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Allyl/Alkyne Coupling Reactions Mediated by Ruthenium(II): Carbon-Carbon Bond Activations and Multicomponent Cycloadditions

by

Christina M. Older 

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Department of Chemistry

Edmonton, Alberta

Spring 2000

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Christina Older Jun 28/2000

501-10101 Saskatchewan Dr.
Edmonton, Alberta

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Allyl/Alkyne Coupling Reactions Mediated by Ruthenium(II): Carbon-Carbon Bond Activations and Multicomponent Cycloadditions** submitted by Christina M. Older in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Dr. Jeffrey Stryker (Supervisor)

Dr. John Vederas

Dr. Josef Takats

Dr. Dennis Hall

Dr. Leonard Wiebe

Dr. Peter Legzdins (External Examiner)

Abstract

A comprehensive investigation of allyl/alkyne coupling reactions mediated by ruthenium(II) templates is presented, including both synthetic and mechanistic aspects. A new carbon-carbon bond activation process is described in which coordinated hexamethylbenzene is converted into pentamethylbenzene under exceptionally mild conditions. The demethylation is integrated into an overall [3 + 2] allyl/alkyne cycloaddition reaction that transforms (η^6-hexamethylbenzene)Ru(η^3-allyl) complexes and disubstituted alkynes into (η^6-*penta*methylbenzene)Ru(η^5-dialkylcyclopentadienyl) complexes and methane. Both model compounds and low temperature NMR experiments are used to investigate the mechanism of this carbon-carbon bond activation reaction. Dissociation of protic acid from an agostic (η^4-hexamethylcyclohexadiene)ruthenium intermediate by reaction with a weak base (typically water) is followed by protolytic activation of the *endo*-methyl group, with "back-side" assistance from the nucleophilic metal center. The protolytic mechanism for dealkylation is relevant to carbon-carbon bond activation reactions observed in previously reported cases of dealkylative ligand aromatization.

The use of more reactive alkynes leads to a large variety of double alkyne insertion products with unusual hapticity patterns. In particular, the insertion of a second alkyne into a DMAD-derived vinyl olefin intermediate results in a broader range of products than has previously been identified for three component [3 + 2 + 2] allyl/alkyne reactions. Products include η^5-cycloheptadienyl complexes, η^1,η^4-methanocyclohexadienyl complexes, acyclic η^2,η^3-heptatrienyl complexes and the unique η^1,η^4-

cycloheptadienyl complexes. Derivatization reactions on the η^1,η^4-cycloheptadienyl complexes involving nucleophilic addition and iodinolysis are also described.

The alkyne coupling reactions of several $(C_6Me_6)Ru$ substituted allyl complexes are also investigated. Disubstituted alkynes generally result in the formation of relatively stable agostic η^3-cyclopentenyl complexes, which undergo further reactions with alkynes, including the highly unusual [5 + 2] ring expansion and constitutes the first such carbon-carbon bond cleavage mediated by a metal other than cobalt.

A high-yield method to prepare complexes of formula $(C_5Me_5)Ru(\eta^3\text{-allyl})L$, where L = alkyne, alkene, CO or PPh_3 is reported. The $(C_5Me_5)Ru(allyl)(alkyne)$ complexes are found to be unusually stable. A wide range of disubstituted alkynes form acyclic η^5-pentadienyl complexes upon warming of these $(C_5Me_5)Ru(allyl)(alkyne)$ complexes. However, $(C_5Me_5)Ru$-mediated allyl alkyne coupling with electron-deficient alkynes leads to η^1,η^4-cycloheptadienyl complexes and to the new acyclic η^1,η^4-heptatrienyl complexes.

Acknowledgements

I would like to express my gratitude to my research advisor, Professor Jeffrey M. Stryker, for allowing me creative freedom and for making these years a special experience.

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Finally, I would like to thank my friends and family for their support and encouragement.

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List of Abbreviations

Å	Angstrom
acac	Acetylacetonato
B	Base
Bu	Butyl group
Bz	Benzyl
COSY	Correlated Spectroscopy
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
Δ	Heating or thermolysis
DMAD	Dimethyl Acetylenedicarboxylate
E	Ester group
Et	Ethyl group
equiv	Equivalents
Fp	$CpFe(CO)_2$
GCOSY	Gradient COSY
HETCORR	Heteronuclear Chemical Shift Correlation
HMB	Hexamethylbenzene
HMBC	Heteronuclear Multiple Bond Coherence
HMQC	Heteronuclear Multiple Quantum Coherence
HOMO	Highest Occupied Molecular Orbital
Hz	Hertz
L	Ligand
LUMO	Lowest Unoccupied Molecular Orbital
M	Metal
Me	Methyl
MO	Molecular Orbital
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect

OAc	Acetate
ORTEP	Oak Ridge Thermal Ellipsoid Program
OTf	Trifluoromethanesulfonate (triflate)
Ph	Phenyl
PMB	Pentamethylbenzene
Pr	Propyl
psig	Pounds per square inch gauge pressure
R	Alkyl Group
S	Solvent
TBDMS	*t*-Butyldimethylsilyl
Tp*	Tris(3,5-dimethylpyrazolyl)borane
TFE	2,2,2-trifluoroethanol
THF	Tetrahydrofuran
TMS	Trimethylsilyl
X	Halogen atom or halide ion

Chapter 1. Introduction and Background

I. General Introduction

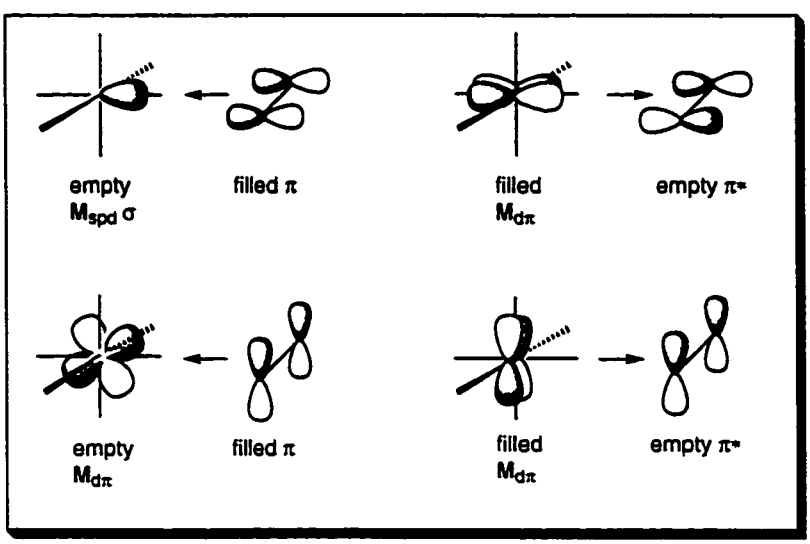
The use of transition metal complexes to mediate the formation of new carbon-carbon bonds has become an important tool in organic synthesis.[1-5] Transformations unprecedented in classical organic chemistry can now be routinely performed using metal complexes to alter the reactivity of the organic moiety. Some of the most important applications of transition metal chemistry to organic synthesis are metal-mediated cyclization reactions. Of particular interest are metal-mediated annulation reactions that involve multiple carbon–carbon bond formations in a selective fashion, since they demonstrate the potential for the efficient construction of complex organic molecules.

Alkynes are one of the more popular substrates for transition-metal-mediated processes since they are highly reactive and readily available. Valuable functionality is preserved in the final product by the incorporation of the surviving double bond. The use of alkynes in transition metal-mediated cyclizations has been extensively reviewed in recent years.[6-8] Metal-alkyne complexes are often quite reactive toward an additional alkyne and also couple readily with alkenes, carbon monoxide, nitriles and ketenes to yield a vast array of organic products. Alkynes have also been shown to react with metal -carbene complexes to give cyclobutenones, cyclopentenediones, phenols, indenes and pyrones.[6] Because of the high reactivity of alkyne metal complexes, the major difficulty

in developing applications for synthesis has been modifying the reaction conditions such that only one product predominates.[1]

The bonding of alkynes to a transition metal center is generally similar to the bonding of alkenes and can also be described using the Dewar-Chatt-Duncanson model.[9] In this description, one filled π orbital of the coordinated alkyne overlaps with a σ-type acceptor orbital on the metal atom; the π^* orbital of the alkyne can also overlap with a filled metal d orbital. The result is a synergistic bonding arrangement that can lead to relatively strong bonding. However, the bonding differs somewhat from that of olefins since a second, orthogonal π orbital is also present in alkynes (Figure 1). In many early transition metal complexes, the metal-alkyne interaction may involve both orthogonal sets of π and π^* orbitals for a formal four-electron donation to a single metal.[5,10] This double interaction can result in remarkably stable alkyne complexes. In contrast, examples of stable complexes where the alkyne is a two-electron donor are far less common. The high reactivity and lability of these two-electron donor alkyne complexes

Figure 1. Bonding in Transition Metal Alkyne Complexes



has been rationalized as a consequence of a four-electron repulsive interaction between the filled perpendicular π orbital, which is not engaged in ligand-to-metal bonding, and a filled d orbital on the metal.[11] A more quantitative description comes from extended Huckel calculations by Hoffman[12a] on d^6-ML_5(alkyne) complexes, which revealed the existence of a high-lying HOMO, formed from the antibonding interaction of a filled metal orbital and the orthogonal π orbital. The generally facile terminal alkyne to vinylidene transformations of these complexes have been attributed to this inherent instability.[12b]

Figure 2. Bonding Modes of Allyl Ligand

η^1-allyl η^3-allyl

Another common organic moiety in organometallic chemistry is the allyl ligand, which generally exists either as an η^1-allyl (σ bonding), or as an η^3-allyl (π bonding) (Figure 2). Metal-allyl complexes are readily prepared from many types of substrates and exhibit a range of reactivities, including nucleophilic attack, electrophilic attack and a wide variety of coupling reactions.[1-4] Many important catalytic processes, including the polymerization and oligomerization of conjugated dienes, involve η^3-allyl complexes as key intermediates.[1] Despite this, relatively few metal-allyl compounds have been developed as useful reagents for organic synthesis. The most widespread synthetic application is the use of catalytic palladium for nucleophilic substitution or alkylation of allylic substrates.[1,13] The reactivity of metal-allyls with alkynes is one potential source of exploitable chemistry that has historically received little attention.

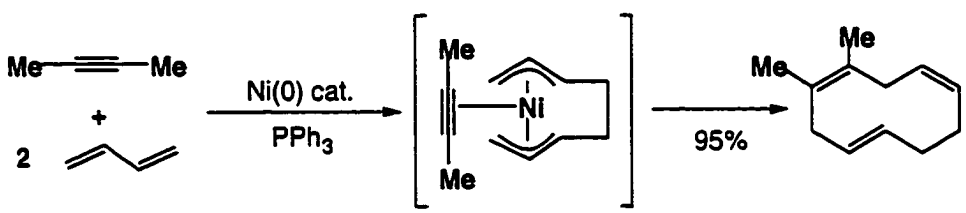
First-row transition metal templates are often preferred for stoichiometric applications in organic synthesis since they are inexpensive, readily available and quite reactive. However, the lability of first-row metals often causes difficulties in the identification and isolation of relevant intermediates. As a result, second- or third-row metals are generally used as model systems for the purpose of probing new reactivity patterns. For this reason ruthenium was selected as a model for possible new organoiron chemistry. The initial aim of this investigation was to explore the alkyne chemistry of selected ruthenium η^3-allyl templates, with an emphasis on finding reactivity patterns that lead to synthetically useful carbocycles. Such fundamental studies could then, in principle, be applied in a synthetic context using iron, where such stoichiometric transformations would be more practical.

II. Metal-mediated Allyl/Alkyne Coupling Reactions

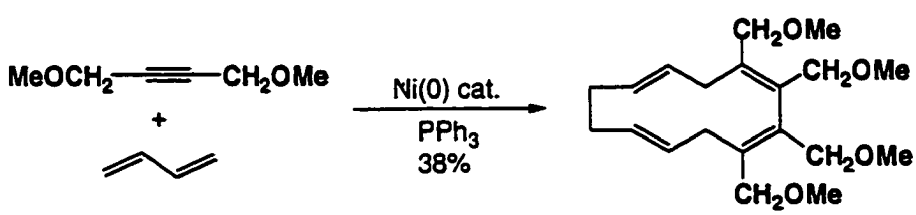
1. Catalytic Allyl/Alkyne Coupling Processes

To date, the most useful applications of allyl/alkyne coupling involve the formation of metal-allyls *in situ*, as part of a catalytic cycle. Subsequent reactions with added alkyne or other reagents free the organic moiety while regenerating the active metal catalyst. In the most popular synthetic processes, products are created from organic precursors in one-pot procedures without requiring the isolation or purification of any transition metal intermediates.

Heimbach reported one of the earliest examples of a metal-allyl coupling with alkynes in 1964 as part of his extensive studies on the nickel-catalyzed oligomerizations of 1,3-butadiene.[14] A nickel(0) catalyst reacts with excess 1,3-butadiene to form the coupled bis-η^3-allylnickel complex which subsequently reacts with a variety of organic substrates (Eq. 1). In the case of alkyne coupling, one equivalent can insert, followed by cyclization to generate disubstituted cyclodecatrienes. In the case of 2-butyne this produces 4,5-dimethyl-*cis,cis,trans*-1,4,7-cyclodecatriene in 95% yield (based on alkyne) with only butadiene oligomers present as readily removed byproducts. This has proven to be a fairly general procedure, since a broad range of alkyl-substituted alkynes can be used, as well as alkynes in which functional groups are separated from the triple bond by at least two methylene units.[15] By increasing the concentration of the alkyne it is also possible to form larger rings, such as 1,2,3,4-(tetramethoxymethyl)-*cis,cis,trans,trans*-1,3,6,10-cyclododecatetraene from 1,4-dimethoxy-2-butyne (Eq. 2), although the yields are lower. These processes have been applied in the synthesis of medium-sized rings of some natural products.[16]

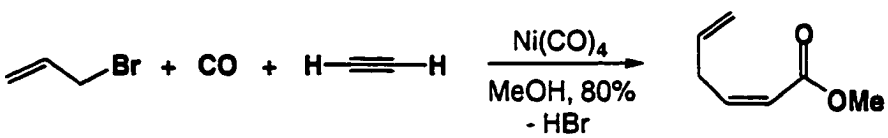


(Eq. 1)



(Eq. 2)

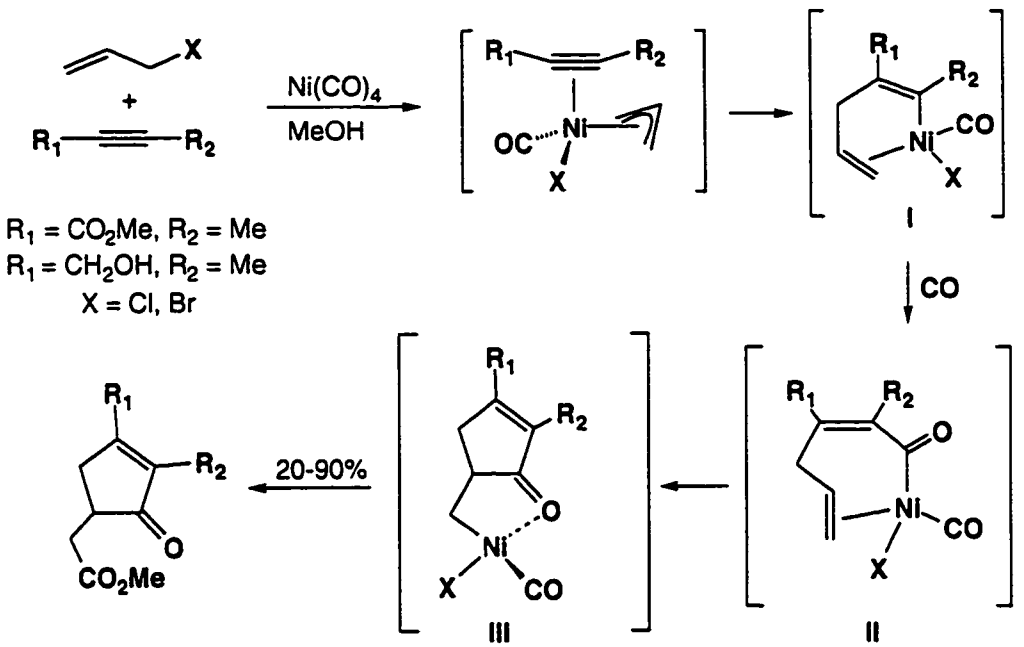
Early work by Chiusoli on the nickel-catalyzed coupling of allyl halide, alkyne and carbon monoxide demonstrated that cyclic products can be formed when the reactions are run under strictly controlled conditions.[17] However, the yields of cycloadducts are generally low and complex mixtures of products are often recovered. Acetylene itself reacts with allyl bromide in the presence of a nickel catalyst and carbon monoxide to produce the linear product *cis*-2,5-hexadienoic acid in yields up to 80% (Eq. 3).[17a] Both linear and cyclization reactions are thought to proceed through an intermediate in which the η^3-allyl and the alkyne both coordinate to the metal center (Scheme 1). The alkyne then inserts into one metal-carbon bond of the allyl to form a vinyl olefin complex **I** that rapidly inserts carbon monoxide to yield an acyl intermediate complex **II**. While this intermediate has not been directly observed, it has been implicated by trapping experiments.[18] Subsequent cyclization of the nickel-acyl complex generally gives 5-substituted 2-cyclopentenones. When the reaction is done in methanol, the terminal functionality is usually a methyl ester but occasionally β-hydride elimination from intermediate **III** occurs instead, resulting in the formation of a methylene group.



(Eq. 3)

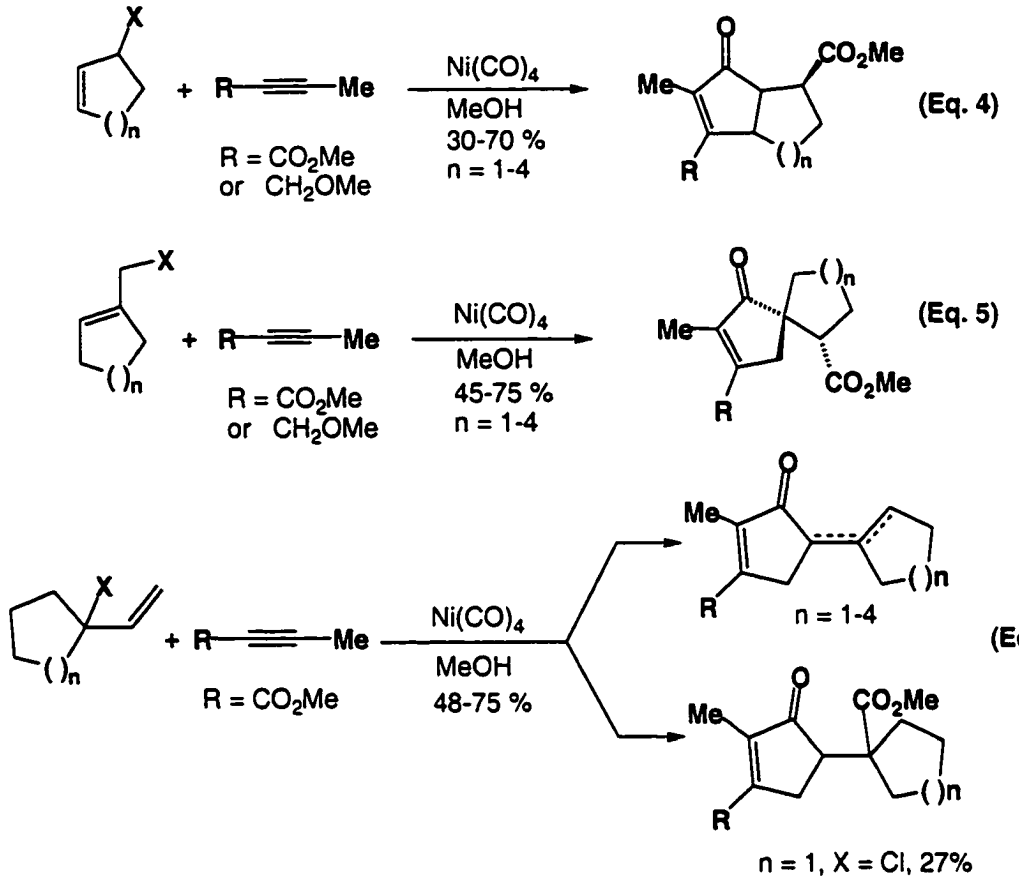
Recent investigations, primarily by Moreto,[19] have concentrated on developing the Chiusoli reaction for applications in organic synthesis. Factors influencing the reaction pathway have been studied in detail and some conclusions have been drawn. Although many alkynes can be used in this reaction, the best results are obtained using

Scheme 1

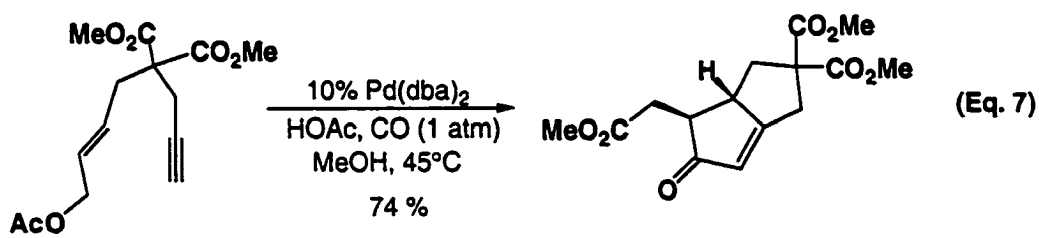


highly polarized alkynes such as methyl 2-butynoate or but-2-yn-1-ol. The preference for electron deficient alkynes in this reaction complements the electronic requirements of the better-known Pauson-Khand[20] reaction: in the Pauson-Khand reaction, electron-deficient alkynes give rise to acyclic byproducts and loss of regioselectivity. The Chiusoli reaction has also been found to work with a broad range of allylic halides, resulting in the formation of fused bicyclic cyclopentenones, spirocyclic compounds and cycloalkenyl-idenecyclopent-2-enones (Eqs. **4**, **5** and **6**). Several intramolecular examples have been demonstrated as well.[22]

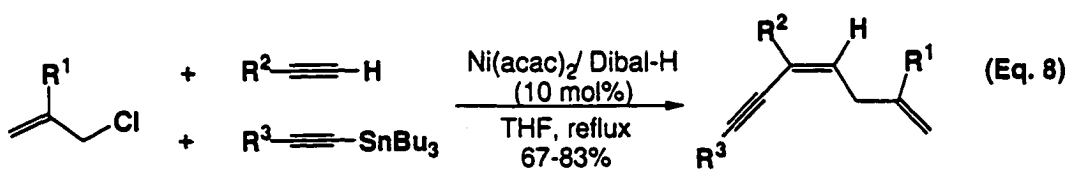
While the chemistry of η^3-allyl palladium complexes has been extensively studied, only a few examples of reactions with alkynes have been reported. Terminal



alkynes have been shown to react with allyl carbonates in the presence of a palladium catalyst to form linear adducts with good regioselectivity and stereoselectivity.[21] Oppolzer[22a] has also reported a palladium-catalyzed intramolecular coupling of allyl and alkyne under a carbon monoxide atmosphere in a reaction that closely parallels the Chiusoli nickel chemistry (Eq. 7).



A recently developed nickel(0) catalyzed process forms 3,6-dien-1-ynes in a regioselective and stereoselective manner. This three-component procedure involves the coupling of allyl chloride, terminal alkyne and an alkynyltin reagent in a single reaction (Eq. 8).[23] The proposed reaction mechanism entails initial generation of a η^3-allyl nickel complex; the allyl ligand then migrates to the terminal alkyne to give a vinylnickel compound in the regiochemical- and stereochemical-determining step. Transmetallation of the tin-acetylide followed by reductive elimination yields the final product and regenerates the nickel catalyst. While a range of terminal alkynes can be used in this reaction, only alkynyltin compounds appear to be effective for the transmetallation; allyl- and vinyltin reagents did not react even over prolonged reaction times. Despite the limitations, this coupling process provides an attractive method for preparing conjugated enynes, and has recently been extended to intramolecular examples.[23a]



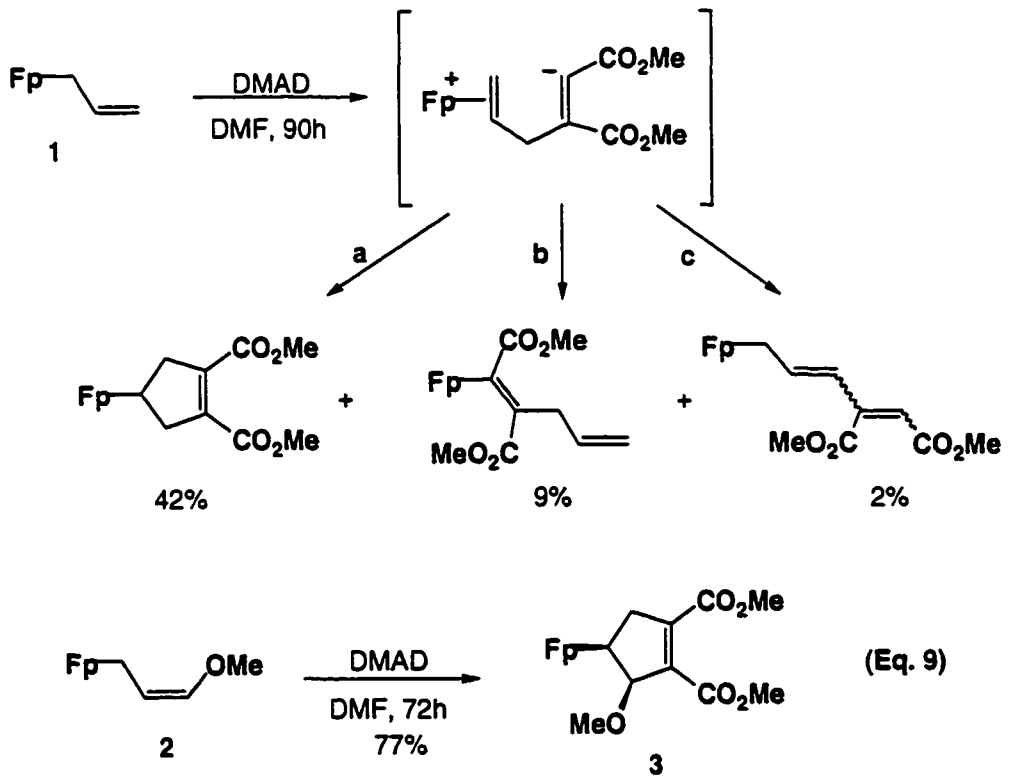
(Eq. 8)

2. Stoichiometric Allyl/Alkyne Coupling Reactions

The reaction of (η^1-allyl)Fp complexes [Fp = (η^5-cyclopentadienyl) iron(dicarbonyl)] with a variety of electrophilic unsaturated moieties has been extensively studied and reviewed.[24] However, only a few examples of reactions with alkynes have been reported.[24c] The reaction of dimethyl acetylenedicarboxylate (DMAD) with η^1-allyl complex **1** results in the formation of three monoadducts in a ratio of 78: 17 : 5 (Scheme **2**). The product distribution can be rationalized by proposing a common zwitterionic

intermediate, formed from nucleophilic attack of the allyl ligand on the free alkyne. The collapse of the dipolar intermediate can follow several routes: (a) cyclization, (b) insertion, and (c) hydride transfer. The latter two processes result in the formation of two different linear products. Use of the more electron rich (η^1-3-methoxyallyl)Fp complex with DMAD significantly alters the reaction pathway, leading only to the [3 + 2] cycloaddition product **3** in 77 % yield (Eq. 9).

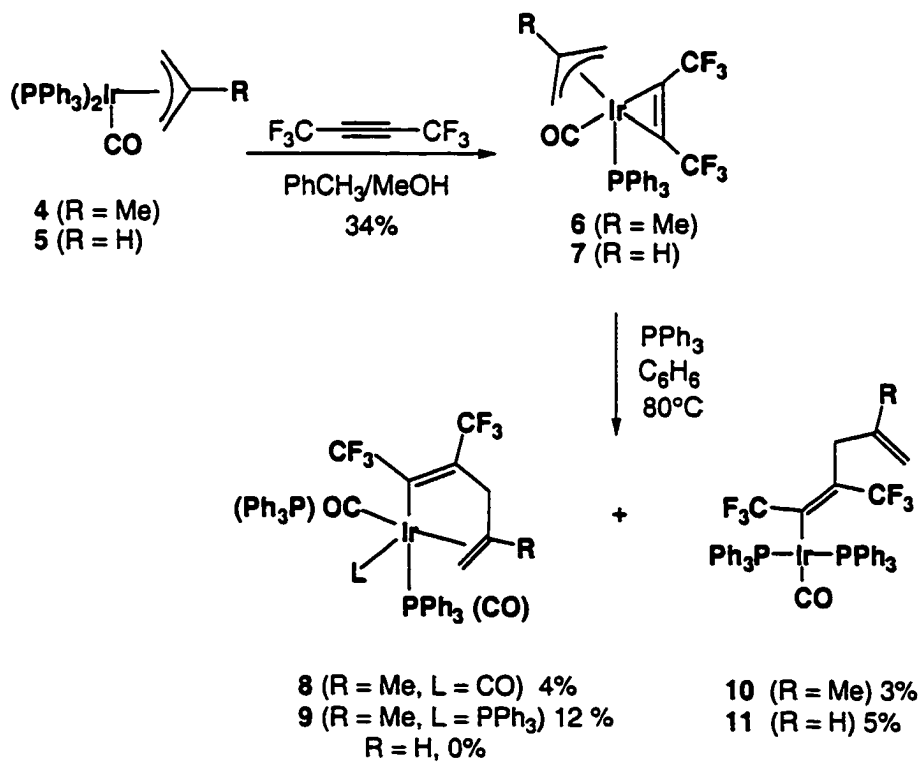
Scheme 2



Isolable allyl/alkyne complexes are generally quite rare due to facile migratory insertions, but Green was able to prepare the first examples of stable η^3-allyl/alkyne complexes using an iridium template (Scheme 3).[25] When (carbonyl)(methylallyl)-

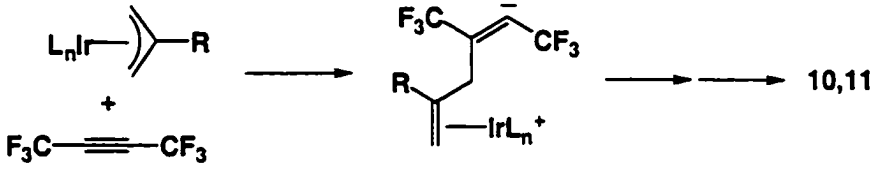
bis(triphenylphosphine)iridium complex **4** is treated with hexafluorobutyne in a toluene/methanol solution, (η^3-methylallyl)Ir(η^2-alkyne) complex **6** is formed in moderate yield. The same reaction with the unsubstituted η^3-allyl complex **5** forms the analogous allyl alkyne complex **7**. Upon mild heating (benzene, 80°C), complex **6** converts to a mixture of 1:1 allyl/alkyne adducts formed through both *cis* and *trans* insertion, while the η^3-allyl analogue forms only the *trans* insertion product **11**, albeit in very poor yield. Ancillary ligand rearrangement accompanies the *cis* insertion, resulting in a mixture of bis(phosphine)carbonyl **8** and bis(carbonyl)phosphine complex **9**. While the *cis* products most likely arise from direct migratory insertion of the alkyne into the allyl ligand, the *trans* product probably forms through nucleophilic attack of the

Scheme 3

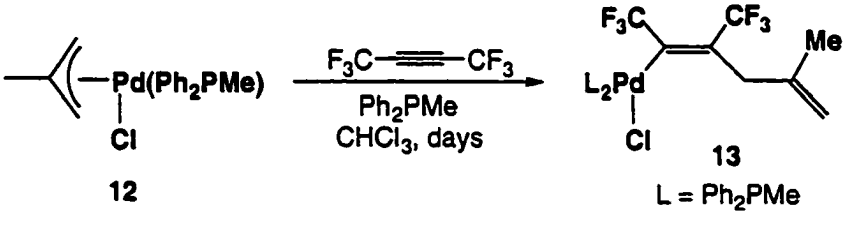


allyl on free alkyne. A dipolar transition state then results, which subsequently collapses to form the final product in a process similar to that previously proposed for the (η^1-allyl)Fp reactivity (Figure 3).

Figure 3. Dipolar Transition State for Allyl/Alkyne Insertion Reactions



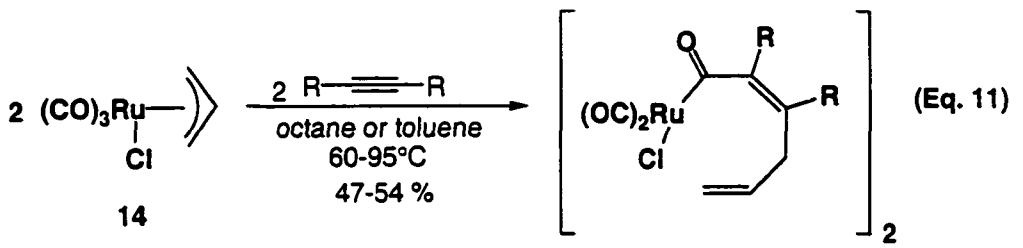
An earlier report by Clark[26] demonstrated a similar single alkyne insertion using a palladium template, although he was unable to isolate the proposed allyl alkyne intermediate. Addition of hexafluorobutyne to the palladium η^3-methylallyl complex **12** initially forms a vinyl olefin complex that exists as a mixture of a dimeric and a monomeric structure, the latter with the pendant olefin coordinated to the metal. However, addition of an equimolar amount of phosphine converts both complexes to the monomeric vinyl complex **13**.



(Eq. 10)

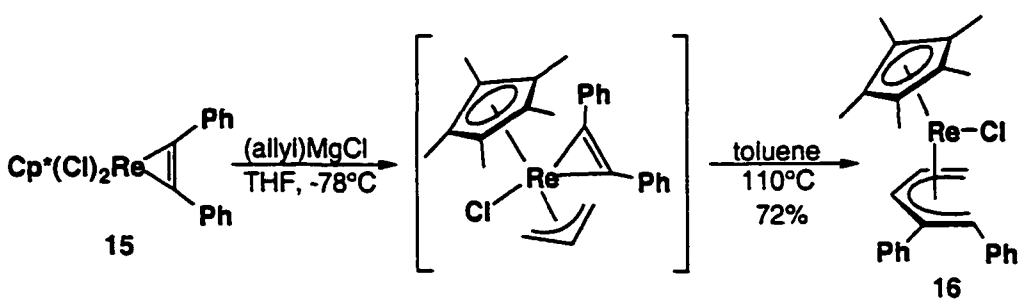
Closely related allyl/alkyne insertion reactions have also been observed for ruthenium allyl complexes.[27] In some examples, further carbon monoxide insertion into the intermediate vinyl olefin leads to the formation of an acyl complex (Eq. 11). Symmetric alkynes (acetylene, diphenylacetylene) yield a single dimeric chloro-bridged

compound. While unsymmetrical alkynes (phenylacetylene, ethyl propiolate) also insert into the η^3-allyl ligand the process is not regioselective, resulting in inseparable mixtures of regioisomers.

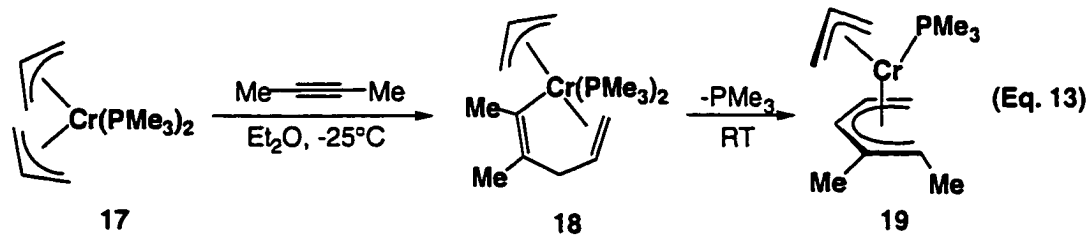


(Eq. 11)

There are several examples of allyl/alkyne insertion reactions in which the initial product undergoes a more extensive rearrangement before reaching the final product. Herrmann,[28] for instance, finds that the stable rhenium alkyne complex **15** reacts with allylmagnesium chloride in tetrahydrofuran to form a transient intermediate that was neither isolated nor characterized, but is presumed to be the η^3-allyl alkyne complex. Heating this compound in toluene at 100°C for 12 hours results in the clean formation of η^5-pentadienyl complex **16** (Eq. **12**). Based on the previous examples, it is likely that the alkyne inserts into the allyl ligand to yield a vinyl olefin complex analogous to compounds **8** and **9**. Thermolysis of this intermediate subsequently causes allylic C-H activation of a methylene hydrogen atom, which is followed by reductive elimination to



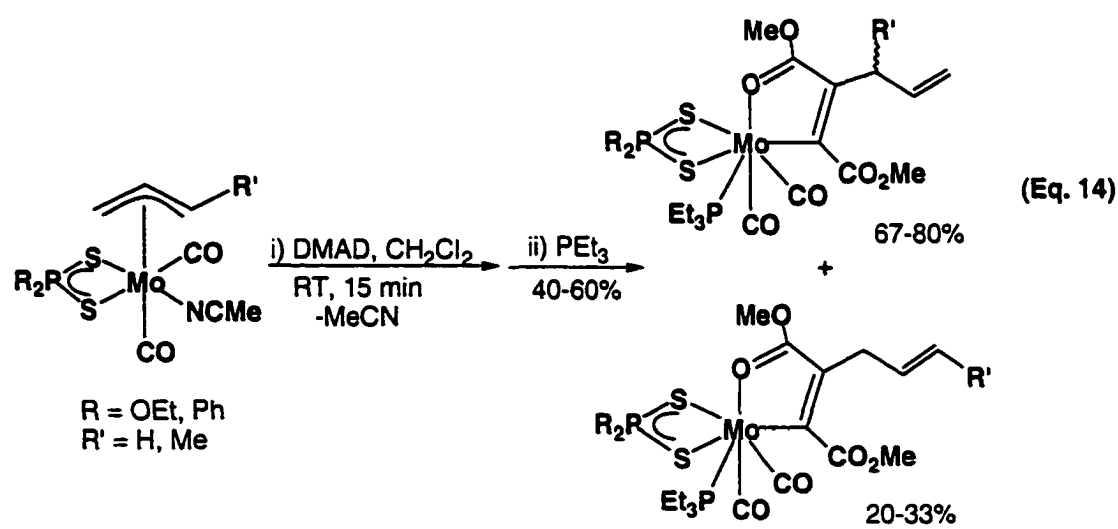
(Eq. 12)



17 18 19 (Eq. 13)

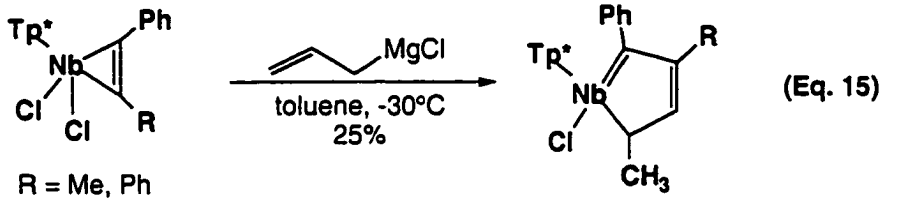
give the final η^5-pentadienyl product **16**. A similar rearrangement was described by Jolly,[29] where the chromium bis(allyl) complex **17** initially reacts with 2-butyne to form the isolable vinyl olefin complex **18** at –25 °C. Warming this compound to room temperature results in conversion to the final η^5-pentadienyl product **19**, under much milder conditions than that reported for the rhenium system.

Molybdenum allyl complexes have been shown to couple with electron-deficient alkynes to yield oxamolybdacyclopentadiene products (Eq. **14**).[30] The alkenyl complexes thus formed are stabilized by intramolecular coordination of the oxygen atom of the ester group on the β-carbon, while the allyl moiety is placed in the *trans* position relative to the metal. In this case the authors propose that the *trans* disposition arises from isomerization of an initial *cis* insertion product.



(Eq. 14)

A different rearrangement is observed in a rare example of early metal allyl-alkyne coupling (Eq. **15**).[31] When the tris(3,5-dimethylpyrazolyl)borate niobium alkyne complex **20** (where the alkyne is a $4e^-$ donor) is treated with allyl magnesium chloride, the product is the niobacyclopentadiene complex **21**. Presumably, this product arises from a metal-mediated 1,3-hydrogen shift after the initial allyl/alkyne coupling.

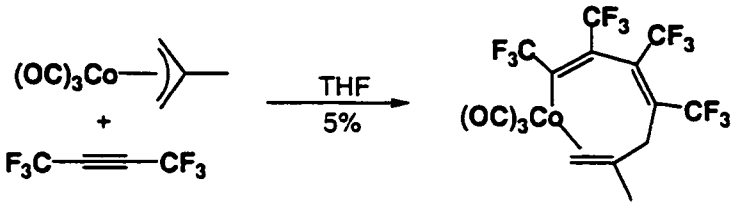


R = Me, Ph

20 **21** **(Eq. 15)**

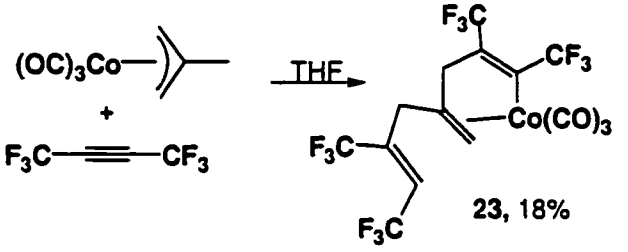
3. Double Alkyne Migratory Insertion Reactions

Several examples of double alkyne insertion into isolable allyl complexes are also known. Both Stone[32a] and Green[32b] report products from double alkyne insertion into the same tris(carbonyl)cobalt methylallyl complex. The earlier report by Stone describes the sequential insertion of two hexafluorobutyne molecules to form alkenyl complex **22** in very low isolated yield (Eq. **16**). However, Green failed to reproduce this reaction, finding instead a different double insertion product **23**, presumably formed by insertion of one alkyne to each end of the methylallyl ligand (Eq. **17**). Green also found a significant amount of the single alkyne insertion product, vinyl olefin complex **24** in the crude reaction mixture. Many other unidentified compounds are formed during this reaction, which is apparently quite sensitive to minor variations in reaction conditions.

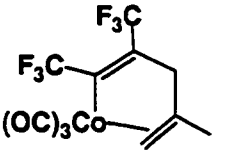


(Eq. 16)

22



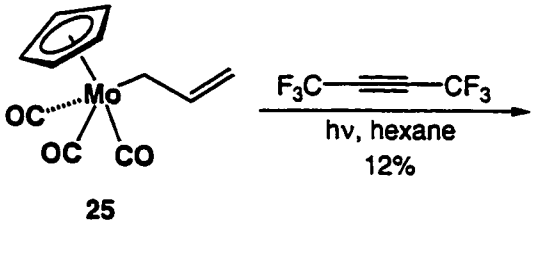
23, 18%



24, 17%

(Eq. 17)

A molybdenum η^1-allyl system has also been reported to insert two equivalents of hexafluorobutyne (Eq. **18**),[33] a reaction proceeding by initial migration of the allyl to generate a *trans* vinyl ligand, which likely arises from a dipolar intermediate similar to that previously described (Figure **3**). A more straightforward *cis* insertion ensues, resulting in the formation of chelating vinyl diene complex **26** in very low yield. The *trans* assignment of the CF_3 groups is based on spectroscopic analysis: only one CF_3 group exhibits J_{FH} coupling to the neighbouring allyl fragment, and this CF_3 substituent also shows no F-F coupling, indicating that the adjacent CF_3 group is in a *trans* orientation. The two other CF_3 groups, assigned to the α and β carbon atoms show mutual coupling (J_{FF} = 12 Hz), but no further splitting of the signals is observed.



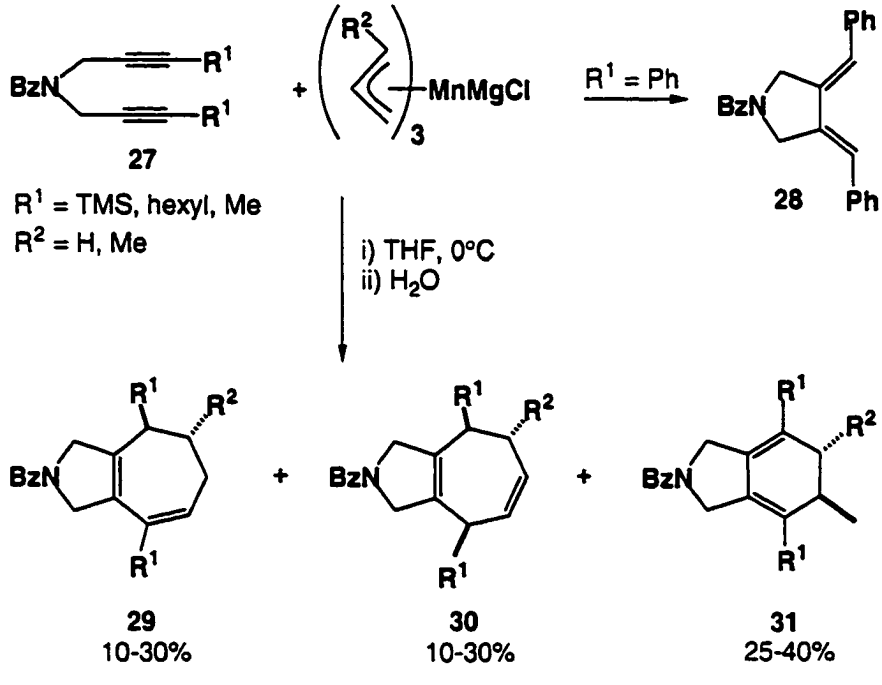
25

26

(Eq. 18)

A more interesting example of double alkyne insertion, recently reported by Oshima, involves an allylmanganate complex.[34] Treatment of selected diynes with triallylmanganate anion results in the production of metal-free bicyclic organic compounds containing mixtures of six- and seven-membered rings (Scheme 4). The reaction is quite specific; only diynes with terminal alkyl or trimethylsilyl substituents afford seven-membered rings (in low yields), while substrates with terminal phenyl groups do not incorporate allyl at all, forming the bis(methylene)azacyclopentane compound **28** instead. Little is known about the mechanism for this reaction, although Oshima proposes that the diyne initially reacts with the triallylmanganate to form a bicyclic manganacyclopentadiene, which then undergoes allyl migration from the manganese to an adjacent carbon. Subsequent ring closure leads to either six- or seven-membered rings, followed by hydrolysis to liberate the organic products.

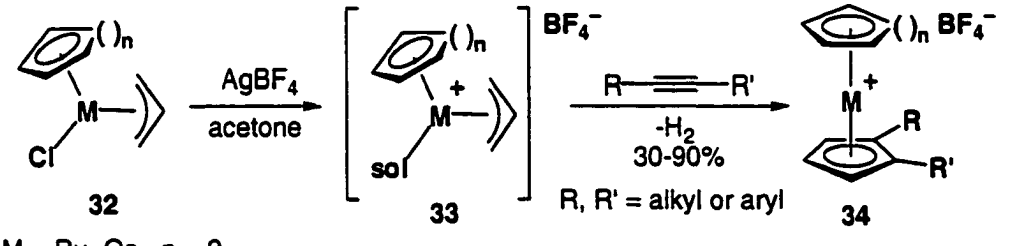
Scheme 4



4. [3 + 2] Allyl/Alkyne Cycloaddition Reactions

Several Group 8 and Group 9 allyl complexes follow an alternative pattern of allyl/alkyne coupling: a [3 + 2] metal-mediated dehydrogenative cycloaddition. Rubezhov[35] provided the first examples of this reaction pattern, using η^3-allyl halide complexes of several late transition metals (Eq. **19**). The addition of silver tetrafluoroborate generates the unsaturated intermediates **33** via halide abstraction, allowing the alkyne to coordinate and insert. Cyclization of the initial insertion product is accompanied by extrusion of dihydrogen to form the metallicenium products **34** in generally good, but variable yields (30-90%). The proposed mechanism of this reaction will be discussed in detail in the following chapter.

(Eq. 19)

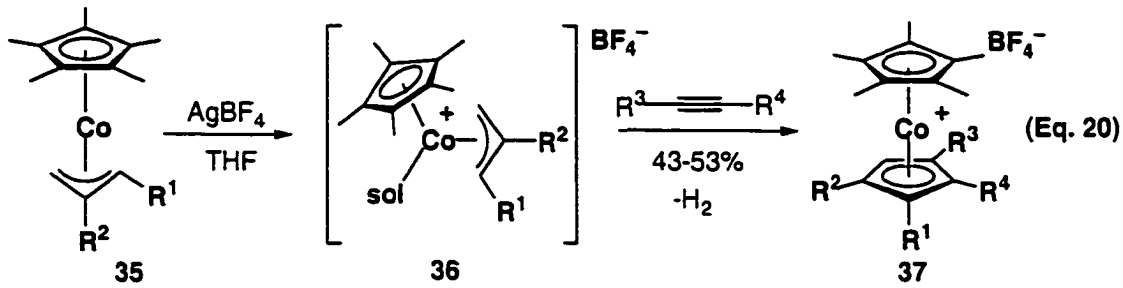


32 **33** **34**

R, R' = alkyl or aryl

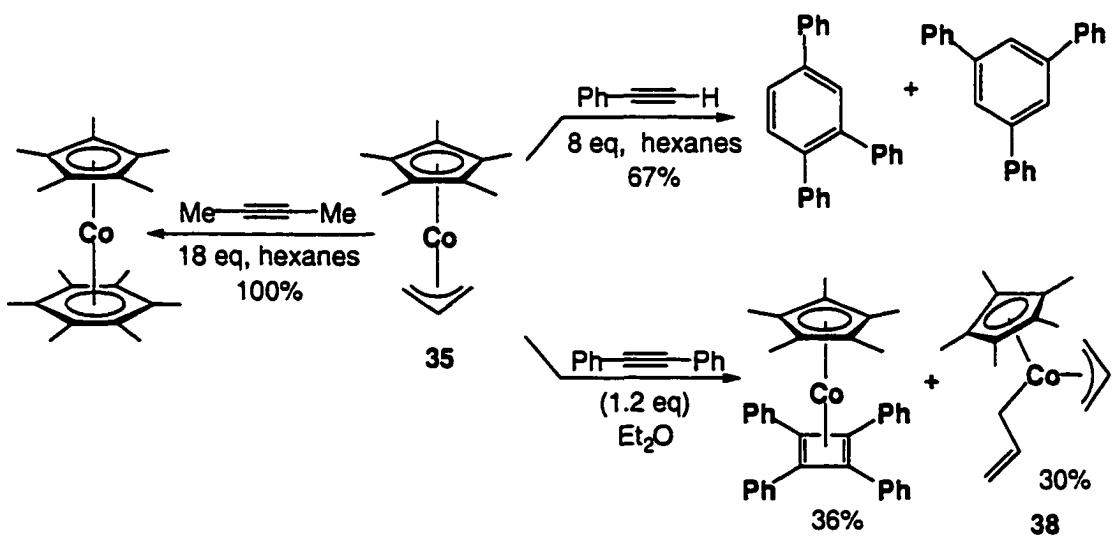
M = Ru, Os n = 2
M = Rh, Ir n = 1

Nehl has also reported a similar [3 + 2] cycloaddition reaction using a cobalt template.[36a] Oxidation of the highly reactive cobalt(II) η^3-allyl **35** to the cobalt(III) allyl cation **36** by silver tetrafluoroborate followed by addition of alkyne in tetrahydrofuran solvent results in the formation of cobalticenium compounds analogous to those isolated by Rubezhov (Eq. **20**). However, a dramatic change in the reactivity pattern is noted when alkyne is allowed to react directly with the neutral cobalt(II) η^3-allyl complex **35**



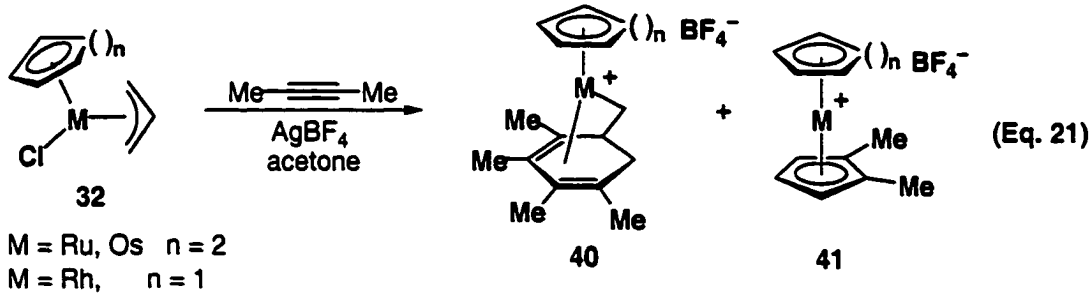
(Scheme 5). Instead of forming allyl/alkyne adducts, the reaction yields a variety of products arising from alkyne dimerization and trimerization, with no apparent incorporation of the allyl ligand. In most cases, the fate of the allyl ligand is unknown, although in the reaction of diphenylacetylene with **35**, (η^5-C_5Me_5)Co(η^1-allyl)(η^3-allyl) (**38**) is isolated along with a η^4-tetraphenylcyclobutadiene cobalt complex. The 17e$^-$ cobalt allyl complex **35** has also been shown to form pyridine rings by the co-cyclization of alkynes and nitriles.[36b]

Scheme 5



5. [3 + 2 + 2] Allyl/Alkyne Cycloaddition Reactions

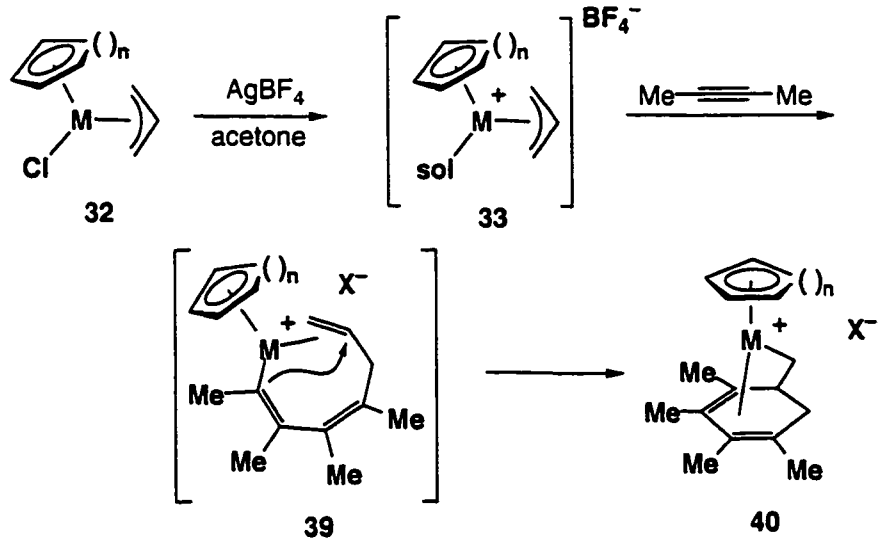
Rubezhov has also reported rare cases of double alkyne insertion into an η^3-allyl ligand using 2-butyne.[37] While the formation of η^1,η^4-methanocyclohexadiene complexes **40** proceeds smoothly in 32-49% isolated yields using several late metal templates, this reactivity pattern is apparently limited just to the case of 2-butyne (Eq. **21**). In the reaction of (η^6-benzene)ruthenium(η^3-allyl)$^+BF_4^-$ (**32**, M = Ru, n = 2) with equimolar 2-butyne, Rubezhov reports a product mixture of 4 : 1 in favour of the bis(adduct) **40** over the single insertion product, complex **41**.[37] The use of a high concentration of 2-butyne results in sole formation of the bis(adduct) **40**. These η^1,η^4-methanocyclohexadiene complexes are thought to proceed from the vinyl diene intermediate complex **39** (Scheme **6**) formed from the sequential insertion of two equivalents of alkyne.



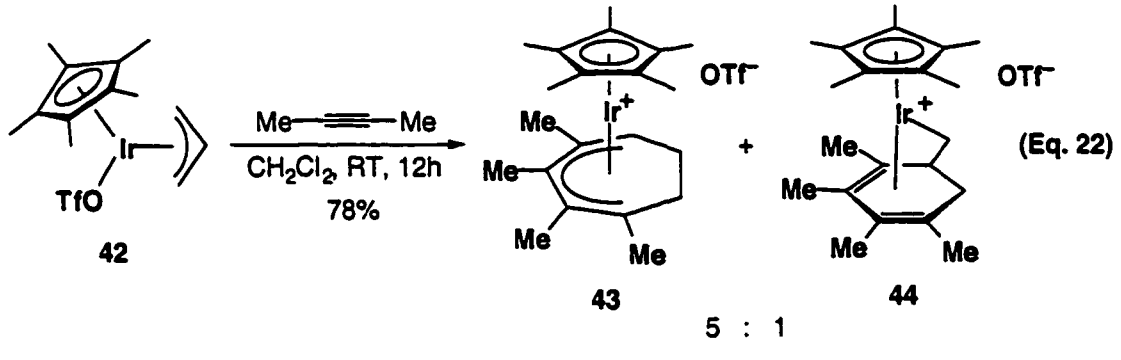
(Eq. 21)

On the basis of this mechanistic proposal, we envisioned that using a different ancillary ligand arrangement might result in an alteration of the reactivity pattern, possibly leading to the production of synthetically useful seven-membered rings. Schwiebert, in this research group, was the first to demonstrate this concept. She showed

Scheme 6

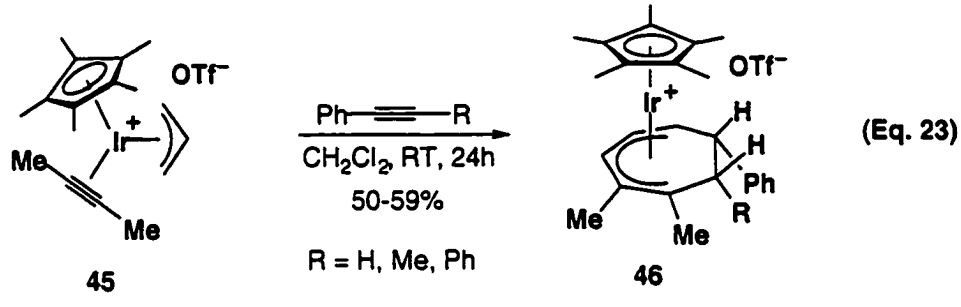


that by using the more sterically demanding pentamethylcyclopentadienyl ligand, the reaction of iridium allyl complex **42** with 2-butyne produces a mixture of seven- and six-membered ring cycloadducts **43** and **44** in a reasonably selective 5:1 ratio (Eq. **22**).[38]



The pentamethylcyclopentadienyl ligand also imparts greater stability to the iridium complexes, allowing Schwiebert to isolate key intermediates in the cyclization pathway. Addition of 2-butyne to a benzene solution of iridium allyl triflate complex **42** results in the formation of a highly labile η^3-allyl alkyne complex **45**, which precipitates

from solution upon addition of diethyl ether. Dissolution of this complex in dichloromethane in the presence of another alkyne yields the seven-membered ring complex **46**, presumably formed via the same process that produces the η^5-cycloheptadienyl complex **43** (Eq. **23**). Also observed during this reaction are varying amounts of isomeric seven-membered complexes (20-50% of the product mixture), which appear to be the result of an alternative sequence of hydride shifts, although these products do not equilibrate under thermolysis conditions.[39]

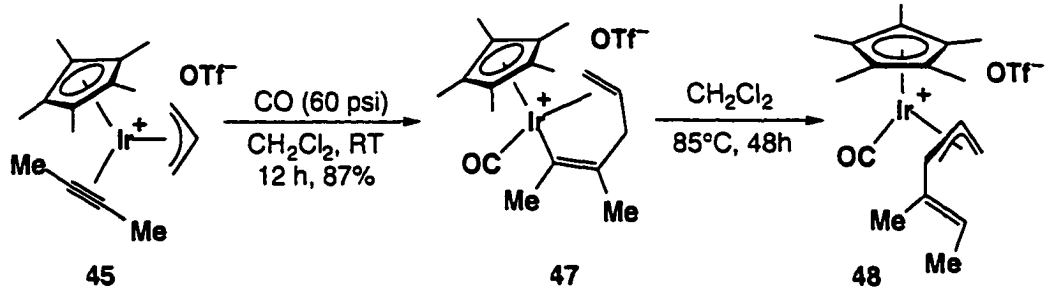


(Eq. 23)

Additional evidence for the mechanistic pathway is obtained by trapping the initial product of allyl/alkyne insertion with carbon monoxide, providing the vinyl olefin carbonyl complex **47** (Eq. **24**) in high yield. Competitive alkyne displacement by carbon monoxide prior to allyl migration also yields a minor amount of $[(C_5Me_5)Ir(\eta^3\text{-}C_3H_5)(CO)]^+OTf^-$ as a byproduct. The vinyl carbonyl complex is presumed to be a stable model for the product initially formed after one equivalent of alkyne inserts into the η^3-allyl, where carbon monoxide replaces a more labile solvent, additional alkyne or triflate ligand in the coordination sphere. Thermolysis of the vinyl olefin complex **47** results in the formation of a product that Schwiebert[39] tentatively assigned as the η^5-1,2-dimethylpentadienyl iridium complex, closely paralleling the allyl/alkyne insertion reaction reported by Herrmann. However, later re-examination of the spectroscopic data

suggests that an η^3-pentadienyl iridium carbonyl structure (**48**) is the more likely assignment.[40]

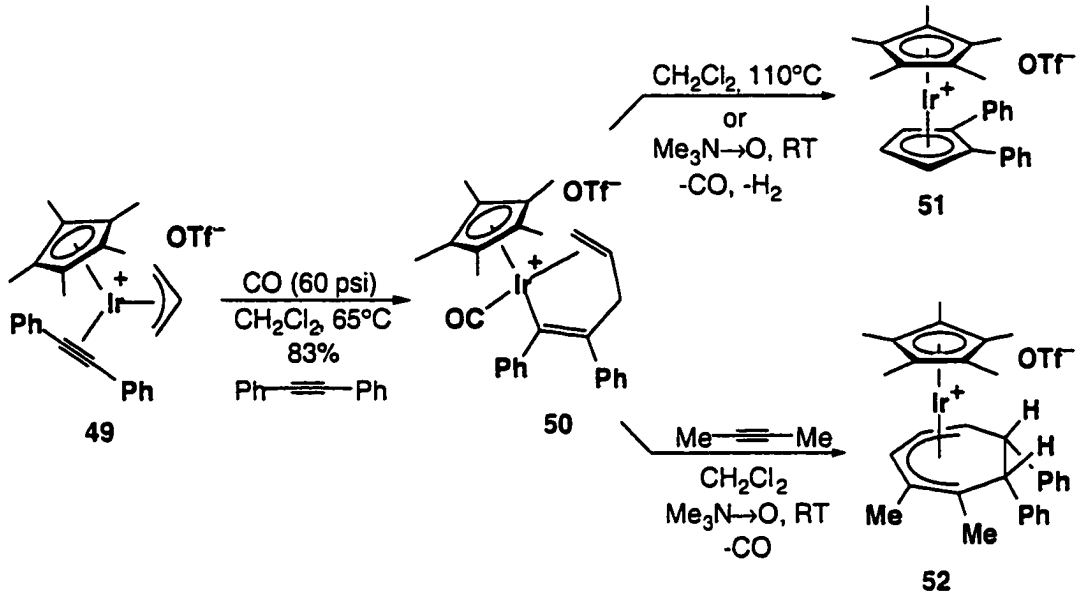
(Eq. 24)



45 47 48

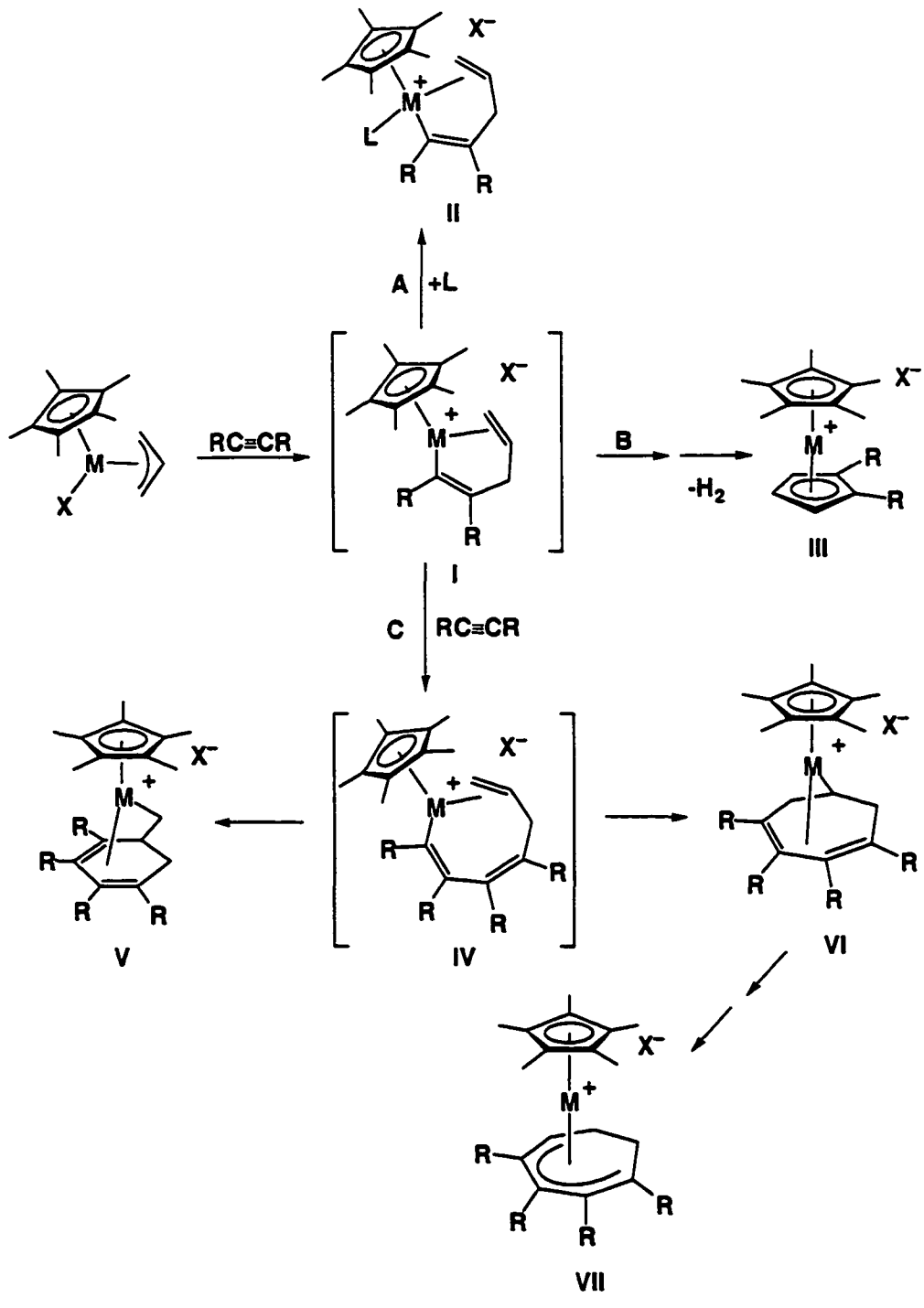
Diphenylacetylene η^3-allyl iridium complex **49** can also be prepared under the same conditions used for the 2-butyne complex **45**. However, treatment of this intermediate with additional diphenylacetylene does not result in the formation of a seven-membered ring, instead directly cyclizing to form the 1,2-diphenyl-cyclopentadienyl complex **51**. It is also possible to intercept the vinyl olefin intermediate by doing the reaction under an atmosphere of carbon monoxide, giving the iridium carbonyl complex **50** (Scheme 7).[39] The reactivity of the vinyl carbonyl complex also varies from that observed for the 2-butyne example. Rather than isomerizing to form an acyclic pentadienyl complex, the treatment of complex **50** with trimethylamine-N-oxide or under thermolysis conditions results in the formation of 1,2-diphenylcyclopentadienyl complex **51**. The reaction of complex **50** with 2-butyne and trimethylamine-N-oxide, however, produces the same seven-membered ring complex **52** observed from the direct reaction of allyl alkyne complex **49** with 2-butyne (Eq. **23**). This complex is also the only seven-membered ring isolated from the reaction of the 2-butyne η^3-allyl complex **45** and diphenylacetylene. Vinyl olefin complexes are thus established as competent intermediates in the [3 + 2 + 2] cycloaddition pathway.

Scheme 7

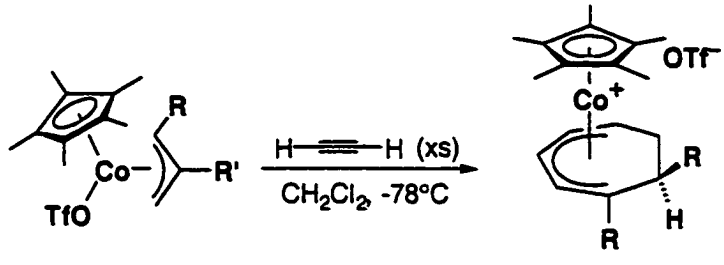


A working mechanistic rationale for seven-membered ring formation by the [3 + 2 + 2] cycloaddition was proposed based on the results from the iridium system (Scheme **8**). Initial insertion of an alkyne molecule into the allyl ligand generates the vinyl intermediate **I**, which may be trapped by added ligand (Path A). Intermediate **I** can subsequently cyclize to the five-membered ring **III** (Path B) or insert a second equivalent of alkyne to form the vinyl diene intermediate **IV** (Path C). Intermediate **IV** then undergoes cyclization to form either a six-membered ring product **V** (as seen by Rubezhov) or an initial seven-membered ring η^1,η^4-carbocycle (**VI**) by migratory insertion. This non-conjugated seven-membered ring intermediate is presumably unstable, rapidly isomerizing via a series of β-hydride elimination and hydride reinsertion to form a stable η^5-cycloheptadienyl product (e.g., **VII**), where the final position of the substituents (R) on sp^2- or sp^3-hybridized carbon positions depends on as yet undetermined factors.

Scheme 8



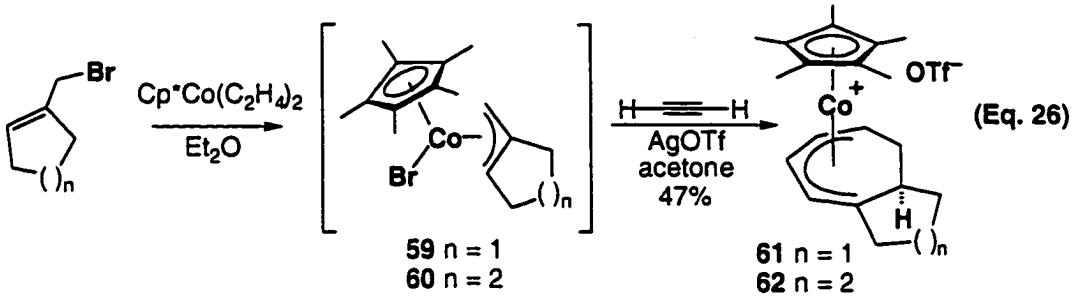
As previously discussed, pentamethylcyclopentadienylcobalt η^3-allyl complexes were found by Nehl to react with alkynes in THF solution to yield only substituted cyclopentadienyl complexes by dehydrogenative [3 + 2] cycloaddition, even in the presence of excess alkyne.[36a] However, Etkin and Dzwiniel in this group later determined that use of a poorly coordinating solvent such as dichloromethane diverts the reaction to a higher-order cycloaddition, producing seven-membered ring complexes from incorporation of two equivalents of alkyne.[41,42] Thus, treatment of allyl, crotyl and 1,2-dimethylallyl cobalt (**53**, **54** and **55**) complexes in dichloromethane with excess acetylene affords η^5-cycloheptadienyl complexes **56**, **57** and **58**, respectively, as air stable solids in good yields after isolation and purification (Eq. **25**). Unlike the closely related iridium system, competitive formation of η^5-cyclopentadienyl or η^1,η^4-methanocyclohexadienyl complexes is not observed, nor are regioisomeric η^5-cycloheptadienyl products detected in the crude reaction mixtures. Synthetically interesting bicyclic η^5-cycloheptadienyl compounds can also be prepared, starting from readily available five- and six-membered ring allylic precursors and acetylene (Eq. **26**). The use of other terminal alkynes also leads to the formation of η^5-cycloheptadienyl complexes in high yield, although phenylacetylene and 3,3-dimethyl-1-butyne afford

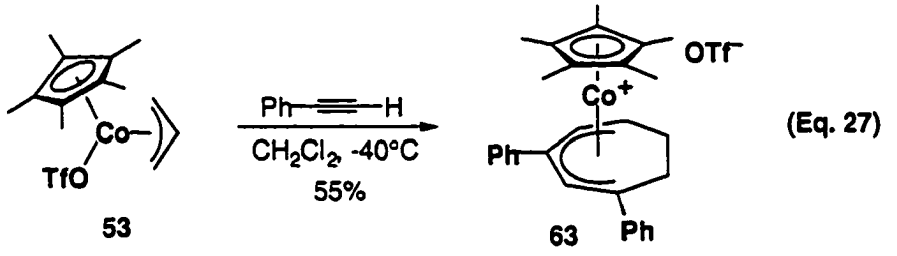


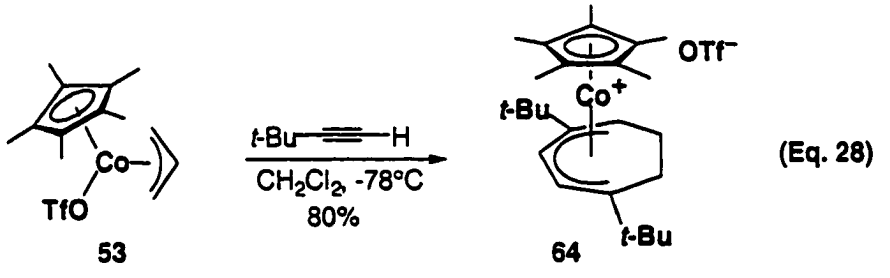
(Eq. 25)

53 (R = H, R' = H)
54 (R = Me, R' = H)
55 (R = Me, R' = Me)

56 (R = H, R' = H) 52%
57 (R = Me, R' = H) 79%
58 (R = Me, R' = Me) 67%

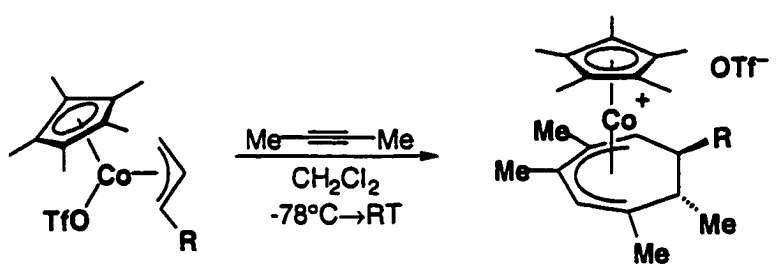






different substitution patterns (Eq. **27** and Eq. **28**), presumably arising from a change in insertion regioselectivity as a function of substituent. However, the use of the less sterically hindered propyne produces a complex mixture of isomeric η^5-cyclopentadienyl products, suggesting that good insertion selectivity is obtained only by using alkynes with sterically well-differentiated substituents. These reactions appear to follow the same [3 + 2 + 2] mechanism presented earlier to rationalize the iridium reactivity.[42]

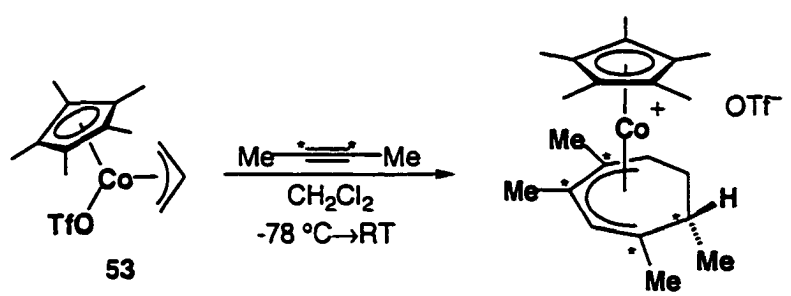
In contrast, simple disubstituted alkynes apparently undergo more complicated transformations. For example, the reactions of cobalt η^3-allyl and η^3-crotyl complexes **53** and **54** with excess 2-butyne result in the formation of the *non-contiguously substituted* η^5-cycloheptadienyl complexes **65** and **66**, respectively (Eq. **29**).[41,43,44] Repeating the reaction of η^3-allyl cobalt complex **53**, but using doubly ^{13}C-labelled 2-butyne yields the quadruply ^{13}C-labelled η^5-tetramethylcycloheptadienyl complex **65**-$^{13}C_4$, conclusively demonstrating that the 2-butyne methyl substituents remain bonded to the labelled carbon atoms throughout the course of the reaction (Eq. **30**). This suggests that the observed products arise from a skeletal rearrangement of the carbon framework, prior to or after cyclization. However, small changes in alkyne substitution suppress this rearrangement: the use of cyclooctyne leads exclusively to the "normal" η^5-cycloheptadienyl product.[43,44]



53 (R = H)
54 (R = Me)

65 (R = H) 81%
66 (R = Me) 58%

(Eq. 29)

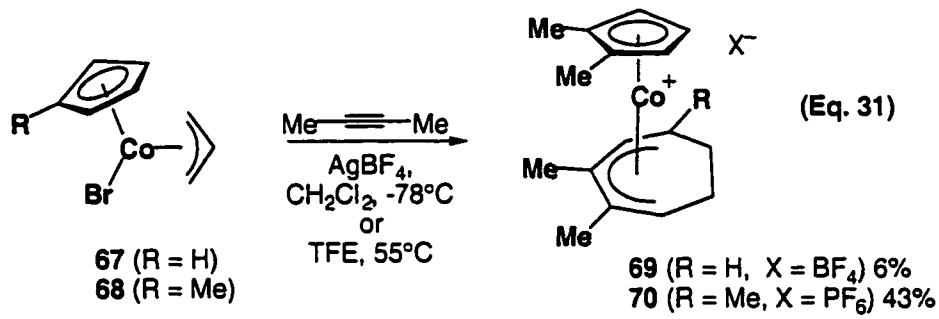


53

65-$^{13}C_4$

(Eq. 30)

Later investigation of less substituted cyclopentadienyl cobalt templates yielded even more unusual reaction products, while also providing critical mechanistic information. Cyclopentadienyl and methylcyclopentadienyl cobalt η^3-allyl complexes **67**



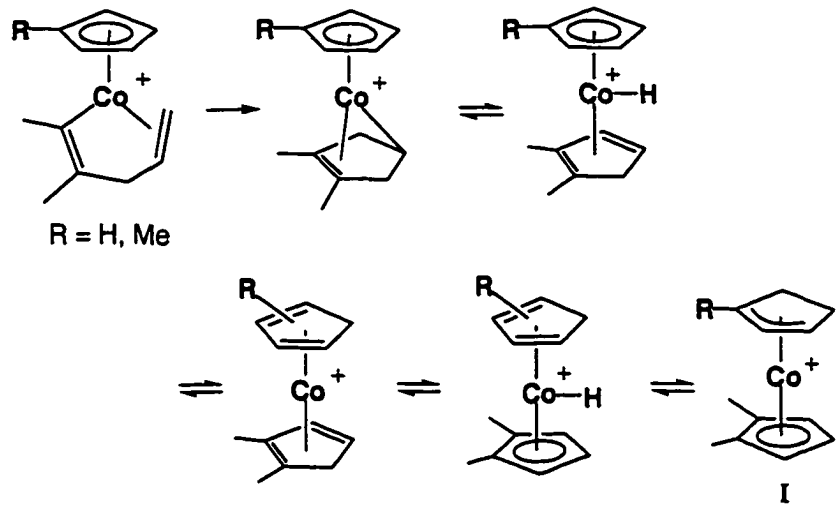
(Eq. 31)

67 (R = H)
68 (R = Me)

69 (R = H, X = BF_4) 6%
70 (R = Me, X = PF_6) 43%

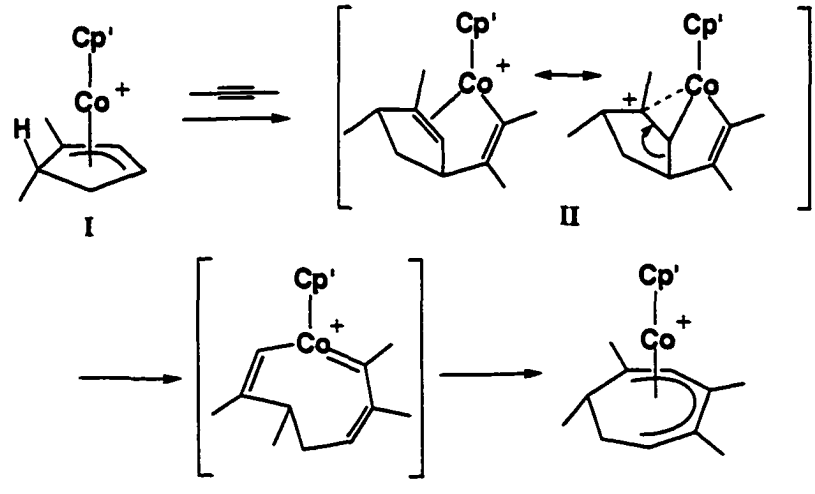
and **68** react with 2-butyne to form η^5-dimethylcyclopentadienyl complexes **69** and **70** containing η^5-cycloheptadienyl ring systems *derived from ring expansion of the original η^5-cyclopentadienyl ancillary ligands* (Eq. **31**).[43,44] It thus appears that (a) cyclization of the vinyl olefin intermediate can be faster than incorporation of the second alkyne, even in reactions that give cycloheptadienyl products, and (b) electrophilic cobalt is capable of activating a carbon-carbon bond in a coordinated five-membered ring under very mild conditions. Based on this information, it was proposed that the η^3-allyl and one equivalent of alkyne initially cyclize to form the η^5-dimethylcyclopentadienyl η^3-cyclopentenyl complex **I**, in the process transferring two hydrogen atoms to the original cyclopentadienyl ring (Scheme **9**). The intermediate **I** then undergoes a second insertion of alkyne, followed by a highly selective carbon-carbon cleavage reaction (Scheme **10**) that leads to the formation of the η^5-cycloheptadienyl ligand. Presumably, a similar process occurs in the reaction of the pentamethylcyclopentadienyl complex with 2-butyne, but the permethylated ring resists disruption, so the reaction proceeds via a

Scheme 9



second alkyne insertion into the intermediate η^3-dimethylcyclopentenyl ring. Two distinct mechanistic pathways therefore exist for cobalt-mediated allyl/alkyne coupling reactions: a [3 +2 + 2] cycloaddition and a [5 + 2] ring expansion, with both processes leading to η^5-cycloheptadienyl products.

Scheme 10



III. Project Goals

The primary objective of this investigation was to explore the fundamental reactivity of alkynes with η^3-allyl ruthenium templates. In particular, we focused on determining those factors controlling the partitioning between the multitude of potential products in the hopes of finding optimal conditions for preparing synthetically useful odd-membered rings. At the same time we also wished to further probe the mechanisms of the seemingly straightforward [3 + 2] cycloaddition and of the more intriguing [3 + 2 + 2] allyl/alkyne reaction pathways.

Schwiebert had previously determined that the sterically large and electron-rich pentamethylpentadienyl iridium template leads to seven-membered carbocycle formation, while the unsubstituted cyclopentadienyl iridium template studied by Rubezhov instead gave rise to six-membered rings while in the presence of excess alkyne. For this reason we chose the isoelectronic η^6-hexamethylbenzene ruthenium template for our initial studies into ruthenium-mediated allyl/alkyne coupling reactions. The hexamethylbenzene ligand should also impart greater stability to the η^6-arene ruthenium complexes, which may allow for a broader range of intermediates to be observed during these reactions.

Chapter 2. [3 + 2] Allyl/Alkyne Coupling Reactions Mediated by the Cationic (η^6-C_6Me_6)Ru(II) Template

I. [3 + 2] Allyl/Alkyne Cycloaddition Reactions

Before beginning an investigation of the (hexamethylbenzene)ruthenium-mediated allyl/alkyne coupling reactions it was necessary to establish an efficient route to the appropriate η^3-allyl complexes. Once a suitable allyl precursor became available, we decided to first evaluate the [3 + 2] allyl/alkyne cycloaddition reaction using this template. We wanted to ascertain whether use of the sterically larger and more electron-rich hexamethylbenzene ligand would significantly affect the formation of the η^5-cyclopentadienyl products from that observed by Rubezhov. We also wished to determine the range of alkynes that would undergo the [3 +2] cycloaddition, as this reaction represents a convergent synthetic route to substituted cyclopentadienyl ligands, and thus may have potentially useful applications in the development of catalyst libraries and for derivatizing alkyne-rich materials and polymers.

1. Preparation of (η^6-C_6Me_6)Ruthenium η^3-Allyl Complexes

One of the most general methods of accessing (η^6-arene)ruthenium(II) complexes is based on the dehydrogenation of 1,3- or 1,4-cyclohexadiene derivatives by ethanolic solutions of $RuCl_3 \cdot xH_2O$.[45] In the case of hexamethylbenzene, however, the cyclohexadiene precursor is not available, so an alternate route was established by

Bennett.[46] The η^6-hexamethylbenzene chloride dimer (**72**) is thus prepared by thermal displacement of a labile *p*-cymene ligand by fusing the readily obtained [(*p*-cymene)$RuCl_2]_2$[45] (**71**) with neat hexamethylbenzene (Eq. **32**).

(Eq. 32)

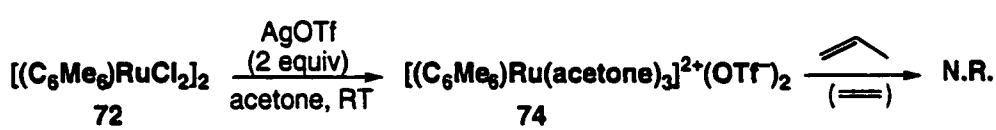
Only a few examples of (η^6-arene)ruthenium allyl complexes are known, mostly involving the parent η^6-benzene template. Zelonka and Baird[47] reported the first synthesis of (η^6-benzene)Ru(η^3-C_3H_5)Cl (**73**), which was prepared by the addition of a large excess (20 equiv) of tetraallyltin to [(η^6-C_6H_6)$RuCl_2]_2$. A more general route to the (η^6-C_6H_6)Ru(η^3-allyl)Cl complexes was later described by Rubezhov,[48] involving the treatment of the dichloride dimer with allylmercuric chlorides (including allyl, methylallyl, crotyl, 1- and 2-phenylallyl and 1-acetyl-2-methylallyl). While both these methods gave satisfactory yields of the desired allyl chloride directly from the ruthenium dichloride dimer, the use of less toxic reagents was preferred for the preparation of the hexamethylbenzene analogues.

A common method for preparing allyl complexes from metal chlorides is the use of Grignard or lithium reagents. However, several research groups have previously reported that Grignard reagents are ineffective for alkylating the parent [(η^6-C_6H_6)$RuCl_2]_2$ dimer, possibly due to its low solubility.[49,45] However, our attempts to add Grignard reagents to the more soluble hexamethylbenzene dimer also did not result in the formation of the desired allyl complex, instead yielding intractable mixtures. One

plausible explanation is that the Grignard reagent acts as a reducing agent, causing the formation of unstable ruthenium(I) complexes that subsequently decompose.

In principle, the most direct access to η^3-allyl complexes involves metal-mediated C-H activation of a simple alkene at an allylic site. Maitlis[50] reported a straightforward method of preparing allyl complexes by allylic activation of alkenes using $[(C_5Me_5)M(acetone)_3]^{2+}(X^-)_2$ (M = Rh, Ir ; X = PF_6). Wakefield later extended this reactivity to a broader range of alkene substrates by the use of ethylene as an "enabling" ligand.[51] Whether the related $[(C_6Me_6)Ru(acetone)_3]^{2+}$ would be able to activate allylic hydrogens in a similar fashion was unknown. A solution of $[(C_6Me_6)Ru(acetone)_3]^{2+}$ $(X^-)_2$ (X = OTf^-, BF_4) (**74**) was thus prepared *in situ* from a suspension of $[(C_6Me_6)RuCl_2]_2$ in acetone by adding 4.0 equivalents of either silver tetrafluoroborate or silver trifluoromethanesulfonate (Scheme **11**).[52] Several attempts were then made to induce the C-H activation of propene, both in the absence or presence of added ethylene, but no evidence of any formed allyl complex was found; only the dicationic acetone complex **74** was ever recovered.

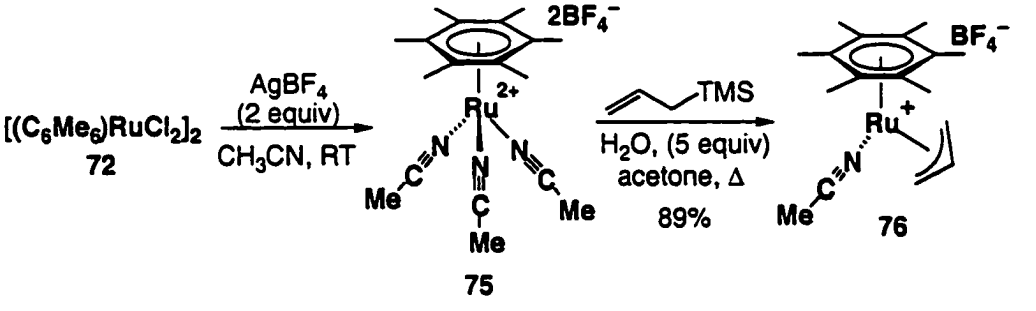
Scheme 11



In cases where metal-mediated allylic C-H activation of an alkene does not readily occur, the more reactive allyltrimethylsilane substrate has been known to undergo C-Si activation, either spontaneously or through addition of an external desilylating agent.[51,53–55] To this end the stable complex $[(C_6Me_6)Ru(CH_3CN)_3]^{2+}(BF_4^-)_2$[45] was

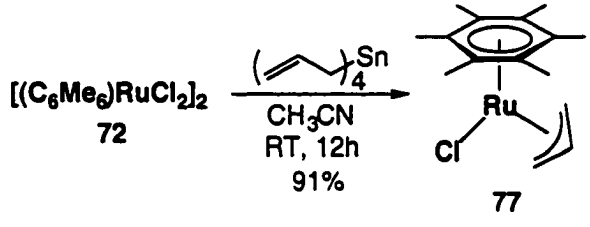
synthesized from addition of 4.0 equivalents silver tetrafluoroborate to an acetonitrile suspension of $[(C_6Me_6)RuCl_2]_2$ (Scheme **12**). Heating the dicationic tris(acetonitrile) complex with excess allytrimethylsilane in acetone solution for an extended period of time results in only partial conversion to the desired $[(C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(CH_3CN)]^+BF_4^-$ (**76**) (approximately 50%). However, addition of several equivalents of water to the reaction mixture significantly increases the yield to 89%. In this case water probably acts as a mild desilylating reagent,[56] although no attempt was made to identify the silyl byproducts of the reaction.

Scheme 12



While a ruthenium η^3-allyl complex was now available, this route presents several problems. The heavy use of silver salts renders this process unattractive as a general method due to the expense of silver reagents. More importantly, the acetonitrile ligand was found to be strongly coordinated to the metal and would exchange with other ligands only slowly; a more labile ancillary ligand was required. For this reason, we returned to the tetraallyltin reagent as a more direct method of obtaining an η^3-allyl complex. Treatment of a suspension of $[(C_6Me_6)RuCl_2]_2$ in acetonitrile with tetraallyltin affords $(C_6Me_6)Ru(\eta^3\text{-}C_3H_5)Cl$ (**77**) in nearly quantitative yield (Eq. **33**). Only one to two

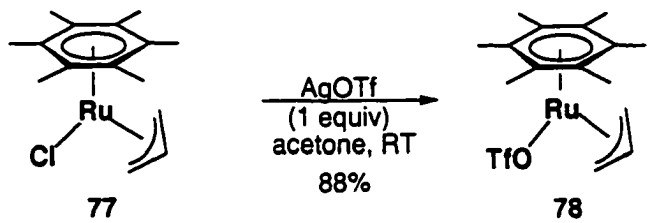
equivalents of tetraallytin are required instead of the twenty equivalents used by Zelonka,[47] which greatly simplifies the isolation and purification of the product. The more convenient tin reagent, allyltriphenyltin, is also effective in forming the allyl chloride, although the yield is somewhat lower (75%) and the byproduct of the reaction, Ph_3SnCl, requires chromatography to separate it from the allyl product. The η^3-allyl ligand configuration in $(C_6Me_6)Ru(\eta^3\text{-}C_3H_5)Cl$ is assigned as *exo* (where the central C-H bond of the allyl is oriented toward the hexamethylbenzene ligand) due to the similarity of the ^1H and ^{13}C NMR spectroscopic data to the analogous $(C_6H_6)Ru(\eta^3\text{-}C_3H_5)I$ complex, which was previously determined to be in the *exo* configuration by X-ray structural analysis.[48b]



(Eq. 33)

The prior success of the iridium and cobalt allyl triflate templates suggested that the $(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-allyl})$ triflate would be a suitable precursor for the alkyne cyclization chemistry. Thus, treatment of the ruthenium allyl chloride **77** with a slight excess of silver triflate provides the triflate complex **78** in high yield as a mildly air-sensitive orange powder (Eq. **34**). The η^3-allyl triflate complex **78** is moderately soluble in benzene, implying inner-sphere coordination of the triflate anion to form a neutral complex in non-polar media. Schwiebert determined that the closely related iridium analogue $(C_5Me_5)Ir(\eta^3\text{-}C_3H_5)(OTf)$ **42** exists in an equilibrium between the neutral, inner-sphere triflate and the charge-separated, outer-sphere complex $[(C_5Me_5)Ir(\eta^3\text{-}$

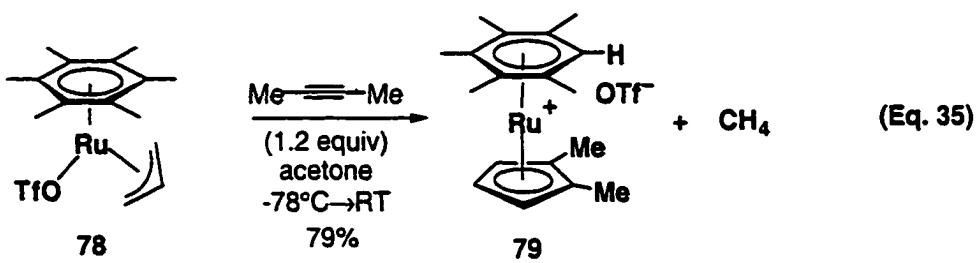
$C_3H_5)]^+OTf^-$, an equilibrium which is highly dependent on the solvent polarity.[38a,39] It is likely that the ruthenium allyl triflate behaves similarly, a hypothesis also supported by the observed shift of the allyl resonances in the ^1H NMR spectrum upon changing solvents: in chloroform-d (or dichloromethane-d_2) a characteristic first order allyl pattern is present, while in benzene-d_6 a second order pattern emerges due to the closer proximity of the central proton and the *syn* proton signals.



77 78 (Eq. 34)

2. Ruthenium-Mediated [3 + 2] Allyl/Alkyne Cycloaddition Reactions

The addition of a slight excess of 2-butyne (1-3 equiv) to the triflate complex **78** at room temperature (in either acetone or dichloromethane) results in the formation of a white crystalline solid in 79% yield (Eq. **35**). Analysis by both ^1H and ^{13}C NMR spectroscopy shows clear evidence of a newly formed disubstituted cyclopentadienyl ligand: a doublet at δ 4.89 (integrating to two hydrogens) and a triplet at δ 4.83



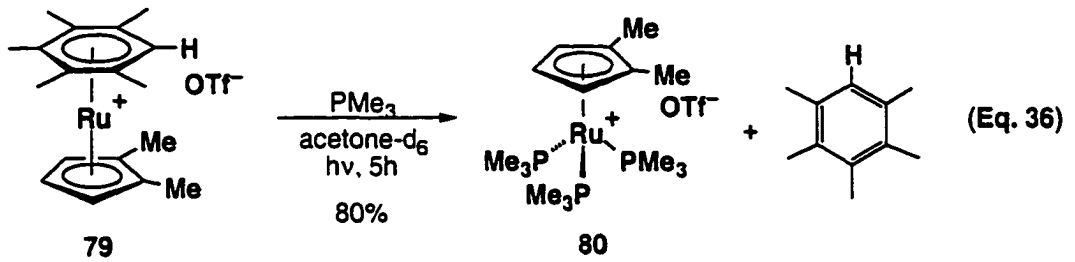
78 79 (Eq. 35)

(integrating to one hydrogen), which exhibit very small vicinal coupling constants ($^3J_{HH}$ = 2.4 Hz) for the methine hydrogen atoms. The methine carbon atoms were determined to have large one-bond carbon-hydrogen coupling constants ($^1J_{CH}$ =175-182 Hz), also characteristic of η^5-cyclopentadienyl ligands.[39,43] However, NMR spectroscopic analysis also reveals that the symmetry of the hexamethylbenzene ligand has been broken. The ^{1}H NMR spectrum exhibits a downfield singlet at δ 6.01 (1H) and three methyl singlets at δ 2.26 (3H), 2.25 (6H), and 2.21 (6H), which is consistent with the presence of an η^6-pentamethylbenzene ligand. The product of allyl triflate **78** is thus identified as the cationic complex [(η^6-pentamethylbenzene)Ru(η^5-dimethylcyclopentadienyl)]$^+$OTf$^-$ (**79**). Elemental analysis of the crystalline product also confirmed the loss of a methyl group.

To determine the ultimate fate of the methyl group, the reaction with 2-butyne was repeated in acetone-d_6 using a sealed NMR tube and monitored by ^{1}H NMR spectroscopy. The formation of methane was detected (δ 0.15 in acetone-d_6) and confirmed by direct comparison to an authentic sample (from natural gas line). No intermediates were observed during the course of this reaction, which goes to completion within a few minutes at room temperature.

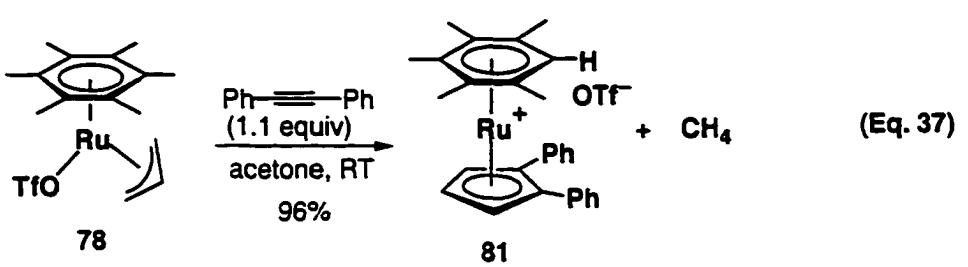
To confirm the presence of an η^6-pentamethylbenzene ligand, a solution of the dimethylcyclopentadienyl complex **79** in a sealed NMR tube was subjected to photolysis conditions (450 W, Hanovia, Pyrex filter) in the presence of three equivalents of trimethylphosphine (Eq. **36**). After five hours of photolysis at room temperature no further changes in the ^{1}H NMR spectrum were observed. The final equilibrium mixture was found to consist of the tentatively assigned [(η^5-$C_5H_3Me_2$)Ru(PMe_3)$_3$]$^+$OTf$^-$, **80**, and starting material (4 : 1), along with free pentamethylbenzene, as determined by ^{1}H

NMR spectroscopy. An authentic sample of commercial pentamethylbenzene was used to verify the presence of the liberated arene. While the cationic tris(phosphine) complex **80** was not isolated from the photolysis reaction mixture, it is spectroscopically very similar to the known complex, $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_3]^+PF_6^-$.[57]

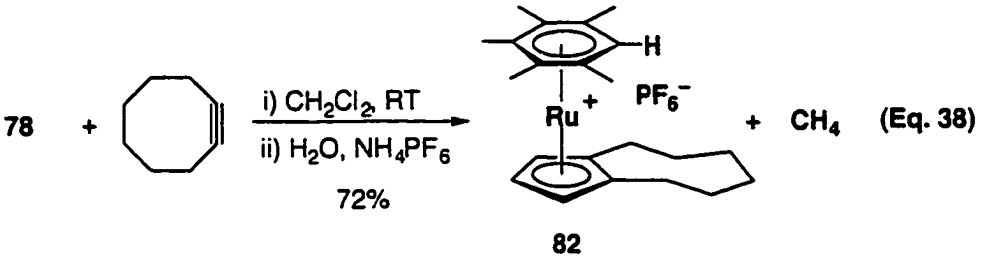


79 **80** **(Eq. 36)**

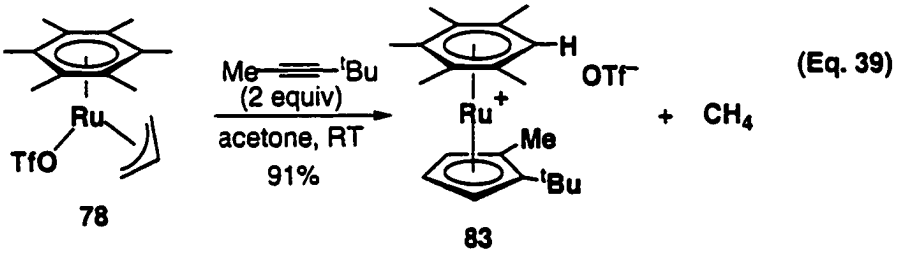
Treatment of allyl triflate **78** with an equivalent of diphenylacetylene also results in the formation of a demethylated product, the η^5-diphenylcyclopentadienyl complex **81** in very high yield (96% after recrystallization) (Eq. **37**). ^{1}H NMR spectroscopic analysis again exhibits a characteristic downfield singlet at δ 6.08 and three methyl singlets between δ 2.20 and δ 2.00 for the coordinated pentamethylbenzene, as well as the cyclopentadienyl resonances at δ 5.41(d, J = 2.5 Hz, 2H) and δ 5.34 (t, J = 2.5 Hz, 1H). The addition of cyclooctyne to the allyl triflate complex **78** also cleanly forms the disubstituted cyclopentadienyl η^6-pentamethylbenzene product **82** (Eq. **38**). The lower yield obtained using this alkyne (72%) results from the need to perform a counterion exchange from triflate to hexafluorophosphate in order to isolate a crystalline product.



78 **81** **(Eq. 37)**



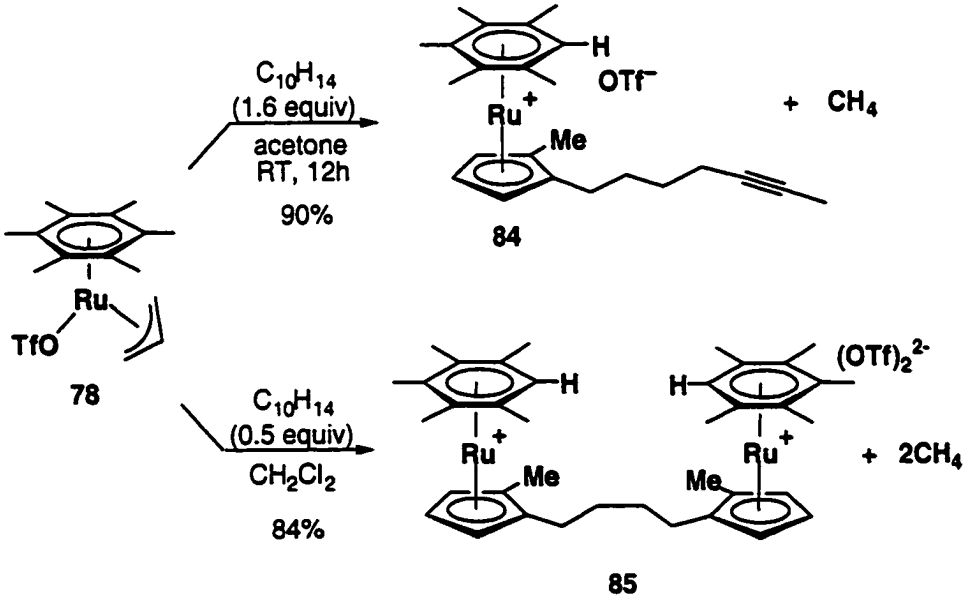
The unsymmetrical alkyne, 4,4-dimethyl-2-pentyne, also gives a high yield of the disubstituted cyclopentadienyl η^6-pentamethylbenzene product **83** in high yield (91% after recrystallization) (Eq. **39**). Unlike the previous examples, the resulting η^5-cyclopentadienyl complex **83** exhibits no plane of symmetry. This is evident from the spectroscopic analysis as both ^1H and ^{13}C NMR spectra reveal that five inequivalent methyl groups for the coordinated pentamethylbenzene ligand, all located between δ 2.40 and δ 2.25 in the ^1H NMR spectrum and between 20.0 and 16.1 ppm in the ^{13}C NMR spectrum.



In contrast to the iridium case,[38b,39] treating ruthenium allyl triflate **78** with one equivalent of 2,8-decadiyne does not result in a seven-membered ring product; instead, the mono(cyclopentadienyl) complex **84** with a pendant alkyne is formed selectively (Scheme **13**). While this compound is initially formed in high yield (approximately 90%) under dilute reaction conditions, it is more difficult to purify than other η^5-cyclopentadienyl ruthenium products since the complex is neither crystalline nor stable

towards standard chromatography conditions. Spectroscopically, the crude compound is quite pure, with characteristic resonances exhibited in the ^{1}H NMR spectrum for the methine hydrogen of the η^6-pentamethylbenzene ligand (δ 5.92, s), and the methyl substituent of the pendant alkyne (δ 1.74, t, J = 2.5 Hz). A weak band appears at 2310 cm^{-1} in the infrared absorption spectrum, indicative of the presence of a free disubstituted alkyne. The use of two equivalents of the allyl triflate **78** results in the formation of the tethered bis(cyclopentadienyl) complex **85**; this compound can also be made by adding an equivalent of allyl triflate **78** to the crude mono(cyclopentadienyl) complex **84**. This tethered dicationic complex (**85**) is readily precipitated as a white powder from hot acetone, and is formed as an inseparable 1 : 1 mixture of the expected diastereomers.

Scheme 13



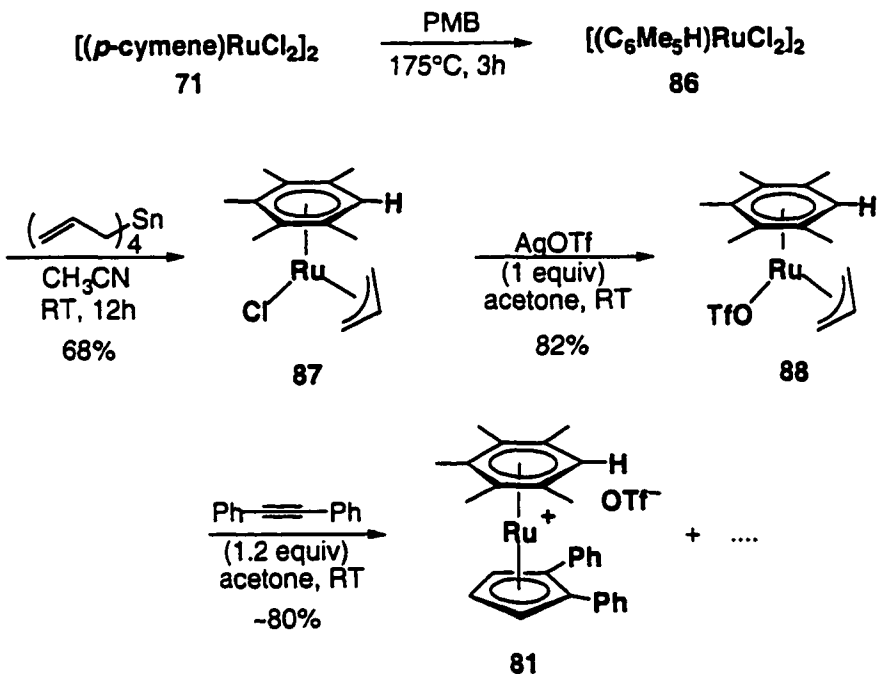
The ruthenium mediated [3 + 2] allyl/alkyne cycloaddition with concomitant demethylation thus appears to be general for dialkyl or diaryl substituted alkynes. No trace of a hexamethylbenzene η^5-cyclopentadienyl product was detected for any of these particular alkynes. In general, the presence of excess alkyne had no significant effect on the course of these reactions. One exception to this is the addition of excess 2-butyne, which results in the formation of a double insertion product that will be discussed further in the following chapter.

Alternative reaction conditions may also be employed to generate the unsaturated ruthenium η^3-allyl complex, aside from the use of triflate as a labile ligand. For example, the *in situ* ionization of the chloride from allyl **77** using silver salt, as previously demonstrated by Rubezhov, provides identical products. The need for silver reagents can be obviated by the use of trifluoroethanol, a highly polar solvent medium; the ruthenium chloride complex **77** readily ionizes in this solvent to provide the unsaturated ruthenium center. While both sets of conditions result in five-membered ring formation accompanied by demethylation, the reactions using the triflate complex **78** generally proceed more cleanly and provide [3 + 2] cycloadducts in higher isolated yields than either of the alternatives.

The loss of the methyl group during the course of this cycloaddition represents a rare example of carbon-carbon bond cleavage under surprisingly mild reaction conditions. One explanation may be that the bond cleavage is driven by relief of the cumulative steric strain experienced by the six mutually buttressed methyl substituents in the hexamethylbenzene ligand. To address this possibility, the pentamethylbenzene ruthenium dimer, $[(\eta^6\text{-}C_6Me_5H)RuCl_2]_2$ **86** was prepared from the *p*-cymene dimer by

ligand exchange under conditions similar to those used to prepare hexamethylbenzene dimer **72** (Scheme **14**). After isolation and purification by recrystallization, the pentamethylbenzene dimer was obtained in approximately 40% yield. The pentamethylbenzene allyl triflate complex **88** was then readily synthesized by the same methodology used to obtain the hexamethylbenzene analogue. The subsequent reaction

Scheme 14



of $(\eta^6\text{-}C_6Me_5H)Ru(\eta^3\text{-}C_3H_5)OTf$ (**88**) and diphenylacetylene provides mainly the η^6-pentamethylbenzene diphenylcyclopentadienyl complex **81** (>80% yield), spectroscopically identical to that obtained from the hexamethylbenzene triflate **78**. Accompanying the major product are trace amounts of several unidentified, but presumably demethylated minor products, as evidenced by singlet resonances between δ

5.95-6.10 and between δ 1.95-2.20 in the ^{1}H NMR spectrum, corresponding to various coordinated tetramethylbenzene ligands. Quantitative dealkylation of the arene ligand thus appears to be limited to the hexamethylbenzene template, supporting a steric origin of the driving force of the reaction. A more in-depth investigation was required, however, to determine the mechanism of the demethylation process.

II. Mechanistic Investigation of the Ruthenium-Mediated [3 + 2] Allyl/Alkyne Cycloaddition Reactions with Concomitant Demethylation

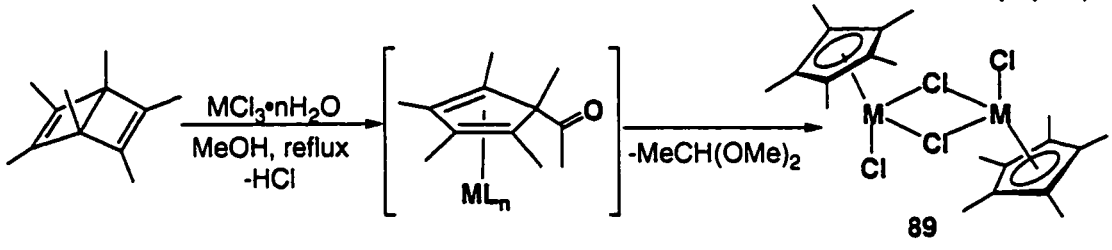
1. Introduction and Background

The use of metal complexes to promote the activation of carbon-carbon bonds is an area of much current interest due to the potential for developing the more efficient utilization of hydrocarbon feedstocks. While carbon-hydrogen bond activation is by now relatively common, examples of carbon-carbon bond activation by soluble metal complexes are far more rare.[58] Several factors, both kinetic and thermodynamic, tend to favour C-H over C-C bond activation: a) the easier approach of the metal center to peripheral C-H bonds, b) the relatively higher abundance of C-H bonds, and c) the generally higher activation barrier for C-C versus C-H oxidative addition due to the more directed nature of the C-C bond.[58a] Gas phase reactions with "bare" atomic metal cations can induce carbon-carbon bond cleavage of alkanes,[59] as can the use of superacids, (such as $HSbF_6 \cdot SbF_5$),[60] although the use of such harsh conditions usually results in low selectivity. Other kinetic and thermodynamic effects that can be used to overcome the barriers to C-C bond activation include the relief of ring strain,[61] coordination-induced proximity (itself encompassing both β-alkyl elimination[62] and oxidative cleavage[63]), ligand aromatization, and combinations of these factors.[64]

While many classes of carbon-carbon bond activation exist, the type that appears to be the most closely related to the observed ruthenium-mediated demethylation process are reactions that result in the formation of an aromatic ligand. In these systems, the

driving force for carbon-carbon bond activation is assumed to be the aromatic stabilization energy gained during the course of the reaction. A classic example, first reported by Maitlis, is the rhodium or iridium trichloride mediated conversion of hexamethyldewarbenzene to the stable η^5-pentamethylcyclopentadienyl metal dimers **89**.[65] Although the reaction sequence involves several steps, including rearrangement of the strained bicyclo[2.2.0] framework, the final one is the scission of the cyclopentadiene-acyl bond (Eq. **40**). In related work, King independently studied the carbon-carbon bond activation of the ring-acetyl bond during reactions of acetyl-pentamethylcyclopentadiene with transition metal complexes.[66]

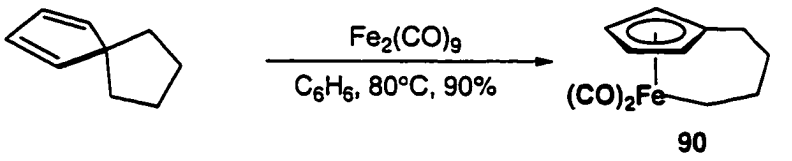
(Eq. 40)



89

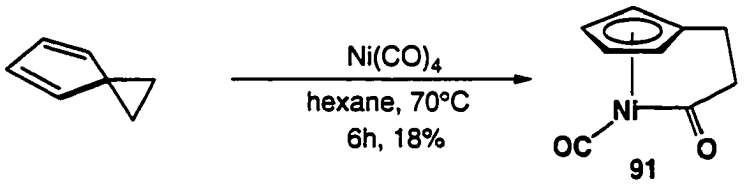
Carbon-carbon activation leading to aromatic ligands is also obtained when iron, nickel, molybdenum, or tungsten carbonyl complexes react with spirocyclic cyclopentadienes (Eqs. **41** and **42**). Eilbracht demonstrated early on that the facile carbon-carbon bond cleavages of these [4.n]spiroalkadiene compounds are most likely driven by the aromaticity of the final product.[67] In most cases, these reactions result in η^5-cyclopentadienyl σ-alkyl complexes such as **90**; sometimes, however, carbon monoxide will insert into the newly formed alkyl bond to give an σ-acyl complex (**91**). Similar chemistry was observed by Green upon co-condensation of molybdenum atoms and spiro[2.4]hepta-4,6-diene.[68] Related to this chemistry is the molybdenum-mediated

reversible rearrangement of an ethyl group to and from a cyclopentadienyl ring (Eq. 43).[68]



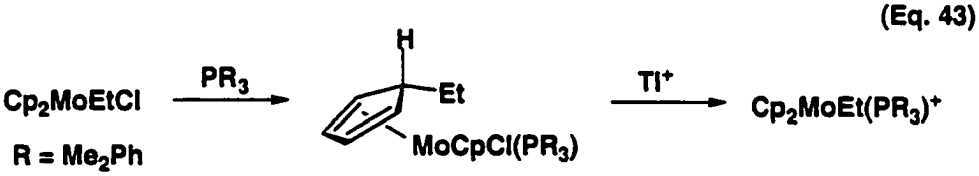
90

(Eq. 41)



91

(Eq. 42)

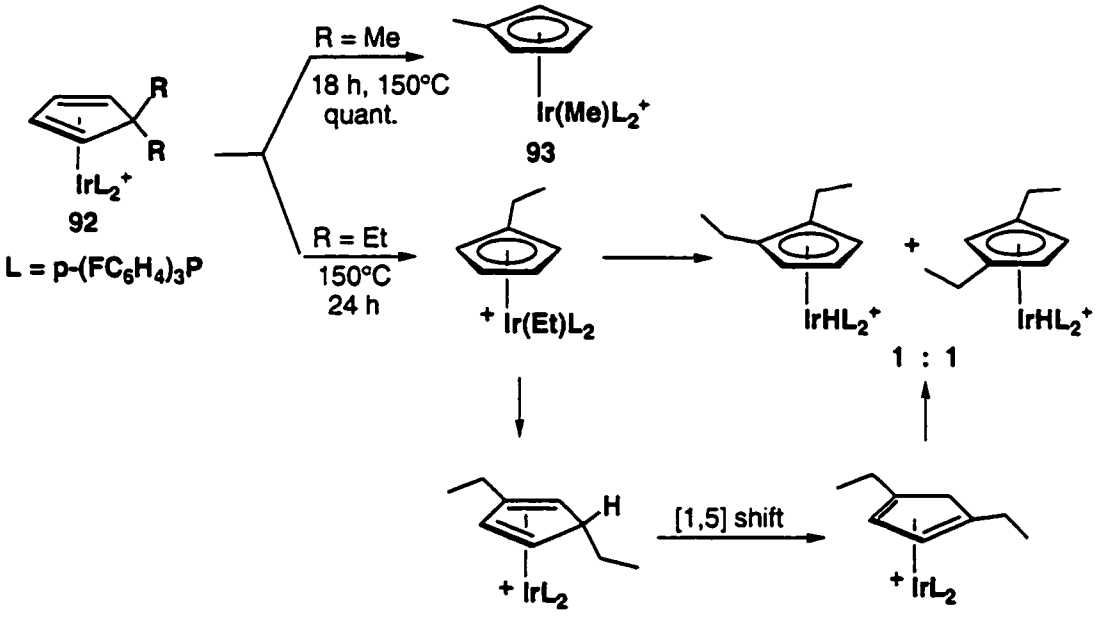


(Eq. 43)

Crabtree has reported carbon-carbon bond activation reactions involving unusual rearrangements during his study of iridium complexes of 1,1-dialkylcyclopentadienes (Scheme **15**).[69] These reactions appear to be greatly dependent on the nature of the alkyl substituent. For example, the 1,1-dimethylcyclopentadiene complex **92** (R = Me) undergoes direct scission of the *endo* methyl group, forming methylcyclopentadienyl complex **93**. However, the diethylcyclopentadiene complex does not undergo reductive elimination of ethane; instead the presumed intermediate, $[(EtCp)Ir(Et)L_2]^+$, rearranges by ethyl migration back to a different carbon atom on the ring. Carbon-hydrogen bond activation then follows, to form a mixture of 1,2- and 1,3-diethylcyclopentadienyl isomers (approximately 1 : 1 ratio). When 1-ethyl-1-methylcyclopentadiene is coordinated to the iridium center, a 3:1 mixture of isomers results where the major

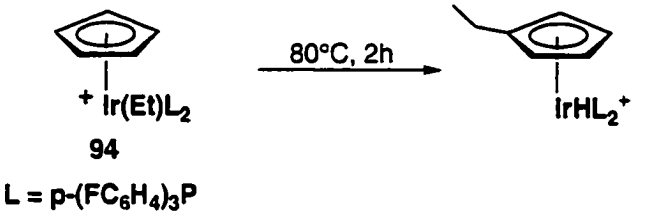
product is the one bearing the *endo*-methyl substituent. Isolation of the major product followed by thermolysis (85°C, 2 hours), results in the selective cleavage of this *endo* methyl group.

Scheme 15



Crabtree rationalizes these differences in reactivity by suggesting that the Ir-Me bond is significantly stronger than the Ir-Et bond. Carbon-carbon bond activation of **92** produces a stable, isolable product $[(MeCp)Ir(Me)L_2]^+$. In contrast, the ethyl analogue is unstable with respect to further rearrangement and forms a new diethylcyclopentadiene ligand. Crabtree then proposes a [1,5]-hydride shift on the *exo* face of the Cp ring in order to place a hydrogen atom *endo* to the metal where it is available for carbon-hydrogen activation, giving the final hydride product. The lability of the Ir-Et bond in

this system is also demonstrated in the related complex **94**, which rearranges upon heating to form an ethylcyclopentadienyl hydride (Eq. **44**).[69]



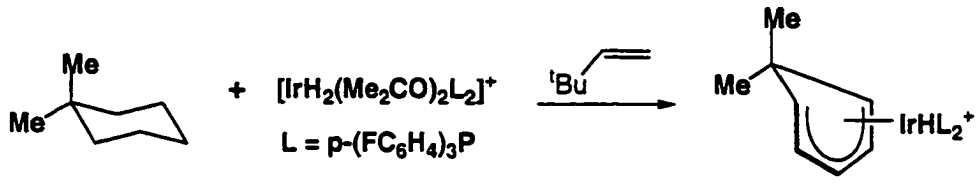
94

L = p-(FC$_6$H$_4$)$_3$P

(Eq. 44)

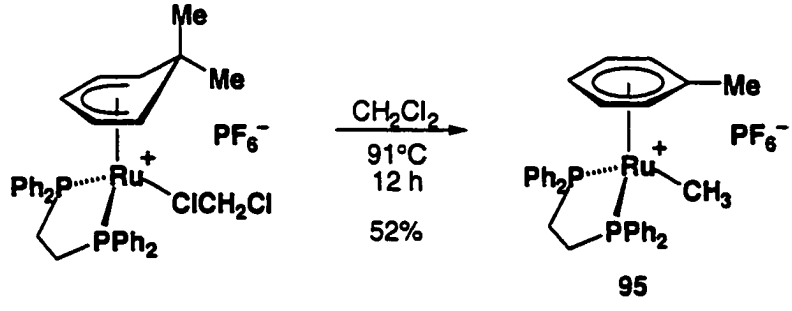
Carbon-hydrogen bond activation of cyclopentadiene substrates has been a common route to forming η^5-cyclopentadienyl ligands; however, competitive carbon-carbon bond cleavage has occasionally been observed during reactions with substituted cyclopentadienes. For instance, Jones[70] finds small amounts of such carbon-carbon bond activation products in the reaction of a rhenium polyhydride complex with methylcyclopentadiene. Hughes[71] has also reported that the standard reaction of pentamethylcyclopentadiene with $Mn_2(CO)_{10}$ actually yields up to 23% (η^5-$C_5Me_4H)Mn(CO)_3$ rather than the desired (η^5-$C_5Me_5)Mn(CO)_3$ due to competitive carbon-carbon bond cleavage.

In marked contrast to the substituted cyclopentadiene systems, there are relatively few examples of carbon-carbon bond activation occurring in substituted cyclohexadienyl derivatives, despite the formation of a thermodynamically stable aromatic ring as a result. The reaction of 6,6-dimethylcyclohexane with Crabtree's iridium precursor resulted only in the formation of a stable 6,6-dimethylcyclohexadienyl hydride iridium complex (Eq. **45**); carbon-carbon bond scission could not be induced, presumably because the iridium is coordinatively saturated at the η^5-cyclohexadienyl stage, whereas the cyclopentadiene derivatives are not.[69] Similarly, Wolczanski finds that initial generation of an unsaturated



(Eq. 45)

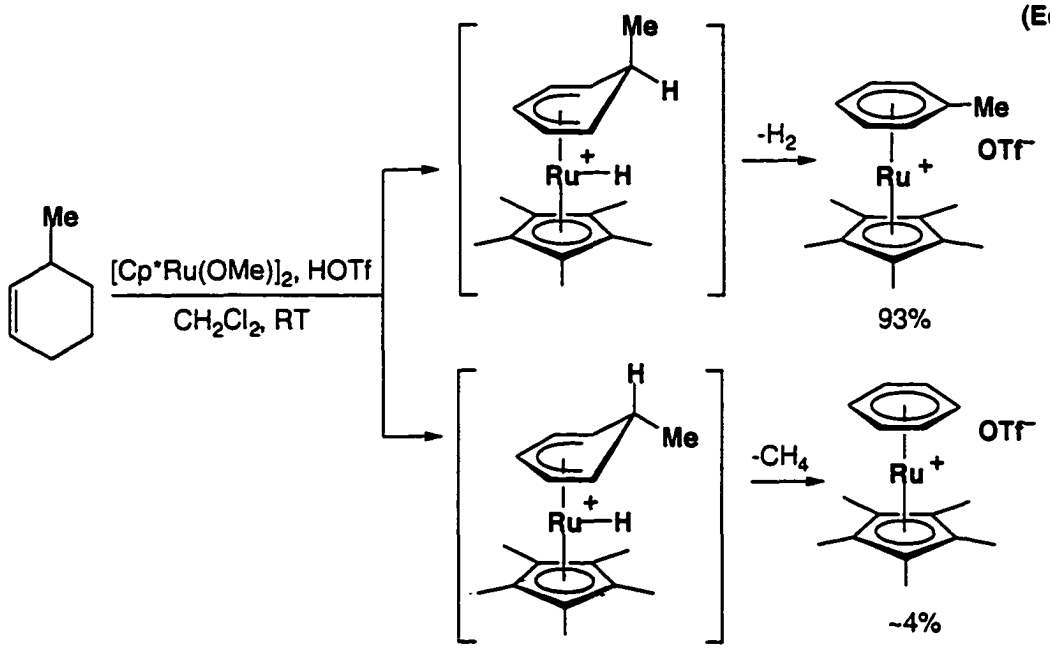
complex is required to induce β-methyl elimination in a 6,6-dimethylcyclohexadienyl ruthenium complex, producing the stable η^6-toluene complex **95** from thermolysis of $[(dppe)Ru(1,1\text{-dimethylcyclohexadienyl})(CH_2Cl_2)]^+PF_6^-$.[72] Even under optimal conditions, prolonged reaction times at high temperatures are still necessary to induce this carbon-carbon bond cleavage (Eq. 46). Addition of a one-electron oxidant to bis(6,6-dimethylcyclohexadienyl)ruthenium also results in aromatization of one ligand to η^6-toluene, although Wolczanski was unable to determine in either case whether the methyl group was lost from the *exo* or *endo* face.



95

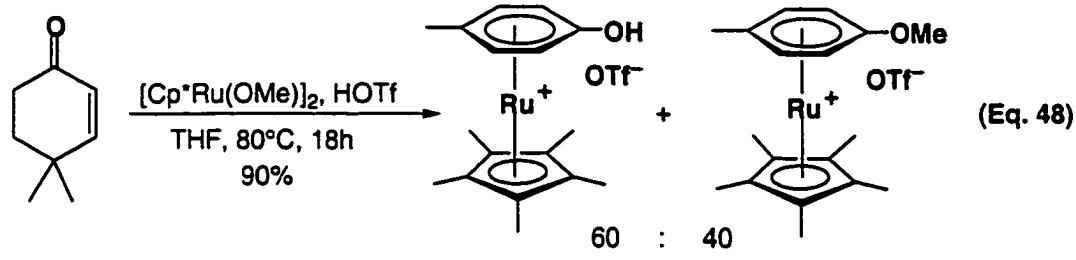
(Eq. 46)

Chaudret found milder examples of dealkylation during his studies on the reactivity of the electrophilic $C_5Me_5Ru^+$ unit.[73] This fragment, prepared *in situ* from $[(\eta^5\text{-}C_5Me_5)Ru(OMe)_2]_2$ and triflic acid, has a high binding affinity for arene ligands, and is also capable of dehydrogenating cyclic olefins to form complexed arenes. When allowed to react with 3-methylcyclohexene below room temperature, the η^6-toluene compound was found to be the primary product; however, a small amount (ca. 4%) of

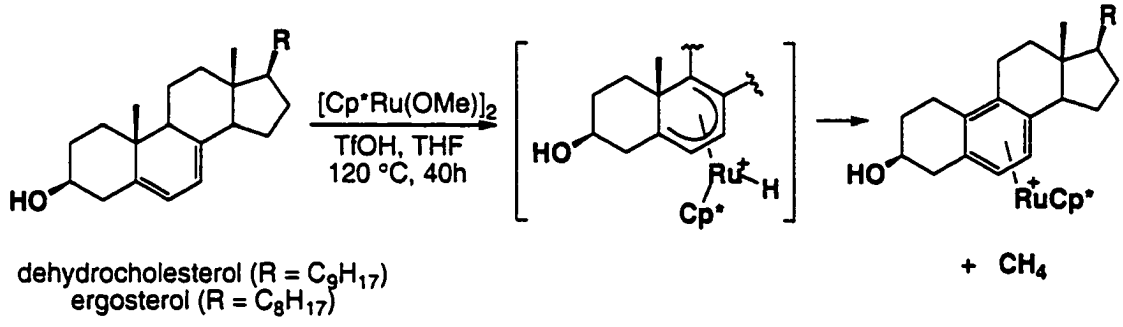


(Eq. 47)

the η^6-benzene complex, resulting from carbon-carbon bond activation, was detected along with traces of methane (Eq. **47**). This reaction was thought to proceed through two separate intermediates, formed through differential coordination of the 3-methylcyclohexene to the two diastereotopic faces of the cyclohexene. To further test this reactivity, the reaction of the electrophilic ruthenium fragment and 4,4-dimethylcyclohexen-1-one was investigated and found to produce a mixture of 4-methylphenol and 4-methylanisole ruthenium complexes (Eq. **48**). Trace amounts of ethane were also detected along with the expected methane and, on the basis of this observation, Chaudret proposed that these dealkylation reactions involve a radical mechanism.[73a] Steroids featuring at least one double bond in the A or B ring (testosterone, progesterone, cholesterol, ergosterol and dehydroisoandrosterone) are also aromatized by this process using forcing conditions (Scheme **16**) with concomitant loss of the 18-methyl group.[73b-d]



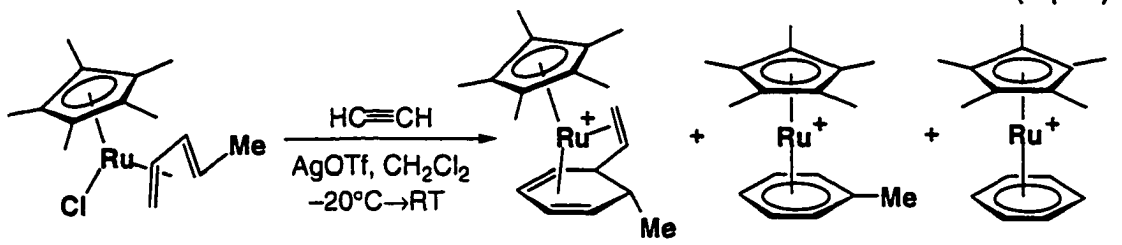
Scheme 16



dehydrocholesterol (R = C_9H_{17})
ergosterol (R = C_8H_{17})

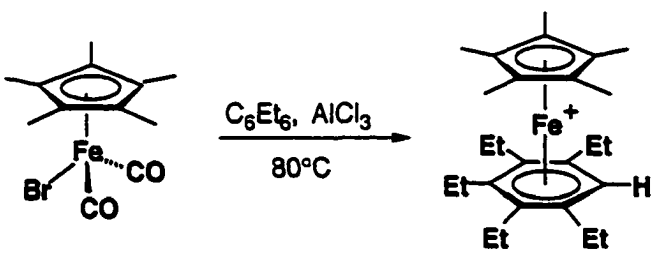
Itoh has reported that a very mild demethylation pathway exists in (η^5-C_5Me_5)Ru-mediated [4 + 2] diene/alkyne cycloaddition reactions, leading to minor amounts of carbon-carbon activation products.[74] When (η^5-C_5Me_5)Ru(η^4-1,3-pentadiene)Cl is treated with silver triflate in the presence of acetylene, a small amount of [(η^5-C_5Me_5)Ru(η^6-C_6H_6)]$^+$OTf$^-$ and methane is recovered along with the η^6-toluene complex and a double-acetylene insertion product (Eq. **49**). The minor dealkylated product was thought to arise from the low stereoselectivity of the cyclization step, resulting in the formation of a small amount of the *endo*-methyl isomer, which subsequently loses methane by the same process initially described by Chaudret.

(Eq. 49)



6.8 : 1 : 1.1

The demethylation of hexamethylbenzene observed during the [3 + 2] allyl/alkyne cyclizations may be related to the well-established dealkylation of polyalkylarenes found during $AlCl_3$-mediated exchange reactions of (cyclopentadienyl)metal complexes (e.g., Eq. **50**).[75,76] Astruc established that these side reactions occur more readily in ruthenium than in the analogous iron systems, and that the source of the hydrogen atom that replaces the alkyl group is proton-containing impurities present in commercial aluminium chloride.[75b] Astruc also determined that there is no dealkylation of the free arene ligand under these reaction conditions and he therefore concludes that the dealkylation occurs at some non-sandwich stage of the reaction, after (or during) coordination of the arene. No further mechanistic investigation on this dealkylation process has been reported.

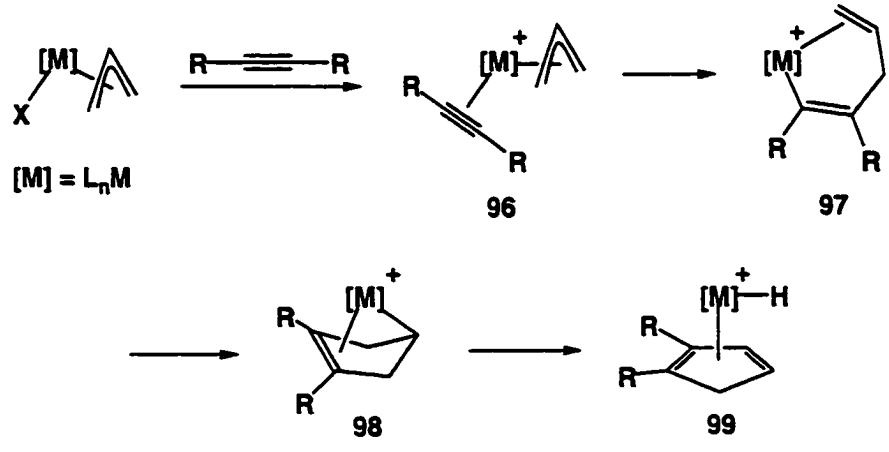


(Eq. 50)

2. Mechanism of General [3 + 2] Allyl/Alkyne Cycloaddition Reactions

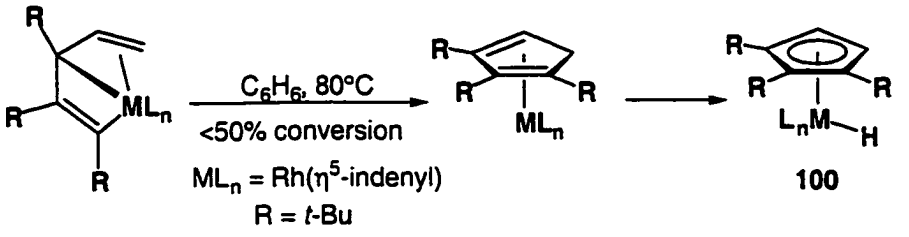
All of the reported dehydrogenative [3 + 2] allyl/alkyne coupling cycloaddition reactions presumably begin with the generation of an unsaturated metal center, either through silver abstraction of a halide ligand or through solvolytic ionization of an anionic ligand (such as triflate or chloride). Alkyne then coordinates to the cationic metal, forming an intermediate η^3-allyl η^2-alkyne complex **96** (Scheme **17**). Such complexes have been isolated by Schwiebert in the isoelectronic iridium system[38,39] and observed spectroscopically at low temperature by Etkin in cobalt.[77] The cationic allyl alkyne complexes of both iridium and cobalt are highly reactive and rapidly form cycloadducts upon warming in a polar solvent. The coordination of alkyne to the metal appears to be relatively weak and reversible, since Rubezhov[35] reports no evidence for alkyne coordination in the coordinating solvents DMSO and acetonitrile and Schwiebert observes substantial alkyne displacement by carbon monoxide during trapping experiments.[39]

Scheme 17



Subsequent migratory coupling of the allyl and alkyne ligands results in the formation of a vinyl olefin complex, **97**. Schwiebert prepared isolable vinyl olefin carbonyl complexes of iridium by using carbon monoxide as a trapping agent, although competitive displacement of the alkyne by CO was also observed.[39] These iridium vinyl olefin complexes were also shown to be competent intermediates in the formation of both five- and seven-membered cycloadducts (Scheme **7**, p 24).

While the vinyl olefin carbonyl complexes prepared by Schwiebert are stable, induced decarbonylation apparently leads to a highly reactive unsaturated intermediate, which is most likely stabilized through the coordination of solvent, triflate anion or additional alkyne. Another structural possibility is the transient formation of an η^2-vinyl ligand, if the metal orbitals are oriented properly.[78] The vinyl olefin intermediates do not always cyclize, as reactions in several related systems give acyclic η^5-pentadienyl products instead.[28,29] The proposed mechanism of this transformation will be discussed in a later chapter. In most cationic systems and in the absence of added alkyne, however intermediate **97** reacts to form a cyclopentadienyl ligand by cyclization followed by loss of hydrogen gas. The most likely mechanism for this step is the migration of the vinyl moiety to the olefin to produce a nonconjugated η^1,η^2-cyclopentenyl complex **98**, which can then undergo facile β-hydride elimination to form cyclopentadiene hydride intermediate **99**. Hughes reports a similar migratory rearrangement in distantly related iridium and rhodium systems (Eq. **51**), starting with 1,3,4,5-η^4-pentadienediyl complexes, resulting in the observed cyclopentadienyl hydride **100**.[79] Other plausible, but less likely, mechanisms for this process have also been proposed.[43]

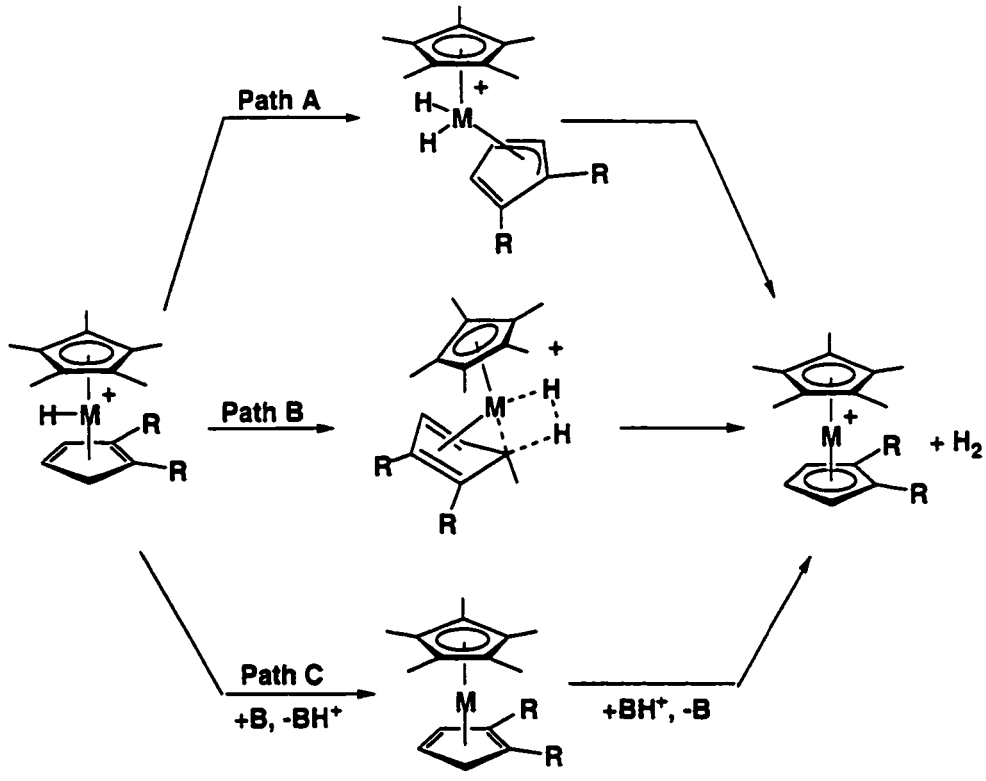


(Eq. 51)

The loss of hydrogen from the cyclopentadiene hydride intermediate could arise from one of several different mechanistic pathways (Scheme **18**), which may depend on the particular system. It is also possible that more than one mechanism operates concurrently. While Rubezhov did not undertake a mechanistic study, he did observe the formation of dihydrogen and stilbene during the reaction of $(C_6H_6)Ru(\eta^3\text{-allyl})^+$ and diphenylacetylene.[35] Many other examples of hydrogen loss or transfer from cyclopentenyl or cyclopentadiene complexes are known. For example, the reaction of nickel(II) bromide with cyclopentenylmagnesium bromide yields (η^5-cyclopentadienyl)(η^3-cyclopentenyl)nickel exclusively, instead of the expected bis(η^3-cyclopentenyl)nickel.[80] Several groups have also reported that the reaction of metal hydrides with cyclopentadiene generates η^5-cyclopentadienyl complexes rather than cyclopentenyl products.[81]

The simplest mechanistic pathway leading to hydrogen loss is the formation of a metal dihydride complex from C-H activation of the doubly allylic methylene in the cyclopentadiene ligand with concomitant ring slippage to an $18e^-$ intermediate (path **A**, Scheme **18**). Reductive elimination from this high oxidation state intermediate produces dihydrogen and the η^5-cyclopentadienyl product. Several stable pentavalent rhodium and iridium alkyl and hydride (or polyhydride)[82] complexes are known, as are several tetravalent ruthenium polyhydride compounds.[82b] The existence of such high valent

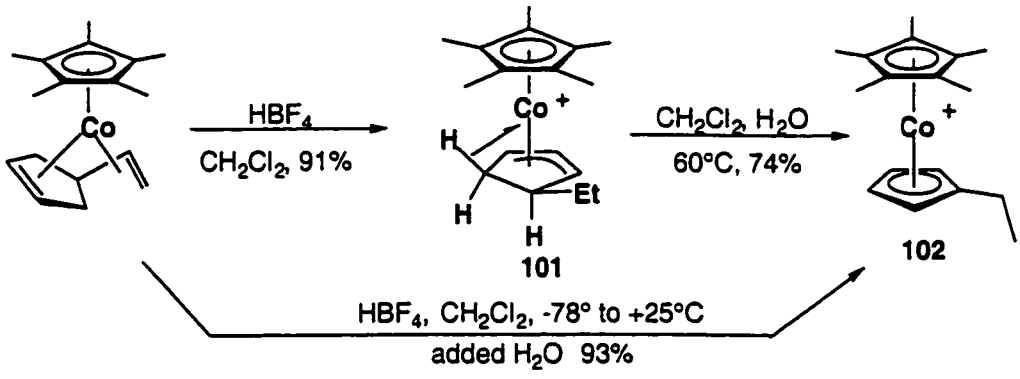
Scheme 18



compounds lends support to the possibility of dihydride intermediates, although this becomes less likely for first row metal complexes such as cobalt. Another possible mechanism is the concerted extrusion of dihydrogen (path **B**), similar to a σ-bond metathesis, which produces the metallicenium cation directly from the cyclopentadiene hydride without the formation of a high oxidation state intermediate. A third possibility involves the mediation of an adventitious Lewis base such as water, solvent, or even the anionic counterion (path **C**). The Lewis base may deprotonate the metal hydride, leaving behind a neutral cyclopentadiene complex which can then undergo hydride abstraction by the protonated base, to yield hydrogen gas. Such a pathway has been proposed in the sulfuric acid protonation of cobalt cyclopentadiene to generate cyclopentadienyl

complexes.[83] Similarly, Spencer reports that the isolable agostic ethylcyclopentenyl complex **101** loses hydrogen only in the presence of water to form the ethylcyclopentadienyl complex **102** (Scheme **19**).[84]

Scheme 19

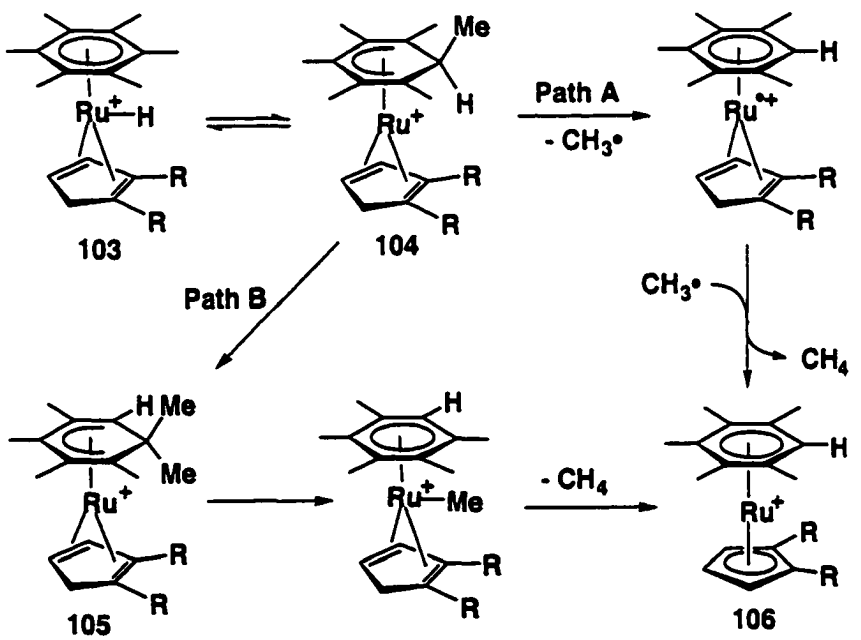


3. Proposed Demethylation Reaction Pathways

While the "normal" mechanism for cyclopentadienyl formation involves the evolution of dihydrogen during the reaction, the hexamethylbenzene ruthenium system proceeds via the dealkylation of hexamethylbenzene and extrusion of methane. Several possible mechanisms for this dealkylation process can be proposed based on relevant precedents. In all of these proposed mechanisms, the reaction follows the "normal" pathway up to the formation of the cyclopentadiene hydride intermediate **103** (Scheme **20**). It is plausible that migration of the hydride to the arene ligand is kinetically faster than the usual dehydrogenation of the cyclopentadiene ligand. While alkyl or hydride migration from a metal center to a coordinated arene is rare, a few examples have been

documented.[85] This migration results in the formation of hexamethylcyclohexadienyl intermediate **104** bearing an *exo*-methyl substituent, perhaps relieving some of the steric strain induced by the six "buttressed" methyl groups. This complex could then suffer direct radical scission (path **A**), as postulated by Chaudret to rationalize the dealkylation of his steroidal substrates.[73b-d] However, the mild conditions of the ruthenium-mediated [3 + 2] cycloaddition compared to the high temperatures and extended reaction times required by Chaudret strongly suggest that an alternative mechanism is more likely.

Scheme 20



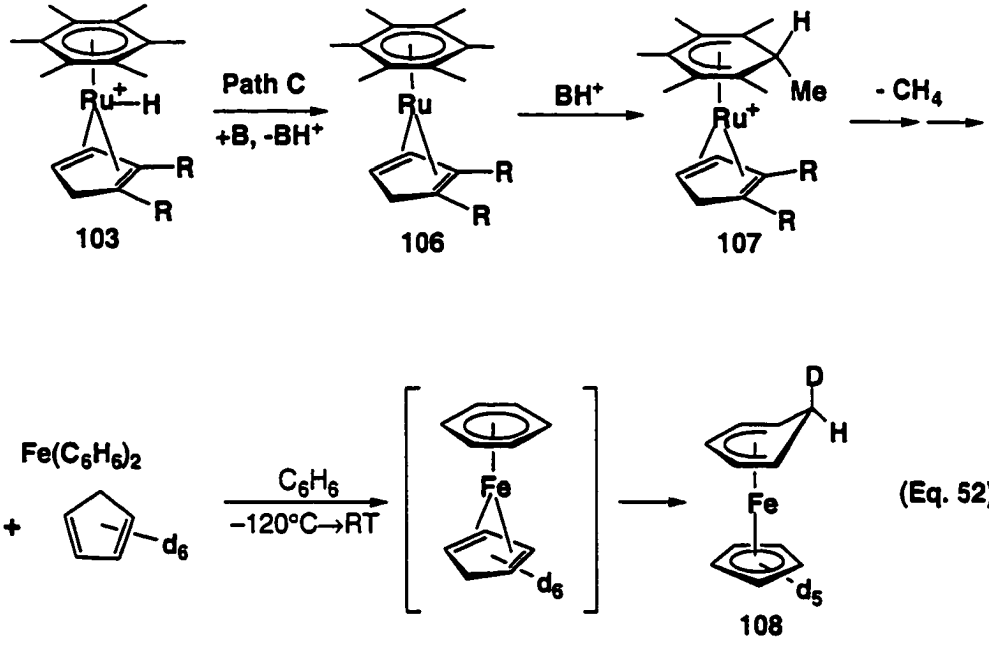
A more interesting, but equally speculative, hypothesis involves 1,2-migration of the *exo*-methyl group in complex **104** to form the geminal dimethyl complex **105** (path **B**), which now projects an *endo*-methyl group into the coordination sphere of the unsaturated ruthenium. Such a "sigmatropic" shift on the *exo* face of a coordinated

ligand is related to the 1,5-hydrogen shift proposed by Crabtree to account for the rearranged products observed in the reactions of 1,1-dialkylcyclopentanes with an unsaturated iridium complex.[69] The subsequent carbon-carbon bond activation then belongs to the relatively common class of proposed *endo* β-alkyl elimination reactions resulting in ligand aromatization. The difficulty with this explanation is that such transformations usually require significantly harsher reactions conditions. As previously discussed, the closely related complex [(dppe)Ru(1,1-dimethylcyclohexadienyl)$(CH_2Cl_2)]^+PF_6^-$, despite having an extremely labile ligand and both *endo*- and *exo*-methyl substituents, still requires 12 hours at 90°C to induce methyl migration to the metal center.[72] However, both Chaudret[73] and Itoh[74] have also demonstrated that a mild demethylation pathway exists in several carbon-carbon activations mediated by ruthenium η^5-methylcyclohexadienyl intermediates.

A logical alternative to both of these proposals involves an intermolecular reaction pathway (Scheme **21**). Adventitious base, potentially including the weakly basic counterion, could deprotonate the cationic ruthenium cyclopentadiene hydride **103**, leaving the neutral ruthenium diene complex **106**; this neutral species could, in principle, be reprotonated on the arene ring to form the hexamethylcyclohexadienyl ruthenium complex **107** bearing an *endo*-methyl group (path **C**). Loss of methane from intermediate **107** would then follow the standard β-alkyl elimination pathway. A related bimolecular mechanism has been implicated in the transfer of a hydrogen (or deuterium) atom from cyclopentadiene to coordinated benzene during metal-vapour synthesis of (cyclohexadienyl)iron(cyclopentadienyl) compounds, although this reaction probably involves hydride rather than proton transfer (Eq. **52**).[86] This reaction pathway, however,

still proposes carbon-carbon bond cleavage of an *endo* methyl group at or below room temperature. Before determining which mechanistic pathway is most plausible, it is necessary to resolve whether it is the *exo* or *endo* methyl substitutent that is cleaved during the course of the [3 + 2] cycloaddition reaction.

Scheme 21



4. Preparation and Reactivity of Model Compounds

4.1 Preparation of Model Compounds and their Reactions with Protic Acids

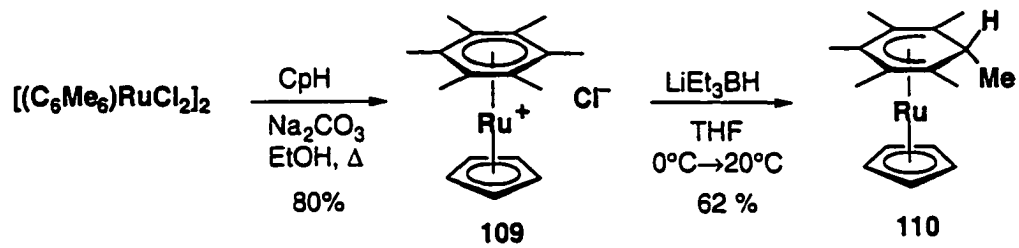
As discussed earlier, the production of methane was confirmed by spectroscopically monitoring the reaction of $(C_6Me_6)Ru(allyl)OTf$ (**78**) with 2-butyne in acetone-d_6 at room temperature. Although methane was detected, no intermediates were

observed during the course of the reaction, *under these conditions*. Since spectroscopic techniques initially appeared to be ineffective in distinguishing between the possible mechanistic pathways, a set of unambiguous model compounds were synthesized to evaluate the competency of putative intermediates.

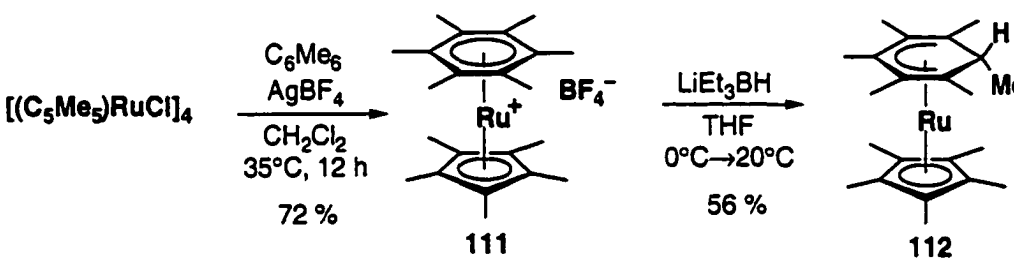
We initially probed whether an *endo*-methyl group on a cyclohexadienyl ligand coordinated to ruthenium is susceptible to carbon-carbon scission, as postulated in both pathways B and C, and as typically invoked in mechanistic rationales for other carbon-carbon bond cleavage processes mediated by transition metals. Because $[(arene)RuCp]^+$ cations readily undergo regioselective nucleophilic addition to the arene ligand[87] and nucleophilic addition to a coordinated ring generally occurs stereospecifically on the *exo* face, hydride addition to cationic (η^6-hexamethylbenzene)ruthenium(η^5-cyclopentadienyl) **109** was expected to provide the necessary *endo*-methyl group. Pauson previously demonstrated such reactions using the analogous iron compound.[88] The known $(C_6Me_6)Ru(C_5H_5)$ cation[89] was thus prepared by modification of an existing literature procedure: ethanolic reduction of Bennett's dimer $[(C_6Me_6)RuCl_2]_2$ using sodium carbonate in the presence of excess cyclopentadiene (Scheme **22**).[90] The product, $[(C_6Me_6)Ru(C_5H_5)]^+Cl^-$ (**109**) was then treated with one equivalent of $LiEt_3BH$ to produce the neutral 1,2,3,4,5,6(*endo*)-hexamethylcyclohexadienyl complex **110** in good yield as a white crystalline solid. ^1H NMR spectroscopic analysis of the compound reveals a quartet at δ 2.21 and a methyl doublet at δ 1.12; the chemical shift is consistent with the presence of an *exo* hydrogen.[88,91] The pentamethylcyclopentadienyl analogue $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*endo*)-hexamethylcyclohexadienyl) (**112**) was also prepared, by $LiEt_3BH$ addition to the known[92b] $(C_5Me_5)Ru(C_6Me_6)$ cation (**111**) (Scheme **23**).

Spectroscopic analysis of this compound shows a quartet at δ 2.44 and a methyl doublet at δ 0.95, similar to the cyclopentadienyl product **110**. Many structurally related complexes bearing a similar *exo* methine hydrogen have been associated with an anomalously low-frequency C-H stretch (~2750-2840 cm^{-1}) in the infrared absorption spectrum;[91] infrared analysis of the pentamethylcyclopentadienyl product **112** shows a strong band at 2847 cm^{-1}, which *may* be attributed to this *exo* C-H stretch.

Scheme 22

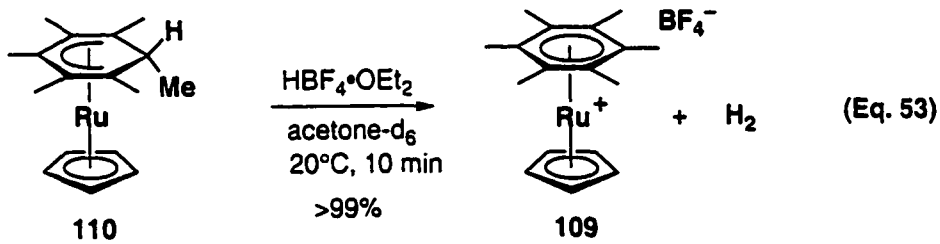


Scheme 23

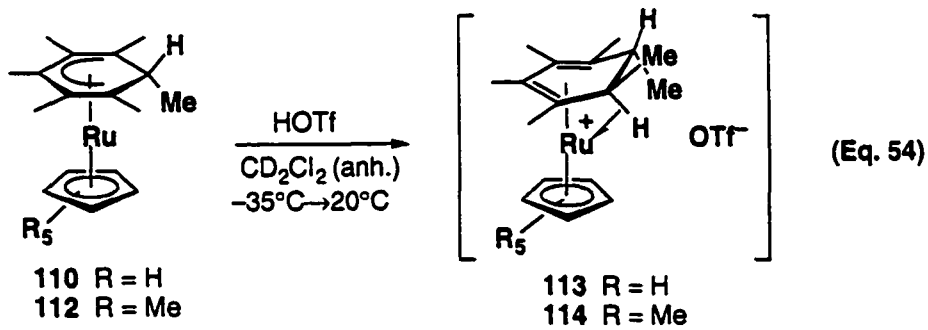


When the hexamethylcyclohexadienyl complex **110** was dissolved in acetone-d_6 and a slight excess of anhydrous tetrafluoroboric acid added at room temperature, the hexamethylbenzene ruthenium cation **109** was rapidly regenerated, presumably via loss of dihydrogen (Eq. **53**). This reactivity implies that the demethylation reaction is *not* occurring through the concerted β-alkyl elimination pathway, ruling out both paths **B** and

C (Schemes **20** and **21**). When the protonation was conducted in rigorously anhydrous dichloromethane-d_2, a new, thermally stable product was immediately formed and identified as $[(C_5H_5)Ru(\eta^4\text{-}1,2,3,4,5(exo),6(endo)\text{-hexamethylcyclohexa-1,3-diene})]^+BF_4^-$ (**113**) (Eq. **54**). The most characteristic signal exhibited by this new complex is an upfield doublet of septets at δ –4.81 (J = 13.3, 2.6 Hz), which is attributed to an agostic hydride ligand undergoing rapid and reversible metal-mediated 1,5-hydride transfers (Scheme **24**). The large 13.3 Hz coupling is due to the *trans* coupling with the neighbouring *exo* hydrogen.



(Eq. 53)

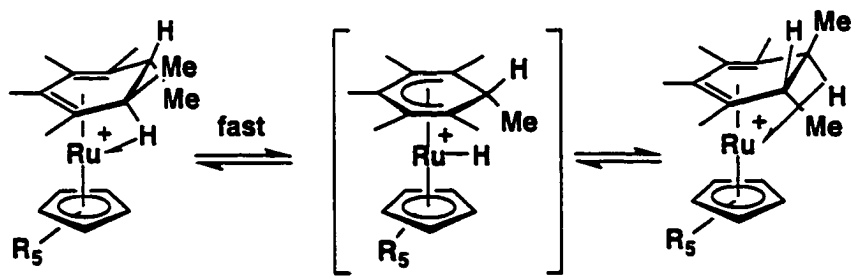


(Eq. 54)

The dynamic behaviour exhibited by this complex is closely related to that of several extensively studied agostic compounds formed upon protonation of symmetrical ruthenium η^5-pentadienyl complexes.[93,94] Consistent with this fluxional structure is a resonance at δ 1.67 (d, J = 2.7 Hz, 6H) shown by homonuclear decoupling experiments to

be coupled to the agostic hydride and assigned to the two methyl substituents flanking the *exo*-hydrogen. The unusually small coupling constant is the result of time-averaged coupling of the two distinct methyl environments. The apparent symmetry of the ^{13}C NMR spectrum is also characteristic: at room temperature, only four methyl signals are detected (aside from the pentamethylcyclopentadienyl signal), rather than the six signals expected for an unsymmetrical species. While no low temperature NMR spectra were obtained for this particular compound, the calculated activation energy for a 1,5-intraligand hydride transfer was found to be less than 30 kJ/mol in the closely related $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-}C_7H_{11})H]^+BF_4^-$ complex.[93b] Attempted isolation of this intermediate results in the development of product mixtures and no further characterization was pursued.

Scheme 24

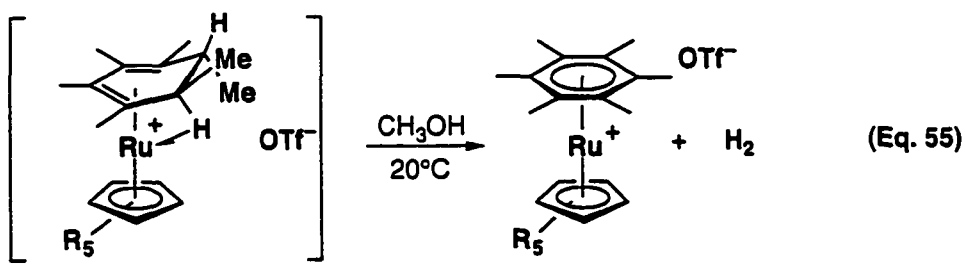


113 R = H
114 R = Me

1,5-Hydride Transfer

When $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*endo*)-hexamethylcyclohexadienyl) complex **112** is similarly treated with excess triflic acid or tetrafluoroboric acid in strictly anhydrous dichloromethane-d_2, and monitored spectroscopically, the isostructural agostic complex **114** is detected (Eq. **54**). In this complex, the agostic signal appears in the ^1H NMR

spectrum as a broad doublet at δ –5.82 (J = 13.0 Hz), shifted upfield from the unsubstituted case, consistent with the greater shielding of the pentamethylcyclopentadienyl ligand. Again the species is fluxional, undergoing rapid intraligand 1,5-hydride transfers as deduced from the low number of signals in the ^{13}C NMR spectrum, which indicates a symmetrical species. Other evidence of fluxionality includes the coupling of the agostic resonance with the resonance at δ 1.44 (d, J = 2.4 Hz, 6H), attributed to the two methyl substituents flanking the *exo*-hydride.



113 R = H
114 R = Me

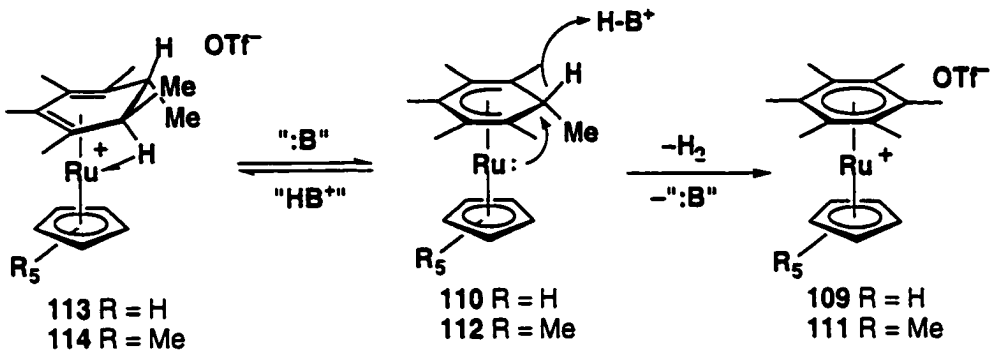
110 R = H (3h)
112 R = Me (5 d)

(Eq. 55)

Both of these agostic hexamethylcyclohexadiene complexes are indefinitely stable in dichloromethane solution so long as anhydrous conditions are maintained. However, when methanol (5-7 equiv) was added to the dichloromethane-d_2 solution of cyclopentadienyl agostic cation **113**, the intermediate loses dihydrogen to form $[(C_6Me_6)Ru(C_5H_5)]^+OTf^-$ over a period of several hours (Eq. **55**). Similarly, the addition of methanol induces the extrusion of dihydrogen from $[(C_5Me_5)Ru(\eta^4$-1,2,3,4,5(*exo*),6(*endo*)-hexamethylcyclohexa-1,3-diene)$]^+OTf^-$ (**114**), although in this case the reaction takes several days to go to completion. The thermal stability of these complexes under strictly anhydrous conditions, along with their sensitivity to a Lewis base such as methanol, strongly suggests that a radical dehydrogenation mechanism is not

operating. Instead, a Bronsted base-promoted pathway is proposed (Scheme **25**), similar to the one described by Spencer[84] for the dehydrogenation of η^3-cyclopentenyl complexes of cobalt. In this mechanism, the agostic η^4-hexamethylcyclohexadiene cation **113** is deprotonated by the Bronsted base in a pre-equilibrium step, regenerating the neutral η^5-hexamethylcyclohexadienyl complex **110**. Hydride is then abstracted from the *exo* face of the neutral complex **110** by the Bronsted acid, releasing hydrogen gas and forming the cationic product.

Scheme 25



113 R = H
114 R = Me

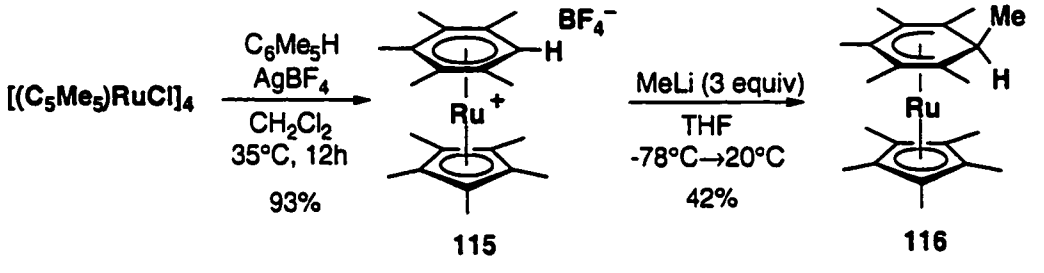
110 R = H
112 R = Me

109 R = H
111 R = Me

Both dehydrogenation reactions were found to be inhibited by excess acid, and the reactions were completely suppressed when the molar amount of protic acid exceeded the amount of base present in the system. This observation strongly suggests that neither the triflate or tetrafluoroborate counterions are basic enough to deprotonate these agostic complexes. The more electron-rich pentamethylcyclopentadienyl ligand is expected to stabilize the agostic cation, thus shifting the pre-equilibrium towards complex **114** and inhibiting the rate of dehydrogenation relative to the unsubstituted cyclopentadienyl complex. This was confirmed by the different reaction rates observed for the methanol-induced dehydrogenation of the two agostic complexes.

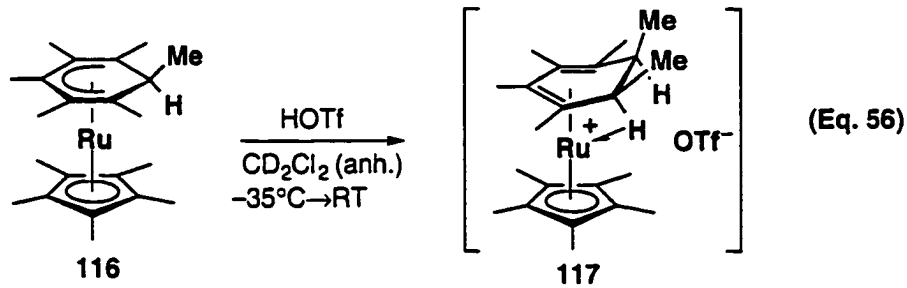
Since the *endo*-methyl complexes **110** and **112** surprisingly do not lead to methane loss, the reactivity of the *exo*-methyl complex was examined. To prepare the relevant model compound, the η^6-pentamethylbenzene complex $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_5H)]^+BF_4^-$ (**115**) was prepared and treated with methyllithium to give $(C_5Me_5)Ru(\eta^5\text{-}1,2,3,4,5,6(exo)\text{-hexamethylcyclohexadienyl})$ (**116**) in moderate yield (Scheme **26**). The addition was confirmed by the presence of an unusually high field methyl doublet at δ 0.11 (J = 6.3 Hz) in the ^{1}H NMR spectrum, accompanied by a quartet resonance for the methine position at δ 1.94. The lowest frequency C-H absorption in the infrared spectrum of *exo*-methyl complex **116** is 2852 cm^{-1}, only marginally higher in energy than the 2847 cm^{-1} absorption observed in the stereoisomeric *endo*-methyl complex **112**.

Scheme 26



The addition of either triflic or tetrafluoroboric acid to complex **116** in anhydrous dichloromethane-d_2 results in the instantaneous formation of a new cationic agostic species, identified as $[(C_5Me_5)Ru(\eta^4\text{-}1,2,3,4,5(exo),6(exo)\text{-hexamethylcyclohexa-1,3-diene})]^+X$ (X = OTf^-, BF_4^-) (**117**) by NMR spectroscopy (Eq. **56**). In contrast to agostic

compounds **113** and **114**, the ^{1}H NMR spectrum of complex **117** at room temperature exhibits only very broad signals, while the ^{13}C NMR spectrum reveals only those signals

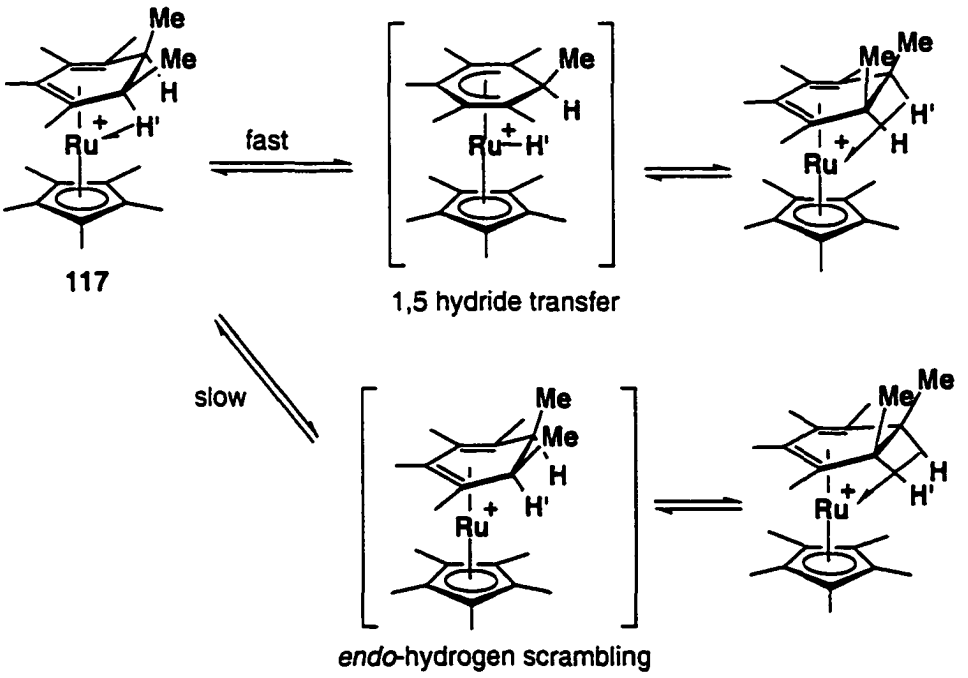


116 **117** (Eq. 56)

corresponding to the pentamethylcyclopentadienyl ligand evident above the baseline noise. Application of a decoupling pulse on the broad agostic resonance at δ –5.73 induces spin saturation transfer, resulting in the complete disappearance of the broad *endo*-hydrogen (1H) signal at δ 2.59. Similarly, a decoupling pulse centered on the methyl signal at δ 0.33 causes the transfer of spin saturation to the methyl resonances at δ 2.37 and δ 1.79, resulting in a marked decrease in the intensity of these signals. Cooling the solution to –80°C fully resolved the ^{13}C NMR spectrum, which clearly defined a symmetrical species. Two of the broad signals in the ^{1}H NMR spectrum also sharpened at this temperature, resolving a quartet at δ 2.53 (J = 6.6 Hz) coupled to a methyl doublet (J = 6.5 Hz) at δ 0.22, the latter shifted considerably further upfield from the 6-*endo*-methyl resonances found in either complex **113** or **114** (at δ 1.12 and 1.21, respectively). The agostic hydride signal, however, remains an unresolved multiplet even at low temperature. The agostic and free methine signals broaden further as a solution of the complex in 1,1,2,2-tetrachloroethane-d_2 is warmed to high temperature, eventually reaching coalescence at approximately 80°C. The spectroscopic evidence thus indicates that two distinct fluxional processes are occurring: a facile 1,5-intraligand hydride

transfer of the agostic hydride, similar to that described for the *endo*-methyl complexes, and a slower scrambling of the two *endo* hydrogen atoms (Scheme **27**). This latter process involves a shift of the agostic interaction to the adjacent *endo* methine hydrogen and is "frozen out" at –80°C, leaving only the low energy 1,5-hydride transfer process. Chaudret spectroscopically observed related, albeit non-fluxional, intermediates in the demethylation of 4,4-dimethylcyclohexen-1-one and of certain steroid substrates, although these complexes were considered to be cationic metal hydrides rather than agostic complexes.[73b-d]

Scheme 27

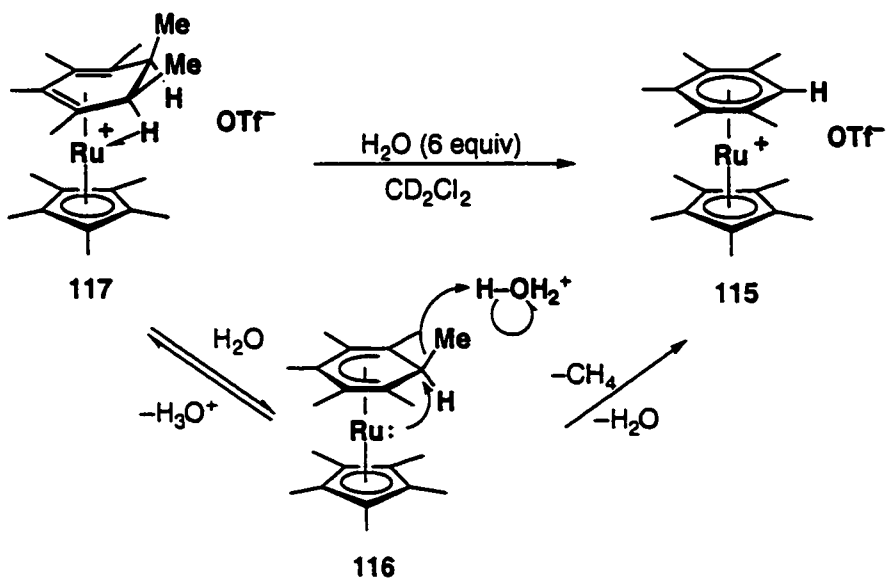


Like the earlier 6-*endo* methyl cations **113** and **114**, $[(C_5Me_5)Ru(\eta^4$-1,2,3,4,5(*exo*),6(*exo*)-hexamethylcyclohexa-1,3-diene)]$^+OTf^-$ (**117**) persists in dichloromethane solution for an extended period of time under strictly anhydrous conditions. However, upon addition of distilled water (~6 equiv) to **117**, clean

conversion to $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_5H)]^+OTf^-$ (**115**) and methane (δ 0.20 in dichloromethane-d_2) occurs in less than one hour at room temperature, as determined by ^1H NMR spectroscopy. Methane extrusion is suppressed in the presence of excess acid, provided that the amount of acid is sufficient to scavenge all of the added or adventitious base present in solution.

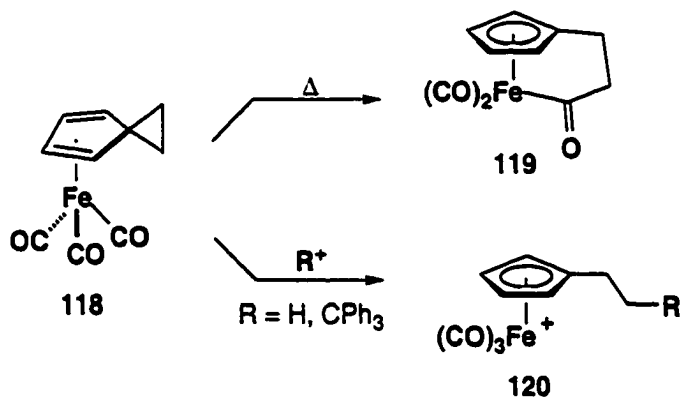
Taken together, these experimental observations strongly suggest that the mechanism for the low temperature demethylation of 6-alkylcyclohexadienyl ligands involves a metal-assisted protolytic activation and that the process is completely selective for activation of the *exo* substituent (Scheme **28**). The reaction proceeds by release of acid from the intermediate agostic cyclohexadiene cation in a pre-equilibrium step, where the base can be either the solvent, added or adventitious water. The reformed 6(*exo*)-hexamethylcyclohexadienyl complex **116** then undergoes protolytic activation of the methyl group, with "back-side" assistance from the nucleophilic metal center. The thermal stability of the agostic cyclohexadiene cation **117** under strictly anhydrous

Scheme 28



conditions is inconsistent with a mechanism involving thermal radical scission of an *exo*-methyl substituent, ruling out Chaudret's proposal of homolytic bond cleavage. A related electrophilic abstraction of an *exo* carbon-carbon bond was recently postulated by Liu *et al.* as part of their investigation of the ring opening reaction of (spiro[2.4]hepta-4,6-diene)tricarbonyl iron **118** (Scheme **29**):[95] while thermolysis results in the formation of the tethered acyl complex ($\eta^5;\eta^1$-$C_5H_4CH_2CH_2C(O))Fe(CO)_2$ (**119**) as earlier demonstrated by Eilbracht,[67i] the addition of a protic or Lewis acid (HBF_4, Ph_3CBF_4) produces the cationic (η^5-cyclopentadienyl)tricarbonyl iron complex **120**.

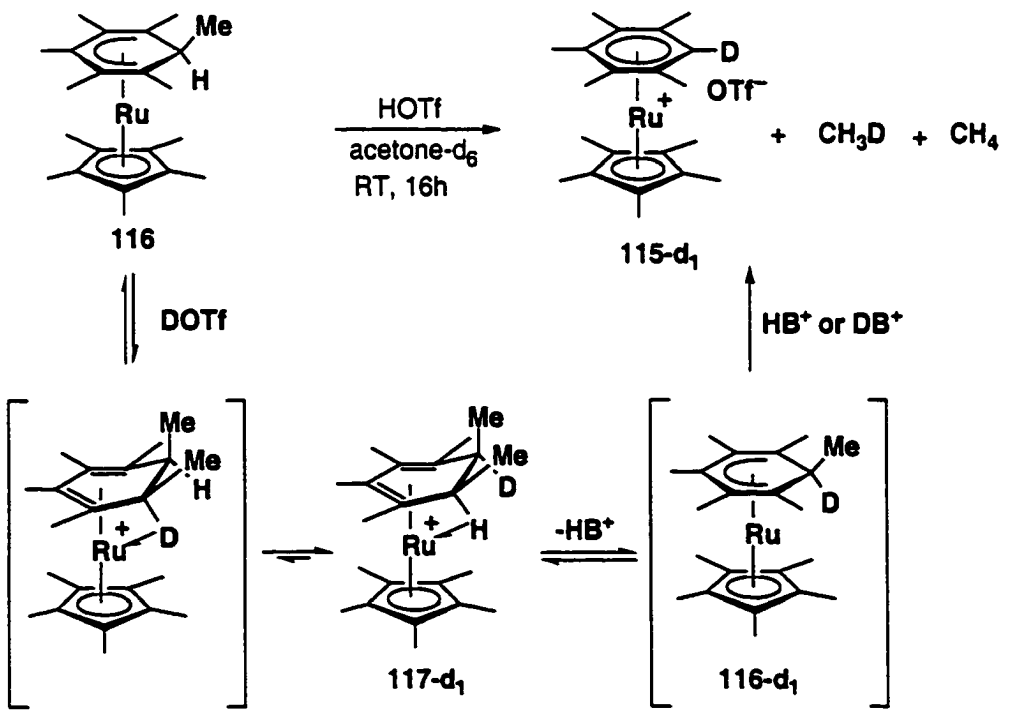
Scheme 29



Treatment of 6(*exo*)-hexamethylcyclohexadienyl complex **116** with triflic acid in acetone-d_6 leads to the immediate formation of the deuterium-labelled agostic intermediate **117**-d_1, as determined by analysis of the ^{1}H NMR spectrum (Scheme **30**). In particular, the signal previously assigned to the 6-*endo* hydrogen (δ 2.70 in acetone-d_6) is absent. This is apparently due to the inadvertent formation of an equivalent of CF_3SO_3D, formed *in situ* by the rapid reaction of triflic acid with acetone-d_6. This reaction is followed by the slow formation of $[(C_5Me_5)Ru(\eta^6$-$C_6Me_5D)]^+OTf^-$, (**115**-d_1) and the

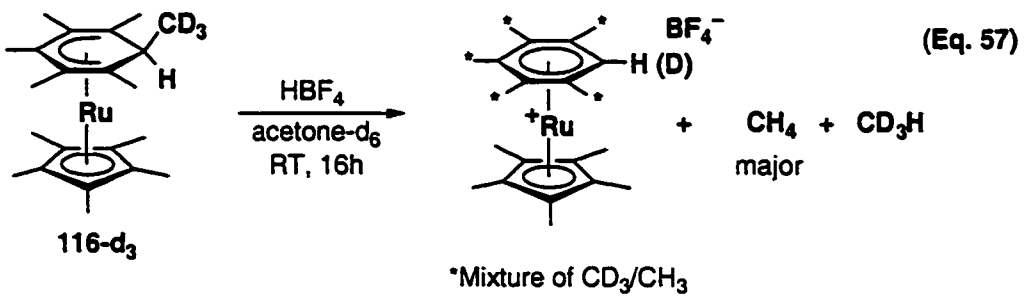
elimination of methane over a period of 20 hours. To the limits of spectroscopic detection, the signal at δ 5.83, previously assigned to the methine hydrogen of the η^6-C_6Me_5H ligand, is not apparent in the final ^1H NMR spectrum. The proposed mechanism of this isotopic labelling experiment is outlined in Scheme **30**. Deuteration of the starting η^5-hexamethylcyclopentadienyl **116** results in the initial formation of an agostic deuteride complex but rapid exchange forms the more thermodynamically stable agostic hydride **117**-d_1. The preference for a hydrogen agostic intermediate arises from the smaller zero-point energy difference between hydrogen and deuterium agostic bonds to the metal, relative to the differences in the terminal C-H and C-D bonds.[96] Deprotonation of the agostic species forms the neutral **116**-d_1, followed by methide abstraction by the protic

Scheme 30



acid to yield the pentamethylbenzene-d_1 cation. The relatively minor amount of CH_3D detected (1:1:1 triplet, δ 0.13 in acetone-d_6) probably arises from the slight excess of CF_3SO_3D present that electrophilically activates the methyl group from intermediate **116**-d_1.

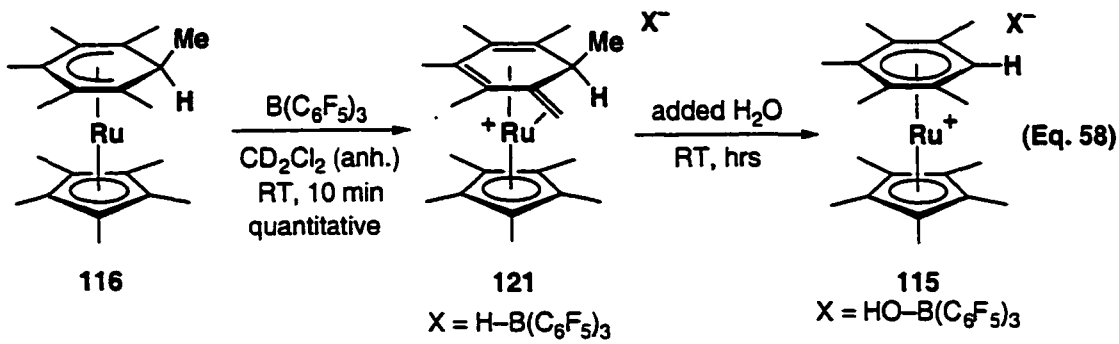
A second and more controlled labelling study was conducted by preparing $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,-pentamethyl-6(*exo*)-CD_3-cyclohexadienyl) (**116**-d_3) by addition of CD_3Li to $[(\eta^5$-$C_5Me_5)Ru(\eta^6$-$C_6Me_5H)]^+BF_4^-$ (**115**). Addition of tetrafluoroboric acid to d_3-labelled **116** in acetone-d_6 regenerates $[(\eta^5$-$C_5Me_5)Ru(\eta^6$-$C_6Me_5H)]^+BF_4^-$, (**115**), after 24 hours but with equivalent deuterium incorporation in all three arene methyl signals, confirming the complete *endo* hydrogen scrambling in this system (Eq. **57**). The integration of the resonance at δ 5.83 was also lower than expected due to partial deuterium incorporation at this position (presumably from the slower isotopic exchange of HBF_4 with acetone-d_6). The major volatile byproduct of this reaction is methane, although a trace of the tentatively assigned CD_3H (br s, δ 0.12 in acetone-d_6) was also detected. A second experiment, conducted in dichloromethane, involves the simultaneous addition of tetrafluoroboric acid and water and also results in equivalent deuterium incorporation into all three arene methyl signals, as determined by ^2H NMR spectroscopy.



(Eq. 57)

4.2 Dealkylation of Model Compounds Using Lewis Acids

To support the determination that protic acid is the agent responsible for abstraction of the *exo*-methyl group, the reactions of other strong electrophiles with $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (**116**) were evaluated. Addition of the strong Lewis acid tris(pentafluorophenyl)borane[97] to **116** in dichloromethane (–35°C) immediately results in hydride abstraction from a peripheral methyl substituent, producing the cationic triene complex **121** (Eq. **58**). This complex exhibits two downfield singlets in the ^{1}H NMR spectrum (δ 4.33 and δ 3.54) corresponding to the two inequivalent methylene hydrogen atoms. The ^{13}C-^{1}H heterocorrelated NMR spectrum (HMQC) demonstrated that these two singlets are directly bonded to the same sp^2 carbon, resonating at 76.2 ppm (J_{CH} = 161 Hz). The chemical shifts strongly suggest that the s-*cis*-s-*trans* triene fragment is η^6-coordinated to the ruthenium metal; a related ruthenium complex has been reported by Chaudret, but with the triene imbedded in a steroid framework.[73c] Also present in the ^{1}H NMR spectrum is the relatively unperturbed *exo*-methyl doublet (J = 6.7 Hz) at δ 0.66 and the corresponding *endo*-hydrogen quartet (J = 6.7 Hz) at δ 1.84.

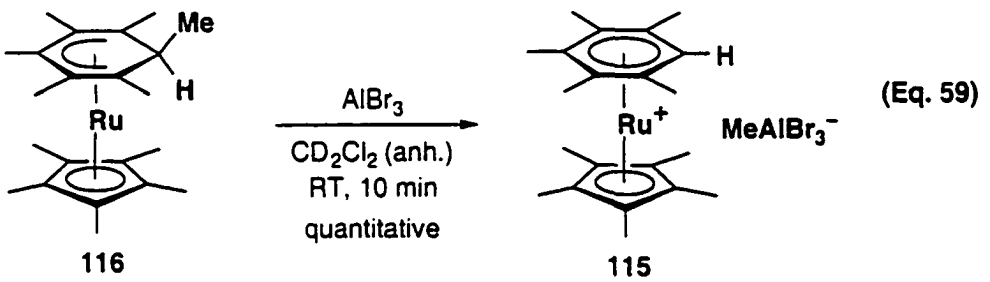


116 **121** **115**

X = H–B(C_6F_5)$_3$ X = HO–B(C_6F_5)$_3$

The presence of even traces of water subsequently cause the η^6-triene complex **121** to convert to the $(C_5Me_5)Ru(\eta^6\text{-}C_6Me_5H)$ cation **115** with concomitant formation of methane. This reaction likely proceeds through reversal of the hydride abstraction upon initial addition of water, followed by electrophilic abstraction by protic acid (formed from the reaction of the Lewis acidic borane reagent with water). The counterion of the final product is tentatively identified as the known borate anion $HO\text{-}B(C_6F_5)_3^-$, based on the broad hydroxyl band at 3670 cm^{-1} found in the infrared spectrum.[98]

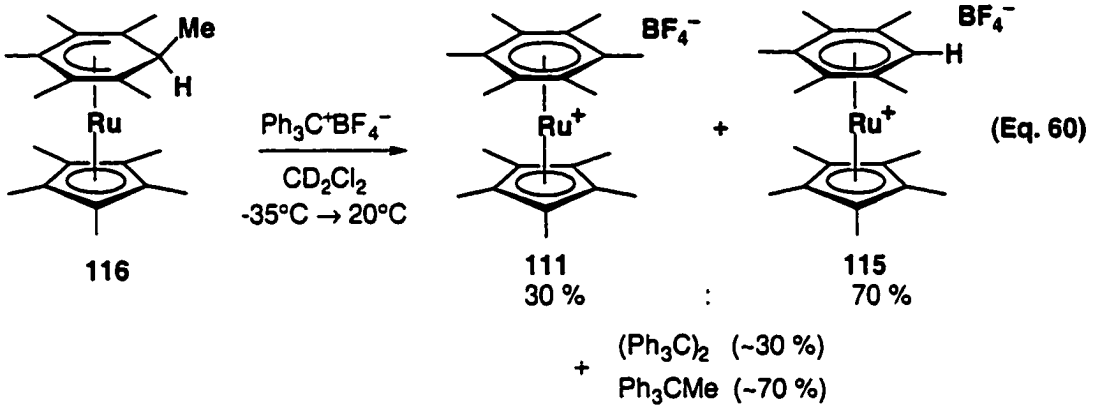
Straightforward demethylation, with no evidence of hydride abstraction, occurs upon addition of anhydrous $AlBr_3$ to 6(*exo*)-hexamethylcyclohexadienyl complex **116**, exclusively forming $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_5H)]^+[MeAlBr_3]^-$ (Eq. **59**). The aluminium methyl signal for the tentatively identified counterion is present in the ^1H NMR spectrum as a broad singlet at δ 0.00.[99]



(Eq. 59)

In contrast, the addition of trityl cation to a cooled solution of $(C_5Me_5)Ru(\eta^5\text{-}$1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) **116** results in immediate conversion to a mixture of both pentamethylbenzene (70%) and hexamethylbenzene (30%) products, **111** and **115**, derived from both *exo*-methyl and *endo*-hydrogen abstraction (Eq. **60**). Also present in solution is 1,1,1-triphenylethane, the expected byproduct from *exo*-methyl

abstraction, in 70% yield. However, instead of the expected triphenylmethane, the observed byproduct of *endo*-hydrogen abstraction is 3-benzhydrylidene-6-triphenylmethyl-1,4-cyclohexadiene (trityl dimer) present in ~30% yield (as measured by ^{1}H NMR spectroscopy).[100] This compound is the dimerization product of trityl radical and strongly suggests that the minor dehydrogenation pathway arises from a competitive electron transfer mechanism. Whether the demethylation process occurs through electron transfer or via direct abstraction is difficult to determine in this case, but the latter pathway is suggested by the isolation of 1,1,1-triphenylethane.

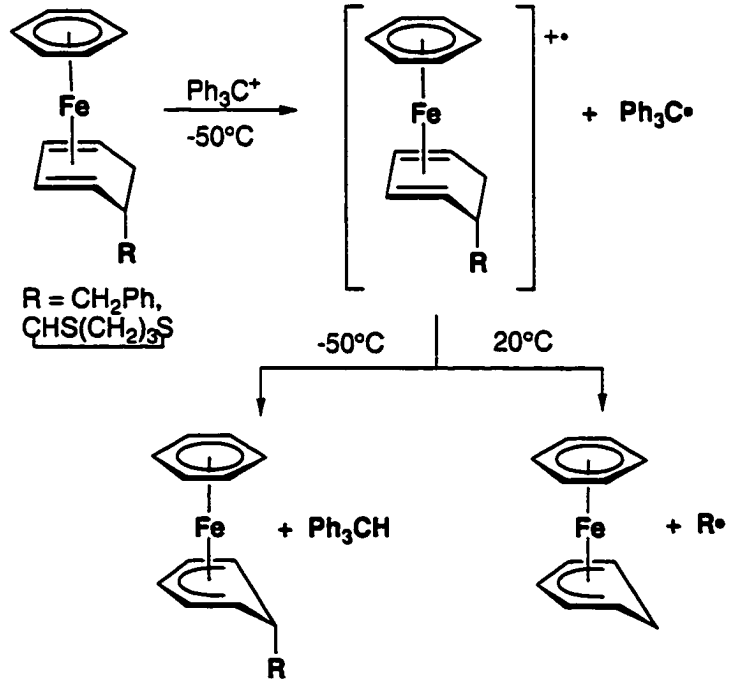


4.3 Oxidatively Induced Reactivity of Model Compounds

Although trityl cation has been widely used as a reagent for the removal of hydride ion from both organic[101] and organometallic[102] substrates, it can also function as a mild one-electron oxidant. On reduction it yields the trityl radical, which reacts with itself to form an equilibrium mixture favouring the diamagnetic dimer. When trityl cation is added to an organometallic complex, it reacts most often by abstraction of an

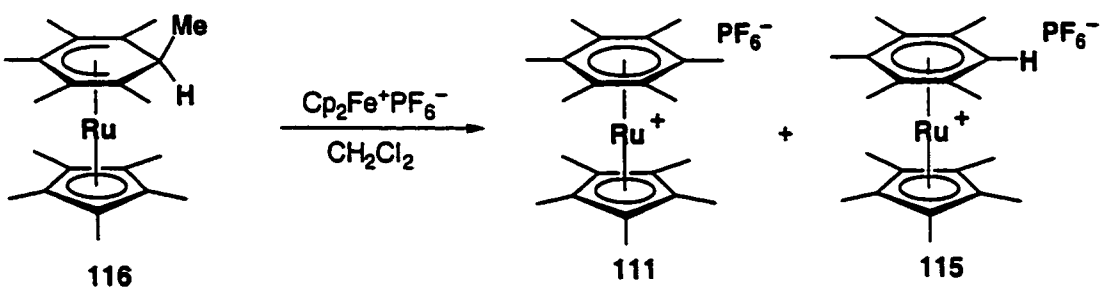
exo-hydrogen from a coordinated ligand, a reaction that may proceed via true hydride abstraction or by electron transfer followed by hydrogen atom abstraction. Trityl cation is also known to remove an *endo*-hydrogen if no *exo*-hydrogen is available, presumably through an electron transfer process.[102] In some cases, however, the use of trityl cation (or NBS, another common oxidant) has been reported to lead to a mixture of *endo*-hydrogen abstraction and *exo*-alkyl or aryl scission.[103] An investigation by Astruc into the reaction of $(\eta^6\text{-}C_6H_6)Fe(\eta^5\text{-}exo\text{-}RC_6H_7)$ (R = benzyl, dithiane) with trityl cation clearly demonstrated that both products were obtained from a common $17e^-$ Fe(I) radical cation intermediate (Scheme **31**).[104] When the reaction of the iron complex and trityl cation is maintained at low temperature, clean *endo*-hydrogen abstraction occurs, presumably through slow hydrogen atom transfer to the iron center. In contrast, when the reaction is conducted at room temperature or is warmed too quickly, cleavage of the *exo*-alkyl radical from the Fe(I) radical intermediate is the favoured mode of decomposition.

Scheme 31

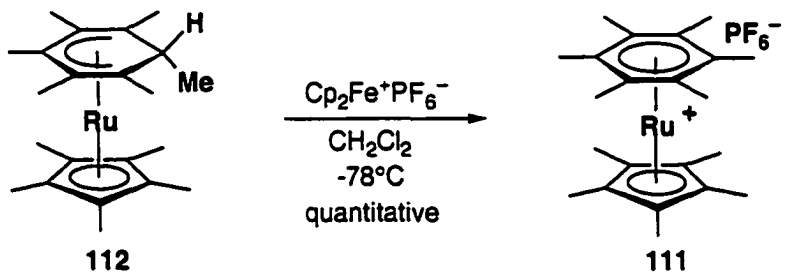


Unlike trityl cation or NBS, $[Cp_2Fe]^+$ reacts solely as an outer-sphere one-electron oxidant;[102] it was thus used to determine how a purely oxidative reaction proceeds. Addition of one equivalent of $[Cp_2Fe]^+PF_6^-$ to $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (**116**) at room temperature in dichloromethane immediately results in the production of a mixture of hexamethylbenzene and pentamethylbenzene cations in a 1 : 4 ratio, close to that observed for the trityl case (Scheme **32**). The gaseous byproducts were not determined in this instance, as this reaction was performed in an open vessel. When this reaction is repeated at low temperature, an immediate deep orange colour develops, suggesting the presence of a metastable $17e^-$ Ru(III) radical cation intermediate. After warming slowly to room temperature, ^1H NMR spectroscopic analysis of the reaction mixture indicates a dramatic increase in the proportion of *endo*-hydrogen loss, giving the hexamethylbenzene to pentamethylbenzene products **111** and **115** in a ratio of 2 : 1 (Scheme **32**). These observations are consistent with Astruc's

Scheme 32



suggestion of a slow *endo*-hydrogen transfer step in the mechanism of oxidatively induced *endo*-hydrogen loss. Adding the ferricinium salt at low temperature to a dichloromethane solution of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (**112**) immediately results in the exclusive loss of *exo*-hydrogen to form the $(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)$ cation **111** (Eq. **61**), evidence that *exo*-hydrogen loss is again kinetically much faster than either *endo*-hydrogen or *endo*-methyl loss.



112 **111** (Eq. 61)

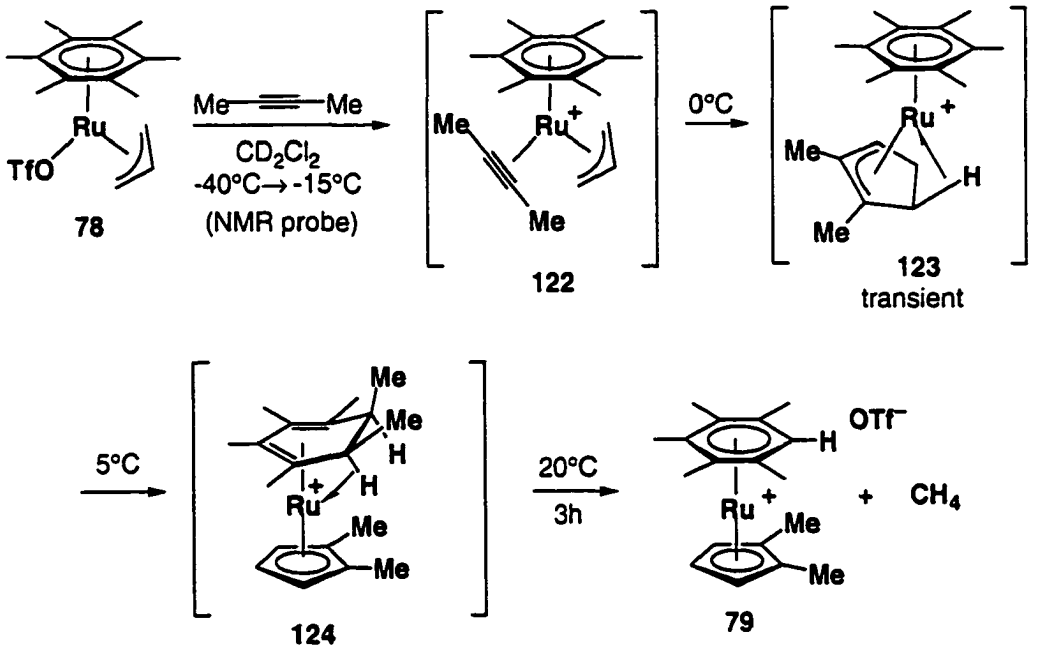
5. The Mechanism of Ruthenium-Mediated [3 + 2] Allyl/Alkyne Cycloaddition with Concomitant Demethylation

The realization that the use of strictly anhydrous dichloromethane allows agostic cations **113**, **114**, and **117** to survive for prolonged periods at room temperature suggested that it might be possible to observe intermediates in the allyl alkyne cyclization reaction. A solution of $(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(OTf)$ (**78**) in dichloromethane-d_2 was thus prepared and excess 2-butyne (3 equiv) added via microliter syringe while the solution was frozen (–196°C) (Scheme **33**). The reaction mixture was slowly warmed to room temperature while being monitored by both ^1H and ^{13}C NMR spectroscopy. Between

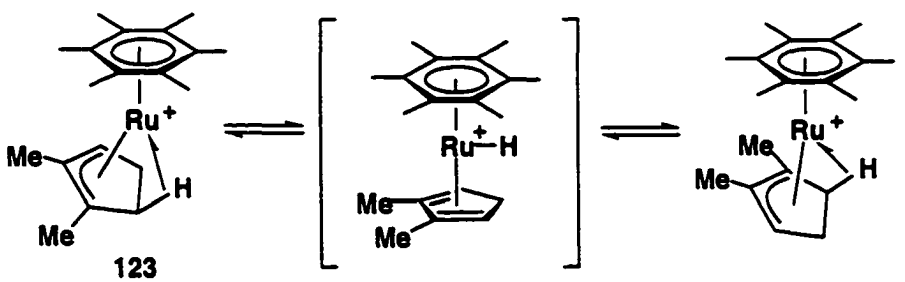
–20°C and –15°C, the starting material slowly disappears and is replaced by a new compound, tentatively identified as the allyl alkyne complex $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(MeC{\equiv}CMe)]^+OTf^-$ (**122**) (Scheme **33**). This new species shows the same characteristic coupling patterns for the allyl resonances as the starting material. The central proton appears as a triplet of triplets at δ 3.41, coupled to two chemically equivalent *syn* protons (δ 3.23, d, J = 6.8 Hz) and two *anti* protons (δ 0.75, d, J = 10.5 Hz). Coupling between the *syn* and *anti* protons, usually 1-2 Hz for several related allyl complexes,[39,43,51] is not resolved in this spectrum. The coordinated 2-butyne methyl groups appear as a singlet at δ 2.08, shifted downfield from free 2-butyne at δ 1.71. The ^{13}C NMR spectrum exhibits a signal for the chemically equivalent terminal allyl carbons at 53.3 ppm, as well as a signal for the central carbon at 87.1 ppm, similar to the allyl carbon resonances observed for $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(CH_3CN)]^+OTf^-$ (**76**). The quaternary carbon signal of coordinated 2-butyne was found at 66.9 ppm, shifted upfield from free 2-butyne at 74.5 ppm. This ^{13}C NMR spectrum closely matches that observed for the isoelectronic iridium complex, $[(C_5Me_5)Ir(\eta^3\text{-}C_3H_5)(MeC{\equiv}CMe)]^+OTf^-$ (**45**).[38,39]

As the temperature of the reaction is gradually warmed from –10°C to 0°C a new species is observed by ^1H NMR spectroscopy, although the concentration of this compound remains low (Scheme **33**). This transient exhibits a hexamethylbenzene singlet at δ 2.22 as well as a methyl singlet at δ 1.88 that integrates to six hydrogens; broad resonances at δ 3.65 (1H) and δ 2.85 (3H), and more significantly at δ –1.42 (1H) are also visible. On the basis of this data, the compound is tentatively identified as the fluxional agostic complex $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_5H_5Me_2)]^+OTf^-$ (**123**), in which the compound is equilibrating from one equivalent agostic structure to the other (Scheme

Scheme 33



Scheme 34



34). This assignment is also supported by several fully characterized analogues that were prepared independently and which will be discussed in later chapters. Above 0°C, both this species and the 2-butyne complex **122** disappear with the formation of a new agostic compound (indicated by a broad singlet at δ –5.03 in the ^{1}H NMR spectrum), which rapidly grows in concentration. By 5°C this complex, consistent with assignment as [(η^5-

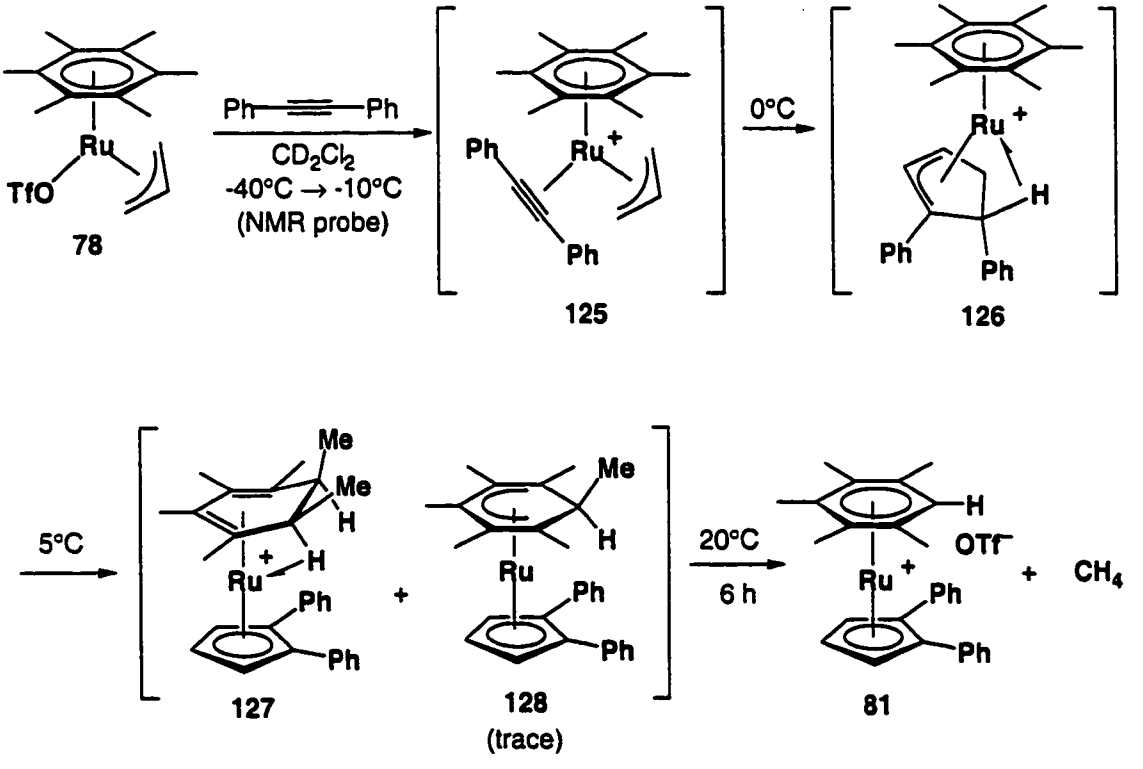
$C_5H_3Me_2)Ru(\eta^4$-1,2,3,4,5(*exo*),6(*exo*)-hexamethylcyclohexa-1,3-diene)]$^+OTf^-$ (**124**), is the major compound present in solution. This compound exhibits a characteristic 1,2-disubstituted cyclopentadienyl pattern of resonances in the ^{1}H NMR spectrum (δ 4.99 (d, J = 2.5 Hz, 2H) and δ 4.78 (t, J = 2.5 Hz, 1H)) similar to known η^5-dimethylcyclopentadienyl ligands.[35-39,43] Also present is an upfield methyl doublet at δ 0.32 coupled to a quartet at δ 2.65, consistent with the *exo* methyl and *endo* hydrogen of a cyclohexadiene ligand; the spectrum is closely analogous to the low temperature spectrum of compound **117**, bearing the same substituted cyclohexadiene ligand. The presence of a narrow methyl doublet (J = 2.5 Hz) that both integrates to six hydrogens and couples to the agostic resonance suggests that a ruthenium-mediated 1,5-hydride transfer occurs rapidly at this temperature. However, there is no indication of *endo* hydrogen scrambling in this instance. It is plausible that the *endo*-scrambling behaviour is limited to the pentamethylcyclopentadienyl analogue, as the more electron-rich and sterically encumbered ligand is more likely to form the required 16e$^-$ unsaturated intermediate. The ^{13}C NMR spectrum is completely consistent with the assigned structure, showing only five methyl signals due to the pseudosymmetry of the fluxional complex. After warming to room temperature, this compound converts to the final pentamethylbenzene product **79** and methane. Within four hours at room temperature the reaction is complete, even under supposedly anhydrous conditions. A small amount of a second product derived from reaction with additional 2-butyne is also present; this product will be discussed in the following chapter.

The reaction of diphenylacetylene with $(\eta^6$-$C_6Me_6)Ru(\eta^3$-$C_3H_5)$(OTf) (**78**) under anhydrous conditions was also monitored spectroscopically (Scheme **35**). Similar to the

reaction of **78** with 2-butyne, the first intermediate is observed between –20° and –10°C and is assigned to the coordinated alkyne complex $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(PhC{\equiv}CPh)]^+$ OTf^- (**125**). The ^1H NMR spectrum is similar to the 2-butyne complex except that the allyl central hydrogen and *syn* hydrogens in the diphenylacetylene complex form a second order pattern due to the proximity of these resonances. The ^{13}C NMR spectrum is also very similar (allyl central carbon at 87.3 ppm, terminal carbons at 53.7 ppm) although the internal alkyne carbons appear at 85.6 ppm, downfield of the more electron-rich butyne signal. As the reaction mixture is warmed to –5°C a new compound forms, associated with a broad singlet at δ –8.63 and a hexamethylbenzene resonance at δ 2.06, suggesting assignment as the agostic cyclopentenyl $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_5H_5Ph_2)]^+OTf^-$ (**126**). The upfield shift of the agostic hydrogen, as well as the presence of several resolved signals between δ 5.30 - 3.30 strongly suggest that the structure of this agostic cyclopentenyl differs considerably from the 2-butyne case. The most plausible explanation for this difference is that this complex is static on the NMR time-scale, and that the agostic hydrogen is located on a carbon with a phenyl substituent: this arrangement has been observed with related, well-characterized 1,2-diphenyl-substituted agostic cyclopentenyl complexes prepared independently (*vide infra*). Further warming of the reaction mixture results in the production of a new cationic agostic complex $[(\eta^5\text{-}C_5H_3Ph_2)Ru(\eta^4\text{-}1,2,3,4,5(exo),6(exo)\text{-hexamethylcyclohexa-1,3-diene})]^+OTf^-$ **127**, which becomes the major species in solution by 10°C. This diphenyl analogue is spectroscopically similar to the previously observed dimethyl complex **124**, exhibiting two cyclopentadienyl signals (doublet at δ 5.38 and a triplet at δ 5.07) as well as the agostic hydrogen as a broad singlet at δ –4.79 in the ^1H NMR spectrum. One *exo*-methyl

group is apparent as a doublet (J = 6.6 Hz, 3H) at δ 0.36 that is coupled to the *endo* hydrogen at δ 2.67. An unusually narrow methyl doublet found at δ 1.80 (J = 2.5 Hz, 6H) again indicates that the complex undergoes a rapid intraligand 1,5-hydride transfer, confirmed by the presence of only four methyl resonances in the ^{13}C NMR spectrum. At room temperature, this compound converts to the final pentamethylbenzene product **81** and methane over the course of six hours, even under strictly anhydrous conditions.

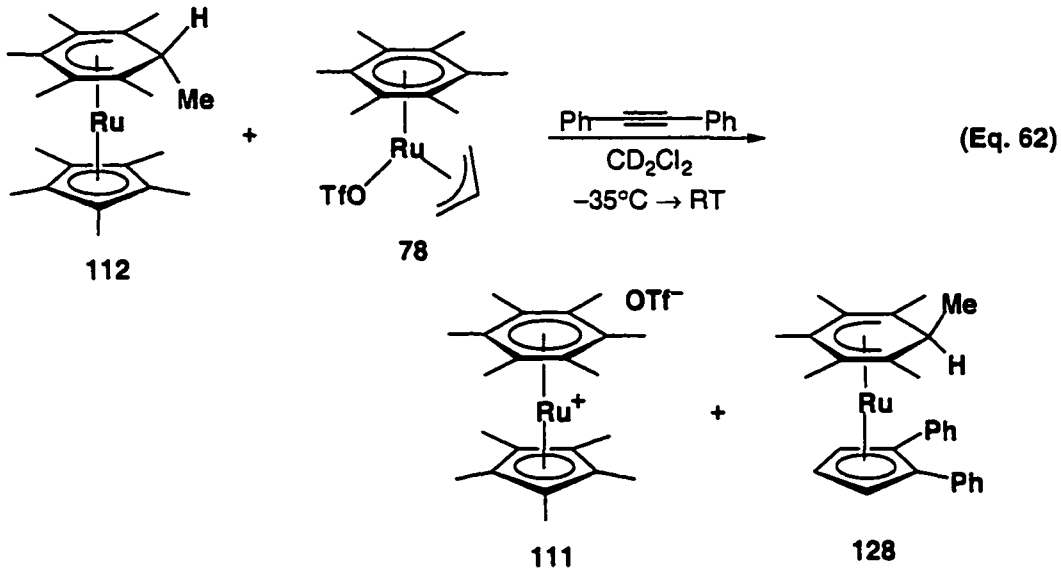
Scheme 35



Also present in solution above 0°C is a small amount of a second diphenylcyclopentadienyl product, one whose concentration remains low during the course of the reaction and which disappears slowly at room temperature. Like the agostic cation **127**, the disubstituted cyclopentadienyl doublet and triplet pattern (J = 2.5 Hz) is

observed, although shifted considerably upfield. Associated with this minor species is an upfield methyl doublet at δ 0.15. On the basis of these observations, this compound was tentatively identified as the neutral (η^5-$C_5H_3Ph_2$)Ru(η^5-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) **128**, which appears to be present in equilibrium with its protonated form. This identification was confirmed by the independent synthesis of complex **128** through treatment of [(η^6-C_6Me_5H)Ru(η^5-$C_5H_3Ph_2$)]$^+$OTf$^-$ (**81**) with methyllithium in tetrahydrofuran at –78°C.

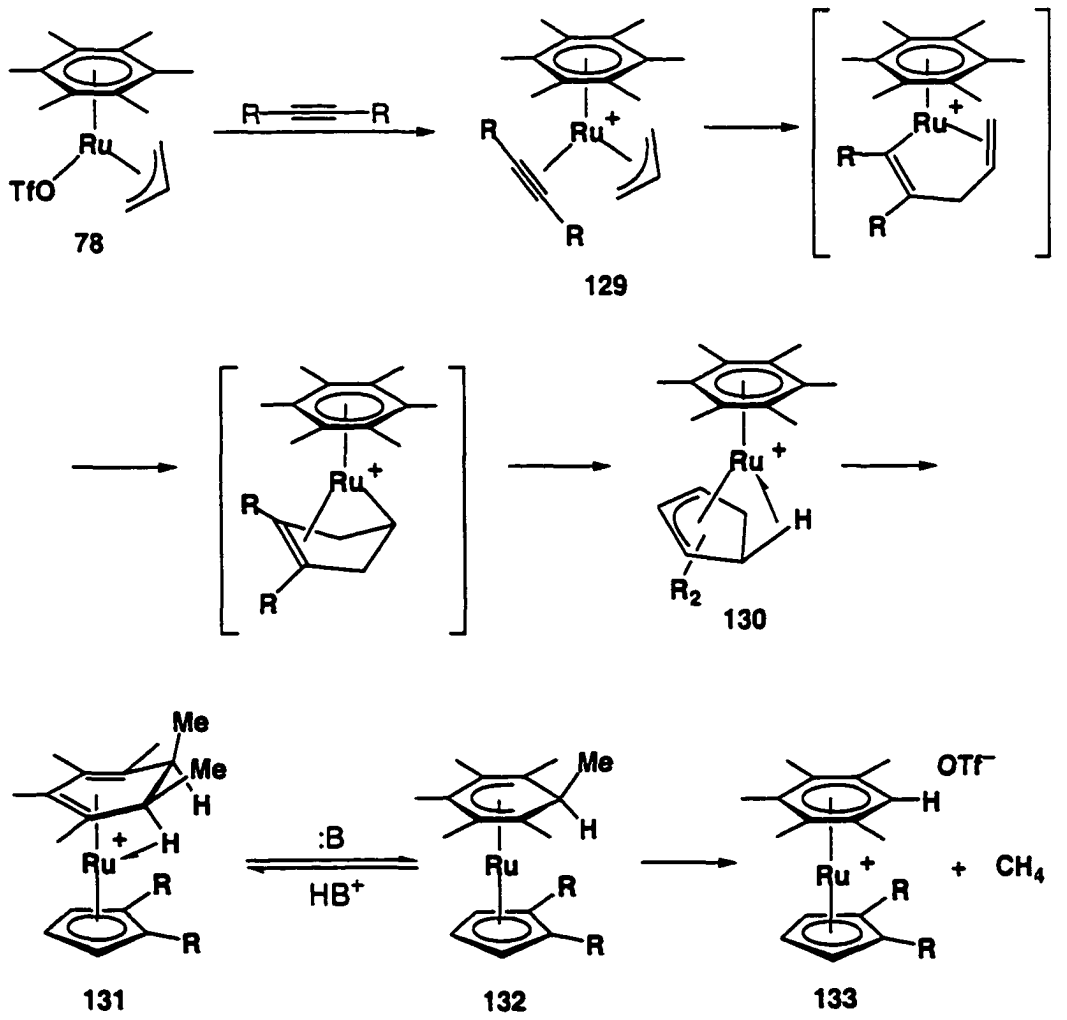
The observation of even a trace amount of the neutral species suggested that it might be possible to trap this intermediate by adding base to the reaction mixture. However, the use of bases such as potassium *t*-butoxide or calcium hydride proved ineffective, since they appear to interfere with the cyclization process. Instead, the presence of liberated acid was confirmed in a crossover experiment using the *exo*-hydrogen complex (C_5Me_5)Ru(η^5-1,2,3,4,5,6(*endo*)-hexamethylcyclohexadienyl) **112** as an acid scavenger during the reaction of diphenylacetylene with allyl triflate **78** (Eq. **62**). The cationic agostic complex **127**, formed during the course of the reaction, thus acts as the source of acid; the acid subsequently abstracts hydride from the *exo*-hydrogen of the η^5-hexamethylcyclohexadienyl complex **112**, to result in the clean formation of [(C_5Me_5)Ru(η^6-C_6Me_6)]$^+$OTf$^-$ and the neutral intermediate **128**. This crossover experiment also confirms that abstraction of the *exo*-hydrogen is kinetically much faster than carbon-carbon bond activation of the *exo*-methyl group.



These experiments better elucidate the mechanism of the [3 + 2] cycloaddition, while also significantly clarifying the demethylation process. The general mechanistic outline for this reaction is thus presented in Scheme **36**. After formation of the allyl alkyne complex **129**, insertion of alkyne yields the vinyl olefin complex (*vide infra*). Migratory cyclization initially forms the non-conjugated η^1-η^2-cyclopentenyl complex, but the complex rapidly rearranges to the more thermodynamically stable agostic η^3-cyclopentenyl complex **130**. The exact structure of this cyclopentenyl intermediate appears to be dependent on the nature of the alkyl or aryl substituents. Two hydrogen atoms from the cyclopentenyl ligand then migrate consecutively to the arene ligand, forming the η^5-cyclopentadienyl ligand at the expense of the arene ligand's residual aromaticity. This newly formed cationic agostic compound **131** exists in equilibrium with its neutral η^5-6(*exo*)-methylcyclohexadienyl counterpart **132**. Eventually, the protic acid formed during the reaction acts to abstract the *exo* methyl group from the neutral species, producing methane and the cationic pentamethylbenzene product **133**. While

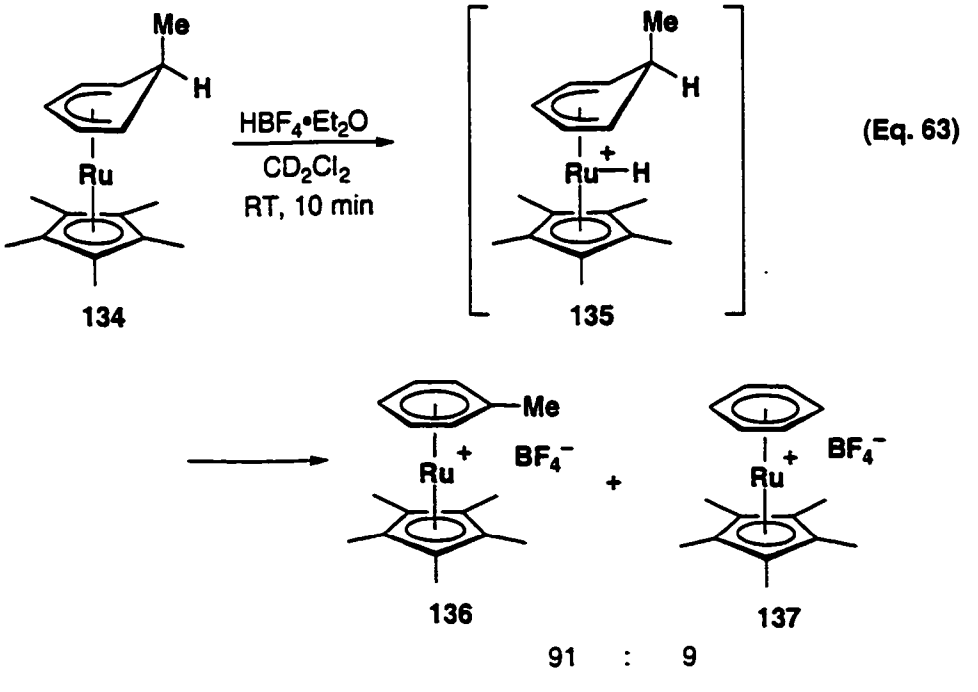
this last step is slow in the total absence of any Lewis base, it proceeds quite rapidly in mildly basic solvents such as acetone or in the presence of trace amounts of water.

Scheme 36



6. Literature Dealkylations Revisited

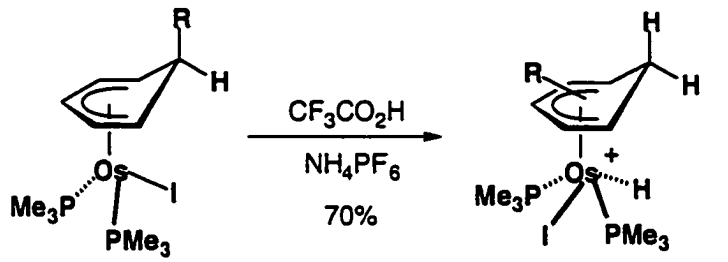
Based on our results, it seems clear that a similar protolytic mechanism is responsible for the low temperature demethylation reactions observed by both Chaudret and Itoh. To test this possibility, the known arene complex $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]^+PF_6^-$[105] was prepared and treated with methyllithium, yielding the neutral *exo*-methylcyclohexadienyl complex **134** in moderate yield. Addition of protic acid to this complex is expected to provide the cationic (and possibly agostic) ruthenium *exo*-methyl cyclohexadienyl hydride complex **135** (Eq. **63**), which is the key intermediate in the major pathway postulated for Chaudret's reaction of the $(C_5Me_5)Ru^+$ fragment with 3-methylcyclohexene and Itoh's [4+2] cycloaddition of coordinated 1,3-pentadiene with acetylene (Eqs. **47** and **49**).



(Eq. 63)

The addition of tetrafluoroboric acid to the *exo*-methylcyclohexadienyl complex **134** in acetone-d_6 at room temperature immediately results in the formation of the known complex $[(C_5Me_5)Ru(\eta^6\text{-toluene})]^+BF_4^-$ (**136**)[92] as the major product with approximately 91% selectivity, as measured spectroscopically (Eq. **63**). Some $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]^+BF_4^-$ (**137**), however, is also detected as a minor product (ca. 9%) resulting from carbon-carbon bond activation. Comparable results are obtained using triflic acid or by performing the reaction in dichloromethane-d_2; no evidence for the formation of a cationic agostic intermediate is observed, even under strictly anhydrous conditions. The ratio of η^6-arene products is very similar to that produced by Itoh,[74] although the proportion of demethylation products is somewhat higher than that reported by Chaudret.[73a] The *exo*-methylcyclohexadienyl ruthenium complex is thus a competent intermediate for both the demethylation and dehydrogenation pathways and therefore it is unnecessary to invoke the concomitant formation of a *endo*-methylcyclohexadienyl isomer to explain the observed alkyl loss. While no intermediates are observed during the course of the reaction, it is reasonable to propose that a fluxional agostic species is formed initially, which undergoes a rapid series of exchanges with the other *endo* hydrogens. This results in the statistical displacement of the methyl substituent to other positions of the cyclohexadienyl ring while providing an *exo*-hydrogen atom that is accessible to electrophilic abstraction, leading to the major product. A similar rearrangement of an *exo*-alkyl cyclohexadienyl substituent is observed upon addition of protic acid to a related osmium complex, although the osmium cation does not undergo ligand aromatization (Eq. **64**).[106] It is also plausible that this same abstraction mechanism

is involved in the coordinated arene dealkylations observed during some $AlCl_3$-mediated ligand exchange reactions with ferrocene and ruthenocene.[75,76]

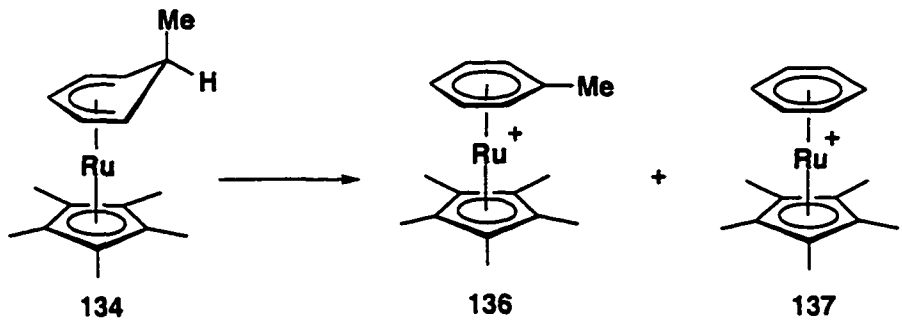


(Eq. 64)

R = Me, *n*-butyl, *t*-butyl

The *exo*-methylcyclohexadienyl ruthenium complex **134** was also treated with a series of Lewis acids and oxidants, the results of which are outlined in Table **1**. While the addition of $AlBr_3$ gave a similar proportion of η^6-toluene to η^6-benzene products as obtained from protic acid, the use of tris(pentafluorophenyl)borane results in the formation of only a trace of the demethylated product. This suggests that a mechanistic pathway for the kinetic abstraction of the *endo*-hydrogen exists that was not available to the more sterically congested hexamethylcyclohexadienyl complex, possibly involving initial coordination of the Lewis acid to the electron-rich metal center. Curiously enough, the use of oxidizing agents such as trityl or ferricinium cation results in a much higher proportion of demethylation, even though oxidizing reagents are generally selected for abstraction of *endo*-hydrogens.[87,88,102b] The use of trityl cation also results in the formation of a third compound which has not been conclusively identified, but appears to arise from trityl addition to the cyclohexadienyl ligand, as deduced by ^{1}H NMR spectroscopy.

Table 1. Product Distribution from Reactions of Lewis Acids With $(C_5Me_5)Ru(\eta^5$-6(*exo*)-methylcyclohexadienyl



134 136 137

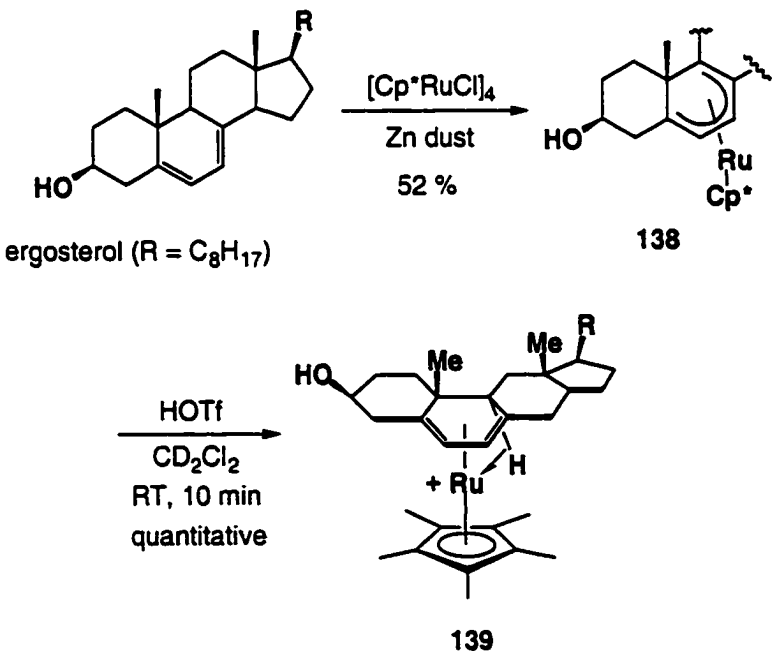
Reaction conditions: (RT)	% of complex 136[a]	% of complex 137[a]
$AlBr_3$, CD_2Cl_2	90	10
$B(C_6F_5)_3$, CD_2Cl_2	99	<1
$Cp_2Fe^+PF_6^-$, CH_2Cl_2,	42	58

[a] As measured by ^1H NMR spectroscopy.

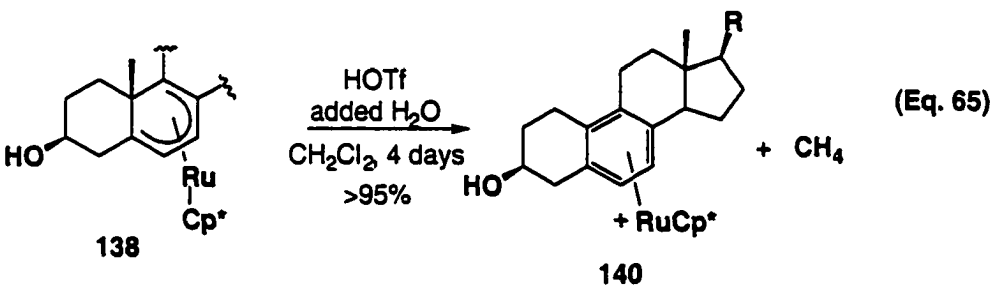
A second look was also taken at the mechanism of aromatization of steroidal substrates by use of electrophilic ruthenium. The ergosterol case was taken as a representative example and the neutral $(C_5Me_5)Ru(\eta^5$-dehydroergosterol) complex **138** prepared by the reaction of $[(C_5Me_5)RuCl]_4$ with ergosterol and Rieke zinc dust (Scheme **37**). Chaudret demonstrated through X-ray structural analysis that coordination in the β-ring of steroid substrates occurs on the α-face, placing the angular methyl group on the opposite face from the ruthenium metal fragment.[73c] Treatment of this neutral species with either triflic or tetrafluoroboric acid in anhydrous dichloromethane produces a stable cationic species **139** spectroscopically similar to the cationic hydride intermediate

previously described by Chaudret. However, the spectroscopic data is more suggestive of an agostic complex than a classical hydride, due to the similarity to the agostic complexes described earlier: a broad singlet at δ –5.00 in the ^{1}H NMR spectrum, and a GCOSY spectrum showing strong correlations of this signal to the δ 1.95-2.40 region. Cationic ergosterol complex **139** appears to be structurally rigid at room temperature on the NMR time-scale, presumably due to the lack of symmetry found in the steroid ligand and the resulting energy difference between the two possible agostic intermediates. Upon the addition of both triflic acid and water to (C_5Me_5)Ru(η^5-9-dehydroergosterol) (**138**), the reaction proceeds quantitatively to produce the aromatized B-ring derivative **140** within four days at room temperature (Eq. **65**). In contrast, under Chaudret's reaction conditions, the conversion typically requires several weeks at room temperature or 40 hours at 120°C. This kinetic difference is probably a result of water being a more

Scheme 37



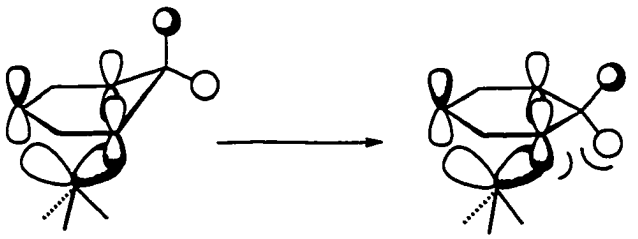
effective Lewis base than the equimolar methanol present in Chaudret's system. It is also plausible that the methanol (in the presence of excess triflic acid) is responsible for the trace amount of ethane observed occasionally in some of Chaudret's reactions, since the $CH_3OH_2^+$ formed may subsequently abstract the *exo*-methyl substituent to produce either hydrogen or ethane, the latter by attack of the electrophilic methyl group on the nucleophilic *exo*-methyl of the steroid complex. However, the *optimal* method for demethylation of the ergosterol ligand involves the treatment of $(C_5Me_5)Ru(\eta^5$-dehydroergosterol) **138** with trityl cation: this reaction proceeds quantitatively to the demethylated product **139** in less than one hour at room temperature. The utility of Chaudret's steroid demethylation can thus be substantially improved by simple modifications in experimental conditions based on this new mechanistic understanding.



(Eq. 65)

The question remains why the straightforward β-alkyl elimination from an *endo*-alkyl cyclohexadienyl complex should remain so elusive. An early paper by Hoffmann[107] on the electronic origin of observed geometrical deformations in such cyclohexadienyl transition metal complexes serves to explain the rarity of this reaction course. Molecular orbital calculations on d^6-(cyclohexadienyl)ML_3 complexes demonstrate that a secondary

Figure 4. MO Interactions for d^6-(Cyclohexadienyl)ML_3 Metal Complexes

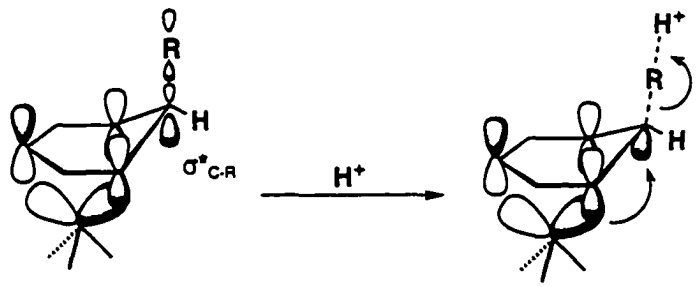


antibonding orbital interaction exists between the metal and the lower methylene carbon-hydrogen bond, causing the methylene group to bend significantly away from the metal (Figure 4). The calculated potential energy curve for distorting this methylene towards planarity shows that a prohibitively high energy barrier is present. Since the cyclohexadienyl ligand cannot approach planarity, the *endo* hydrogen (or carbon) remains inaccessible for metal-mediated bond cleavage. However, this antibonding orbital interaction can be mitigated, either by removal of an ancillary ligand from the complex or via oxidation of the metal center, allowing the β-alkyl elimination to proceed, although such reactions may still require harsh conditions. A similar secondary antibonding interaction was also calculated for related cyclopentadiene complexes, although the magnitude of the interaction was found to be less significant in these systems.

In contrast, the low activation barrier for cleavage of the *exo* substituent can be rationalized by considering that significant stabilization of the transition state may be provided by the interaction of a filled metal-centered molecular orbital[107] with the σ*-orbital of the activated bond (Figure 5). A similar molecular orbital interaction is considered responsible for the low frequency C-H vibrational mode observed for the *exo* carbon-hydrogen bond in the infrared spectra of other η^5-cyclohexadienyl and η^4-

cyclopentadienyl complexes.[88,91] This bonding interaction transforms smoothly into a metal-arene orbital as the bent cyclohexadienyl ring converts to the planar arene ligand. The metal is, in effect, displacing the *exo*-substituent by a concerted nucleophilic substitution with electrophilic assistance from the proton, which functions to stabilize the anionic alkyl leaving group.

Figure 5. MO Interactions for Dealkylation Reaction



R = H, CH_3

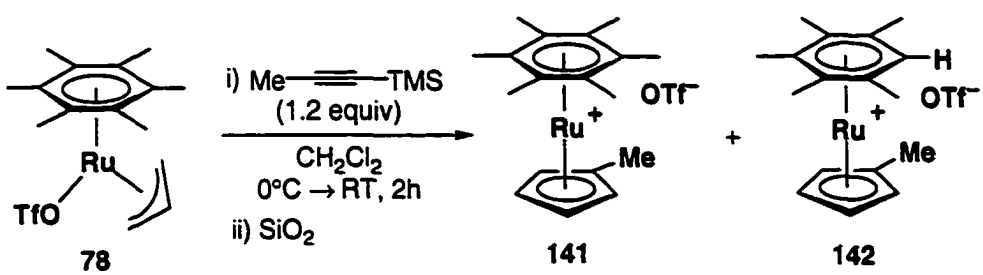
7. Conclusion

Through the use of model studies and low temperature NMR spectroscopy we have better elucidated the mechanism of the ruthenium mediated allyl/alkyne [3 + 2] cycloaddition and determined that the integrated demethylation process follows a protolytic reaction pathway. This is the first recognized example of a strong, apparently unactivated carbon-carbon bond being cleaved by electrophilic abstraction under mild conditions. It is plausible, however, that several related examples of dealkylation involving electrophilic ruthenium or iron systems follow a similar reaction pathway. The use of an electron transfer reagent functions to induce oxidative carbon-carbon bond activation of these complexes, although this can also lead to competitive *endo*-hydrogen

abstraction. These radical reactions can be controlled to some extent by changes in reaction temperature. Both the electrophilic abstraction and the oxidatively induced carbon-carbon bond scission represent surprisingly mild reaction conditions for the dealkylation of *exo*-substituted cyclohexadienyl complexes.

III. Ruthenium-Mediated [3 + 2] Coupling Reactions of Silyl-Substituted Alkynes

An intriguing discovery was that the cycloaddition reaction could be diverted away from the dealkylation process by the use of silyl-substituted alkynes. Thus, treatment of (η^6-C_6Me_6)Ru(η^3-allyl)OTf **78** with 1-(trimethylsilyl)propyne (1.2 equiv) in dichloromethane results in the formation of two η^5-methylcyclopentadienyl products, complexes **141** and **142**, after purification by chromatography (Eq. **66**). Both products have lost the silyl substituent, either during the course of the reaction or at some point in the purification process. The major product, **141**, retains the η^6-hexamethylbenzene ligand while the minor product is the demethylated η^6-pentamethylbenzene complex **142**, produced in a ratio of 1.5 : 1, respectively. ^{1}H NMR spectroscopic analysis of the crude product mixture, however, indicates that the initial minor product is likely the (η^6-C_6Me_5H)Ru(η^5-1-silyl-2-methylcyclopentadienyl) **145** [δ 6.09 (s, 1H, $C_6Me_5\underline{H}$), 4.95 (br s, 3H, $C_5\underline{H}_3Me(SiMe_3)$)]; the silyl group is subsequently lost, presumably during chromatography on silica gel. The hexamethylbenzene complex **141** is apparent in the initial crude product mixture, suggesting that in this case the silyl group is lost during the [3 + 2] cycloaddition reaction. Unfortunately, a complex mixture of singlets is observed

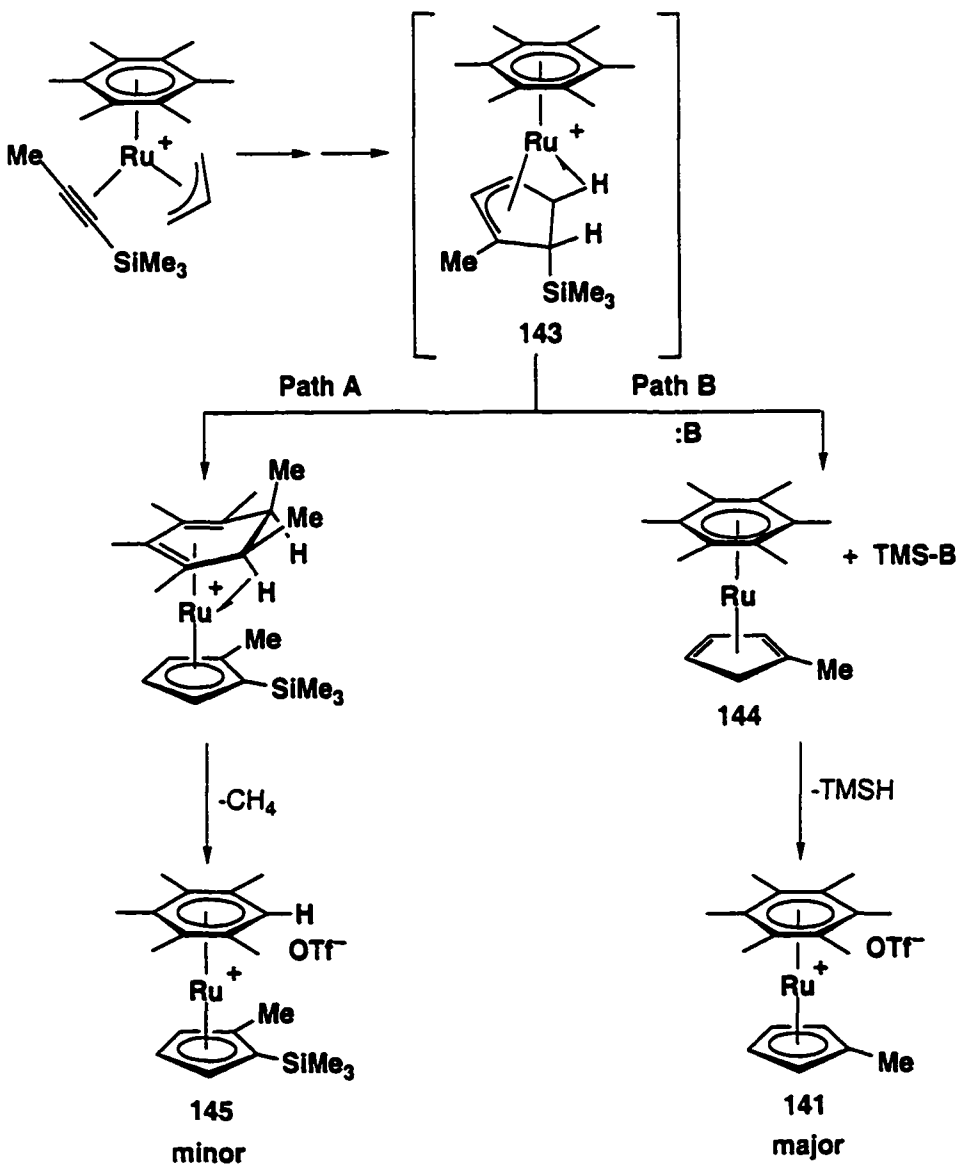


(Eq. 66)

in the silyl region of the crude ^{1}H NMR spectrum (δ 0.4 – δ 0.0), giving little information on the silyl products formed during this reaction.

An integrated mechanistic proposal can be constructed, based on the mechanism earlier outlined for the [3 + 2] cycloaddition with concomitant demethylation (Scheme 38). Initial alkyne insertion is followed by migratory cyclization to form the η^1,η^2-

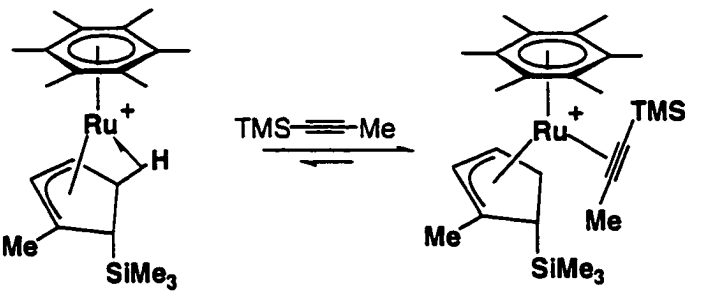
Scheme 38



cyclopentenyl intermediate, which rearranges to a more stable agostic η^3-cyclopentenyl complex **143**. For steric reasons, the most likely arrangement of the η^3-cyclopentenyl complex is with the silyl group located on a carbon not directly coordinated to the metal center. At this η^3-cyclopentenyl stage, a kinetic partition then selects between nucleophilic abstraction of the *exo* silyl group (path B) or transfer of two cyclopentenyl hydrogen atoms to the arene ligand (path A). The nucleophile in the former pathway could be adventitious base present in the reaction (e.g., H_2O), or possibly the triflate counterion.[53,56] Subsequent electrophilic abstraction of an *exo* hydride from the neutral intermediate **144** either by the trimethylsilyltriflate or adventitious protic acid then results in formation of the hexamethylbenzene product **141**. In contrast, the latter pathway (path B) follows the standard arene dealkylation mechanism, resulting in the formation of the minor η^6-pentamethylbenzene cyclopentadienyl **145** and methane.

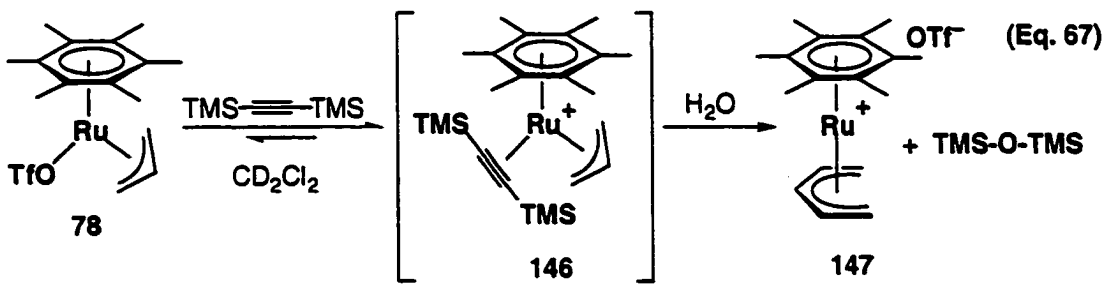
The ratio of pentamethylbenzene to hexamethylbenzene product can be influenced somewhat by adjusting the reaction conditions. Addition of excess 1-(trimethylsilyl)propyne (>20 equiv) increases the selectivity in favour of the hexamethylbenzene product, producing a 9 : 1 ratio, as measured spectroscopically. This phenomenon can be rationalized by proposing that excess alkyne can coordinate to the unsaturated η^3-cyclopentenyl complex **143** but does not insert (Scheme **39**). The coordination by excess alkyne would be expected to suppress the interligand hydrogen transfer, thus inhibiting the dealkylation pathway. The desilylation pathway, however, is apparently not significantly affected by the coordination of alkyne, resulting in an increased ratio of the hexamethylbenzene product.

Scheme 39



143

An even more unusual reaction is observed upon treatment of ruthenium allyl triflate **78** with bis(trimethylsilyl)acetylene. The reaction gives a single *acyclic* product, the doubly-desilylated acyclic η^5-pentadienyl compound **147**, while retaining the hexamethylbenzene ligand. The ^{1}H NMR spectrum of this complex exhibits mirror-plane symmetry, with a downfield signal at δ 5.75 (t, 1H) assigned to the central hydrogen of the pentadienyl ligand. The two equivalent terminal *anti* hydrogens are located further upfield (at δ 1.07) than the *syn* hydrogens (at δ 2.79), the higher shielding caused by closer metal proximity. Both the ^{1}H and ^{13}C NMR spectra closely resemble those of other known acyclic ruthenium η^5-pentadienyl complexes.[93,94,109] During the course of the reaction, hydrogen atoms have replaced both silyl groups, even as the reaction pathway is diverted from the "normal" dealkylative cycloaddition process.



In an attempt to gain more information about the mechanism of this transformation, the reaction was repeated in anhydrous dichloromethane-d_2 while being monitored by ^1H and ^{13}C NMR spectroscopy (Eq. **67**). Addition of an equimolar amount of bis(trimethylsilyl)acetylene results in a mixture of starting material, free alkyne and a new ruthenium complex, tentatively identified as the cationic allyl alkyne complex **146**. Both the ^1H NMR and ^{13}C NMR spectrum of this compound closely resemble those obtained for the previously discussed hexamethylbenzene allyl alkyne complexes **122** and **125**. The silyl methyl groups of coordinated bis(trimethyl)acetylene appear as a singlet at δ 0.23 (18 H) in the ^1H NMR spectrum and at 2.3 ppm in the ^{13}C NMR spectrum. The internal carbons of the coordinated alkyne appear at 110.8 ppm, which is shifted slightly upfield from the free alkyne (at 114.1 ppm), a phenomenon noted for the other ruthenium η^3-allyl alkyne examples. A second equivalent of bis(trimethylsilyl)acetylene completely converts this mixture to the allyl alkyne complex, indicating that an equilibrium exists between the allyl triflate starting material and the cationic bis(trimethylsilyl)acetylene complex. The allyl alkyne complex appears to be stable with respect to further reactivity under these conditions: even after four hours at room temperature, no traces of any new products are detected.

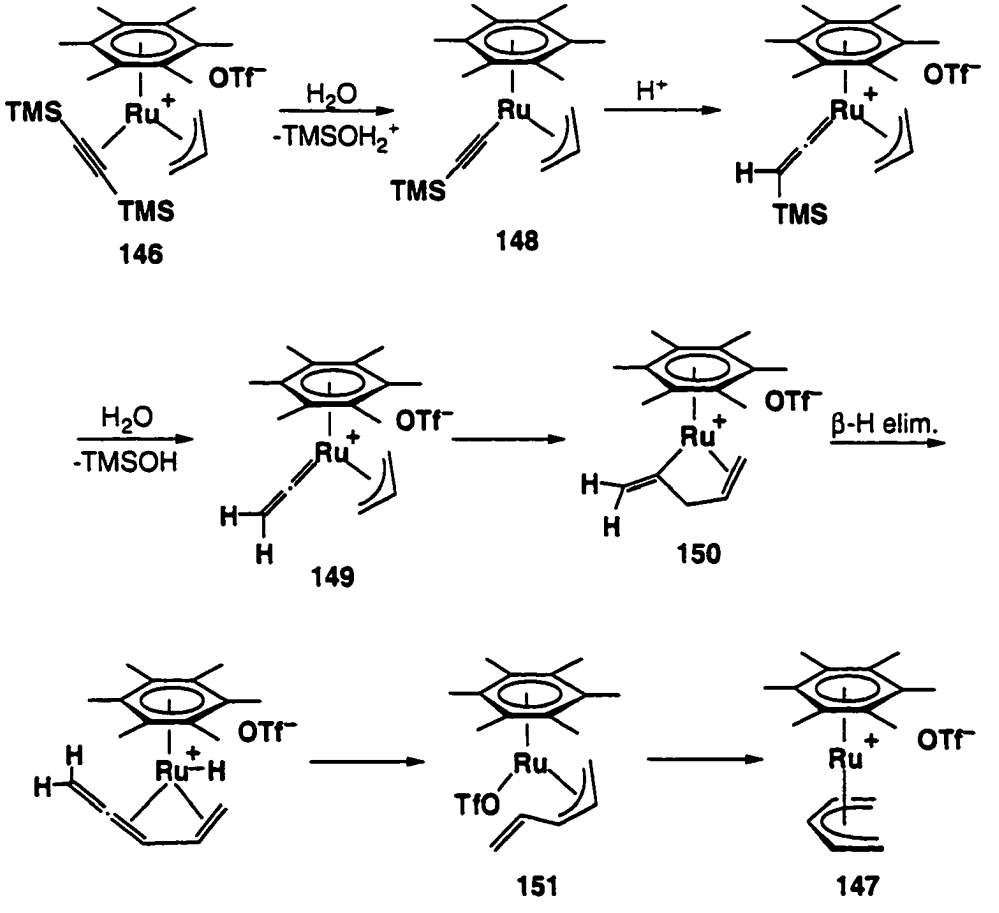
Although stable in anhydrous dichloromethane-d_2, the alkyne complex rapidly converts to the acyclic η^5-pentadienyl product **147** upon addition of water. The reaction is complete within 10 minutes at room temperature but, unfortunately, no intermediates are observed spectroscopically. However, a new upfield signal at δ 0.11 in the ^1H NMR spectrum is formed concurrently with the pentadienyl complex **147**. Over a period of 24 hours, this signal slowly disappears and is replaced by a new singlet at 0.06 ppm, which

is attributed to the formation of hexamethyldisiloxane by comparison to an authentic sample. Based on the formation of this material, the initially observed upfield signal is probably due to the formation of trimethylsilanol during the course of the reaction. The facile dehydration of silyl alcohols to form silyl ethers in the presence of trace acid or base is well precedented.[109]

The exact mechanism of this double desilylation reaction is unclear, although it is certain that the presence of water is required to effect the conversion. The observed stability of the allyl alkyne complex **146** in anhydrous solvent suggests that neither direct allyl-alkyne coupling, nor an initial [1,2]-silyl shift on the coordinated alkyne to form a bis(trimethylsilyl)vinylidene complex occurs, although an equilibrium with the vinylidene strongly favouring the alkyne complex cannot be completely ruled out.[110] A second possibility is that water acts to convert the bis(trimethyl)acetylene to the terminal alkyne, (trimethylsilyl)acetylene, which can then insert and subsequently rearrange to form the final product. However, treatment of the ruthenium allyl triflate complex **78** with 1.5 equivalents of (trimethylsilyl)acetylene under otherwise identical reaction conditions results in a complex mixture of products, none of which corresponds to the observed acyclic η^5-pentadienyl complex **147**.

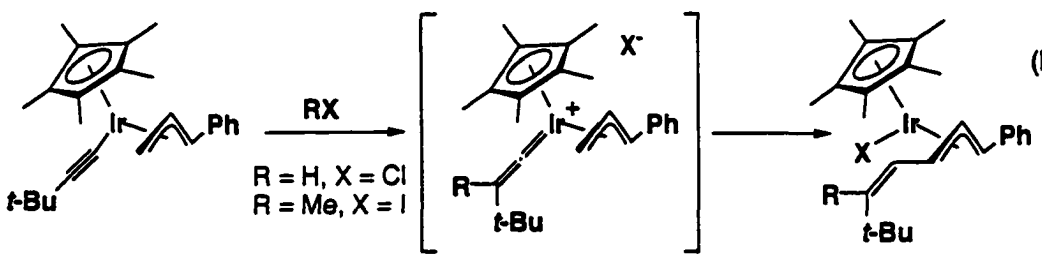
The most plausible rationalization, then, is that water acts as a nucleophile to desilylate the coordinated alkyne, resulting in the formation of $TMSOH_2^+$ and the neutral η^3-allyl acetylide complex **148** (Scheme **40**). While fluoride is a more common desilylating agent,[54-55] water is a strong enough nucleophile to abstract silyl groups from electrophilically activated substrates such as those coordinated to a cationic metal center.[56] A similar process was demonstrated earlier in the preparation of [(η^6-

Scheme 40



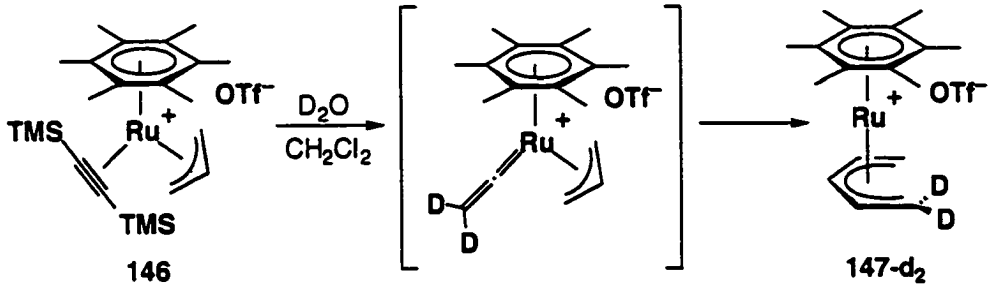
$C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(CH_3CN)]^+BF_4^-$ **76** (*vide supra*) using allyltrimethylsilane in wet solvent. We then propose that protonation of the neutral acetylide **148** generates a cationic ruthenium η^3-allyl vinylidene complex. The addition of electrophiles to the β-carbon of a σ-acetylide ligand to yield a metal-vinylidene complex is well known.[111] While it is possible that the second silyl group is lost at some later stage of the reaction, it is more likely that the second desilylation occurs at this point, since silyl-substituted vinylidene complexes have been shown to be very sensitive to water and other proton sources.[112] Once the bulky silyl group is replaced to yield the unsubstituted vinylidene

complex **149**, the α-carbon of the vinylidene ligand becomes more susceptible to attack by the nucleophilic terminal carbon of the allyl. The initial product from the coupling of vinylidene and η^3-allyl ligands is the strained η^1,η^2-pentadienyl complex **150**, which can undergo β-hydride elimination and reinsertion to form the more stable η^3-pentadienyl triflate complex **151**. Rotation of the pendant alkene around the carbon single bond followed by coordination to the metal thus results in the formation of the final η^5-pentadienyl product. Chin, *et al.*, have recently demonstrated a similar coupling reaction, in which a related iridium η^3-allyl σ-acetylide complex is treated with an equivalent of HCl or MeI to yield the η^3-pentadienyl product (Eq. **68**).[111a] It is also plausible that the allene intermediate loses a proton to the solvent medium and then reprotonates to directly yield complex **147**.



In an attempt to confirm the proposed mechanism, a deuterium labelling experiment was performed. Thus, allyl alkyne complex **146**, formed *in situ*, was treated with D_2O instead of water. Analysis of the crude labelled product, **147**-d_2, by ^2H NMR spectroscopy revealed that two deuterium atoms were incorporated exclusively at one terminus of the η^5-pentadienyl ligand (Eq **69**). This establishes that the desilylated vinylidene complex **148** is a plausible intermediate in the overall transformation. It is

likely that this reaction pathway becomes available only because bis(trimethylsilyl)-acetylene is too large to undergo a "normal" migratory coupling process.



146 147-d_2 (Eq. 69)

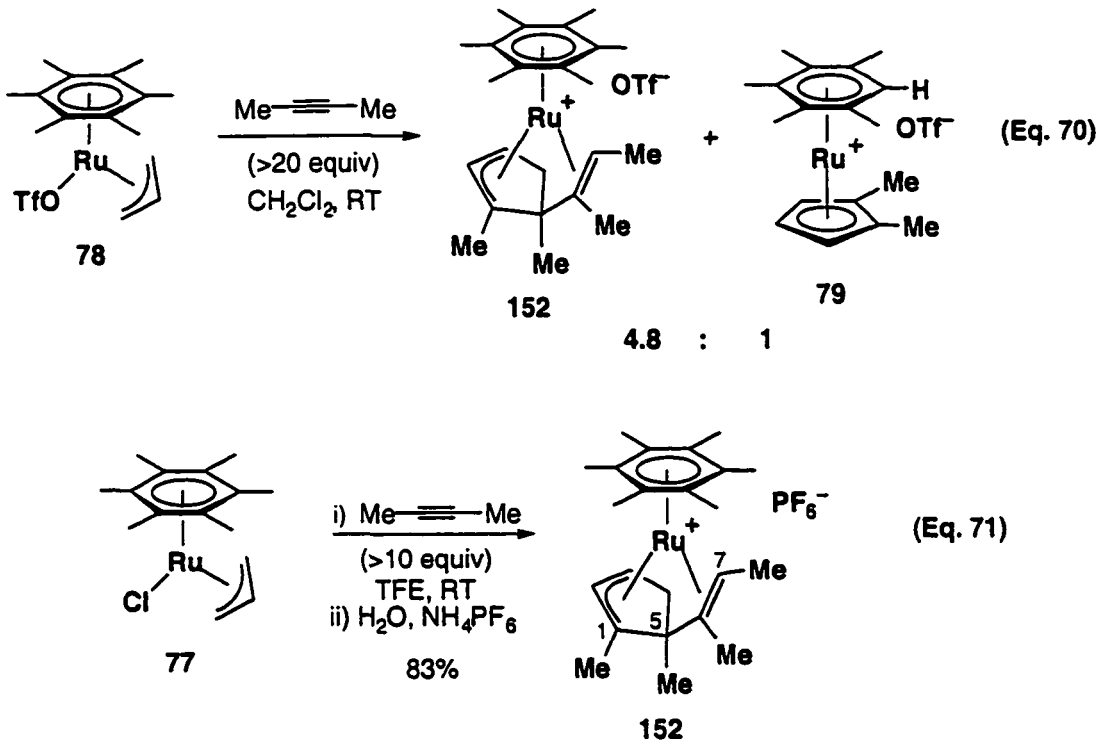
Chapter 3. [3 + 2 + 2] Allyl/Alkyne Coupling Reactions Mediated by the Cationic (η^6-C_6Me_6)Ru(II) Template

I. [3 + 2 + 2] Cycloaddition Reactions of Cationic η^3-Allyl Ruthenium Complexes

Although the [3 + 2] allyl/alkyne cycloaddition proved to be far more complex than originally expected, our primary interest is in developing the potentially useful [3 + 2 + 2] allyl/alkyne cycloaddition reactions for synthetic applications. In general, as discussed in Chapter 2, most of the dialkyl- and diaryl-substituted alkynes that were tested using the cationic (η^6-C_6Me_6)Ru(η^3-allyl) template yield only [3 + 2] allyl/alkyne monoadducts, even in the presence of excess alkyne. However, the use of more reactive alkynes can lead to an astonishing variety of double alkyne insertion products with unusual hapticity patterns.

1. The [3 + 2 + 2] η^3-Allyl/2-Butyne Cycloaddition Reaction

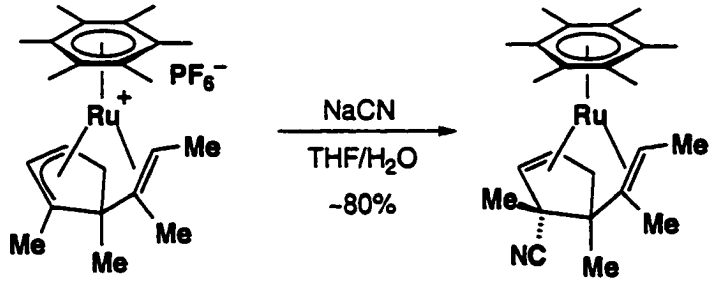
Of those assayed, the only dialkyl-substituted alkyne that results in the formation of a double alkyne insertion product is 2-butyne. While addition of equimolar amounts of 2-butyne to (η^6-C_6Me_6)Ru(η^3-allyl) triflate (**78**) yields (η^6-C_6Me_5H)Ru(η^5-dimethylcyclopentadienyl) complex **79** (Chapter 2), a different product is observed when a large excess of 2-butyne is used. Thus, treatment of η^3-allyl triflate complex **78** with 20 equivalents of 2-butyne in dichloromethane yields a mixture of pentamethylbenzene



complex **79** and the new hexamethylbenzene complex **152**, which incorporates two equivalents of 2-butyne, formed in a ratio of 1 : 4.8 (Eq. **70**). Use of the ruthenium allyl chloride complex **77** in trifluoroethanol was found to give the bis-adduct **152** more cleanly, using only ten equivalents of 2-butyne and with no trace of the monoadduct (Eq. **71**). Although the yield of this reaction is relatively high (83%), purification proved to be difficult, as the initial complex slowly converts to a second, unidentified product, accompanied by a significant amount of decomposition. The ^{1}H NMR spectroscopic analysis of the crude product indicates that the initial hexamethylbenzene product has four non-aromatic methyl groups, three of which are singlets, (at δ 1.77, 1.68 and 1.00) and one doublet (at δ 1.69, J = 6.2 Hz). This methyl doublet signal is coupled to a downfield quartet at δ 3.15 (H_7), which in turn correlates to a sp^2-hybridized carbon signal at 65.1 ppm (C_7) in the gated ^{13}C NMR spectrum, with a $^{1}J_{CH}$ coupling of 159 Hz. Together, the

evidence indicates that a terminal dimethylvinyl group is present. On the basis of further spectroscopic analysis (including HMQC and HMBC spectra) the hexamethylbenzene bis-adduct was tentatively identified as the cationic 1,5,6,7-tetramethyl-5-vinylcyclopentenyl complex **152**. However, all attempts to obtain analytically pure crystals for combustion analysis and X-ray crystallography for this compound failed.

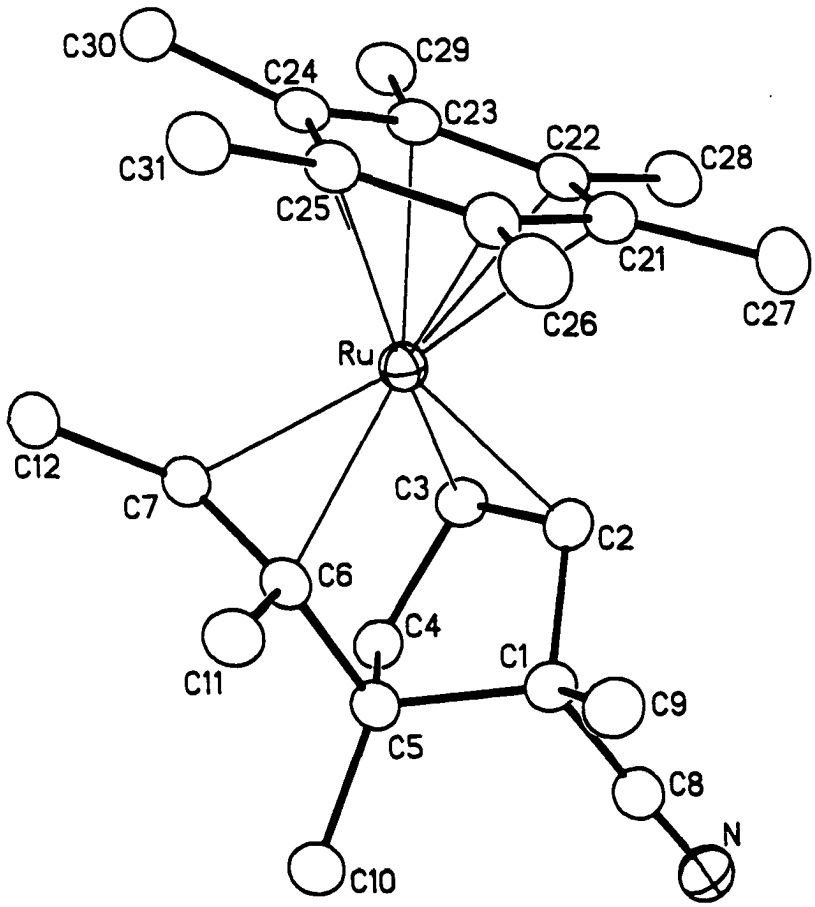
Since we were unable to obtain suitable crystals of the cationic bis-2-butyne adduct, a derivative was prepared in the hope that it would be more crystalline and less prone to thermal decomposition. Addition of cyanide provides a clean reaction, resulting in the formation of a yellow, mildly air-sensitive crystalline material (Eq. **72**). Slow recrystallization at low temperature (–35°C) yields a small amount of X-ray diffractable crystals. The purified material was subjected to both spectroscopic and X-ray analysis. The complex proved to be the neutral, non-conjugated 1,5,6,7-tetramethyl-1-cyano-5-vinylcyclopentene complex **153** (Figure **6**). The identity of this derivative is fully consistent with the initial assignment of complex **152**.



152 **153** **(Eq. 72)**

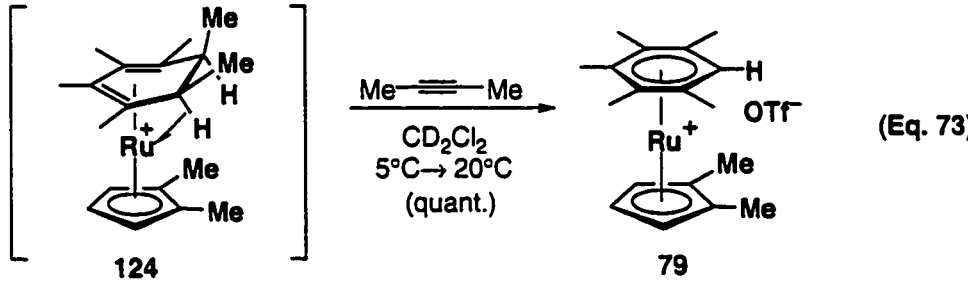
Several NMR experiments were performed in order to obtain more information on the mechanism of the double 2-butyne insertion. As previously described (see Chapter 2, Scheme **33**, p. 81), the addition of an equimolar amount of 2-butyne to allyl triflate

Figure 6. ORTEP[113] Plot of Complex **153** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9804



Final Residuals: $R_1 = 0.0466$; $wR_2 = 0.1341$. Data obtained at -60°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.
Selected Bond Distances (Å): Ru-C2, 2.108(4); Ru-C3, 2.146(4); Ru-C6, 2.160(5); Ru-C7, 2.162(4); N-C8, 1.153(6); C1-C2, 1.527(6); C1-C5, 1.578(6); C1-C8, 1.472(6); C1-C9, 1.531(6); C2-C3, 1.429(6); C3-C4, 1.520(6); C4-C5, 1.543(6); C5-C6, 1.548(7); C5-C10, 1.513(6); C6-C7, 1.419(6); C6-C11, 1.522(6); C7-C12, 1.506(5).
Selected Bond Angles (deg.): C2-C1-C5, 98.1(3); C2-C1-C8, 110.0(4); C2-C1-C9, 113.7(4); C5-C1-C8, 110.5(4); C5-C1-C9, 118.5(4); C8-C1-C9, 105.9(4); C1-C2-C3, 110.3(4); C2-C3-C4, 105.8(4); C3-C4-C5, 100.8(3); C1-C5-C4, 99.1(3); C1-C5-C6, 106.5(3); C1-C5-C10, 114.7(4); C4-C5-C6, 107.1(4); C4-C5-C10, 113.7(4); C6-C5-C10, 114.4(4); C5-C6-C7, 118.9(4); C5-C6-C11, 115.4(4); C7-C6-C11, 117.1(4); C6-C7-C12, 122.5(4); N-C8-C1, 178.6(5).

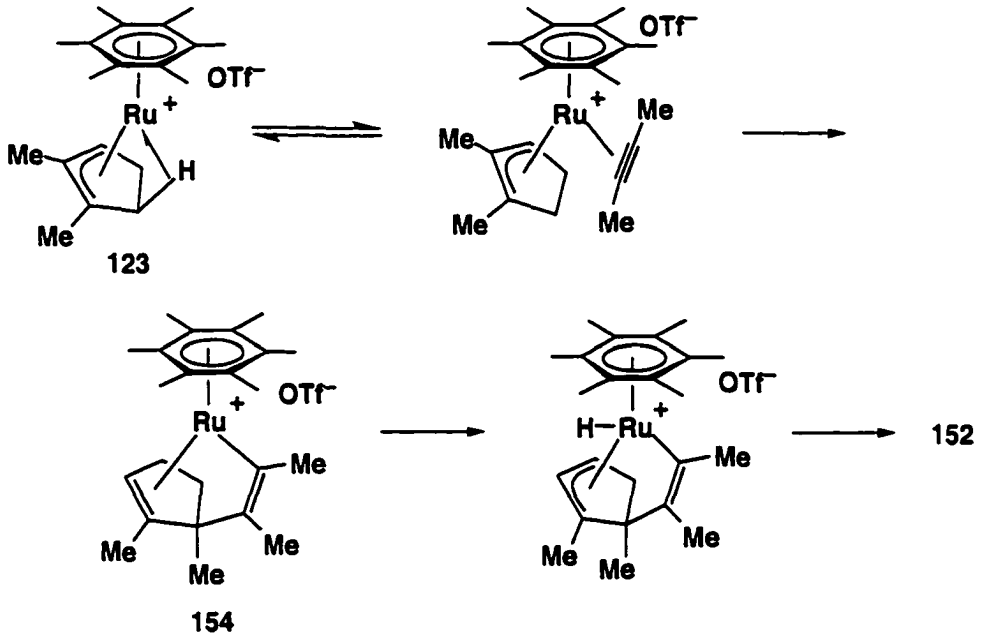
complex **78** at low temperature in anhydrous dichloromethane-d_2 followed by careful warming results in the formation of cationic agostic η^4-cyclohexadiene complex **124**. Once this intermediate is formed, only the demethylated cyclopentadienyl complex **79** is observed even if excess 2-butyne is subsequently added to the reaction mixture (Eq. **73**). This indicates that the double hydrogen atom transfer to the arene ring is irreversible and that insertion of the second equivalent of 2-butyne leading to complex **152** must occur before the intraligand transfer.



(Eq. 73)

The most plausible mechanism for the formation of the 5-vinylcyclopentenyl product **152** is thus outlined in Scheme **41**. As described earlier, the 2-butyne initially coordinates and then inserts to form a vinyl olefin intermediate, followed by migratory cyclization to yield the η^1, η^2-cyclopentenyl complex (Chapter 2, Scheme **33**). This complex rearranges to form the spectroscopically observed η^3-dimethylcyclopentenyl complex **123**, which was tentatively identified earlier as a fluxional agostic complex by low temperature NMR spectroscopy. In the presence of excess 2-butyne, a second alkyne coordinates and inserts to form the vinylcyclopentene complex **154**, a process very similar to that proposed for cobalt [5 + 2] ring expansion reactions.[43,44] However, in contrast to the cobalt reactivity, 2-butyne must insert into the more substituted end of the ruthenium

Scheme 41

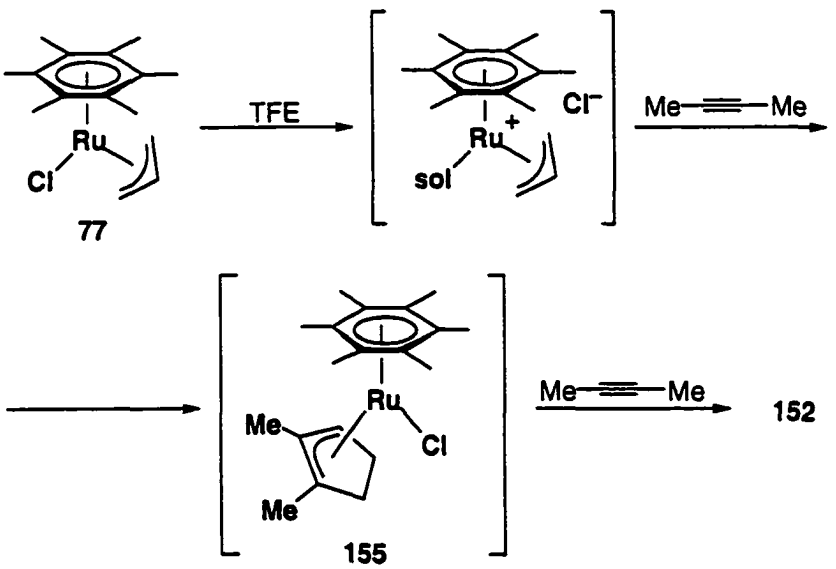


η^3-cyclopentenyl ligand. The insertion is followed by allylic C-H activation and subsequent reductive elimination to form the final vinylcyclopentenyl complex **152**, which must be faster than the [5 + 2] ring expansion required to produce an η^5-heptadienyl product. This difference may be attributed to kinetic differences arising from the far more readily oxidized Ru(II) intermediate **154** compared to the Co(III) system, and possibly to the greater accessibility of the methylene hydrogen atom to the ruthenium metal center compared to cobalt.

The fact that the reaction of allyl chloride complex **77** with 2-butyne occurs in trifluoroethanol merits further discussion. Trifluoroethanol is a highly polar solvent that promotes ionization of the chloride ligand, yielding a solvated outer sphere anion and a cationic unsaturated ruthenium center which is able to coordinate additional alkyne (Scheme **42**). After initial alkyne insertion and migratory cyclization provides the

unsaturated η^3-cyclopentenyl complex **123**, it is plausible that chloride re-coordinates, trapping the new η^3-allyl as the neutral chloride complex **155**, instead of forming the agostic complex observed during the reaction of the triflate complex in dichloromethane. However, the η^3-cyclopentenyl chloride complex **155** can subsequently dissociate the chloride ligand and the unsaturated ruthenium thus formed inserts additional 2-butyne to form the bis-adduct **152**.

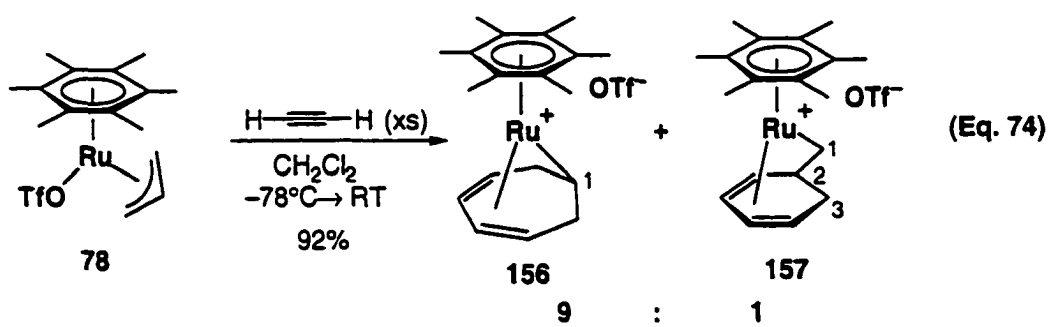
Scheme 42



In moving to the η^6-hexamethylbenzene ancillary ligand from the unsubstituted η^6-benzene ligand studied by Rubezhov, it thus appears that we promote five-membered ring products instead of seven-membered ring formation, as originally intended. To suppress the formation of five-membered ring adducts, we assayed the reactivity of terminal alkynes, since a sterically small, reactive alkyne is more likely than a large, disubstituted alkyne to insert twice prior to migratory cyclization.

2. [3 + 2 + 2] η^3-Allyl/Terminal Alkyne Cycloaddition Reactions

While neither Schwiebert nor Rubezhov detected tractable products from reactions of acetylene and either the iridium[38,39] or ruthenium systems,[35] Dzwiniel and Etkin demonstrated that reactions with acetylene produce seven-membered ring complexes from a variety of cobalt allyl templates.[42,43] The addition of acetylene to a dichloromethane solution of $(C_6Me_6)Ru(\eta^3$-allyl) triflate **78** at low temperature, followed by warming to room temperature initially provides an inseparable mixture of two η^6-hexamethylbenzene bis(acetylene) products **156** and **157** in a ratio of 9 : 1 (Eq. 74). The major product (**156**) exhibits mirror-plane symmetry in both the ^1H and ^{13}C NMR spectra, consistent with the formation of an unsubstituted seven-membered ring. However, unlike previously identified cobalt η^5-cycloheptadienyl adducts, the ^1H NMR spectrum of **156** reveals an upfield signal at δ –0.09 that integrates to one hydrogen; ^1H-^{13}C HETCORR spectroscopic



(Eq. 74)

analysis establishes that this proton signal correlates to an unusually upfield carbon resonance at –38.1 ppm in the ^{13}C NMR spectrum. On the basis of this spectroscopic data, the major compound is identified as the η^1,η^4-cycloheptadienyl complex **156**, with the

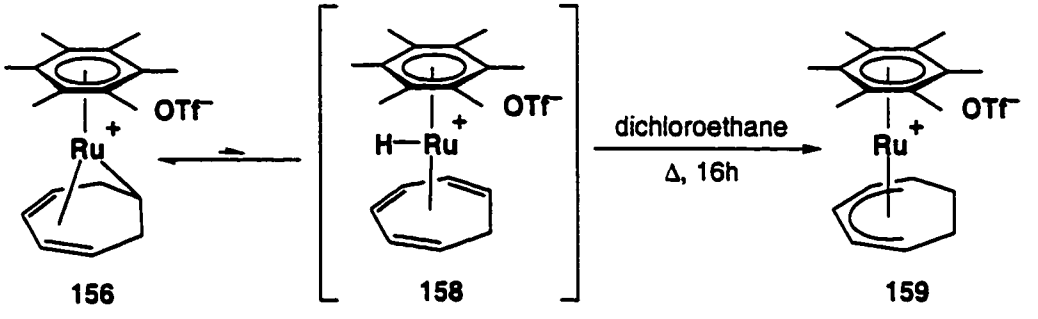
upfield carbon being assigned to the ipso carbon σ-bonded to the ruthenium metal center (C_1). While such a structure has previously been proposed as a plausible intermediate in the formation of η^5-cycloheptadienyl complexes from [3 + 2 + 2] cycloadditions, no such complex has ever been directly observed; complex **156** thus represents a new hapticity pattern for the coordination of a seven-membered ring to a metal.

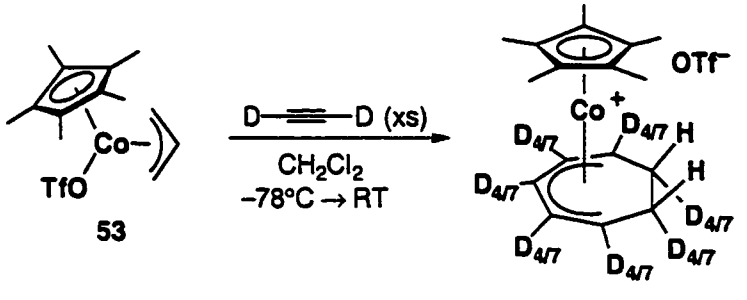
The minor product, **157**, while also incorporating two equivalents of acetylene, exhibits no apparent symmetry in the ^1H or ^{13}C NMR spectrum. The spectroscopic analysis indicates the formation of a compound very similar in structure to the tetramethyl-η^1,η^4-methanocyclohexadienyl complex **40** isolated by Rubezhov. The ^1H NMR spectrum exhibits two downfield triplet signals at δ 5.36 and δ 4.53 with a mutual coupling of 5.5 Hz, which are assigned to the internal diene protons H_5 and H_6, respectively. Similar to the Rubezhov complex, the two methylene protons H_{3exo} and H_{3endo} appear as a broad singlet at δ 1.07 due to the close proximity of chemical shifts. Also of note is a narrow doublet at δ 0.99 attributed to H_{1b}, which exhibits unusually small geminal coupling of 3.2 Hz to H_{1a} at δ 1.21, characteristic of a geminal pair of hydrogens adjacent to an electropositive metal center.[114] The carbon attached directly to the ruthenium atom, C_1, which appears at 0.13 ppm in the ^{13}C NMR spectrum, is shifted downfield from the reported carbon resonance at –8.96 ppm for the analogous η^6-benzene complex.

While ^1H NMR spectroscopy of the major, seven-membered ring product appeared to indicate a static structure, decoupling experiments proved that the complex was in fact fluxional. Application of a decoupling pulse to the resonances located at δ 5.33 ($H_{4/5}$), 3.53 ($H_{3/6}$), 2.15 ($H_{2exo/7exo}$) and –0.09 (H_1) each resulted in a marked decrease in the intensity of these same signals, a phenomenon due to spin saturation transfer (SST). The

only ring hydrogen signal apparently not affected by SST is the resonance found at 3.73 ppm, assigned to the two *endo* methylene hydrogens ($H_{2endo/7endo}$). These findings are consistent with an equilibrium wherein the observed η^1,η^4-cycloheptadienyl ruthenium complex **156** is converting via β-hydride elimination to the undetected cationic η^4-triene hydride complex **158** and back to one of two degenerate η^1,η^4-isomers, in a reaction that is slow on the NMR spectroscopic time-scale (Scheme **43**). This process results in the pairwise exchange of all but the two *endo* methylene ring hydrogens if labelled acetylene-d_2 is used. A similar scrambling process was observed in the reaction of cobalt η^3-allyl triflate complex **53** with acetylene-d_2 (Eq. **75**), although Etkin was unable to conclusively determine the mechanism by which the scrambling occurred.[41]

Scheme 43





(Eq. 75)

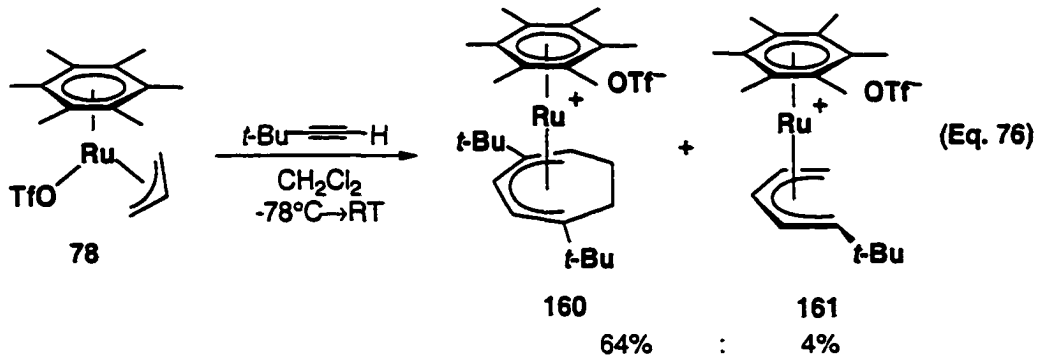
The slow conversion of η^1,η^4-cyclohexadienyl complex **156** to a new hexamethylbenzene product is observed when the mixture of the two acetylene adducts remains in a dichloromethane solution for a prolonged period of time. The conversion is accomplished more rapidly and quantitatively upon heating to reflux for sixteen hours (Scheme **43**). The minor product **157** is unaffected by this thermolysis. The isomerized product **159** is isolated from the minor methanocyclohexadienyl complex **157** by flash chromatography on silica gel using 5% methanol/dichloromethane as eluent and proved to be spectroscopically identical to the known $[(C_6Me_6)Ru(\eta^5\text{-cycloheptadienyl})]^+Cl^-$.[90] This complex was thus independently synthesized from the sodium carbonate reduction of Bennett's dichloro dimer **72** in ethanol while in the presence of excess cycloheptatriene.

Interestingly, the addition of an equimolar amount of acetylene to the allyl triflate complex **78** results in the formation of a mixture of the six- and seven-membered ring products **157** and **156**, along with a high proportion of starting material; no five-membered ring products are detected. This implies that, for acetylene at least, the second insertion of the alkyne is much faster than migratory cyclization to form a five-membered ring.

The isolation of the η^1,η^4-cycloheptadienyl "intermediate" confirms much of the proposed mechanism for the formation of seven-membered ring systems from the cycloaddition of a metal allyl complex and two alkynes. The discovery that such compounds can be fluxional also clarifies some of the earlier results found using the iridium and cobalt templates. For example, the deuterium labelling studies performed by Etkin[41] (*e.g.*, Eq. **75**) can now be rationalized by proposing that a similar equilibrium exists between various cobalt η^1,η^4-cycloheptadienyl isomers and the cobalt η^4-triene hydride prior to the slower conversion to the final η^5-cycloheptadienyl product. Schwiebert[39]

observed in the iridium system the formation of isomeric mixtures of seven-membered ring products that were related by hydride shifts, although she was unable to equilibrate these compounds under thermolysis conditions (Chapter 1, Eq. **23**, p. 22). These results can be rationalized, however, by proposing that the hydride shifts occur by β-elimination and reinsertion at the η^1,η^4-cycloheptadienyl intermediate stage and that the observed η^5-cycloheptadienyl products are formed irreversibly and are thermodynamically stable.

The [3 + 2 + 2] double alkyne cycloaddition was conducted using other unsymmetrical alkynes, although the formation of multiple regioisomers limits the utility of these reactions to those involving terminal alkynes with large substituents. Treatment of allyl triflate complex **78** with excess 3,3-dimethyl-1-butyne (4 equiv) at low temperature for example, results in a mixture of two products after warming to room temperature (Eq. **76**). These products can be readily separated by flash chromatography, giving the major product **160** as an orange crystalline material in 64% yield; however, only a small amount (4%) of the pure minor product **161** could be isolated due to interference from other impurities present in the reaction mixture. Extensive spectroscopic analysis (^{1}H, ^{13}C NMR) of the major compound was used to identify this product as the η^5-cycloheptadienyl

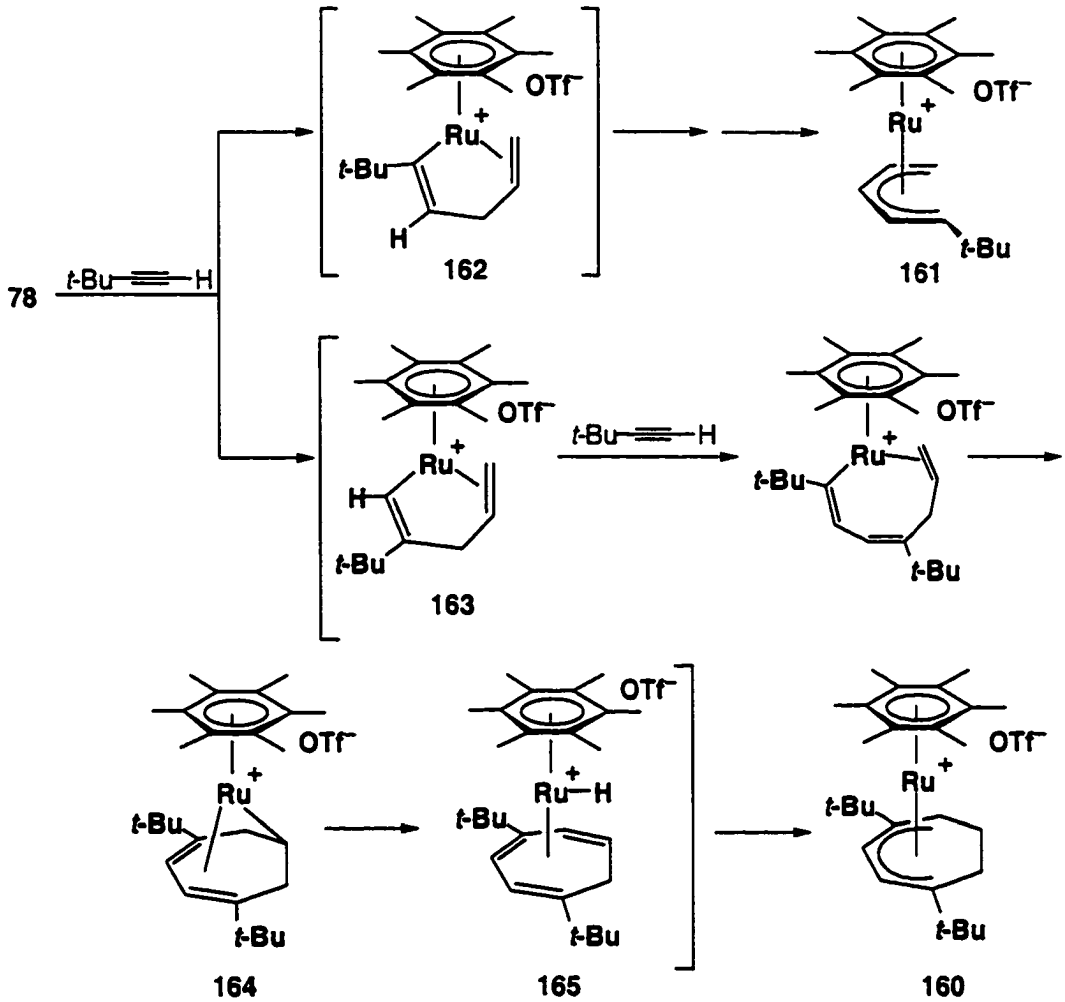


complex **160**, as both the ^{1}H and ^{13}C NMR spectra show a strong similarity to the analogous cobalt complex also obtained from 3,3-dimethyl-1-butyne.[42,43] Like the cobalt compound, the ^{1}H NMR spectrum of complex **160** exhibits an isolated AX spin system, with doublets at δ 6.05 and δ 5.40 for H_3 and H_2, respectively, consistent with a 1,4 substitution pattern. An upfield resonance at δ 0.05 (td, J = 12.1, 4.4 Hz) assigned as H_{7endo}, is considered highly characteristic of unsymmetrical η^5-cycloheptadienyl complexes and also closely matches that found for the cobalt complex.[43]

While only a small amount of the minor compound **161** was cleanly isolated, ^{1}H NMR spectroscopic analysis clearly indicates the formation of an acyclic η^5-pentadienyl structure. Comparison of the vicinal hydrogen coupling constants and chemical shifts to known η^5-pentadienyl ruthenium complexes suggest that the *t*-butyl substituent is located at one terminus of the pentadienyl ligand, *syn* to the neighbouring hydrogen.[93,94] Perhaps surprisingly, no trace of an η^1,η^4-cycloheptadienyl product was detected in the crude reaction mixture with this alkyne.

Even though the major product from this reaction was easily identified, the mechanism of its formation is not clearly understood. If the η^5-1,4-bis(*t*-butyl)cycloheptadienyl complex **160** is formed through the "normal" [3 + 2 + 2] reaction mechanism, then a partitioning must occur subsequent to the first alkyne insertion (Scheme **44**). The 1,4-substitution pattern displayed by the major product cannot arise from the same vinyl olefin intermediate **162** that leads to the minor acyclic pentadienyl complex **161**. To obtain the 1,4-substitution pattern found in complex **160**, the first alkyne must insert such that the *t*-butyl substituent is placed away from the ruthenium metal center to

Scheme 44

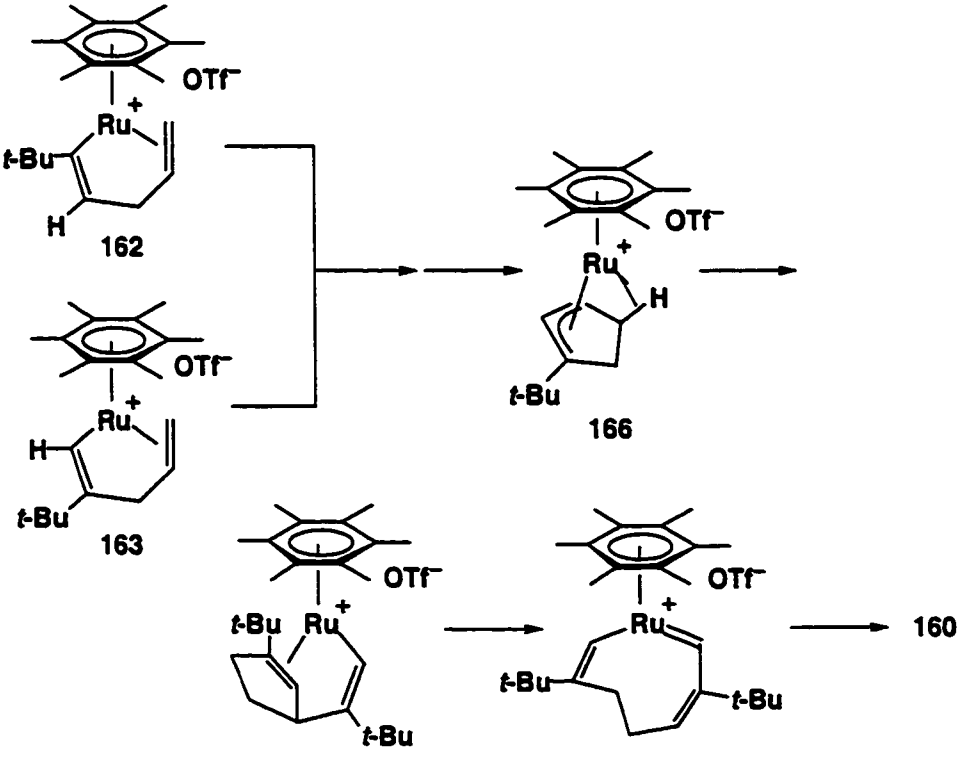


form vinyl olefin **163**, while, in contrast, the second alkyne must insert such that the *t*-butyl group is situated on the α-carbon. Migratory cyclization then results in the formation of an initial η^1,η^4-cycloheptadienyl complex (**164**) with mirror-plane symmetry. β-Hydride elimination subsequently gives the cationic triene hydride **165**, followed by a selective hydride insertion to produce the final η^5-cycloheptadienyl product. In principle, several isomers are possible from hydride rearrangements at the η^1,η^4-cycloheptadienyl stage, but

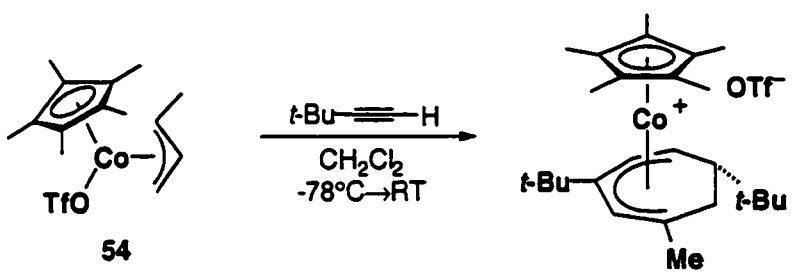
only a single bis(adduct) has ever been isolated from reactions with 3,3-dimethyl-1-butyne using the ruthenium or cobalt systems.

An alternative proposal suggests that the bis(adduct) is formed through the highly unusual [5 + 2] ring expansion mechanism (Scheme **45**), similar to that determined for some cobalt systems.[43,44] Migratory cyclization of either vinyl olefin intermediate **162** or **163** and subsequent rearrangement should eventually lead to the formation of η^3-cyclopentenyl complex **166**. Coordination and regioselective insertion of a second equivalent of 3,3-dimethyl-1-butyne to the less substituted end of the allyl ligand can then occur, preferentially placing the *t*-butyl group away from the metal. Carbon-carbon bond cleavage of the five-membered ring followed by ring closure to a seven-membered ring then yields the stable η^5-cycloheptadienyl complex **160**, without the opportunity for further rearrangement.

Scheme 45



In an attempt to distinguish between these two possible mechanisms, the reaction was repeated using equimolar 3,3-dimethyl-1-butyne. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicates formation of a complex mixture, including the starting material, the acyclic η^5-pentadienyl complex **161**, as well as some η^5-1,4-bis(*t*-butyl)cycloheptadienyl complex **160**. Unfortunately, few conclusions about the actual mechanism can be derived from such complexity, as either process can lead to all of the observed products. However, the reaction of $(C_5Me_5)Co(\eta^3$-crotyl)(OTf) **54** with excess 3,3-dimethyl-1-butyne is known to proceed via the [5 + 2] ring expansion mechanism to give the same "tail-to-tail" insertion pattern found in the ruthenium η^5-cycloheptadienyl product, although a slightly different rearrangement sequence takes place in this case (Eq. 77).[43] While the cobalt reaction confirms the plausibility of a ring expansion mechanism for the ruthenium η^3-allyl example, it does not prove that the reaction follows this pathway.



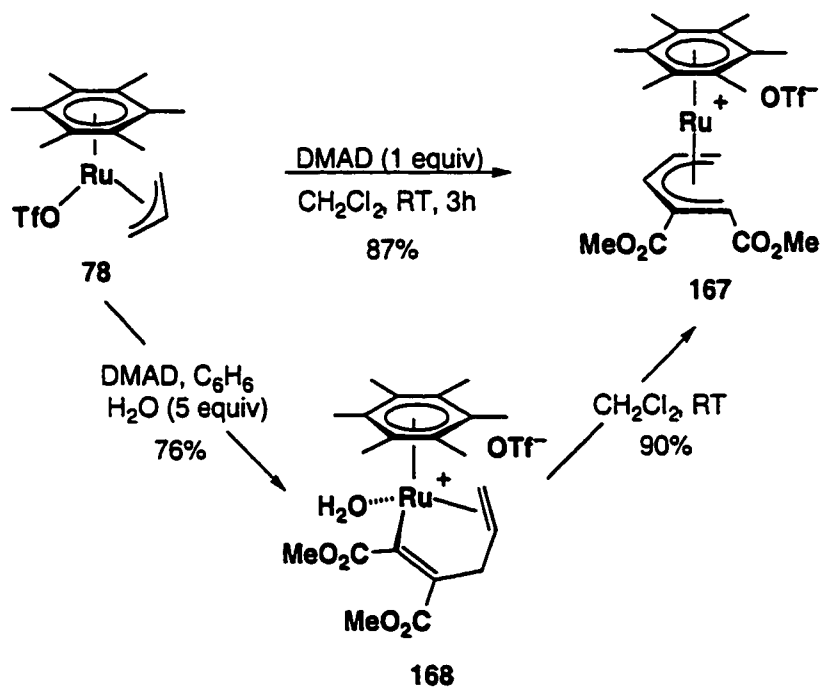
(Eq. 77)

In contrast to the reaction of 3,3-dimethyl-1-butyne, treatment of $(C_6Me_6)Ru(\eta^3$-allyl)(OTf) **78** with phenylacetylene produces no tractable products. Even the addition of excess alkyne (5 equiv) results in a significant proportion of recovered starting material, along with a variety of other ruthenium compounds, suggesting that an uncontrolled oligomerization process may be occurring.

3. [3 + 2] Allyl/DMAD Coupling Reactions

Although Rubezhov reported that no tractable products were isolated from the reaction of the (η^6-benzene)Ru(η^3-allyl) cation with dimethyl acetylenedicarboxylate (DMAD), the η^6-hexamethylbenzene ruthenium system yields a rich chemistry with this alkyne. The reaction of ruthenium η^3-allyl triflate **78** with an equimolar amount of DMAD in dichloromethane smoothly forms a single hexamethylbenzene monoadduct **167** within a few hours at room temperature (Scheme **46**). The product can be readily purified and isolated by crystallization from acetone/diethyl ether, giving pale yellow crystals in 90%

Scheme 46



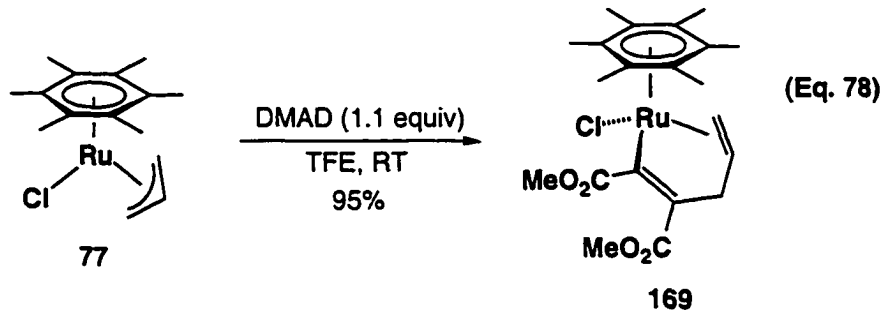
yield. Analysis by ^{1}H and ^{13}C NMR spectroscopy indicates that the compound is an acyclic η^5-pentadienyl complex containing two ester groups. The presence of the two esters is confirmed by strong bands at 1735 cm^{-1} and 1714 cm^{-1} ($\upsilon_{C=O}$) in the infrared absorption spectrum, as well as a strong band at 1266 cm^{-1} and a medium intensity one at 1030 cm^{-1} (υ_{C-O}). In addition to the expected ABMX spin system, the ^{1}H NMR spectrum also shows a singlet at δ 1.20, integrating to one hydrogen: the upfield shift of this resonance suggests that this hydrogen atom is located at the pentadienyl terminus, oriented *anti*, towards the metal. The product is therefore identified as $[(C_6Me_6)Ru(\eta^5$-1,2-dicarbomethoxypentadienyl)]$^{+}OTf^{-}$, **167**, with the two adjacent carbomethoxy groups *cis* to one another.

An attempt was made to trap the ruthenium η^3-allyl DMAD complex via the precipitation technique developed by Schwiebert.[38,39] Thus, a benzene solution of allyl triflate **78** was treated with an equivalent of DMAD and diethyl ether added to reduce the polarity of the solution prior to cooling the reaction mixture. The cationic alkyne complex did not immediately precipitate, as was previously observed in the iridium system, although a small amount of a brown, microcrystalline material, **168**, began to deposit after several days (Scheme **46**). Analysis by ^{1}H and ^{13}C NMR spectroscopy immediately confirmed that this product was not the expected alkyne complex. The ^{1}H NMR spectrum exhibits two different methyl ester signals, at δ 3.82 and δ 3.63, as well as one doublet at δ 4.68 and a complex multiplet at δ 4.59. Also present is a doublet of doublets at δ 3.18 (J = 18.4, 7.0 Hz) and a doublet at δ 2.99 (J = 18.4 Hz), corresponding to a geminal hydrogen pair. Both the ^{1}H and ^{13}C NMR spectra show strong similarities to the spectroscopy reported by Schwiebert for the iridium vinyl olefin complexes **47** and **50** (Chapter 1, p. 23).

Infrared absorption spectroscopy confirmed the presence of two ester groups (1701 and 1654 cm^{-1}, $\upsilon_{C=O}$) but also present in the spectrum is a broad, strong band at 3068 cm^{-1}; the ^1H NMR spectrum also exhibits a sharp singlet at δ 5.04 integrating to two hydrogens that does not correlate to any carbon resonance. These observations strongly suggest that a molecule of water is coordinated to the ruthenium center, a fact later confirmed by elemental analysis of the product.

The deliberate addition of five equivalents of water to a benzene solution of the allyl triflate **78** and excess DMAD forms the vinyl olefin complex **168** much more efficiently; the addition of diethyl ether then precipitates the product in 76% yield as analytically pure material. Water thus effectively traps the vinyl olefin complex after initial insertion of the alkyne, although this process is specific to DMAD among all the alkynes investigated. Heating a solution of complex **168** in anhydrous dichloromethane, or treating it with a dehydrating reagent (*e.g.*, $MgSO_4$ or molecular sieves) rapidly transforms the aqua complex into the η^5-pentadienyl complex **167** in high yield.

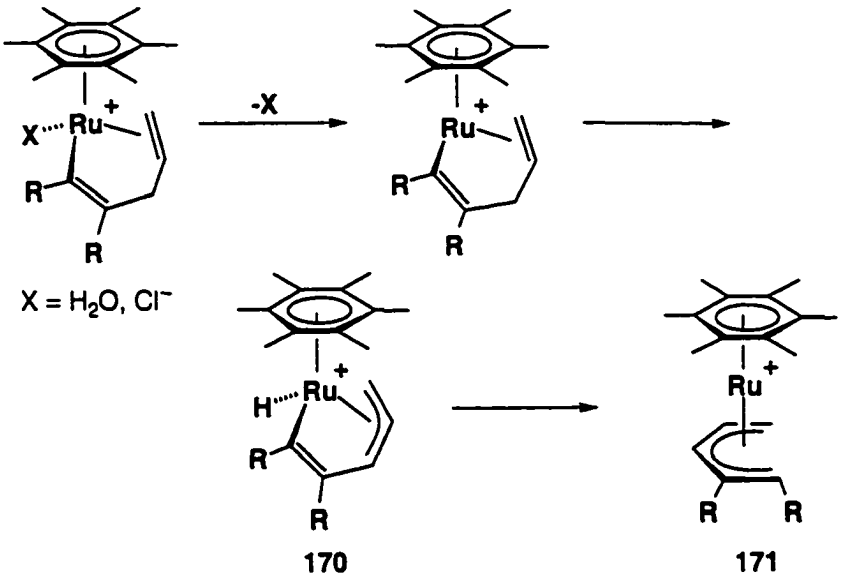
Another method of trapping this vinyl olefin intermediate is realized upon treatment of (C_6Me_6)Ru(allyl)Cl **77** with DMAD in trifluoroethanol at room temperature (Eq. **78**). This reaction proceeds to form neutral (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentadienyl)Cl **169** in very high yield (>95%) and the product is readily purified by simple recrystallization of the crude residue to provide dark brown crystals. The ^1H and ^{13}C NMR spectra are very similar to those exhibited by the cationic aqua complex **168** described above. It appears that this reaction is also specific to DMAD; no other alkynes provide vinyl olefin complexes using this trifluoroethanol procedure.



77 169 (Eq. 78)

Unlike the acyclic η^5-pentadienyl complex produced from desilylation of BTMSA, (see Chapter 2, Scheme **40**, p. 104) the formation of DMAD η^5-pentadienyl product does not involve a metal-vinylidene intermediate, as shown by the final disposition of the methyl ester substituents. Instead, the reaction of η^3-allyl complexes **77** or **78** with DMAD appears to be more closely related to the allyl/alkyne coupling reactions reported by Herrmann and Jolly.[28,29] The process that converts the vinyl olefin complexes **168** or **169** to η^5-pentadienyl **167** complex involves the overall transfer of an allylic hydrogen to the vinyl carbon. Although the mechanism for this process is not known, the most plausible reaction pathway is outlined in Scheme **47**. As shown experimentally, an empty coordination site is required before the reaction can proceed. Removal of the coordinated ligand can occur either thermally (for coordinated H_2O) or through use of a halide abstracting reagent (for chloride). We then propose that the unsaturated ruthenium center activates one allylic methylene hydrogen atom to generate the cationic Ru(IV) hydride intermediate **170**. Subsequent reductive coupling of the resulting hydride with the vinyl moiety results in the formation of the η^5-pentadienyl ligand, a process that is entirely analogous to the previously discussed conversion of allyl chloride **77** to vinylcyclopentenyl complex **152**.

Scheme 47

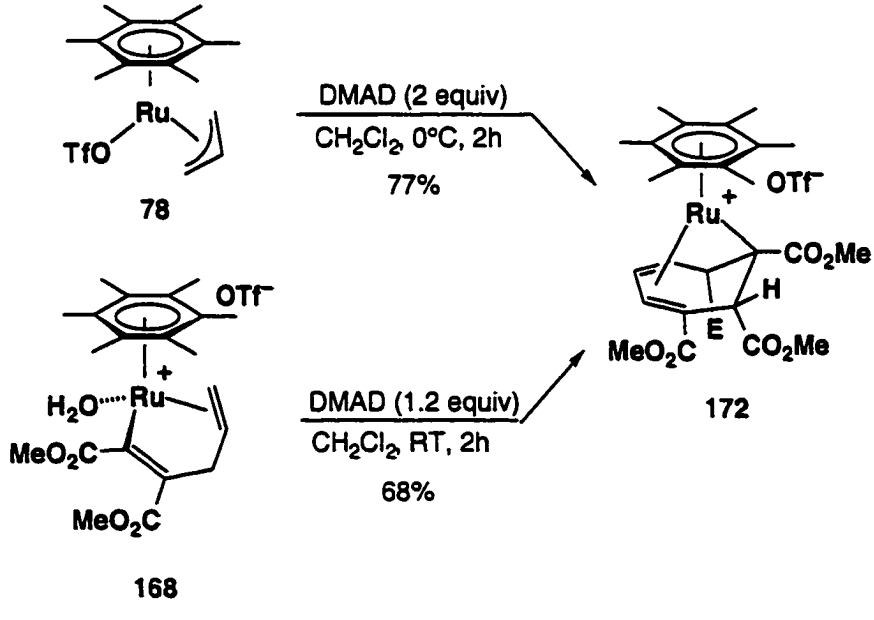


The difference in reactivity between dialkyl- and the dicarbomethoxy-substituted alkynes is intriguing. It appears that the electron-withdrawing ester groups act to stabilize the vinyl olefin intermediate by suppressing the migratory cyclization process that leads to five-membered ring formation. Electronegative substituents on the α-carbon are well known to result in shorter, stronger metal-carbon bonds, and these bonds are thus less susceptible to migratory coupling reactions.[115] By inhibiting the migration of the vinyl carbon, carbon-hydrogen activation becomes the kinetically preferred pathway for this alkyne.

4. [3 + 2 + 2] Allyl/DMAD/Alkyne Coupling Reactions

The addition of two equivalents of DMAD to (η^6-C_6Me_6)Ru(η^3-allyl)OTf **78** in anhydrous dichloromethane results in the formation of a very different product from the

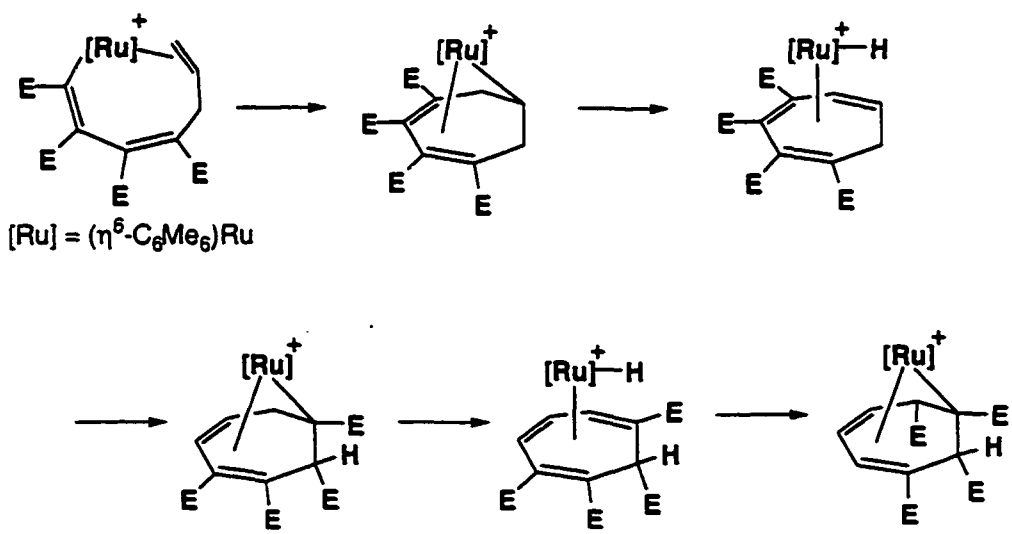
η^5-pentadienyl complexes formed by the reaction with equimolar DMAD. This new compound is readily purified by flash column chromatography on silica gel followed by recrystallization, giving yellow crystals of complex **172** in 77% yield (Eq. **79**). An identical product is also obtained by treating the isolated vinyl olefin complex **168** with an equivalent of DMAD, although this reaction is not as clean. Trace quantities of other products can be observed when more than two equivalents of DMAD are used, possibly arising from further DMAD insertions into acyclic or cyclic intermediates. In both the ^1H and ^{13}C NMR spectra, complex **172** exhibits signals consistent with four methyl ester groups, as well as revealing an upfield singlet carbon resonance at −15.5 ppm (C_1) consistent with the formation of an η^1,η^4-cycloheptadienyl complex. Unlike the unsubstituted η^1,η^4-cycloheptadienyl complex **156** derived from acetylene, however, this compound does not convert to a η^5-cyclopentadienyl structure upon heating, nor is there any evidence of fluxional behaviour.



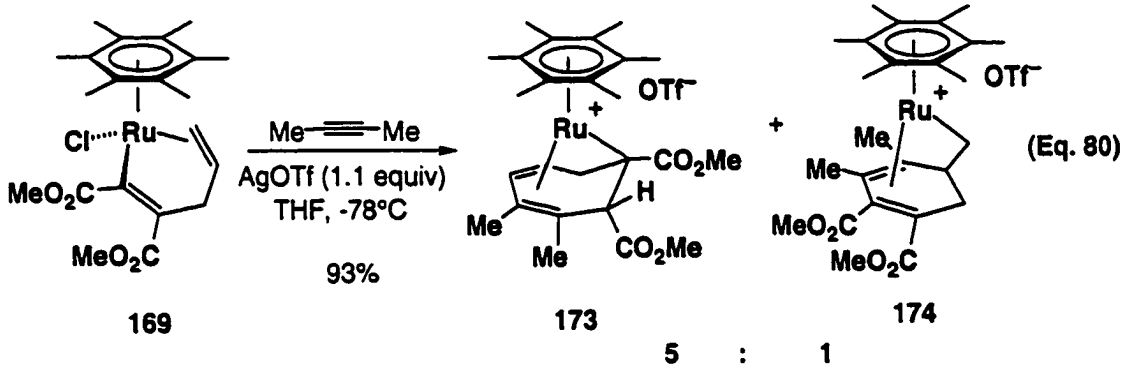
(Eq. 79)

Based on the lack of signals upfield of δ 4.00 in the ^{1}H NMR spectrum (other than the hexamethylbenzene and methyl ester singlets), and on analysis by ^{1}H-^{13}C heterocorrelated spectroscopy, the structure of this product was tentatively identified as the η^1,η^4-cycloheptadienyl complex **172**. One of the methyl ester groups is located on the ipso carbon. Other salient ^{1}H NMR spectroscopic data are presented in Table **2** (p. 133). The hapticity of complex **172** is supported by the spectroscopic similarity to crystallographically characterized complexes of the same general structure (*vide infra*). To obtain this complex, however, the initially formed η^1,η^4-cycloheptadienyl complex from migratory cyclization must undergo an extensive sequence of β-hydride elimination and reinsertion reactions, as outlined in Scheme **48**. A similar rearrangement process is thought to lead to isomeric products observed by Schwiebert in the iridium system[39] (*vide supra*), although in this ruthenium reaction only a single η^1,η^4-cycloheptadienyl complex is detected and no further isomerization to an η^5-cycloheptadienyl ligand is observed.

Scheme 48



The ability to isolate the vinyl olefin intermediate from DMAD insertion also raised the first general opportunity to incorporate a different alkyne in the second insertion step that occurs during [3 + 2 + 2] cycloadditions. Thus, treatment of vinyl olefin complex **169** with 2-butyne and AgOTf in tetrahydrofuran results in clean formation of two products, complexes **173** and **174**, in a ratio of 5 : 1 (Eq. **80**). The two adducts are readily separated and purified by chromatography on flash silica gel, followed by recrystallization of each product from dichloromethane/diethyl ether. Both complexes are obtained as yellow crystals, the major product **173** in 78% yield and the minor product **174** in 15% yield. The major product exhibits an upfield resonance at –25.2 ppm in the ^{13}C NMR spectrum, characteristic of the η^1,η^4-cycloheptadienyl structure. Both the ^1H and ^{13}C NMR spectra of this material show signals indicative of two methyl ester groups, as expected. Unlike the



169 **173** **174**

5 : 1

product obtained from the reaction with two equivalents of DMAD, however, the major complex also exhibits signals in the ^1H NMR spectrum consistent with two hydrogen atoms of a methylene unit, at δ 3.24 and 2.22 (H_{7endo} and H_{7exo}, respectively) with a mutual coupling of 15.5 Hz (Table **2**, p. 133). Both signals correlate to a carbon resonance located at 30.5 ppm in the ^{13}C NMR spectrum. Further analysis by standard spectroscopic techniques, including ^1H-^{13}C HETCORR and long-range heterocorrelated ^1H-^{13}C

(BIRDTRAP) experiments, led to the identification of the major product as the η^1,η^4-cycloheptadienyl complex **173**. An X-ray diffraction analysis carried out on this product confirmed both the unusual η^1,η^4 -hapticity pattern and the disposition of the two methyl ester groups. Other salient features of the solid-state molecular structure determination are provided in Figure 7.

Like the bis(DMAD) adduct, the structure of η^1,η^4-cycloheptadienyl complex **173** indicates that the initial η^1,η^4-coordinated seven-membered ring obtained from migratory cyclization subsequently rearranges to give the final isomer (Scheme 49). This rearrangement is not as extensive as the previous example, although both compounds result in an ester group located on the ipso carbon. Once again, attempts to isomerize the η^1,η^4-cycloheptadienyl complex to its η^5-isomer by thermolysis proved unsuccessful.

Scheme 49

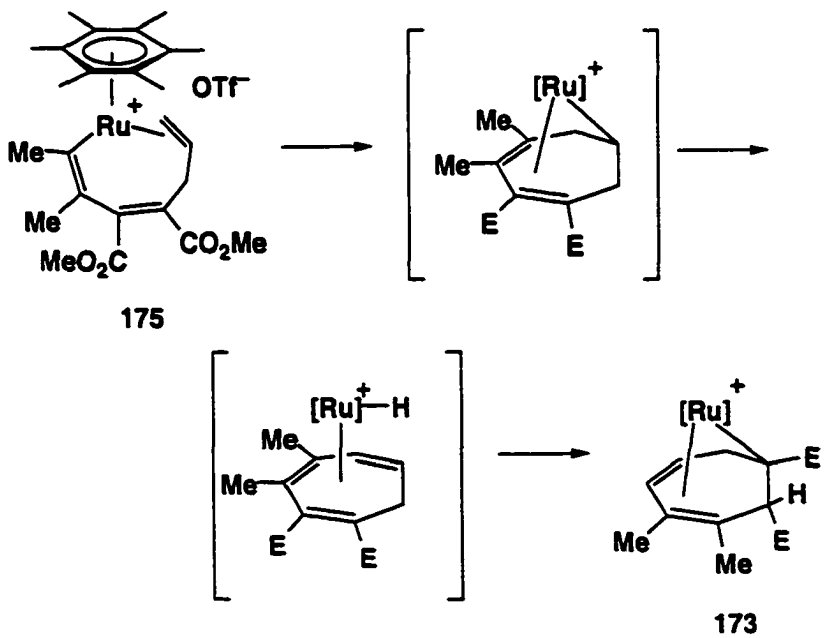
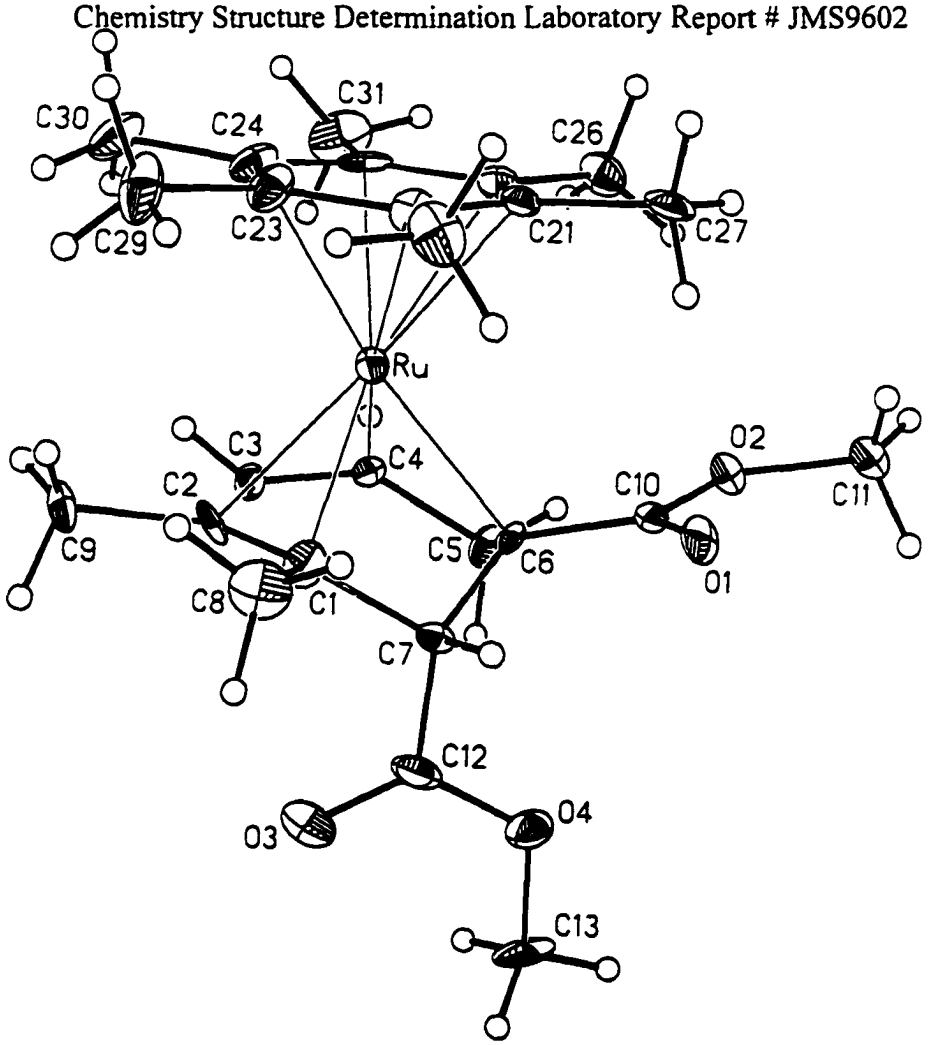


Figure 7. ORTEP[113] Plot of Complex **173** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9602

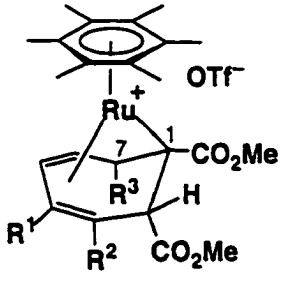


Final Residuals: $R_1 = 0.0975$; $wR_2 = 0.2685$. Data obtained at -50°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): Ru-C1, 2.26(2); Ru-C2, 2.224(15); Ru-C3, 2.163(14); Ru-C4, 2.235(14); Ru-C6, 2.203(12); C1-C2, 1.43(2); C1-C7, 1.50(2); C1-C8, 1.49(2); C2-C3, 1.43(2); C2-C9, 1.50(2); C3-C4, 1.39(2); C4-C5, 1.48(2); C5-C6, 1.51(2); C6-C7, 1.49(2); C6-C10, 1.48(2); C7-C12, 1.49(2).

Selected Bond Angles (deg): C2-C1-C7, 120.8(14); C2-C1-C8, 121.5(14); C7-C1-C8, 113.6(13); C1-C2-C3, 124.4(13); C1-C2-C9, 120.4(14); C3-C2-C9, 114.7(13); C2-C3-C4, 131.2(14); C5-C6-C7, 116.2(13); C5-C6-C10, 117.3(12); C7-C6-C10, 112.4(12); C1-C7-C6, 105.6(11); C1-C7-C12, 115.9(14); C6-C7-C12, 115.6(13); C3-C4-C5, 128.1(14); C4-C5-C6, 103.5(11).

Table 2. Comparative ^{1}H NMR Spectroscopic Data for DMAD-Derived η^1,η^4-Cycloheptadienyl Complexes[a]



172 R^1 = H, R^2 = R^3 = CO_2Me
173 R^1 = R^2 = Me, R^3 = H
176 R^1 = -$(CH_2)_6$-, R^3 = H
178 R^1 = R^2 = R^3 = H

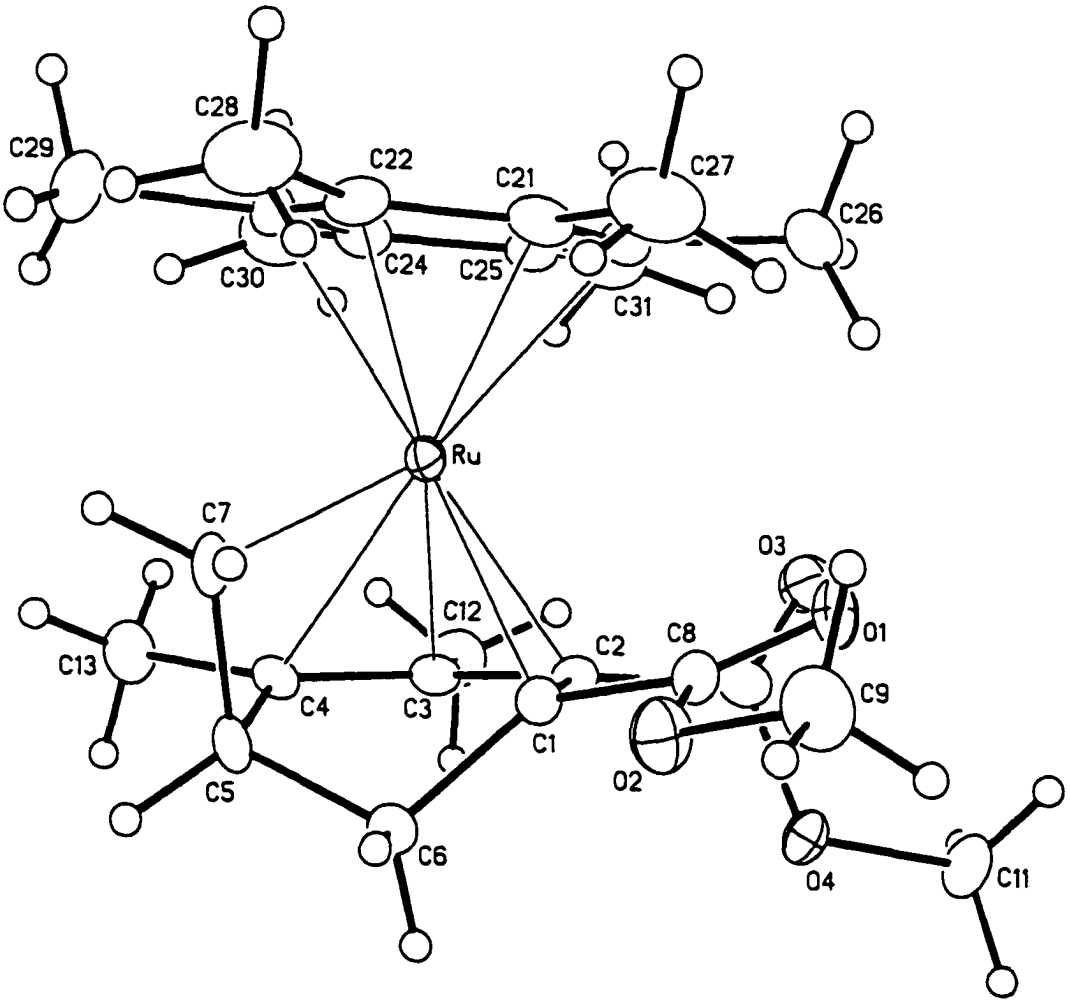
Assignment	172	173	176	178
H_2 $J_{2\text{-}3}$ $J_{2\text{-}7endo}$	5.03 (s) b b	4.18 (d) b 1.3 Hz	4.23 (d) b 1.2 Hz	4.23 (d) 9.0 Hz 1.2 Hz
H_3 $J_{3\text{-}4}$	b	b	b	4.16 (t) 8.3 Hz
H_4 $J_{4\text{-}5}$	6.59 (d) 8.2 Hz	b	b	5.62 (t) 7.9 Hz
H_5 $J_{5\text{-}6}$	5.75 (t) 8.4 Hz	5.30 (d) 8.9 Hz	5.62 (d) 9.2 Hz	5.43 (t) 8.0 Hz
H_6 $J_{6\text{-}7endo}$ $J_{6\text{-}7exo}$	4.16 (t) 8.4 Hz b	3.90 (td) 8.7 Hz 2.2 Hz	3.80 (td) 9.0 Hz 1.9 Hz	4.03 (td) 8.4 Hz 2.6 Hz
H_{7endo} $J_{7endo\text{-}7exo}$	4.52 (d) b	3.24 (ddd) 15.4 Hz	3.27 (ddd) 15.5 Hz	3.33 (ddd) 15.3 Hz
H_{7exo}	b	2.22 (ddd)[b]	d	2.09 (ddd)[c]

[a] Spectra were taken in $CDCl_3$ at room temperature. [b]Not applicable due to non-hydrogen substituent. [c]Additional splitting observed due to long-range coupling. [d]Resonance partially obscured by other signals.

X-ray crystallography was also used to unambiguously determine the structure of the minor product, which was identified as the η^1,η^4-methanocyclohexadienyl complex **174** (Figure **8**). Spectroscopic analysis reveals a distinctive doublet of triplets at δ 3.08 (J = 4.4, 2.2 Hz) in the ^{1}H NMR spectrum (Table **3**), correlated to a carbon resonance at 44.5 ppm in the ^{13}C NMR spectrum ($^1J_{CH}$ = 141 Hz) and assigned to H_2 and C_2 respectively. As with other known η^1,η^4-methanocyclohexadienyl complexes, the resonance attributed to H_{1b} (at δ 1.15) is a narrow doublet, showing a characteristic geminal coupling constant of only 3.3 Hz to H_{1a} (at δ 1.46). These signals also correlate to a triplet resonance at 5.7 ppm ($^1J_{CH}$ = 137 Hz) in the ^{13}C NMR spectrum, which is shifted considerably upfield from a normal sp^3-hybridized carbon and is assigned to the carbon directly σ-bonded to the ruthenium metal. This carbon resonance is not shifted as far upfield as is the ipso carbon signals found for the η^1,η^4-cycloheptadienyl complexes, but it is consistent with the ipso carbon signal found for the acetylene-derived η^1,η^4-methanocyclohexadienyl complex **157**.

Treatment of vinyl olefin complex **169** with AgOTf in the presence of cyclooctyne also results in the clean formation of two products but with less selectivity, in a ratio of 2.6 : 1 (Eq. **81**). These products can be readily separated and purified by standard chromatography and both yield yellow crystals after recrystallization from dichloromethane/diethyl ether. The major product was isolated in 63% yield and was identified as η^1,η^4-cycloheptadienyl complex **176** due to the close similarity of both its ^{1}H and ^{13}C NMR spectrum to that exhibited by the 2-butyne complex **173** (Table **2**, p. 133). The characteristic upfield resonance of C_1 is located at –27.6 ppm in the ^{13}C NMR spectrum. The minor product was also identified on the basis of spectroscopic analysis as η^1,η^4-methanocyclohexadienyl complex **177**, isolated in 24% yield. Like the 2-butyne

Figure 8. ORTEP[113] Plot of Complex **174** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9604

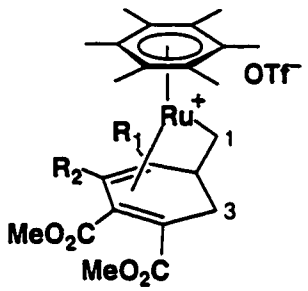


Final Residuals: $R_1 = 0.0585$; $wR_2 = 0.1689$. Data obtained at -50°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): Ru-C1, 2.221(6); Ru-C2, 2.143(6); Ru-C3, 2.232(6); Ru-C4, 2.286(6); Ru-C7, 2.172(6); C1-C2, 1.429(8); C1-C6, 1.511(8); C1-C8, 1.492(8); C2-C3, 1.435(8); C2-C10, 1.498(9); C3-C4, 1.416(9); C3-C12, 1.497(9); C4-C5, 1.517(9); C4-C13, 1.508(9); C5-C6, 1.509(9); C5-C7, 1.506(9).

Selected Bond Angles (deg.): C2-C1-C6, 116.8(5); C2-C1-C8, 115.7(5); C6-C1-C8, 120.5(5); C1-C2-C3, 115.4(5); C1-C2-C10, 122.9(5); C3-C2-C10, 120.9(6); C2-C3-C4, 117.5(6); C2-C3-C12, 121.2(6); C4-C3-C12, 121.2(6); C3-C4-C5, 122.7(6); C3-C4-C13, 121.6(6); C5-C4-C13, 114.6(6); C4-C5-C6, 111.8(5); C4-C5-C7, 96.8(5); C6-C5-C7, 104.8(5); C1-C6-C5, 105.4(5).

Table 3. Comparative ^{1}H NMR Spectroscopic Data for DMAD-Derived η^1,η^4-Methanocyclohexadienyl Complexes[a]

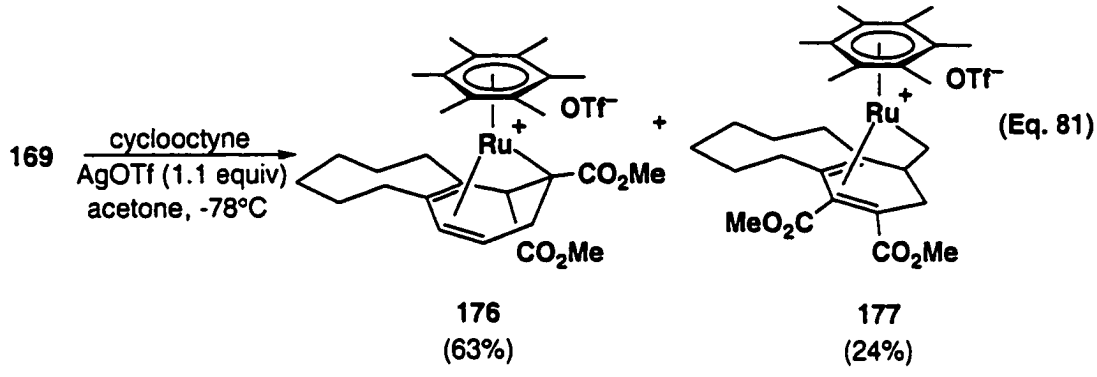


174 $R^1 = R^2 = Me$
177 $R^1 = -(CH_2)_6-$
184 $R^1 = Ph$, $R^2 = H$

Assignment	174	177	184
H_{1a} J_{1a-2} $J_{1a-3exo}$	1.46 (m) 4.4 Hz 2.3 Hz	c	1.40 (m) d d
H_{1b} J_{1b-1a}	1.15 (d) 3.3 Hz	1.17 (d) 2.0 Hz	1.41 (br s) c
H_2 $J_{2-3endo}$ J_{2-3exo}	3.08 (dt) 2.2 Hz 2.3 Hz	3.23 (dt) 2.3 Hz 2.5 Hz	3.70 (br s) 2.1 Hz 1.6 Hz
H_{3endo} $J_{3endo-3exo}$	1.63 (dd) 12.1 Hz	1.69 (dd) 12.0 Hz	1.70 (dd) 12.6 Hz
H_{3exo}	0.84 (dt)	0.80 (dt)	1.22 (dt)
H_6	b	b	6.06 (s)
H_7	b	b	b

[a] Spectra were taken in $CDCl_3$ at room temperature. [b]Not applicable due to non-hydrogen substituent. [c]Chemical shift not determined as the resonance is obscured by overlapping signals. [d]Numerical value for the coupling constant not obtained due to second order character or complexity of the signal.

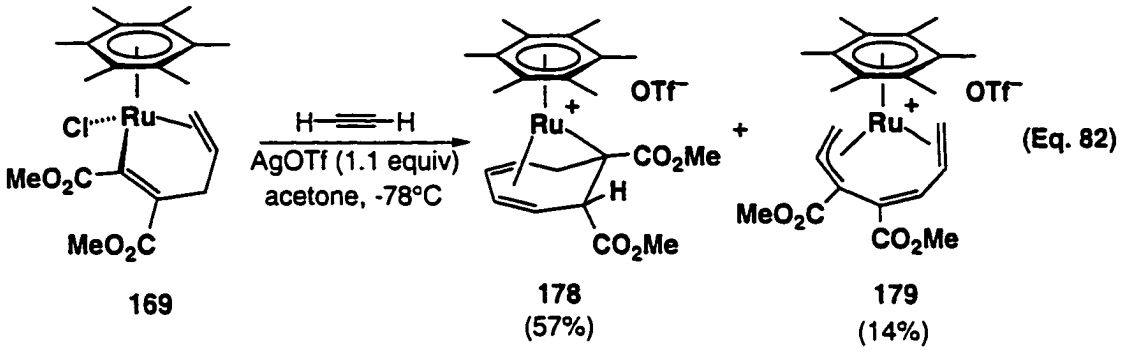
minor product, complex **177** exhibits in the ^{1}H NMR spectrum a doublet of triplets at δ 3.23 (J = 5.0, 2.3 Hz, H_2) and a narrow doublet at δ 1.17 (J = 2.0 Hz) attributed to H_{1b} (Table **3**).



176 (63%) **177** (24%)

The reaction of chloride complex **169** with acetylene at low temperature again gives a η^1,η^4-cycloheptadienyl complex as the major product, although this reaction is not as clean as the previous examples (Eq. **82**). The major compound, identified as η^1,η^4-cycloheptadienyl complex **178**, is isolated from the reaction mixture in 57% by flash chromatography on silica gel using 3% methanol/dichloromethane as eluent, followed by recrystallization from dichloromethane/diethyl ether. Complex **178** exhibits a similar coupling pattern in the ^{1}H NMR spectrum to those observed for the previously isolated η^1,η^4-cycloheptadienyl complexes (Table **2**), as well as displaying the characteristic upfield resonance at –27.5 ppm attributed to the σ-carbon in the ^{13}C NMR spectrum.

The minor product was also isolated by chromatography, in 14% yield, but the spectroscopy of this compound does not correspond to that previously observed for the η^1,η^4-methanocyclohexadienyl minor complexes. The ^{1}H NMR spectrum exhibits two isolated multispin systems, while the ^{13}C NMR spectrum does not display any significantly

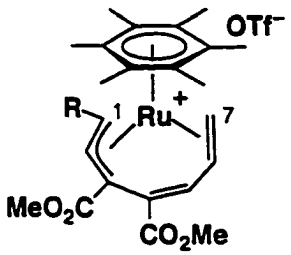


169 178 (57%) 179 (14%)

shielded carbon resonances (Table 4), suggesting that this complex is acyclic rather than a cycloadduct. X-ray diffractable crystals of this minor product were obtained by recrystallization of the more crystalline hexafluorophosphate salt, prepared by ion exchange using excess NH_4PF_6 in water. X-ray crystallography subsequently identified this byproduct to be the unusual acyclic η^2,η^3-heptatrienyl complex **179** (Figure 9).

The acyclic minor product can, in principle, be obtained through a metal-mediated alkyne-to-vinylidene rearrangement related to the mechanism proposed earlier to rationalize the formation of acyclic η^5-pentadienyl complex **147** from BTMSA and ruthenium allyl **78** (Scheme **40**, page 102). A more likely hypothesis, however, is that insertion of acetylene yields a vinyl diene intermediate, **180** (Scheme **50**). A kinetic partition then results, with the major pathway proceeding through a migratory cyclization to form the initial η^1,η^4-cycloheptadienyl complex, while the minor pathway proceeds via a metal-mediated [1,5]-hydride shift, presumably involving the Ru(IV) intermediate **181**, as illustrated. The latter process is closely related to the mechanism earlier proposed for the formation of 1,2-dicarbomethoxy η^5-pentadienyl complex **167** (Scheme **48**). In order to distinguish between the proposed mechanisms, the reaction was repeated using doubly

Table 4. Comparative ^{1}H and ^{13}C NMR Spectroscopic Data for DMAD Derived η^3,η^2-Heptatrienyl Complexes[a]

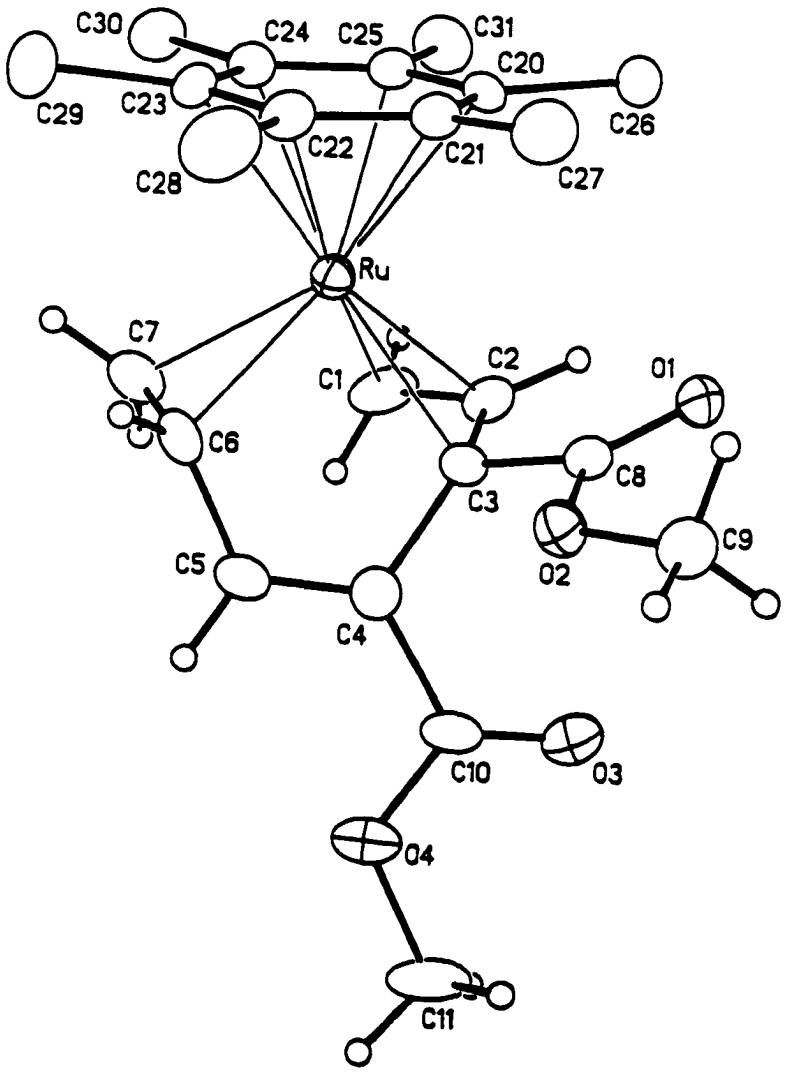


179 R = H
182 R = TMS

^{1}H NMR	179	182		^{13}C NMR	179	182
H_{1syn} $J_{1syn\text{-}1anti}$ $J_{1syn\text{-}2}$	3.73 (dd) 2.0 Hz 7.5 Hz	b		C_1	55.7	59.0
H_{1anti} $J_{1anti\text{-}2}$	1.64 (dd) 11.4 Hz	1.17 (d) 13.9 Hz		C_2	89.2	94.6
H_2	4.70 (dd)	4.91 (d)		C_3	107.2	109.2
H_5 $J_{5\text{-}6}$	6.87 (d) 1.7 Hz	6.87 (d) 1.9 Hz		C_4	133.9	135.9
H_6 $J_{6\text{-}7syn}$ $J_{6\text{-}7anti}$	4.45 (ddd) 9.5 Hz 12.9 Hz	4.20 (dt) 9.4 Hz 12.7 Hz		C_5	146.9	146.0
H_{7syn}	3.17 (d)	3.16 (d)		C_6	78.5	74.9
H_{7anti}	2.97 (d)	2.98 (d)		C_7	62.8	70.0

[a] Spectra were taken in $CDCl_3$ at room temperature. [b] Not applicable due to non-hydrogen substituent.

Figure 9. ORTEP[113] Plot of Complex **179** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9701



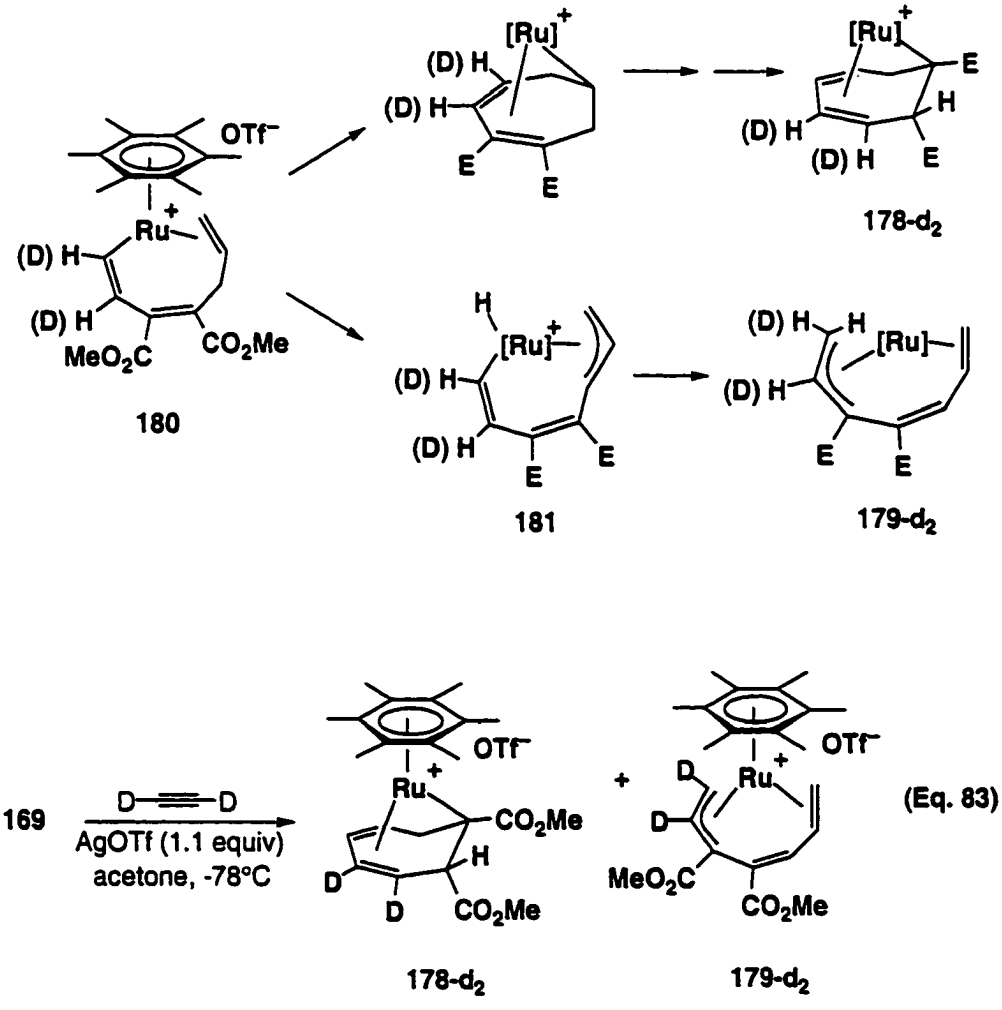
Final Residuals: $R_1 = 0.0390$; $wR_2 = 0.1085$. Data obtained at -60°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): Ru-C1, 2.217(6); Ru-C2, 2.148(6); Ru-C3, 2.215(6); Ru-C6, 2.196(6); Ru-C7, 2.219(7); C1-C2, 1.423(11); C2-C3, 1.421(9); C3-C4, 1.493(10); C3-C8, 1.502(8); C4-C5, 1.304(10); C4-C10, 1.520(11); C5-C6, 1.449(10); C6-C7, 1.371(10).

Selected Bond Angles (deg.): C1-C2-C3, 118.1(6); C2-C3-C4, 122.9(5); C2-C3-C8, 114.5(5); C4-C3-C8, 114.4(5); C3-C4-C5, 118.4(7); C3-C4-C10, 115.6(6); C5-C4-C10, 126.0(7); C4-C5-C6, 120.9(7); C5-C6-C7, 119.2(7).

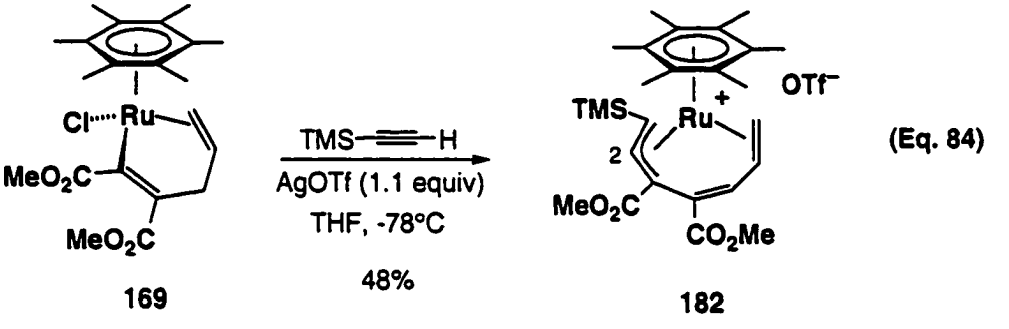
deuterium-labelled acetylene (Eq. 83). Spectroscopic analysis of the crude product mixture revealed that deuterium incorporation in the major η^1,η^4-cycloheptadienyl product, as expected, occurs exclusively in the H_3 and H_4 positions. In the minor acyclic product, deuterium is incorporated exclusively in the H_{1syn} and H_2 positions, conclusively demonstrating that this product is *not* formed through a vinylidene intermediate.

Scheme 50



A similar acyclic complex is the only product isolated, in 48% yield, from the reaction of complex **169** with trimethylsilylacetylene (Eq. 84), although several

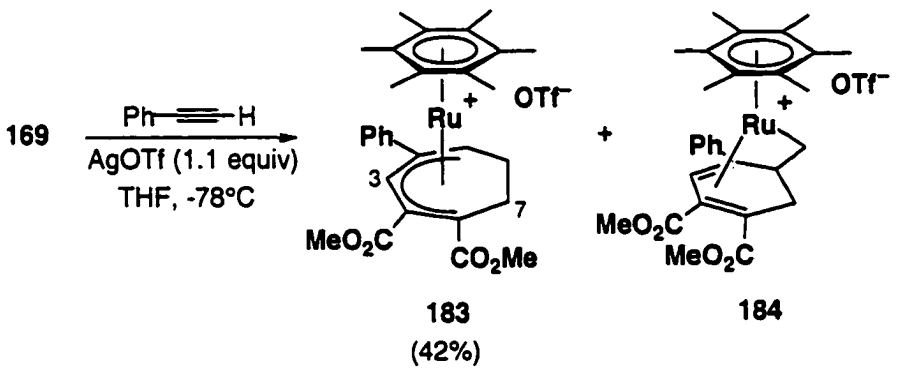
uncharacterized minor products were also detected spectroscopically. Both ^{1}H and ^{13}C NMR spectra of the major product closely parallel those observed for the acyclic η^2,η^3-heptatrienyl complex **179** (Table 4). By comparing the ^{1}H NMR spectroscopic data of these complexes, it is clear that the trimethylsilyl substituent is located at the terminus of the allyl moiety, *syn* to the adjacent hydrogen atom (H_2). This indicates that the insertion of trimethylsilylacetylene primarily proceeds via migration of the vinyl moiety to the unsubstituted end of the alkyne, yielding a vinyl diene intermediate with the bulky trimethylsilyl group surprisingly located adjacent to the ruthenium center.



(Eq. 84)

The reaction of vinyl olefin **169** with phenylacetylene results in the formation of two compounds in a ratio of approximately 2 : 1, although only the major product **183** could be isolated cleanly from the reaction mixture (Eq. **85**). Chromatography on silica gel followed by careful recrystallization from dichloromethane/diethyl ether returns the pure product as a bright yellow crystalline material in 42% yield. Spectroscopic analysis by ^{1}H and ^{13}C NMR spectroscopy indicates that this product is not the expected η^1,η^4-cycloheptadienyl complex but, surprisingly, its valence isomer, the η^5-cycloheptadienyl complex **183**. Overall, the ^{1}H and ^{13}C NMR spectra display a strong similarity to those of the related cobalt η^5-cycloheptadienyl complexes.[42-44] The ^{1}H NMR spectrum exhibits a

characteristic upfield ddd pattern at δ 0.50 (J= 13.3, 11.6, 5.2 Hz), assigned to H_{7b}; also present is a downfield singlet at δ 6.65, assigned to H_3. The minor product, although not isolated, is tentatively identified as the η^1,η^4-methanocycloheptadienyl complex **182** based on the similarity of its ^{1}H NMR spectrum to those of the previous examples (Table 3). As in the case of trimethylsilylacetylene addition, it appears that the vinyl moiety migrates to the unsubstituted end of the coordinated phenylacetylene, forming a single α-phenyl vinyl intermediate that leads to both the major and minor products. However, we are uncertain why this reaction uniquely produces the conjugated ring system.



Treating vinyl olefin complex **169** with diphenylacetylene under the same reaction conditions results in the clean formation of only the DMAD-derived acyclic η^5-pentadienyl complex **167**; it thus appears that this alkyne is too sterically bulky to undergo insertion. The use of 1-(trimethylsilyl)propyne or bis(trimethylsilyl)acetylene likewise returns only the acyclic monoadduct **167**. However, the addition of 3,3-dimethylbutyne yields a complex mixture of products; the two major compounds present are tentatively identified as different η^1,η^4-cycloheptadienyl complexes based on preliminary ^{1}H NMR spectroscopic analysis of the product mixture, but these compounds could not be isolated cleanly.

The addition of silver salts to vinyl chloride complex **169** in the presence of alkyne is not the only method by which a second alkyne can be introduced. The addition of alkyne to a solution of the aqua complex **168** in acetone, or addition of alkyne to a trifluoroethanol solution of vinyl chloride **169** results in the formation of the same products. However, the ratio of major to minor products is generally lower under both of these alternative conditions, as illustrated in Table **5** for the addition of 2-butyne. The differences in product partitioning is, we believe, primarily due to the different temperatures required to induce the formation of an open coordination site; halide abstractions by silver reagents occur well below room temperature, while thermal dissociation of water or the chloride ligand only occurs at room temperature. Using different solvents for the silver-mediated halide abstraction process results in a more subtle effect: polar solvents such as acetone give marginally higher ratios of seven- membered ring to six-membered ring products compared to the use of dichloromethane or 2-butanone.

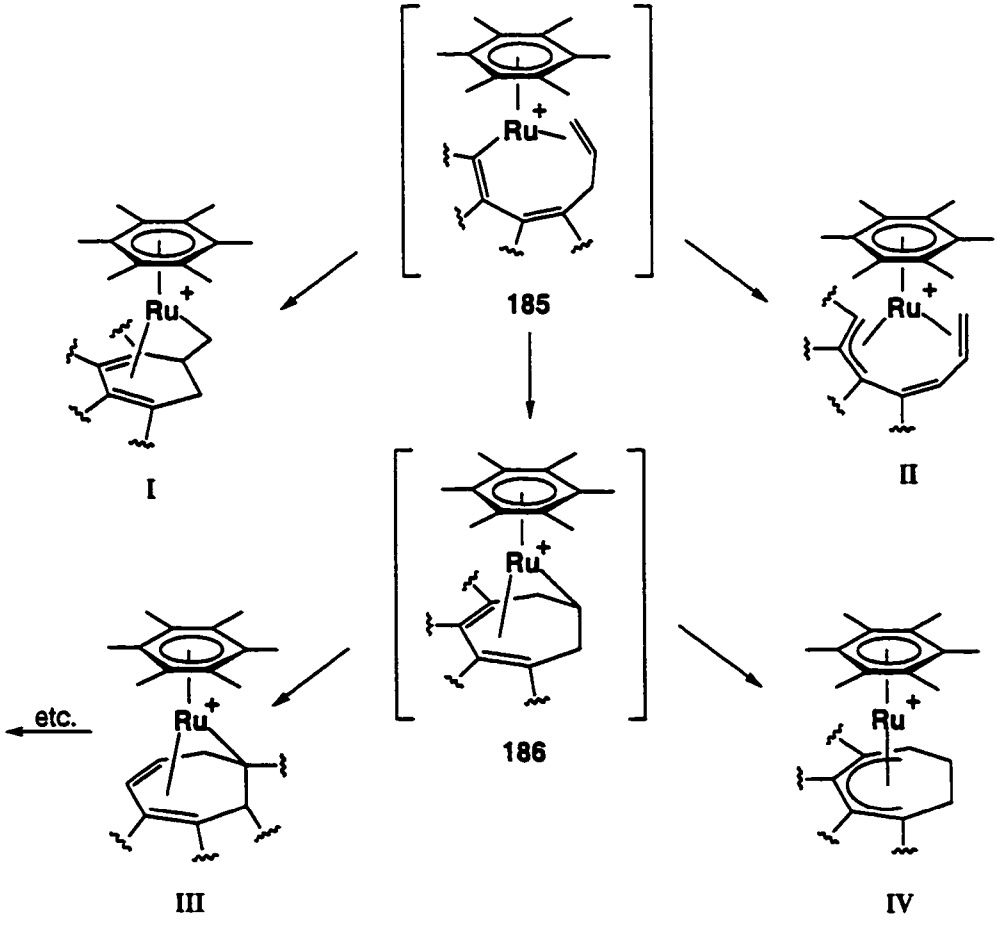
Table 5. Effect of Reaction Conditions on Product Distribution for DMAD Derived 2-Butyne Adducts

Reaction Conditions:	Product Ratio of Complex **173** to **174**
Complex **169**, AgOTf, 2-butyne (5 equiv), THF: -78°C to RT	5 : 1
Complex **169**, 2-butyne (5 equiv), TFE: RT, 3h	2 : 1
Complex **168**, 2-butyne (5 equiv), acetone: 0°C to RT, 2h	3.5 : 1

However, the less polar tetrahydrofuran solvent leads to a greater proportion of the acyclic heptadienyl byproduct compared to the seven-membered ring product.

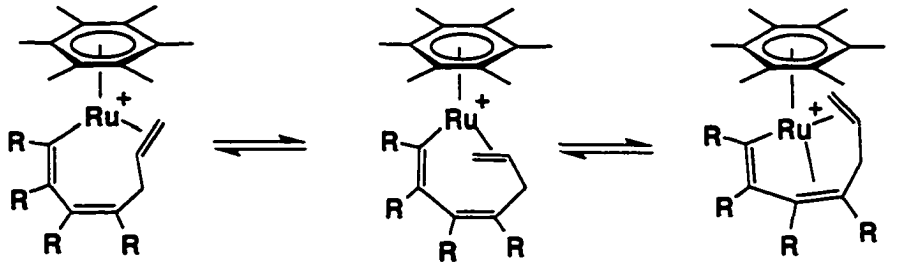
In general, the insertion of a second alkyne into a DMAD-derived vinyl olefin intermediate results in a much broader range of products than has previously been identified for three component [3 + 2 + 2] allyl/alkyne reactions.[37-44] Besides the expected η^5-cycloheptadienyl products **IV**, the dominant η^1,η^4-cycloheptadienyl complexes **III**, the minor η^1,η^4-methanocyclohexadienyl complexes **I** and acyclic η^2,η^3-heptatrienyl complexes **II** have been isolated and fully characterized (Scheme **51**). While the

Scheme 51



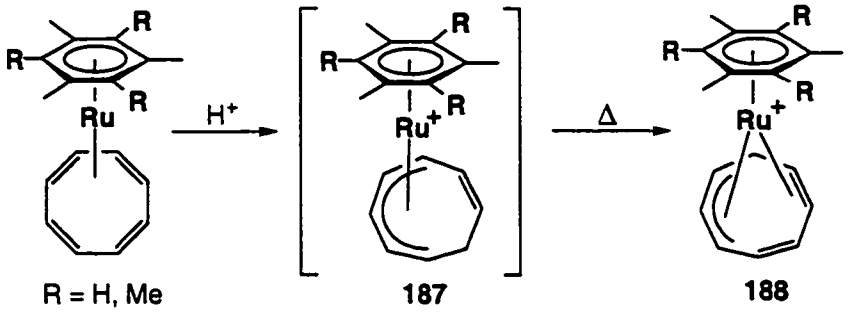
complexity of these reactions may limit general organic synthetic applications (as does the expense of stoichiometric ruthenium), these reactions do provide valuable mechanistic information about the [3 + 2 + 2] allyl/alkyne cyclization process. Each of the products obtained is derived from a common vinyl diene intermediate **185**, formed from alkyne insertion into an initial vinyl olefin complex. This putative intermediate has never been isolated or observed in any reaction, although it is proposed to be the key intermediate in the "normal" [3 + 2 + 2] cycloaddition mechanism. The vinyl diene intermediate **185**, arbitrarily depicted as a $16e^-$ complex, may exist in a variety of coordination and conformational states (Figure **10**): in principle, an unsaturated structure may have the pendant alkene oriented so that the terminal carbon is pointed away from the metal-carbon σ-bond (intermediate **V**) or towards the metal-carbon bond σ-bond (intermediate **VI**); alternatively, the internal alkene may be coordinated to form a saturated structure (intermediate **VII**). It is also plausible that these structures are interconverting and that the equilibrium may be strongly influenced by substituents and solvent choice. One reasonable possibility is that these conformationally and electronically different intermediates are responsible for the observed product partitioning. For instance, intermediate **V** would readily lead to the η^1,η^4-methanocyclohexadienyl product due to proximity effects, while intermediates **VI** or **VII** may lead preferentially to seven-membered ring formation. The lack of direct experimental evidence for this putative intermediate and the possible importance of its relationship to the final product distribution suggest that computational modeling of this system may give valuable insights into the various factors controlling the reaction partitioning.

Figure 10. Possible Coordination Modes of Intermediate **185**



V VI VII

The most interesting aspect of this chemistry is the prevalence of kinetically and/or thermodynamically favoured η^1,η^4-cycloheptadienyl complexes. While the only precedented bonding for coordinated seven-membered rings of this type is the η^5-coordination mode, slightly larger rings readily accommodate alternative non-conjugated bonding modes, especially in complexes of second and third row transition metals. For example, protonation of (η^6-arene)Ru(cyclooctatetraene) complexes (arene = hexamethylbenzene or mesitylene) kinetically produces an isolable η^5-cyclooctatrienyl complex **187**, but upon heating, this product converts to the non-conjugated η^3,η^2-cyclooctatrienyl isomer **188** (Eq. **86**).[116] A comparison of solid-state molecular structures obtained for these two complexes suggests that relief of strain in the eight-membered ring may be an important factor in thermodynamically favouring the less conjugated η^3,η^2-coordination mode, although it is insufficient to disfavour η^5-pentadienyl bonding in the corresponding iron tricarbonyl system (*vide infra*, p. 166). It is probable that the more diffuse and flexible second and third row metal orbitals also act to stabilize the less planar non-conjugated structures relative to the more compact and planar η^5-conformation.



(Eq. 86)

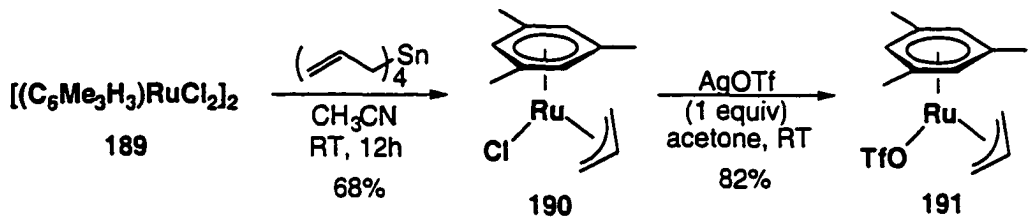
The reaction of acetylene with η^3-allyl triflate complex **78** clearly yields a kinetic η^1,η^4-seven-membered ring complex **156** that only slowly converts to the thermodynamic η^5-cycloheptadienyl complex **159** (Scheme **43**), revealing that a significant kinetic barrier exists between the two isomers. However, the isolated η^1,η^4-complexes derived from initial DMAD insertion do not convert to η^5-isomers even after prolonged heating at high temperature, indicating that the η^1,η^4-complexes are either thermodynamic products or that the kinetic barrier to isomerization is insurmountable under these reaction conditions. The fact that at least one example (phenylacetylene) returns a η^5-cycloheptadienyl product at low temperature suggests that η^5-isomers are, in fact, kinetically accessible. It is probable that the ester substituent strengthens the carbon-ruthenium σ–bond to the extent that the η^1,η^4-cycloheptadienyl isomer becomes thermodynamically competitive with the η^5-isomer. In this case, relatively small differences in substituents may be responsible for the final determination of the thermodynamic product.

5. Evaluation of the η^6-Mesitylene Ruthenium Template

To probe the role of the ancillary ligand in the [3 + 2 + 2] allyl/alkyne product partitioning, the effects of altering the arene ligand from hexamethylbenzene to mesitylene

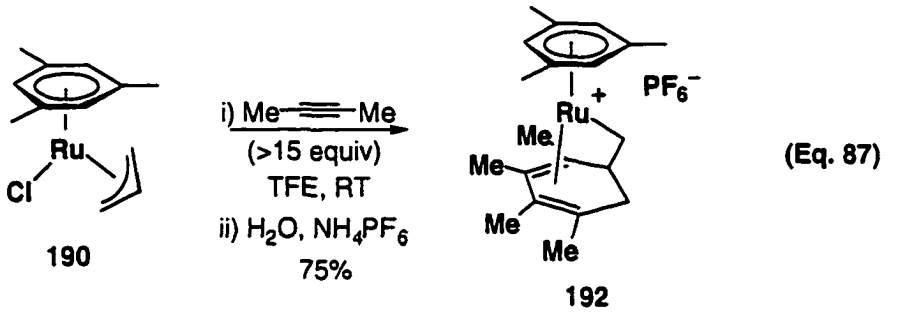
were evaluated. Compared to the hexamethylbenzene ligand, mesitylene is less electron rich and sterically smaller, although larger and more electron rich than the unsubstituted η^6-benzene ligand previously studied by Rubezhov.

Scheme 52



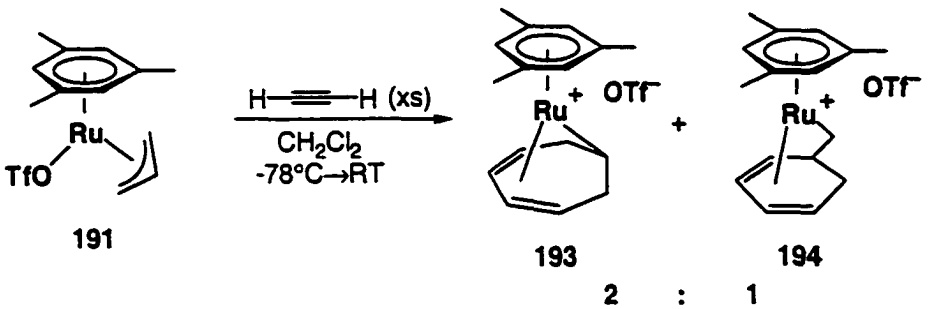
The η^3-allyl chloride complex **190** was thus readily prepared from the known η^6-mesitylene dichloride dimer[45] **189** using the same alkylation process used earlier for the hexamethylbenzene template (Scheme **52**). Addition of an equimolar amount of silver triflate also proceeds to form η^3-allyl triflate complex **191** in high yield. In trifluoroethanol, only a single product **192** is formed upon treatment of the mesitylene η^3-allyl chloride **190** with a large excess of 2-butyne (Eq. **87**). This compound was isolated by initial ion exchange to provide the hexafluorophosphate salt, followed by recrystallization to give pale yellow crystals in 75% yield. Analysis of the pure compound (by ^{1}H NMR and gated ^{13}C NMR spectroscopy) identified the product as η^1,η^4-tetramethylmethanocyclohexadienyl complex **192**, completely analogous to the compound isolated by Rubezhov from the reaction of the unsaturated η^6-benzene allyl complex with 2-butyne.[37] When the reaction is instead performed using the mesitylene allyl triflate complex **191** in dichloromethane, a mixture of the methanocyclohexadienyl complex **192** and an unidentified second product is formed in a ratio of 1 : 1. After several days in

solution, the latter compound converts to an inseparable mixture of two new products, but the identity of these derivatives could not be established.



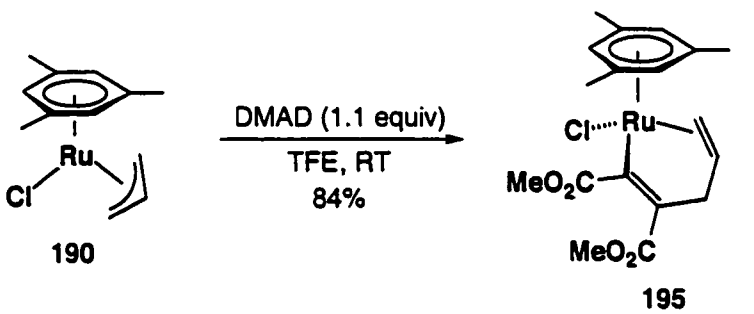
(Eq. 87)

Addition of acetylene to $(\eta^6\text{-}C_6Me_3H_3)$Ru(allyl)OTf complex **191** at low temperature in dichloromethane also results in an initial mixture of two products, formed in a ratio of 2 : 1 (Eq. **88**). These products are easily recognizable as η^1,η^4-cycloheptadienyl complex **193** and η^1,η^4-methanocyclohexadienyl complex **194**, respectively, due to the close similarity of the crude ^{1}H NMR spectrum to that obtained from the reaction of acetylene with the hexamethylbenzene template. Maintaining the dichloromethane solution of the crude reaction mixture at room temperature for two days results in the disappearance of the η^1,η^4-cycloheptadienyl complex **193**. Surprisingly, this material does not convert to the expected mesitylene η^5-cycloheptadienyl complex, but instead proceeds to a mixture of two new, as yet unidentified, complexes. The minor η^1,η^4-methanocyclohexadienyl complex, **194**, is not affected under these reaction conditions.

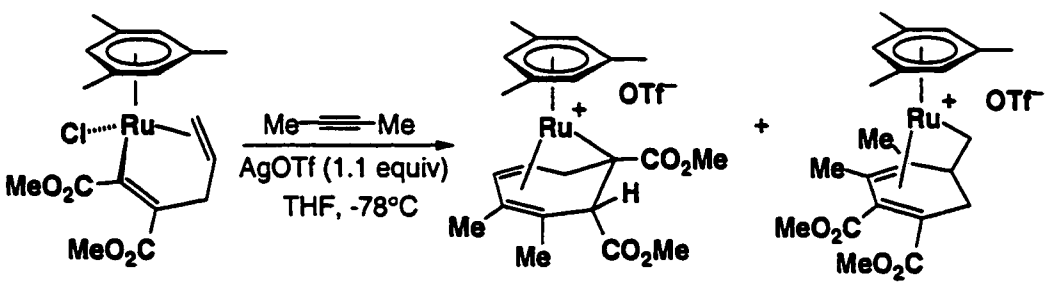


(Eq. 88)

Treatment of the mesitylene allyl triflate complex **191** with two equivalents of DMAD does not yield the expected seven-membered ring; instead, a complex mixture of unidentified products is formed. However, the mesitylene η^1,η^2-dicarbomethoxy-pentadienyl chloride complex **195** can be prepared in high yield using the same procedure used to obtain the hexamethylbenzene counterpart (Eq. **89**). Addition of an equimolar amount of silver triflate and 2-butyne to this complex results in the clean formation of the analogous η^1,η^4-cycloheptadienyl complex **196** and η^1,η^4-methanocyclohexadienyl complex **197**, although in a lower ratio of 1.3 to 1 (Eq. **90**). Surprisingly, the use of acetylene under these conditions leads to an intractable mixture of products, possibly due to multiple insertions of this alkyne.



190 **195** (Eq. 89)



195 **196** **197** (Eq. 90)

1.3 : 1

Using mesitylene as an ancillary ligand thus inhibits premature cyclization to five-membered ring after the initial alkyne insertion, as revealed in the reaction with 2-butyne. After the second alkyne insertion, however, the smaller, less electron rich arene ligand clearly favours cyclization to form the six-membered ring. Our original hypothesis that the larger and more electron rich ligand would promote seven-membered ring cyclization over six-membered ring formation is thus confirmed, although exactly how the ancillary ligand affects the migratory ring closure remains speculative.

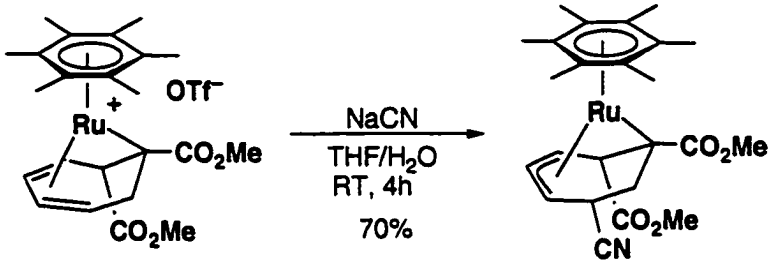
II. The Reactivity of DMAD-Derived η^1,η^4-Cycloheptadienyl Complexes

The cationic η^1,η^4-cycloheptadienyl complexes formed from the [3 + 2 + 2] allyl/alkyne cycloaddition process represent the first stable structures displaying this hapticity pattern in a seven-membered ring. It was thus decided to briefly explore the reactivity of these novel compounds and compare the results to the reactivity of the better known cationic η^5-cycloheptadienyl complexes.

1. Nucleophilic Addition

The reaction of sodium cyanide with the cationic η^1,η^4-cycloheptadienyl complex **178** derived from DMAD and acetylene proceeds to give a single product in good yield (Eq. **91**). The cyanide adduct is both air stable and crystalline, providing bright yellow crystals in 70% yield. Although the product was identified spectroscopically, crystals were obtained by slow recrystallization from a toluene/pentane mixture and subsequent X-ray diffraction analysis unambiguously established that the product is the η^1,η^3-6-cyanocycloheptendiyl complex **198**. Salient features of the structure determination are

presented in Figure 11. The nucleophile attacks the less hindered terminus of the diene ligand, rather than adding to the ipso carbon, as originally predicted.

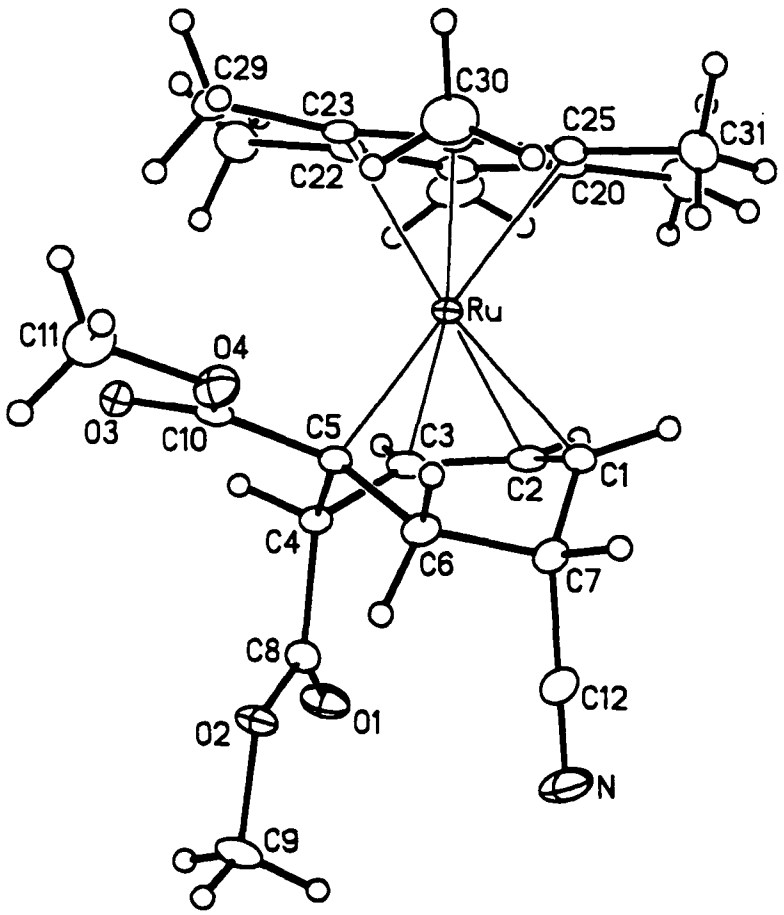


178 198 (Eq. 91)

The ^{1}H NMR spectrum displays a distinctive pattern (Table 6), with the most downfield signal being a broad doublet at δ 4.64 (assigned to H_2) and two protons at δ 2.53 and 2.23 (H_{7exo} and H_{7endo}, respectively), which exhibit a geminal coupling of 14.2 Hz. As well, the coupling between H_6 (at δ 2.79) and the adjacent H_{7exo} is unusually small, being approximately 0 Hz. The cyanide carbon is located as a singlet at 122.5 ppm in the gated ^{13}C NMR spectrum. Surprisingly, the ipso carbon is found as a broad singlet at 21.7 ppm, a downfield shift of more than 40 ppm from the ipso carbon resonance exhibited by the cationic starting material, complex **178**. A comparison of the X-ray analysis data indicates little difference in either the carbon-ruthenium bond length or bond angle between the two compounds, suggesting that a significant change in metal center anisotropy occurs upon addition of a nucleophile and is largely responsible for the large downfield shift.

While the η^1,η^4-cycloheptadienyl hapticity pattern is new, the η^1,η^3-cycloheptendiyl bonding pattern of the cyanide adduct is not. Studies of nucleophilic

Figure 11. ORTEP[113] Plot of Complex **198** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9806

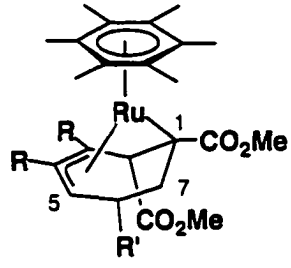


Final Residuals: $R_1 = 0.0299$; $wR_2 = 0.0784$. Data obtained at -60°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): Ru-C1, 2.156(4); Ru-C2, 2.138(4); Ru-C3, 2.193(4); Ru-C5, 2.214(4); N-C12, 1.142(6); C1-C2, 1.430(6); C1-C7, 1.523(6); C2-C3, 1.398(6); C3-C4, 1.496(5); C4-C5, 1.538(5); C4-C8, 1.518(5); C5-C6, 1.525(5); C5-C10, 1.470(5); C6-C7, 1.522(6); C7-C12, 1.469(6).

Selected Bond Angles (deg.): C2-C1-C7, 125.3(4); C1-C2-C3, 122.2(4); C2-C3-C4, 123.7(4); C3-C4-C5, 106.0(3); C3-C4-C8, 112.7(3); C5-C4-C8, 122.9(3); C4-C5-C6, 118.6(3); C4-C5-C10, 111.4(3); C6-C5-C10, 112.9(3); C5-C6-C7, 111.1(3); C1-C7-C6, 111.9(3); C1-C7-C12, 111.6(4); C6-C7-C12, 112.0(4); N-C12-C7, 178.9(5).

Table 6. Comparative ^{1}H NMR Spectroscopic Data for η^1,η^3-Cycloheptendiyl Complexes[a]

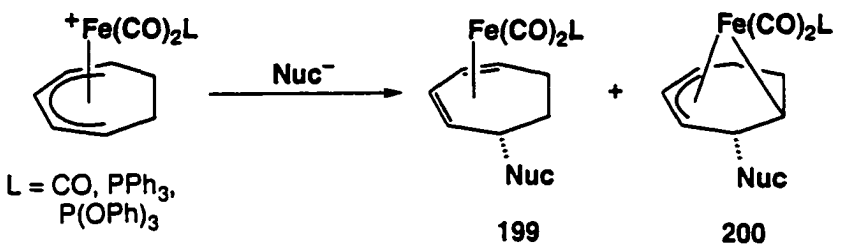


198 R = H, R' = CN
201 R = Me, R' = CN
204 R = Me, R' = OMe
205 R = H, R' = OMe

Assignment	198	201	204	205
H_2 J_{2-3}	4.64 (br d) 7.2 Hz	4.72 (br s) b	4.68 (br s) b	4.64 (br d) 7.3 Hz
H_3 J_{3-4}	3.59 (t) 6.9 Hz	b	b	3.65 (t) 6.9 Hz
H_4 J_{4-5}	2.90 (t) 7.0 Hz	b	b	3.20 (dd)[d] 7.9 Hz
H_5 J_{5-6}	3.11(t) 7.9 Hz	3.05 (d) 8.3 Hz	3.39 (dd) 7.6 Hz	3.47 (t)[d] 7.0 Hz
H_6 J_{6-7a}	2.79 (dd) 11.3 Hz	2.79 (ddd)[c] 11.8 Hz	4.06 (t) 7.7 Hz	4.03 (t) 7.3 Hz
H_{7a} J_{7a-7b}	2.23 (dd) 14.2 Hz	3.24 (dd) 14.2 Hz	2.25 (dd) 14.0 Hz	2.33 (dd) 14.2 Hz
H_{7b}	2.79 (d)	2.43 (d)	2.63 (d)	2.72 (d)

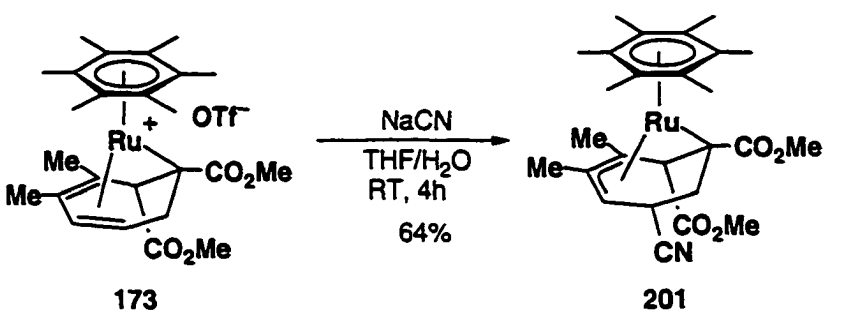
[a] Spectra were taken in C_6D_6 at room temperature. [b]Not applicable due to non-hydrogen substituent. [c]Additional splitting observed due to small coupling (1.0 Hz) to H_{7b}. [d]Resonance partially obscured by other signals.

additions to η^5-cycloheptadienyl iron complexes have generally found a mixture of two addition products, η^4-cycloheptadiene **199** and η^1,η^3-cycloheptendiyl **200**, where the product ratios depend on the nature of the nucleophile and the nature of the ancillary ligands attached to the metal (Eq. **92**).[117, 118] Similar behaviour has been noted for related ruthenium[119] and osmium η^5-cycloheptadienyl and η^5-cyclohexadienyl complexes, although the tendency to form σ-π-allyl complexes increases down the triad and is especially pronounced for osmium.[120]



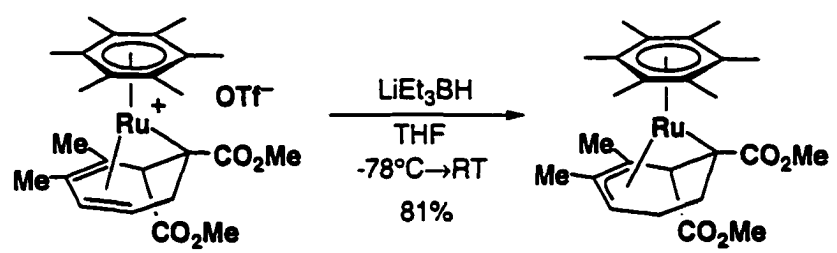
(Eq. 92)

The 2-butyne-derived counterpart, complex **201**, results from the addition of sodium cyanide to the dimethyl η^1,η^4-cycloheptadienyl complex **173** (Eq. **93**). The yellow crystals isolated from this reaction exhibit a very similar ^{1}H NMR spectrum in solution, with the most downfield signal being a singlet at δ 4.72, assigned to H_2 (Table **6**). Present in the ^{13}C NMR spectrum is the cyanide carbon resonance at 122.4 ppm, as well as the ipso carbon signal at 21.8 ppm.

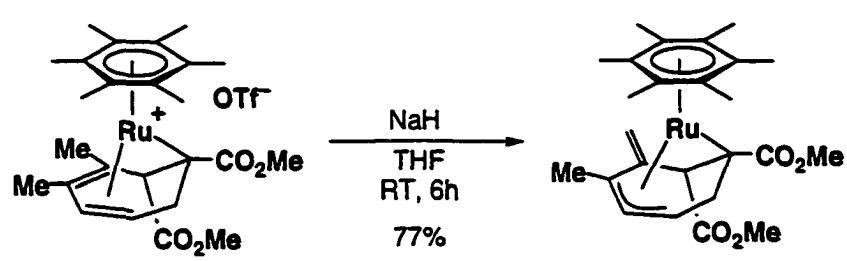


(Eq. 93)

Further attempts were made to add nucleophiles to dimethyl η^1,η^4-cycloheptadienyl complex **173** using a variety of reagents. Hydride addition can be cleanly achieved using $LiEt_3BH$ at low temperature (Eq. **94**), yielding the analogous η^1,η^3-cycloheptendiyl complex **202**. While the ^1H NMR spectrum of this material is generally similar to the cyanide adducts described above, the two sp^3-hybridized methylene pairs are present as unresolved complex signals. Other nucleophiles, such as methyl lithium, sodium malonate, and the potassium enolate of propiophenone apparently result in the formation of inseparable mixtures of nucleophilic addition and deprotonation products, as judged by the inspection of crude product mixtures by ^1H NMR spectroscopy. Treatment with the more strongly basic sodium hydride results in clean deprotonation of one of the methyl groups, giving the *exo*-methylene substituted η^1,η^3-cycloheptendiyl complex **203** (Eq. **95**). The *exo*-methylene protons appear as two inequivalent downfield signals at δ 5.42 and 5.33, both coupled weakly to the neighbouring triplet signal at δ 4.01, assigned to H_2.

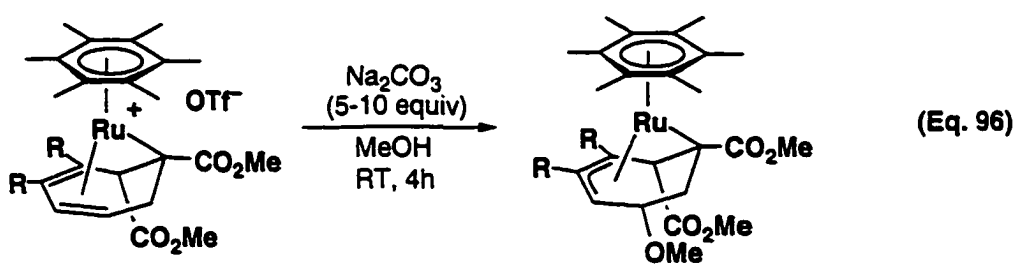


173 **202** **(Eq. 94)**



173 **203** **(Eq. 95)**

Sodium methoxide, prepared *in situ* from Na_2CO_3 and methanol, also adds cleanly to both η^1,η^4-cycloheptadienyl complexes **173** and **178** (Eq. **96**). The resulting η^1,η^3-6-methoxycycloheptendiyl products, **204** and **205**, are isolated as yellow air-stable crystals. Both the ^1H and ^{13}C NMR spectra exhibited by these complexes are very similar to those obtained for the products of cyanide addition (Table **6**). One notable difference in the ^1H NMR spectrum is the reduction of $J_{6\text{-}7endo}$ from approximately 11.5 Hz in the cyanide adducts to 7.5 Hz for the methoxy-substituted complexes, presumably due to the change in substituent electronegativities. Unlike the cyanide adducts, however, the η^1,η^3-6-methoxycycloheptendiyl complexes are found to react with silica gel. When a slurry made from silica gel and a diethyl ether solution of 6-methoxy substituted complex **205** is stirred at room temperature for several hours, the starting material is slowly converted to an air-sensitive, pentane soluble compound that is tentatively identified as the η^4-cycloheptatriene complex **206** (Eq. **97**). The ^1H NMR spectrum of **206** indicates the presence of a single sp^3-hybridized methylene unit, with two proton signals located at δ 3.07 and 1.49 (H_{7a} and H_{7b}) that display a very large geminal coupling of 20 Hz. Coupled to these methylene protons are two multiplet signals at δ 5.96 and 5.33 (H_5 and H_6, respectively); the downfield chemical shift of these signals suggest that they

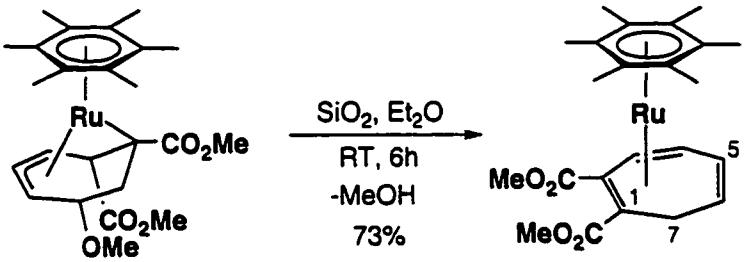


(Eq. 96)

173 R = Me
178 R = H

204 R = Me, 88%
205 R = H, 79%

correspond to the non-coordinated alkene. When the dimethyl analogue, complex **200**, is subjected to the same reaction conditions (flash silica gel, diethyl ether), an initial mixture of the deprotonation compound, η^1,η^3-cycloheptendiyl complex **203**, and a second unidentified product is formed in a ratio of 1 : 1, while longer reaction time results in the formation of a complex mixture of several unidentified compounds.



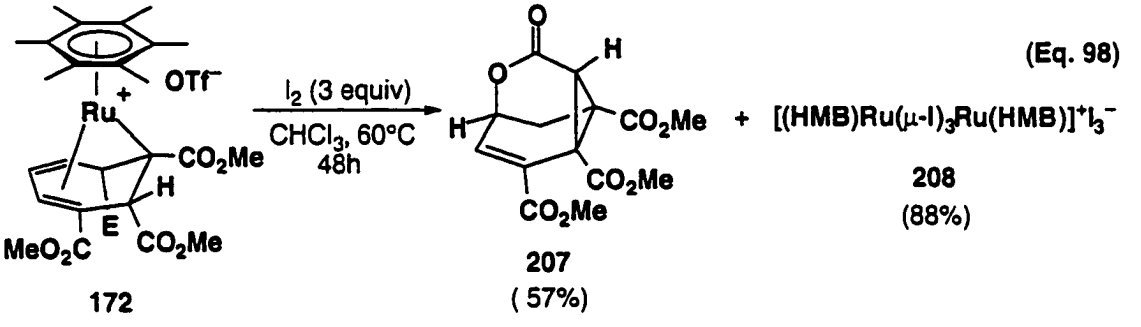
205 **206** **(Eq. 97)**

We had originally hoped that the addition of nucleophiles to the cationic η^1,η^4-cycloheptadienyl complexes would result in the formation of Ru(0) η^4-cycloheptadiene products. For our purposes, the formal reduction of the metal is desirable since oxidative removal of the functionalized organic fragment is more feasible at the reduced metal center. Unfortunately, the Ru(II) η^1,η^3-cycloheptendiyl complexes that are formed upon nucleophilic addition are quite inert. Attempts to remove the organic moiety by thermolysis, carbonylation or hydrogenation result only in the recovery of starting material.

2. Iodinolysis: Oxidative Removal of Seven-Membered Rings

It is possible to liberate the seven-membered ring organic fragment from the ruthenium metal template by the use of iodine in a one-pot method that proceeds by an

extensive transformation of the ring. Treatment of η^1,η^4-tetracarbomethoxycyclo-heptadienyl complex **172** in chloroform with three equivalents of iodine at room temperature thus results in the slow formation of black crystals (complex **208**) and a single organic compound (**207**) over a period of several weeks. The reaction can be accelerated by heating to reflux temperature, reducing the reaction time to two days (Eq. **98**).



172

207
(57%)

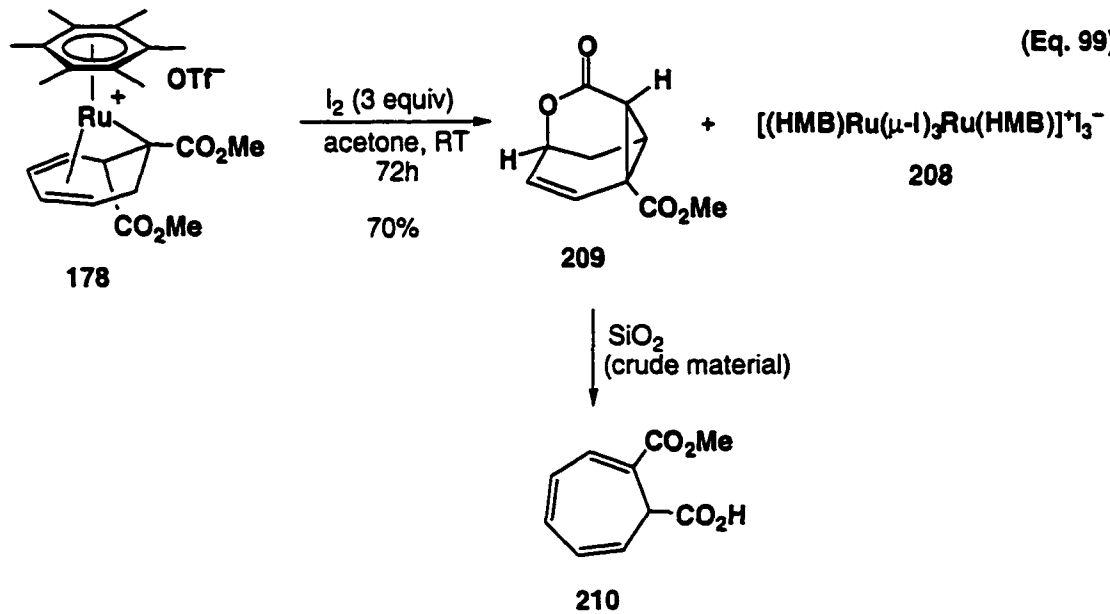
208
(88%)

(Eq. 98)

The organic compound **207** derived from this reaction is isolated by flash chromatography as a yellow oil in moderate yield. High resolution mass spectrometry of this material gives $C_{14}H_{14}O_8$ as the molecular formula. The ^1H NMR spectrum also reveals that only three methyl ester groups are present in the organic product, although four carbonyl carbons are found in the ^{13}C NMR spectrum (at 168.1, 166.6, 164.2 and 164.1 ppm). Other relevant ^1H and ^{13}C NMR data are presented in Table **7**. Of particular importance is the carbon signal at 35.0 ppm, assigned to C_2; the large carbon-hydrogen coupling constant of 178 Hz, combined with the upfield shift, indicates the presence of a cyclopropyl ring. Both direct ^1H-^{13}C correlation (HETCORR) and long range ^1H-^{13}C correlation spectroscopy (BIRDTRAP) were used to confirm the interesting tricyclic structure of compound **207**.

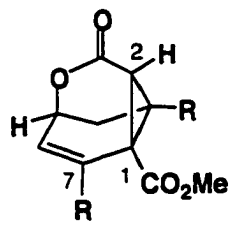
The black crystals formed during this reaction were found to be completely insoluble in most organic solvents and only marginally soluble in acetonitrile; a ^{1}H NMR spectrum taken in acetonitrile-d_3 revealed only one resonance, a singlet at δ 2.17 that corresponds to the hexamethylbenzene ligand. X-ray crystallography of crystals obtained directly from the reaction mixture was used to identify this material as the triple iodide-bridged complex $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}I)_3Ru(\eta^6\text{-}C_6Me_6)]^+$ **208** bearing the unusual I_3^- counterion (Figure **12**). The related η^6-benzene chloride-bridged dimer is well known, and has been prepared with a variety of counterions.[45,121-123] Elemental analysis of the black precipate, however, indicates that it has a chemical composition closer to $C_{12}H_{18}RuI_4$ than the expected $C_{12}H_{18}RuI_3$, suggesting the presence of other compounds.

A similar, but faster, reaction is observed when the η^1,η^4-dicarbomethoxy-cycloheptadienyl complex **178** is treated with excess iodine (Eq. **99**). After two or three days at room temperature, black crystals of complex **208** are removed by filtration, leaving only the organic compound **209** in the filtrate. This organic product exhibits ^{1}H



(Eq. 99)

Table 7. Comparative ^{1}H and ^{13}C NMR Spectroscopic Data for Tricyclic Products of Iodinolysis[a]

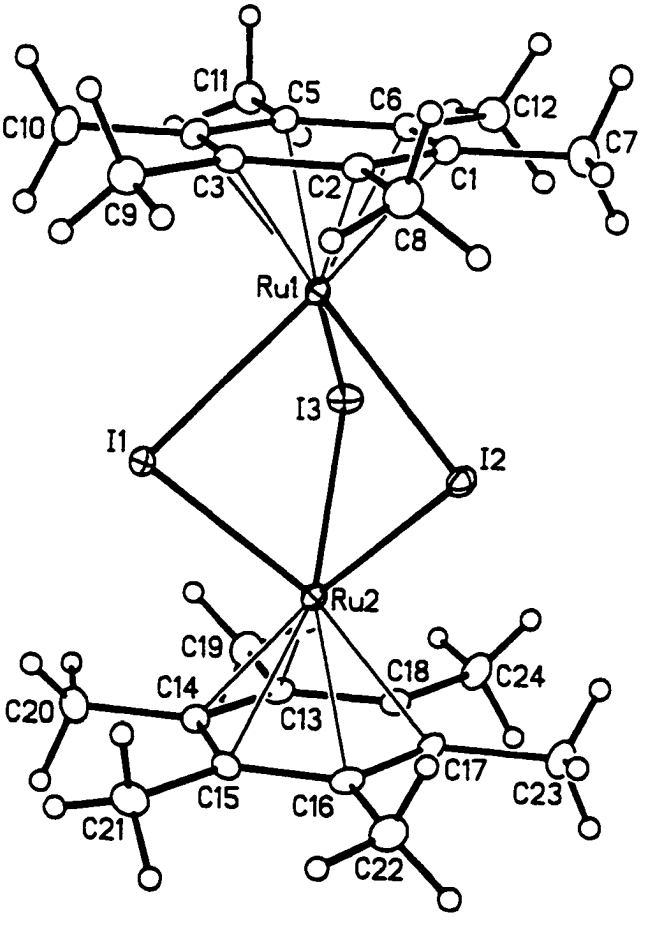


207 R = CO_2Me
209 R = H

^{1}H NMR	**207**	**209**	^{13}C NMR	**207**	**209**
H_2 J_{2-3}	3.65 (s) b	3.06 (d) 7.8 Hz	C_1	39.3 (s)	31.6 (s)
H_3 J_{3-4a} J_{3-4b} J_{3-5}	b	2.71 (dq) 2.6 Hz 2.6 Hz 2.6 Hz	C_2 $^{1}J_{CH}$	35.0 (d) 178 Hz	22.6 (d) 177 Hz
H_{4a} J_{4a-4b} J_{4a-5}	2.27 (dd) 15.0 Hz 4.0 Hz	2.27 (ddd)[d] 14.4 Hz 3.9 Hz	C_3 $^{1}J_{CH}$	32.3 (s)	34.5 (d) 176 Hz
H_{4b} J_{4b-5}	1.55 (ddd)[c] 1.7 Hz	1.55 (dt) 2.3 Hz	C_4 $^{1}J_{CH}$	21.4 (t) 137 Hz	20.0 (t) 134 Hz
H_5 J_{5-6} J_{5-7}	5.02 (ddd) 7.0 Hz b	4.86 (m) 6.5 Hz 0.6 Hz	C_5 $^{1}J_{CH}$	67.3 (d) 161 Hz	68.3 (d) 154 Hz
H_6 J_{6-7}	7.18 (dd) b	6.18 (dd) 9.5 Hz	C_6 $^{1}J_{CH}$	133.7 (d) 174 Hz	128.5 (d) 169 Hz
H_7	b	6.86 (dd)	C_7 $^{1}J_{CH}$	132.6 (s)	124.6 (d) 172 Hz

[a] Spectra were taken in $CDCl_3$ at room temperature. [b] Not applicable due to non-hydrogen substituent. [c] Additional splitting observed due to small coupling (0.5 Hz) to H_6. [d] Additional splitting observed due to small coupling (1.8 Hz) to H_6.

Figure 12. ORTEP[113] Plot of for Complex **208** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9928



Final Residuals: $R_1 = 0.0358$; $wR_2 = 0.0920$. Data obtained at -80°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): I1-Ru1, 2.7420(6); I1-Ru2, 2.7492(6); I2-Ru1, 2.7394(6); I2-Ru2, 2.7414(6); I3-Ru1, 2.7422(6); I3-Ru2, 2.7358(6); Ru1-C1, 2.201(5); Ru1-C2, 2.203(5); Ru1-C3, 2.201(5); Ru1-C4, 2.213(6); Ru1-C5, 2.205(6); Ru1-C6, 2.210(5); Ru2-C13, 2.206(5); Ru2-C14, 2.183(5); Ru2-C15, 2.200(5); Ru2-C16, 2.209(6); Ru2-C17, 2.196(6); Ru2-C18, 2.197(5).

Selected Bond Angles (deg): Ru1-I1-Ru2, 81.741(17); Ru1-I2-Ru2, 81.930(17); Ru1-I3-Ru2, 81.981(17); I1-Ru1-I2, 82.109(17); I1-Ru1-I3, 81.837(17); I2-Ru1-I3, 81.246(17); I1-Ru2-I3, 81.821(17); I2-Ru2-I3, 81.324(17).

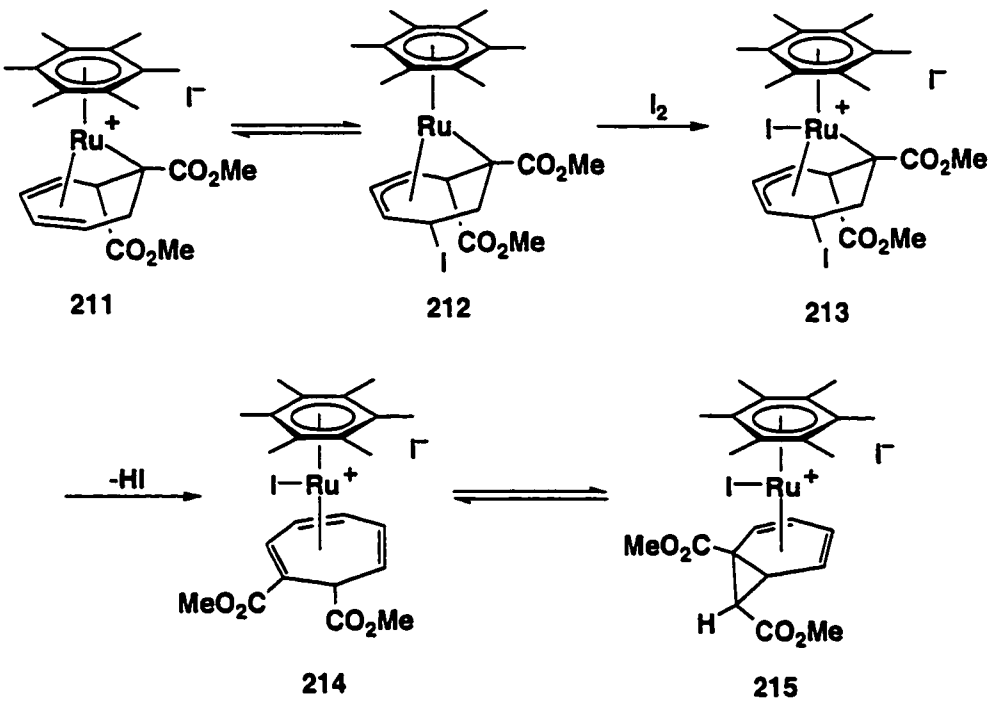
and ^{13}C NMR spectra similar to those observed for the tetracarbomethoxy analogue (Table 7), while high resolution mass spectrometry indicates a consistent chemical formula of $C_{10}H_{10}O_4$. When the crude residue from the reaction is directly chromatographed on silica gel (diethyl ether) without any prior purification, compound **209** is replaced with a new organic compound, **210**. This product also gives the molecular ion composition as $C_{10}H_{10}O_4$, although both the ^1H NMR spectrum and infrared spectrometry now indicate the presence of a carboxylic acid group. This strongly suggests that the lactone ring of tricyclic compound **207** opens during silica gel chromatography of the crude material and the resulting norcaradiene intermediate then undergoes a valence tautomerization to the cycloheptatriene compound **210**. The electrocyclic norcaradiene-cycloheptatriene rearrangement is known to occur readily at room temperature, especially if electron-withdrawing groups are present.[124] It is possible to isolate the initial tricyclic compound **209** cleanly by rinsing a chloroform solution of the crude residue with aqueous sodium thiosulfate solution prior to chromatography. The sodium thiosulfate solution removes excess iodine and also neutralizes acidic byproducts that may be responsible, along with the silica gel itself, for the ring-opening reaction.

When only one equivalent of iodine is used in the reaction of diester complex **178**, the sole product obtained is a complex that exhibits an identical resonance pattern in the ^1H NMR spectrum to that of the starting material, but with slightly different chemical shifts. This suggests that the first equivalent of iodine in the iodinolysis reaction is involved in a counterion exchange, presumably producing I^+OTf^- as a byproduct.[125] A second equivalent of iodine then converts the η^1,η^4-cycloheptadienyl iodide complex to the final products. However, the black crystals isolated from the reaction using only two

equivalents of iodine, which otherwise appear to be identical to those formed from three equivalents of iodine, provide elemental analysis data indicating a chemical formula of $C_{12}H_{18}RuI_2$. One explanation for this difference is that the counterion of complex **208** may be either I_3^- or I^-, depending on the reaction stoichiometry.

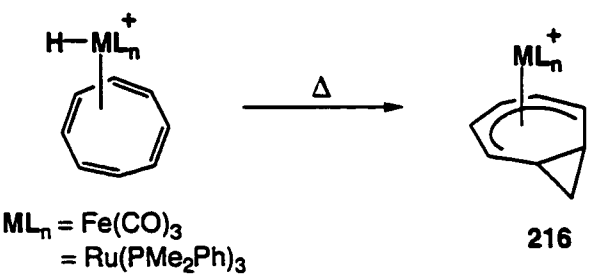
The iodinolysis reactions are complex and involve multistep processes to obtain the final products. Several distinct but related mechanistic proposals can be developed to rationalize the iodinolysis process, although only a few variations will be discussed here (Scheme **53**). As shown earlier, the first equivalent of iodine clearly reacts with the starting η^1,η^4-cycloheptadienyl **178** by counterion exchange, providing the η^1,η^4-cycloheptadienyl iodide complex **211**. This cationic complex can then undergo nucleophilic attack by the I^- at the most reactive C_6 position to yield the neutral η^1,η^3-6-iodocycloheptendiyl complex **212**. Subsequent electrophilic attack by I_2 at the metal forms a new, cationic, high valent ruthenium complex **213**. Elimination of HI from this species, either by a metal-mediated mechanism or via a simple *trans* elimination, results in the formation of the cationic Ru(II) η^4-cycloheptatriene complex **214**, which may undergo ring closure to the cyclopropyl diene ligand while still coordinated to the metal. If the organic moiety dissociates as the cycloheptatriene fragment, prior to ring closure, it is expected to remain as the seven-membered ring based on known norcaradiene reactions.[123] Similar rearrangements on a metal template have been observed to yield stable cationic 2–6-η^5-bicyclo[5.1.0]octadienyl complexes **216** upon protonation of some η^4-coordinated cyclooctatetraene complexes of iron and ruthenium (Eq. **100**).[126] Another plausible mechanism (Scheme **54**) involves spontaneous rearrangement of the σ-π-allyl

Scheme 53



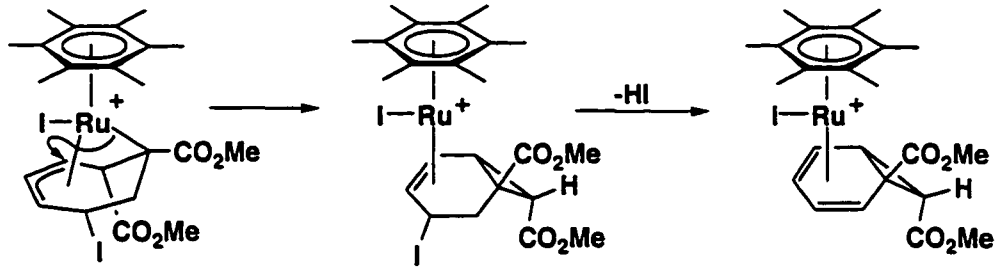
ligand of cationic complex **213**, yielding the bicyclic alkene intermediate **217** that can then eliminate HI to form complex **215**.

To rationalize the demethylation and formation of the observed lactone product, it is necessary to propose the cleavage of one methyl ester under the reaction conditions. Methyl esters undergo demethylation upon treatment with lithium iodide, but this

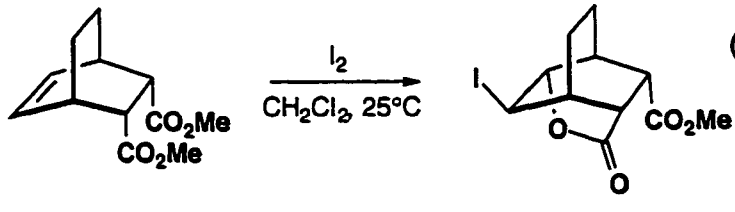


(Eq. 100)

Scheme 54



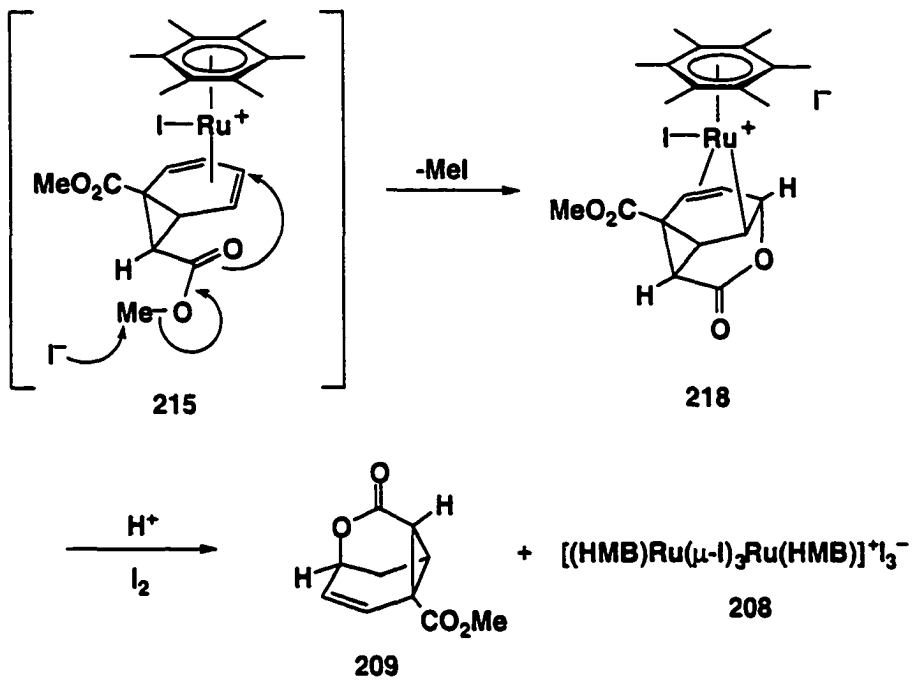
reaction generally requires elevated temperatures.[127] However, iodine itself cleaves the methyl ester and promotes lactone formation in the reaction of dimethyl *endo,endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate at room temperature (Eq. **101**), a process initiated by iodonium ion formation.[128] It is believed that the strained bicyclo[2.2.2] ring fixes the ester carbonyl in position to stabilize the cationic charge development at the reaction site, increasing the rate of the reaction. A similar process presumably occurs after the rearrangement to the coordinated norcaradiene complex **215** (Scheme **55**), to yield the tricyclic organic structure found in complex **218**; this process is likely promoted by the electron-withdrawing properties of the cationic ruthenium center bound to the diene ligand. The non-conjugated σ-bond in complex **218** is then be susceptible to electrophilic attack by HI, the byproduct of an earlier step (Scheme **53** or **54**). This reaction produces the final tricyclic structure of compound **209**, which dissociates from



(Eq. 101)

the ruthenium metal center in the presence of iodine. In principle, the lactonization could occur after decomplexation of the norcaradiene fragment, although no evidence for an intermediate organic compound is found during these two reactions.

Scheme 55

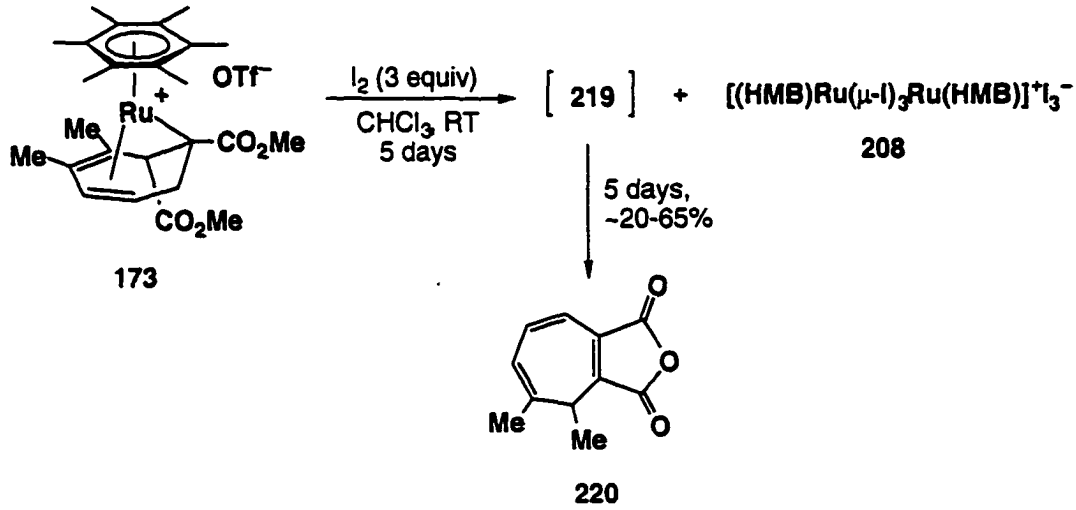


Addition of excess bromine (3 equivalents) to η^1,η^4-cycloheptadienyl complex **178** results in a rapid reaction that yields a dark orange precipitate and a complex mixture of organic products. Elemental analysis of the precipitate is consistent with the formulation $(C_6Me_6)RuBr_4$, similar to the precipitate obtained from iodinolysis. The mixture of organic products most likely results from the higher reactivity, lower selectivity, and the irreversibility of bromine reactions compared to iodine.

Finally, the iodinolysis of the 2-butyne derived η^1,η^4-cycloheptadienyl complex **173** proceeds to a different organic product (Scheme **56**). One major difference in this

reaction is that a *minimum* of three equivalents of iodine is required to completely remove the organic moiety from the metal, instead of the two equivalents consumed in the previous two examples. After several days at room temperature, a black crystalline precipitate is formed that is identical to the cationic dimer **208** isolated from the earlier reactions. Unfortunately, the initial organic compound **219** produced shows very broad signals in the ^{1}H NMR spectrum and has not been conclusively identified. When the reaction mixture is left undisturbed for a further five days, however, this intermediate species slowly converts to bicyclic anhydride **220**, although the isolated yield is quite variable. This second product is a waxy yellow solid and is readily isolated by sublimation from the crude reaction mixture. The structure was identified as 6,7-dimethyl-1,6-cycloheptatrienedicarboxylic anhydride **220** by a combination of spectroscopic and analytical methods. Both elemental analysis and mass spectral data confirm the chemical formula of $C_{10}H_{10}O_3$. The compound exhibits ^{1}H and ^{13}C NMR spectra consistent with a cycloheptatriene structure; also apparent is the loss of both

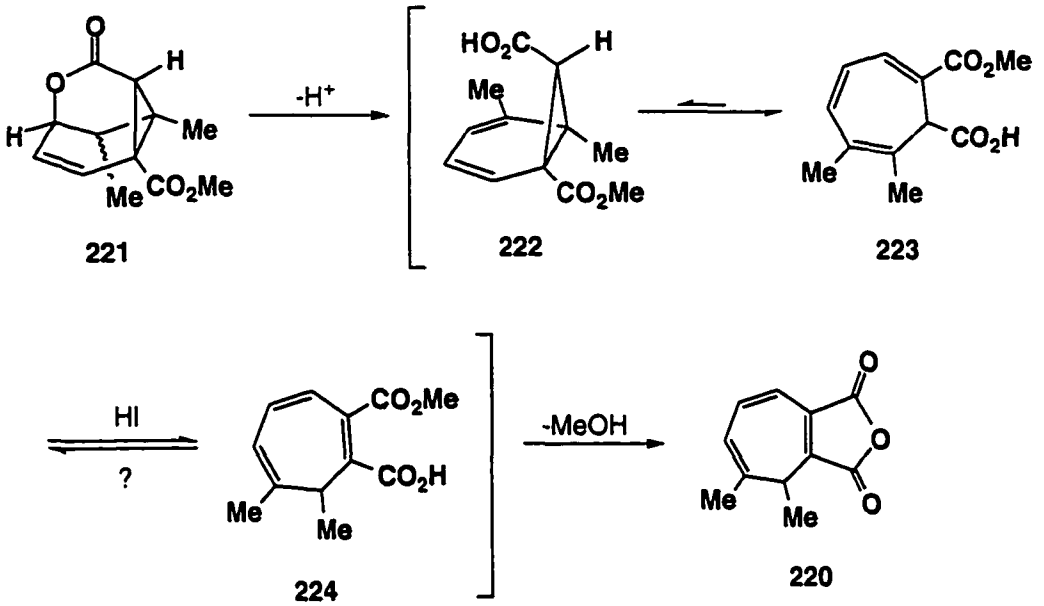
Scheme 56



methyl ester signals. Infrared spectrometry reveals strong absorptions at 1843 and 1767 cm^{-1}, characteristic of the carbonyl stretches of the five-membered ring conjugated anhydride.[129]

Treatment of η^1,η^4-cycloheptadienyl complex **173** with two equivalents of iodine results in the formation of a mixture of the counterion exchange product and the unknown intermediate organic species **219** in an approximate ratio of 1 : 1, along with the formation of some black precipitate of complex **208**. This observation indicates that the intermediate formed from a second equivalent of iodine reacts more quickly with any excess iodine present than the η^1,η^4-cycloheptadienyl iodide complex formed from the first equivalent. The addition of a third equivalent of iodine results in the complete conversion of this mixture to organic compound **219** and the ruthenium cluster **208**. It is likely that this reaction initially proceeds in the same fashion as the previous iodinolysis reactions (Scheme **57**). Once the tricyclic organic product **221** is formed, however, it is plausible that the lactone ring opens more readily than the earlier examples, due to the presence of a methyl group on the bridgehead. The resultant norcaradiene compound **222** then rapidly undergoes an electrocyclic rearrangement to form the cycloheptatriene **223**. The observed broadness of intermediate **219** in the ^1H NMR spectrum may be due to the cycloheptatriene compound undergoing reversible cycloheptatriene-norcaradiene tautomerizations at room temperature and/or the cycloheptadiene undergoing acid-catalyzed hydrogen shifts. Eventually the anhydride is formed, locking the organic structure in place. Another possibility is that iodine oxidizes the cycloheptatriene compound **223** to a tropylium cation, a reaction that has been previously demonstrated

Scheme 57



221 222 223 224 220

using bromine;[130] however, it is difficult to rationalize the subsequent reduction of the tropylium cation under these reaction conditions. In general, this transformation of the η^1,η^4-cycloheptadienyl ligand to the final organic product is not readily understood and the variable yield of anhydride **218** suggests that unknown factors also influence the final steps of the reaction.

These novel iodinolysis reactions are unusual because they involve mild oxidation of an already cationic ruthenium(II) complex, as well as resulting in selective demetallation of the η^1,η^4-cycloheptadienyl ligand in a single reaction. By comparison, addition of excess iodine to the six-membered ring adduct, η^1,η^4-methanocyclohexadienyl complex **174**, yields only the counterion exchange product; no further reaction is observed even after prolonged reaction. Similarly, the reaction of the unsubstituted η^5-cycloheptadienyl complex **159** with excess iodine returns a complex that

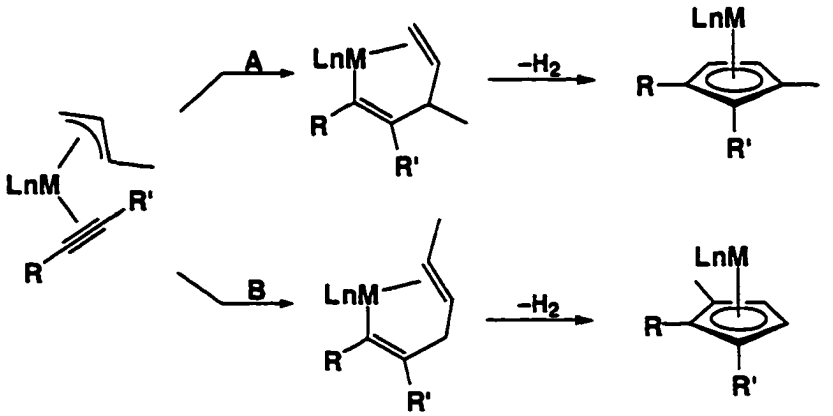
is spectroscopically identical to the starting material due to simple counterion exchange. The oxidative removal of coordinated ligands by iodinolysis thus appears to be limited to the η^1,η^4-coordinated seven-membered rings, which are the unique products of the [3 + 2 + 2] cycloaddition reaction.

Chapter 4. Substituted Allyl/Alkyne Coupling Reactions Mediated by the Cationic (η^6-C_6Me_6)Ru(II) Template

1. Introduction and Background

The placement of a substituent on the η^3-allyl ligand has significant effects on its subsequent reactivity. In particular, in a terminally substituted η^3-allyl complex, the two ends of the allyl ligand are dissimilar, so migratory insertion of an alkyne can potentially form two different vinyl olefin complexes (Figure **13**). However, despite an extensive investigation of substituted allyls in the cobalt system, no conclusive evidence has been obtained that would indicate a preference for alkyne insertion on the less substituted side of the allyl ligand (path B), although this has been the general assumption.[43] This migration regioselectivity has been surprisingly difficult to determine, since the only

Figure 13. Regioisomers Formed from Crotyl/Alkyne Cycloaddition



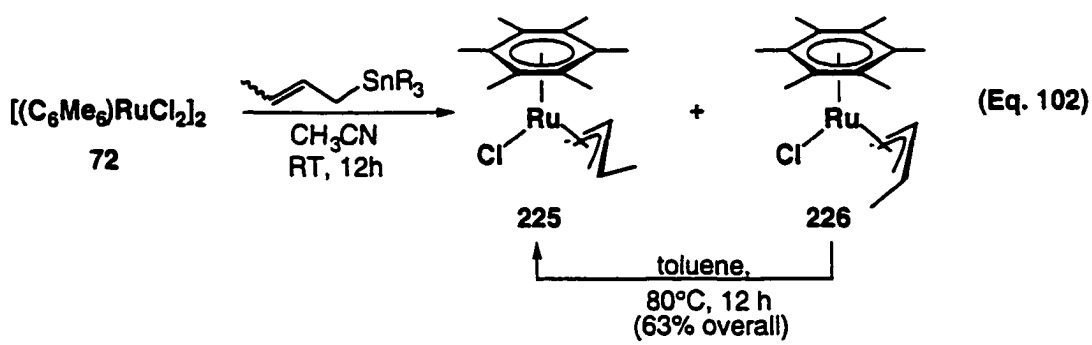
consequence of insertion of a symmetric alkyne into opposite ends of a terminally substituted allyl ligand is the formation of enantiomeric five- or seven-membered ring products. An unsymmetrical alkyne would, in principle, distinguish which end of the substituted allyl is reactive in the migratory insertion, although this is complicated by uncertainty about the alkyne's preferred direction of insertion and by the possibility of competing [5 +2] cycloaddition reactions under some reaction conditions.

By investigating the reactivity of substituted η^3-allyl ruthenium complexes with a selection of alkynes we hoped to determine whether substituents on the η^3-allyl ligand significantly alter the partitioning between the five, six and seven-membered ring products. We also intended to probe further the regioselectivity of the initial alkyne insertion, using the unsymmetrical η^3-allyl ligands as a tool to distinguish between regioisomeric pathways. In the end, we succeeded in resolving some of the consequences of allyl substitution on both the reaction partitioning and stereochemistry, and, as a significant bonus, we have obtained important mechanistic information relevent to recently discovered cobalt-mediated carbon-carbon activation/ring expansion reactions.[43,44]

2. Preparation of Substituted η^3-Allyl Ruthenium Complexes

The simplest terminally-substituted allyl ligand is the 1-methylallyl (crotyl) ligand, and this became our initial synthetic target. While the preparation of the η^3-allyl ruthenium complex **77** involved the commercially available tetraallyltin or allyltriphenyltin reagents, the analogous crotyl tin reagents require synthesis. The

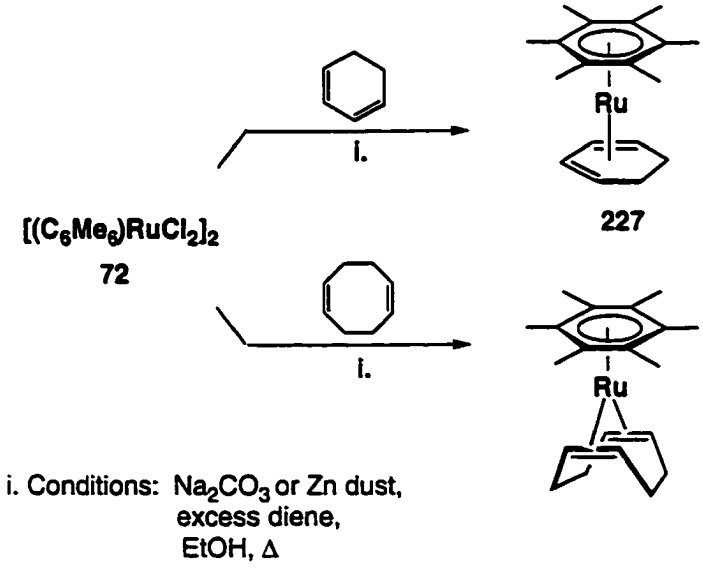
reaction of tributyltin chloride with crotyl Grignard readily provides the required crotyl tin reagent, although it is formed as an inseparable mixture of both *cis*- and *trans*-(2-butenyl)tributylstannane, along with the (1-methyl-2-propenyl)stannane isomer.[131] However, treatment of a suspension of $[(C_6Me_6)RuCl_2]_2$ in acetonitrile with this mixture of isomeric crotyl tin compounds results in the initial formation of two different ruthenium complexes, in a ratio of approximately 1 : 1 (Eq. **102**). Based on the ^1H NMR spectroscopic analysis of the crude residue, the two products were identified as $(C_6Me_6)Ru(\eta^3$-*exo,syn*-crotyl)Cl (**225**) and $(C_6Me_6)Ru(\eta^3$-*exo,anti*-crotyl)Cl (**226**). Traces of a third isomer also appear in the reaction mixture, tentatively identified as an *endo* crotyl isomer. The crude reaction mixture is both thermally unstable and air-sensitive, decomposing to a black material upon exposure to air or heat. However, careful removal of the tin residues before heating of the ruthenium mixture in toluene results in the smooth conversion of the *anti* isomer to the thermodynamically more stable *syn* isomer. The isolated $(C_6Me_6)Ru(\eta^3$-*exo,syn*-crotyl)Cl complex **225** was found to be air-stable and is readily purified by recrystallization from a toluene/pentane mixture, giving an overall yield of 63% from the ruthenium dimer **72**.



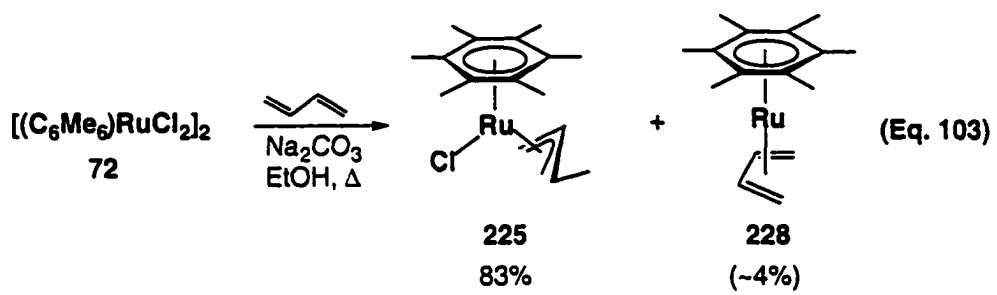
(Eq. 102)

Although the use of tin reagents is effective, a simpler and more convenient synthetic route to terminally substituted allyls was sought. One attractive alternative is the conversion of a diene ligand to an allyl complex upon protonation, a procedure that is well established in the cobalt system.[43] However, few useful methods for preparing arene-olefin complexes of zerovalent ruthenium exist in the literature. Bennett reported that ethanolic reduction of $[(C_6Me_6)RuCl_2]_2$ using sodium carbonate or zinc dust in the presence of 1,5-cyclooctadiene or 1,3-cyclohexadiene results in the formation of ruthenium diene complexes in good yield (Scheme **58**).[90,52] In contrast, the reaction of $[(C_6Me_6)RuCl_2]_2$, sodium carbonate and cycloheptatriene in alcohol does not give the expected ruthenium triene complex, but instead yields the protonated η^5-cycloheptadienyl complex, (Chapter 3, p. 117). It is therefore not surprising that the ethanolic reduction of $[(C_6Me_6)RuCl_2]_2$ using sodium carbonate in the presence of 1,3-butadiene results primarily in the formation of the thermodynamic crotyl isomer, $(C_6Me_6)Ru(\eta^3$-*exo,syn*-

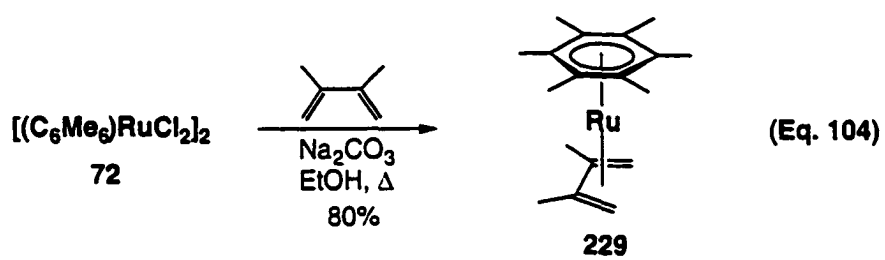
Scheme 58



crotyl)Cl (**225**) in high yield, along with a small amount (~4%) of the coordinated butadiene complex **228** (Eq. **103**). The butadiene byproduct **228** is readily separated from the crotyl chloride complex **225** by extraction from the crude residue with pentane. When the reduction is conducted in the presence of 2,3-dimethylbutadiene, however, the only product isolated is the η^4-2,3-dimethylbutadiene complex (**229**) (Eq. **104**). It appears that under these reaction conditions an equilibrium exists between the Ru(0) diene complexes and the Ru(II) η^3-allyl complexes, which is dependent on the nature of the diene.

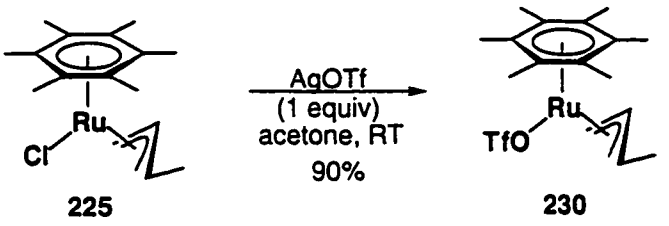


(Eq. 103)



(Eq. 104)

Treatment of the ruthenium crotyl chloride **225** with a slight excess of silver triflate provides the triflate complex **230** in high yield as an air-sensitive orange powder (Eq. **105**). This product was identified as the *exo,syn*-isomer based on the similarity of the coupling constants in the ^{1}H NMR spectrum to those of the starting chloride complex and due to its spectroscopic similarity to the unsubstituted η^3-allyl triflate complex **78**.

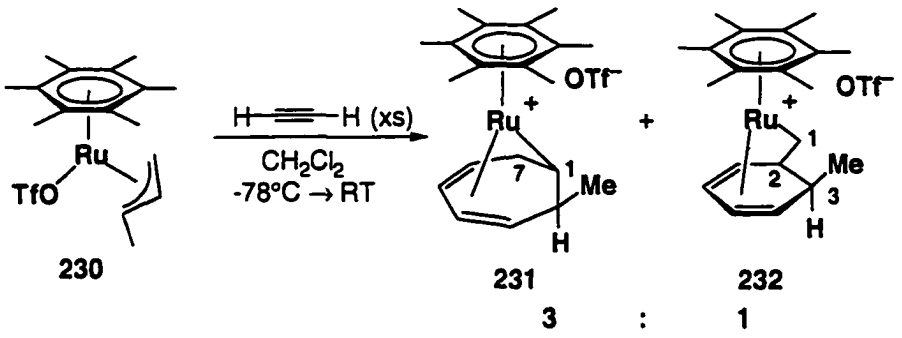


225 230 (Eq. 105)

3. Ruthenium-Mediated Coupling of the η^3-Crotyl ligand with Alkynes

3.1 The Reaction of η^3-Crotyl Ruthenium Triflate Complex with Acetylene

The addition of acetylene to a dichloromethane solution of (C_6Me_6)Ru(crotyl) triflate **230** at low temperature, followed by warming to room temperature, initially provides an inseparable mixture of two cycloaddition products, **231** and **232** in a ratio of 3 : 1 (Eq. **106**). The major complex **231** is identified as the η^1,η^4-2(*endo*)-methylcycloheptadienyl complex based on the similarity of the ^{1}H and ^{13}C NMR spectra to those previously obtained for the unsubstituted η^1,η^4-cycloheptadienyl complex **156** (*vide supra*). Unlike complex **156**, however, the η^1,η^4-2-methylcycloheptadienyl complex **231** does not exhibit mirror plane symmetry due to the presence of the crotyl-derived methyl substituent. The ^{13}C NMR spectrum reveals the upfield signal characteristic of a ruthenium η^1,η^4-cycloheptadienyl complex at –29.1 ppm (attributed to C_1). In the ^{1}H NMR spectrum, the upfield signal at δ –0.55, assigned to H_1, appears as a doublet with a coupling constant of 8.5 Hz due to coupling only to the adjacent H_{7endo}, with no apparent coupling to either H_{7exo} or to H_2. On the basis of this observation, the methyl group is tentatively assigned to be *endo* to the ruthenium center, similar to the stereoselectivity observed in cycloadditions using the crotyl cobalt complexes.[42-44]

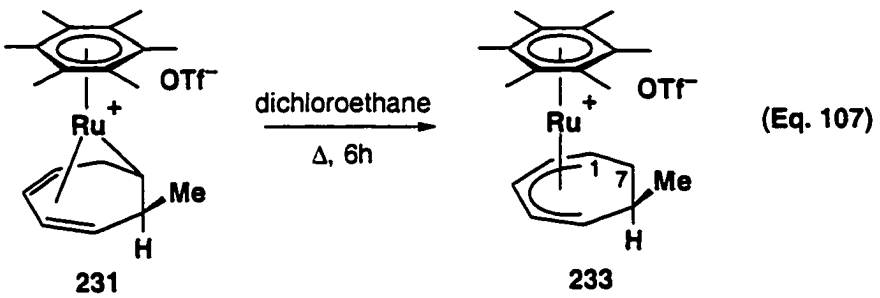


(Eq. 106)

The minor product, complex **232**, is readily identified as an η^1,η^4-methanocyclohexadienyl complex based on its spectroscopic similarity to the parent η^1,η^4-methanocyclohexadienyl complex **157**. The presence of a characteristic narrow doublet in the ^{1}H NMR spectrum at δ 0.87 ($J_{1b\text{-}1a}$ = 3.1 Hz), attributed to H_{1b}, suggests that the crotyl-derived methyl substituent is located on C_3. However, the stereochemistry of the methyl group is more difficult to determine and is tentatively assigned as *endo* by analogy to the major product. The location of the methyl group on C_3 suggests that, for the minor product at least, the migratory insertion of acetylene occurs to the substituted end of the allyl ligand.

Heating the mixture of η^1,η^4-2-methylcycloheptadienyl complex **231** and η^1,η^4-3-methylmethanocyclohexadienyl complex **232** in dichloroethane results in the conversion of both compounds to new products. As expected, the major η^1,η^4-2-methylcycloheptadienyl complex undergoes a quantitative transformation to η^5-6-methylcycloheptadienyl complex **233** (Eq. **107**). The ^{1}H and ^{13}C NMR spectra of this complex are very similar to those obtained for the analogous cobalt complexes and confirm the assignment of the methyl substituent as *endo*. More surprising is the transformation of the minor η^1,η^4-3-methylmethanocyclohexadienyl complex **231** to a

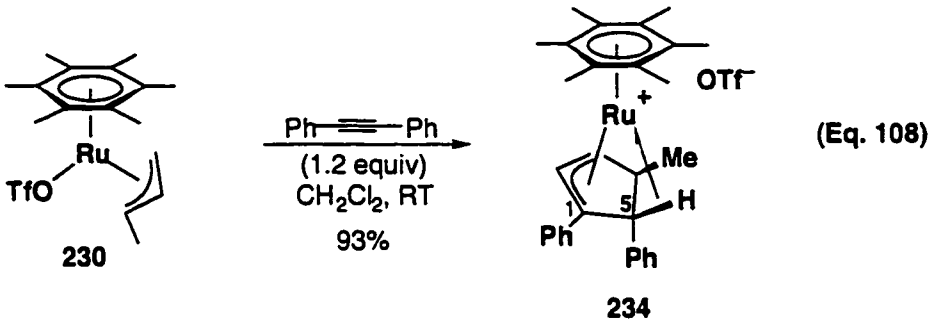
new product, as no previous η^1,η^4-methanocyclohexadienyl complex proved to be thermally labile. Unfortunately, this reaction is accompanied by a significant amount of decomposition and the identity of this thermolysis product could not be established.



(Eq. 107)

3.2 The Reaction of η^3-Crotyl Ruthenium Triflate Complex with Substituted Alkynes

Addition of diphenylacetylene to a solution of crotyl triflate **230** in either acetone or dichloromethane does not result in the expected demethylated pentamethylbenzene η^5-cyclopentadienyl product. Although only a single hexamethylbenzene product is isolated from the reaction (Eq. **108**), the compound displays none of the characteristic spectroscopic features of an η^5-cyclopentadienyl complex; instead, the ^{1}H NMR spectrum displays signals corresponding to four cyclopentenyl ring hydrogens, indicating that the dehydrogenation of the five-membered ring does not occur. The most characteristic spectroscopic feature exhibited by this new complex is an upfield signal at δ –9.45, attributed to an agostic hydride. This signal appears as a doublet (J = 12.7 Hz), where the large coupling is due to the *trans* coupling with a neighbouring *exo* hydrogen. The signal for this *exo* hydrogen (H_{4exo}) is found at δ 3.83 in the ^{1}H NMR spectrum and is coupled to a methyl signal at δ 0.93 (d, J = 6.4 Hz), as well as the H_3 signal at δ 3.65



(Eq. 108)

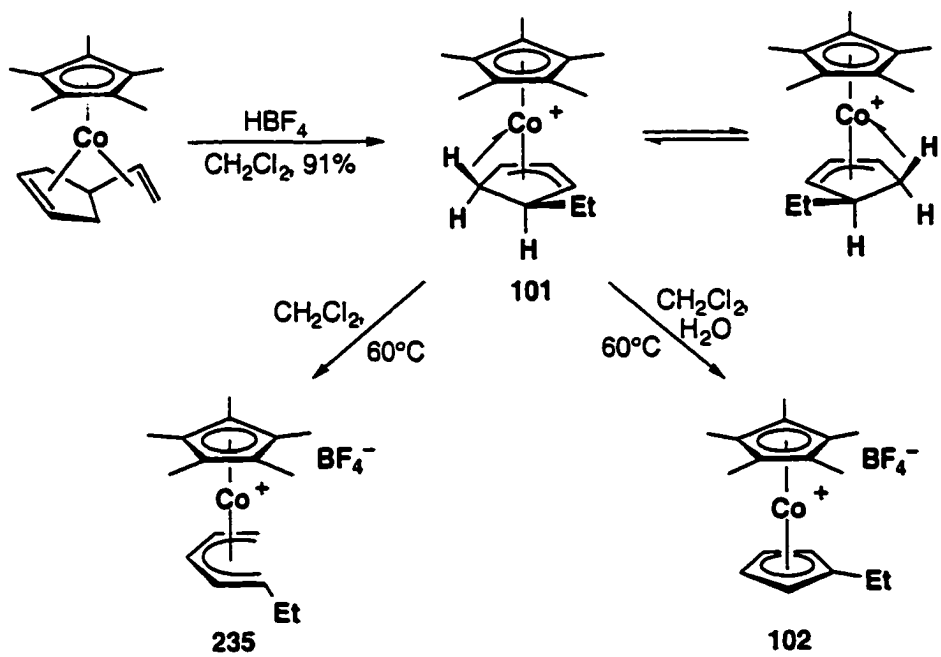
(d, J = 3.2 Hz). Also present in the ^{1}H NMR spectrum is a downfield doublet at δ 5.79 (J = 3.2 Hz, 1H) assigned to the olefinic H_2. Based on these observations, the product is identified as the agostic η^3-1,5-diphenyl-4-methylcyclopentenyl complex **234**, with the methyl substituent originally derived from the crotyl ligand located *endo* to the ruthenium center. The spectroscopic analysis also establishes that the agostic hydrogen is positioned adjacent to a phenyl group. The ^{13}C NMR spectrum exhibits a peak at 41.2 ppm (C_5) with $^1J_{CH}$ = 78 Hz, the low value of the coupling constant being characteristic of an agostic metal-hydrogen interaction.[96a] Analytically pure material is provided in high yield by recrystallization from an anhydrous tetrahydrofuran/diethyl ether mixture, although diffractable crystals could not be obtained by this method.

The structure of this agostic η^3-cyclopentenyl complex is similar to that proposed for the η^3-diphenylcyclopentenyl complex **126** (Chapter 2, Scheme **35**, p. 85), which was observed at low temperature by ^{1}H NMR spectroscopy. One important difference is the thermal stability of the crotyl-derived complex **234** compared to the η^3-diphenylcyclopentenyl complex **126**; the latter compound rapidly loses methane above 0°C, while the isolated η^3-methyl-diphenylcyclopentenyl complex **234** only slowly converts to new products at room temperature. The thermal stability of this agostic complex is primarily due to the *endo* position of the methyl substituent, since the lack of

two available *endo* hydrogen atoms inhibits the ruthenium-mediated conversion of the η^3-cyclopentenyl moiety to an η^5-cyclopentadienyl ligand.

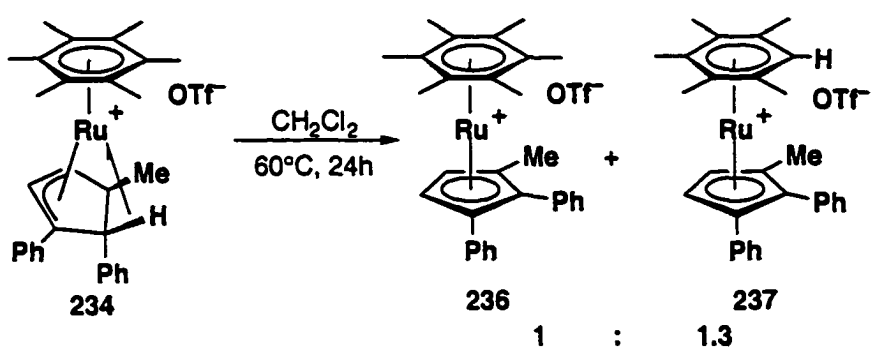
Spencer has reported a similar, isolable, agostic η^3-cyclopentenyl cobalt complex **101**, synthesized from the protonation of the neutral (4-vinylcyclopentene)cobalt(I) complex (Scheme **59**), where the ethyl substituent is also *endo* to the metal center.[84] This agostic cobalt complex, however, undergoes rapid [1,4]-hydride shifts on the NMR time-scale. Interestingly, heating the η^3-cyclopentenyl cobalt complex **101** to 60°C either in the solid state or in an anhydrous dichloromethane solution results in the ring opening of the cyclopentenyl ring, producing the acyclic η^5-4-ethylpentadienyl complex **235**. In contrast, heating the agostic cobalt complex in the presence of trace amounts of water results in the dehydrogenation of the η^3-cyclopentenyl ligand to form the mixed sandwich

Scheme 59



complex **102**, a reaction somewhat analogous to the water induced dealkylation and dehydrogenation reactions reported for the ruthenium-mediated [3 + 2] cycloaddition (Chapter 2).

Heating the trisubstituted ruthenium η^3-cyclopentenyl complex in dichloromethane results in a different reactivity pattern than that observed for the η^3-cyclopentenyl cobalt complex. After 48 hours at 60°C, the η^3-cyclopentenyl ruthenium complex **234** completely disappears and is replaced by an inseparable mixture of hexamethyl- and pentamethylbenzene η^5-trimethylcyclopentadienyl complexes **236** and **237** in a ratio of 1 : 1.3 (Eq **109**). Similar results were obtained upon thermolysis of the η^3-cyclopentenyl complex **234** in acetone solution. The hexamethylbenzene complex **236** was identified by two downfield doublets at δ 5.15 and δ 4.89 (J = 2.5 Hz) in the ^{1}H NMR spectrum, attributed to the two methine hydrogen atoms of the η^5-$C_5H_2MePh_2$ ligand and by the resonance at δ 2.14 (integrating to 18 hydrogens) for the equivalent hexamethylbenzene methyl groups. The pentamethylbenzene analogue **237** was recognized by the characteristic downfield singlet at δ 5.88 (integrating to one hydrogen), corresponding to the pentamethylbenzene methine hydrogen, and by two

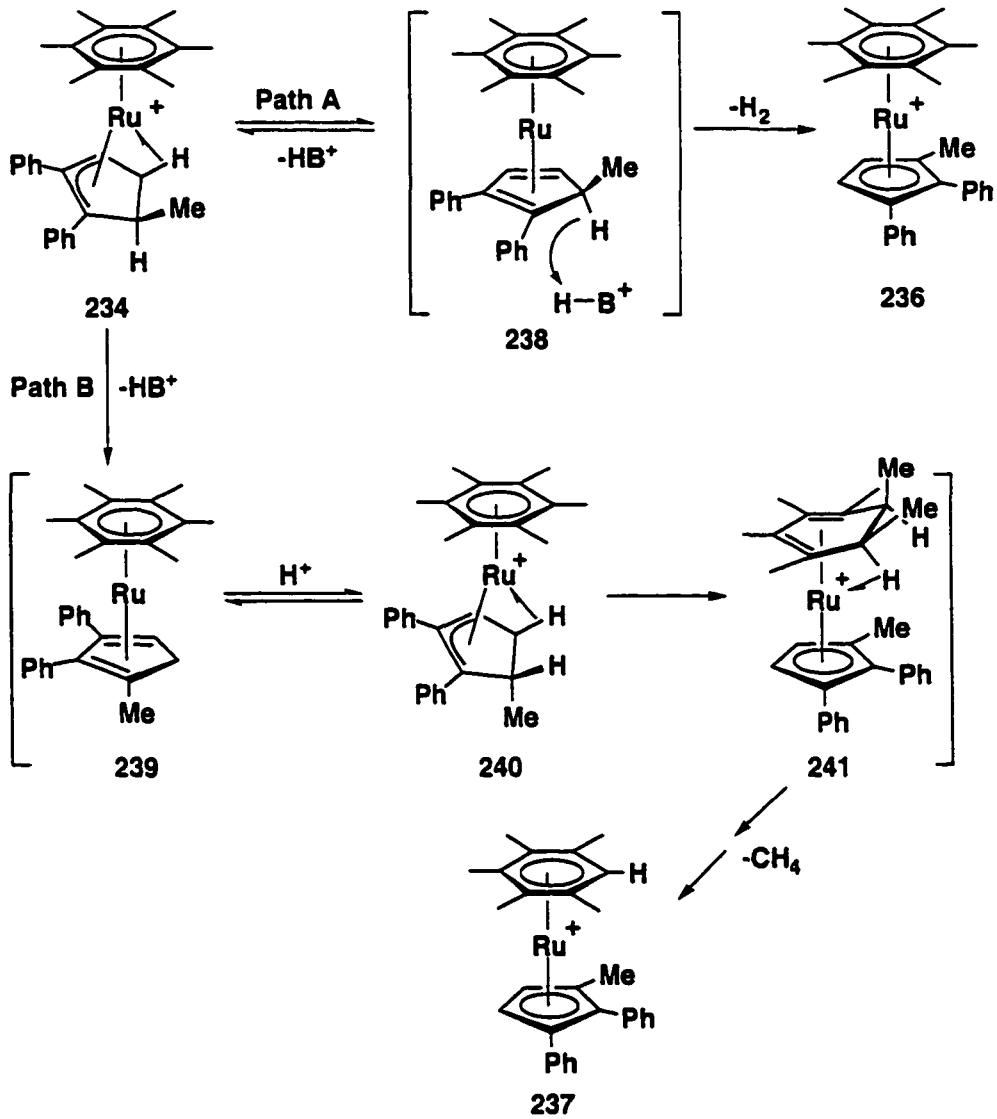


(Eq. 109)

doublets at δ 5.24 and δ 4.98 (J = 2.6 Hz) corresponding to the methine hydrogen atoms of the η^5-cyclopentadienyl ligand. Thus both dehydrogenation and demethylation processes are available to the *endo*-methyl η^3-cyclopentenyl ruthenium complex.

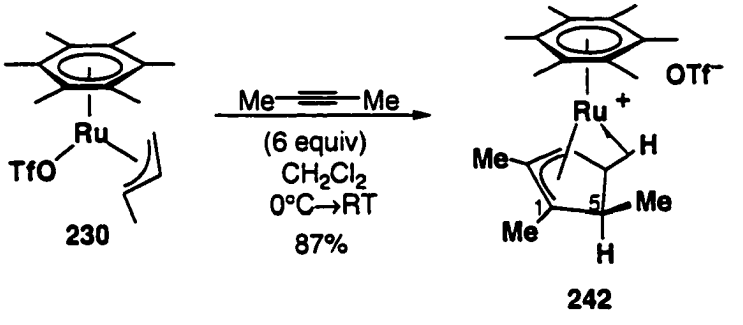
It is clear that the presence of the *endo*-methyl substituent inhibits the "normal" ruthenium-mediated demethylation and dehydrogenation processes, so in order to produce the η^5-cyclopentadienyl ligand, variant mechanisms must be operating (Scheme **60**). We speculate that reversible deprotonation of cationic η^3-cyclopentenyl complex **234** by adventitious base forms the neutral η^4-cyclopentadiene complex **238** by removing the agostic hydrogen while retaining the *endo*-methyl substituent (Path A). Hydride can then be abstracted from the *exo* face of the neutral complex **238** by the previously formed protic acid, releasing hydrogen gas and forming the cationic hexamethylbenzene product **236**. This process is closely related to the mechanism earlier proposed for the dehydrogenation of [(C_5Me_5)Ru(η^4-1,2,3,4,5(*exo*),6(*endo*)-hexamethylcyclohexa-1,3-diene)]$^+$OTf$^-$ (**114**) (Chapter 2), and also to that proposed by Spencer for the water-promoted dehydrogenation of *endo*-ethyl η^3-cyclopentenyl cobalt complex **101** (Scheme **59**). In contrast, the formation of the pentamethylbenzene η^5-trimethylcyclopentadiene product (Path B) probably involves initial loss of the *endo*-methyl stereochemistry. This can occur, we propose by selective deprotonation of the *exo* hydrogen located adjacent to the methyl substituent, yielding the neutral η^4-cyclopentadiene complex **239**. Protonation of this diene complex at the ruthenium metal eventually forms a new cationic agostic η^4-cyclohexadiene complex **241**, via migration of the hydrogen atoms to the arene ring. Subsequent extrusion of methane forms the final pentamethylbenzene product **237**.

Scheme 60



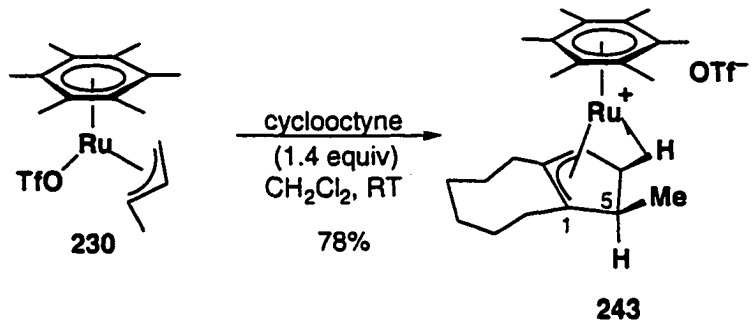
Treatment of crotyl triflate complex **230** with 2-butyne (1-6 equiv) also results in the formation of an unusually stable agostic hydride product, η^3-trimethylcyclopentenyl complex **242** (Eq. **110**). The ^{1}H NMR spectrum of this complex displays an upfield resonance at δ −11.11 (td, J = 12.7, 1.5 Hz) for the agostic hydrogen atom. The large triplet coupling is due to both the geminal hydrogen and to the *trans* relationship to the coupling with a neighbouring *exo* hydrogen. The signal for this adjacent *exo* hydrogen

(H_5) is found at δ 3.34 in the ^{1}H NMR spectrum and is additionally coupled to a methyl resonance at δ 0.98 (d, J = 6.2 Hz). The structure of the agostic η^3-trimethylcyclopentenyl is similar to that earlier proposed for the η^3-dimethylcyclopentenyl complex **123** observed at low temperature (Chapter 2, Schemes **33** and **34**, p. 82), although the crotyl-derived product **242** appears to be static on the NMR time-scale. Heating an acetone or dichloromethane solution of η^3-trimethylcyclopentenyl complex **242** to 60°C for 24 hours results in a the formation of mixture of hexamethyl- and pentamethylbenzene η^5-trimethylcyclopentadienyl products, in a ratio of 1 : 1.4, as previously observed for the diphenylacetylene cycloadduct.



(Eq. 110)

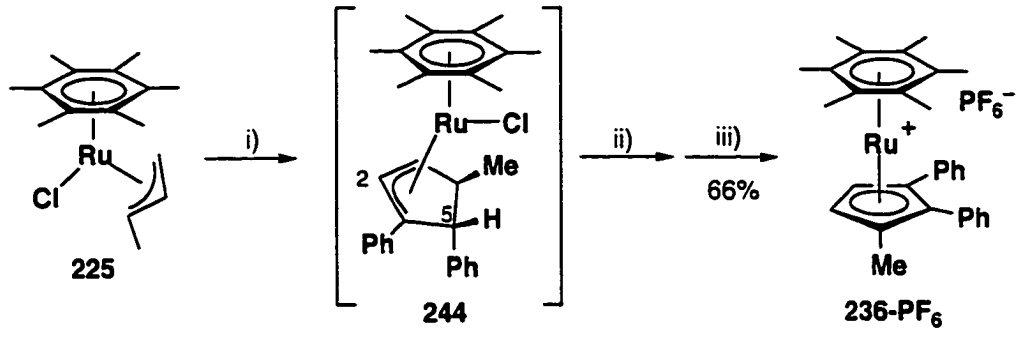
The addition of cyclooctyne (1.4 equiv) to the crotyl triflate complex **230** also results in the formation of a trisubstituted agostic η^3-cyclopentenyl product, complex **243** (Eq. **111**). The ^{1}H NMR spectrum exhibits a characteristic upfield doublet of doublets −11.12 (J = 15.7, 13.1 Hz, 1H) for the agostic hydrogen atom resonance, as well as a downfield doublet at δ 5.41 (J = 3.1 Hz, 1H, H_3) and a complex signal at δ 3.48 (dqd, J = 12.5, 6.2, 2.8 Hz, 1H, H_5). The disposition of the agostic hydrogen is thus similar to that observed for η^3-trimethylcyclopentenyl complex **242**.



(Eq. 111)

The agostic η^3-cyclopentenyl ruthenium complexes can also be obtained from the crotyl chloride complex by *in situ* reaction with silver salts in the presence of the alkyne. This *in situ* ionization proceeds equally well using either silver tetrafluoroborate or silver triflate. However, an attempt to avoid the use of silver reagents by using the ionizing solvent 2,2,2-trifluoroethanol (TFE) leads instead to an intriguing result. When a solution of crotyl chloride complex **225** in TFE is treated with equimolar diphenylacetylene and the reaction analyzed before reaching completion, the ^{1}H NMR spectrum of the crude reaction mixture indicates the formation of two products, one a non-agostic intermediate (Eq. **112**). The intermediate complex is tentatively identified as (C_6Me_6)Ru(η^3-cyclopentenyl) chloride complex **244**. This complex displays in the ^{1}H NMR spectrum a singlet at δ 3.98 (H_5), a narrow doublet at δ 3.85 (J = 2.5 Hz, H_2), a narrow triplet at δ 3.61 (H_3), and a complex signal around δ 2.37 (H_4). The second product is readily identifiable as hexamethylbenzene η^5-diphenylmethylcyclopentadienyl complex **236**-Cl. Dissolving the crude reaction mixture in TFE for another 2 hours at room temperature results in the complete conversion of η^3-cyclopentenyl chloride complex **244** to the hexamethylbenzene η^5-cyclopentadienyl complex **236**-Cl. No trace of the pentamethylbenzene η^5-cyclopentadienyl complex was observed in the ^{1}H NMR

(Eq. 112)

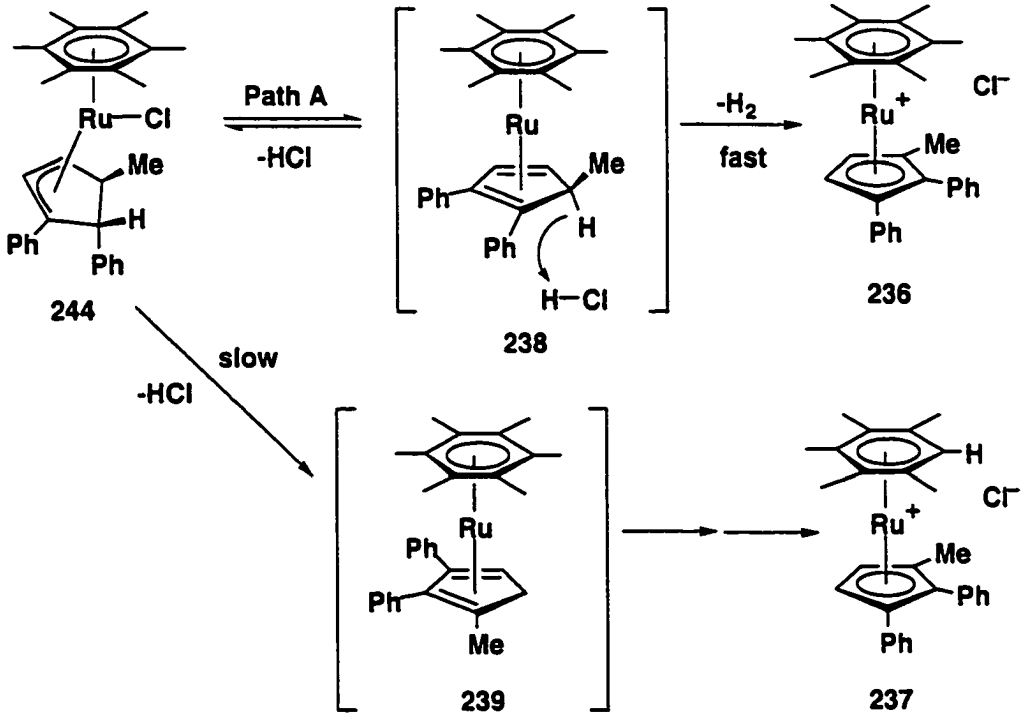


Conditions i) Ph—≡—Ph (1.2 equiv), TFE, RT ii) TFE, RT, 2h iii) H_2O, NH_4PF_6

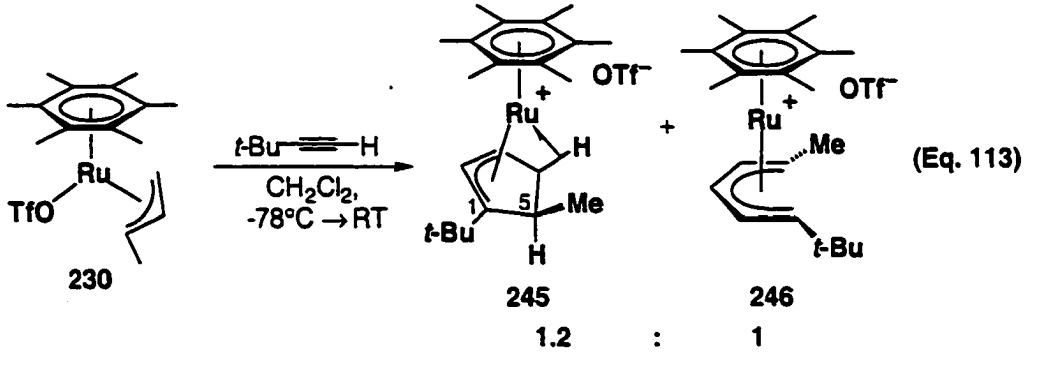
spectrum of the final reaction mixture. The $[(C_6Me_6)Ru(\eta^5\text{-}C_5H_2Me_3)]^+PF_6^-$ complex, was also obtained in good yield from the treatment of allyl chloride complex **225** with 2-butyne in trifluoroethanol. It is clear that the trifluoroethanol solvent significantly alters the kinetic partitioning between the dehydrogenation and demethylation processes, resulting in the reaction exclusively following the dehydrogenation mechanistic pathway (Scheme **61**). This is plausibly due to the higher acidity of the solvent medium (pKa of trifluoroethanol = 14.0[132]), increasing the rate of electrophilic abstraction of the *exo* hydride from complex **238**, relative to the rate of deprotonation from the *exo* face of the η^3-cyclopentenyl ligand.

Treatment of hexamethylbenzene crotyl triflate complex **230** with the unsymmetric alkyne 3,3-dimethyl-1-butyne (4 equiv) at low temperature results in the formation of a mixture of two products after warming to room temperature (Eq. **113**). The major product is tentatively identified as the agostic η^3-cyclopentenyl complex **245**, where the *t*-butyl substituent is adjacent to the *endo* methyl group. This structural assignment is based on ^1H NMR decoupling experiments, which demonstrate that a narrow vicinal coupling exists between the signal at δ 4.90 (d, J = 3.1 Hz, 1H, H_2) and a

Scheme 61

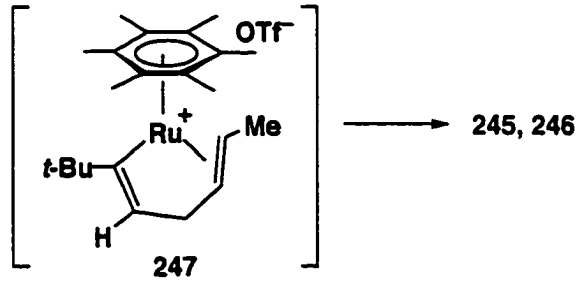


resonance at δ 3.04 (dd, J = 3.1, 1.6 Hz, 1H, H_3), consistent with the two adjacent methine hydrogen atoms of an η^3-cyclopentenyl ligand. The second product is readily identified as *acyclic* η^5-pentadienyl complex **246**; analysis of the vicinal hydrogen coupling constants and chemical shifts of the ^{1}H NMR spectrum indicates that both the *t*-butyl and methyl substituents are located at opposite termini of the pentadienyl ligand



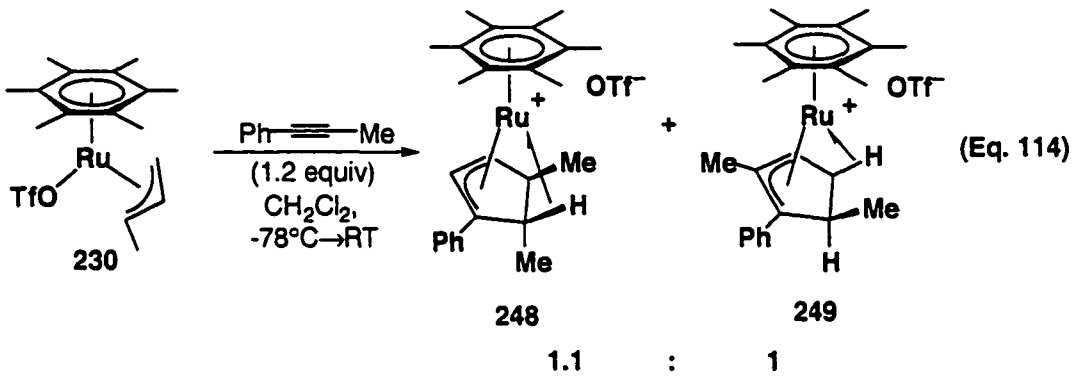
and that both are oriented *syn* to the neighbouring hydrogens. It is plausible that both products are formed from a common vinyl olefin intermediate (Figure **14**), produced from the migratory coupling of the unsubstituted end of the crotyl ligand with the terminal end of the alkyne, placing the bulky *t*-butyl group adjacent to the ruthenium metal center.

Figure 14. Proposed Common Intermediate for Complexes **245** and **246**



The addition of 1-phenyl-1-propyne to a solution of crotyl triflate **230** at low temperature also results in the formation of an inseparable mixture of two products, although in this case both products are agostic η^3-cyclopentenyl complexes (Eq. **114**). Spectroscopic analysis of the crude reaction mixture (^{1}H NMR) indicates that the major product has the agostic hydride located adjacent to an *exo* methyl group; the agostic resonance is found at δ –10.12 (dquin, J = 12.7, 3.8 Hz) and is coupled to the methyl resonance located at δ 1.27 (d, J = 4.0 Hz). Based on these observations, the major product is identified as η^3-1-phenyl-4,5-dimethylcyclopentenyl complex **248**. The minor product exhibits an agostic resonance at δ –10.29 (dd, J = 12.9, 5.0 Hz) and is tentatively identified as η^3-1-phenyl-2,5-dimethylcyclopentenyl complex **249**, a regioisomer of the major product, based on the close spectroscopic analogy to agostic complex **242**. Heating a dichloromethane solution of the crude reaction mixture results in the formation

of two hexamethylbenzene and two pentamethylbenzene η^5-cyclopentadienyl products, which were neither separated nor fully characterized.



While the coupling of η^3-allyl ruthenium complexes with dimethyl acetylenedicarboxylate (DMAD) results in a variety of interesting products, the treatment of η^3-crotyl triflate complex **230** with DMAD unfortunately produces a complex product mixture. Treatment of a trifluoroethanol solution of crotyl chloride complex **225** with either an excess or stoichiometric amount of DMAD similarly results in the formation of intractable product mixtures.

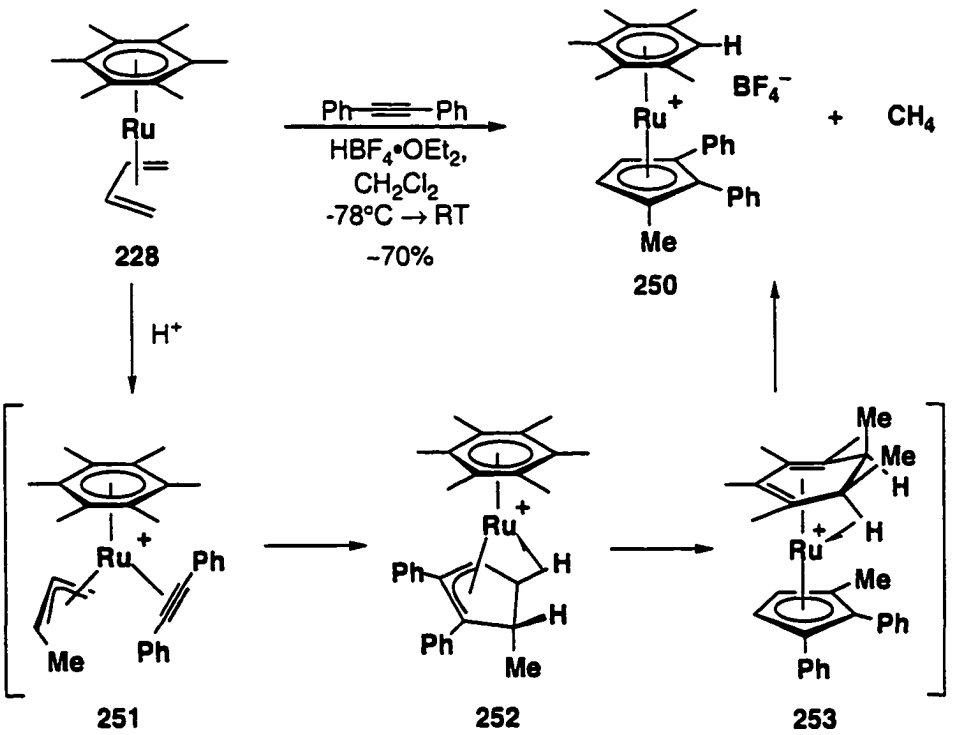
3.3 The Origin of the endo-Methyl Stereochemistry

The ruthenium-mediated coupling of the η^3-crotyl *syn,exo* ligand with alkynes thus proceeds to either five-, six-, or seven-membered rings, each bearing a methyl substituent exclusively located *endo* to the metal center. In the case of the five-membered ring products, the stereochemistry of this methyl group is subsequently lost during thermolysis. The *endo*-selectivity is directly linked to the unusual stability of the agostic η^3-cyclopentenyl ruthenium complexes by inhibiting the normal dehydrogenation

and demethylation processes. The same *endo* stereoselectivity was observed by Dzwiniel and Etkin in the cobalt-mediated reactions of terminally substituted allyls to form η^5-cycloheptadienyl complexes, regardless of whether the product was obtained from the [3 + 2 + 2] or the [5 + 2] cycloaddition pathways.[41-44] However, in contrast to the stable ruthenium η^3-cyclopentenyl complexes, the cobalt template appears to more readily eliminate dihydrogen during [3 + 2] cycloaddition to form the η^5-cyclopentadienyl ligand, despite the presence of the *endo*-methyl group.[36,43]

We propose that the *endo*-methyl stereochemistry of the crotyl/alkyne coupling products is a consequence of the *exo,syn* geometry of the crotyl ligand; migration of the *syn* crotyl ligand to the alkyne is expected to place the methyl substituent *endo* to the metal center. In the case of the cobalt template, protonation of a butadiene ligand proceeds to form the thermodynamically most stable *exo, syn* η^3-crotyl isomer very rapidly, with no opportunity to isolate or trap a kinetically formed *anti* isomer. However, in the ruthenium template, the *anti* crotyl ligand is reasonably stable to isomerization, as evidenced in the preparation of the η^3-crotyl chloride complexes **225** and **226** using tin reagents (*vide supra*). In order to confirm the origin of the *endo* selectivity, the neutral ruthenium η^4-butadiene complex **228** (isolated as a minor byproduct in the large scale production of crotyl chloride **225**) was treated with strong acid at low temperature in the presence of diphenylacetylene (Scheme **62**). After warming to room temperature, the exclusive product isolated from the reaction mixture is the pentamethylbenzene complex $[(\eta^6\text{-}C_6Me_5)Ru(\eta^5\text{-}C_5Ph_2Me)]^+BF_4^-$ (**250**) rather than an agostic complex analogous to that obtained from the *syn*-crotyl precursor under identical reaction conditions. Presumably, the reaction proceeds by initial formation of the unsaturated

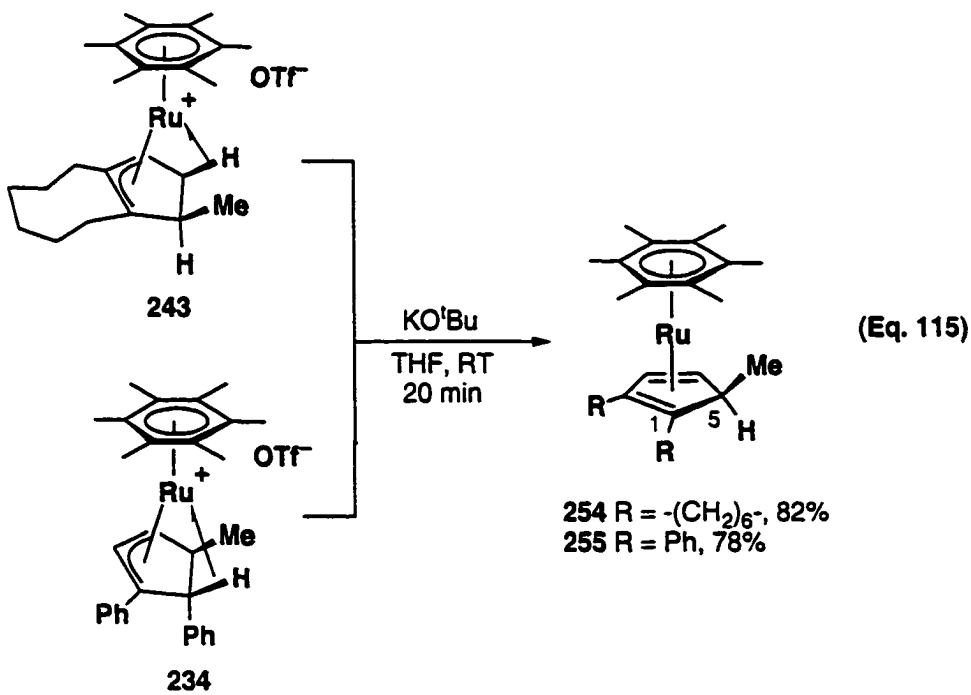
Scheme 62



ruthenium η^3-*exo,anti*-crotyl complex, which is then trapped by an equivalent of diphenylacetylene to form the alkyne intermediate **251**. Insertion of the alkyne followed by migratory cyclization to a five-membered ring eventually yields the agostic η^3-cyclopentenyl ruthenium complex **252**, but with the methyl substituent located *exo* to the ruthenium center, this complex rapidly transfers the two *endo* hydrogen atoms to the hexamethylbenzene ligand to form the η^4-hexamethylcyclohexadiene intermediate **253**. Subsequent loss of methane results in the exclusive formation of the observed pentamethylbenzene η^5-cyclopentadienyl product at or below room temperature, consistent with the facile demethylation observed during [3 + 2] cycloadditions using the parent allyl complex (Chapter 2).

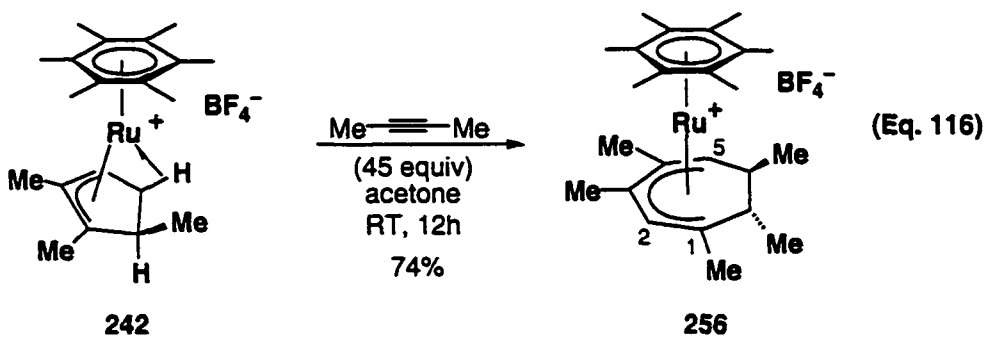
3.4 Reactivity of Cationic (C_6Me_6)Ru(η^3-cyclopentenyl) Complexes

The unusual stability of the agostic ruthenium η^3-cyclopentenyl complexes raises a unique opportunity to explore the reactivity of these compounds. Treatment of the cyclooctyne-derived η^3-cyclopentenyl complex **243** with potassium *tert*-butoxide in tetrahydrofuran leads to the formation of the neutral η^4-cyclopentadiene complex **254** in high yield (Eq. **115**). The trisubstituted ruthenium η^4-cyclopentadiene complex was isolated as a pentane soluble, pale yellow solid that decomposes rapidly on exposure to either water or oxygen. In the ^{1}H NMR spectrum, this complex exhibits a quartet at δ 3.77 (H_5), as well as a methyl doublet at δ 1.30, indicating that the *endo* methyl substituent is unaffected by the deprotonation reaction. The cyclopentadienyl methine hydrogen atoms are located as doublets at δ 4.19 (H_3) and 1.93 (H_4), mutually coupled by a small vicinal coupling of 2.7 Hz. A similar complex, **255**, was obtained by adding potassium *tert*-butoxide to η^3-diphenylmethylcyclopentenyl complex **234**.



(Eq. 115)

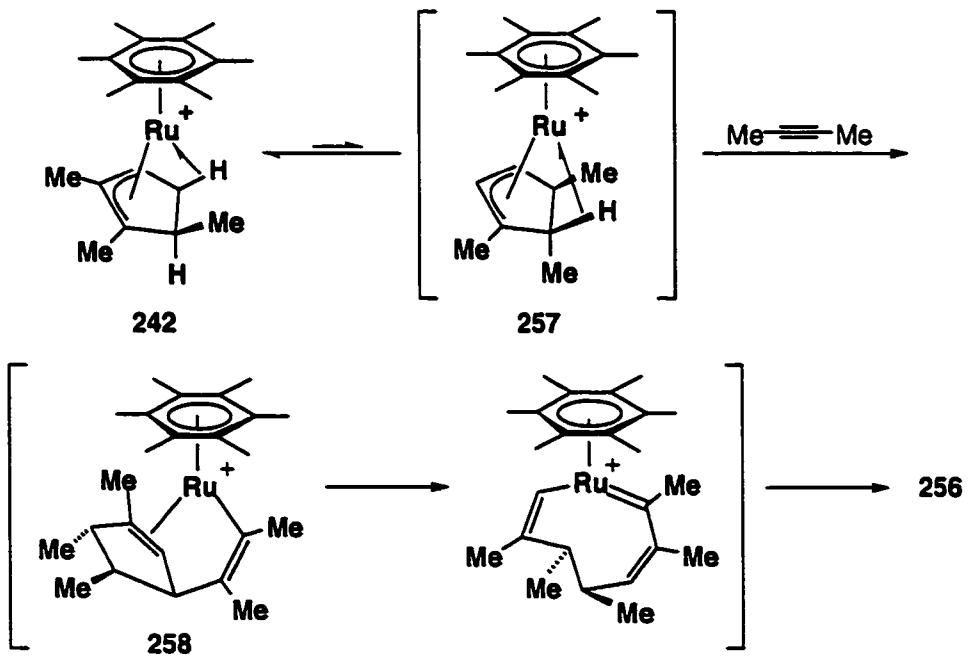
Since the η^3-cyclopentenyl ligand formed from the original crotyl/alkyne coupling is a new, substituted η^3-allyl ligand, these complexes could, in principle, react further with additional alkyne. In particular, the agostic η^3-cyclopentenyl complexes are closely related to key intermediates postulated for the mechanism of the cobalt-mediated [5 + 2] ring-expansion (Chapter 1, Scheme **9** and **10**, p. 30). It is perhaps not surprising that treatment of η^3-trimethylcyclopentenyl complex **242** at room temperature with a large excess of 2-butyne leads to slow conversion to give the ring-expanded η^5-pentamethylcycloheptadienyl complex **256** (Eq. **116**). Analysis by both ^1H and ^{13}C NMR spectroscopy reveals that the cycloheptadienyl ligand has the identical substitution pattern to the one established for η^5-pentamethylcycloheptadienyl cobalt complex **66**, derived from the "abnormal" reaction of $(C_5Me_5)Co(\eta^3\text{-crotyl})(OTf)$ **54** and 2-butyne (Eq. **29**, p. 28).[43,44] Like the cobalt complex, the ruthenium η^5-pentamethylcyclo-heptadienyl product exhibits a downfield singlet attributed to H_2 at δ 4.76, and a characteristic upfield signal at δ 0.47 (dq, J = 13.5, 6.8 Hz) corresponding to H_{7endo}. This reaction is the first conclusive demonstration that the [5 + 2] ring expansion involves the intermediate formation of an agostic η^3-cyclopentenyl complex, and constitutes the first such carbon-carbon bond cleavage mediated by a metal other than cobalt.



242 **256** (Eq. 116)

The proposed mechanism for this ring expansion is outlined in Scheme **63**. One interesting aspect of this reaction is that in order to obtain the isolated product, an undetected equilibrium must exist between the η^3-cyclopentenyl complex **242** and a second, rearranged η^3-cyclopentenyl complex **257**. Coordination of 2-butyne to transient **257** is followed by coupling of the alkyne at the less substituted terminus of this η^3-allyl ligand, providing vinylcyclopentene intermediate **258**. This is in direct contrast to the reaction of the unsubstituted η^3-allyl ruthenium chloride complex **77** with excess 2-butyne, where 2-butyne inserts into the more substituted end of the intermediate η^3-cyclopentenyl ligand (Chapter 3, Scheme **41**, p. 112). The vinylcyclopentene complex **258** then fragments to the proposed vinyl alkylidene intermediate and recloses to a seven-membered ring, as postulated for the cobalt chemistry. Although an *endo* hydrogen atom

Scheme 63



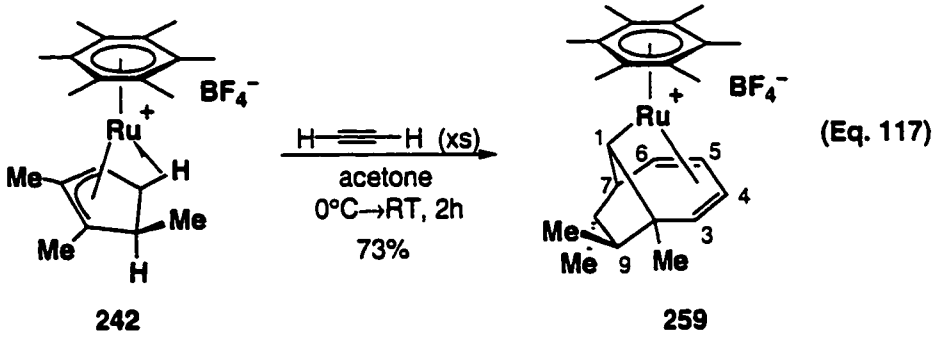
is available in complex **258** for allylic C-H activation, it is possible that the presence of the flanking *endo* methyl groups inhibits this ruthenium-mediated rearrangement by altering the conformation of the ring, preventing the formation of a η^3,η^2-5-vinylcyclopentenyl product (*vide infra*).

To maximize the production of η^5-pentamethylcycloheptadienyl complex **256**, a very high concentration of 2-butyne is required. Under these conditions the formation of a significant amount of free hexamethylbenzene is observed, presumably produced from the cyclotrimerization of 2-butyne, catalyzed by a trace amount of a ruthenium decomposition product. At lower 2-butyne concentrations (in either dichloromethane or acetone), significant amounts of the pentamethylbenzene η^5-cyclopentadienyl byproduct are formed. In particular, the presence of triflate as a counterion results in the recovery of a high proportion of the pentamethylbenzene η^5-cyclopentadienyl complex **237**, a phenomenon that can be avoided by using the tetrafluoroborate counterion. This curious effect was also noted for the cobalt-mediated [5 + 2] ring expansion reactions,[43] although the reason for it is not well understood. The addition a large excess of 2-butyne to a trifluoroethanol solution of crotyl chloride **225** also provides a product mixture consisting of the η^5-cycloheptadienyl complex **256** and the hexamethylbenzene η^5-trimethyl-cyclopentadienyl complex in a ratio of 1 : 2, respectively.

The fact that relatively forcing conditions are necessary to prepare the η^5-cycloheptadienyl product in high yield suggests that the ruthenium-mediated [5 + 2] ring-expansion process is not as facile as the corresponding cobalt reaction. This may be due to the less electrophilic nature of the ruthenium template compared to cobalt, making the

carbon-carbon bond cleavage more difficult. No other reactions of **242** with alkynes result in the formation of ring-expansion η^5-cycloheptadienyl products.

Acetylene reacts with the agostic η^3-trimethylcyclopentenyl complex **242** in a different fashion than that observed with 2-butyne (Eq. **117**). The product surprisingly incorporates two equivalents of alkyne, proceeding via a "normal" [3 + 2 + 2] allyl/alkyne coupling reaction, resulting in the formation of the η^1,η^4-bicyclo-[4.2.1]nonadienyl complex **259**. The ^{13}C NMR spectrum of this complex exhibits the upfield signal at –20.1 ppm ($^1J_{CH}$ = 150 Hz), characteristic of an η^1,η^4-coordinated seven-membered ring. The disposition and stereochemistry of the three methyl substituents were confirmed by extensive spectroscopic analysis including GCOSY, HMQC and HMBC experiments.

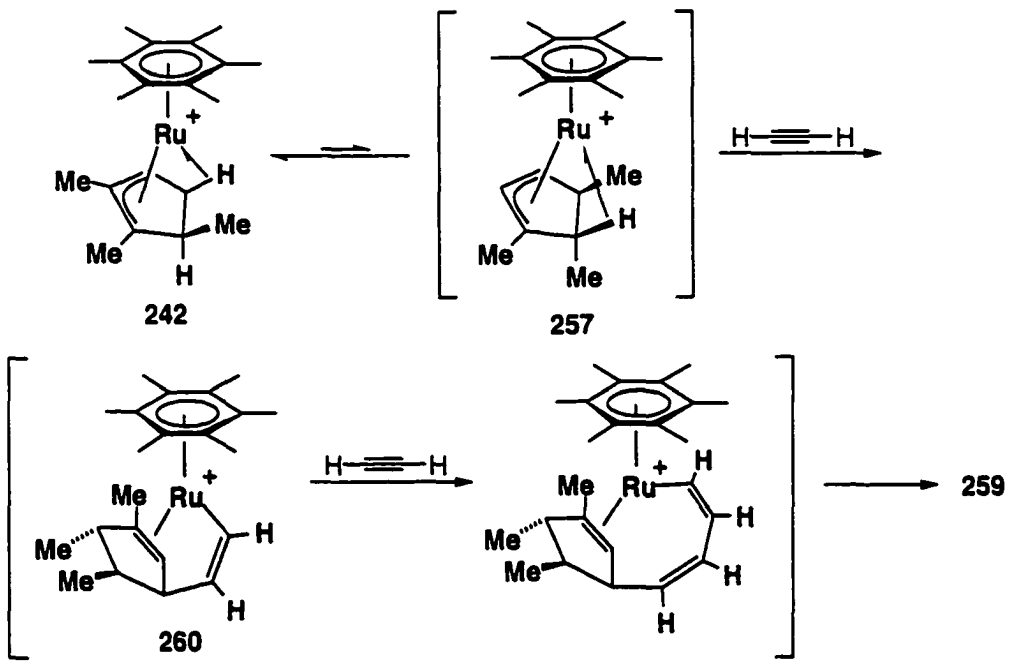


242 **259** **(Eq. 117)**

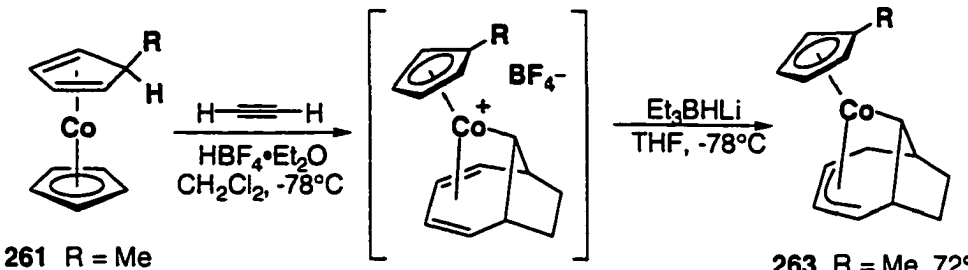
As with the previously described 2-butyne insertion, the first step of the proposed mechanism involves an equilibration to the more reactive agostic η^3-cyclopentenyl complex **257** before the insertion of the first equivalent of acetylene (Scheme **64**). The alkyne inserts into the allylic ligand to form vinylcyclopentene **260** and is rapidly followed by insertion of a second equivalent of acetylene, rather than undergoing C-C bond activation. Although Scheme **64** illustrates that the alkyne insertion occurs at the

less substituted terminus of the η^3-cyclopentenyl ligand, it is equally possible that the insertion occurs at the more substituted site. The extended vinylcyclopentene intermediate then undergoes migratory closure to form a seven-membered ring, resulting in the unusual bicyclic structure. The ability of acetylene to insert twice under these reaction conditions must be at least partially due to its small size and high reactivity compared to the sterically larger 2-butyne.

Scheme 64



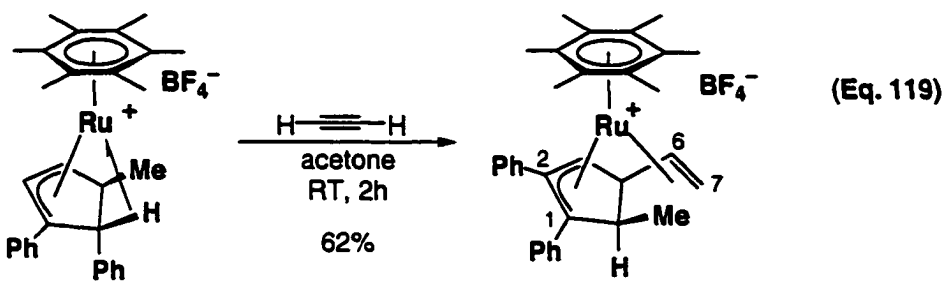
Dzwiniel later obtained similar compounds from the reaction of several cobalt cyclopentadiene complexes with tetrafluoroboric acid and excess acetylene (Eq. **118**). However, unlike the ruthenium complex **259**, the cobalt complexes are not stable enough to isolate directly; instead, the crude products are treated with Et_3BHLi to provide the stable, although air-sensitive, cycloadducts **263** and **264**.[43]



261 R = Me
262 R = *t*-Bu

263 R = Me, 72%
264 R = *t*-Bu, 81%

Surprisingly, when the diphenylacetylene-derived η^3-cyclopentenyl complex **234** is treated with excess acetylene, the only product detected is the η^3,η^2-vinylcyclopentenyl complex **265** (Eq. **119**), which is isolated in 62% yield after recrystallization. Only a single equivalent of alkyne undergoes insertion, unambiguously at the less hindered end of the η^3-allyl ligand, prior to allylic C-H activation. Reductive elimination then results in the formation of the observed terminal vinyl group. This process is identical to that earlier proposed for the formation of the 5-vinylcyclopentenyl complex **152** from the reaction of η^3-allyl triflate **78** and excess 2-butyne (Chapter 3, Scheme **41**, p. 112). Why the vinylcyclopentene intermediate in this case undergoes activation of the allylic hydrogen faster than the insertion of a second alkyne is not known, but we speculate that the sterically bulky phenyl groups may alter the cyclopentenyl conformation enough to promote the allylic C-H activation.



234 **265**

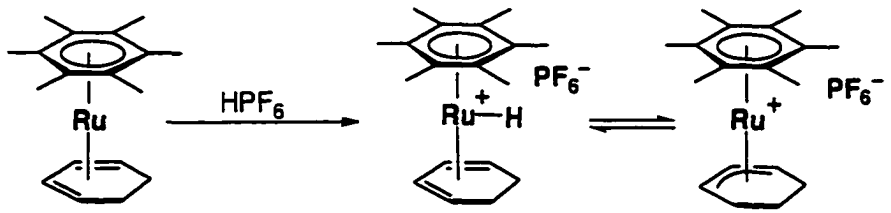
Treatment of the cyclooctyl-substituted η^3-cyclopentenyl complex **243** with excess acetylene unfortunately results in a complex mixture of products. Several of the major products, however, could be identified by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. Characteristic ^{1}H NMR signals for the hexamethylbenzene η^5-cyclopentadienyl complex are evident, as are resonances attributed to a η^1,η^4-bicyclo-[4.2.1]nonadienyl complex. A third product has also been tentatively identified as an η^3,η^2-vinylcyclopentenyl product analogous to complex **265**. Several of the components of this product mixture proved to be thermally unstable and no further attempts to isolate or purify the reaction products were made.

4. Reactions of Other Substituted Allyl Ruthenium Cations with Alkynes

4.1 Reactions of (C_6Me_6)Ru(η^3-cyclohexenyl) Cation

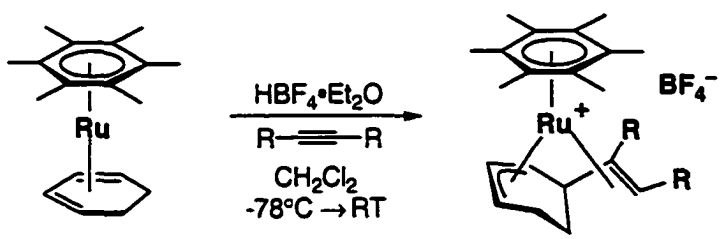
To further our investigation of allyl/alkyne coupling, the reactions of other, easily accessible, substituted allyl complexes were probed. In particular, Bennett[52] earlier described the behaviour of the ruthenium cation obtained from the addition of hexafluorophosphoric acid to (C_6Me_6)Ru(η^4-cyclohexadiene) (**227**). He reported that in the solid state the product cation appeared to be an unsaturated sixteen electron η^3-cyclohexenyl species (**266**), while in solution the *endo* hydrogen atoms migrate rapidly between carbon and ruthenium on the NMR time-scale (Eq. **120**). However, addition of carbon monoxide rapidly leads to the formation of a cationic CO complex with a static

η^3-allyl ligand, and we were therefore confident that the addition of an alkyne would trap the η^3-cyclohexenyl ruthenium complex.



227 266 (Eq. 120)

Thus, a single product is obtained from the reaction of $(C_6Me_6)Ru(\eta^4$-cyclohexadiene),[46b] tetrafluoroboric acid and 2-butyne in dichloromethane (Eq. **121**). The η^3,η^2-vinylcyclopentenyl structure assigned to the fully characterized product **267** is indicated by the appearance of a quartet at δ 5.23 (J = 6.5 Hz, 1H) and a corresponding methyl doublet at δ 2.06 (J = 6.3 Hz, 3H) in the ^{1}H NMR spectrum, consistent with the presence of a dimethylvinyl substituent.[43] A related product, **268**, is isolated in 70% yield from the reaction of $(C_6Me_6)Ru(\eta^4$-cyclohexadiene), tetrafluoroboric acid and acetylene. It appears, unfortunately, that metal-mediated allylic C-H activation is the kinetically preferred pathway for the coupling of alkynes with the η^3-cyclohexenyl ligand.

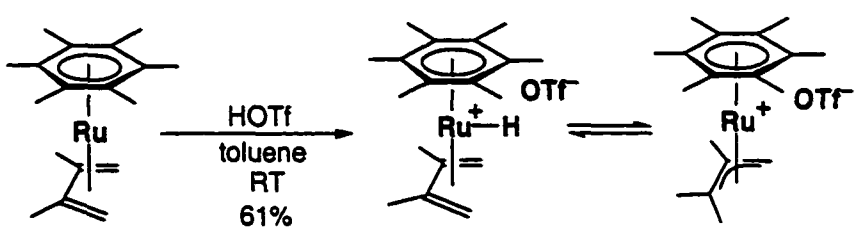


227 (Eq. 121)

267 R = Me, 60%
268 R = H, 70%

4.2 Reactions of $(C_6Me_6)Ru(\eta^3$-1,1,2-trimethylallyl) Cation

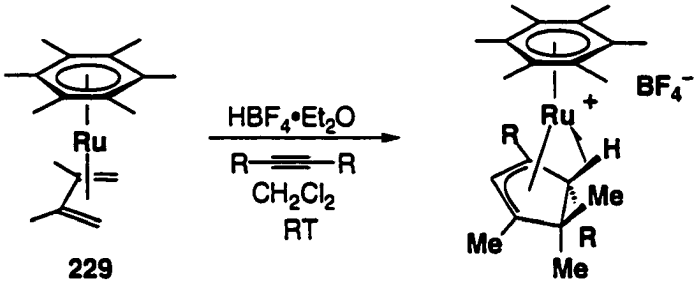
The protonation of $(C_6Me_6)Ru(\eta^4$-2,3-dimethylbutadiene) (**229**) with triflic acid results in the formation of a single cationic species that exhibits dynamic behaviour in solution (Eq. **122**). Consistent with a fluxional structure, complex **269** shows time-averaged symmetry in both the ^1H NMR and ^{13}C NMR spectra at room temperature. Only singlet resonances are observed in the ^1H NMR spectrum at room temperature, at δ 2.66 (2H), δ 2.32 (18H), δ 2.00 (6H) and δ –1.60 (3H), while in the ^{13}C NMR spectrum only three carbon signals are observed for the η^3-allyl ligand at 91.2, 25.4 and 17.7 ppm. No further characterization of this cationic product was attempted. Based on the similarity of the spectroscopic evidence to that of the fluxional η^3-cyclohexenyl complex **266** described by Bennett, complex **269** is presumably interconverting between the diene hydride and the unsaturated ruthenium η^3-allyl complex, although rapidly interconverting agostic η^3-allyl complexes are also possible. Low temperature NMR spectroscopy will be required to distinguish between these possible ground-state structures.



229 **269** (Eq. 122)

However, when the fluxional cationic complex **269**, prepared *in situ* from the addition of tetrafluoroboric acid to a dichloromethane solution of $(C_6Me_6)Ru(\eta^4$-2,3-dimethylbutadiene), was treated with 2-butyne, a single agostic product **270** (Eq. **123**) is

obtained within two hours at room temperature. The ^{1}H NMR spectrum exhibits the agostic hydrogen resonance at δ −11.22 (q, J = 3.9 Hz, 1H), similar to the agostic η^3-cyclopentenyl complex **134** derived from the crotyl complex. The correlated carbon signal at 45.4 ppm in the ^{13}C NMR spectrum shows an unusually small carbon-hydrogen coupling of 65 Hz, characteristic of an agostic hydride interaction.[96a] The addition of diphenylacetylene to the η^3-1,1,3-trimethylallyl cation, also provides an η^3-cyclopentenyl complex **271**, although in this case the reaction requires three days at room temperature to go to completion. Prolonged heating of either of these cyclopentenyl products in dichloromethane results only in decomposition, even in the presence of excess alkyne.



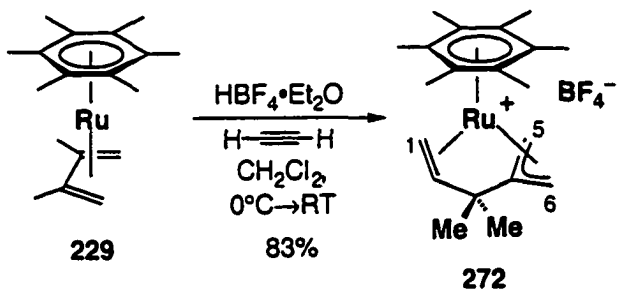
229

270 R = Me, 63%
271 R = Ph, 75%

(Eq. 123)

The addition of excess acetylene to a dichloromethane solution of cationic allyl complex **269**, generated *in situ*, surprisingly does not result in the formation either a five- or a seven-membered ring. Instead, the product arises from incorporation of a single equivalent of alkyne, providing the unusual acyclic $\eta^3;\eta^2$ allyl olefin complex **272** exclusively in high yield (Eq. **124**). The ^{1}H NMR spectrum displays only two methyl singlets besides the C_6Me_6 resonance, as well as exhibiting two isolated spin systems (Table **8**). The ^{1}H NMR spectroscopic data indicates that the η^3-allyl ligand is unsymmetrical and highly distorted. HMBC spectroscopic experiments also reveal long-

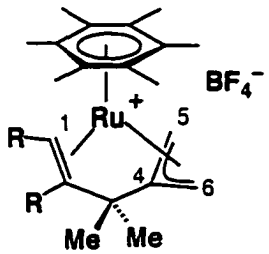
range correlations between the quaternary carbon located at 30.9 ppm (assigned to C_3) and proton signals at δ 4.04 (H_{6syn}), 2.46 (H_{1anti}), 1.49 (H_{6anti}), δ 2.34 (H_2) and δ 0.72 (H_{5syn}), among others. A solid-state molecular structure was obtained for complex **272** to confirm the unusual η^3,η^2 hapticity pattern; salient features of the structure determination are presented in Figure **15**.



229 **272** **(Eq. 124)**

The mechanism proposed for the formation of complex **272** is outlined in Scheme **65**. Insertion of acetylene unambigously occurs at the doubly substituted end of the η^3-allyl ligand, resulting in the formation of vinyl olefin **274**. Similar to the mechanism of acyclic η^5-pentadienyl formation (*vide supra*), this step is followed by a metal-mediated allylic C-H activation, although of the adjacent methyl group. This results in the formation of the unusual *endo* 2-substituted η^3-allyl ligand of intermediate **275**. Reductive coupling of the ruthenium hydride and vinyl group subsequently provides the final product. Why the allylic C-H activation of the methyl group is preferred over cyclization to a five-membered ring is difficult to address. One possibility is that the alkyne substituents of 2-butyne or diphenylacetylene interact with the geminal dimethyl pair to cause a change in conformation that inhibits the C-H activation. Alternatively, the agostic η^3-cyclopentenyl products may arise from insertion of the more bulky

Table 8. Comparative ^{1}H and ^{13}C NMR Spectroscopic Data for η^{4}-2,3-Dimethylbutadiene Derived Acyclic Products[a]



272 R = H
276 R = CO_2Me

^{1}H NMR	**272**	**276**		^{13}C NMR	**272**	**276**
H_{1syn} $J_{1syn\text{-}1anti}$ $J_{1syn\text{-}2}$	1.83 (dd) 1.5 Hz 7.3 Hz	2.79 (s)		C_1	51.5	43.2
H_{1anti} $J_{1anti\text{-}2}$	2.46 (dd) 11.5 Hz	b		C_2	50.4	94.0
H_2	2.34 (dd)	b		C_3	30.9	34.3
H_{5syn} $J_{5syn\text{-}5anti}$ $J_{5syn\text{-}6syn}$	2.28 (dd) 1.9 Hz 3.9 Hz	2.63 (dd) 2.0 Hz 3.6 Hz		C_4	92.1	101.5
H_{5anti}	0.72 (d)	1.36 (d)		C_5	47.5	53.9
H_{6syn}	4.04 (d)	4.56 (d)		C_6	59.6	64.0
H_{6anti}	1.49 (s)[c]	1.94 (s)				

[a] Spectra were taken in $CDCl_3$ at room temperature. [b] Not applicable due to non-hydrogen substituent. [c] GCOSY indicates long-range H-H coupling to H_{5anti}.

Figure 15. ORTEP[113] Plot of Complex **272** from University of Alberta

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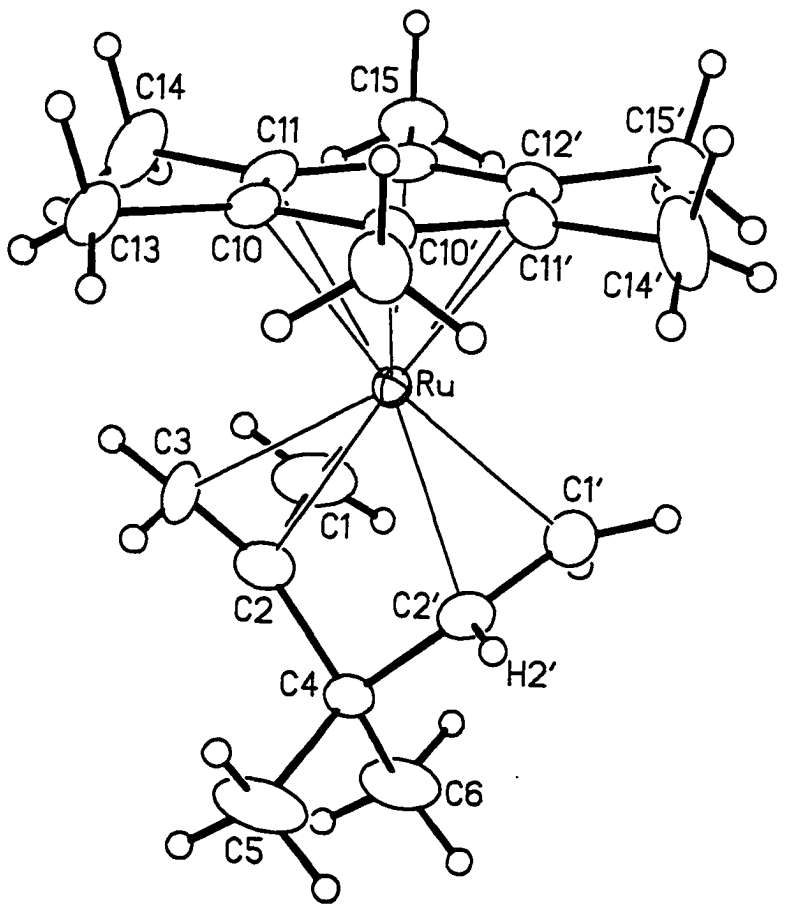
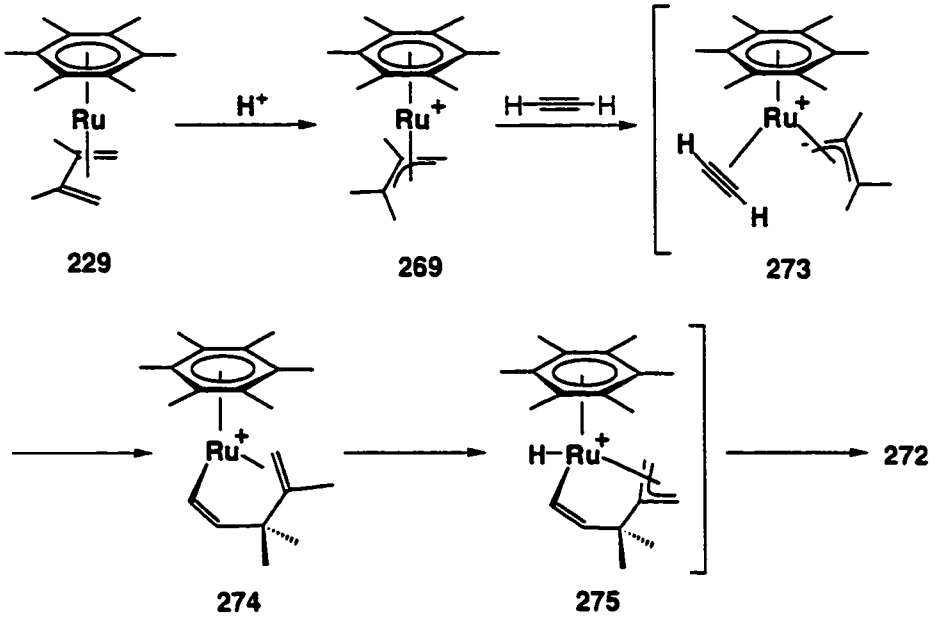


Final Residuals: $R_1 = 0.0511$; $wR_2 = 0.1533$. Data obtained at -80°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.
Selected Bond Distances (Å): Ru-C1, 2.205(7); Ru-C2, 2.203(6); Ru-C3, 2.175(13); Ru-C10, 2.283(5); Ru-C11, 2.248(5); Ru-C12, 2.263(5); C1-C2, 1.392(10); C2-C3, 1.187(17); C2-C4, 1.501(7); C4-C5, 1.528(11); C4-C6, 1.513(11).
Selected Bond Angles (deg) C1-C2-C3, 105.4(15); C1-C2-C4, 121.3(8); C3-C2-C4, 128.5(16); C2-C4-C2, 97.2(6); C2-C4-C5, 112.8(5); C2-C4-C6, 114.4(5); C5-C4-C6, 105.5(7).

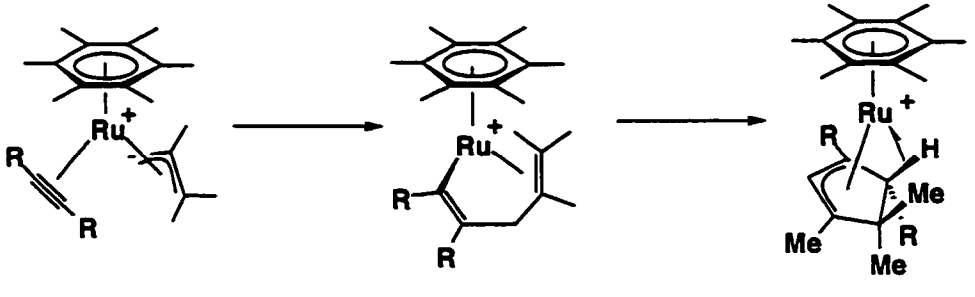
Scheme 65



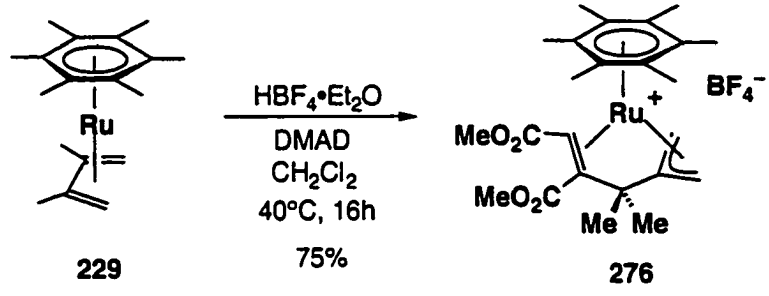
disubstituted alkynes into the sterically *less* substituted side of the allyl ligand, resulting in a different vinyl olefin intermediate that subsequently closes to a five-membered ring (Scheme **66**).

An analogous acyclic product is obtained upon treatment of the unsaturated η^3-1,1,2-trimethylallyl complex with excess DMAD, although this reaction proceeds much more slowly than the acetylene reaction (Eq. **125**). The product, complex **276**, is isolated

Scheme 66



in 75% yield as an orange powder after recrystallization from acetone/diethyl ether. Analysis of complex **276** by ^{1}H and ^{13}C NMR indicates a strong spectroscopic similarity to complex **275**; pertinent data is provided in Table **8**.



229 **276** (Eq. 125)

5. Conclusion

The presence of one or more substituents on the η^3-allyl ligand clearly has a major effect on ruthenium-mediated allyl/alkyne coupling reactions. Only the addition of acetylene follows the "normal" [3 + 2 + 2] pathway upon reaction with the η^3-crotyl complex. While the unsubstituted η^3-allyl triflate **78** complex yields primarily the seven-membered ring product **156** after treatment with excess acetylene (Eq. **74**, p. 114), the crotyl triflate complex **230** provides a mixture of the six- and seven-membered ring adducts in a ratio of 1 : 3, respectively. This comparison demonstrates that the presence of the methyl substituent adversely affects the selectivity of the product partitioning. The reactions with all other alkynes result in closure to a five-membered ring prior to the introduction of a second equivalent of alkyne. More highly substituted allyl ligands generally react to yield monoadducts upon treatment with excess alkyne, with a few notable exceptions.

The regioselectivity of the initial alkyne insertion into the substituted allyl ligand is a more complex issue. Although the majority of the isolated products do not provide evidence for the insertion regiochemistry, the reaction products that do suggest that the insertion selectivity is controlled by both electronic and steric components. With alkynes presenting a minimal steric profile, such as acetylene, alkyne coupling is generally observed at the more hindered terminus of the allyl ligand. Steric factors appear to dominate in reactions with larger alkynes and in reactions involving the more highly congested η^3-cyclopentenyl complexes.

The demonstration that the unusual [5 + 2] ring expansion process can be mediated by a η^6-arene ruthenium template suggests an interesting area for further exploration. While only one example of the [5 + 2] cycloaddition was found during the course of this investigation, this may be in part be due to the steric limits imposed by the bulky C_6Me_6 ancillary ligand and to the less electrophilic character of the second row, low valent metal. A smaller, less electron-rich, ancillary ligand may thus result in a more electrophilic and less congested template that allows for a broader range of alkynes to participate in this potentially valuable process.

Chapter 5. Allyl/Alkyne Coupling Reactions Mediated by the Neutral (η^5-C_5Me_5)Ru(II) Template

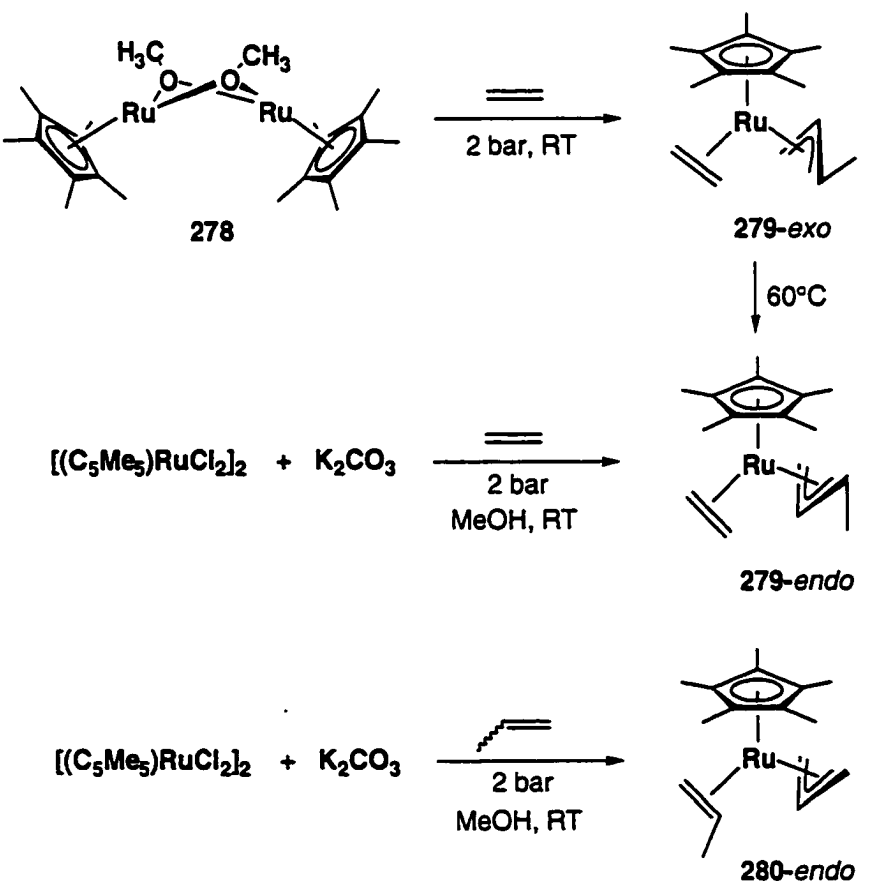
Although the cationic η^6-arene ruthenium template provides a wide variety of reaction patterns, we wished to evaluate the effect of changing the formal electronic charge on the metal from cationic to neutral, without substantially altering either the steric profile at the metal or the molecular orbitals involved. While this change is not easily probed in the iridium and cobalt systems, in ruthenium this can be readily accomplished by altering the ancillary ligand from a neutral η^6-arene to an anionic η^5-cyclopentadienyl ligand. The (C_5Me_5)Ru(II) template was chosen for study as being more likely to result in the formation of seven-membered rings from double alkyne insertion, as well as generally being more stable as a result of the steric and electron-donating effects of the five methyl groups.

1. The Preparation and Reactivity of (C_5Me_5)Ru(η^3-allyl)(η^2-alkyne) Complexes

Several complexes of the general form (C_5R_5)Ru(η^3-allyl)L have been reported,[133] although no general synthetic routes to such complexes have been developed. Moreover, very few methods are known for the preparation of complexes (C_5Me_5)Ru(η^3-allyl)L where L is neither CO or phosphine, which were desired for our studies into Ru(II)-

mediated allyl/alkyne coupling reactions. Koelle has shown that the coordinatively unsaturated ruthenium complex $[(C_5Me_5)Ru(OMe)]_2$ **278** reacts with ethylene to provide the air-stable $(C_5Me_5)Ru(\eta^3\text{-crotyl})(\eta^2\text{-}C_2H_4)$ **279-*exo***, the η^3-crotyl ligand being formed from a metal-mediated coupling of two ethylene units (Scheme **67**).[134] When the reaction mixture is subsequently warmed to 60°C or, alternatively, when the reaction is conducted as a one-pot synthesis starting from $[(C_5Me_5)RuCl_2]_2$, potassium carbonate, and methanol in the presence of ethylene, the thermodynamic isomer **279-*endo*** is obtained in high selectivity. The use of propene under the latter reaction conditions leads to the

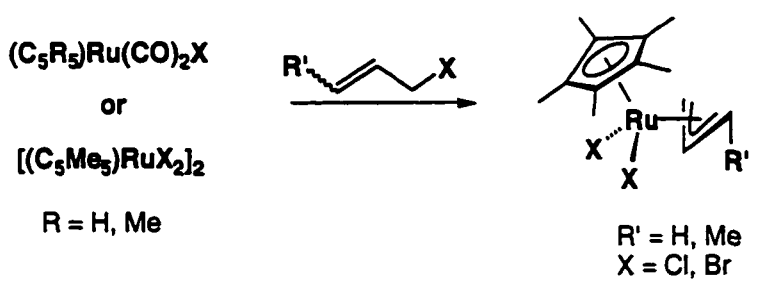
Scheme 67



formation of unsubstituted complex $(C_5Me_5)Ru(\eta^3\text{-allyl})(\eta^2\text{-}C_3H_6)$ (**280**-*endo*), via C-H activation of the olefin, rather than coupling to form the expected η^3-hexenyl complex. In both cases, the structure of the product complexes were confirmed by X-ray analysis.

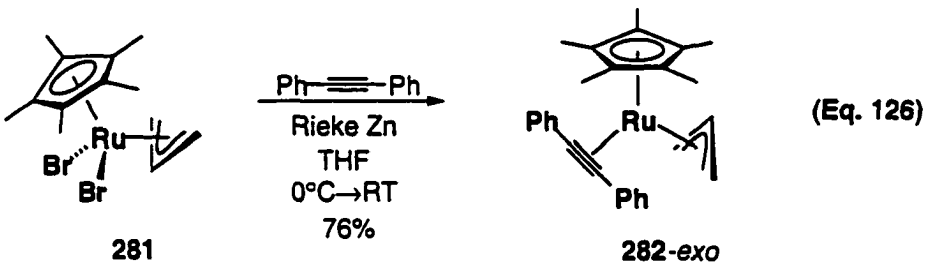
For a detailed investigation into the coupling of η^3-allyl ruthenium complexes with alkynes, however, it was necessary to find an efficient, high-yield synthesis of neutral $(C_5Me_5)Ru(II)$ η^3-allyl complexes in which the extent of substitution on the allyl ligand could be readily varied. Pertinent to this requirement, Itoh *et al.*, recently described the preparation of new Ru(IV) η^3-allyl complexes of the general formula $(C_5R_5)Ru(\eta^3\text{-allyl})X_2$ (R = H, Me; X = Cl, Br) by oxidative addition of allylic halides to one of several Ru(II) precursors (Scheme **68**).[135] We postulated that reduction of these Ru(IV) allyl dihalide complexes in the presence of alkyne would lead to the desired Ru(II) allyl alkyne complexes and to subsequent coupling reactions.

Scheme 68



Thus, the treatment of $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$ **281**[135] with Rieke zinc[136b] in the presence of one equivalent of diphenylacetylene provides the allyl alkyne complex **282**-*exo* in good yield (Eq. **126**). This complex is unusually stable, showing little tendency to react further at room temperature, and can be readily recrystallized from cold pentane to

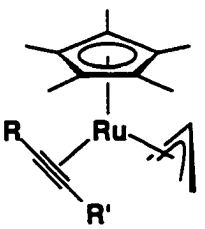
give analytically pure orange crystals. Relevant ^{1}H and ^{13}C NMR spectroscopic data are presented in Table 9 and indicate a close similarity to $[(C_6Me_6)Ru(\eta^3\text{-allyl})(PhC{\equiv}CPh)]^{+}OTf^{-}$ **126**, described previously (Chapter 2, p. 85). However, it should be noted that the chemical shifts of the allylic proton resonances in the ^{1}H NMR spectrum are upfield from those observed for the cationic hexamethylbenzene analogue, as expected for the more electron-rich neutral C_5Me_5 template. Interestingly, while the allyl carbon resonances of alkyne complex **282**-*exo* are also shifted considerably upfield of those observed for the hexamethylbenzene complex **125**, the sp-hybridized diphenylacetylene carbon signals are shifted ~9 ppm *downfield* to 98.1 ppm, very close to the signal found for uncomplexed diphenylacetylene at 101 ppm.



281 **282**-*exo* **(Eq. 126)**

The spectroscopic assignments of this complex are also in agreement with the NMR spectra obtained for the crotyl complex **279**-*exo* described by Koelle[134a] and for the analogous *exo* $(C_5Me_5)Ir$ complexes reported by Wakefield.[51] The *exo* orientation of the diphenylacetylene complex **282**-*exo* was confirmed through difference NOE measurements: irradiation of the C_5Me_5 resonance leads to a large enhancement of the resonance assigned to $H_{central}$ (10%), indicating that this proton is pointing up towards the C_5Me_5 ligand.

Table 9. Comparative ^{1}H and ^{13}C NMR Spectroscopic Data for $(C_5Me_5)Ru(\eta^3\text{-allyl})(\eta^2\text{-alkyne})$ Complexes[a]

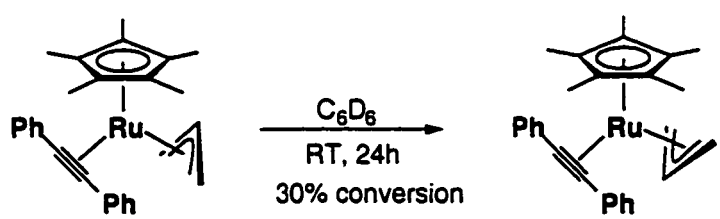


282-*exo* R = R' = Ph
284 R = R' = Me
286 R = R' = TMS
287 R = Me, R' = TMS

Assignment	**282**-*exo*	**284**	**286**	**287**
$H_{central}$ $J_{central\text{-}syn}$ $J_{central\text{-}anti}$	3.12 (tt) 6.4 Hz 9.5 Hz	3.08 (tt) 6.2 Hz 9.0 Hz	3.00 (tt) 6.3 Hz 9.5 Hz	3.00 (tt) 6.2 Hz 9.2 Hz
H_{syn}	2.85 (d)	2.58 (d)	2.60 (d)	2.66 (dd)[b] 2.47 (dd)[b]
H_{anti}	0.44 (d)	–0.04 (d)	–0.73 (d)	0.18 (d) –0.29 (d)
$C_{central}$	79.6	77.0	79.3	78.1
$C_{terminal}$	44.8	43.2	44.0	45.0 42.5
C_{alkyne}	98.1	74.0	111.7	89.0 70.3

[a] Spectra were taken in C_6D_6 at room temperature. [b]Additional splitting observed due to H_{syn1}-H_{syn2} coupling of 2.0 Hz.

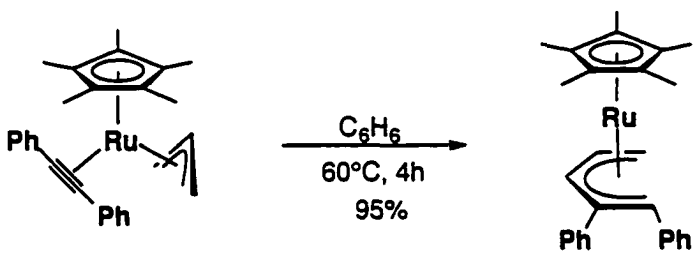
Although no coupling of the allyl and alkyne ligands is apparent at room temperature, slow conversion to the η^3-allyl isomer **282**-*endo* is observed when diphenylacetylene complex **282**-*exo* is left standing in a benzene solution for prolonged periods of time (30% conversion after 24 hours) (Eq. **127**). This new η^3-allyl alkyne complex exhibits the central hydrogen signal at δ 2.37 (tt, J = 6.5, 10.5 Hz) in the ^{1}H NMR spectrum, while the *syn* proton resonances are found as a doublet at δ 3.27 (d, J = 6.6 Hz) and the *anti* resonances are located at δ 1.17 (d, J = 10.4 Hz). The upfield shift of $H_{central}$ and the downfield shift of the *syn* and *anti* protons in the *endo* isomer is considered diagnostic for several closely related allyl complexes.[51] The conversion of the kinetic *exo* η^3-allyl alkyne complex **282**-*exo* to the **282**-*endo* isomer is consistent with the η^3-allyl alkene isomerization reactions reported by both Koelle[134] and Wakefield.[51] In this case, however, it is difficult to distinguish whether the presence of the *endo* isomer is due to an equilibrium process or if it is indeed the thermodynamically more stable isomer, since the conversion is very slow at room temperature, and heating induces the coupling reaction.



282-*exo* **282**-*endo* **(Eq. 127)**

A variety of reducing reagents were screened for the reduction of $(C_5Me_5)Ru(\eta^3$-allyl$)Br_2$ in the presence of diphenylacetylene. Although Rieke magnesium, sodium amalgam, and samarium iodide (2 equiv) are all effective, Rieke zinc is the most

convenient. It is easy to handle, readily prepared on a multigram scale, and remains active when stored under an inert atmosphere for a period of several months.[136] Freshly acid-washed zinc dust also reduces $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$, but this reaction is much slower than the reaction using the more highly activated Rieke zinc. The Ru(IV) complex $(C_5Me_5)Ru(\eta^3\text{-allyl})Cl_2$ is an equally effective precursor for the zinc reduction reactions.

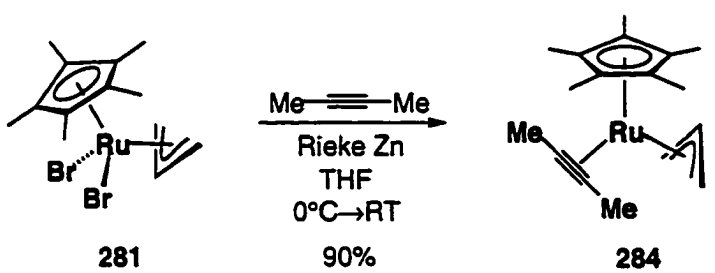


282-*exo* **283** **(Eq. 128)**

The thermolysis of $(C_5Me_5)Ru(\eta^3\text{-allyl})(PhC{\equiv}CPh)$ **282-*exo*** at higher temperature results in the quantitative formation of the acyclic η^5-pentadienyl complex **283** within a few hours (Eq. **128**). Recrystallization from cold pentane returns analytically pure material as air-stable, yellow crystals. This material exhibits the characteristic η^5-pentadienyl pattern in the ^{1}H NMR spectra; salient ^{1}H NMR spectral data is presented in Table **10**. As with all other η^5-pentadienyl products acquired through ruthenium-mediated allyl/alkyne coupling, the alkyne-derived substituents are oriented *cis* to one another. The allyl/alkyne coupling reaction presumably follows the same allylic C-H activation mechanism postulated for the formation of acyclic η^5-pentadienyl products in the cationic series (*vide supra*). This is the first example in this study where the reaction of a η^3-allyl complex with this alkyne results in the formation of an *acyclic* product;

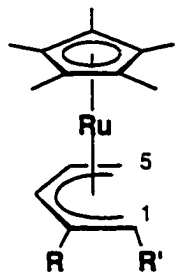
coupling reactions with diphenylacetylene invariably lead to five-membered ring products in the cationic ruthenium, iridium and cobalt systems.

The reaction of $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$, Rieke zinc, and excess 2-butyne in tetrahydrofuran follows the same general pattern as the diphenylacetylene reaction (Eq. **129**). The η^3-allyl alkyne complex **284** is isolated in good yield as a yellow crystalline material, although the 2-butyne product is far more thermally labile than the diphenylacetylene complex. While the 2-butyne complex **284** can be stored indefinitely in the solid state at low temperature (–20°C to –80°C) and is air-stable, the compound decomposes to unidentifiable products when stored at room temperature or left under vacuum for a prolonged period of time. The increased kinetic lability of the 2-butyne complex compared to that of the analogous diphenylacetylene complex **282** parallels the expected difference in the thermodynamic stability of these complexes. The repulsive interaction between electrons in the filled overlapping ruthenium and perpendicular alkyne orbital should be substantially larger for the electron-donating 2-butyne ligand, compared to diphenylacetylene. The ruthenium-alkyne bond for 2-butyne should also involve less metal-alkyne d→π* back-donation than bonding in the more electron-poor alkynes such as diphenylacetylene. In general, however, the ^1H and ^{13}C NMR spectra of



281 90% **284** **(Eq. 129)**

Table 10. Comparative ^{1}H NMR Spectroscopic Data for $(C_5Me_5)Ru(\eta^5$-pentadienyl) Complexes[a]



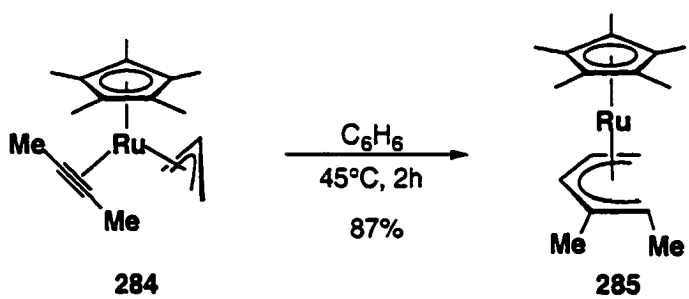
283 R = R' = Ph
285 R = R' = Me
288 R = Me, R' = TMS
289 R = $-(CH_2)_6-$
290 R = Me, R' = Ph
291 R = Ph, R = C(O)Me

Assign.	283	285	288	289	290	291
H_1	1.23 (s)	0.24 (q)[a]	−1.27 (s)	0.12 (dd)[a]	0.99 (s)	1.05 (s)
H_3 J_{3-4}	5.19 (d) 5.9 Hz	4.71 (d) 5.8 Hz	4.61(d) 6.1 Hz	4.59 (d) 6.0 Hz	4.74 (d) 6.0 Hz	5.11(d) 5.8 Hz
H_4 $J_{4\text{-}5syn}$ $J_{4\text{-}5anti}$	3.78 (td) 8.6 Hz 9.0 Hz	3.74 (td) 8.5 Hz 8.7 Hz	3.62 (td) 8.8 Hz 8.9 Hz	3.77 (td) 8.6 Hz 8.6 Hz	3.72 (td) 8.8 Hz 9.0 Hz	3.74 (td) 8.7 Hz 5.8 Hz
H_{5syn} $J_{5syn\text{-}5anti}$	2.46 (dd) 2.8 Hz	2.22 (dd) 2.6 Hz	2.25 (dd) 2.9 Hz	2.25 (dd) 2.6 Hz	2.39 (dd) 2.8 Hz	2.43 (dd) 3.0 Hz
H_{5anti}	1.31 (dd)	0.67 (dd)	1.12 (dd)	0.76 (dd)	1.25 (dd)	1.11

[a] Spectra were taken in C_6D_6 at room temperature. [b]Additional splitting observed due to coupling with substituent.

2-butyne complex **284** closely resembles those obtained for diphenylacetylene complex **282**-*exo* (Table **9**), although the H_{syn} and H_{anti} resonances of the allyl are shifted still further upfield due to the relatively electron-rich 2-butyne ligand. The internal alkyne carbon resonances are located at 74.0 ppm in the ^{13}C NMR spectrum, compared to 73.6 ppm for uncomplexed 2-butyne.

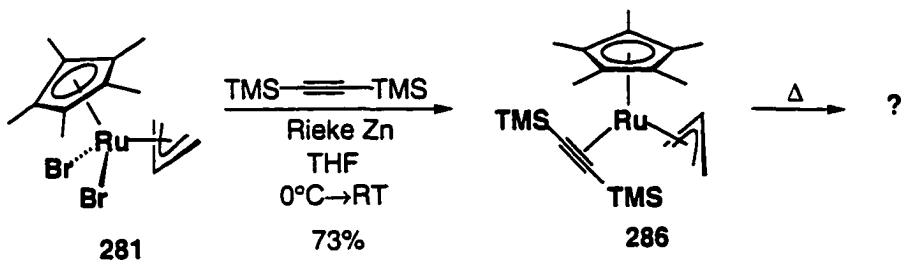
Coupling of the η^3-allyl and 2-butyne ligands occurs at a lower temperature than that necessary to induce the coupling of the diphenylacetylene complex. When a solution of 2-butyne complex **284** in benzene is left standing at room temperature, a slow conversion to η^5-1,2-dimethylpentadienyl complex **285** is observed. The conversion to the η^5-pentadienyl product is accomplished more rapidly and quantitatively by warming a benzene solution of the alkyne complex to 45°C for a few hours (Eq. **130**). ^1H NMR data for η^5-1,2-dimethylpentadienyl complex **285** are presented in Table **10**. An attempt to force double alkyne insertion by thermolysis of the 2-butyne complex **284** in the presence of a large excess of 2-butyne results only in the formation of intractable product mixtures.



284 **285** **(Eq. 130)**

The reduction of $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$ in the presence of bis(trimethylsilyl)-acetylene (BTMSA) also leads to the formation of an isolable allyl alkyne complex in good yield (Eq. **131**). ^1H and ^{13}C NMR spectroscopic data for alkyne complex **286** are presented in Table **9**. In contrast to the previous two examples, however, thermolysis of

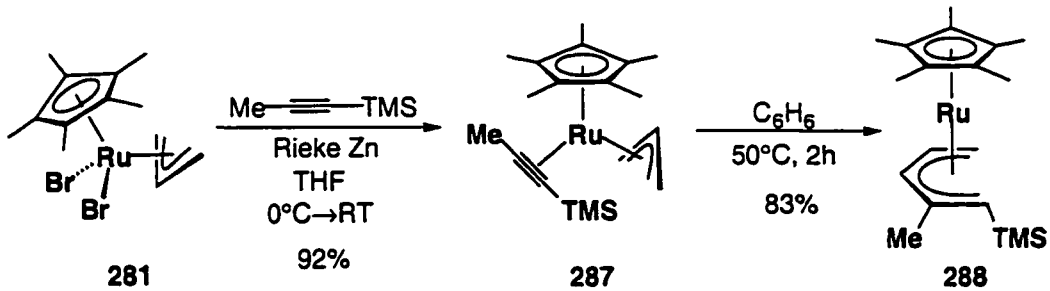
BTMSA complex **286** does not yield an η^5-pentadienyl complex, but instead leads to the formation of several unidentified products. It is plausible that the sterically bulky trimethylsilyl groups inhibit the normal migratory coupling of the allyl and alkyne ligands.



(Eq. 131)

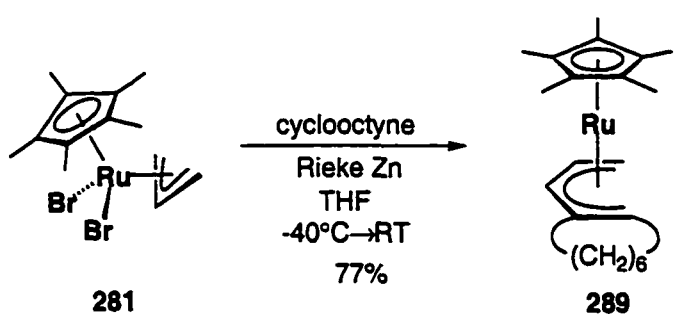
The unsymmetrical alkyne, 1-(trimethylsilyl)propyne, yields allyl alkyne complex **287** in high yield by zinc reduction of $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$ (Eq. **132**). The lack of symmetry of the alkyne ligand results in the loss of symmetry for the entire complex, leading to chemically inequivalent carbon termini in the allyl ligand and to inequivalent *syn* and *anti* proton pairs (Table **9**). Thermolysis of complex **287** leads to the formation of a single η^5-pentadienyl product, complex **288**, isolated as a yellow crystalline material. The unusually far upfield singlet present at δ –1.27 (1H, H_1) in the ^{1}H NMR spectrum of this complex strongly suggests that the trimethylsilyl group is located at the terminus of the pentadienyl ligand (Table **10**). The regioselectivity of this reaction suggests that the initial migratory allyl/alkyne coupling occurs at the sterically less hindered end of the alkyne ligand, and supports our assumption that the lack of coupling for BTMSA complex **286** has a steric origin.

(Eq. 132)



281 287 288

In contrast to the previous alkynes, zinc reduction of $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$ in the presence of cyclooctyne does not yield an isolable allyl alkyne complex; instead, the disubstituted η^5-pentadienyl product **289** is isolated, even when the reaction is kept at low temperature (Eq. **133**). The η^5-pentadienyl complex **289** is isolated as an air-sensitive yellow powder; relevant ^1H and ^{13}C NMR data for this material are presented in Table **10**. While cyclooctyne is expected to have a strong d→π* backbonding interaction with the ruthenium center, the inherent ring strain of cyclooctyne presumably activates the alkyne towards coupling with the allyl ligand.

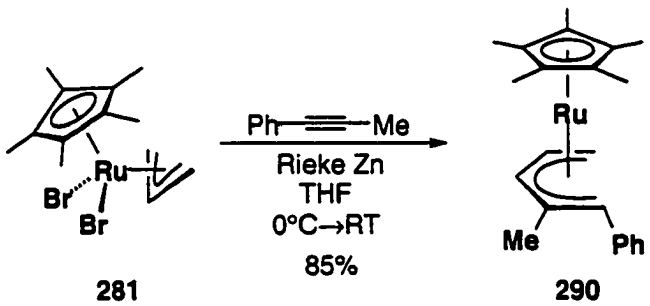


281 289

(Eq. 133)

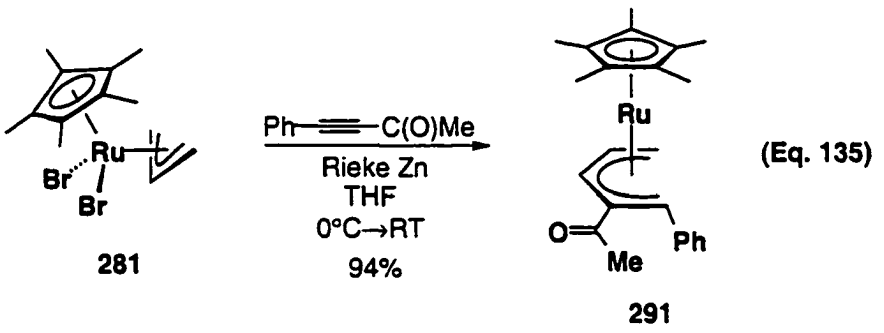
Curiously, the reaction of $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$, Rieke zinc, and 1-phenyl-propyne also results in the rapid formation of a single η^5-pentadienyl product, with only traces of the allyl alkyne intermediate detected in the crude reaction mixture (Eq. **134**).

The presence of an upfield singlet at δ 0.99 in the ^{1}H NMR spectrum of complex **290** establishes that the phenyl group is located at the terminus of the pentadienyl ligand (Table **10**). The regioselectivity of the allyl/alkyne coupling once again places the sterically larger alkyne substituent adjacent to the ruthenium metal center. The migratory coupling of the allyl ligand with coordinated 1-phenylpropyne occurs at a faster rate than the coupling of either 2-butyne or diphenylacetylene, most likely due to the polarization of the unsymmetrical alkyne ligand.



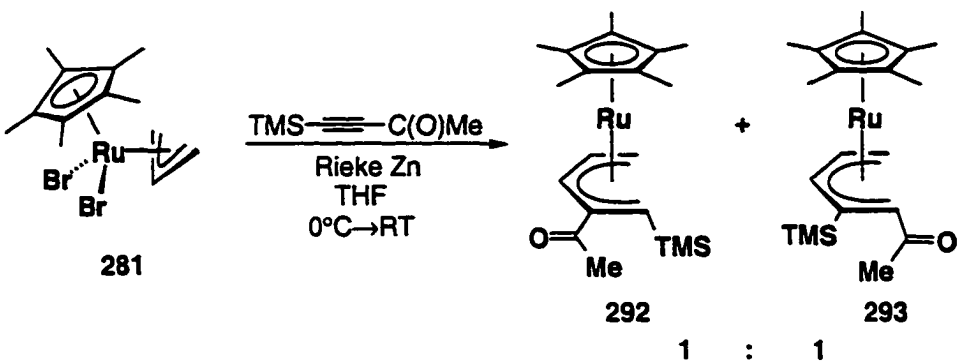
281 **290** **(Eq. 134)**

The zinc reduction of $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$ in the presence of the electron-deficient alkyne 4-phenyl-3-butyn-2-one also rapidly yields a single η^5-pentadienyl product in high yield (Eq. **135**). In this case a more extensive use of NMR spectroscopy was required to determine the regioselectivity of the alkyne insertion and both HMQC and HMBC spectroscopy were essential to unambiguous characterization. The presence of long-range heterocorrelations between the carbon resonance at 53.7 ppm (C_1) and the phenyl protons at δ 6.93 as well as between the carbon signal at 127.3 ppm (C_{Ph}) and a proton at δ 1.05 (assigned to H_1) establish that the phenyl substituent is located at one terminus of the η^5-pentadienyl ligand.



281 291 (Eq. 135)

The exclusive formation of acyclic η^5-pentadienyl products gives us our first opportunity to assess systematically the factors that determine the regiochemistry of alkyne insertion in the migratory coupling of alkyne and η^3-allyl ligands. Based on the reactions described, it appears that the regioselectivity is predominately governed by steric effects: the allyl ligand preferentially couples to the end of the alkyne with the sterically smaller substituent. However, treatment of $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$ with Rieke zinc in the presence of 4-trimethylsilyl-3-butyn-2-one yields an inseparable mixture of two η^5-pentadienyl complexes, **292** and **293**, in a ratio of approximately 1 : 1, instead of just the expected regioisomer **292** (Eq. **136**). This strongly suggests that there is also an electronic component to the regioselectivity of the allyl/alkyne coupling, one that leads to placement of the electron-withdrawing substituent adjacent to the metal. In the case of



281 292 + 293 (Eq. 136)

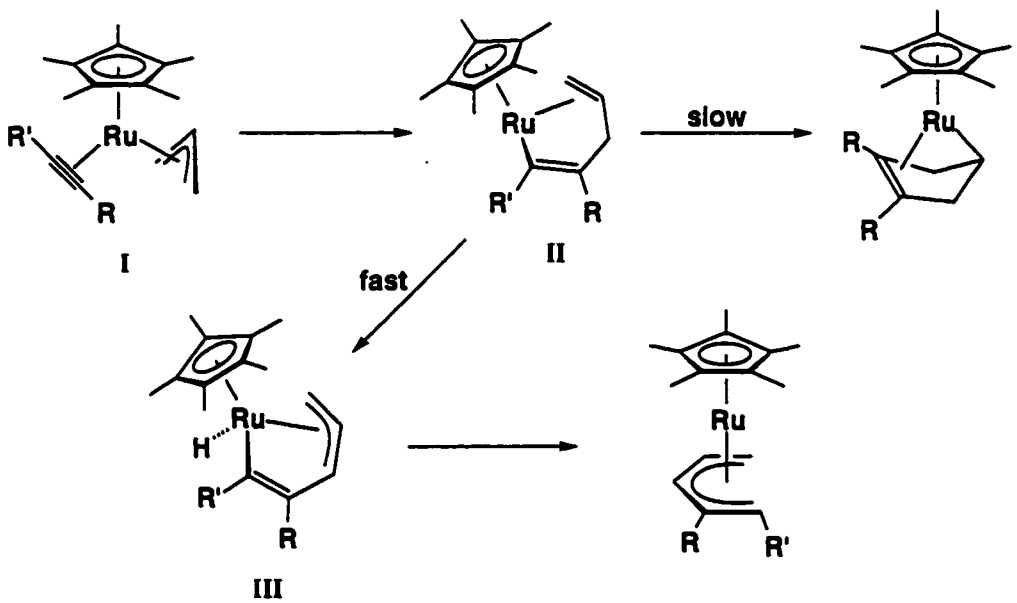
1 : 1

4-trimethylsilyl-3-butyn-2-one, the steric and electronic components of the substituents are evidently balanced, resulting in a mixture of pentadienyl products. Rationalizing the high regioselectivity observed for 4-phenyl-3-butyn-2-one is more problematic: one possible explanation is that phenyl itself acts as an electron-withdrawing group, and this electronic component, combined with its larger steric profile, may lead to selective coupling of the allyl ligand with the acetyl-substituted end of the alkyne. Since the carbon-carbon bond formation of the allyl/alkyne coupling step is unlikely to be reversible, the final product presumably reflects the kinetic selectivity of the initial allyl/alkyne coupling and does not necessarily produce the most thermodynamically stable η^5-pentadienyl complex.

The (C_5Me_5)Ru-mediated allyl/alkyne coupling to form η^5-pentadienyl complexes is thus general for a wide range of disubstituted alkynes. Unfortunately, the zinc reduction of $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$ in the presence of terminal alkynes is not so straightforward. Attempts to reduce the Ru(IV) dibromide complex **281** in the presence of excess acetylene results in the recovery of only a small amount of unidentifiable products while the use of phenylacetylene yields an intractable mixture of products. It is possible that the terminal alkynes undergo metal-mediated alkyne-vinylidene rearrangement prior to an uncontrolled oligomerization. Another possibility is that the terminal alkynes react rapidly with a Ru(III) intermediate formed during the zinc reduction reaction. The use of the electron-deficient alkyne DMAD during the reduction process also results in the formation of a complex mixture of products, although in this case it may be due to the competitive reaction of DMAD with Rieke zinc.

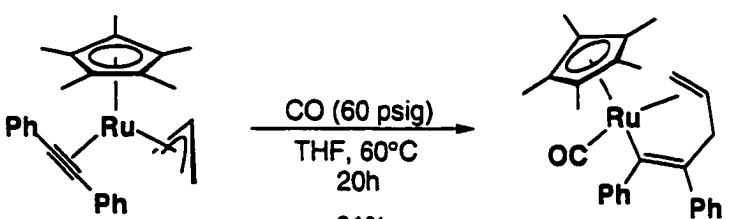
Although the inability to use terminal alkynes in this reaction is disappointing,

several conclusions can be drawn from the reactions with disubstituted alkynes. It is evident that, by altering the ruthenium template from the cationic η^6-hexamethylbenzene system to the neutral η^5-pentamethylcyclopentadienyl, the C-H bond activation that forms the η^5-pentadienyl products becomes the kinetically preferred pathway over cyclization (Scheme 69). This may in part be due to the more electronic rich pentamethylcyclopentadienyl ligand better stabilizing the Ru(IV) oxidation state of the postulated hydride intermediate **III** relative to the cationic (η^6-arene)Ru template. Since electron-rich systems are also known to have slower rates of migratory insertion reactions compared to more electrophilic systems,[137] migratory cyclization of the vinyl olefin **II** to form cyclic products is presumably inhibited as well.



1.1 Reactions of $(C_5Me_5)Ru(\eta^3\text{-allyl})(\eta^2\text{-alkyne})$ Complexes with Carbon Monoxide

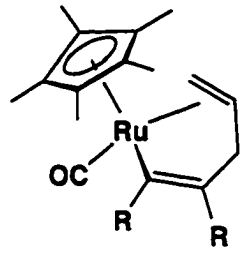
The vinyl olefin intermediate in the allyl/alkyne coupling reaction can be intercepted by the use of carbon monoxide as a trapping reagent.[39] Thus, heating diphenylacetylene complex **282** under carbon monoxide pressure (60 psig) suppresses the formation of the η^5-pentadienyl product by trapping the initial product of allyl/alkyne coupling, resulting in the formation of vinyl olefin complex **294** (Eq. **137**). This product is purified by recrystallization from diethyl ether/methanol and has been fully characterized by both spectroscopic and analytical techniques. The ^1H and ^{13}C NMR spectroscopic data are fully consistent with the presence of a vinyl olefin moiety, based on the comparison to known complexes[39] (Table **11**). The presence of the carbonyl ligand is supported by the infrared spectrum, which exhibits a carbonyl stretch at 1933 cm^{-1}, and by the ^{13}C NMR spectrum, which reveals a typical carbonyl resonance at 211.0 ppm.



282 **294** **(Eq. 137)**

As previously observed in the iridium system,[39] the treatment of 2-butyne complex **284** with carbon monoxide leads to a mixture of the vinyl olefin complex **295** and η^3-allyl carbonyl complex **296** (*vide infra*) (Scheme **70**). However, when the reaction is carried out in the presence of excess 2-butyne, the formation of the η^3-allyl

Table 11. Comparative ^{1}H and ^{13}C NMR Spectroscopic Data for η^{1},η^{2}-Pentadienyl Carbonyl Complexes[a]



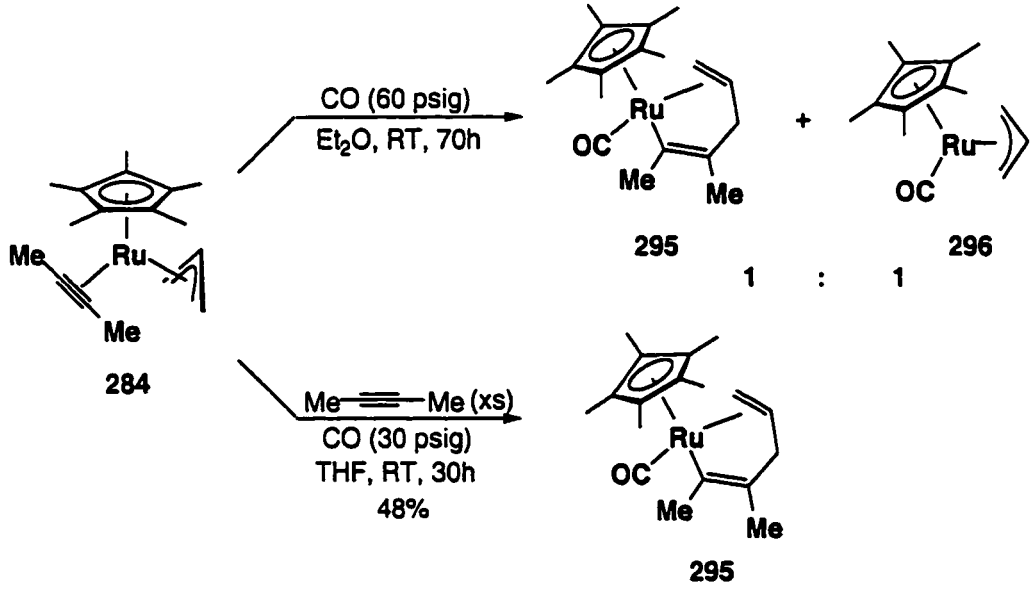
294 R = Ph
295 R = Me

^{1}H NMR	**294**	**295**		^{13}C NMR	**294**	**295**
$\mathbf{H_{3a}}$ $J_{3a\text{-}3b}$ $J_{3a\text{-}4}$	3.88 (dd) 16.4 Hz 6.4 Hz	3.04 (br dd)[b] 16.0 Hz 6.7 Hz		$\mathbf{C_1}$	152.0	142.0
$\mathbf{H_{3b}}$ $J_{3b\text{-}4}$	2.59 (dd) 7.3 Hz	2.29 (br dd)[b] 7.5 Hz		$\mathbf{C_2}$	151.7	142.1
$\mathbf{H_4}$ $J_{4\text{-}5anti}$ $J_{4\text{-}5syn}$	2.34 (dddd) 12.0 Hz 8.0 Hz	3.34 (dddd) 12.0 Hz 8.3 Hz		$\mathbf{C_3}$ J_{CH}	47.8 (t) 124 Hz	46.0
$\mathbf{H_{5anti}}$	3.03 (d)	2.84 (d)		$\mathbf{C_4}$ J_{CH}	72.7 (d) 152 Hz	72.7
$\mathbf{H_{5syn}}$	2.11 (d)	2.14 (d)		$\mathbf{C_5}$ J_{CH}	48.8 (t) 158 Hz	47.5

[a] Spectra were taken in C_6D_6 at room temperature. [b]GCOSY indicates long-range H-H coupling to both Me groups.

carbonyl complex is inhibited, and the reaction exclusively provides the vinyl olefin complex. Decomposition of the starting alkyne complex during this reaction remains a significant problem, however, resulting in a lower yield than that obtained for the diphenylacetylene reaction. The product, vinyl olefin complex **295**, is air-stable and readily recrystallized from diethyl ether/methanol to provide analytically pure material. The carbonyl ligand of complex **295** is established by the absorption at 1938 cm^{-1} in the infrared spectrum and by the carbonyl resonance at 211.5 ppm in the ^{13}C NMR spectrum. Both the ^{1}H and ^{13}C NMR spectra closely resemble those obtained for the diphenylacetylene-derived carbonyl complex (Table **11**).

Scheme 70



The reaction of η^3-allyl 1-(trimethylsilyl)propyne complex **287** with carbon monoxide leads to a mixture of the η^3-allyl carbonyl complex **296** and the η^5-pentadienyl complex **288**. Attempts to prevent substitution of the alkyne ligand by carbon monoxide by the addition of excess 1-(trimethylsilyl)propyne does result in a small reduction in the

amount of η^3-allyl carbonyl complex produced, but the excess alkyne also apparently inhibits the allyl/alkyne coupling reaction, resulting in the recovery of a significant proportion of starting material. While this observation is not well understood, it may be due to the large silyl group adjacent to the ruthenium acting to inhibit reactions at the metal center.

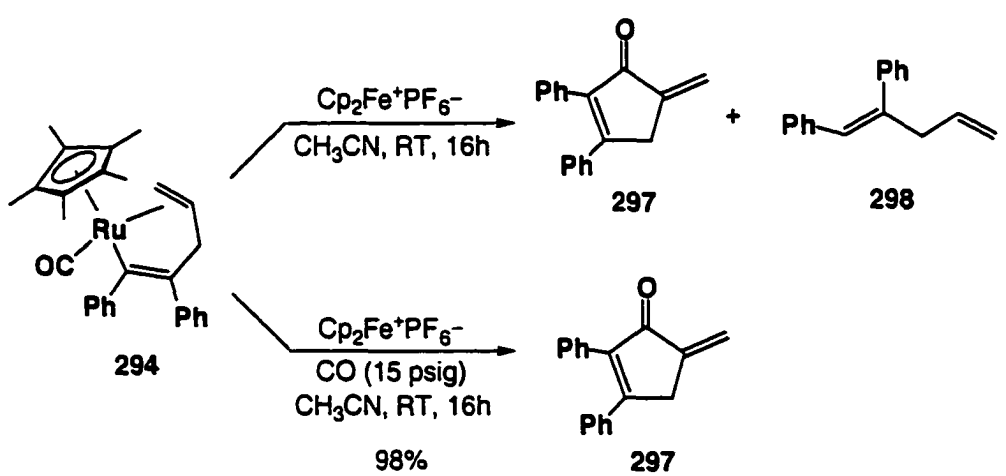
1.2 The Reactivity of $(C_5Me_5)Ru(\eta^1,\eta^2$-pentadienyl)(CO) Complexes

An investigation of the chemistry of the carbonyl-trapped vinyl olefin complexes **294** and **296** was undertaken to probe further migratory coupling reactivity. Thermolysis of the diphenyl-substituted vinyl olefin complex **294** in toluene at 110°C for a prolonged period results only in the clean recovery of starting material, even upon addition of Lewis acids to promote migratory insertion.[115,137] At higher temperatures, decomposition becomes evident. Photolysis of complex **294** in toluene at room temperature also has little effect.

One-electron oxidation of transition metal complexes provides tremendous rate enhancements for elementary processes such as ligand dissociation, substitution, structural isomerization, reductive elimination, and migratory insertion.[138] In particular, one-electron oxidants have been used to induce migrations of alkyl ligands to coordinated carbonyls to form metal acyl complexes, a reactivity pattern that has been observed for a wide variety of transition metal complexes.[139] Thus, an investigation into the reactivity of the vinyl olefin carbonyl complexes upon treatment with oxidants was undertaken, with the goal of promoting migratory insertion of the carbonyl ligand.

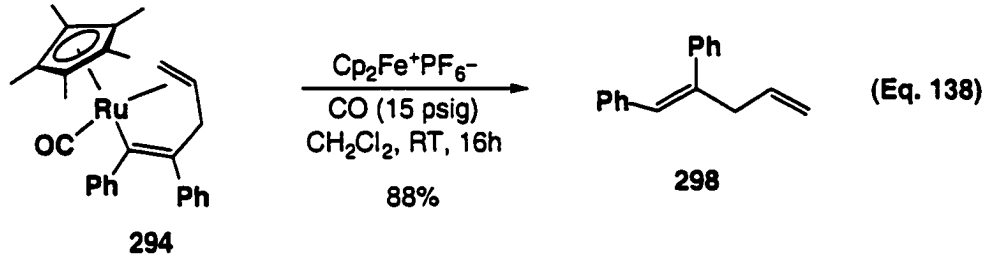
Although the diphenylacetylene-derived carbonyl complex **294** is completely unreactive at temperatures up to the onset of decomposition, carbonyl insertion is induced at room temperature upon treatment with a one-electron oxidant. The addition of excess ferricinium hexafluorophosphate to carbonyl complex **294** in acetonitrile at room temperature results in the formation of the known organic products 2,3-diphenyl-5-methylenecyclopent-2-en-1-one **297**[140d] and 1,2-diphenyl-1,4-pentadiene[39] **298** (Scheme **71**). Performing the reaction under an atmosphere of carbon monoxide in a sealed vessel provides the highest selectivity for the formation of cyclopentenone **297**, which is isolated in 98% yield after purification by flash chromatography on silica gel. Only a trace of the linear diene **298** is formed under these reaction conditions. The use of a sub-stoichiometric amount of $[Cp_2Fe]^+PF_6^-$ (0.25 equiv) results in the recovery of starting material along with the formation of a small amount of the organic product, indicating that this induced cyclization reaction is not catalytic in oxidant.

Scheme 71



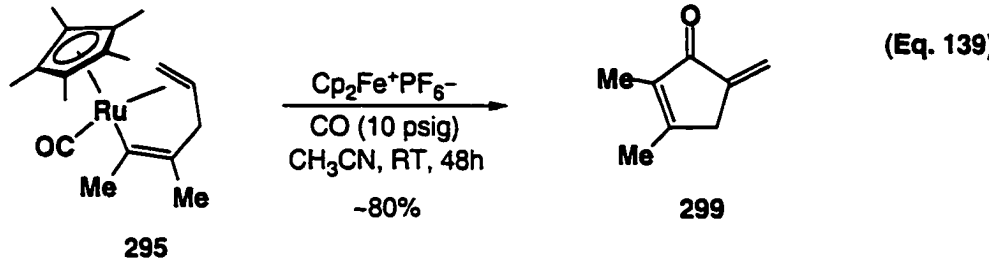
The solvent used for the oxidation of vinyl olefin complex **294** has a dramatic effect on the product partitioning. When the oxidation is carried out in the non-

coordinating solvent dichloromethane, the only organic product detected is 1,2-diphenyl-1,4-pentadiene, even in the presence of carbon monoxide (Eq. **138**). Surprisingly, the same oxidation reaction in tetrahydrofuran yields no identifiable products, while the use of methanol as solvent results only in the recovery of starting material. Coordinating solvents such as acetonitrile presumably serve to stabilize electronically and coordinatively unsaturated intermediates; the addition of a strongly coordinating ligand such as carbon monoxide can similarly affect the reaction, although in this case the presence of both carbon monoxide and a coordinating solvent are required for optimal conversion.



(Eq. 138)

The treatment of the 2-butyne-derived carbonyl complex **295** with excess ferricinium in acetonitrile under carbon monoxide pressure yields 2,3-dimethyl-5-methylenecyclopent-2-en-1-one **299** as the exclusive organic product (Eq. **139**). This compound is isolated as a volatile oil in approximately 80% yield after chromatography



(Eq. 139)

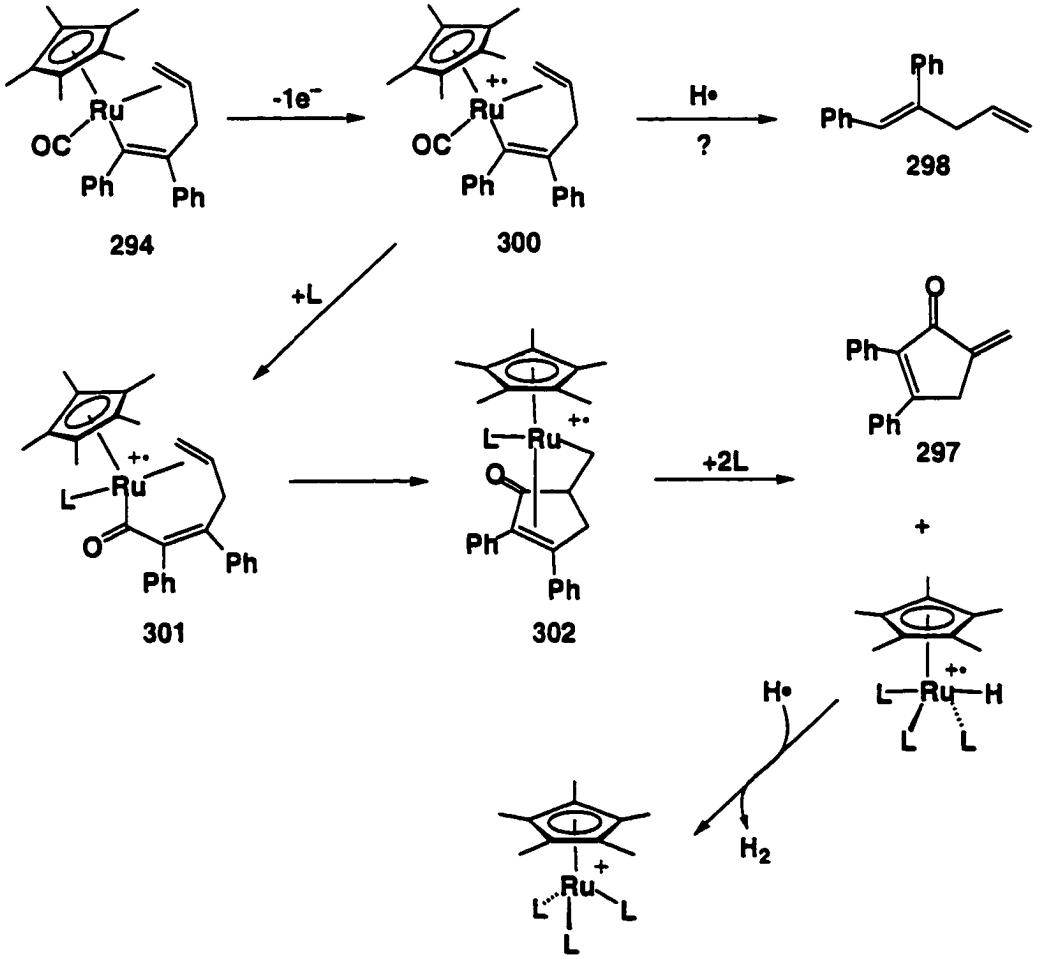
on silica gel. Compound **299** is also known as methylenomycin B, a natural cyclopentanoid antibiotic that has been synthesized previously by a variety of methods.[140]

The fate of the ruthenium subsequent to release of the organic moiety is also dependent on the choice of solvent. Oxidation of vinyl olefin complex **294** in dichloromethane or in tetrahydrofuran in the absence of added carbon monoxide results in the formation of a complex mixture of unidentifiable diamagnetic $(C_5Me_5)Ru$ complexes. However, yellow crystals of an organometallic product are isolated from the oxidation reaction carried out in acetonitrile under a CO atmosphere. Spectroscopic data (^1H NMR, IR) and elemental analysis of this material are consistent with the formation of a mixture of two complexes of the formula $[(C_5Me_5)Ru(CH_3CN)L_2]^+PF_6^-$ (L = CH_3CN or CO).

A mechanistic rationale consistent with the observed effects of solvent and added carbon monoxide can be constructed (Scheme **72**). Treatment of vinyl olefin complex **294** with ferricinium hexafluorophosphate initiates the reaction by an outer-sphere one-electron transfer, forming the cationic Ru(III) intermediate **300** and ferrocene. The coordination of the donor acetonitrile ligand gives a $19e^-$ intermediate, which induces the alkyl-to-acyl migration to generate complex **301**, a reaction pattern that has been extensively investigated.[139] Replacement of the donor solvent with π-acidic carbon monoxide in a non-coordinating solvent diverts the reaction pathway away from migratory insertion; instead, the organic moiety abstracts hydrogen radical, possibly from the solvent, to form 1,4-pentadiene **298**. This abstraction manifold is not well understood and may involve the release of the organic moiety as a vinyl radical that is then quenched; alternatively, the cationic Ru(III) complex **300** may abstract H• to form a

diamagnetic hydride complex that subsequently undergoes reductive elimination of the pentadiene fragment. A third possibility is that complex **300** undergoes σ-bond metathesis of one of the methyl groups of the pentamethylcyclopentadienyl ligand, resulting in a "tuck-in complex" that decomposes to produce the pentadiene moiety.[141] No control reactions were conducted in deuterated solvent, leaving us uncertain if the source of hydride is the solvent or the pentamethylcyclopentadienyl ligand.

Scheme 72



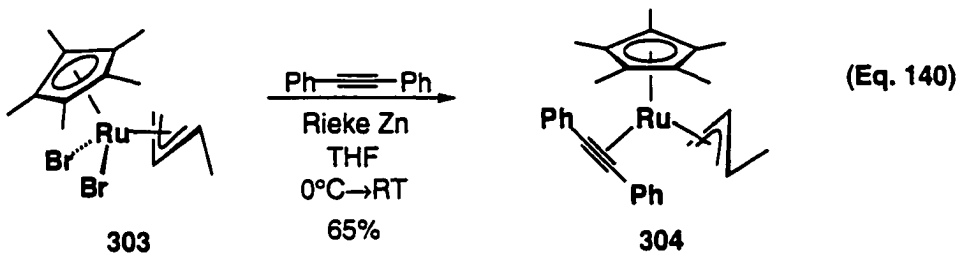
The oxidatively-induced carbonyl insertion that forms acyl complex **301** then undergoes migratory cyclization to generate complex **302** containing the cyclopentenone ring. Subsequent β-hydride elimination releases the methylenecyclopent-2-en-1-one moiety while also producing a Ru(III) hydride byproduct, which is subsequently reduced to a cationic divalent $(C_5Me_5)Ru(L_3)$ complex (L = CH_3CN or CO), presumably through the extrusion of hydrogen gas. The overall process that produces the cyclopentenone involves allyl/alkyne coupling, carbonyl insertion, migratory cyclization and β-hydride elimination, and is very reminiscent of the nickel-catalyzed Chiusoli cycloaddition of alkynes, allyl halides and carbon monoxide (Chapter 1, p. 6) although the ruthenium-mediated process is not catalytic in metal.

One-electron oxidation of the otherwise unreactive ruthenium carbonyl complexes **294** and **295** thus provides a rich reactivity manifold in which the distribution of products appears to be determined by the partitioning between ligand coordination and hydrogen atom abstraction. Either pathway can be accessed selectively by the choice of solvent and by providing additional carbon monoxide. The oxidation of the ruthenium complex not only reduces the kinetic barrier to carbonyl insertion, but also shifts the preferred reactivity pattern from C-H activation to migratory cyclization.

1.3 Effects of Allyl Substitution on (C_5Me_5)Ru-Mediated Allyl/Alkyne Coupling

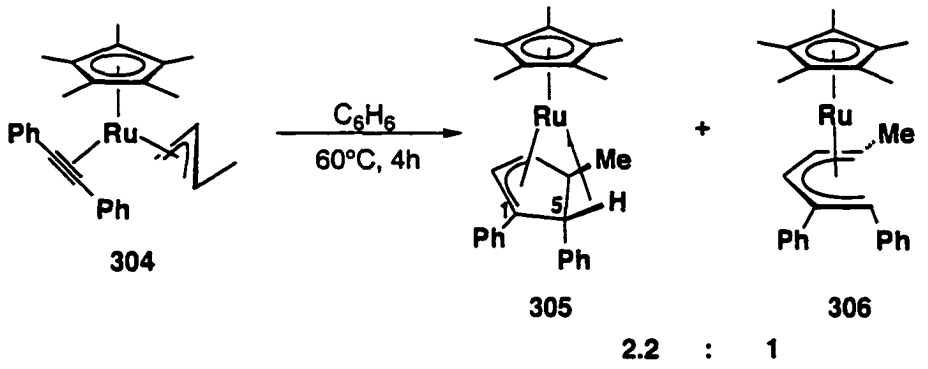
Substituted allyl complexes $(C_5Me_5)Ru(\eta^3\text{-}C_3H_4R)Br_2$, with a variety of ligand substituents are readily prepared using the oxidative addition process developed by Itoh. The presence of a substituent on the η^3-allyl ligand, however, complicates the

allyl/alkyne coupling manifold. The initial formation of the substituted η^3-allyl alkyne complexes proceeds smoothly enough: treatment of $(C_5Me_5)Ru(\eta^3\text{-crotyl})Br_2$ with Rieke zinc in the presence of diphenylacetylene, for example, provides the crotyl alkyne complex **304** (Eq. **140**). Similar to the allyl analogue, the crotyl complex **304** is stable at room temperature and can be recrystallized from cold pentane to afford orange crystals in 65% yield. The configuration of the η^3-crotyl ligand is assigned as *exo, syn* on the basis of both the observed chemical shifts and the coupling constants in the ^{1}H NMR spectrum



303 **304** **(Eq. 140)**

The central proton signal of the crotyl ligand is observed at δ 3.04 (td, J = 9.1, 6.5 Hz) while the methyl group appears as a doublet at δ 1.72 (J = 6.1 Hz). The loss of symmetry in this complex due to the presence of the methyl substituent results in the appearance of inequivalent H_{anti} resonances, which are found at δ 0.68 (dq, J = 9.0, 6.1 Hz) and δ 0.53 (d, J = 9.3 Hz) in the ^{1}H NMR spectrum. Similarly, the ^{13}C NMR spectrum of complex **304** displays two distinct signals at 98.2 and 97.9 ppm, corresponding to the inequivalent alkyne carbons of the coordinated diphenylacetylene. Heating $(C_5Me_5)Ru(\eta^3\text{-crotyl})(PhC{\equiv}CPh)$ **304** in benzene for several hours results in the conversion of the alkyne complex to two new products, **305** and **306**, in a ratio of 2.2 : 1, respectively (Eq. **141**). The major product, complex **305**, exhibits in the ^{1}H NMR spectrum an unusually upfield resonance at δ –4.89 (d, J = 11.9 Hz), strongly suggestive of an agostic hydride. Also found in the ^{1}H NMR spectrum is a downfield doublet at δ 4.67 (J = 3.5 Hz, H_2),

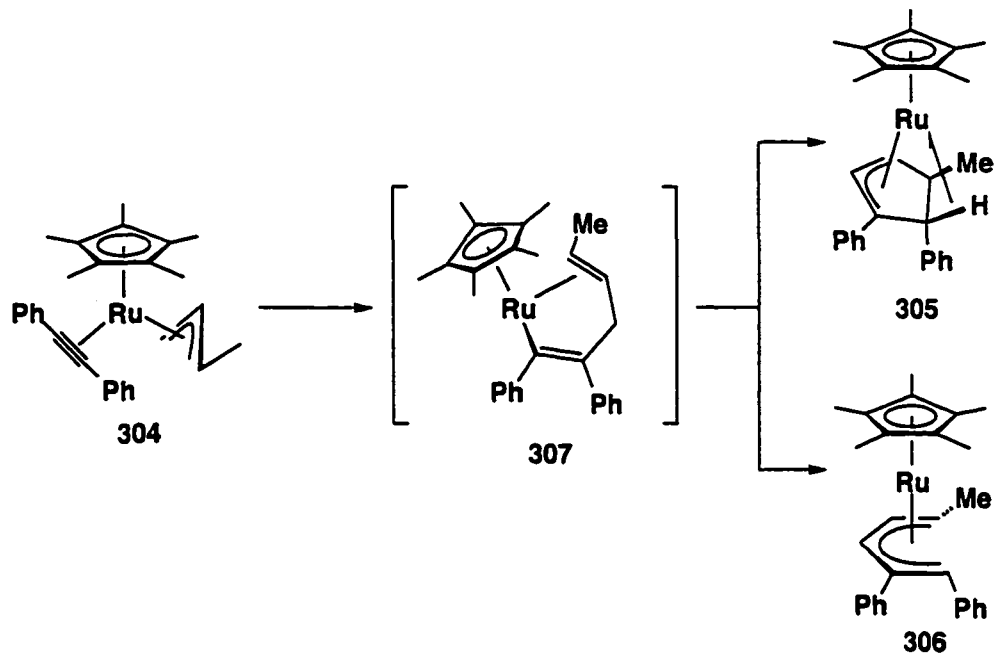


(Eq. 141)

another doublet at δ 2.94 (J = 3.7 Hz, H_3), and a resonance at δ 3.74 (dq, J = 11.8, 5.9 Hz) attributed to H_{4exo}. While the chemical shifts are different from that observed in the ^{1}H NMR spectrum of the analogous cationic (η^6-C_6Me_6)Ru(η^3-cyclopentenyl) complex **234** (Chapter 4, Eq. **108**, p. 181), the coupling constants throughout are nearly identical. This complex is thus tentatively identified as the agostic η^3-1,5-diphenyl-4-methylcyclopentenyl complex **305**, with the methyl substituent originally derived from the crotyl ligand located *endo* to the ruthenium center. The minor product exhibits the typical acyclic η^5-pentadienyl pattern in the ^{1}H NMR spectrum, while analysis of the vicinal coupling constants indicates that the methyl group is located at the terminus of the η^5-pentadienyl ligand. No attempt was made to separate or further characterize these complexes.

It is likely that both products **305** and **306** arise from the common vinyl olefin intermediate **307**, which is formed by migratory insertion of the alkyne into the unsubstituted end of the allyl ligand (Scheme **73**). Should this be the case, it is not clear why the presence of a third substituent should cause competitive cyclization, considering that all previous examples of allyl/alkyne coupling with the neutral (C_5Me_5)Ru template follow the allylic C-H activation pathway. Alternatively, if the initial alkyne insertion

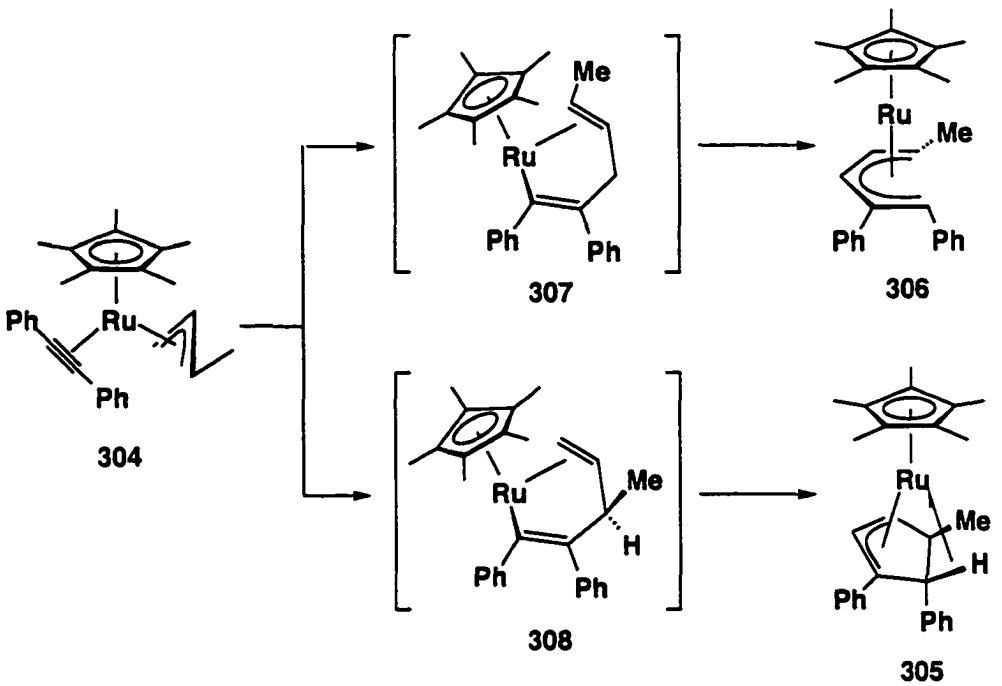
Scheme 73



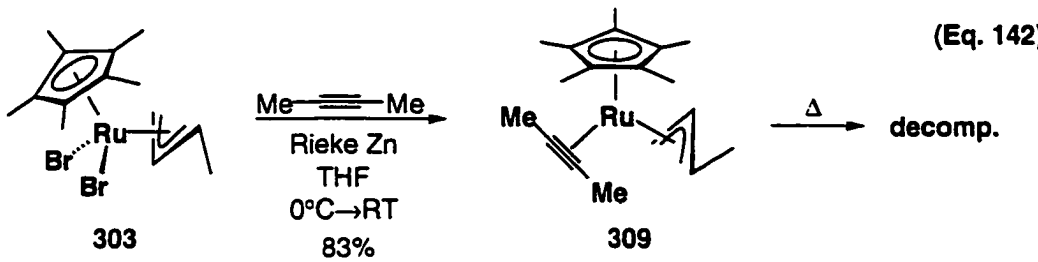
into the crotyl ligand is not regioselective, it is possible that isomeric vinyl olefin intermediates **307** and **308** may form (Scheme **74**). While intermediate **307** can readily undergo metal-mediated C-H activation to form the acyclic η^5-pentadienyl product **306**, vinyl olefin complex **308** has an *endo* methyl group that prevents the metal-mediated allylic activation without isomerizing the coordination geometry. It is then plausible that migratory cyclization becomes the lowest energy reaction pathway available to this intermediate.

The reaction of $(C_5Me_5)Ru(\eta^3\text{-crotyl})Br_2$, Rieke zinc, and 2-butyne in tetrahydrofuran provides the crotyl alkyne complex **309** in good yield (Eq. **142**). Similar to the allyl complex **284**, the η^3-crotyl 2-butyne complex is thermally labile at room temperature and is best stored at low temperature under an inert atmosphere. The ^1H NMR spectrum of this material closely resembles that of the diphenylacetylene complex

Scheme 74



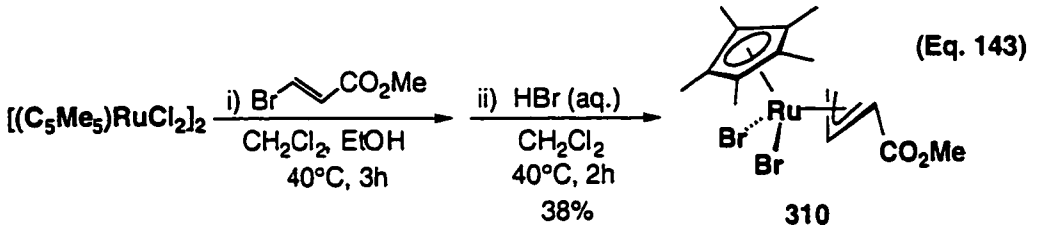
304, although many of the proton resonances are considerably shifted upfield by the more electron-rich 2-butyne ligand. The most downfield signal is attributed to $H_{central}$, located at δ 3.05 (td, J = 8.5, 6.2 Hz) with the resonance at δ 2.40 (d, J = 6.1 Hz) assigned to H_{syn}. The two inequivalent H_{anti} proton signals are found at δ 0.11 (dq, J = 8.3, 6.3 Hz) and δ 0.03 (d, J = 8.6 Hz). The absence of symmetry in this complex results in two mutually coupled methyl resonances at δ 2.12 (q, J = 1.6 Hz) and δ 2.20 (q, J = 1.6 Hz), corresponding to the coordinated 2-butyne methyl groups. In the ^{13}C NMR spectrum there are also two distinct signals present at 75.0 ppm and 73.5 ppm for the inequivalent alkyne carbons of the coordinated 2-butyne. Attempts to induce allyl/alkyne coupling in this complex by heating in the presence of 2-butyne results only in the decomposition of the starting material, giving unidentifiable products.



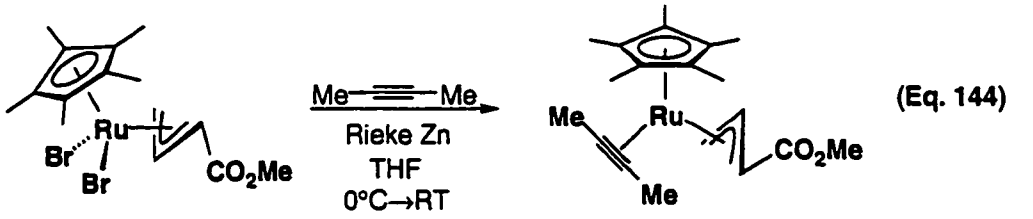
(Eq. 142)

To determine the effect of an electron-withdrawing substituent on the allyl/alkyne coupling, the ester-substituted allyl complex $(C_5Me_5)Ru(\eta^3\text{-}1\text{-}(CO_2Me)C_3H_4)Br_2$ (**310**) was prepared using Itoh's oxidative addition process.[135a] Thus, the Ru(III) dichloro dimer was treated with methyl 4-bromocrotonate, followed by halide exchange to provide the *endo,syn* η^3-allyl dibromide complex **310** (Eq. **143**). Although the material balance of this reaction is disappointing, the product is readily recrystallized to afford analytically pure red crystals in 38% yield. The Rieke zinc reduction of dibromide complex **310** proceeds in high yield in the presence of excess 2-butyne to form the alkyne complex **311** as a bright yellow crystalline material (Eq. **144**). In direct contrast to the previously prepared η^3-allyl and η^3-crotyl 2-butyne complexes **284** and **309**, complex **311** is stable at room temperature and under vacuum. Analysis of this complex by ^{1}H NMR spectroscopy indicates a pattern very similar to that found for the η^3-crotyl 2-butyne complex **309**, although the hydrogen resonances are shifted considerably downfield: the signal attributed to $H_{central}$ is located at δ 4.32 (td, J = 8.1, 6.4 Hz), H_{syn} at δ 2.52 (d, J = 6.4 Hz), and the inequivalent H_{anti} signals are found at δ 1.28 (d, J = 8.1 Hz) and δ 0.64 (d, J = 8.1 Hz). Based on this observation, the allyl ligand in complex **311** is tentatively assigned as having the expected *exo,syn* configuration. 2-Butyne complex **311** is surprisingly inert toward heating, showing no signs of allyl/alkyne coupling up to the onset of decomposition. It appears that the electron-withdrawing ester substituent

stabilizes the 2-butyne complex, simultaneously inhibiting the allyl/alkyne coupling reaction.



310 (Eq. 143)

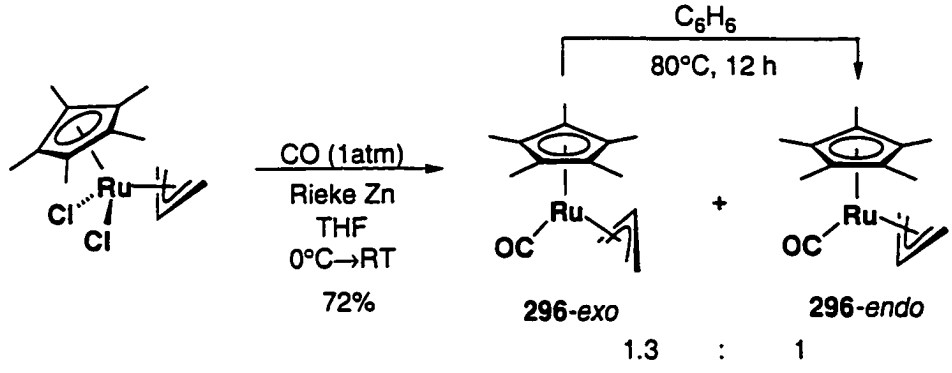


310 311 (Eq. 144)

2. Reduction of $(C_5Me_5)Ru(\eta^3$-allyl) Dihalide Complexes with Non-Alkyne Ligands

The success of the zinc reduction route to the ruthenium(II) η^3-allyl alkyne complexes encouraged us to investigate the range of ligands that could be used in place of an alkyne. A general, high-yield method to prepare complexes of formula $(C_5Me_5)Ru(\eta^3$-allyl)L could have several potential applications, particularly for developing catalyst precursors.

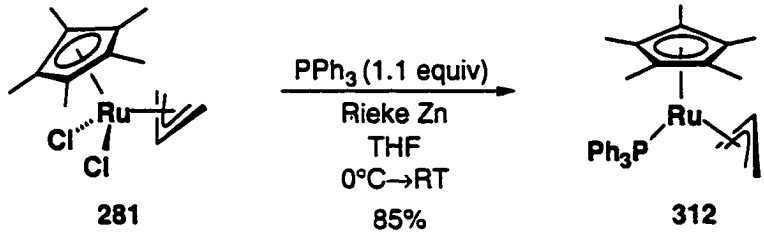
The Rieke zinc reduction of $(C_5Me_5)Ru(\eta^3$-allyl)Cl_2 under an atmosphere of carbon monoxide provides $(C_5Me_5)Ru(\eta^3$-allyl)CO as a mixture of isomers, **296**-*exo* and **296**-*endo*, in a ratio of 1.3 : 1, respectively (Eq. **145**). The configurational assignment of the two isomers was determined by comparison of the ^{1}H NMR spectra to those of known allyl complexes and by NOE difference measurements. Heating a mixture of both isomers in benzene for 24 hours results in the conversion of the *exo* isomer to the



(Eq. 145)

thermodynamically more stable *endo* isomer. Although this conversion is in accord with the allyl ligand isomerization reactions observed for the $(C_5Me_5)Ru(II)$ alkyne and olefin complexes, it is in direct contrast with the behaviour reported for the $(C_5H_5)Ru(\eta^3$-allyl)CO counterparts. In the cyclopentadienyl ruthenium system, the configurational isomerization from the *endo* to the thermodynamically more stable *exo*-allyl carbonyl complex has been described by several groups.[142] This difference can probably be attributed to steric interactions with the large pentamethylcyclopentadienyl ligand.

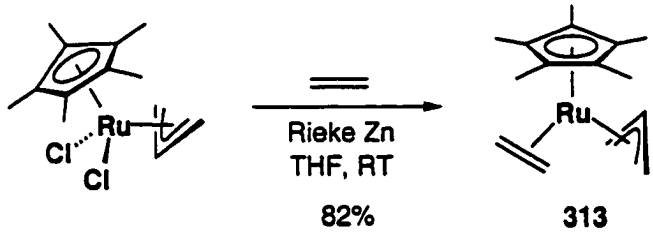
The *exo* isomer of the phosphine complex **312** is the only product isolated upon treatment of $(C_5Me_5)Ru(\eta^3$-allyl)Cl_2 with Rieke zinc in the presence of triphenylphosphine (Eq. **146**). The ^1H NMR spectrum exhibits the characteristic pattern of an *exo* allyl ligand with the exception that the H_{anti} resonances at δ 0.63 show an



(Eq. 146)

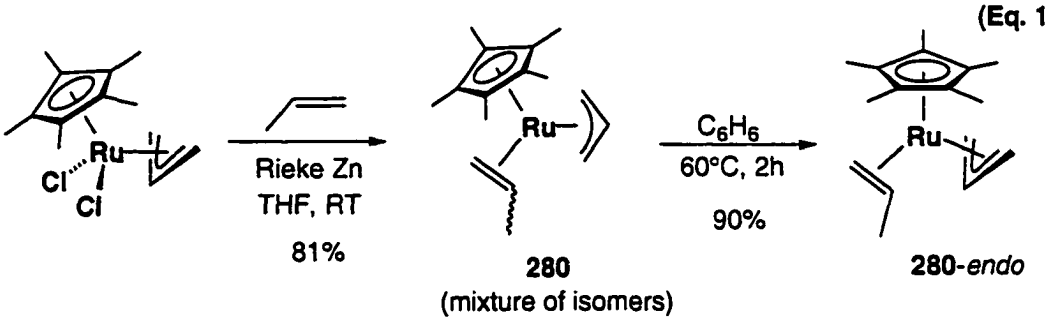
additional large coupling constant of 16.5 Hz, caused by $^{3}J_{H\text{-}P}$ coupling between the protons and the phosphine ligand. Prolonged heating of complex **312** in benzene has no effect on the configuration of the allyl ligand.

The reaction of $(C_5Me_5)Ru(\eta^3\text{-allyl})Cl_2$, Rieke zinc and ethylene in tetrahydrofuran provides the η^3-allyl η^2-ethylene complex **313** in good yield as a pale yellow crystalline material (Eq. **147**). The ^{1}H NMR spectrum of this material indicates that while complex **313** is mostly present as the *exo* isomer, a small amount (~ 8%) of the *endo* isomer is also detectable. However, no equilibrium studies were carried out on this complex.



(Eq. 147)

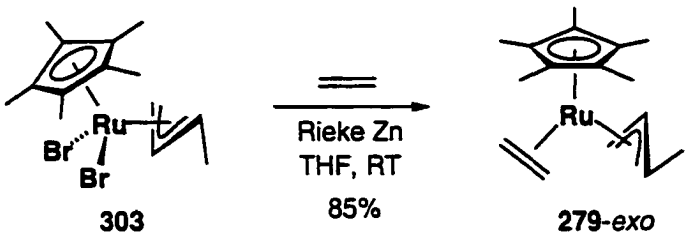
A more complicated result is obtained from the presence of propene in the zinc reduction reaction. Thus, treatment of $(C_5Me_5)Ru(\eta^3\text{-allyl})Cl_2$ with Rieke zinc under an atmosphere of propene results in the formation of a yellow, crystalline material that is thermally labile. While the mass spectral data of this material is consistent with assignment as the η^3-allyl η^2-propene complex **280**, the ^{1}H NMR spectrum exhibits resonances for at least three different isomers. Heating this mixture in the presence of excess propene in a sealed flask results in the smooth conversion to a fourth, previously undetected isomer, the known complex $(C_5Me_5)Ru(\eta^3\text{-allyl})$(propene) **280**-*endo*.[134] This isomer is quite stable in comparison to those initially formed during the reduction



(Eq. 148)

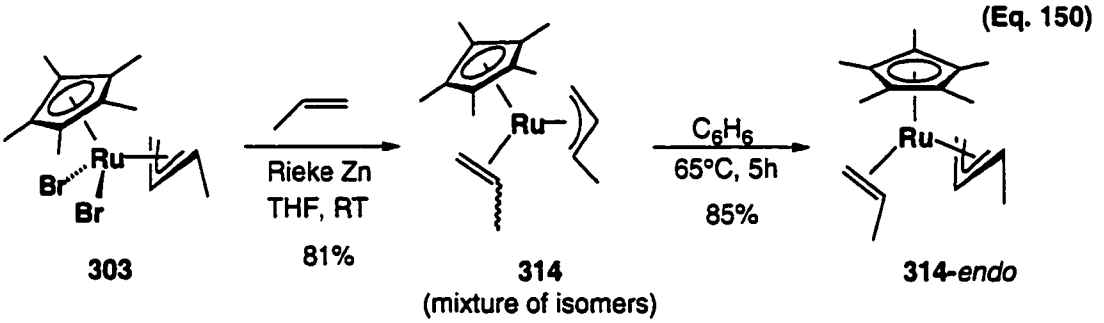
reaction and is readily recrystallized from diethyl ether/methanol. A similar difference in lability between the *exo* and the thermodynamic *endo* isomer for the analogous iridium compounds was investigated by Wakefield using molecular orbital calculations.[51] He determined that there was a marked increase in back-bonding to the olefin when the allyl ligand is in the *endo* configuration which is responsible for the added stability of the thermodynamic isomer.

Reductions of the η^3-crotyl dibromide complex in the presence of olefins correspond closely to the reactions of the unsubstituted η^3-allyl compound. Thus, the Rieke zinc reduction of crotyl dibromide **303** under an atmosphere of ethylene produces the η^3-crotyl η^2-ethylene complex in good yield as a pale yellow crystalline single isomer (Eq. **149**). This material is spectroscopically identical to the known *exo, syn* complex **279-*exo*** obtained as the kinetic product from the reaction of $[(C_5Me_5)Ru(OMe)]_2$ and ethylene.[134]



(Eq. 149)

As expected, treatment of crotyl dihalide **303** with Rieke zinc under an atmosphere of propene provides a yellow crystalline material that is very thermally labile and must be stored under an inert atmosphere at low temperatures (–35°C) (Eq. **150**). Analysis of this material by ^{1}H NMR spectroscopy shows it to be a complex mixture of isomers, with mass spectral data consistent with assignment as $(C_5Me_5)Ru(\eta^3$-crotyl)(propene) **314**. Thermolysis of this mixture in benzene under a propene atmosphere causes the conversion of the material to a single new isomer in high yield, identified as the *endo,syn* crotyl complex **314**-*endo*. This complex is thermally stable and can be recrystallized from diethyl ether/methanol.

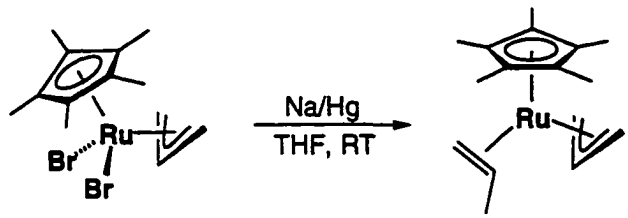


303 **314** (mixture of isomers) **314**-*endo*

(Eq. 150)

An attempt was also made to prepare the coordinated tetrahydrofuran complex by reduction of the allyl dibromide complex **281** in tetrahydrofuran in the absence of added ligand. However, treatment of $(C_5Me_5)Ru(\eta^3$-allyl)Br_2 with sodium amalgam in tetrahydrofuran provides the $(C_5Me_5)Ru(\eta^3$-allyl)(propene) complex **280**-*endo* as the only identifiable product (Eq. **151**). This complex is isolated in approximately 40% yield as the thermodynamically most stable *endo* isomer after chromatography over deactivated alumina. The same reactivity is observed when the allyl dibromide complex **281** is treated with Rieke zinc, although this reaction is much slower than the sodium amalgam

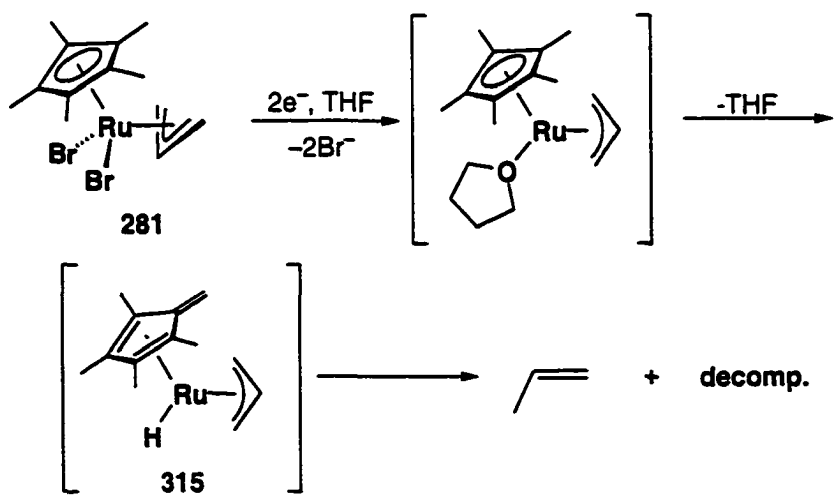
reduction. The most plausible source of propene in this reaction is the allyl ligand itself (Scheme **75**); the unsaturated intermediate formed after reduction presumably disproportionates by C-H activation of one of the methyl substituents of the η^5-C_5Me_5 ligand to form the "tuck-in" product, η^6-tetramethylfulvene hydride complex **315**, which



281 **280-*endo*** (ca. 40%) **(Eq. 151)**

may then decompose by reductive elimination of propene. The propene thus produced is available for coordination to another ruthenium center, forming the observed η^2-alkene complex **280**-*endo* in less than 50% yield. It thus appears that tetrahydrofuran is not a strong enough ligand to stabilize the Ru(II) intermediate, as was hoped. The metal-mediated C-H activation of pentamethylcyclopentadienyl ring methyl groups is known in several systems, including ruthenium.[141]

Scheme 75



281 **315**

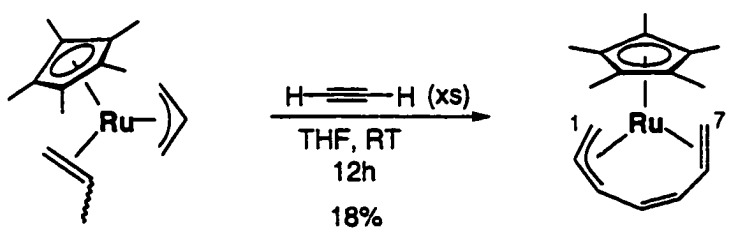
The reduction of Ru(IV) η^3-allyl dihalide complexes with Rieke zinc is an efficient, general route to a variety of complexes of formula $(C_5Me_5)Ru(\eta^3\text{-allyl})L$, where L is carbonyl, phosphine or olefin. The use of other poorly π-acidic ligands is not as successful; zinc reduction of dibromide complex **281** in the presence of excess acetonitrile, for example, results in the formation of a single pentamethylcylopentadienyl product, but it is not the expected η^3-allyl acetonitrile complex. The identity of this complex, however, has not yet been established.

3. Displacement of η^2-Propene Ligand with Alkynes

The complex mixture of isomers initially formed from the reduction of $(C_5Me_5)Ru(\eta^3\text{-allyl})Br_2$ **281** under a propene atmosphere incorporates a labile η^2-olefin ligand that can be readily displaced by a stronger ligand. This suggested an alternative route to $(C_5Me_5)Ru(\eta^3\text{-allyl})(\eta^2\text{-alkyne})$ complexes, particularly for those alkynes that do not give tractable products from the direct zinc reduction procedure. This entry into the allyl/alkyne chemistry has resulted in the discovery of additional reactivity patterns that can be mediated by the neutral ruthenium(II) system.

Treatment of the η^3-allyl propene complex **280** with excess acetylene provides a single product, the bis(acetylene) adduct **316**, albeit in low isolated yield (Eq. **152**). Decomposition of the starting material to give ruthenium powder is a significant problem during the course of this reaction. Once formed, however, the final product is both thermally and air stable and is readily purified by recrystallization from diethyl ether/methanol, providing bright yellow crystals in 18% yield. The acyclic η^2,η^3-

heptatrienyl structure assigned to the fully characterized product is suggested by the downfield chemical shifts of the internal, non-coordinating, olefin protons, located at δ 5.83 (dd, J = 5.5, 0.9 Hz, H_5) and δ 5.40 (dd, J = 5.5, 2.3 Hz, H_4) in the ^{1}H NMR spectrum. The small coupling constants to H_3 and H_6 reveal a non-planar geometry, consistent with the proposed non-conjugated structure. This complex is the first example of the neutral (C_5Me_5)Ru template incorporating two equivalents of alkyne in reaction with the η^3-allyl ligand. The mechanism of its formation is presumed to be analogous to the one earlier proposed for the closely related cationic complex, $[(\eta^6\text{-}C_6Me_6)Ru(\eta^2,\eta^3\text{-}$ 3,4-dicarbomethoxyheptatrienyl)]$^+$OTf$^-$ **179** derived from DMAD (Chapter 3, Eq. **82**). It would appear that the small size and high reactivity of acetylene again promotes the insertion of two equivalents of alkyne, but the subsequent C-H activation is preferred over cyclization as the primary reaction manifold for this neutral Ru(II) system.



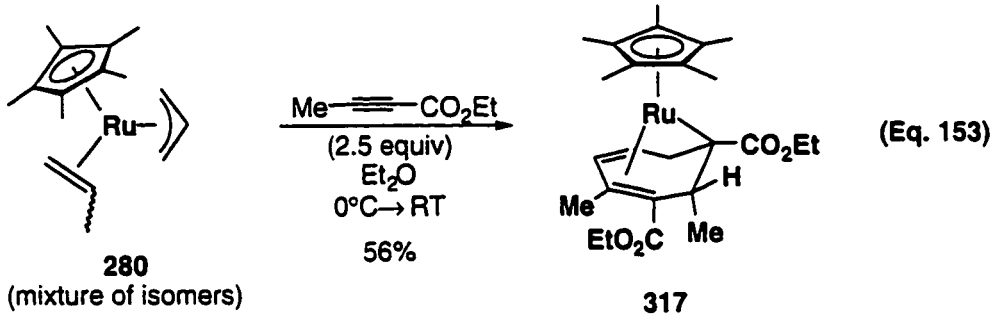
280
(mixture of isomers)

316

(Eq. 152)

Surprisingly, the treatment of the thermally labile mixture of η^3-allyl η^2-propene isomers with excess ethyl 2-butynoate leads to the formation of a single seven-membered ring product, complex **317** (Eq. **153**). This compound is isolated by chromatography on silica gel using 15% pentane/diethyl ether as eluent, which provides the product as bright yellow crystals in moderate yield. Analysis of this material by both ^{1}H and ^{13}C NMR spectroscopy indicates the product is an η^1,η^4-cycloheptadienyl complex by analogy to

the corresponding cationic products described previously; pertinent data is provided in Table **12**. In particular, the product exhibits in the ^{13}C NMR spectrum an unusually upfield carbon singlet at –32.9 ppm, assigned to the ipso carbon (C_1); the extreme chemical shift of this carbon resonance is characteristic of the η^1,η^4-cycloheptadienyl complexes. The disposition of both the ethyl ester and methyl substituents in this complex was determined unambiguously through the use of HMBC spectroscopy.



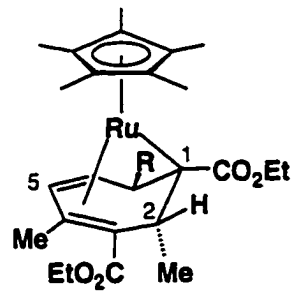
280
(mixture of isomers)

317

(Eq. 153)

This reaction is the first demonstration that the [3 + 2 + 2] allyl/alkyne cycloaddition reaction can indeed be mediated by a neutral metal, expanding the number of potential metal templates available for the development of synthetic applications. The formation of complex **317** is assumed to follow the analogous pathway to that outlined earlier for the formation of the cationic η^1,η^4-cyloheptadienyl complexes (Chapter 3, Scheme **49**). The isolation of yet another η^1,η^4-seven-membered ring ligand also confirms the stability of this unique hapticity pattern for ruthenium complexes. Thermolysis of complex **317** in benzene does not provide the η^5-cycloheptadienyl isomer, but instead leads to a complex mixture of unidentified products. This suggests that this compound is not as stable as the previous DMAD-derived η^1,η^4-cycloheptadienyl complexes, which were relatively inert under thermolysis conditions.

Table 12. Comparative ^{1}H and ^{13}C NMR Spectroscopic Data for Ethyl 2-Butynoate-Derived $(C_5Me_5)Ru(\eta^1,\eta^4$-Cycloheptadienyl) Complexes[a]



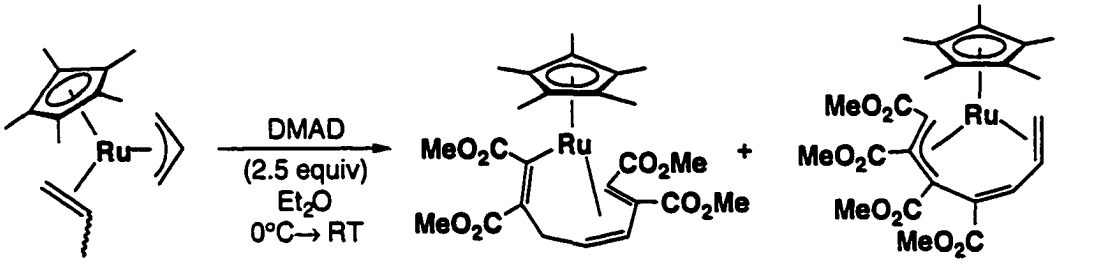
317 R = H
323 R = Me

^{1}H NMR	317	323		^{13}C NMR	317	323
H_2 $J_{2\text{-Me}}$	4.09 (q) 7.2 Hz	4.27 (q) 7.2 Hz		C_1	–32.9	–32.6
Me	0.45 (d)	0.4 (d)		C_2 J_{CH}	38.9 (d) 135 Hz	40.4 (d) 134 Hz
Me	2.29 (s)	2.27 (s)		C_3	38.3	37.3
H_5 $J_{5\text{-}6}$	4.30 (d) 8.5 Hz	4.16 (d) 8.9 Hz		C_4	104.3	104.1
H_6 $J_{6\text{-}7endo}$ $J_{6\text{-}7exo}$	3.11 (td) 8.0 Hz 1.4 Hz	2.62 (dd) b 2.0 Hz		C_5 J_{CH}	97.3 (d) 156 Hz	94.8 (d) 159 Hz
H_{7endo} $J_{7endo\text{-}7exo}$	3.18 (dd) 13.8 Hz	b		C_6 J_{CH}	40.6 (d) 157 Hz	46.9 (d) 156 Hz
H_{7exo}	2.99 (dd)	3.23(qd)		C_7 J_{CH}	28.8 (t) 130 Hz	34.7 (d) 136 Hz

[a] Spectra were taken in $CDCl_3$ at room temperature. [b] Not applicable due to non-hydrogen substituent.

A very different insertion pattern is observed in the reaction of propene complex **280** with DMAD (Eq. **154**). Two compounds are isolated from this reaction after purification by chromatography on silica gel; the major product is obtained as a bright orange crystalline material, formed in 61% yield, while the minor product is found as yellow crystals in only 12% yield. The major product is identified as the unusual *acyclic* η^1,η^4-tetracarbomethoxyheptatrienyl complex **318**, where one equivalent of alkyne appears to have inserted on each side of the original η^3-allyl ligand. This assignment is based on both extensive spectroscopic analysis (including ^1H, ^{13}C NMR, GCOSY, HMQC and HMBC experiments) and comparison to the crotyl analogue **325**, for which an X-ray crystal structure has been obtained (*vide infra*). Selected ^1H and ^{13}C NMR data for this complex are provided in Table **13**. The minor product, complex **319**, is easily recognized spectroscopically as bearing an acyclic η^2,η^3-heptatrienyl ligand due to the close similarity of the ^1H and ^{13}C NMR spectra to that of the previously assigned η^2,η^3-heptatrienyl complexes, **316**.

(Eq. 154)



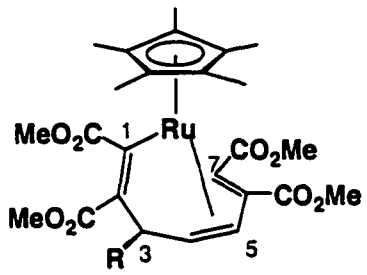
280
(mixture of isomers)

318
61%

319
12%

The unusual insertion pattern seen in the major product **318** can be rationalized in two ways, one highly speculative. In this speculative scenario, a seven-membered ring, formed by the normal sequential insertion pathway, undergoes an unprecedented ring-

Table 13. Comparative ^{1}H and ^{13}C NMR Spectroscopic Data for DMAD-Derived $(C_5Me_5)Ru(\eta^1,\eta^4$-heptadienyl) Complexes[a]

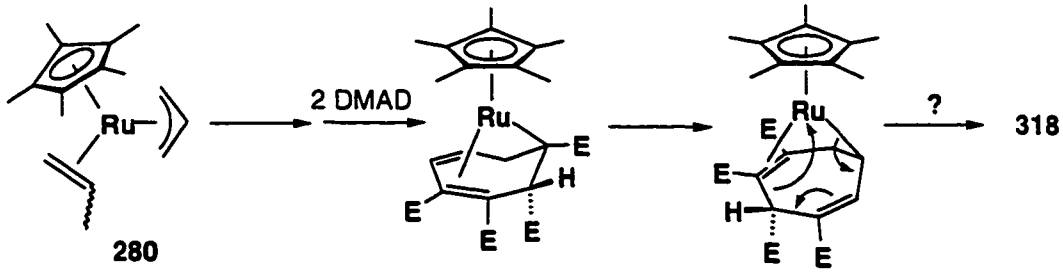


318 R = H
325 R = Me

^{1}H NMR	318	325		^{13}C NMR	318	325
H_{3endo} $J_{3endo-3exo}$ $J_{3endo-4}$	3.31 (dd) 17.7 Hz 9.5 Hz	b		C_1	179.7	176.6
H_{3exo} J_{3exo-4}	1.95 (dd) 6.2 Hz	2.30(qd) 5.2 Hz		C_2	139.7	144.1
H_4 J_{4-5}	4.04 (dt) 8.6 Hz	3.45 (dd) 8.7 Hz		C_3 J_{CH}	35.4 (t) 129 Hz	41.4 (d) 129 Hz
H_5 J_{5-7}	4.30 (dd) 0.8 Hz	4.83 (dd) 0.7 Hz		C_4 J_{CH}	72.5 (d) 153 Hz	80.7 (d) 146 Hz
H_6	b	b		C_5 J_{CH}	88.6 (d) 168 Hz	87.0 (d) 167 Hz
H_7	1.91 (d)	1.70 (d)		C_6	92.3	92.7
				C_7 J_{CH}	56.9 (d) 168 Hz	58.4 (d) 169 Hz

[a] Spectra were taken in $CDCl_3$ at room temperature. [b] Not applicable due to non-hydrogen substituent.

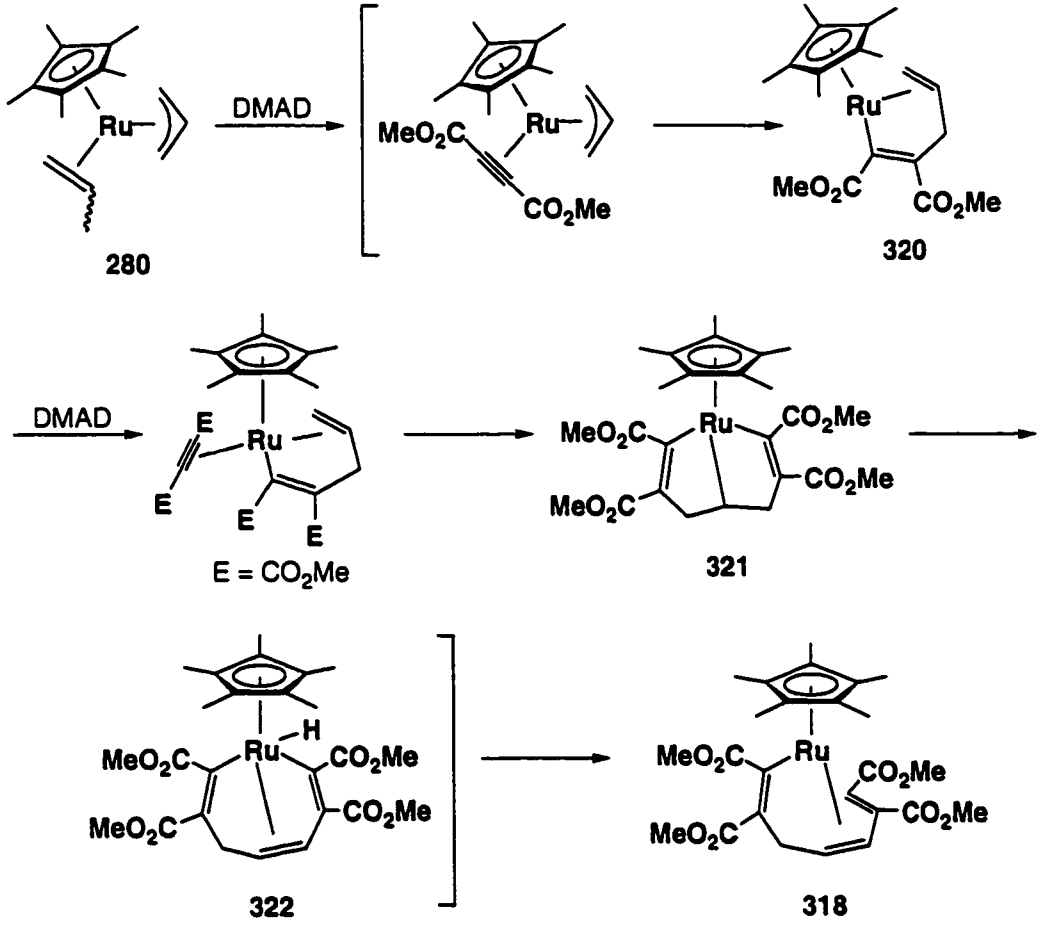
Scheme 76



opening by cleavage of a carbon-carbon single bond to provide the final product (Scheme **76**). The reaction of ethyl 2-butynoate to yield η^1,η^4-cycloheptadienyl **317** demonstrates that formation of a seven-membered ring is possible in this system, although the fact that this complex converts to a multitude of products upon mild heating suggests that clean ring-opening of the cycloheptadienyl ligand is an unlikely event.

A more plausible mechanism involves the coupling of one alkyne to each end of the η^3-allyl ligand (Scheme **77**). Although this is the first occurrence of this particular reaction pattern in our ruthenium systems, Green has reported a related product from the reaction of the tri(carbonyl)cobalt(2-methylallyl) complex with hexafluorobutyne (Chapter 1, Eq. **17**, p. 16).[25] The initial alkyne insertion in this proposed mechanism presumably follows the usual reaction pathway: initial ligand exchange with an equivalent of DMAD, followed by alkyne insertion to form vinyl olefin intermediate **320**. However, rather than inserting a second equivalent of DMAD into the metal-carbon σ-bond as expected, the coordinated alkyne instead undergoes oxidative coupling with the pendant alkene to give the divinyl intermediate **321**. This unsaturated Ru(IV) intermediate can then undergo β-hydride elimination to form the divinyl hydride **322**, with subsequent reductive coupling yielding the diene moiety of the final η^1,η^4-heptatrienyl product **318**.

Scheme 77

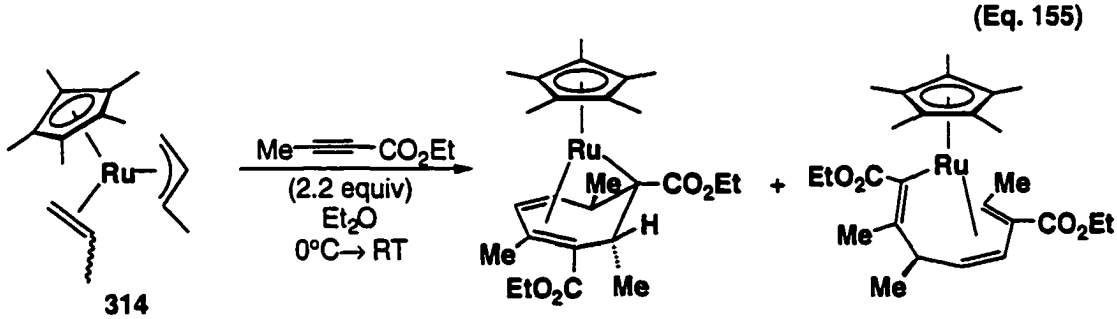


Although unexpected in this context, the metal-mediated oxidative coupling of alkenes and alkynes is well known. In particular, (η^5-C_5H_5)Ru and (η^5-C_5Me_5)Ru complexes have been extensively investigated as catalysts for alkene/alkyne coupling reactions by several groups.[144,145] While alkyne insertion into the metal-carbon σ-bond would normally be considered more facile, it may be that the stabilization provided by the electron-withdrawing ester substituent strengthens this metal-carbon bond to the extent that the coupling of the alkyne and pendant alkene becomes competitive. The formation of the minor acyclic η^2,η^3-heptatrienyl complex **319**, which presumably arises

from the "normal" sequential double insertion of DMAD, clearly defines that the energy difference between these two pathways is small.

Treatment of η^3-crotyl η^2-propene complex **314** (consisting of the kinetic mixture of thermally labile isomers) with ethyl 2-butynoate provides both the η^1,η^4-cycloheptadienyl complex **323** analogous to **317** and the acyclic η^1,η^4-heptatrienyl complex **324** (Eq. **155**), the latter as a minor byproduct. These products were separated and purified by bench-top chromatography on silica gel using 8% diethyl ether/hexane as eluent. Pertinent ^{1}H and ^{13}C NMR spectroscopic data on the major product, complex **323**, are presented in Table **12** (p. 250); the data correspond closely to the analysis of complex **317**. The disposition of the ethyl ester and methyl substituents in the minor η^1,η^4-heptatrienyl complex **324** was established through extensive analysis (including ^{1}H and ^{13}C NMR spectroscopy, as well as HMQC and HMBC experiments), which suggests a structural homology with DMAD adduct **318**.

(Eq. 155)



314
(mixture of isomers)

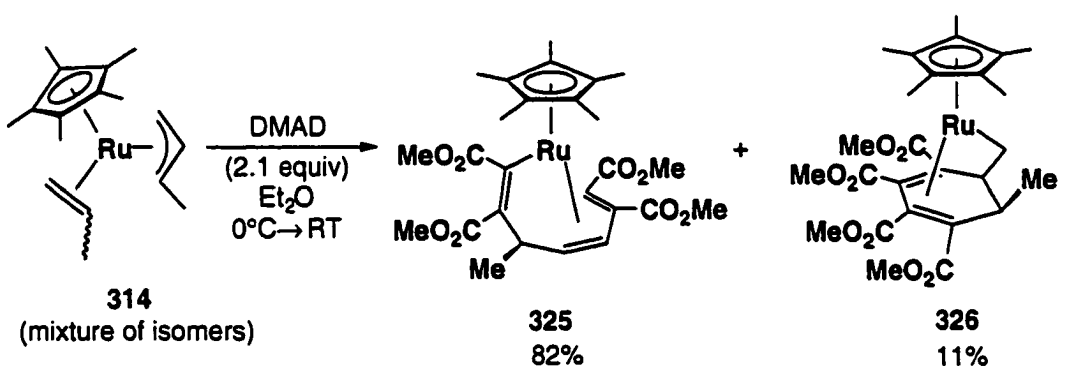
323
48%

324
16%

Finally, the addition of excess DMAD to a solution of crotyl complex **314** in diethyl ether also results in the formation of the two products, the now expected acyclic η^1,η^4-heptatrienyl complex **325** and, surprisingly, a small amount of η^1,η^4-

methanocyclohexadienyl complex **326** (Eq. **156**). Both products were separated and purified by chromatography on silica gel using 15% pentane/diethyl ether as eluent. The major product, isolated in 82% yield, provides diffractable orange crystals after slow recrystallization from dichloromethane/pentane; salient features of the structure determination are presented in Figure **16**. Consistent with earlier examples of crotyl alkyne coupling, the methyl substituent derived from the η^3-crotyl ligand is located *endo* to the ruthenium center. Selected ^1H and ^{13}C NMR spectroscopic data for complex **325** data are provided in Table **13** (p. 252), demonstrating a close structural relationship to DMAD adduct **318**.

(Eq. 156)



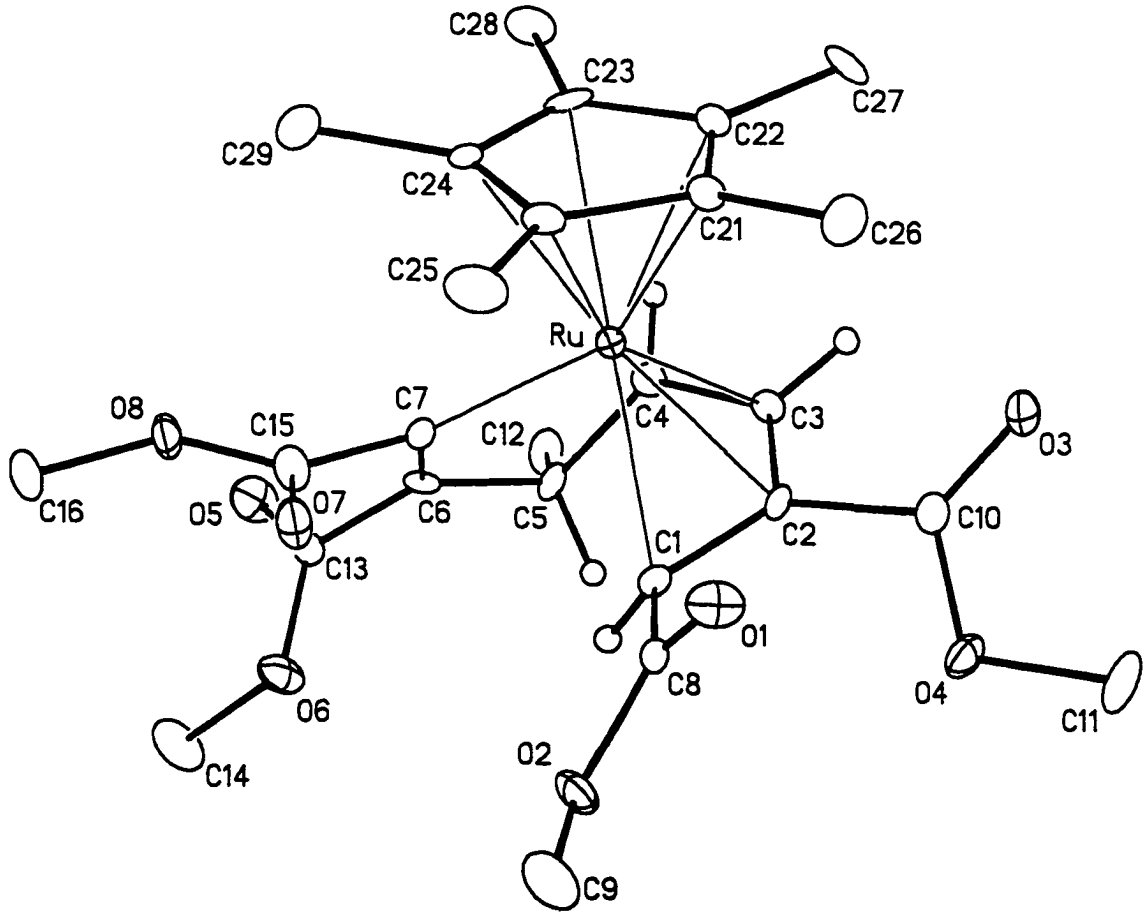
314
(mixture of isomers)

325
82%

326
11%

The minor product from the reaction of crotyl complex **314** with two equivalents of DMAD, η^1,η^4-methanocyclohexadienyl complex **326**, is very curious since the minor product from the same reaction with the η^3-allyl complex **280** is an *acyclic* η^2,η^3-heptatrienyl complex. Both of these minor products, however, derive from the "normal" double alkyne insertion sequence, so the difference can presumably be attributed to the subtle structural and energetic differences that control the partioning among the cyclization and allylic activation pathways.

Figure 16. ORTEP[113] Plot of Complex **325** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9717



Final Residuals: $R_1 = 0.0722$; $wR_2 = 0.1419$. Data obtained at -50°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): Ru-C1, 2.199(8); Ru-C2, 2.152(9); Ru-C3, 2.132(10); Ru-C4, 2.169(11); Ru-C7, 2.116(10); C1-C2, 1.425(13); C1-C8, 1.482(14); C2-C3, 1.435(13); C2-C10, 1.514(13); C3-C4, 1.393(13); C4-C5, 1.534(13); C5-C6, 1.499(14); C5-C12, 1.540(14); C6-C7, 1.319(14); C6-C13, 1.517(14); C7-C15, 1.52(2).

Selected Bond Angles (deg): C2-C1-C8, 119.3(9); C1-C2-C3, 121.6(9); C1-C2-C10, 124.1(9); C3-C2-C10, 114.3(9); C2-C3-C4, 124.1(10); C3-C4-C5, 127.6(9); C4-C5-C6, 107.5(9); C4-C5-C12, 109.6(9); C6-C5-C12, 117.5(9); C5-C6-C7, 117.1(10); C5-C6-C13, 116.0(10); C7-C6-C13, 126.6(11); C6-C7-C15, 119.7(9).

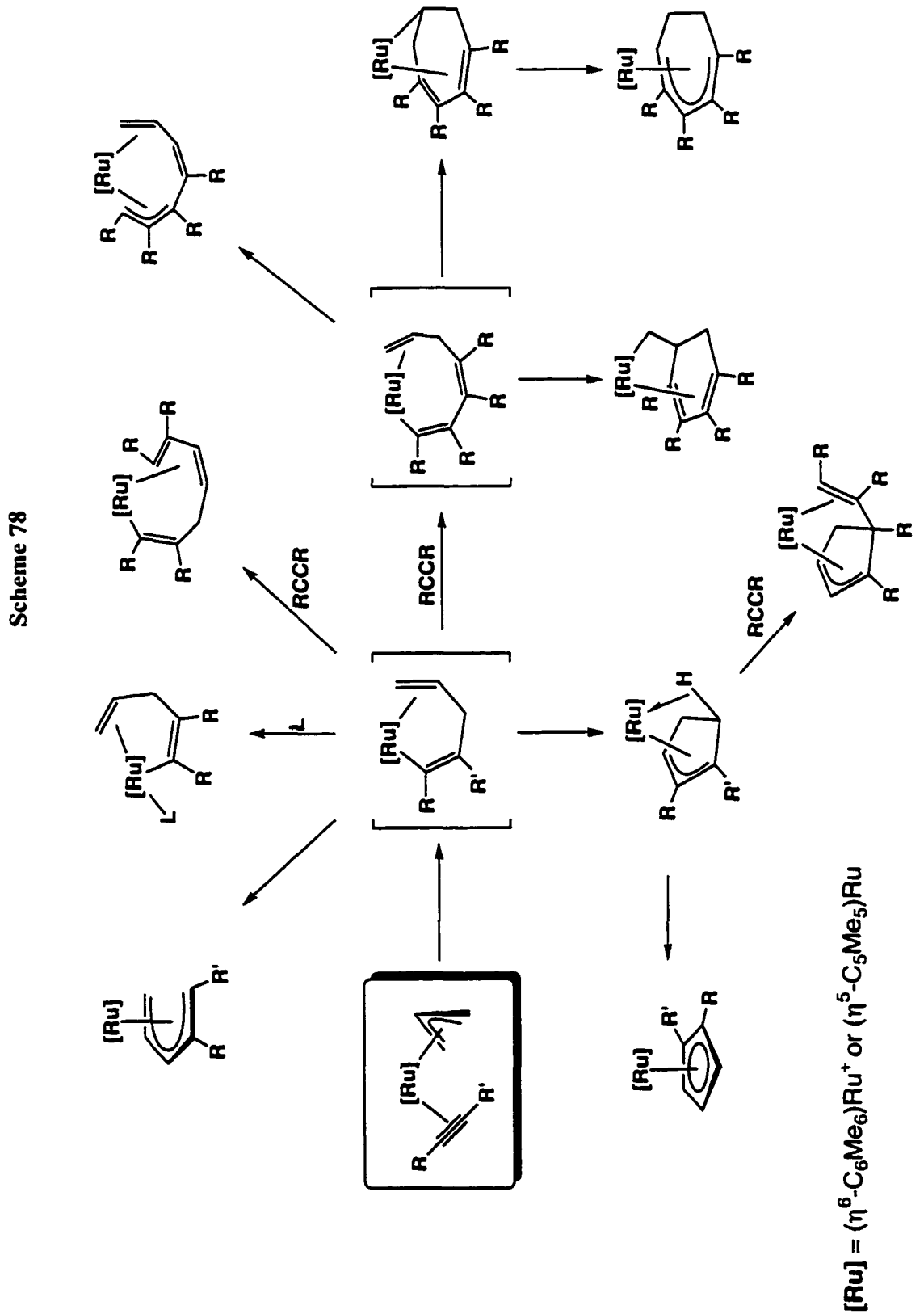
4. Conclusion

The comparison of the cationic η^6-arene and neutral η^5-pentamethyl-cyclopentadienyl Ru(II) templates leads to some interesting inferences. Although both templates generally provide [3 + 2] monoadducts from the reaction of the η^3-allyl ligand with a disubstituted alkyne, the cationic template yields primarily cyclic products while the neutral system preferentially forms acyclic complexes (Scheme **78**). This difference in reactivity is rationalized by both the inhibition of the migratory cyclization process and the greater accessibility of the Ru(IV) oxidation state for the less electrophilic pentamethylcyclopentadienyl template. Together, these effects promote the C-H bond activation pathway that results in the formation of acyclic η^5-pentadienyl products.

For both templates, the presence of electron-withdrawing substituents on the alkyne can lead to both cyclization and the formation of seven-membered ring products. Presumably this is promoted by the extra stabilization provided to the vinyl olefin intermediates by the electron-withdrawing substituent that permits the insertion of a second equivalent of alkyne. However, in the neutral (C_5Me_5)Ru(II) template, this sometimes lead to competitive alkyne/alkene coupling instead of sequential double alkyne insertion. Unfortunately, seven-membered ring formation is limited to only a few examples with either template, although the cationic system provides an intriguing complement to the reactivity of the cationic cobalt system developed by Etkin and Dzwiniel.[41-44]

In this investigation of the allyl/alkyne coupling chemistry of ruthenium(II) allyl complexes, we have isolated and characterized a bewildering variety of products. In the process, we have also contributed to a better understanding of many of the factors that

Scheme 78



[Ru] = $(\eta^6\text{-}C_6Me_6)Ru^+$ or $(\eta^5\text{-}C_5Me_5)Ru$

control the partitioning between the large number of potential reaction pathways available to ruthenium(II). This information should prove valuable in promoting selective seven-membered ring formation using other templates currently under investigation.

5. Future Research Topics

While ruthenium(II)-mediated allyl/alkyne coupling reactions are unsuitable for general organic synthetic applications due to both the complexity of the reaction manifold and the expense of stoichiometric ruthenium, this investigation has proved invaluable for providing important details about the mechanisms of these multicomponent reactions. Although this investigation was limited to the study of metal-mediated allyl/alkyne coupling, it is likely that an examination of the coupling of η^3-allyl ruthenium ligands with other reactive organic moieties, such as isocyanides, will lead to other potential applications.

This investigation focused on reactions mediated by ruthenium(II) templates, although this is not the only oxidation state available to ruthenium. Both ruthenium(III) and ruthenium(IV) η^3-allyl templates may be accessible and could potentially lead to the discovery of additional reactivity patterns upon treatment with alkynes. In particular, these higher oxidation states may evidence a greater propensity to form cyclic products due to the increased electrophilicity of the higher oxidation state metal.

However, for practical applications to organic synthesis, it is necessary for the metal involved in a stoichiometric reaction to be inexpensive, such as iron. Previous

studies on related iridium and cobalt systems have demonstrated that the economical, first row cobalt templates are *more* selective for seven-membered ring formation than is the expensive iridium template. The differences in reactivity between the apparently related iron and ruthenium systems are not trivial, however, so it is uncertain how much of this investigation will be relevant to developing a practical iron template for allyl/alkyne coupling reactions.

Chapter 6. A Preliminary Investigation of Iron(II) Templates

While ruthenium(II) complexes were found to mediate a broad range of allyl/alkyne coupling reactions, it is hoped that analogous iron templates will lead to reactivity patterns more suitable for applications in organic synthesis. To this end, an investigation into potential iron(II) templates was initiated. Preliminary results indicate that although the cationic iron(II) templates are difficult to synthesize, the neutral (C_5Me_5)iron(II) template mediates both allyl/alkyne and allyl/alkene coupling reactions.

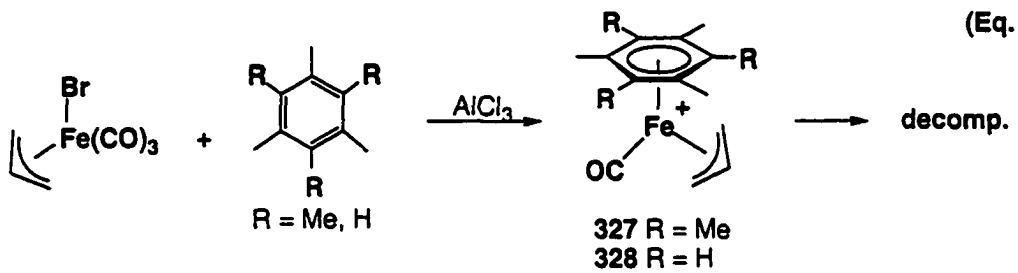
1. Reactivity of Cationic Fe(η^3-allyl) Templates

Compared to the wealth of ruthenium examples, half-sandwich (η^6-arene)iron(II) complexes are extremely rare. Most (η^6-arene)iron compounds are prepared from the conventional Fischer-Hafner synthesis, which provides sandwich complexes such as $[Fe(\eta^6\text{-arene})_2]^{2+}$,[75a] or from specialized metal vapour techniques, which have been used to generate a number of highly reactive iron(0) complexes.[145]

The only known route to (η^6-arene)iron complexes containing an η^3-allyl ligand was recently reported by Wright.[146] These carbonyl complexes, $[(\eta^6\text{-arene})Fe(\eta^3\text{-allyl})(CO)]^+PF_6^-$ (arene = benzene, hexamethylbenzene, mesitylene), are formed in the reaction of (allyl)$FeBr(CO)_3$ with arenes in the presence of a strong Lewis acid (Eq. **157**). The yields of the arene products are moderate and very dependent on the reaction

conditions, as the complexes lie on a reaction sequence that ultimately produces $[Fe(\eta^6\text{-arene})_2]^{2+}$ complexes.

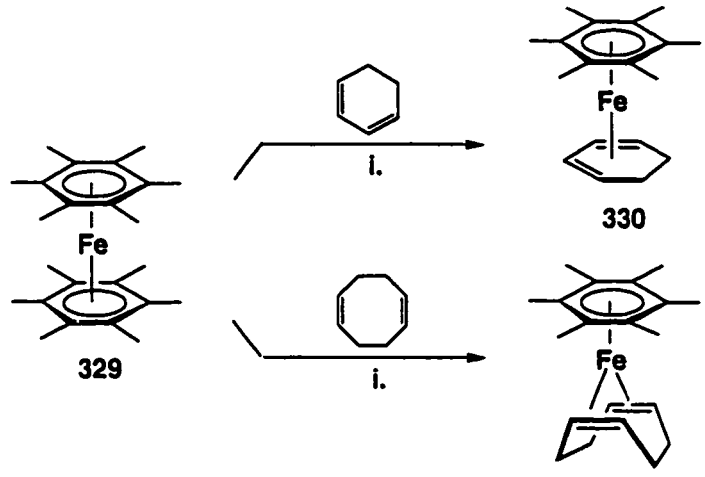
Unfortunately, all attempts to remove the carbonyl ligand of complex **327** or **328** by either photolysis or by treatment with trimethylamine N-oxide to allow alkyne coordination in the presence of excess alkyne proved unsuccessful. In each case, preferential dissociation of the arene ligand was observed, although the identity of the final iron product was not determined.



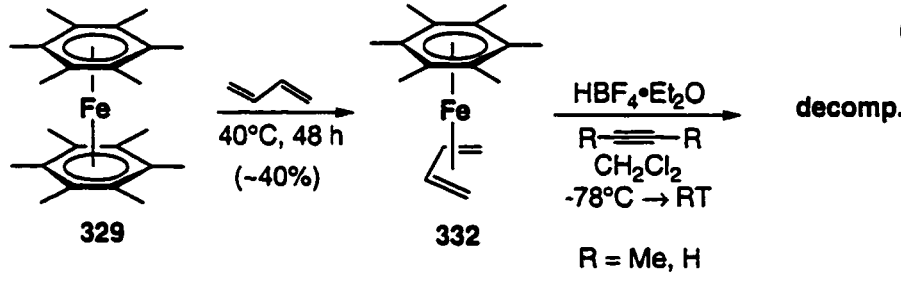
(Eq. 157)

An alternate route to the desired iron(II) η^3-allyl complexes was then devised, involving the protonation of highly reactive $(\eta^6\text{-arene})Fe(\eta^4\text{-diene})$ complexes in the presence of excess alkyne. Although many of these iron(0) compounds are prepared by metal vapour synthesis,[145] the η^6-hexamethylbenzene iron(0) η^4-diene complexes are available through ligand exchange techniques (Scheme **79**).[90,147] Thermal decomposition of the unusual $20e^-$ species, bis(hexamethylbenzene)iron(0) **329**,[148] prepared from sodium amalgam reduction of $[Fe(\eta^6\text{-}C_6Me_6)_2]^{2+}$, produces the η^4-diene iron(0) complexes **330** and **331**, while liberating an equivalent of hexamethylbenzene, as long as the reaction is conducted in neat diene. These diene complexes are subsequently isolated by fractional sublimation as extremely air-sensitive, dark red crystalline materials.

Scheme 79



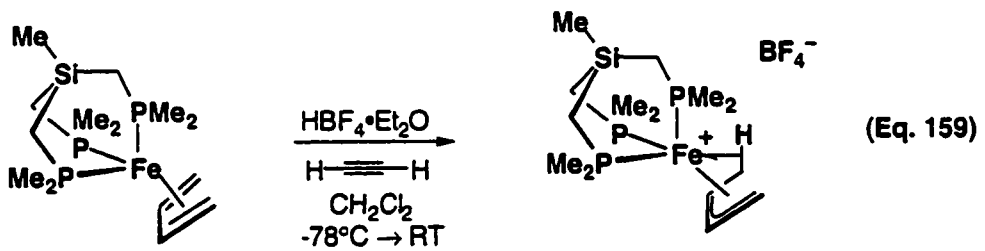
Unfortunately, our attempts to add protic acids to such $(C_6Me_6)Fe(\eta^4$-diene) complexes in the presence of excess alkyne lead only to the formation of decomposition products, consisting primarily of free hexamethylbenzene and iron(II) salts. The $(C_6Me_6)Fe(\eta^4$-butadiene) complex **332**, prepared in an analogous fashion, similarly decomposed upon addition of acid (Eq. **158**).



(Eq. 158)

Clearly, the lability of the η^6-arene ligands is a significant problem with these iron systems. As a more stable alternative to the η^6-hexamethylbenzene ancillary ligand, the use of the tridentate trialkylphosphine ligand, $MeSi(CH_2PMe_2)_3$ (SiP_3) was evaluated.

This ligand is a bulky six-electron donor similar to hexamethylbenzene, but is much less likely to dissociate from the iron center due to the greater donating character of the phosphine groups.[149] Thus, the known $(SiP_3)Fe(\eta^4\text{-butadiene})$[149] complex **333** was prepared and treated with tetrafluoroboric acid in the presence of excess acetylene (Eq. **159**). However, the only product isolated from the reaction mixture is a red crystalline material that does not incorporate any alkyne. This material is tentatively identified as the agostic η^3-crotyl complex **334**, on the basis of ^{1}H NMR spectroscopic analysis. A closely related agostic complex is formed upon protonation of the tris(phosphine) complex $(PMe_3)_3Fe(\eta^4\text{-butadiene})$.[150] Although the agostic appears to prevent the coordination of alkyne in this template, it is plausible that the *syn*-crotyl isomer would mediate allyl/alkyne coupling.



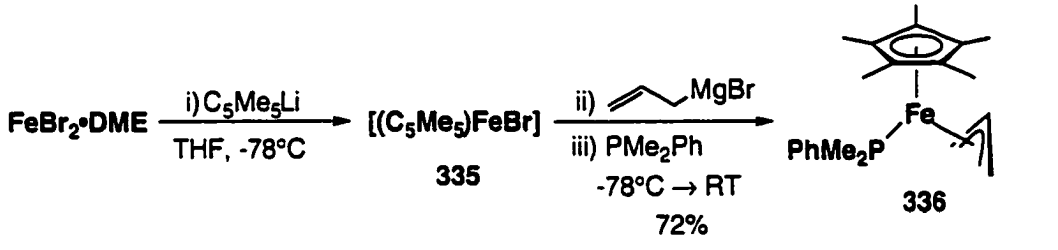
333 **334** **(Eq. 159)**

2. Reactivity of Neutral $(C_5Me_5)Fe(\eta^3\text{-allyl})$ Template

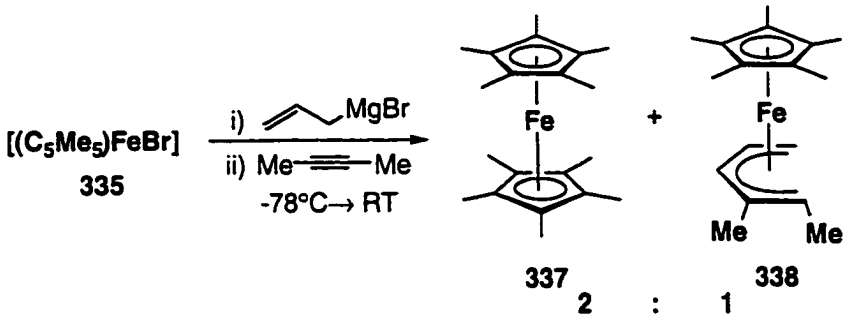
In comparison to the $(\eta^6$-arene)iron chemistry, the corresponding $(\eta^5$-cyclopentadienyl)iron chemistry is well-established. Several complexes of the formula $(C_5Me_5)Fe(\eta^3\text{-allyl})L$ (L = CO, PR_3) have been previously reported,[151] although the synthetic routes used are not suitable for our purposes. However, a report by Kölle[152]

outlines a method of preparing the transient complex $(C_5Me_5)FeBr$ **335** at –80°C from the reaction of $FeBr_2$•DME and C_5Me_5Li. This reactive species can then be treated with C_5H_5Li or carbon monoxide to synthesize $(C_5Me_5)Fe(C_5H_5)$ or $(C_5Me_5)Fe(CO)_2Br$, respectively. Using this method, complex **335** (prepared *in situ*) was treated with allylmagnesium bromide and dimethylphenylphosphine, providing the known[151a] complex $(C_5Me_5)Fe(\eta^3\text{-allyl})PMe_2Ph$ **336** in good yield (Eq. **160**). This one-pot procedure represents a significant improvement on the literature synthesis of η^3-allyl complex **336** and demonstrates the feasibility of preparing η^3-allyl iron complexes by this route.

(Eq. 160)

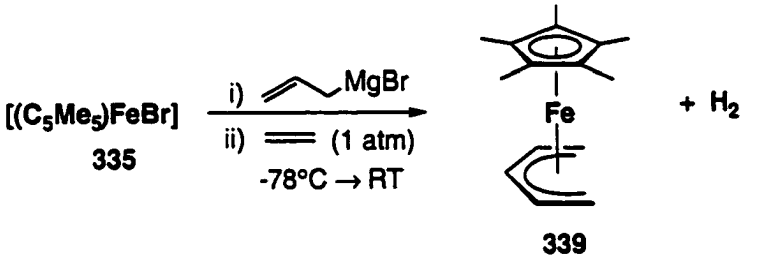


When the iron bromide complex **335** was prepared *in situ* and treated with allylmagnesium bromide in the presence of excess 2-butyne (7.8 equiv), two products were observed in the crude reaction mixture (Eq. **161**). The major product is easily identified as decamethylferrocene (**337**) while the minor product is assigned as $(C_5Me_5)Fe(\eta^5\text{-}1,2\text{-dimethylpentadienyl})$ **338** on the basis of the close spectroscopic resemblance to the ruthenium analogue **285**.



(Eq. 161)

Curiously, conducting the allylation reaction under an ethylene atmosphere does not produce the expected η^2-ethylene complex. Instead, the major product is tentatively identified as the $(C_5Me_5)Fe(\eta^5$-pentadienyl) **339**, apparently arising from coupling of an intermediate η^3-allyl η^2-ethylene complex with subsequent dehydrogenation. This reaction demonstrates that allyl/alkene coupling is feasible using the neutral $(C_5Me_5)Fe(II)$ template and suggests potentially interesting new areas of research.



(Eq. 162)

While this preliminary investigation of iron(II) chemistry serves primarily to highlight the potential difficulties of extending allyl/alkyne cycloadditions to the first row metal, further experimentation may lead to more promising results.

Experimental Procedures

Reagents and Methods. All manipulations on air sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques, or in a Vacuum Atmospheres He-553-2 Dri-lab equipped with a Mo-41-1 inert gas purifier and a CD-882 Dri-Cold Freezer maintained at –35°C. Vacuum transfer of volatile reagents was performed at high vacuum (10^{-5} mm Hg) using a MKS Baratron digital pressure transducer for measurement of gas pressure in known volume flasks. Toluene, benzene, tetrahydrofuran, diethyl ether, hexane and pentane were distilled from sodium/ benzophenone ketyl or sodium (potassium)/benzophenone ketyl. Reagent grade acetone was degassed and stored under nitrogen with no further purification. Dichloromethane and acetonitrile were distilled from calcium hydride and degassed. Acetylene was used without further purification. Unless stated otherwise, all reactions were carried out under a nitrogen atmosphere. Photolysis was carried out using a Hanovia 450 watt high pressure mercury lamp filtered through Pyrex. Reactions requiring greater than atmospheric pressure were carried out in reactors consisting of a thick-walled bottle, commercially available from Fisher-Porter, fitted with a safety pressure release, a sample withdrawal port, and a quick-connect hookup. IR spectra were recorded on a Nicolet Magna IR 750 or a Nicolet 20SX spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), Bruker AM-360 (^{1}H, 360 MHz), Bruker AM-300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) or a Varian Unity-Inova 300 (^{1}H, 300 MHz) spectrometer. High resolution mass spectra were obtained on a Kratos MS-50 spectrometer (electron impact ionization (EI)) and elemental analyses were performed by the University of Alberta Microanalysis Laboratories.

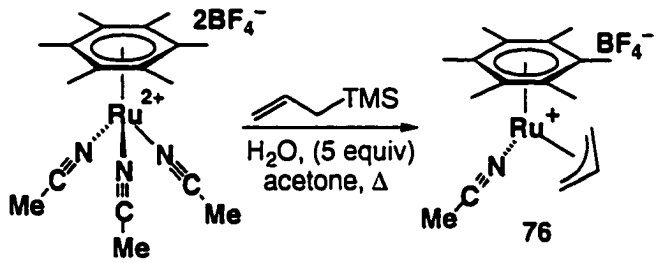
Further Notes on Spectroscopic Methods. Chemical shifts are reported relative to residual protiated solvent. In ^{1}H NMR spectral data, values of the coupling constants are either obtained directly from the spectrum, or extracted using standard homonuclear decoupling techniques. Although generally measured to ±0.1 Hz, J values are self-consistent only to ±1 Hz. GCOSY denotes the standard COSY experiment, acquired using field gradients. Data for the ^{1}H-^{1}H COSY or GCOSY is presented such that correlations are listed only once. Values of $^1J_{CH}$ are obtained either directly from the gated decoupled spectrum, or from the coupled HMQC spectrum. ^{1}H-^{13}C HETCORR and ^{1}H-^{13}C BIRDTRAP experiments are recorded at the ^{13}C frequency of the spectrometer, while HMQC and HMBC are recorded at the ^{1}H frequency.

The following compounds were prepared by published procedures: $[(C_6Me_6)RuCl_2]_2$ (**72**),[46b] $[(C_6Me_6)Ru(CH_3CN)_3]^+BF_4^-$ (**75**),[45] cyclooctyne,[153] $[(C_5Me_5)RuCl_2]_2$,[154] $[(C_5Me_5)RuCl]_4$,[92a] $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (**137**),[105] $[Cp_2Fe]^+PF_6^-$,[102a] $[(C_6Me_6)Ru(\eta^5\text{-cycloheptadienyl})]^+Cl^-$ (**159**),[90] $[(C_6Me_3H_3)RuCl_2]_2$ (**189**),[45] $(C_6Me_6)Ru(\eta^4\text{-cyclohexadiene})$ (**227**),[90] $(C_5Me_5)Ru(C_3H_5)Br_2$ (**281**),[135a] $(C_5Me_5)Ru(1\text{-}MeC_3H_4)Br_2$ (**303**),[135a] $(C_6Me_6)Fe(\eta^3\text{-allyl})(CO)$ (**327**),[146] $(C_6Me_3H_3)Fe(\eta^3\text{-allyl})(CO)$ (**328**),[146] $(C_6Me_6)_2Fe$ (**329**),[149] $(MeSi(CH_2PMe_2)_3)Fe(\eta^4\text{-1,3-butadiene})$ (**333**),[149] $FeBr_2$•DME.[152]

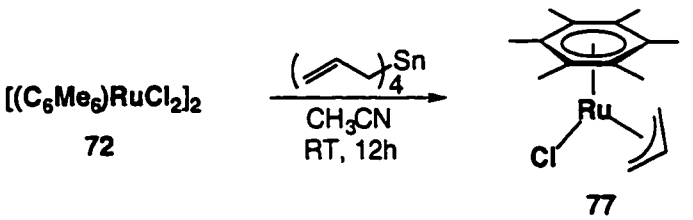
2,8-Decadiyne was prepared by the reaction of 1,7-octadiyne (Aldrich) and 2 equivalents of butyllithium at -78°C followed by treatment with 2 equivalents of methyl iodide, warming to room temperature, and stirring for several hours before standard aqueous workup and distillation.

Rieke zinc was prepared by lithium reduction of anhydrous $ZnCl_2$ using a catalytic amount of napthalene as the electron carrier, according to the procedure developed by Rieke.[136b] The Rieke zinc was subsequently stored under inert atmosphere for time periods lasting up to three months.

Chapter 2 Experimental

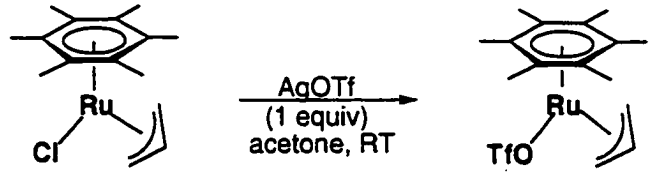


$[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(CH_3CN)]^+BF_4^-$ (76). A yellow solution of $[(C_6Me_6)Ru(CH_3CN)_3]^{2+}(BF_4^-)_2$ (0.060 g, 0.107 mmol) in 4 mL degassed acetone was placed in a small two-necked round-bottom equipped with reflux condenser and septum. Allyltrimethylsilane (0.100 mL, 0.629 mmol) and distilled water (0.100 mL) were then added by syringe and the reaction mixture was heated to reflux for 10 hours. Afterwards the solvent was evaporated under reduced pressure to give an orange solid. After thorough drying the product was recrystallized from acetone/diethyl ether to afford 0.041 g (89%) of orange needles. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.36 (tt, J = 11.0, 6.8 Hz, 1H, $H_{central}$), 3.14 (d, J = 6.8 Hz, 2H, H_{syn}), 2.45 (s, 3H, $\underline{CH_3}CN$), 2.15 (s, 18 H, C_6Me_6), 1.87 (d, J = 11.1 Hz, 2H, H_{anti}); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 125.5 ($CH_3\underline{C}N$), 99.3 ($\underline{C}_6Me_6$), 88.9 ($C_{central}$), 52.3 ($C_{terminal}$), 15.7 ($C_6\underline{Me}_6$), 3.8 ($\underline{CH_3}CN$). Analysis calculated for $C_{17}H_{26}BF_4NRu$: C, 47.24%; H, 6.06%; N, 3.24%; found: C, 47.06%; H, 5.95%; N, 3.16%.



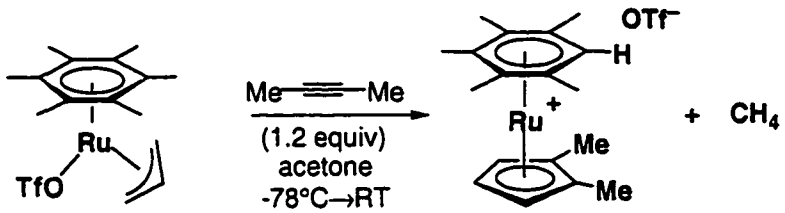
77

(η^6-C_6Me_6)Ru(η^3-C_3H_5)Cl (77). A 300 mL, oven-dried Schlenk flask was charged with $[(C_6Me_6)RuCl_2]_2$ (1.60 g, 2.39 mmol) and 200 mL of acetonitrile and the resulting red slurry placed under nitrogen. Tetraallyltin (1.36 mL, 4.80 mmol) was added via syringe and the reaction mixture stirred at room temperature for 12 hours, giving a clear orange solution (1.1 equivalents of tetraallytin is also effective but longer reaction times are required). Acetonitrile was removed by rotary evaporation leaving an oily orange residue. This crude mixture was placed under vacuum, then transferred to the dry box where it was rinsed with several portions of diethyl ether to remove triallyltin chloride and unreacted tetraallyltin. The crude product was then recrystallized from toluene/hexane to give 1.48 g (91%) of orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.31 (tt, J = 11.0, 6.8 Hz, 1H, $H_{central}$), 3.14 (d, J = 6.8 Hz, 2H, H_{syn}), 2.31 (d, J = 10.9 Hz, 2H, H_{anti}), 2.05 (s, 18H, C_6Me_6); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 96.2 ($\underline{C}_6Me_6$), 88.7 ($C_{central}$), 53.8 ($C_{terminal}$), 15.3 ($C_6\underline{Me}_6$). Analysis calculated for $C_{15}H_{23}ClRu$: C, 53.01%; H, 6.82%; found: C, 52.96%; H, 6.89%.



77 78

(η^6-C_6Me_6)Ru(η^3-C_3H_5)OTf (78). A solution of (C_6Me_6)Ru(η^3-C_3H_5)Cl (1.007 g, 2.96 mmol) in acetone (100 mL) was degassed and placed under nitrogen atmosphere. A solution of AgOTf (0.776 g, 3.02 mmol, 1.02 equiv) in acetone (5 mL) was then added via syringe and a white precipitate was immediately observed. The reaction mixture was allowed to stir at room temperature for a further 2 hours. The mixture was quickly filtered through Celite to remove insoluble silver salts and the bright orange solution concentrated in vacuo. The resulting air sensitive solid was transferred to the dry box where it was dissolved in toluene and filtered through Celite again to remove any remaining traces of silver salt. The toluene was removed by evaporation under reduced pressure to give 1.185 g (88%) of an orange solid (pure by 1H NMR), which was kept stored under nitrogen. This solid slowly turns brown on exposure to oxygen. IR ($CHCl_3$ cast, cm^{-1}): 1389 (m), 1251 (s), 1168 (s), 1045 (m), 1032 (m), 650 (m), 637 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 3.63 (d, J = 6.8 Hz, 2H, Hsyn), 3.38 (m, 1H, $H_{central}$), 2.45 (d, J = 11.3 Hz, 2H, H_{anti}), 2.15 (s, 18H, C_6Me_6); $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ 98.2 (C_6Me_6), 93.1 ($C_{central}$), 58.3 ($C_{terminal}$), 15.6 (C_6Me_6). Triflate carbon signal was not observed. Analysis calculated for $C_{16}H_{23}F_3O_3RuS$: C, 42.38%; H, 5.11%; found: C, 42.53%; H, 5.08%.

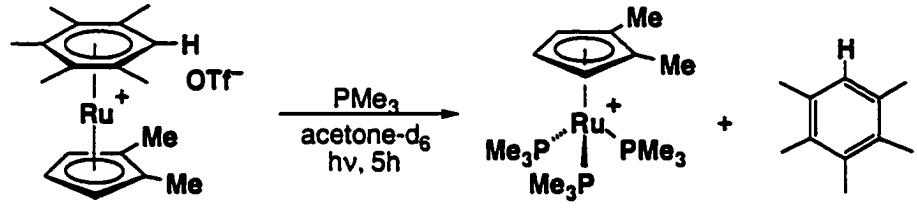


78 79

[(η^6-C_6Me_5H)Ru(η^5-$C_5H_3Me_2$)]$^+$OTf$^-$ (79). A solution of (η^6-C_6Me_6)Ru(η^3-C_3H_5)OTf (0.060 g, 0.132 mmol) in approximately 1.5 mL of acetone was placed in a small, oven-dried glass reaction bomb equipped with stir-bar, and degassed via three freeze-pump-thaw cycles. 2-Butyne (0.0086 g, 0.159 mmol, 1.2 equiv) was then added by vacuum transfer to the solution. The reaction mixture was allowed to warm to room temperature at which point the solution rapidly turned colour from orange to yellow. After 30 minutes the solvent was evaporated under reduced pressure to give a light yellow solid. The product was recrystallized from acetone/diethyl ether to afford 0.051 g (79%) of small white needles. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.01 (s, 1H, $C_6Me_5\underline{H}$), 4.89 (d, J = 2.4 Hz, 2H, $C_5\underline{H}_3Me_2$), 4.83 (t, J = 2.4 Hz, 1H, $C_5\underline{H}_3Me_2$), 2.26 (s, 3H, $C_6\underline{Me}_5H$), 2.25 (s, 6H, $C_6\underline{Me}_5H$), 2.21 (s, 6H, $C_6\underline{Me}_5H$), 1.77 (s, 6H, $C_5H_3\underline{Me}_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 99.5 (s, $\underline{C}_6Me_5H$), 99.2 (s, $\underline{C}_6Me_5H$), 99.0 (s, $\underline{C}_6Me_5H$), 95.0 (s, $\underline{C}_5H_3Me_2$), 89.4 (d, $^1J_{CH}$ = 173.7 Hz, $\underline{C}_6Me_5H$), 81.4 (d, $^1J_{CH}$ = 175.8 Hz, $\underline{C}_5H_3Me_2$), 79.2 (d, $^1J_{CH}$ = 181.4 Hz, $\underline{C}_5H_3Me_2$), 18.9 (q, $^1J_{CH}$ = 128.5 Hz, $C_6\underline{Me}_5H$), 15.8 (q, $^1J_{CH}$ = 129.0 Hz, $C_6\underline{Me}_5H$), 15.3 (q, $^1J_{CH}$ = 128.1 Hz, $C_6\underline{Me}_5H$), 10.2 (q, $^1J_{CH}$ = 128.5 Hz, $C_5H_3\underline{Me}_2$). Triflate carbon signal was not observed. ^{1}H-^{13}C HETCORR (100 MHz, $CDCl_3$): δ 89.4 ($\underline{C}_6Me_5H$)↔ δ 6.01 ($C_6Me_5\underline{H}$); δ 81.4 ($\underline{C}_5H_3Me_2$) ↔ δ 4.89 ($C_5\underline{H}_3Me_2$); δ 79.2 ($\underline{C}_5H_3Me_2$) ↔ δ 4.83 ($C_5\underline{H}_3Me_2$); δ 18.9 ($C_6\underline{Me}_5H$) ↔ δ 2.25

($C_6\underline{Me}_5H$); δ 15.8 ($C_6\underline{Me}_5H$) ↔ δ 2.26 ($C_6\underline{Me}_5H$); δ 15.3 ($C_6\underline{Me}_5H$) ↔ δ 2.21 ($C_6\underline{Me}_5H$); δ 10.2 ($C_5H_3\underline{Me}_2$) ↔ δ 1.77 ($C_5H_3\underline{Me}_2$). Analysis calculated for $C_{19}H_{25}F_3O_3RuS$: C, 46.43%; H, 5.13%; found: C, 46.70%; H, 4.84%.

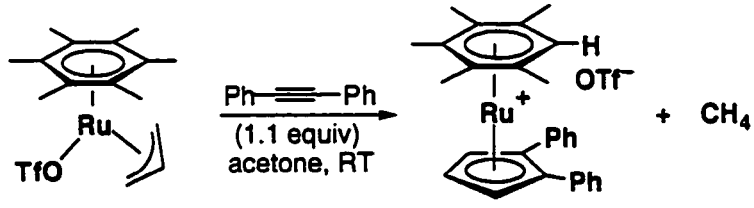
Detection of Methane. A solution of [(η^6-C_6Me_6)Ru(η^3-C_3H_5)OTf (0.016 g, 0.035 mmol) in approximately 0.4 mL of acetone-d6 was transferred to an NMR tube equipped with a Schlenk line adapter. The solution was degassed by three freeze-pump-thaw cycles and 2-butyne (0.0022 g, 0.040 mmol) added via vacuum transfer. The reaction was placed under a nitrogen atmosphere and sealed, then warmed to room temperature and allowed to stand for 24 hours. At this time the ^{1}H NMR spectrum showed complete conversion to [(η^6-C_6Me_5H)Ru(η^5-$C_5H_3Me_2$)]$^+$OTf$^-$, plus an additional singlet at δ 0.15. A sample of methane (natural gas line) was added via gas-tight syringe and the upfield signal increased in intensity accordingly.



79 80

Decomplexation and Identification of C_6Me_5H. A solution of [(η^6-C_6Me_5H)Ru(η^5-$C_5H_3Me_2$)]$^+$OTf$^-$ (**79**) (0.010 g, 0.020 mmol) in approximately 0.4 mL of acetone-d_6 was transferred to an NMR tube equipped with a Schlenk line adapter. The solution was degassed by three freeze-pump-thaw cycles and trimethylphosphine (0.005 g, 0.065 mmol) added via vacuum transfer. The NMR tube was then photolyzed for 5

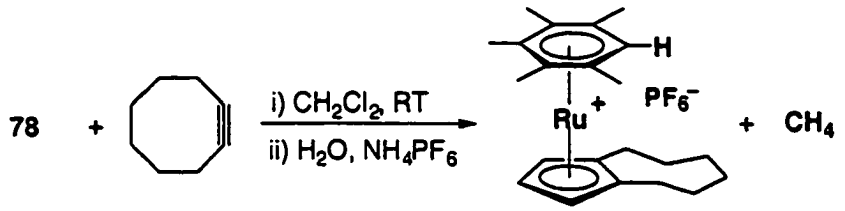
hours, at which point no further changes were observed in the ^{1}H NMR spectrum. The final reaction mixture was found to consist of $[(\eta^5\text{-}C_5H_3Me_2)Ru(PMe_3)_3]^+OTf^-$ (**80**) (tentatively assigned) and starting material (4:1), along with free pentamethylbenzene, as determined by ^{1}H NMR spectroscopy. An authentic sample of pentamethylbenzene (Lancaster) was added and the corresponding peaks [^{1}H NMR (300 MHz, acetone-d_6): δ 6.75 (s, 1H, $C_6Me_5\underline{H}$), 2.17 (s, 6H, $C_6\underline{Me_5}H$), 2.15 (s, 3H, $C_6\underline{Me_5}H$), 2.11 (s, 6H, $C_6\underline{Me_5}H$)] were observed to increase in intensity accordingly. ^{1}H NMR (300 MHz, acetone-d_6) of $[(\eta^5\text{-}C_5H_3Me_2)Ru(PMe_3)_3]^+OTf^-$ (**80**): δ 4.90 (d, J = 2.5 Hz, 2H, $C_5\underline{H_3}Me_2$), 4.64 (t, J = 2.5 Hz, 1H, $C_5\underline{H_3}Me_2$), 1.95 (q, $J_{H\text{-}P}$ = 1.25 Hz, 6H, $C_5H_3\underline{Me_2}$), 1.59 (m, 'goal-post' pattern, 27H, PMe_3). This material was not isolated or further characterized.



78 81

[(η^6-C_6Me_5H)Ru(η^5-$C_5H_3Ph_2$)]$^+$OTf$^-$ (81). Diphenylacetylene (0.013 g, 0.073 mmol) and (η^6-C_6Me_6)Ru(η^3-C_3H_5)OTf (0.030 g, 0.066 mmol) were placed in a small Schlenk flask capped with a rubber septum. A nitrogen atmosphere was established by evacuating and backfilling three times. Acetone (2 mL) was added via syringe and the resultant solution was stirred under nitrogen at room temperature for 1 hour. The solvent was then removed *in vacuo* to yield a bright yellow residue from which the

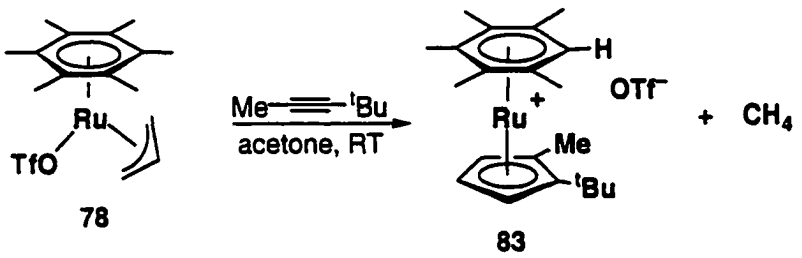
product was recrystallized from acetone/diethyl ether to give 0.039 g (96%) of white needles. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33-7.29 (m, 6H, H_{Ph}), 7.20-7.17 (m, 4H, H_{Ph}), 6.08 (s, 1H, $C_6Me_5\underline{H}$), 5.41 (d, J = 2.5 Hz, 2H, $C_5\underline{H}_3Ph_2$), 5.34 (t, J = 2.5 Hz, 1H, $C_5\underline{H}_3Ph_2$), 2.15 (s, 3H, $C_6\underline{Me}_5H$), 2.12 (s, 6H, $C_6\underline{Me}_5H$), 2.04 (s, 6H, $C_6\underline{Me}_5H$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 130.5, 129.0, 128.9, 128.7, 100.5, 100.2, 98.0, 90.7, 82.4, 81.2, 18.9, 16.0, 15.3. Triflate carbon signal was not observed. Analysis calculated for $C_{29}H_{29}F_3O_3RuS$: C, 56.58%; H, 4.75%; found: C, 56.38%; H, 4.62%.



82

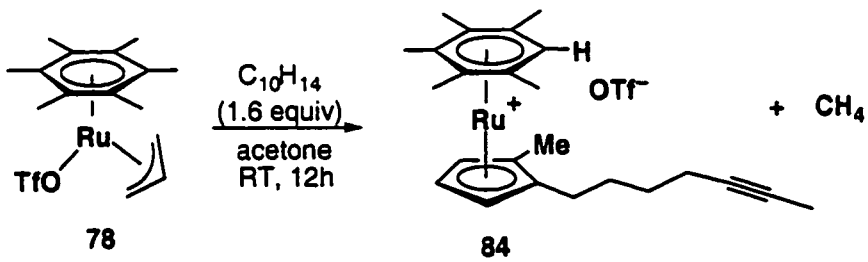
[(η^6-C_6Me_5H)Ru(η^5-$C_5H_3(CH_2)_6$)]$^+PF_6^-$ (82). A solution of (C_6Me_6)Ru(η^3-C_3H_5)OTf (0.030 g, 0.066 mmol) in 5 mL of dichloromethane was prepared in a small Schlenk flask equipped with a rubber septum and placed under a nitrogen atmosphere. Freshly distilled cyclooctyne (0.025 mL, 0.20 mmol) was introduced via microliter syringe. The reaction mixture was allowed to stir at room temperature for 4 hours before removing the solvent *in vacuo*. The crude product was converted to the more crystalline hexafluorophosphate salt by dissolving the brown residue in a minimum of warm distilled water and adding an excess of NH_4PF_6. A white precipitate immediately formed and collected by filtration. The crude product was recrystallized from dichloromethane/diethyl ether to yield 0.025 g (72%) of colourless needles. ^{1}H

NMR (300 MHz, $CDCl_3$): δ 6.06 (s, 1H, $C_6Me_5\underline{H}$), 4.97 (t, J = 2.4 Hz, 1H, $C_5\underline{H}_3(CH_2)_6$), 4.88 (d, J = 2.4 Hz, 2H, $C_5\underline{H}_3(CH_2)_6$), 2.29 (s, 9H, $C_6\underline{Me}_5H$), 2.24 (s, 6H, $C_6\underline{Me}_5H$), 2.19 (m, 2H, cyclooctyl ring, partially obscured), 2.04 (m, 2H, cyclooctyl ring), 1.46-1.24 (m, 6H, cyclooctyl ring); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 99.4, 99.3, 99.2, 99.0, 89.6, 81.0, 80.5, 30.8, 25.4, 24.2, 19.3, 16.4, 15.6, triflate carbon signal not observed. Analysis calculated for $C_{22}H_{31}F_6PRu$: C, 48.80%; H, 5.77%; found: C, 49.09%; H, 6.03%.



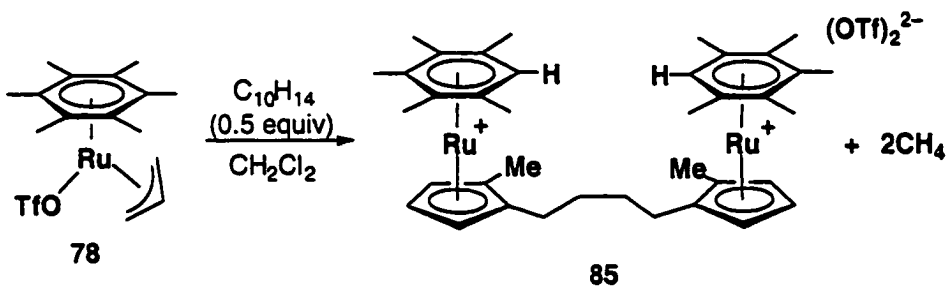
[(η^6-C_6Me_5H)Ru(η^5-$C_5H_3Me^tBu$]$^+OTf^-$ (83). A solution of $(C_6Me_6)Ru(\eta^3\text{-}C_3H_5)OTf$ (0.054 g, 0.119 mmol) in approximately 4 mL of acetone was placed in a small, oven-dried glass reaction bomb and degassed via several freeze-pump-thaw cycles. 4,4-Dimethyl-2-pentyne (0.60 mmol) was then added by vacuum transfer to the solution. The reaction mixture was allowed to warm to room temperature with stirring; the solution gradually turned colour from orange to bright yellow. After 1 hour the solvent was evaporated under reduced pressure to give a yellow solid. To remove some of the coloured impurities the residue was dissolved in dichloromethane and washed through a silica gel plug with a 10% methanol/dichloromethane solution and the yellow filtrate concentrated by rotary evaporation. The product was then recrystallized from

acetone/diethyl ether to afford 0.058 g (91%) of ivory crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.99 (s, 1H, $C_6Me_5\underline{H}$), 4.90 (t, J = 2.5 Hz, 1H, $C_5\underline{H}_3Me^tBu$), 4.87 (dd, J = 2.5, 1.6 Hz, 1H, $C_5\underline{H}_3Me^tBu$), 4.85 (dd, J = 2.4, 1.6 Hz, 1H, $C_5\underline{H}_3Me(C(CH_3)_3)$), 2.39 (s, 3H, $C_6\underline{Me}_5H$), 2.34 (s, 3H, $C_6\underline{Me}_5H$), 2.32 (s, 3H, $C_6\underline{Me}_5H$), 2.29 (s, 3H, $C_6\underline{Me}_5H$), 2.25 (s, 3H, $C_6\underline{Me}_5H$), 1.91 (s, 3H, $C_5H_3\underline{Me}^tBu$), 1.21 (s, 9H, $C_5H_3Me^t\underline{Bu}$); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl3): δ 99.9, 99.8, 99.5, 99.1, 99.0, 92.9, 89.4, 85.2, 80.0, 79.7, 31.6, 30.7, 20.0, 18.9, 16.9, 16.3, 16.1, 13.1. One quaternary signal and the triflate carbon signal were not observed. Analysis calculated for $C_{22}H_{31}F_3O_3RuS$: C, 49.52%; H, 5.86%; found: C, 49.43%; H, 5.84%.



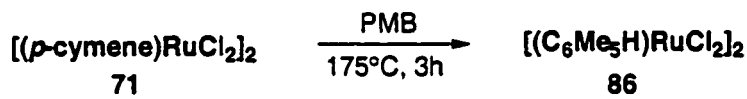
[(η^6-C_6Me_5H)Ru(η^5-$C_5H_3Me((CH_2)_4C{\equiv}CMe)$]$^+OTf^-$ (84). A solution of (C_6Me_6)Ru(η^3-C_3H_5)OTf (0.021 g, 0.046 mmol) in 10 mL degassed acetone was prepared in a small Schlenk flask equipped with a stir-bar and rubber septum then placed under a nitrogen atmosphere. Freshly distilled 2,8-decadiyne (0.013 mL, 0.073 mmol) was added via microliter syringe and the solution stirred overnight at room temperature. The solvent was then evaporated under low pressure leaving 0.024 g (90%) of an oily yellow residue. Further attempts at purification of this crude product resulted only in decomposition. IR (CH_2Cl_2 cast, cm^{-1}): 2924 (m), 2310 (w), 1458

(m), 1267 (s), 1150 (s), 1031 (s), 637 (s). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.92 (s, 1H, $C_6Me_5\underline{H}$), 4.75-4.90 (m, 3H, $C_5\underline{H}_3Me((CH_2)_4C{\equiv}CMe)$, 2.27 (s, 3H, $C_6\underline{Me}_5H$), 2.24 (s, 3H, $C_6\underline{Me}_5H$), 2.23 (s, 3H, $C_6\underline{Me}_5H$), 2.22 (s, 3H, $C_6\underline{Me}_5H$), 2.21 (s, 3H, $C_6\underline{Me}_5H$), 2.06-2.19 (m, 4H, $C_5H_3Me((\underline{CH_2})_4C{\equiv}CMe)$), 1.78 (s, 3H, $C_5H_3\underline{Me}((CH_2)_4C{\equiv}CMe)$), 1.74 (t, J = 2.5 Hz, 3H, $C_5H_3Me((CH_2)_4C{\equiv}C\underline{Me})$), 1.38-1.62 (m, 4H, $C_5H_3Me((\underline{CH_2})_4C{\equiv}CMe)$); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 100.3, 99.9, 99.6, 99.4, 95.1, 89.7, 82.4, 81.0, 79.7, 78.7, 76.2, 29.3, 28.7, 25.3, 19.5, 19.4, 18.7, 17.1, 16.3, 15.7, 10.6, 3.5, 1.1. One quaternary carbon signal and the triflate carbon signal were not observed.

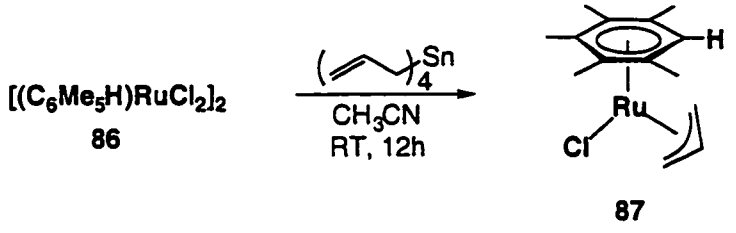


[(η^6-C_6Me_5H)Ru (η^5-$C_5H_3Me(CH_2CH_2$-)]$_2^{2+}$($OTf)_2^{2-}$ (85). A small Schlenk flask was charged with (C_6Me_6)Ru(η^3-C_3H_5)OTf (0.045 g, 0.100 mmol) and placed under a nitrogen atmosphere. Freshly distilled, degassed dichloromethane (3.0 mL) was added by syringe and the orange solution cooled to 0°C. 2,8-Decadiyne (0.009 mL, 0.050 mmol) was then added via syringe and the solution stirred at 0°C for 20 minutes, than warmed to room temperature and stirred for a further 2 hours. The solvent was removed *in vacuo* to give a solid white residue that was dissolved in hot acetone and diethyl ether then added to precipitate the product as a white powder (0.042 g, 84%).

This product was determined to be a 1:1 mixture of diastereomers by ^{1}H NMR spectroscopic analysis. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.92 (s, 2H, $C_6Me_5\underline{H}$), 5.03 (ap. q, J = 2.2 Hz, 2H, $C_5\underline{H}_3MeR$), 4.77 (ap. t, J = 1.3 Hz, 4H, $C_5\underline{H}_3MeR$), 2.28 (s, 6H, $C_6\underline{Me}_5H$), 2.26 (s, 6H, $C_6\underline{Me}_5H$), 2.24 (s, 3H, $C_6\underline{Me}_5H$), 2.23 (s, 3H, $C_6\underline{Me}_5H$), 2.22 (s, 6H, $C_6\underline{Me}_5H$), 2.21 (s, 6H, $C_6\underline{Me}_5H$), 2.10 - 2.07 (m, 4H, CH_2), 1.79 (s, 6H, $C_5H_3\underline{Me}R$), 1.52 - 1.44 (m, 4H, CH_2); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 100.2, 99.9, 99.6, 95.0, 89.8, 82.2, 81.5, 79.7, 29.6, 25.3, 25.2, 19.4, 19.2, 16.3, 15.8, 15.6, 10.6. Triflate carbon signal was not observed. Analysis calculated for $C_{40}H_{52}F_6O_6Ru_2S_2$: C, 47.61%; H, 5.19%; found: C, 47.53%; H, 5.15%.

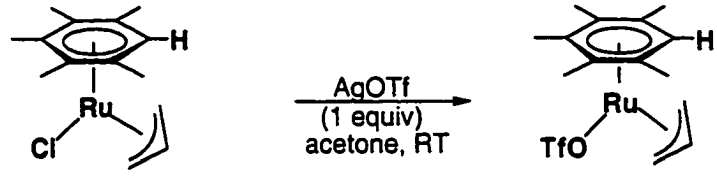


[(η^6-C$_6$Me$_5$H)RuCl$_2$]$_2$ (86). A mixture of [(*p*-cymene)$RuCl_2$]$_2$ (0.100 g, 0.163 mmol) and pentamethylbenzene (1.75 g, 10.9 mmol) was placed in a small oven-dried glass bomb along with 0.5 mL of dichloromethane. The sealed bomb was heated to 175°C (oil bath) with stirring for 2.5 hours. The melt was allowed to cool to room temperature, then dissolved in chloroform and filtered to remove decomposed material. The solvent was removed by rotary evaporation and the residue washed repeatedly with hexanes to remove excess pentamethylbenzene. The remaining dark orange solid was then recrystallized from chloroform/hexane to give dark red needles (approximately 0.045 g, 40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.98 (s, 1H, $C_6Me_5\underline{H}$), 2.08 (s, 6H, $C_6\underline{Me}_5H$), 2.00 (s, 9H, $C_6\underline{Me}_5H$). This material was used without further purification or characterization.



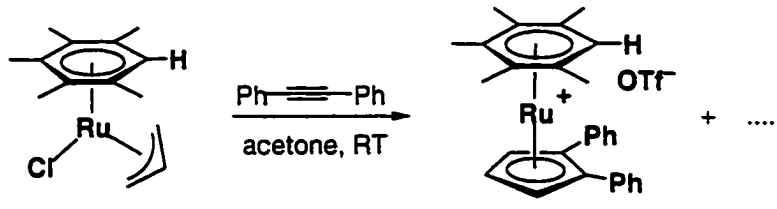
87

(η^6-C_6Me_5H)Ru(η^3-C_3H_5)Cl (87). A small Schlenk flask equipped with stir-bar and rubber septum was charged with [(η^6-C_6Me_5H)$RuCl_2$]$_2$ (0.034 g, 0.055 mmol) and 5 mL degassed acetonitrile added and the red slurry placed under nitrogen atmosphere. Tetraallyltin (0.038 mL) was added via syringe and the reaction stirred at room temperature for 6 hours, gradually turning the red suspension to a light yellow solution. The acetonitrile was then removed under low pressure and the residue dried under vacuum overnight. The crude product was rinsed with several portions of hexanes (3 x 5 mL) to remove tin byproducts. The remaining orange solid was dissolved in hot toluene and filtered through Celite. Light orange crystals were obtained by recrystallization from toluene/hexane (approximately 0.035 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.13 (s, 1H, $C_6Me_5\underline{H}$), 3.51 (m, 1H, $H_{central}$), 3.31 (d, J = 6.9 Hz, 2H, H_{syn}), 2.34 (d, J = 11.1 Hz, 2H, H_{anti}), 2.15 (s, 3H, $C_6\underline{Me}_5H$), 1.99 (s, 6H, $C_6\underline{Me}_5H$), 1.98 (s, 6H, $C_6\underline{Me}_5H$). Analysis calculated for $C_{14}H_{21}ClRu$: C, 51.61%; H, 6.50%; found: C, 51.12%; H, 6.65%.



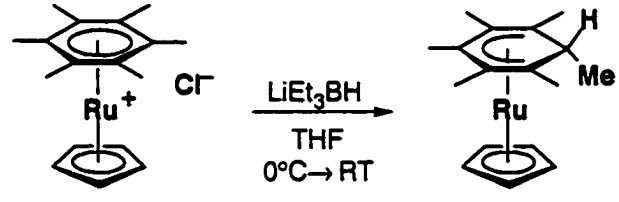
87 88

(η^6-C_6Me_5H)Ru(η^3-C_3H_5)OTf (88). A small Schlenk flask was charged with (η^6-C_6Me_5H)Ru(η^3-C_3H_5)Cl (0.014 g, 0.043 mmol) and 2 mL of acetone added and the resulting solution was degassed. Silver triflate (0.011 g, 0.043 mmol) dissolved in 1 mL of acetone was then added by syringe, resulting in the rapid precipitation of silver chloride. The mixture was stirred at room temperature for 1 hour then quickly filtered through Celite and the filtrate evaporated *in vacuo*. The yellow residue was taken into the drybox, dissolved in benzene and filtered again through Celite to remove residual silver chloride. The benzene was then evaporated under reduced pressure. An air-sensitive orange powder was isolated, which was pure by ^{1}H NMR spectroscopic analysis, in approximately 85% yield (0.016 g) and stored under nitrogen. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.55 (s, 1H, $C_6Me_5\underline{H}$), 3.76 (d, J = 6.8 Hz, 2H, H_{syn}), 3.52 (m, 1H, $H_{central}$), 2.42 (d, J = 11.3 Hz, 2H, H_{anti}), 2.20 (s, 3H, $C_6\underline{Me}_5H$), 2.03 (s, 6H, $C_6\underline{Me}_5H$), 1.91 (s, 6H, $C_6\underline{Me}_5H$).



87 81

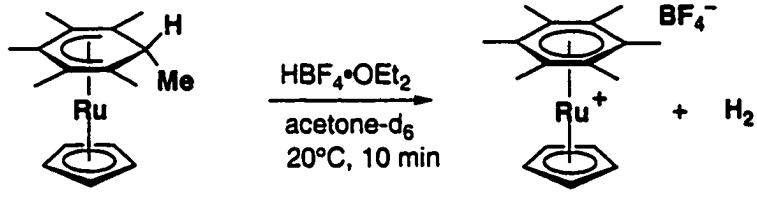
Reaction of (η^6-C_6Me_5H)Ru(η^3-C_3H_5)OTf with Diphenylacetylene. Diphenylacetylene (0.009 g, 0.073 mmol) and (η^6-C_6Me_5H)Ru(η^3-C_3H_5)OTf (0.015 g, 0.040 mmol) were placed in a small Schlenk flask capped with a rubber septum. A nitrogen atmosphere was established by evacuating and backfilling three times. Acetone (2 mL) was added via syringe and the resultant solution was stirred under nitrogen at room temperature overnight. The solvent was then removed *in vacuo* to yield a bright yellow residue. The ^1H NMR spectrum of the crude residue revealed that the major product (>80%) was spectroscopically identical to [(C_6Me_5H)Ru(η^5-$C_5H_3Ph_2$)]$^+OTf^-$ (**81**). Trace amounts of further demethylated products may have formed as evidenced by singlets between δ 5.95-6.10 and between δ 1.95-2.20.



109 110

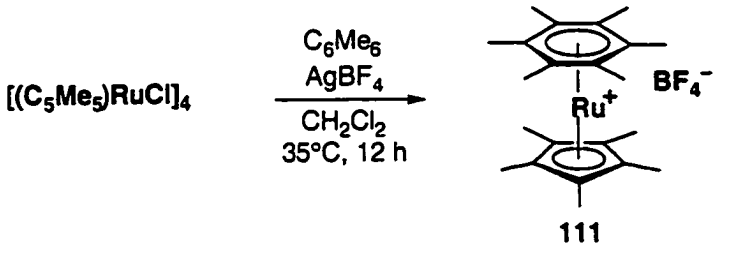
(C_5H_5)Ru(η^5-1,2,3,4,5,6(*endo*)-hexamethylcyclohexadienyl) (110). A suspension of [(C_5H_5)Ru(η^6-C_6Me_6)]$^+Cl^-$ (0.055 g, 0.151 mmol) in tetrahydrofuran (3 mL) was cooled to 0°C and $LiEt_3BH$ (1.0 M in THF, 0.18 mL, 0.18 mmol, 1.2 equiv) added via syringe. After stirring at 0°C for 30 minutes the reaction was warmed to room temperature for

another hour before removing the solvent *in vacuo*. The residue was triturated with 2 x 3 mL pentane and the pentane extracts filtered through Celite and dried to a white solid. The crude product was then redissolved in pentane and filtered through a plug of alumina (5% H_2O). After evaporation of pentane the product (0.031 g, 62%) was obtained as off-white crystals and used without further purification. ^1H NMR (400 MHz, CD_2Cl_2): δ 4.36 (s, 5H, C_5H_5), 2.41 (s, 3H, CH_3), 2.21 (q, J = 7.1 Hz, 1H, *exo*-H), 1.94 (s, 6H, CH_3), 1.35 (s, 6H, CH_3), 1.12 (d, J = 7.1 Hz, 3H, *endo*-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 91.9, 91.2, 78.3, 39.9, 37.0, 18.9, 17.6, 17.4, 17.1.



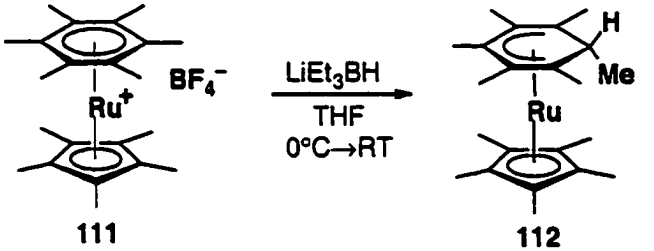
110 109

Addition of HBF_4•Et_2O in acetone-d_6. An acetone-d_6 solution of $(C_5H_5)Ru(\eta^5$-1,2,3,4,5,6(*endo*)-hexamethylcyclohexadienyl) (0.010 g, 0.030 mmol) was placed into an NMR tube equipped with a septum. Tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) (0.004 mL, 0.045 mmol) was then added via microsyringe and the resultant solution analyzed by ^1H NMR spectroscopy. Clean conversion of starting material to $[(C_5H_5)Ru(\eta^6\text{-}C_6Me_6)]^+BF_4^-$ was observed within 10 minutes at room temperature.



111

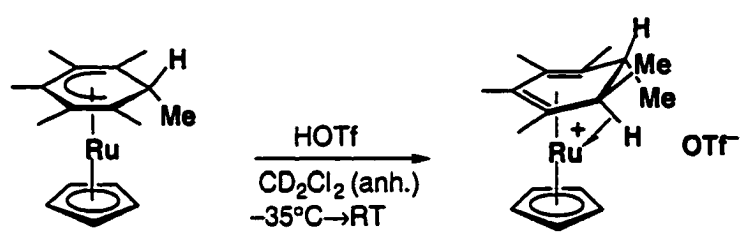
$[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+BF_4^-$ (111). A Schlenk flask equipped with a septum was charged with $[(C_5Me_5)RuCl]_4$ (0.100 g, 0.368 mmol/Ru), hexamethylbenzene (0.310 g, 1.90 mmol) and silver tetrafluoroborate (0.076 g, 0.390 mmol). Dichloromethane (6 mL) was added by syringe and the reaction mixture immediately turned dark green. The reaction was then heated to a gentle reflux for five hours, gradually turning light brown with a grey precipitate. The solution was then filtered through Celite to remove silver salts and the filtrate evaporated to dryness. The tan residue was rinsed with hexane to remove excess hexamethylbenzene, then dissolved into a minimum of dichloromethane and the product precipitated using diethyl ether. A white powder was collected (0.131 g, 73%), which was spectroscopically identical to the known $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+OTf^-$.[92b]



111 112

$(C_5Me_5)Ru(\eta^5\text{-}1,2,3,4,5,6(\textit{endo})\text{-hexamethylcyclohexadienyl})$ (112). A suspension of $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+BF_4^-$ (0.050 g, 0.103 mmol) in tetrahydrofuran (3 mL) was cooled to 0°C and $LiEt_3BH$ (1.0 M in THF, 0.11 mL, 0.11 mmol, 1.07 equiv) added via

syringe. After stirring at 0°C for 30 minutes the reaction was warmed to room temperature for 1 hour before removing the solvent *in vacuo*. The residue was triturated with 2 x 3 mL pentane and the pentane extracts filtered through Celite and then dried to a white solid. The crude product was then redissolved in pentane and filtered through a plug of alumina (5% H_2O). After evaporation of pentane the product (0.023 g, 56%) was obtained as a white crystalline solid and used without further purification. IR (CH_2Cl_2 cast, cm^{-1}): 2967 (s), 2898 (s), 2870 (s), 2847 (s), 1375 (s), 1026 (m); ^1H NMR (400 MHz, CD_2Cl_2): δ 2.44 (q, J = 7.1 Hz, 1H, *exo*-H), 2.07 (s, 3H, CH_3), 1.64 (s, 6H, CH_3), 1.61 (s, 15H, C_5Me_5), 1.05 (s, 6H, CH_3), 0.95 (d, J = 7.1 Hz, 3H, *endo*-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 96.8, 89.9, 87.0, 41.1, 35.3, 17.4, 15.9, 15.3, 15.0, 10.0; MS *m/z* calculated for $C_{22}H_{34}{}^{102}Ru$ (M^+): 400.1704; found: 400.1655 (28.08%); calculated for $C_{22}H_{33}{}^{102}Ru$ (M-H): 399.1626; found: 399.1625 (100.00%); calculated for $C_{21}H_{31}{}^{102}Ru$ (M-CH_3): 385.1469; found: 385.1464 (4.41%).

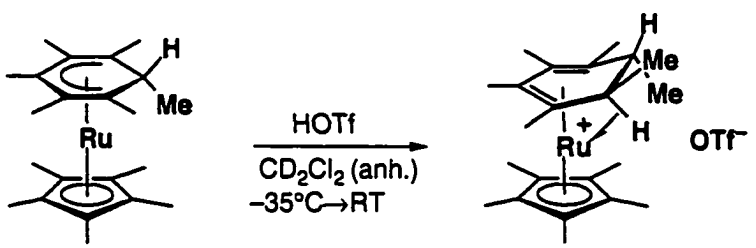


110 113

[(C_5H_5)Ru(η^4-1,2,3,4,5(*exo*),6(*endo*)-hexamethylcyclohexa-1,3-diene)]$^+BF_4^-$ (113). A CD_2Cl_2 solution of (C_5H_5)Ru(η^5-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (0.016 g, 0.049 mmol) was placed into an NMR tube equipped with a small septum. Tetrafluoroboric acid (diethyl ether complex, 85%) was then added (0.008 mL, 0.064 mmol) via microliter syringe and the resulting yellow solution analyzed by ^1H NMR

spectroscopy. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.14 (s, 5H, C_5H_5), 2.82, (s, 3H, CH_3), 2.50 (dq, J = 13.2, 6.6 Hz, 1H, *exo*-H), 2.17 (s, 6H, CH_3), 1.67 (d, J = 2.7 Hz, 6H, CH_3), 1.31 (d, J = 6.7 Hz, 3H, *endo*-CH_3), –4.81 (d of sept, J = 13.3, 2.6 Hz, 1H, H_{ag}).

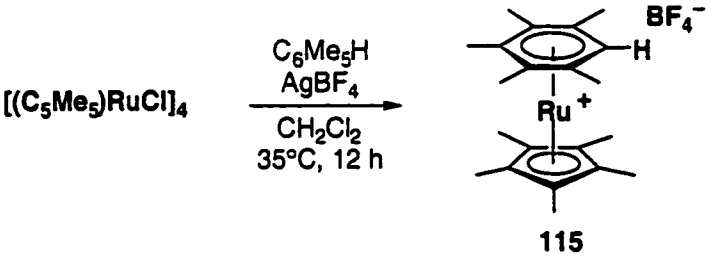
Addition of MeOH. Excess MeOH (0.008 mL, 6.5 equiv) was added via microsyringe to the CD_2Cl_2 solution of [$(C_5H_5)Ru(\eta^4$-1,2,3,4,5(*exo*),6(*endo*)-hexamethylcyclohexa-1,3-diene)]$^+BF_4^-$ prepared above and the reaction monitored spectroscopically. Complete conversion to [$(C_5H_5)Ru(\eta^6$-$C_6Me_6)]^+BF_4^-$ was observed within 4 hours at room temperature, along with traces of decomposition.



112 114

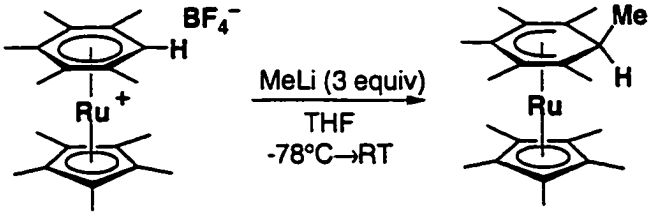
[$(C_5Me_5)Ru(\eta^4$-1,2,3,4,5(*exo*),6(*endo*)-hexamethylcyclohexa-1,3-diene)]$^+$OTf$^-$ (114). An anhydrous CD_2Cl_2 solution of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*endo*)-hexamethylcyclohexadienyl) (0.030 g, 0.075 mmol) was placed into an NMR tube equipped with a septum. Triflic acid (0.007 mL, 0.079 mmol) was then added via microliter syringe and the resulting solution analyzed by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.44 (dq, J = 13.0, 6.6 Hz, 1H, *exo*-H), 2.40 (s, 3H, CH_3), 1.85 (s, 6H, CH_3), 1.77 (s, 15H, C_5Me_5), 1.44 (d, J = 2.4 Hz, 6H, CH_3), 1.21 (d, J = 6.6 Hz, 3H, *endo*-CH_3), –5.82 (br d, J = 13.0 Hz, H_{ag}); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 101.9, 99.9, 96.8, 67.1, 42.1, 16.9, 16.0, 14.9, 14.2, 9.7. Triflate carbon signal was not observed.

Addition of MeOH. Excess MeOH (0.011 mL, 6.0 equiv) was added via microliter syringe to the CD_2Cl_2 solution of $[(C_5Me_5)Ru(\eta^4\text{-}1,2,3,4,5(exo),6(endo)\text{-}$ hexamethylcyclohexa-1,3-diene)]$^+OTf^-$ prepared above and the reaction monitored spectroscopically. After 24 hours only 21% conversion to $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+OTf^-$ was observed.



115

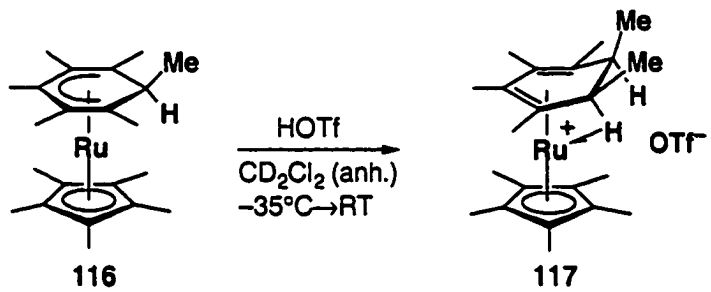
$[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_5H)]^+BF_4^-$ (115). A similar procedure to that described for the preparation of $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+BF_4^-$ (**111**) was followed, except that pentamethylbenzene is used in place of hexamethylbenzene. Thus, a mixture of $[(C_5Me_5)RuCl]_4$ (0.300 g, 1.10 mmol/Ru), pentamethylbenzene (0.840 g, 5.66 mmol) and silver tetrafluoroborate (0.218 g, 1.12 mmol) in 12 mL dichloromethane was kept at a gentle reflux for 5 hours. A bright white powder (0.483 g, 93%) was isolated after recrystallization from dichloromethane/diethyl ether. ^1H NMR (400 MHz, CD_2Cl_2): δ 5.46 (s, 1H, $C_6Me_5\underline{H}$), 2.10 (s, 6H, $C_6\underline{Me}_5H$), 2.06 (s, 3H, $C_6\underline{Me}_5H$), 2.03 (s, 6H, $C_6\underline{Me}_5H$), 1.71 (s, 15H, $C_5\underline{Me}_5$); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 99.2, 99.1, 98.7, 93.1, 91.5, 17.9, 14.7, 14.2, 9.4. Analysis calculated for $C_{21}H_{31}RuBF_4$: C, 53.51%; H, 6.63%; found: C, 53.38%; H, 6.52%.



115 116

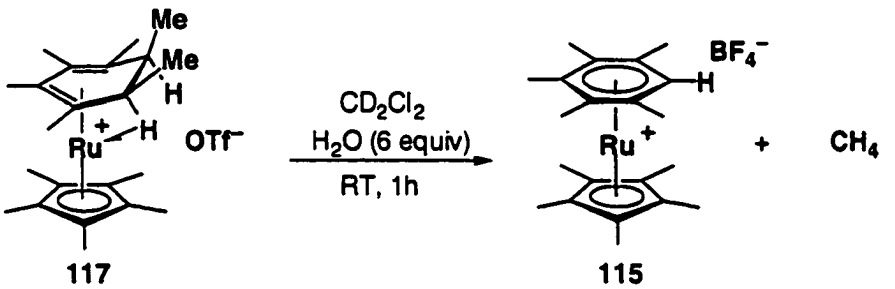
(C_5Me_5)Ru(η^5-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (116). A suspension of [(C_5Me_5)Ru(η^6-C_6Me_5H)]$^+BF_4^-$ (0.165 g, 0.350 mmol) in 6 mL of tetrahydrofuran was cooled to –78°C using a dry ice/acetone bath and MeLi (1.4 M in diethyl ether, 0.75 mL, 1.05 mmol, 3.0 equiv) added via syringe. The reaction was stirred at –78°C for several hours before gradually being warmed to room temperature. The resulting yellow solution was then evaporated under low pressure and the residue triturated with several portions of pentane. The combined pentane extracts were filtered through Celite and the yellow filtrate concentrated to a solid. After thorough drying *in vacuo* the yellow solid was dissolved in pentane and filtered through a plug of alumina (5% H_2O), giving a colourless filtrate. This filtrate was concentrated under low pressure to give 0.058 g (42%) of white crystalline material, which was used without further purification. IR (CH_2Cl_2 cast, cm^{-1}): 2959 (s), 2937 (s), 2902 (s), 2881 (s), 2852 (s), 1376 (m), 1265 (m), 1017(m), 740 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 2.02 (s, 3H, CH_3), 1.94 (q, J = 6.3 Hz, 1H, *endo*-H), 1.60 (s, 21H, 2 x CH_3 and C_5Me_5), 1.31 (s, 6H, CH_3), 0.11 (d, J = 6.3 Hz, 3H, *exo*-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 88.1, 86.7, 86.5, 50.2, 39.9, 20.3, 20.2, 15.3, 14.4, 10.0; MS *m/z* calculated for $C_{22}H_{34}{}^{102}Ru$ (M^+): 400.1704; found: 400.1687 (3.81%); calculated for $C_{22}H_{33}{}^{102}Ru$ (M-H): 399.1626; found: 399.1644 (6.55%); calculated for $C_{21}H_{31}{}^{102}Ru$ (M-CH_3): 385.1469; found: 385.1464 (100.00%).

$(C_5Me_5)Ru(\eta^5$-1,2,3,4,5-pentamethyl-6(*exo*)-CD_3-cyclohexadienyl) (116-d_3). A similar procedure to that described above was followed. A cold (–78°C) suspension of $(C_5Me_5)Ru(\eta^6\text{-}C_6Me_5H)]^+BF_4^-$ (0.050 g, 0.106 mmol) in tetrahydrofuran was prepared and CD_3Li (approximately 0.3 M in diethyl ether, 1.06 mL, 3.0 equiv) added by syringe. The flask was then warmed to room temperature, and the product isolated as previously described. Pale yellow crystals were collected (0.015 g, 37%). ^1H NMR (400 MHz, CD_2Cl_2): δ 2.02 (s, 3H, CH_3), 1.93 (br s, 1H, *endo*-H), 1.60 (s, 21H, CH_3 and C_5Me_5), 1.31 (s, 6H, CH_3).



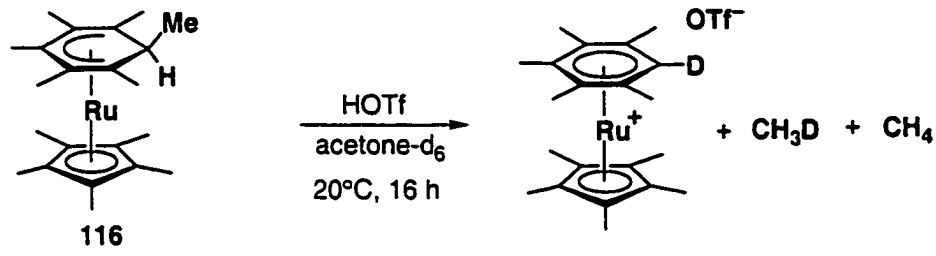
[$(C_5Me_5)Ru(\eta^4$-1,2,3,4,5(*exo*),6(*exo*)-hexamethylcyclohexa-1,3-diene)]$^+OTf^-$ (117). An anhydrous CD_2Cl_2 solution of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethyl-cyclohexadienyl) (0.015 g, 0.038 mmol) was placed into an NMR tube equipped with a small rubber septum. Triflic acid (0.004 mL, 0.045 mmol) was then added via syringe and the resulting solution analyzed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, at both room temperature and at –80°C. ^1H NMR (400 MHz, CD_2Cl_2, 20°C): δ 2.59 (br s, 1H, *endo*-H), 2.37 (br s, 3H, CH_3), 1.79 (br s, 12H, CH_3), 1.77 (s, 15H, C_5Me_5), 0.33 (br s, 3H, *exo*-CH_3), -5.73 (br s, 1H, H_{ag}); ^1H NMR (400 MHz, CD_2Cl_2, –80°C): δ 2.53 (br q, J = 6.6 Hz, 1H, *endo*-H), 2.25 (s, 3H, CH_3), 1.71 (s, 12H, CH_3), 1.67 (s, 15H, C_5Me_5), 0.22 (d, J

= 6.5 Hz, 3H, *exo*-CH_3), –5.40 (br s, 1H, H_{ag}); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 20°C): δ 96.8, 9.8, (all other signals broadened into the baseline); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, –80°C): δ 98.6, 96.1, 95.6, 74.0, 51.2, 22.4, 19.8, 14.0, 12.8, 9.2. Triflate carbon signal was not observed. Qualitative spin saturation transfer experiments (400 MHz, CD_2Cl_2, 20°C): irradiation of δ –5.73 (H_{ag}) ↔ disappearance of signal at δ 2.59 (*endo*-H); irradiation of δ 0.33 (*exo*-CH_3) ↔ disappearance of signal at δ 1.79 (12H, CH_3) and diminution of signal at δ 2.37 (3H, CH_3).

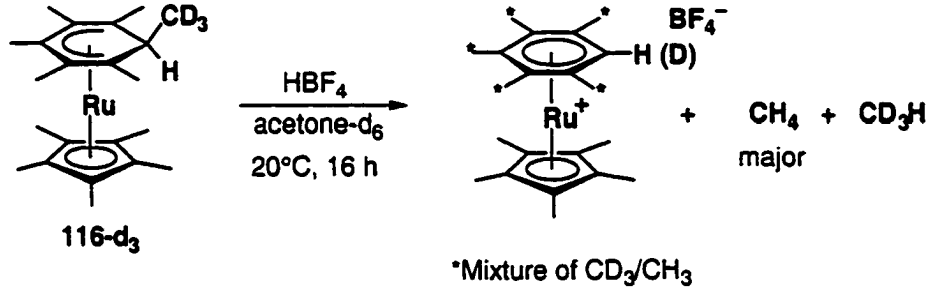


117 115

Addition of water. Excess distilled water (0.004 mL, 5.9 equiv) was added via microliter syringe to the CD_2Cl_2 solution of [(C_5Me_5)Ru(η^4-1,2,3,4,5(*exo*),6(*exo*)-hexamethylcyclohexa-1,3-diene)] $^+OTf^-$ prepared above. The NMR tube was shaken for 1 minute then the reaction monitored by ^1H NMR spectroscopy in 10 minute intervals. After 50 minutes the conversion of [(C_5Me_5)Ru(η^4-1,2,3,4,5(*exo*),6(*exo*)-hexamethylcyclohexa-1,3-diene)]$^+OTf^-$ to [(C_5Me_5)Ru(η^6-C_6Me_5H)]$^+OTf^-$ and methane (δ 0.20 in CD_2Cl_2) was complete.

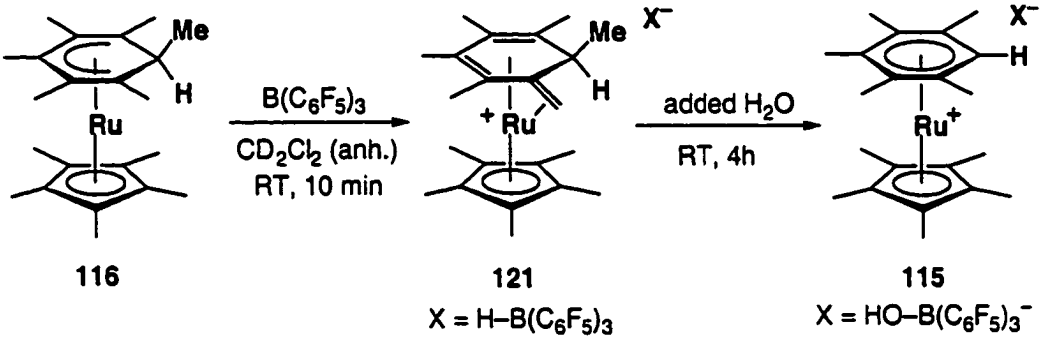


Addition of CF_3SO_3H in acetone-d_6. An acetone-d_6 solution of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (0.015 g, 0.038 mmol) was placed into an NMR tube equipped with a septum and sealed. Triflic acid (0.004 mL, 0.045 mmol) was then added via syringe and the reaction was monitored spectroscopically. After 20 minutes at room temperature ^{1}H NMR showed complete conversion of starting material to $[(C_5Me_5)Ru(\eta^4$-1,2,3,4,5(*exo*),6(*exo*)-hexamethylcyclohexa-1,3-diene)]$^+OTf^-$ **(117)** along with traces of $[(C_5Me_5)Ru(\eta^6$-$C_6Me_5D)]^+OTf^-$. After 24 hours at room temperature conversion to $[(C_5Me_5)Ru(\eta^6$-$C_6Me_5D)]^+OTf^-$ was complete, accompanied by the formation of methane (δ 0.15 in acetone-d_6) and CH_3D (1:1:1 triplet at δ 0.13 in acetone-d_6).



Addition of protic Acids to $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5-pentamethyl-6(*exo*)-CD_3-cyclohexadienyl) (116-d_3). A dichloromethane solution of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5-pentamethyl-6(*exo*)-CD_3-cyclohexadienyl) (0.015 g, 0.037 mmol) was placed into an

NMR tube and capped with a small rubber septum. The solution was then frozen using liquid nitrogen (–196°C) and triflic acid (0.004 mL, 0.045 mmol) added via microsyringe, followed quickly by addition of an excess of distilled water (0.004 mL, 0.22 mmol, 6 equiv). The NMR tube was rapidly warmed to room temperature and allowed to stand for a further 2 hours. Subsequent analysis of the solution mixture by ^{2}H NMR spectroscopy indicates deuterium incorporation at δ 2.07, 2.03 and 2.00 in a 2 : 1 : 2 ratio, respectively, consistent with equal incorporation of CD_3 at each of the arene methyl positions. Also present is a broad upfield signal at approximately δ 0.12, suggesting a small amount of CD_3H was alsoformed.

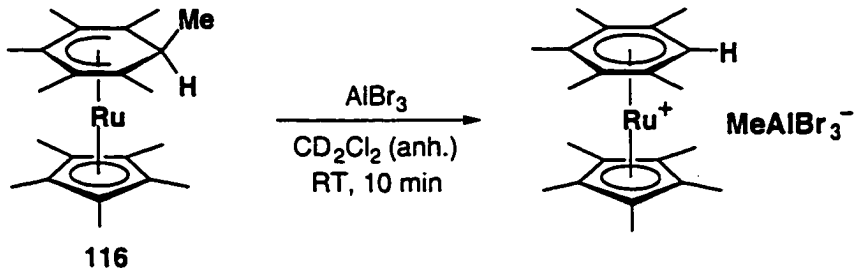


116 121 X = H–B(C6F5)3 115 X = HO–B(C6F5)3⁻

[(C5Me5)Ru(η6-1,2,3,4,6(*exo*)-pentamethyl-5-methylenecyclohexa-1,3-diene)]+ HB(C6F5)3- (121). An NMR tube was charged with a solution of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (0.012 g, 0.030 mmol) in anhydrous CD_2Cl_2 and the tube cooled to –35°C. Immediately upon addition of tris(pentafluorophenyl)borane (0.016 g, 0.031 mmol) the colourless solution turned bright yellow. Spectroscopic analysis (^{1}H, ^{13}C NMR, HMQC) of the reaction mixture showed quantitative formation of the product within 10 minutes. ^{1}H NMR (400 MHz, CD_2Cl_2):

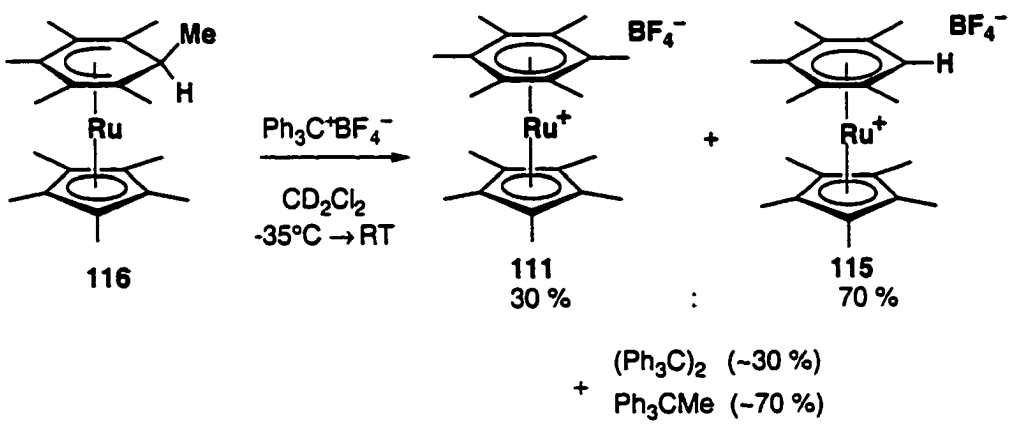
δ 4.33 (s, 1H, $HC_6Me_5C\underline{H}_2$), 3.54 (s, 1H, $HC_6Me_5C\underline{H}_2$), 2.02 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.84 (q, J = 6.7 Hz, 1H, *endo*-H), 1.67 (s, 15H, C_5Me_5), 1.48 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 0.66 (d, J = 6.7 Hz, 3H, *exo*-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, $^1J_{CH}$ obtained from HMQC spectrum): δ 106.4 (s, $H\underline{C}_6Me_5CH_2$), 98.7 (s, $H\underline{C}_6Me_5CH_2$), 96.3 (s, $\underline{C}_5Me_5$), 94.5 (s, $H\underline{C}_6Me_5CH_2$), 89.6 (s, $H\underline{C}_6Me_5CH_2$), 76.2 (d, $^1J_{CH}$ = 161 Hz, $HC_6Me_5\underline{C}H_2$), 55.7 (s, $H\underline{C}_6Me_5CH_2$), 40.2 (d, $^1J_{CH}$ = 133 Hz, CH), 21.0 (q, $^1J_{CH}$ = 133 Hz, *exo*-CH_3), 18.9 (q, $^1J_{CH}$ = 129 Hz, CH_3), 14.9 (q, $^1J_{CH}$ = 130 Hz, CH_3), 13.4 (q, $^1J_{CH}$ = 130 Hz, CH_3), 13.0 (q, $^1J_{CH}$ = 129 Hz, CH_3), 9.7 (q, $^1J_{CH}$ = 127 Hz, C_5Me_5); HMQC (300 MHz, CD_2Cl_2): δ 76.2 (CH_2) ↔ δ 4.33, 3.54 (CH_2); δ 40.2 (CH) ↔ δ 1.84 (CH); δ 21.0 (CH_3) ↔ δ 0.66 (CH_3); δ 18.9 (CH_3) ↔ δ 1.39 (CH_3); δ 14.9 (CH_3) ↔ δ 1.48 (CH_3); δ 13.4 (CH_3) ↔ δ 1.88 (CH_3); δ 13.0 (CH_3) ↔ δ 2.02 (CH_3); δ 9.7 (C_5Me_5) ↔ δ 1.67 (C_5Me_5).

Addition of Water. Excess distilled water (0.004 mL, 7.5 equiv) was added via microsyringe to the anhydrous CD_2Cl_2 solution of [(C_5Me_5)Ru(η^6-1,2,3,4,6(*exo*)-pentamethyl-5-methylenecyclohexa-1,3-diene)]$^+HB(C_6F_5)_3^-$ prepared above. The NMR tube was shaken for 1 minute then the reaction monitored by ^1H NMR spectroscopy. After 4 hours the conversion of starting material to [(C_5Me_5)Ru(η^6-C_6Me_5H)]$^+HOB(C_6F_5)_3^-$ and methane (δ 0.20 in CD_2Cl_2) was complete. IR (CH_2Cl_2 cast, cm^{-1}): 3670 (br), 1644 (m), 1515 (s), 1465 (s), 1089 (s), 976 (s).



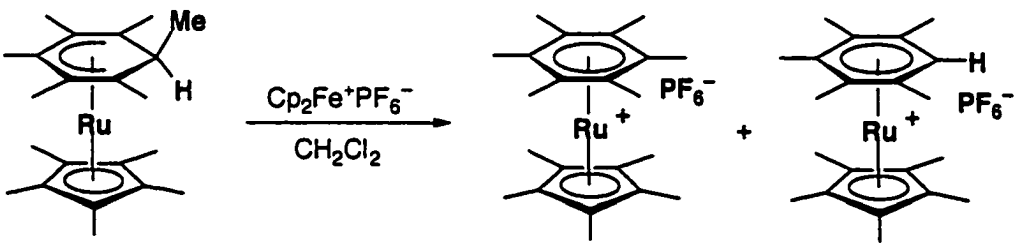
116

Reaction of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) with $AlBr_3$. A solution of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (0.010 g, 0.025 mmol) in CD_2Cl_2 was loaded into an NMR tube and anhydrous $AlBr_3$ (0.008 g, 0.030 mmol) added. The NMR tube was capped and shaken for a minute. After 10 minutes standing at room temperature ^1H NMR spectroscopic analysis indicates only a single product formed in quantitative yield, $[(C_5Me_5)Ru(\eta^6$-$C_6Me_5H)]^+MeAlBr_3^-$, based on spectroscopic comparison with the well-characterized triflate analogue. ^1H NMR (360 MHz, CD_2Cl_2): δ 5.37 (s, 1H, $C_6Me_5\underline{H}$), 2.10 (s, 6H, $C_6\underline{Me}_5H$), 2.06 (s, 3H, $C_6\underline{Me}_5H$), 2.03 (s, 6H, $C_6\underline{Me}_5H$), 1.71 (s, 15H, $C_5\underline{Me}_5$), 0.00 (br s, 3H, $\underline{Me}AlBr_3$).



Reaction of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) with Ph_3CBF_4. A solution of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl)

(**116**) (0.010 g, 0.025 mmol) in anhydrous CD_2Cl_2 was cooled to –35°C and triphenylcarbenium tetrafluoroborate (0.009 g, 0.027 mmol) added. The solution immediately turned bright yellow and was placed into an NMR tube. Subsequent ^1H NMR analysis indicates only the final products are present, with no trace of any intermediates. $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_5H)]^+BF_4^-$ (70%) and $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+BF_4^-$ (30%) are apparent as is Ph_3CMe (^1H NMR, (300 MHz, CD_2Cl_2): δ 7.37-7.06 (m, 15H, H_{PH}), 2.17 (s, 3H, Me)), (~70%), and trityl dimer [^1H NMR, (300 MHz, CD_2Cl_2,): δ 7.33-7.15 (m, 21H), 6.95 (dd, J = 8.1, 1.8 Hz, 4H), 6.23 (dd, J = 10.5, 2.0 Hz, 2H), 5.97 (dd, J = 10.5, 3.8 Hz, 2H), 5.13 (br s, 1H)] in 30% yield.

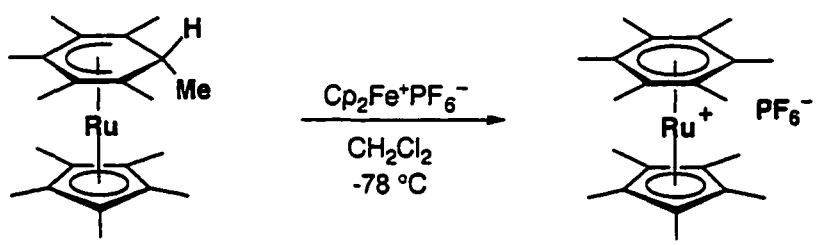


116 **111** **115**

Reaction of $(C_5Me_5)Ru(\eta^5\text{-}1,2,3,4,5,6(exo)\text{-}hexamethylcyclohexadienyl)$ (116) with $[Cp_2Fe]^+PF_6^-$ at –78°C. A blue suspension of $[Cp_2Fe]^+PF_6^-$ (0.009 g, 0.027 mmol) in 2 mL dichloromethane was cooled to –78°C in a dry ice/acetone bath and a solution of $(C_5Me_5)Ru(\eta^5\text{-}1,2,3,4,5,6(exo)\text{-}hexamethylcyclohexadienyl)$ (0.011 g, 0.027 mmol) in 1 mL dichloromethane was slowly added via syringe. The reaction mixture turned from blue to orange within 5 minutes and the cold bath was removed. Upon rapid warming to room temperature the reaction lightened to pale yellow and the solvent was then removed under low pressure. ^1H NMR spectroscopic analysis of the yellow residue indicates that

66% $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+PF_6^-$ and 33% $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_5H)]^+PF_6^-$ are present, along with a quantitative amount of ferrocene.

Reaction of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (116) with $[Cp_2Fe]^+PF_6^-$ at room temperature The reaction was performed as above except that no cold bath was used. Upon addition of starting material the reaction immediately turned pale yellow, and the reaction was stirred for a further 10 minutes. Solvent was then removed *in vacuo* and the residue analyzed by ^1H NMR spectroscopy. $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+PF_6^-$ was present in 30% yield, and $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_5H)]PF_6$ in 70% yield along with a quantitative amount of ferrocene.



112 111

Reaction of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*endo*)-hexamethylcyclohexadienyl) with $[Cp_2Fe]^+PF_6^-$ at –78°C. A blue suspension of $[Cp_2Fe]^+PF_6^-$ (0.009 g, 0.027 mmol) in 2 mL dichloromethane was cooled to –78°C in a dry ice/acetone bath and a solution of $(C_5Me_5)Ru(\eta^5$-1,2,3,4,5,6(*endo*)-hexamethylcyclohexadienyl) (**112**) (0.011 g, 0.027 mmol) in 1 mL dichloromethane added slowly via syringe. The reaction mixture immediately faded from blue to a pale yellow solution, and the cold bath was removed. After warming to room temperature the solvent was removed under reduced pressure. ^1H

NMR spectroscopic analysis of the yellow residue indicates complete conversion to $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+PF_6^-$ along with a quantitative amount of ferrocene.

Variable Temperature Experiments:

2-Butyne. An NMR tube was charged with a solution of $(C_6Me_6)Ru(C_3H_5)OTf$ (0.015 g, 0.033 mmol) in anhydrous CD_2Cl_2, and capped with a septum while still under an N_2 atmosphere. The solution was then frozen using liquid nitrogen and 2-butyne (0.013 mL, 0.165 mmol, 5.0 equiv) added via microliter syringe. The probe on the Bruker AM-400 NMR spectrometer was precooled to –20°C before insertion of the cold sample. The reaction was subsequently monitored spectroscopically while gradually increasing the temperature in 5°C increments, allowing 30 minutes at each temperature. There were little or no temperature dependent chemical shifts noted in this temperature range.

Between –20°C and –15°C the slow formation of compound **122**, tentatively identified as $[(C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(MeC{\equiv}CMe)]^+OTf^-$ was observed, accompanied by the complete disappearance of starting material. Little change was observed until 0°C, when signals from several new compounds began to appear: compound **C**, tentatively identified as $[(\eta^5\text{-}C_5H_3Me_2)Ru(\eta^4\text{-}1,2,3,4,5(exo),6(exo)\text{-hexamethylcyclohexa-1,3-diene})]^+OTf^-$ and compound **152**, derived from insertion of a second equivalent of 2-butyne. Traces of a transient compound were also present at 0°C, tentatively identified as $[(C_6Me_6)Ru(\eta^3\text{-}C_5H_5Me_2)]^+OTf^-$, **123**, but the signals were broad and quickly disappeared as the reaction warmed further. At 5°C, any remaining traces of compound **122** disappeared rapidly with a concomitant increase in the concentrations of compounds

124 and **152**. After 30 minutes at 5°C only **124** and complex **152** were left; after an hour at 5°C traces of the final product, $[(\eta^5\text{-}C_5H_3Me_2)Ru(\eta^6\text{-}C_6Me_5H)]^+OTf^-$ (**79**), and methane began to appear. After 3 hours at room temperature the bis-adduct **152** and the pentamethylbenzene product **79** are the only ruthenium species remaining.

$[(C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(CH_3C{\equiv}CCH_3)]^+OTf^-$ (122). ^{1}H NMR (400 MHz, CD_2Cl_2, −15°C): δ 3.41 (tt, J = 10.5, 6.9 Hz, 1H, $H_{central}$), 3.23 (d, J = 6.8 Hz, 2H, H_{syn}), 2.13 (s, 18H, C_6Me_6), 2.08 (s, 6H, $C\underline{H}_3C{\equiv}CC\underline{H}_3$), 0.75 (d, J = 10.5 Hz, 2H, H_{anti}); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, −15°C): δ 106.9, 87.1, 66.9, 53.3, 15.8, 10.1. Triflate carbon signal was not observed.

$[(C_6Me_6)Ru(\eta^3\text{-}C_5H_5Me_2)]^+OTf^-$ (123). ^{1}H NMR (400 MHz, CD_2Cl_2, 0°C): δ 3.65 (br s, 1H), 2.87-2.82 (m, 3H), 2.22 (s, 18H, C_6Me_6), 1.88 (s, 6H, CH_3), −1.42 (br s, 1H).

$[(\eta^5\text{-}C_5H_3Me_2)Ru(\eta^4\text{-}1,2,3,4,5(exo),6(exo)\text{-hexamethylcyclohexa-1,3-diene})]^+OTf^-$ (124). ^{1}H NMR (400 MHz, CD_2Cl_2, 5°C): δ 4.99 (d, J = 2.5 Hz, 2H, $C_5\underline{H}_3Me_2$), 4.78 (t, J = 2.5 Hz, 1H, $C_5\underline{H}_3Me_2$), 2.67 (q, J = 6.6 Hz, 1H, *endo*-H), 2.65 (s, 3H, CH_3), 2.01 (s, 6H, CH_3), 1.90 (d, J = 2.5 Hz, 6H), 1.84 (s, 6H, CH_3), 0.32 (d, J = 6.6 Hz, 3H, *exo*-CH_3), −5.03 (br s, 1H, H_{ag}); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 5°C): δ 101.7, 100.7, 97.8, 85.9, 83.0, 75.6, 52.3, 23.1, 21.2, 15.9, 15.8, 11.1. Triflate carbon signal was not observed.

Diphenylacetylene. A solution of $(C_6Me_6)Ru(C_3H_5)OTf$ (**78**) (0.015 g, 0.033 mmol) in 0.30 mL anhydrous CD_2Cl_2 was placed in an NMR tube and capped with a small septum while under a nitrogen atmosphere. The solution was then frozen using liquid nitrogen and a solution of diphenylacetylene (0.006 g, 0.033 mmol, 1.0 equiv) in 0.10 mL CD_2Cl_2

added via syringe. The reaction mixture was briefly thawed to melting temperature and shaken before inserting the sample into the precooled probe (–20°C) on the Bruker AM-400 NMR spectrometer. The reaction was subsequently monitored spectroscopically while gradually increasing the temperature in 5°C increments, usually allowing 30 minutes at each temperature. There were little or no observed temperature dependent chemical shifts noted in this temperature range.

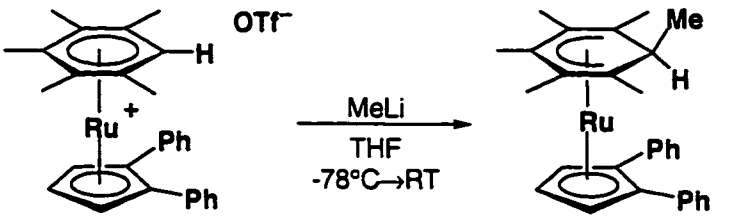
Between –20°C and –10°C the slow disappearance of the starting material was observed with concomitant formation of compound **125**, tentatively identified as $[(C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(PhC{\equiv}CPh)]^+OTf^-$. The reaction was held at –10°C for 1 hour to allow the starting material to complete the conversion to **125**. At –5°C several new compounds began to appear: compound **126**, tentatively identified as $[(C_6Me_6)Ru(\eta^3\text{-}C_5H_5Ph_2)]^+OTf^-$, and a trace amount of compound **128**, $(\eta^5\text{-}C_5H_3Ph_2)Ru(\eta^5$-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (spectroscopically identical to the independently prepared compound - see following reaction), as well as a small amount of compound **127**, $[(\eta^5\text{-}C_5H_3Ph_2)Ru(\eta^4$-1,2,3,4,5(*exo*),6(*exo*)-hexamethylcyclohexa-1,3-diene)$]^+OTf^-$. As the reaction was warmed to 0°C the signals corresponding to compound **125** began to decrease in intensity at a rapid rate while compounds **126** and **127** were growing at an approximately 1 : 1 ratio, whereas compound **128** was still only present in trace amounts. Between 0°C and 5°C compound **125** completely disappeared, compound **126** began to decrease in signal intensity while compound **127** continued to increase. At 10°C, compound **126** had disappeared, leaving compound **127** as the major species present along with the trace of compound **128**. Above 10°C small amounts of methane and the final product, $[(\eta^5\text{-}C_5H_3Ph_2)Ru(\eta^6\text{-}C_6Me_5H)]^+OTf^-$ (**81**), began to

appear. After 6 hours at room temperature the conversion to the final product **81** and methane was complete.

[(C_6Me_6)Ru(η^3-C_3H_5)(PhC≡CPh)]$^+$OTf$^-$ (125). ^{1}H NMR (400 MHz, CD_2Cl_2, -10°C): δ 7.71 (dt, J = 7.4, 1.0 Hz, 4H, H_{Ph}), 7.52 (t, J = 7.5 Hz, 4H, H_{Ph}), 7.42 (t, J = 7.4 Hz, 2H, H_{Ph}), 3.69-3.60 (m, AB pattern, 3H, H_{syn} and $H_{central}$), 2.11 (s, 18H, C_6Me_6), 1.09 (d, J = 10.2 Hz, 2H, H_{anti}); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, –10°C): δ 131.9, 129.2, 129.1, 125.5, 110.2, 87.3, 85.6, 53.7, 16.5. Triflate carbon signal was not observed.

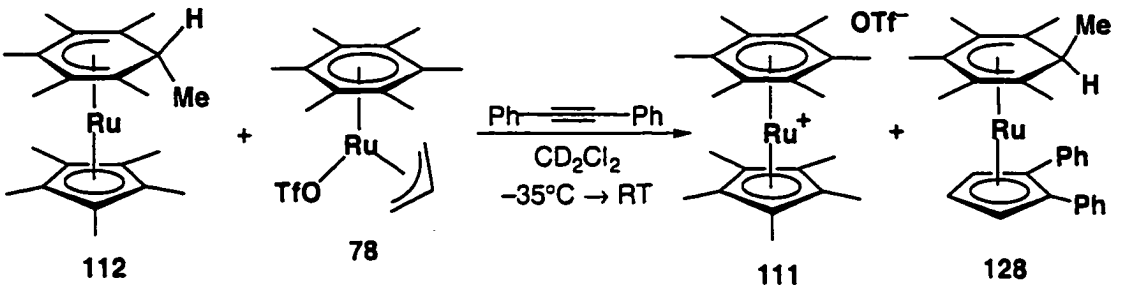
[(C_6Me_6)Ru(η^3-$C_5H_5Ph_2$)]$^+$OTf$^-$ (126). ^{1}H NMR (400 MHz, CD_2Cl_2, 0°C, partial data only): δ 5.24 (br s, 1H), 4.05 (v. br s, 1H), 3.31 (m, 1H), 2.06 (s, 18H, C_6Me_6), –8.63 (br s, 1H).

[(η^5-$C_5H_3Ph_2$)Ru(η^4-1,2,3,4,5(*exo*),6(*exo*)-hexamethylcyclohexa-1,3-diene)]$^+$OTf$^-$ (127). ^{1}H NMR (400 MHz, CD_2Cl_2, 10°C): δ 7.37-7.30 (m, 10H, H_{Ph}), 5.38 (d, J = 2.7 Hz, 2H, $C_5\underline{H}_3Ph_2$), 5.07 (t, J = 2.7 Hz, 1H, $C_5\underline{H}_3Ph_2$), 2.67 (q, J = 6.6 Hz, 1H, *endo*-H), 2.57 (s, 3H, CH_3), 1.85 (s, 6H, CH_3), 1.80 (d, J = 2.5 Hz, 6H, CH_3), 0.36 (d, J = 6.6 Hz, 3H, *exo*-CH_3), –4.79 (br s, 1H, H_{ag}); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 10°C): δ 130.1, 129.9, 129.6, 129.1, 103.2, 97.9, 86.9, 86.8, 74.2, 52.8, 22.8, 20.5, 16.7, 16.2. Triflate carbon signal was not observed.

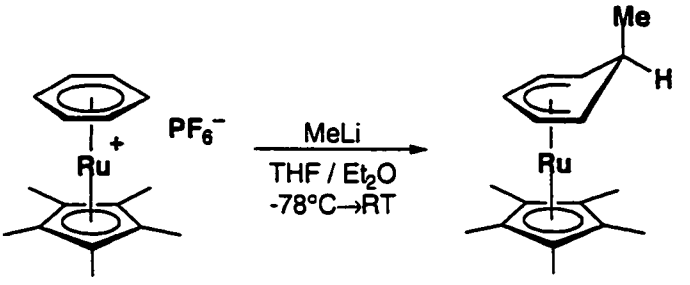


81 128

Independent synthesis of (η^5-$C_5H_3Ph_2$)Ru(η^5-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (128). A suspension of [(η^5-$C_5H_3Ph_2$)Ru(η^6-C_6Me_5H)]$^+$OTf$^-$ (0.055 g, 0.089 mmol) in 4 mL tetrahydrofuran was cooled to –78°C using a dry ice/acetone bath and MeLi (1.4 M in diethyl ether, 0.15 mL, 0.21 mmol, 2.4 equiv) added via syringe. The reaction was stirred at –78°C for several hours before gradually warmed to room temperature. The resulting yellow solution was then evaporated under low pressure and the residue triturated with several portions of hexane (3 x 2 mL). The combined hexane extracts were filtered through Celite and the yellow filtrate concentrated to a solid. After thorough drying in vacuo the solid was then dissolved in pentane and filtered through a plug of alumina (5% H_2O). The filtrate was concentrated under low pressure to yield 0.016 g (37%) of pale yellow crystalline material. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.19-7.10 (m, 10H, H_{Ph}, partially obscured), 4.70 (t, J = 2.5 Hz, 1H), 4.65 (d, J = 2.5 Hz, 2H), 2.23 (q, J = 6.4 Hz, 1H), 2.12 (s, 3H, CH_3), 1.63 (s, 6H, CH_3), 1.44 (s, 6H, CH_3), 0.15 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 137.2, 129.4, 128.0, 125.9, 94.4, 90.9, 88.3, 81.3, 78.4, 50.3, 43.2, 22.1, 20.8, 16.2, 15.4; MS m/z calculated for $C_{29}H_{32}{}^{102}Ru$ (M+): 482.1548; found: 482.1543 (1.54%); calculated for $C_{29}H_{31}{}^{102}Ru$ (M-H): 481.1469; found: 481.1458 (2.80%); calculated for $C_{28}H_{29}{}^{102}Ru$ (M-CH_3): 467.1313; found: 467.1325 (100.00%).

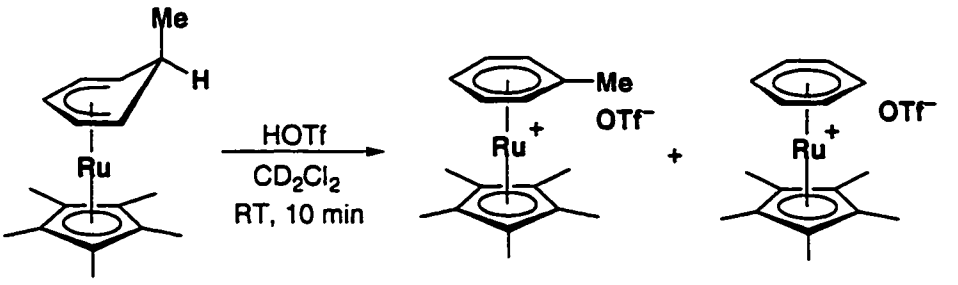


Crossover Experiment: trapping of (η^5-$C_5H_3Ph_2$)Ru(η^5-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl) (128). An anhydrous CD_2Cl_2 solution of (C_5Me_5)Ru(η^5-1,2,3,4,5,6(*endo*)-hexamethylcyclohexadienyl), **112**, (0.014 g, 0.035 mmol) and diphenylacetylene (0.008 g, 0.045 mmol) was prepared and placed in an NMR tube capped with a small septum; the solution was then cooled in the drybox freezer (–35°C) for 20 minutes. An orange solution of (C_6Me_6)Ru(η^3-C_3H_5)OTf (**78**) (0.017 g, 0.037 mmol) in ~0.2 mL CD_2Cl_2 was then added to the cooled reaction mixture. After the reaction was warmed to room temperature the resulting yellow solution was analyzed by ^{1}H NMR spectroscopy, which indicated the quantitative formation of [(C_5Me_5)Ru(η^6-C_6Me_6)]$^+$OTf$^-$, as well as the formation of (η^5-$C_5H_3Ph_2$)Ru(η^5-1,2,3,4,5,6(*exo*)-hexamethylcyclohexadienyl), **128**, spectroscopically identical to the independently synthesized compound. The solvent was then removed under reduced pressure, the residue triturated with 3 mL of pentane, and the pentane extract filtered through Celite and dried to a pale yellow solid (0.012 g, approximately 71%; some diphenylacetylene was still present).



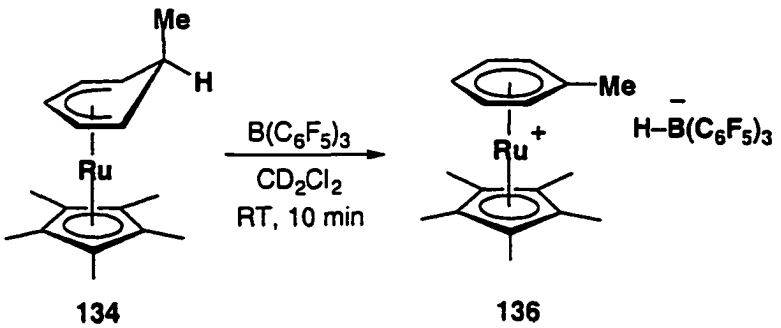
134

(C_5Me_5)Ru(η^5-6(*exo*)-methylcyclohexadienyl) (135). A suspension of [(C_5Me_5)Ru(η^6-C_6H_6)]$^+PF_6^-$ (**134**) (0.210 g, 0.457 mmol) in 20 mL diethyl ether was cooled to 0°C using an ice bath and MeLi (1.4 M in diethyl ether, 0.36 mL, 0.50 mmol, 1.1 equiv) added via syringe. No reaction was observed until 3 mL tetrahydrofuran was added. The reaction was stirred at 0°C for 1 hour before gradually warmed to room temperature for another 4 hours. The bright orange solution was then evaporated under low pressure and the residue triturated with several portions of hexane (3 x 2 mL). The combined hexane extracts were filtered through Celite and the orange filtrate concentrated to an oily residue. After thorough drying *in vacuo* the red residue was dissolved in pentane and filtered through a plug of alumina (5% H_2O), giving a nearly colourless filtrate. This filtrate was concentrated under reduced pressure to yield 0.086 g (57%) of a pale yellow crystalline material, which was used without further purification. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.13 (td, J = 4.7, 0.9 Hz, 1H, H_3), 3.89 (tt, J = 4.8, 1.3 Hz, 2H, H_2 and H_4), 2.22-2.20 (m, 3H, H_3, H_5 and H_6), 1.88 (s, 15H, C_5Me_5), 0.12 (d, J = 5.9 Hz, CH_3); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 89.2, 80.5, 79.3, 36.7, 34.6, 28.0, 11.5; MS *m/z* calculated for $C_{17}H_{24}{}^{102}Ru$ (M^+): 330.0922; found: 330.0906 (5.97%); calculated for $C_{17}H_{23}{}^{102}Ru$ (M-H): 329.0843; found: 329.0869 (8.77%); calculated for $C_{16}H_{21}{}^{102}Ru$ (M-CH_3): 315.0687; found: 315.0686 (100.00%).



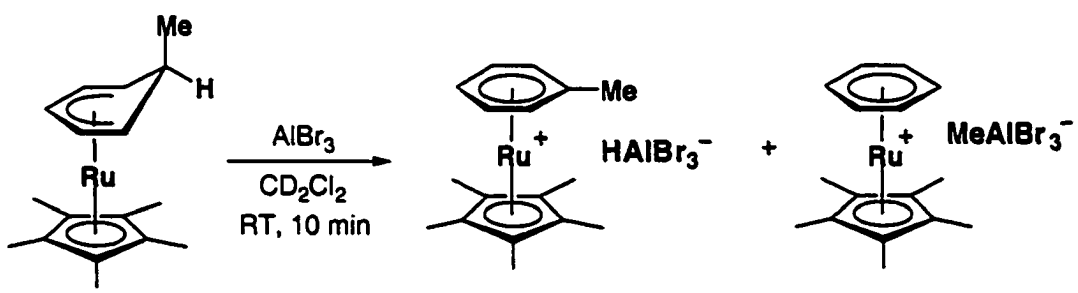
134 136 137

Addition of Protic Acids to $(C_5Me_5)Ru(\eta^5$-6(*exo*)-methylcyclohexadienyl). A solution of $(C_5Me_5)Ru(\eta^5$-6(*exo*)-CH_3-$C_6H_6)$ (0.015, 0.046 mmol) in anhydrous CD_2Cl_2 was placed into an NMR tube, which was then capped with a rubber septum. Triflic acid (0.004 mL, 0.045 mmol) was then added via microsyringe and the resulting solution analyzed by ^1H NMR spectroscopy. In less than 10 minutes at room temperature the reaction had gone to completion, giving $[(C_5Me_5)Ru(\eta^6$-$CH_3C_6H_5)]^+OTf^-$ (**136**) (spectroscopically identical to the known literature compound) with approximately 91% selectivity. The remaining 9% was identified as the demethylated product, $[(C_5Me_5)Ru(\eta^6$-$C_6H_6)]^+OTf^-$ (**137**) based on comparison to authentic material. Comparable results were obtained from the analogous reaction of $(C_5Me_5)Ru(\eta^5$-6(*exo*)-methylcyclohexadienyl) (0.015 g, 0.046 mmol) with excess tetrafluoroboric acid in acetone–d_6.



134 136

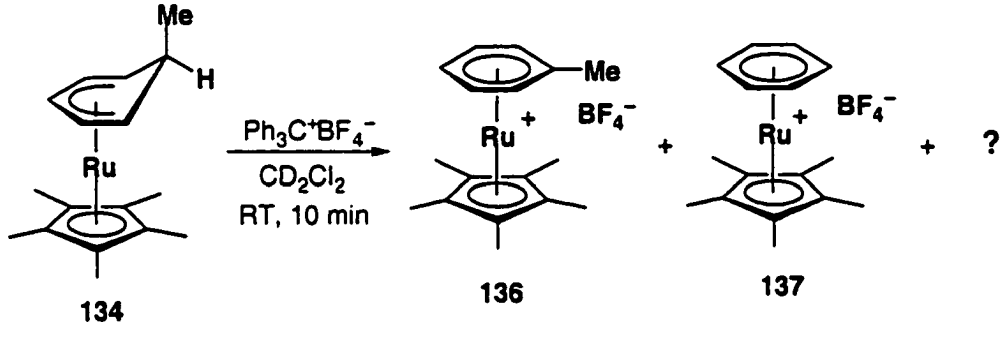
Reaction of $(C_5Me_5)Ru(\eta^5$-6(*exo*)-methylcyclohexadienyl) with $B(C_6F_5)_3$. A solution of $(C_5Me_5)Ru(\eta^5$-6(*exo*)-methylcyclohexadienyl) (**135**) (0.020 g, 0.060 mmol) in anhydrous CD_2Cl_2 was loaded into an NMR tube and tris(pentafluorophenyl)borane (0.035 g, 0.068 mmol) quickly added. The NMR tube was then capped and shaken for one minute. After 10 minutes standing at room temperature, ^{1}H NMR spectroscopic analysis of the colourless solution indicates $[(C_5Me_5)Ru(\eta^6\text{-}CH_3C_6H_5)]^+HB(C_6F_5)_3^-$ (*ca.* 99%) as the major product. Only a small trace of $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]^+$ (<1%) was observed in the ^{1}H NMR spectrum.



134

Reaction of $(C_5Me_5)Ru(\eta^5$-6(*exo*)-methylcyclohexadienyl) with $AlBr_3$. A solution of $(C_5Me_5)Ru(\eta^5$-6(*exo*)-methylcyclohexadienyl) (**135**) (0.025 g, 0.076 mmol) in anhydrous CD_2Cl_2 was loaded into an NMR tube and anhydrous $AlBr_3$ (0.021 g, 0.079 mmol) added. The NMR tube was then capped and shaken for a minute. After 10 minutes standing at

room temperature, ^{1}H NMR spectroscopic analysis of the colourless solution indicates a mixture of $[(C_5Me_5)Ru(\eta^6\text{-}CH_3C_6H_5)]^+$ (*ca.* 90%) and $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]^+$ (*ca.* 10%) with no trace of starting material. The counterions are presumed to be $HAlBr_3^-$ and $MeAlBr_3^-$, respectively, although no attempt was made to isolate these complexes.

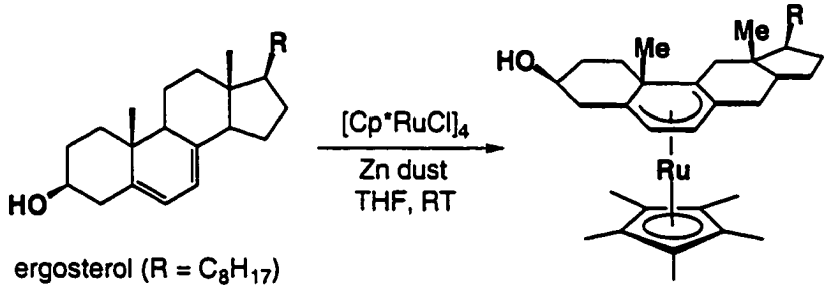


134 136 137

Reaction of $(C_5Me_5)Ru(\eta^5\text{-}6(exo)\text{-methylcyclohexadienyl})$ with Ph_3CBF_4. A solution of $(C_5Me_5)Ru(\eta^5\text{-}6(exo)\text{-methylcyclohexadienyl})$ (**135**) (0.015 g, 0.045 mmol) in anhydrous CD_2Cl_2 was loaded into an NMR tube and Ph_3CBF_4 (0.015 g, 0.045 mmol) added. The NMR tube was then capped and shaken for one minute. After 10 minutes standing at room temperature, ^{1}H NMR spectroscopic analysis of the colourless solution indicates a complex mixture containing $[(C_5Me_5)Ru(\eta^6\text{-}CH_3C_6H_5)]^+BF_4^-$ and $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]^+BF_4^-$ in a ratio of approximately 2.2 : 1. Also present is a third complex, which is tentatively identified as a trityl adduct.

Reaction of $(C_5Me_5)Ru(\eta^5\text{-}6(exo)\text{-methylcyclohexadienyl})$ with $[Cp_2Fe]^+PF_6^-$ at room temperature. A blue suspension of $[Cp_2Fe]^+PF_6^-$ (0.025 g, 0.076 mmol) in 2 mL dichloromethane was prepared and a solution of $(C_5Me_5)Ru(\eta^5\text{-}6(exo)\text{-}$

methylcyclohexadienyl) (0.025 g, 0.076 mmol) in 2 mL dichloromethane added slowly via cannula. The reaction mixture immediately turned from the blue suspension to a pale yellow solution. After stirring at room temperature for 30 minutes the solvent was removed under reduced pressure. ^{1}H NMR spectroscopic analysis of the yellow residue indicates conversion to $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (*ca.* 58%) and $[(C_5Me_5)Ru(\eta^6\text{-}CH_3C_6H_6)]^+PF_6^-$ (*ca.* 42%) along with a quantitative amount of ferrocene.

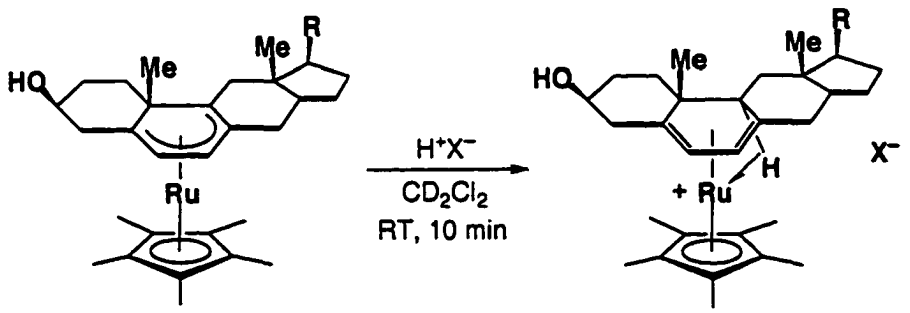


ergosterol (R = C_8H_{17})

138

$(C_5Me_5)Ru(\eta^5\text{-9-dehydroergosterol})$ (138). In the drybox, a Schlenk flask was charged with $[(C_5Me_5)RuCl]_4$ (0.130 g, 0.478 mmol/Ru) and ergosterol (0.20 g, 0.504 mmol, 1.05 equiv). Tetrahydrofuran (6 mL) was added and the reaction stirred at room temperature for 6 h, gradually turning deep green. Afterwards, Rieke zinc dust (0.100 g) was added and the reaction mixture stirred for a further 10 hours, turning the green solution nearly colourless. The solvent was then evaporated under reduced pressure and the residue triturated with several portions of hexane (3 x 2 mL) and the combined hexane extracts filtered through Celite. The filtrate was evaporated to a light brown foam, then dissolved in tetrahydrofuran and filtered through a plug of alumina (5% H_2O). The solvent was removed under reduced pressure to yield 0.157 g (52%) of a tan solid, which was used

without further purification. ^{1}H NMR (400 MHz, C_6D_6, select data only): δ 5.28 and 5.21 (AB pattern, J = 7.5 Hz, 2H, H_{22}/H_{23}), 5.11 and 3.59 (d, J = 4.8 Hz, 2H, H_6/H_7), 3.97-3.85 (m, 1H, H_3) 1.70 (s, 15H, C_5Me_5), 1.10 (d, J = 6.6 Hz, 3H), 1.01 (d, J = 6.9 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.90 (d, J = 6.7 Hz, 3H, Me-28/Me-27/Me-25/Me-21), 0.75 and 0.54 (s, 3H, Me-19/Me-18); ^{13}C NMR (100 MHz, C_6D_6): δ 136.2, 132.3 (C_{22}/C_{23}), 95.8, 92.1 (C_5/C_8), 87.2 (C_5Me_5), 79.3, 78.5, (C_6/C_7), 75.5 (C_9), 69.9 (C_3), 55.2, 51.4 (C_{14}/C_{17}), 44.2 (C_{10}), 42.4 (C_{13}), 43.3, 41.0, 38.6 ($C_{26}/C_{24}/C_{20}$), 37.7, 36.4, 33.4, 32.9, 29.8, 25.2, 23.7 ($C_{16}/C_{15}/C_{12}/C_{11}/C_4/C_2/C_1$), 22.6, 21.3, 20.2, 19.9, 17.9 (C_{28}/ C_{27}/ $C_{25}/C_{21}/C_{19}$), 11.3 (C_{18}), 10.9 (C_5Me_5); MS *m/z* calculated for $C_{38}H_{58}{}^{102}RuO$ (M^+): 632.3534; found: 632.3405 (2.83%); calculated for $C_{37}H_{55}{}^{102}Ru$) (M-CH_3): 617.3297; found: 617.3288 (100.00%).



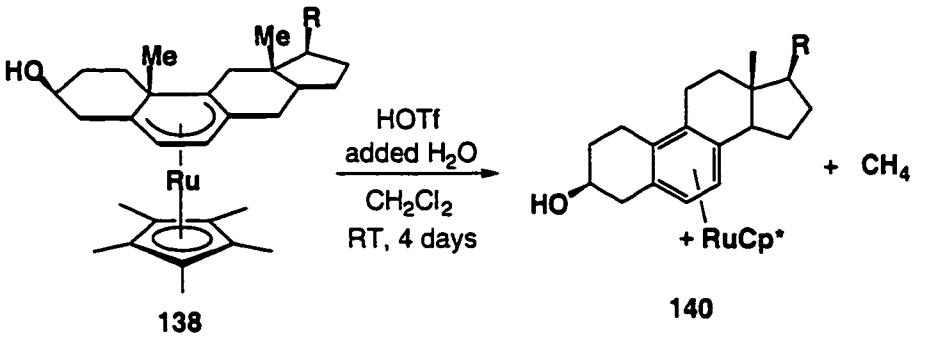
138 **139**

X = BF_4, OTf

[(C_5Me_5)Ru(η^4-ergosterol)]$^+BF_4^-$ (139). A solution of (C_5Me_5)Ru(η^5-dehydoergosterol) (**138**) (0.027 g, 0.043 mmol) in anhydrous dichloromethane-d_2 was placed into an NMR tube and capped with a small rubber septum. Tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) was then added (0.008 mL, 0.064 mmol) via microliter

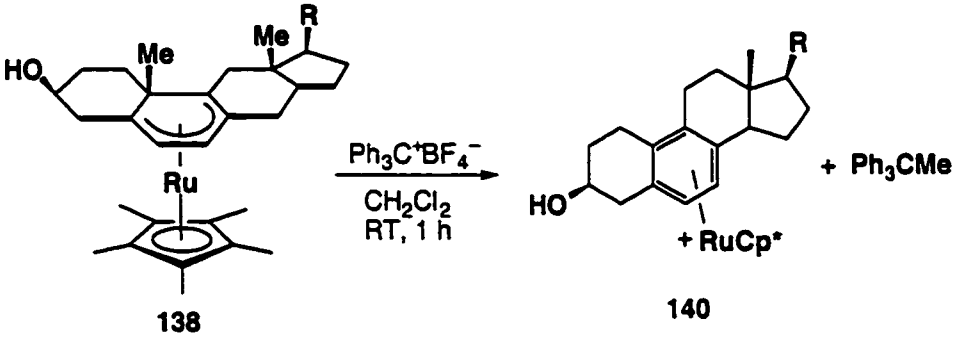
syringe and the resulting yellow solution analyzed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. (Chemical shifts vary slightly depending on amount of excess acid.)

Alternative Method: $[(C_5Me_5)Ru(\eta^4\text{-ergosterol})]^+OTf^-$ (139). A solution of $(C_5Me_5)Ru(\eta^5\text{-dehydroergosterol})$ (0.022 g, 0.035 mmol) in distilled diethyl ether (3 mL) was prepared in a small Schlenk flask. Triflic acid (0.004 mL, 0.045 mmol) was added via microliter syringe and the reaction stirred for 1 hour. Within 20 minutes an oily yellow residue deposited from the solution. The solution was decanted and the residue rinsed with several portions of diethyl ether, before drying the residue under vacuum. The resulting yellow foam was analyzed spectroscopically but was not further purified. ^{1}H NMR (400 MHz, CD_2Cl_2, select data only): δ 6.26 and 4.65 (d, J = 5.7 Hz, 2H, H_6/H_7), 5.30, 5.14 (AB pattern, J = 7.2 Hz, 2H, H_{22}/H_{23}), 4.08-3.90 (m, 1H, H_3), 1.91 (s, 15H, C_5Me_5), 1.00 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.83 (d, J = 6.8 Hz, 3H, Me-28/Me-27/Me-25/Me-21), 0.65, 0.55 (s, 3H, Me-19/Me-18), -5.00 (br s, 1H, H_{ag}); $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2): δ 134.9, 133.4 (C_{22}/C_{23}), 103.8 (C_8), 97.6 (C_5Me_5), 88.7, 88.6 (C_6/C_7), 81.6 (C_5), 79.7 (C_3), 68.1 (br, C_9), 54.7, 51.0 (C_{14}/C_{17}), 45.8, 42.2(C_{10}/C_{13}), 43.2, 40.5, 33.4 ($C_{26}/C_{24}/C_{20}$), 39.2, 36.3, 31.0, 29.0, 24.9, 24.0, ($C_{16}/C_{15}/C_{12}/C_{11}/C_4/C_2/C_1$), 26.1, 21.0, 20.0, 19.8, 17.6, ($C_{28}/C_{27}/C_{25}/C_{21}/C_{19}$), 10.8 ($C_{18}$), 10.6 ($C_5Me_5$). Triflate carbon signal was not observed.



138 140

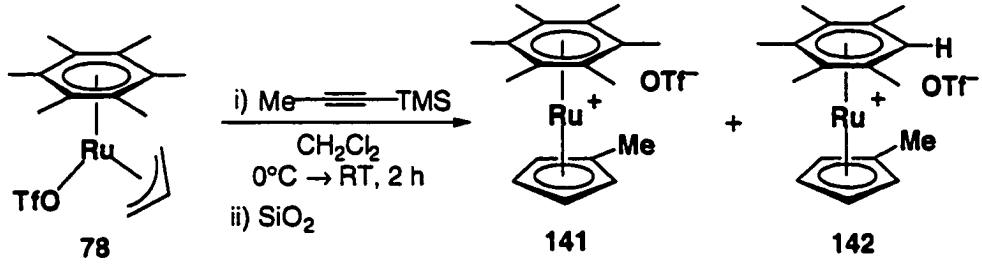
Dealkylation and Aromatization of $(C_5Me_5)Ru(\eta^5$-9-dehydroergosterol). A solution of $(C_5Me_5)Ru(\eta^5$-dehydroergosterol) (**138**) (0.044 g, 0.032 mmol) in distilled dichloromethane (2 mL) was prepared in a small Schlenk flask. Tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) was added via microsyringe (0.013 mL, 0.075 mmol) and the reaction stirred for 5 minutes before adding distilled water (0.006 mL, 0.33 mmol, 10.4 equiv). After 4 days stirring at room temperature the solvent was removed under reduced pressure, leaving a tan solid as residue. Spectroscopic analysis of the residue showed clean conversion to the aromatized B-ring derivative $[(C_5Me_5)Ru(\eta^6$-neoergosterol)$]^+BF_4^-$, **140**, which was spectroscopically consistent with the compound reported by Chaudret.[73b]



138 140

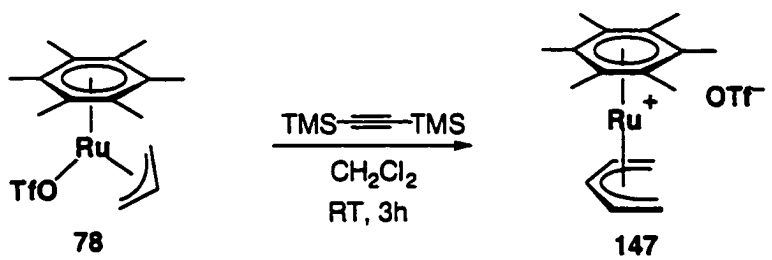
Reaction of $(C_5Me_5)Ru(\eta^5$-9-dehydroergosterol) with Ph_3CBF_4. In the drybox, a solution of $(C_5Me_5)Ru(\eta^5$-dehydroergosterol) (**138**) (0.015 g, 0.024 mmol) in 3 mL of

tetrahydrofuran was placed in a small Schlenk flask. A yellow slurry of triphenylcarbenium tetrafluoroborate (0.009 g, 0.027 mmol) was added dropwise over 5 minutes; the trityl precipitate rapidly disappeared and the solution turned light brown in colour. The reaction was stirred for another hour then the solvent removed *in vacuo*. Spectroscopic analysis of the residue in acetone-d_6 indicates clean conversion to the aromatized derivative $[(C_5Me_5)Ru(\eta^6\text{-neoergosterol})]^+BF_4^-$ (**140**) and Ph_3CCH_3.



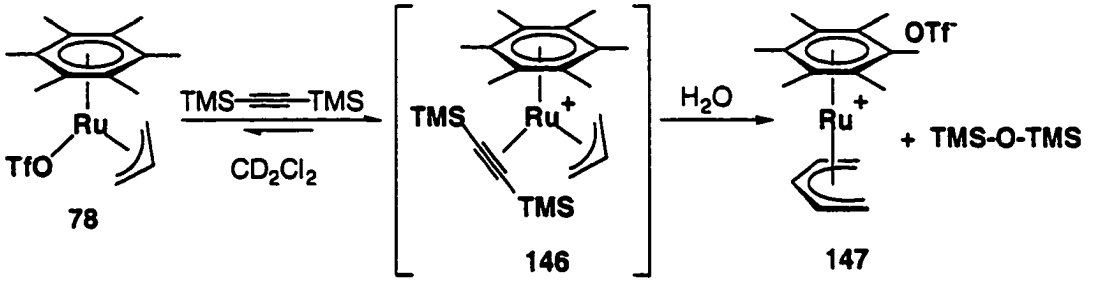
$[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_5H_4Me)]^+OTf^-$ (141). A small Schlenk flask was charged with $(C_6Me_6)Ru(\eta^3\text{-}C_3H_5)OTf$ (0.050 g, 0.110 mmol) and placed under a nitrogen atmosphere. Freshly distilled, degassed dichloromethane (1.5 mL) was added by syringe and the orange solution cooled to 0°C. 1-(Trimethylsilyl)propyne (0.33 mL, 2.22 mmol, 20 equiv) was then added via syringe and the solution stirred at 0°C for 2 hours, gradually turning brown. The solvent was then removed under reduced pressure, leaving an oily brown residue. ^1H NMR spectrum of the crude residue indicatess a 9 : 1 mixture of $[(C_6Me_6)Ru(\eta^5\text{-}C_5H_4Me)]^+OTf^-$ (**141**) and the tentatively identified $[(C_6Me_5H)Ru(\eta^5\text{-}C_5H_3Me(SiMe_3))]^+OTf^-$ (**145**): ^1H NMR (300 MHz, $CDCl_3$) partial data only: δ 6.09 (s, 1H, $C_6Me_5\underline{H}$), 4.95 (br s, 3H, $C_5\underline{H}_3Me(SiMe_3)$). The major compound was isolated by chromatography on a silica gel column using

10% methanol/dichloromethane as eluent, followed by recrystallization from dichloromethane/ diethyl ether to give 0.034 g (63%) of colourless needles. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.91 (t, J = 1.8 Hz, 2H, $C_5\underline{H}_4Me$), 4.84 (t, J = 1.8 Hz, 2H, $C_5\underline{H}_4Me$), 2.37 (s, 18H, $C_6\underline{Me}_6$), 1.83 (s, 3H, $C_5H_4\underline{Me}$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 99.1, 96.1, 81.9, 81.7, 17.4, 11.8. Triflate carbon signal was not observed. Analysis calculated for $C_{19}H_{25}F_3O_3RuS$: C, 46.43%; H, 5.13%; found: C, 46.37%; H, 4.94%. After chromatography the minor component was now tentatively identified in solution as the desilylated $[(C_6Me_5H)Ru(\eta^5\text{-}C_5H_4Me)]^+OTf^-$ (**142**) by the characteristic ^{1}H NMR spectroscopic signatures. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.13 (s, 1H, $C_6Me_5\underline{H}$), 4.98 (t, J = 1.5 Hz, 2H, C_5H_4Me), 4.95 (t, J = 1.5 Hz, 2H, C_5H_4Me), 2.33 (s, 3H, C_6Me_5H), 2.30 (s, 6H, C_6Me_5H), 2.28 (s, 6H, C_6Me_5H), 1.88 (s, 3H, C_5H_4Me).



$[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_5H_7)]^+OTf^-$ (147). A solution of $(C_6Me_6)Ru(\eta^3\text{-}C_3H_5)OTf$ (0.052 g, 0.115 mmol) in 3 mL degassed dichloromethane was prepared in a small Schlenk flask equipped with stir-bar and rubber septum. Freshly distilled bis(trimethylsilyl)acetylene (0.031 mL, 0.137 mmol, 1.2 equiv) was added via microliter syringe and the solution stirred for 3 hours at room temperature. The dichloromethane was evaporated under low pressure leaving an oily brown residue that

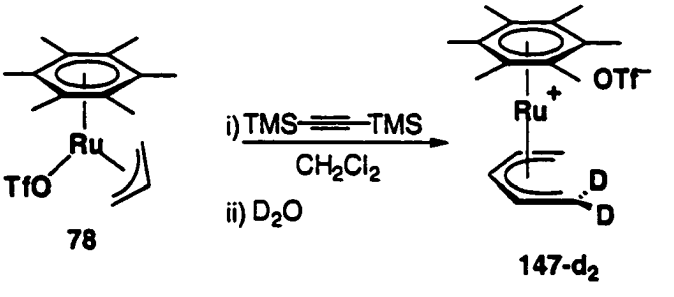
was filtered through a plug of silica gel (on the bench top) to remove coloured impurities using 10% methanol/dichloromethane as eluent. The product was then recrystallized by layering diethyl ether on acetone, yielding 0.032 g (58%) of large tan needles. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.75 (t, J = 6.2 Hz, 1H, H_3), 4.67 (ddd, J = 10.0, 8.9, 6.1 Hz, 2H, $H_{2/4}$), 2.79 (dd, J = 8.7, 3.1 Hz, 2H, $H_{1syn/5syn}$), 2.31 (s, 18H, $C_6\underline{Me_6}$), 1.07 (dd, J = 9.8, 3.0 Hz, 2H, $H_{1anti/5anti}$); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 104.7, 96.3, 91.6, 54.2, 16.8. Triflate carbon signal was not observed. Analysis calculated for $C_{18}H_{25}F_3O_3RuS$: C, 45.09%; H, 5.25%; found: C, 44.97%; H, 5.00%.



Preparation of [(η^6-C_6Me_6)Ru(η^3-C_3H_5)(TMS—≡—TMS)]$^+$OTf$^-$ (146). A solution of (η^6-C_6Me_6)Ru(η^3-C_3H_5)OTf (0.024 g, 0.053 mmol) in approximately 0.4 mL anhydrous degassed dichloromethane-d_2 was placed in an NMR tube. Freshly distilled bis(trimethylsilyl)acetylene (0.024 mL, 0.106 mmol, 2.0 equiv) was added via microliter syringe and the resulting dark orange solution analyzed by ^{1}H and ^{13}C NMR spectroscopy. The only ruthenium complex detected in solution was the alkyne complex **146**, present in near quantitative yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.68 (tt, J = 11.0, 6.4 Hz, 1H, $H_{central}$), 2.87 (dt, J = 6.3, 1.1 Hz, 2H, H_{syn}), 2.29 (s, 18 H, C_6Me_6), 1.78 (d, J = 11.1, 1.1 Hz, 2H, H_{anti}), 0.23 (s, 18H, TMS); ^{13}C{^{1}H} NMR (100

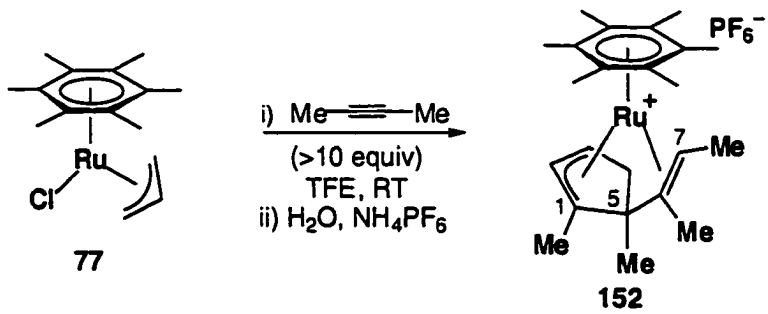
MHz, CD_2Cl_2): δ 110.8, 101.6, 87.8, 47.5, 16.9, 2.3. Triflate carbon signal was not observed. No changes were observed after 4 hours at room temperature while the solution was kept tightly sealed.

Addition of Water. Distilled water (0.003 mL, 0.167 mmol, 3.1 equiv) was added via microliter syringe to the solution of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_3H_5)(TMS{-}{\equiv}{-}TMS)]^+OTf^-$ (**146**) prepared above and the reaction mixture quickly analyzed by ^1H NMR spectroscopy. In less than 10 minutes the alkyne complex had completely converted to the η^5-pentadienyl product **147**; a new upfield signal at δ 0.11 (s, 18H) was also detected that was tentatively identified as the byproduct trimethylsilanol. The reaction mixture was allowed to stand for a further 24 hours before being analyzed again by ^1H NMR spectroscopy; the ruthenium complex remained unchanged but the trimethylsilanol signal had disappeared, to be replaced by a new signal at δ 0.06 (s, 18 H), identified as hexamethyldisiloxane. This identification was confirmed by comparison to an authentic sample.



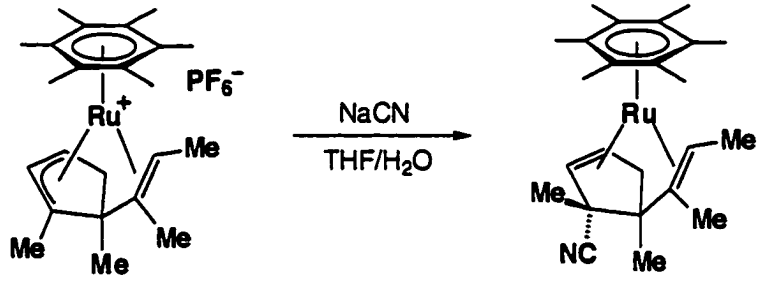
Addition of D_2O. A solution of $(C_6Me_6)Ru(\eta^3\text{-}C_3H_5)OTf$ (0.024 g, 0.053 mmol) in 2 mL degassed anhydrous dichloromethane was prepared in a small Schlenk flask equipped with stir-bar and rubber septum. Freshly distilled bis(trimethylsilyl)acetylene (0.024 mL, 0.106 mmol, 2.0 equiv) was added via microliter syringe and the solution

stirred for 20 minutes at room temperature. Excess D_2O (0.005 mL, 0.25 mmol, 4.7 equiv) was then added by microsyringe and the reaction stirred for a further 10 minutes. The dichloromethane was evaporated under low pressure to yield a tan solid. Analysis of the crude product by ^1H NMR spectroscopy revealed clean formation of the acyclic η^5-pentadienyl complex, where the signals at δ 2.79 and δ 1.07 now integrate to only one hydrogen each. The ^2H NMR spectrum only exhibits signals at δ 2.79 and δ 1.07, indicating that deuterium was exclusively incorporated at the H_{1syn} and H_{1anti} positions.



[(C_6Me_6)Ru((1,2,3:6,7-η)-1,5,6,7-tetramethyl-5-vinylcyclopentenyl)]$^+PF_6^-$ (152). A small Schlenk flask equipped with stir-bar and septum was charged with (C_6Me_6)Ru(C_3H_5)Cl (0.200 g, 0.589 mmol) and a nitrogen atmosphere was established. Trifluoroethanol (5.0 mL) was added, forming an intense orange solution. With rapid stirring 2-butyne (0.50 mL, 6.39 mmol, 10.8 equiv) was added by pipette and the reaction flask was sealed. After stirring for 30 minutes the solvent was removed *in vacuo*, leaving an oily orange residue. This residue was dried under vacuum for several hours before the crude product was extracted into 2 x 5 mL warm distilled water, and the aqueous solution filtered through Celite. Excess NH_4PF_6 (0.200 g, 1.23 mmol) was then added to the filtrate and the precipitate collected and thoroughly dried, giving 0.272 g (83%) of yellow powder. Further attempts at purification results in slow, partial conversion to an unidentified isomer accompanied by significant decomposition. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.51 (d, J = 3.6 Hz, 1H, H_2), 3.15 (q, J = 6.2 Hz, 1H, H_7), 3.07 (dd, J = 3.5, 1.5 Hz, 1H, H_3), 2.11 (s, 18H, C_6Me_6), 1.77 (s, 3H, CH_3), 1.69 (d, J = 6.3 Hz, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 0.80 (2H, AB pattern, H_{4a} and H_{4b}); ^{13}C NMR (100

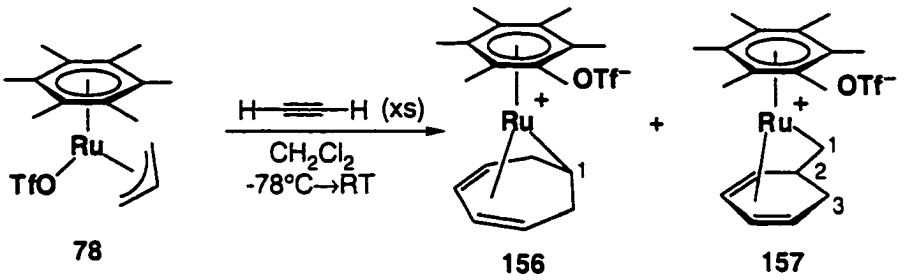
MHz, $CDCl_3$): δ 102.1 (s, $\underline{C}_6Me_6$), 83.4 (d, $^1J_{CH}$ = 176 Hz, C_2), 65.2 (s, C_6), 65.1 (d, $^1J_{CH}$ = 159 Hz, C_7), 63.5 (s, C_1), 52.9 (d, $^1J_{CH}$ = 168 Hz, C_3), 44.1 (s, C_5), 35.9 (t, $^1J_{CH}$ = 135 Hz, C_4), 19.4 (q, $^1J_{CH}$ = 125 Hz, CH_3), 15.9 (q, $^1J_{CH}$ = 126 Hz, $C_6\underline{Me}_6$), 14.5 (q, $^1J_{CH}$ = 125 Hz, CH_3), 14.4 (q, $^1J_{CH}$ = 125 Hz, CH_3), 13.4 (q, $^1J_{CH}$ = 125 Hz, CH_3); HMQC (300 MHz, $CDCl_3$): δ 83.4 (C_2) ↔ δ 3.51 (H_2); δ 65.1 (C_7) ↔ δ 3.15 (H_7); δ 52.9 (C_3) ↔ δ 3.07 (H_3); δ 35.9 (C_4) ↔ δ 0.80 (H_{4a} and H_{4b}); δ 19.4 (CH_3) ↔ δ 1.00 (CH_3); δ 15.9 (C_6Me_6) ↔ δ 2.11 (C_6Me_6); δ 14.5 (CH_3) ↔ δ 1.77 (CH_3); δ 14.4 (CH_3) ↔ δ 1.68 (CH_3); δ 13.4 (CH_3) ↔ δ 1.69 (CH_3); HMBC (300 MHz, $CDCl_3$): δ 83.4 (C_2) ↔ δ 1.77, 0.80; δ 65.2 (C_6)↔ δ 3.15, 1.68, 1.00, 0.80; δ 65.1 (C_7) ↔ δ 1.69; δ 63.5 (C_1) ↔ δ 3.51, 1.77, 1.00; δ 52.9 (C_3) ↔ δ 3.51, 0.80; δ 44.1 (C_5) ↔ δ 3.51, 3.15, 1.77, 1.68, 1.00, 0.80; δ 35.9 (C_4) ↔ δ 3.51, 1.00; δ 19.4 (CH_3) ↔ δ 0.80.



152 153

(C_6Me_6)Ru(2,3:6,7-η)-1,5,6,7-tetramethyl-1-cyano-5-vinylcyclopentene) (153). A solution of (**152**) (0.200 g, 0.359 mmol) in tetrahydofuran (5 mL) was prepared and a NaCN solution (0.090 g, 1.84 mmol, 5.12 equiv) in 1 mL distilled water was added via syringe. The reaction was then allowed to stir at room temperature for two hours before removing the solvent under low pressure. The residue was dried thoroughly under vacuum before the flask was removed to the drybox, where the residue was triturated

with 2 x 4 mL diethyl ether and the combined fractions filtered through alumina (5% H_2O). The filtrate was concentrated to give 0.135 g (86%) of yellow, mildly air-sensitive crystals. X-ray quality crystals were grown by layering pentane on a concentrated toluene solution and cooling at –35°C (drybox freezer) for several days. ^{1}H NMR (400 MHz, C_6D_6): δ 2.55 (q, J = 6.6 Hz, 1H, H_7), 1.86 (d, J = 4.8 Hz, 1H, H_2), 1.74 (dd, J = 4.8, 1.8 Hz, 1H, H_3), 1.57 (s, 3H, CH_3), 1.56 (s, 18H, C_6Me_6), 1.50 (dd, J = 12.9, 1.8 Hz, 1H, H_{4a}), 1.30 (d, J = 12.9 Hz, 1H, H_{4b}), 1.21 (d, J = 6.6 Hz, 3H, CH_3), 1.14 (s, 3H, CH_3), 1.10 (s, 3H, CH_3); ^{13}C NMR (75 MHz, C_6D_6): δ 124.9 (s, $\underline{C}N$), 98.3 (s, $\underline{C}_6Me_6$), 67.0 (s, C_6), 64.5 (d, $^1J_{CH}$ = 163 Hz, C_2), 56.5 (s, C_1), 50.6 (d, $^1J_{CH}$ = 152 Hz, C_7), 49.8 (s, C_5), 41.9 (d, $^1J_{CH}$ = 160 Hz, C_3), 36.7 (t, $^1J_{CH}$ = 127 Hz, C_4), 22.0 (q, $^1J_{CH}$ = 125 Hz, CH_3), 18.3 (q, $^1J_{CH}$ = 122 Hz, CH_3), 17.4 (q, $^1J_{CH}$ = 122 Hz, CH_3), 15.7 (q, $^1J_{CH}$ = 125 Hz, $C_6\underline{Me}_6$), 14.1 (q, $^1J_{CH}$ = 126 Hz, CH_3); HMQC (300 MHz, C_6D_6): δ 64.5 (C_2) ↔ δ 1.86 (H_2); δ 50.6 (C_7) ↔ δ 2.55 (H_7); δ 41.9 (C_3) ↔ δ 1.74 (H_3); δ 36.7 (C_4) ↔ δ 1.50 (H_{4a}) and 1.30 (H_{4b}); δ 22.0 (CH_3) ↔ δ 1.57 (CH_3); δ 18.3 (CH_3) ↔ δ 1.10 (CH_3); δ 17.4 (CH_3) ↔ δ 1.21 (CH_3); δ 15.7 ($C_6\underline{Me}_6$) ↔ δ 1.56 ($C_6\underline{Me}_6$); δ 14.1 (CH_3) ↔ δ 1.14 (CH_3); HMBC (300 MHz, C_6D_6): δ 67.0 (C_6) ↔ δ 1.21, 1.14, 1.10; δ 64.5 (C_2) ↔ δ 1.74, 1.30; δ 56.5 (C_1) ↔ δ 1.86, 1.74, 1.30, 1.14; δ 50.6 (C_7) ↔ δ 1.21; δ 49.8 (C_5) ↔ δ 2.55, 1.86, 1.74, 1.30, 1.14, 1.10; δ 41.9 (C_3) ↔ δ 1.86, 1.30; δ 36.7 (C_4) ↔ δ 1.86, 1.74, 1.14; δ 18.3 (CH_3) ↔ δ 2.55. MS *m/z* calculated for $C_{24}H_{35}N^{102}Ru$ (M^+): 439.1813; found: 439.1811(53.23%); calculated for $C_{23}H_{32}N^{102}Ru$ (M-CH_3): 424.1578; found: 424.1565 (25.06%); calculated for $C_{19}H_{27}{}^{102}Ru$ (M-C_5H_8N): 357.1156; found: 357.1138 (100.00%).

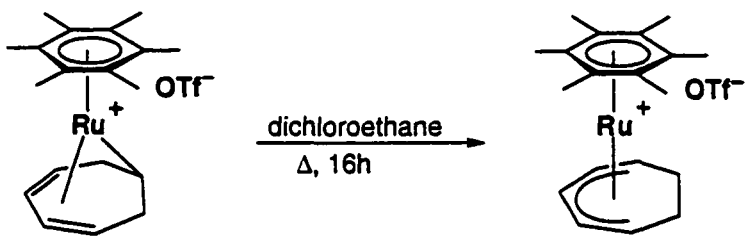


78 156 157

Reaction of $(C_6Me_6)Ru(C_3H_5)OTf$ (78) with Acetylene. In the drybox $(C_6Me_6)Ru(C_3H_5)OTf$ (0.050 g, 0.110 mmol) was placed in a Schlenk flask equipped with stir-bar and septum. The flask was sealed and removed to the Schlenk line where dichloromethane (4 mL) was added by syringe. The orange solution was then cooled to –78°C using a dry ice/acetone bath and the septum wired on. Acetylene was bubbled through the solution for 5 minutes before slowly removing the cold bath. Once the reaction neared room temperature the solvent was immediately removed *in vacuo*, leaving a tan solid. Initial analysis of the crude residue by ^1H NMR spectroscopy indicates two products **156** and **157** in an approximate 9 : 1 ratio, respectively. **$[(C_6Me_6)Ru((1:3,4,5,6-\eta)cycloheptadienyl)]^+OTf^-$ (156).** ^1H NMR (400 MHz, $CDCl_3$): δ 5.33-5.29 (m, AA´XX´ pattern, 2H, H_4/H_5), 3.53 (br t, J = 6.9 Hz, 2H, H_3/H_6), 3.73 (dt, J = 13.5, 8.5 Hz, 2H, H_{2endo}/H_{7endo}), 2.23 (s, 18H, C_6Me_6), 2.15 (d, J = 13.8 Hz, 2H, H_{2exo}/H_{7exo}, partially obscured), –0.09 (t, J = 8.8 Hz, 1H, H_1). Qualitative spin saturation transfer experiments (300 MHz, $CDCl_3$): irradiation at δ 5.32, 3.53, 2.15 or –0.09 ↔ disappearance or diminution of signals at 5.32, 3.53, 2.15 and –0.09. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 107.6, 97.7, 44.1, 33.5, 16.3, –38.1. Triflate carbon signal was not observed. ^1H-^{13}C HETCORR (100 MHz, $CDCl_3$): δ 97.7 (C_4/C_5) ↔ δ 5.30 (H_4/H_5);

δ 44.1 (C_3/C_6) ↔ δ 3.53 (H_3/H_6); δ 33.5 (C_2/C_7) ↔ δ 3.73, 2.15 (H_2/H_7); δ 16.3 (C_6Me_6) ↔ δ 2.23 (C_6Me_6); δ –38.1 (C_1) ↔ δ –0.09 (H_1);

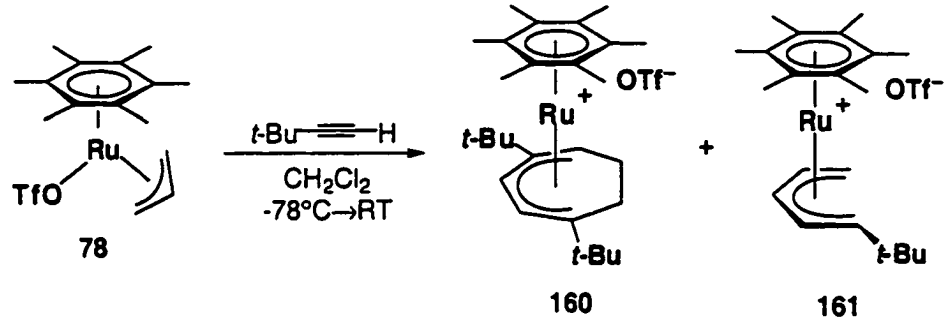
[(C_6Me_6)Ru((1:4,5,6,7-η)methanocyclohexadienyl)]$^+$OTf$^-$ (157) (Characterized as a 1 : 9 mixture with complex **156**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.36 (t, J = 5.5 Hz, 1H, H_5), 4.53 (t, J = 5.5 Hz, 1H, H_6), 3.96 (br s, 1H, H_4), 3.48 (t, J = 5.6 Hz, 1H, H_7), 3.15 (br s, 1H, H_2), 2.24 (s, 18H, C_6Me_6), 1.21 (br s, 1H, H_{1a}), 1.07 (br s, 2H, H_{3endo} and H_{3exo}), 0.99 (d, J = 3.2 Hz, 1H, H_{1b}); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 106.8, 91.6, 86.8, 70.5, 62.3, 37.3, 24.4, 16.4, 0.13. Triflate carbon signal was not observed.



156 **159**

[(C_6Me_6)Ru(η^5-cycloheptadienyl)]$^+$OTf$^-$ (159). The mixture of complexes **156** and **157** from the previous reaction was placed into a small roundbottom flask equipped with a stir bar, nitrogen inlet and condenser. Dichloroethane (3 mL) was added and the mixture heated to reflux for 12 hours. Afterwards the solvent was removed under reduced pressure and the tan residue dried. ^{1}H NMR spectroscopic analysis of the residue demonstrated that complex **156** had cleanly converted to [(C_6Me_6)Ru(η^5-cycloheptadienyl)]OTf **159** which is spectroscopically identical to the known literature compound, while complex **157** had remained unchanged. The η^5-cycloheptadienyl

product is isolated by chromatography on silica gel using 10% methanol/ dichloromethane as eluent, followed by recrystallization from acetone/ diethyl ether.

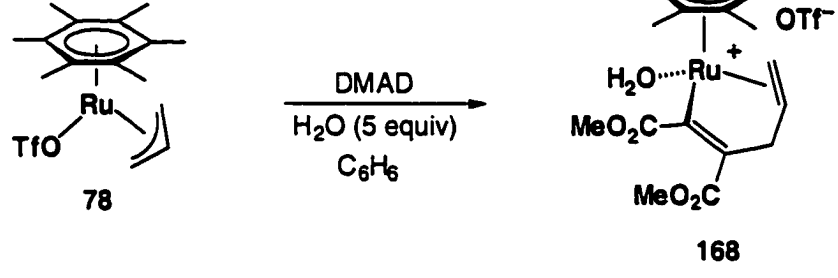


[(C_6Me_6)Ru(η^5-1,4-bis(*t*-butyl)cycloheptadienyl)]$^+$OTf$^-$ (160). In the drybox, (C_6Me_6)Ru(C_3H_5)OTf (0.045 g, 0.099 mmol) was placed in a Schlenk flask equipped with stir-bar and septum. The sealed flask was removed to the Schlenk line and anhydrous dichloromethane (3 mL) added. The solution was then cooled to –78°C and 3,3-dimethyl-1-butyne (0.050 mL, 0.40 mmol, 4 equiv) added via syringe. After 10 min at –78°C the cold bath was removed and the reaction was allowed to warm to room temperature for a further hour. The solvent was then removed under low pressure and the oily orange residue dried under vacuum. The products were separated and purified by chromatography on silica gel using 2% ethanol/dichloromethane. An orange fraction was collected and dried to give 0.052 g (64%) of orange foam as the major product **160**. Analytically pure product could be obtained after careful recrystallization from dichloromethane/diethyl ether. A second, pale yellow fraction was collected to give 0.003 g (4%) of the minor product **161**.

[(C_6Me_6)Ru(η^5-1,4-bis(*t*-butyl)cycloheptadienyl)]$^+$OTf$^-$ (160). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (d, J = 5.7 Hz, 1H, H_3), 5.40 (d, J = 5.6 Hz, 1H, H_2), 3.81 (br s, 1H, H_5),

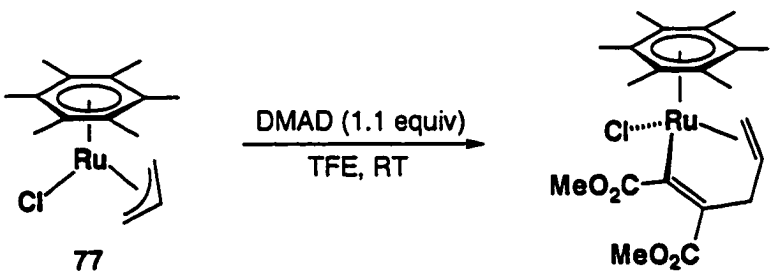
2.75 (dtd, J = 14.8, 4.2, 1.3 Hz, 1H, H_{6endo}), 2.60-2.45 (m, 1H, H_{6exo}), 2.29 (s, 18H, C_6Me_6), 1.56 (ddd, J = 12.3, 6.8, 1.4 Hz, 1H, H_{7exo}), 1.17 (s, 9H, $C(C\underline{H}_3)_3$), 1.07 (s, 9H, $C(C\underline{H}_3)_3$), 0.05 (td, J = 12.1, 4.4 Hz, 1H, H_{7endo}); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 139.5, 116.0, 102.2, 85.5, 81.7, 63.3, 50.2, 39.4, 37.2, 30.4, 28.7, 27.5, 17.8. The triflate carbon signal was not observed. Analysis calculated for $C_{28}H_{43}F_3O_3RuS$: C, 54.44%; H, 7.02%; found: C, 54.27%; H, 6.84%.

$[(C_6Me_6)Ru(\eta^5$-1-*t*-butylpentadienyl)$]^+OTf^-$ (161) (partial data only): ^1H NMR (400 MHz, $CDCl_3$): δ 6.37 (t, J = 6.8 Hz, 1H, H_3), 4.80 (ddd, J = 10.1, 8.6, 6.8 Hz, 1H, H_4), 4.24 (dd, J = 9.5, 6.5 Hz, 1H, H_2), 3.22 (d, J = 9.3 Hz, 1H, H_{1anti}), 2.57 (dd, J = 8.7, 3.0 Hz, 1H, H_{5syn}), 2.28 (s, 18H, C_6Me_6), 0.82 (s, 9H, $C(\underline{C}H_3)_3$). One proton signal was obscured.



$[(C_6Me_6)Ru((1:4,5-\eta)$-1,2-dicarbomethoxypentadienyl)$(OH_2)]^+OTf^-$ (168). In the drybox $(C_6Me_6)Ru(C_3H_5)OTf$ (0.545 g, 1.20 mmol) was placed in a 50 mL Schlenk flask equipped with stir-bar and septum, and the flask removed to the Schlenk line. Benzene (15 mL) was added, forming an orange solution, and dimethyl acetylenedicarboxylate (0.252 mL, 2.05 mmol, 1.70 equiv) added by syringe. The solution was allowed to stir at room temperature for 2 hours before adding 0.100 mL (5 equiv) of distilled water.

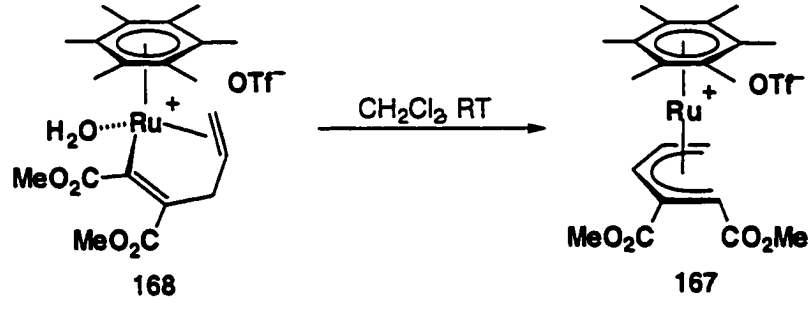
Diethyl ether (15 mL) was added, and the flask cooled without stirring to –20°C overnight. The next day the brown precipitate was filtered off and rinsed with 3 mL of diethyl ether and dried, giving 0.560 g (76%) of analytically pure complex **168**. IR (CH_2Cl_2 cast, cm^{-1}): 3068 (br), 1701 (s), 1654 (s), 1236 (s), 1218 (s), 1025 (s), 637 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 5.04 (s, 2H, H_2O), 4.68 (d, 1H, J = 9.0 Hz, H_{5syn}), 4.59-4.52 (m, 1H, H_4), 3.82 (s, 3H, CO_2CH_3), 3.63 (s, 3H, CO_2CH_3), 3.57 (d, 1H, J = 13.3 Hz, H_{5anti}), 3.18 (dd, 1H, J = 18.4, 7.0 Hz, H_{3endo}), 2.99 (d, J = 18.4 Hz, H_{3b}), 2.05 (s, 18H, C_6Me_6); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 175.7, 169.8, 161.7, 138.6, 105.3, 94.8, 70.6, 51.9, 51.7, 35.3, 15.6. The triflate carbon signal was not observed. Analysis calculated for $C_{22}H_{31}F_3O_8RuS$: C, 43.06%; H, 5.09%; found: C, 43.17%; H, 4.93%.



77 169

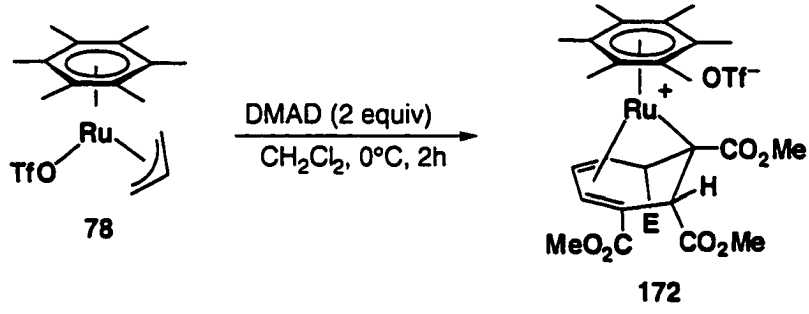
(C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentadienyl)Cl (169). A bright orange solution of $(C_6Me_6)Ru(C_3H_5)Cl$ (0.220 g, 0.647 mmol) in 4 mL trifluoroethanol was placed in a small Schlenk flask under a nitrogen atmosphere. Dimethyl acetylenedicarboxylate (0.096 mL; 0.780 mmol, 1.2 equiv) was added via syringe and the reaction stirred at room temperature, gradually turning dark brown in colour. After 4 hours the solvent was removed *in vacuo*, leaving an oily brown residue. The crude product was then extracted up into a minimum of warm toluene and the solution filtered

through Celite. Hexane was layered on the filtrate and the mixture cooled to –20°C overnight. The next day the product was filtered off as a brown microcrystalline solid (0.295 g, 95%). IR ($CHCl_3$ cast, cm^{-1}): 1706 (s), 1693 (s), 1572 (m), 1258 (m), 1225 (s), 750 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 4.59-4.52 (m, 1H, H_4), 3.66 (s, 3H, CO_2CH_3), 3.59 (d, 1H, J = 8.8 Hz, H_{5syn}), 3.58 (d, 1H, J = 14.0 Hz, H_{5anti}), 3.57 (s, 3H, CO_2CH_3), 3.12 (dd, 1H, J = 17.6, 6.8 Hz, H_{3a}), 3.02 (dd, J = 17.6, 3.1 Hz, H_{3b}), 2.02 (s, 18H, C_6Me_6); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 177.4, 174.5, 162.2, 128.3, 105.3, 86.4, 66.2, 51.2, 50.6, 35.7, 15.6. Analysis calculated for $C_{21}H_{29}RuClO_4$: C, 52.33%; H, 6.06%; found: C, 52.83%; H, 6.07%.



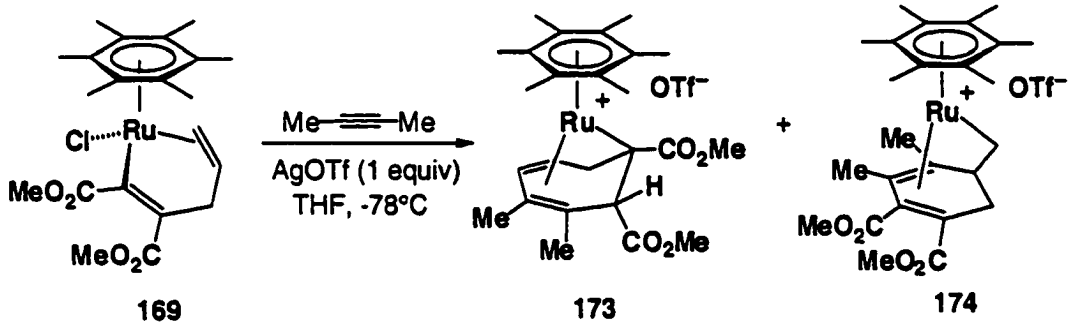
[(C_6Me_6)Ru(η^5-1,2-dicarbomethoxypentadienyl)]$^+$OTf$^-$ (167). A brown solution of [(C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentenyl)(OH_2)]$^+$OTf$^-$ (0.040 g, 0.065 mmol) in dichloromethane (2 mL) was stirred at room temperature for 20 hours, gradually lightening in colour to pale yellow. The solvent was removed under reduced pressure, leaving a yellow foam as residue. Pale yellow crystals were precipitated from acetone/ diethyl ether, giving 0.035 g (90%) of analytically pure product. IR (CH_2Cl_2 cast, cm^{-1}): 1735 (s), 1714 (s), 1266 (s), 1030 (m), 637 (s); ^1H NMR (300 MHz, $CDCl_3$): δ 6.14 (d, J = 6.3 Hz, 1H, H_3), 5.23-5.12 (m, 1H, H_4), 3.83 (s, 3H, CO_2CH_3), 3.77 (s, 3H, CO_2CH_3),

3.35 (dd, J = 9.1, 3.7 Hz, 1H, H_{5syn}), 2.27 (s, 18H, C_6Me_6), 1.63 (dd, J = 10.5, 3.8 Hz, 1H, H_{5anti}), 1.20 (s, 1H, H_1); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 171.2, 167.2, 107.6, 99.9, 95.5, 91.9, 59.9, 53.6, 52.0, 48.0, 16.3. Triflate carbon signal was not observed. Analysis calculated for $C_{22}H_{29}F_3O_7RuS$: C, 44.37%; H, 4.91%; found: C, 44.42%; H, 4.85%.



[(C_6Me_6)Ru((1:3,4,5,6-η)-1,2,3,7-tetracarbomethoxycycloheptadienyl)]$^+$OTf$^-$ (172). A solution of (C_6Me_6)Ru(C_3H_5)OTf (0.110 g, 0.243 mmol) in dichloromethane was cooled to 0°C using an ice bath and dimethyl acetylenedicarboxylate (0.061 mL, 0.50 mmol, 2.0 equiv) added by syringe. After two hours stirring at 0°C, the ice bath was removed and stirring continued for another 12 hours at room temperature. After evaporation of the solvent, the residue was taken up into a minimum of dichloromethane and purified by flash chromatography on silica gel, using 5% methanol/dichloromethane as eluent. The isolated yield of the yellow solid was 0.137 g (77%). An analytical sample was prepared by careful recrystallization from dichloromethane/diethyl ether. IR (CH_2Cl_2 cast, cm^{-1}): 1736 (v br s), 1715 (s), 1689 (s), 1266 (s), 1223 (s), 638 (m); ^1H NMR (300 MHz, $CDCl_3$): δ 6.59 (d, J_{4-5} = 8.2 Hz, 1H, H_4), 5.75 (t, $J_{5-4} = J_{5-6}$ = 8.4 Hz, 1H, H_5), 5.03 (s, 1H, H_2), 4.52 (d, J_{4-5} = 8.3 Hz, 1H, H_7), 4.16 (t, $J_{6-5} = J_{6-7}$ = 8.4 Hz, 1H,

H_6), 3.923 (s, 3H, $CO_2\underline{Me}$), 3.920 (s, 3H, $CO_2\underline{Me}$), 3.46 (s, 3H, $CO_2\underline{Me}$), 3.43 (s, 3H, $CO_2\underline{Me}$), 2.10 (s, 18H, $C_6\underline{Me}_6$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.4 (s, $\underline{C}O_2Me$), 169.9 (s, 2 x $\underline{C}O_2Me$), 169.0 (s, $\underline{C}O_2Me$), 110.4 (s, $\underline{C}_6Me_6$), 100.3 (d, $^1J_{CH}$ = 169 Hz, C_4), 98.7 (d, $^1J_{CH}$ = 169 Hz, C_5), 53.6 (q, $^1J_{CH}$ = 125 Hz, CO_2Me), 53.0 (q, $^1J_{CH}$ = 125 Hz, CO_2Me), 51.8 (m, 2 x CO_2Me, C_6), 48.1 (s, C_3), 46.2 (d, $^1J_{CH}$ = 133 Hz, C_2), 45.4 (d, $^1J_{CH}$ = 137 Hz, C_7), 15.4 (q, $^1J_{CH}$ = 130 Hz, $C_6\underline{Me}_6$), −15.5 (s, C_1); ^1H-^{13}C HETCORR (100 MHz, $CDCl_3$): δ 100.3 (C_4) ↔ δ 6.59 (H_4); δ 98.7 (C_5) ↔ δ 5.75 (H_5); δ 53.6 (CO_2Me) ↔ δ 3.923 (CO_2Me); δ 53.0 (CO_2Me) ↔ δ 3.920 (CO_2Me); δ 51.8 (C_6, 2 x CO_2Me) ↔ δ 3.43, 3.43 (2 x CO_2Me), 4.16 (H_6); δ 46.2 (C_2) ↔ δ 5.03 (H_2); δ 45.4 (C_7) ↔ δ 4.53 (H_7); δ 15.1 (C_6Me_6) ↔ δ 2.10 (C_6Me_6). Analysis calculated for $C_{28}H_{35}F_3O_{11}RuS$: C, 45.59%; H, 4.78%; found: C, 45.20%; H, 4.72%.



169 173 174

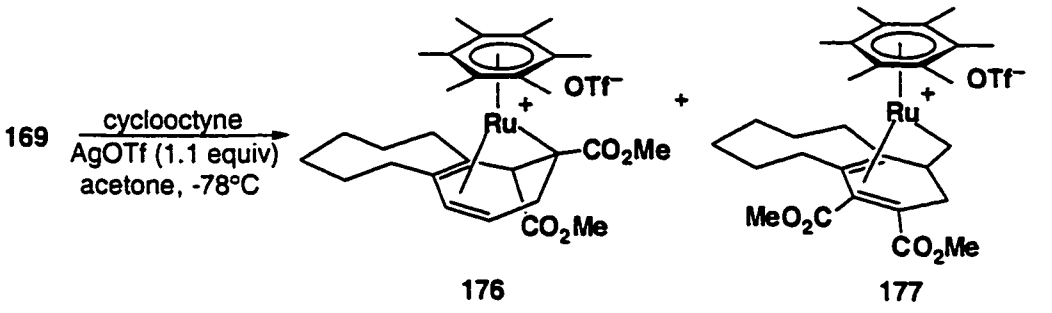
Reaction of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentenyl)Cl (169) with 2-Butyne. A solution of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentenyl)Cl (0.200 g, 0.415 mmol) in tetrahydrofuran (6 mL) was cooled to −78°C using a dry ice/acetone bath. 2-Butyne (0.165 mL, 2.11 mmol, 5 equiv) was added via syringe, then a solution of AgOTf (0.120 g, 0.467 mmol, 1.12 equiv) in 2 mL tetrahydrofuran was introduced via

cannula. The reaction mixture was stirred at –78°C for several hours then gradually allowed to warm to room temperature. After filtration through Celite to remove AgCl, the solvent was evaporated under low pressure and the residue was purified by chromatography on silica gel, using 4% methanol/dichloromethane as eluent. The first yellow fraction collected proved to be the minor product **174**, which was dried and recrystallized from dichloromethane/diethyl ether, giving 0.040 g (15%) of yellow crystals. The second fraction collected, the major product, complex **173**, was treated similarly, yielding 0.260 g (78%) of bright yellow crystals.

[(C_6Me_6)Ru((1:3,4,5,6-η)-1,2-dicarbomethoxy-3,4-dimethylcycloheptadienyl)]$^+$OTf$^-$ (173). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.30 (d, $J_{5\text{-}6}$ = 8.9 Hz, 1H, H_5), 4.18 (d, $J_{2\text{-}7endo}$ = 1.3 Hz, 1H, H_2), 3.90 (ap. td, 1H, $J_{6\text{-}5}$ = 8.7 Hz, $J_{6\text{-}7endo}$ = 8.7 Hz, $J_{6\text{-}7exo}$ = 2.2 Hz, H_6), 3.83 (s, 3H, $CO_2\underline{Me}$), 3.50 (s, 3H, $CO_2\underline{Me}$), 3.24 (ddd, $J_{7endo\text{-}7exo}$ = 15.4 Hz, $J_{7endo\text{-}6}$ = 8.5 Hz, $J_{7endo\text{-}2}$ = 1.4 Hz, 1H, H_{7endo}), 2.26 (s, 3H, CH_3), 2.22 (ddd, $J_{7exo\text{-}7endo}$ = 15.5 Hz, $J_{7exo\text{-}6}$ = 2.1 Hz, $J_{7exo\text{-}5}$ = 1.1 Hz, 1H, H_{7exo}), 2.13 (s, 18H, $C_6\underline{Me}_6$), 1.87 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 177.4 ($\underline{C}O_2Me$), 171.0 ($\underline{C}O_2Me$), 112.2 (C_4), 107.7 ($\underline{C}_6Me_6$), 97.9 (C_5), 57.0 (C_2), 56.2 (C_3), 52.2 ($CO_2\underline{Me}$), 51.6 ($CO_2\underline{Me}$), 50.4 (C_6), 30.5 (C_7), 22.9 (CH_3), 22.4 (CH_3), 15.1 ($C_6\underline{Me}_6$), –25.2 (C_1); ^{1}H-^{13}C HETCORR (100 MHz, $CDCl_3$): δ 97.9 (C_5) ↔ δ 5.30 (H_5); δ 57.0 (C_2) ↔ δ 4.18 (H_2); δ 52.2 ($CO_2\underline{Me}$) ↔ δ 3.83 ($CO_2\underline{Me}$); δ 51.6 ($CO_2\underline{Me}$) ↔ δ 3.50 ($CO_2\underline{Me}$); δ 50.4 (C_6) ↔ δ 3.90 (H_6); δ 30.5 (C_7) ↔ δ 3.24 (H_{7endo}) and 2.22 (H_{7exo}); δ 22.4 (CH_3) ↔ δ 2.26 (CH_3); δ 22.9 (CH_3) ↔ δ 1.87 (CH_3); δ 15.1 ($C_6\underline{Me}_6$) ↔ δ 2.13 ($C_6\underline{Me}_6$); ^{1}H-^{13}C BIRDTRAP (100 MHz, $CDCl_3$): δ 177.4 (CO_2Me) ↔ δ 3.83, 4.18; δ 171.0 (CO_2Me) ↔ δ 3.50, 4.18; δ 112.2 (C_3) ↔ δ 1.87, 2.26, 3.90, 4.18; δ 107.7 (C_6Me_6) ↔ δ 2.13; δ 57.0 (C_2) ↔ δ 1.87;

δ 56.2 (C_3) ↔ δ 1.87, 2.26, 4.18, 5.30; δ 52.2 (CO_2Me) ↔ δ 3.83; δ 51.6 (CO_2Me) ↔ δ 3.50; δ 15.1 (C_6Me_6) ↔ δ 2.13; δ –25.2 (C_1) ↔ δ 4.18. Analysis calculated for $C_{26}H_{35}F_3O_7SRu$: C, 48.07%; H, 5.43%; found: C, 48.20%; H, 5.34%.

[(C_6Me_6)Ru((1:4,5,6,7-η)-4,5-dicarbomethoxy-6,7-dimethylmethanocyclohexa-dienyl)]$^+$OTf$^-$ (**174**) (minor product). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89 (s, 3H, CO_2Me), 3.70 (s, 3H, CO_2Me), 3.08 (dt, J = 4.4, 2.2 Hz, 1H, H_2), 2.10 (s, 18H, $C_6\underline{Me}_6$), 1.88 (s, 3H, CH_3), 1.63 (dd, J = 12.1, 2.0 Hz, 1H, H_{3endo}), 1.48 (s, 3H, CH_3), 1.46 (m, partially obscured, 1H, H_{1a}), 1.15 (d, J = 3.3 Hz, 1H, H_{1b}), 0.84 (dt, J = 12.1, 2.3 Hz, 1H, H_{3exo}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7 (s, $\underline{C}O_2CH_3$), 167.7 (s, $\underline{C}O_2CH_3$), 111.3 (s, $\underline{C}_6Me_6$), 97.3 (s, C_5), 94.3 (s, C_6), 70.1 (s, C_4), 63.4 (s, C_7), 53.4 (q, $^1J_{CH}$ = 125 Hz, $CO_2\underline{Me}$), 52.2 (q, $^1J_{CH}$ = 125 Hz, $CO_2\underline{Me}$), 44.5 (d, $^1J_{CH}$ = 141 Hz, C_2), 24.4 (t, $^1J_{CH}$ = 140 Hz, C_3), 17.7 (q, $^1J_{CH}$ = 125 Hz, CH_3), 15.5 (q, $^1J_{CH}$ = 129 Hz, $C_6\underline{Me}_6$), 12.9 (q, $^1J_{CH}$ = 129 Hz, CH_3), 5.7 (t, $^1J_{CH}$ = 137 Hz, C_1); ^{1}H-^{13}C HETCORR (100 MHz, $CDCl_3$): δ 53.4 ($CO_2\underline{Me}$) ↔ δ 3.89 ($CO_2\underline{Me}$); δ 52.2 ($CO_2\underline{Me}$) ↔ δ 3.70 ($CO_2\underline{Me}$); δ 44.5 (C_2) ↔ δ 3.08 (H_2); δ 24.4 (C_3) ↔ δ 1.63, 0.84 (H_{3endo} and H_{3exo}); δ 17.7 (CH_3) ↔ δ 1.48 (CH_3); δ 15.5 ($\underline{C}_6Me_6$) ↔ δ 2.10 ($C_6\underline{Me}_6$); δ 12.9 (CH_3) ↔ δ 1.88 (CH_3); δ 5.7 (C_1) ↔ δ 1.45, 1.15 (H_{1a} and H_{1b}).



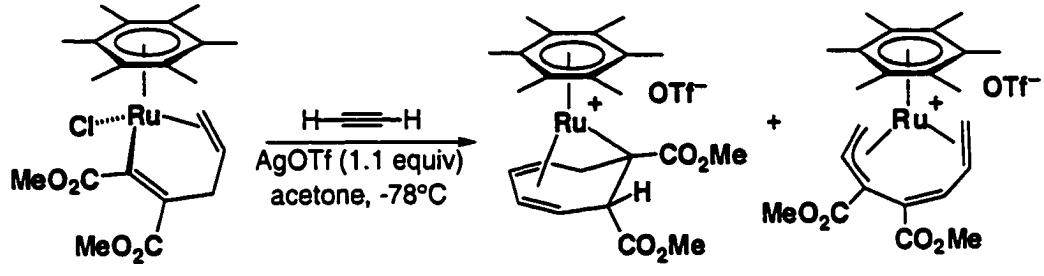
176 177

Reaction of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentenyl)Cl (169) with Cyclooctyne. A solution of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentadienyl)Cl (0.100 g, 0.207 mmol) in acetone (5 mL) was cooled to –78°C using a dry ice/acetone bath. Freshly prepared cyclooctyne (0.084 mL, 6.21 mmol, 3.0 equiv) was added via syringe, then a solution of AgOTf (0.060 g, 0.234 mmol, 1.13 equiv) in 1 mL acetone was introduced by syringe. The reaction mixture was stirred at –78°C for several hours then gradually allowed to warm to room temperature. After filtration through Celite to remove AgCl, the solvent was evaporated under low pressure and the residue purified by chromatography on silica gel, using 5 % methanol/dichloromethane as the eluent. The first yellow fraction collected proved to be the minor product, complex **177**, which was dried and recrystallized from dichloromethane/diethyl ether, giving 0.035 g (24 %), of pale yellow crystals. The second fraction collected, the major compound **176**, was treated similarly, yielding 0.092 g (63 %) of bright yellow crystals.

$[(C_6Me_6)$Ru((1:3,4,5,6-η)-1,2-dicarbomethoxy-3-$(CH_2)_6$-4-cycloheptadienyl)$]^+OTf^-$ (176). IR ($CHCl_3$ cast, cm^{-1}): 1737 (s), 1686 (s), 1265 (s), 1198 (s), 1010 (s), 637 (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.62 (d, $J_{4\text{-}5}$ = 9.2 Hz, 1H, H_5), 4.23 (br s, 1H, H_2), 3.84 (s, 3H, $CO_2\underline{Me}$), 3.49 (s, 3H, $CO_2\underline{Me}$), 3.80 (td, $J_{6\text{-}5} = J_{6\text{-}7endo}$ = 9.0 Hz, $J_{6\text{-}7exo}$= 1.9 Hz,

1H, H_6), 3.27 (ddd, $J_{7endo\text{-}7exo}$ = 15.5 Hz, $J_{7endo\text{-}6}$ = 8.5 Hz, $J_{7endo\text{-}2}$ = 1.2 Hz, 1H, H_{7endo}), 2.12 (s, 18H, $C_6\underline{Me}_6$), 2.55-1.36 (series of multiplets, 13H, H_{7exo} and cyclooctyl CH_2's); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 177.5, 171.0, 118.7, 114.2, 108.1, 98.1, 60.2, 56.1, 52.6, 52.4, 51.6, 37.9, 35.4, 31.7, 31.6, 26.9, 24.0, 15.5, –27.6, triflate carbon signal was not observed. Analysis calculated for $C_{30}H_{41}F_3O_7SRu$: C, 51.20%; H, 5.87%; found: C, 51.07%; H, 5.85%.

Complex 177 (minor product). ^1H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H, $CO_2\underline{Me}$), 3.72 (s, 3H, $CO_2\underline{Me}$), 3.23 (dt, J = 5.0, 2.3 Hz, 1H, H_2), 2.43 (dt, J = 12.0, 5.2 Hz, 1H, cyclooctyl ring), 2.12 (s, 18H, $C_6\underline{Me}_6$), 1.69 (dd, J = 12.0, 2.3 Hz, 1H, H_{3endo}), 1.17 (d, J = 2.0 Hz, H_{1b}), 0.80 (dt, J = 12.0, 2.5 Hz, 1H, H_{3exo}), 2.15-0.98 (series of multiplets, 12H, H_{1a} and cyclooctyl ring CH_2's).



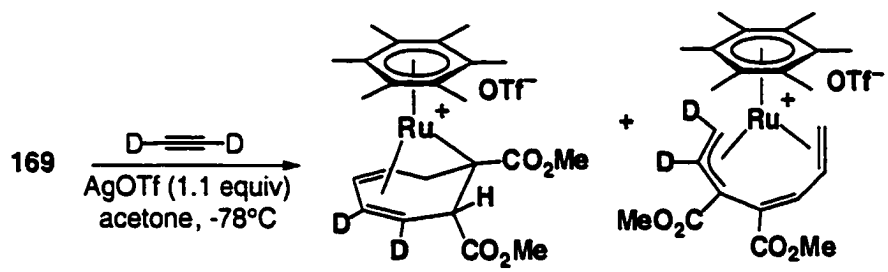
Reaction of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentenyl)Cl (169) with Acetylene. A solution of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentadienyl)Cl (0.200 g, 0.415 mmol) in acetone (5 mL) was cooled to –78°C using a dry ice/acetone bath. Acetylene was bubbled through the solution for 5 minutes before adding a solution of AgOTf (0.110 g, 0.428 mmol, 1.03 equiv) in 1 mL acetone via syringe. The reaction

flask was sealed and allowed to warm slowly to room temperature; the reaction mixture gradually turned black as it warmed up. After stirring at room temperature for 1 hour the reaction mixture was filtered through Celite, giving an orange filtrate that was dried *in vacuo*. The residue was found to be a mixture of two compounds, which were separated and purified by flash chromatography (3 % methanol/dichloromethane on silica gel). The first fraction off the column was found to be primarily the minor product, complex **179** along with traces of several other compounds. This compound was further purified by dissolving the impure residue in a minimum of hot water then adding excess NH_4PF_6 to precipitate the ion-exchange product, which was then filtered, dried, and recrystallized (dichloromethane/ diethyl ether) to yield 0.036 g (14 %) of yellow crystals. The second fraction proved to be the clean major product, complex **178**, and was further purified by recrystallization from dichloromethane/diethyl ether to give 0.148 g (57 %), of bright yellow crystals.

[(C_6Me_6)Ru((1:3,4,5,6-η)-1,2-dicarbomethoxycycloheptadienyl)]$^+$OTf$^-$ (178). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.62 (t, $J_{4\text{-}5} = J_{4\text{-}3} = 7.9$ Hz, 1H, H_4), 5.43 (t, $J_{5\text{-}6} = J_{5\text{-}4} = 8.0$ Hz, 1H, H_5), 4.23 (br d, $J_{2\text{-}3} = 9.0$ Hz, 1H, H_2), 4.16 (t, $J_{3\text{-}2} = J_{3\text{-}4} = 8.3$ Hz, 1H, H_3), 4.03 (td, $J_{6\text{-}5} = J_{6\text{-}7endo} = 8.4$ Hz, $J_{6\text{-}7exo} = 2.6$ Hz, 1H, H_6), 3.83 (s, 3H, $CO_2\underline{Me}$), 3.50 (s, 3H, $CO_2\underline{Me}$), 3.33 (ddd, $J_{7endo\text{-}7exo} = 15.3$ Hz, $J_{7endo\text{-}6} = 8.6$ Hz, $J_{7endo\text{-}2} = 1.2$ Hz, 1H, H_{7endo}), 2.19 (s, 18H, $C_6\underline{Me}_6$), 2.09 (ddd, $J_{7exo\text{-}7endo} = 15.3$ Hz, $J_{7exo\text{-}6} = 2.5$ Hz, $J_{7exo\text{-}5} = 1.5$ Hz, 1H, H_{7exo}); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 177.2 ($\underline{C}O_2Me$), 171.1 ($\underline{C}O_2Me$), 109.7 ($\underline{C}_6Me_6$), 100.0 (C_4), 99.8 (C_5), 52.4 ($CO_2\underline{Me}$), 51.8 ($CO_2\underline{Me}$), 50.4 (C_3), 48.8 (C_6), 48.2 (C_2), 30.5 (C_7), 15.1 ($C_6\underline{Me}_6$), –27.1 (C_1). Triflate carbon signal was not observed.

Analysis calculated for $C_{23}H_{31}F_6O_4PRu$: C, 44.74%; H, 5.06%; found: C, 44.31%; H, 4.82%.

[(C_6Me_6)Ru((1,2,3: 6,7-η)-3,4-dicarbomethoxyheptatrienyl)]$^+PF_6^-$ (179). ^{1}H NMR (400 MHz, $CDCl_3$, PF_6 salt): δ 6.87 (d, $J_{5\text{-}6}$ = 1.7 Hz, 1H, H_5), 4.70 (dd, $J_{2\text{-}1anti}$ = 11.3 Hz, $J_{2\text{-}1syn}$ = 7.5 Hz, 1H, H_2), 4.45 (ddd, $J_{6\text{-}7syn}$= 12.9 Hz, $J_{6\text{-}7anti}$ = 9.5 Hz, $J_{6\text{-}5}$ = 1.9 Hz, 1H, H_6), 3.85 (s, 3H, $CO_2\underline{Me}$), 3.73 (dd, $J_{1syn\text{-}2}$ = 7.5 Hz, $J_{1syn\text{-}1anti}$ = 2.0 Hz, 1H, H_{1syn}), 3.60 (s, 3H, $CO_2\underline{Me}$), 3.17 (d, $J_{7syn\text{-}6}$ = 9.2 Hz, 1H, H_{7syn}), 2.97 (d, $J_{7anti\text{-}6}$ = 13.0 Hz, 1H, H_{7anti}), 2.11 (s, 18H, $C_6\underline{Me}_6$), 1.64 (dd, $J_{1anti\text{-}2}$ = 11.4 Hz, $J_{1anti\text{-}1syn}$ = 2.0 Hz, 1H, H_{1anti}); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, BPh_4 salt): δ 171.3 ($\underline{C}O_2Me$), 170.8 ($\underline{C}O_2Me$), 164.0 (C_{ipso}), 146.9 (C_5), 136.2 (C_{Ph}), 133.9 (C_4), 125.5 (C_{Ph}), 121.7 (C_{Ph}), 109.6 ($\underline{C}_6Me_6$), 107.2 (C_3), 89.2 (C_2), 78.5 (C_6), 62.8 (C_7), 55.7 (C_1), 52.8 ($CO_2\underline{Me}$), 52.2 ($CO_2\underline{Me}$), 15.1 ($C_6\underline{Me}_6$); ^1H-^{13}C HETCORR (100 MHz, $CDCl_3$, BPh_4 salt): δ 146.9 (C_5) ↔ δ 6.87 (H_5); δ 89.2 (C_2) ↔ δ 4.70 (H_2); δ 78.5 (C_6) ↔ δ 4.45 (H_6); δ 62.8 (C_7) ↔ δ 2.97 (H_{7syn}), 3.17 (H_{7anti}); δ 55.7 (C_1) ↔ δ 1.64 (H_{1anti}), 3.73 (H_{1syn}); δ 52.8 (CO_2Me) ↔ δ 3.85 (CO_2Me); δ 52.2 (CO_2Me) ↔ δ 3.60 (CO_2Me); δ 15.1 (C_6Me_6) ↔ δ 2.11 (C_6Me_6).



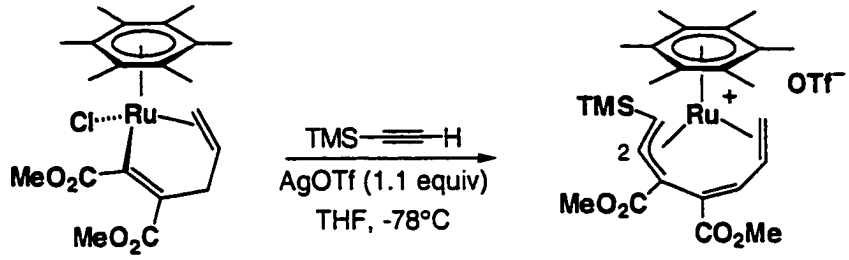
178-d_2 **179-d_2**

Reaction of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentenyl)Cl (169) with Acetylene-d_2. A solution of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentenyl)Cl

(0.020 g, 0.042 mmol) in acetone (2 mL) was cooled to 0°C using a ice bath and a solution of AgOTf (0.011 g, 0.043 mmol, 1.03 equiv) in 1 mL acetone was added by pipette. Acetylene-d_2, prepared by slowly adding D_2O to CaC_2 solid under a nitrogen atmosphere, was then bubbled through the acetone solution. After 20 minutes the reaction flask was sealed, the ice bath removed and the reaction stirred at room temperature for 1 hour. Afterwards, the reaction mixture was filtered through Celite, and the orange filtrate dried under reduced pressure. The crude product mixture was then analyzed by ^{1}H NMR spectroscopy. No further attempt was made to isolate or purify the deuterium labelled products.

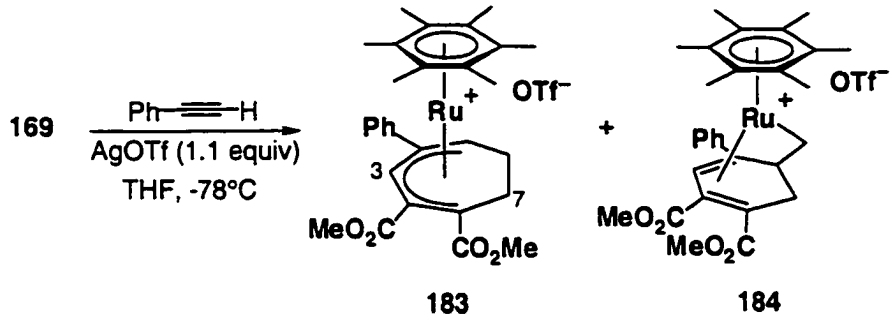
Complex 178-d_2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.43 (d, J= 8.0 Hz, 1H, H_5), 4.23 (br s, 1H, H_2), 4.03 (td, J= 8.4, 2.6 Hz, 1H, H_6), 3.83 (s, 3H, CO_2Me), 3.50 (s, 3H, CO_2Me), 3.33 (ddd, J= 15.3, 8.6, 1.2 Hz, 1H, H_{7endo}), 2.19 (s, 18H, C_6Me$_6$), 2.09 (ddd, J= 15.3, 2.5, 1.5 Hz, 1H, H_{7exo}). Positions H_3 and H_4 are deuterated.

Complex 179-d_2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.87 (d, J= 1.7 Hz, 1H, H_5), , 4.45 (ddd, J= 12.9, 9.5, 1.9 Hz, 1H, H_6), 3.85 (s, 3H, CO_2Me), 3.60 (s, 3H, CO_2Me), 3.17 (d, J = 9.2 Hz, 1H, H_{7syn}), 2.97 (d, J= 13.0 Hz, 1H, H_{7anti}), 2.11 (s, 18H, C_6Me$_6$), 1.62 (s, 1H, H_{1anti}). Positions H_2 and H_{1syn} are deuterated.



169 182

[(C_6Me_6)Ru((1,2,3: 6,7-η)-3,4-dicarbomethoxy-1-(trimethylsilyl)heptatrienyl)]$^+$OTf$^-$ (182). A solution of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentadienyl)Cl (0.083 g, 0.172 mmol) in tetrahydrofuran (3 mL) was cooled to –78°C using a dry ice/acetone bath. Trimethylsilylacetylene (0.121 mL, 0.856 mmol, 5 equiv) was added via syringe, then a solution of AgOTf (0.051 g, 0.20 mmol, 1.15 equiv) in 1 mL tetrahydrofuran was introduced by syringe. The reaction mixture was stirred at –78°C for several hours then gradually allowed to warm to room temperature. After filtration through Celite to remove AgCl, the solvent was evaporated under low pressure and the residue purified by chromatography on silica gel, using 4% methanol/dichloromethane as the eluent. The major product, complex **182**, was isolated as a yellow oil (0.057 g, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.87 (d, $J_{5\text{-}6}$ = 1.9 Hz, 1H, H_5), 4.91 (d, $J_{2\text{-}1anti}$ = 13.9 Hz, 1H, H_2), 4.20 (ddd, $J_{6\text{-}7anti}$ = 12.7 Hz, $J_{6\text{-}7syn}$ = 9.4 Hz, $J_{6\text{-}5}$ = 1.9 Hz, 1H, H_6), 3.88 (s, 3H, $CO_2\underline{Me}$), 3.61 (s, 3H, $CO_2\underline{Me}$), 3.16 (d, $J_{7syn\text{-}6}$ = 9.4 Hz, 1H, H_{7syn}), 2.98 (d, $J_{7anti\text{-}6}$ = 12.8 Hz, 1H, H_{7anti}), 2.11 (s, 18H, $C_6\underline{Me}_6$), 0.92 (d, $J_{1anti\text{-}2}$ = 13.9 Hz, 1H, H_{1anti}), 0.25 (s, 9H, $Si(\underline{CH}_3)_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 171.8, 163.8, 146.0, 135.9, 110.5, 109.2, 94.6, 74.9, 70.0, 59.0, 52.9, 52.3, 15.9, 0.09. The triflate carbon signal was not observed.

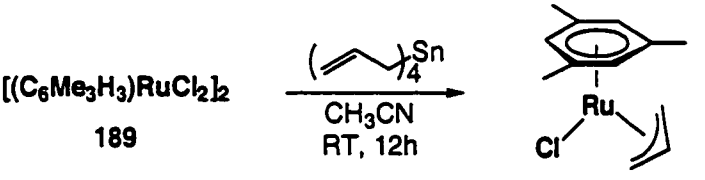


Reaction of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentenyl)Cl (169) with Phenylacetylene. A solution of (C_6Me_6)Ru((1:4,5-η)-1,2-dicarbomethoxypentadienyl)Cl (0.100 g, 0.207 mmol) in acetone (5 mL) was cooled to –78°C using a dry ice/acetone bath. Phenylacetylene (0.045 mL, 0.41 mmol, 1.98 equiv) was added via syringe, then a solution of AgOTf (0.060 g, 0.23 mmol, 1.13 equiv) in 1 mL acetone introduced by syringe. The reaction mixture was stirred at –78°C for several hours then gradually allowed to warm to room temperature to stir for another 5 hours. After filtration through Celite to remove AgCl, the solvent was evaporated under low pressure and the residue purified by chromatography on silica gel, using 3% ethanol/dichloromethane as the eluent. The first yellow fraction collected proved to be the primarily the major product, complex **183**, which was further purified by careful recrystallization using dichloromethane/diethyl ether, giving 0.061 g (42%), of bright yellow crystals. The second fraction collected proved to be a mixture of complex **184** and another, unidentified, product.

$[(C_6Me_6)Ru(\eta^5$-1,2-dicarbomethoxy-4-phenylcycloheptadienyl)$]^+OTf^-$ (183). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 5H, Ph), 6.65 (s, 1H, H_3), 4.89 (td, J = 3.3, 1.0 Hz, 1H, H_5), 3.88 (s, 3H, $CO_2\underline{Me}$), 3.80 (s, 3H, $CO_2\underline{Me}$), 2.65 (dddd, J = 15.7, 11.6, 9.0, 3.7

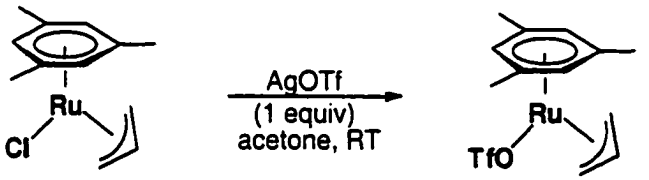
Hz, 1H, H_{6b}), 2.38 (dddd, J = 15.7, 5.2, 2.9, 1.4 Hz, 1H, H_{6a}), 2.15 (dddd, J = 13.4, 9.0, 1.4, 1.0 Hz, 1H, H_{7endo}), 1.94 (s, 18H, $C_6\underline{Me}_6$), 0.50 (ddd, $J_{7exo\text{-}7endo}$ = 13.3 Hz, $J_{7exo\text{-}6}$ = 11.6 Hz, $J_{7exo\text{-}5}$ = 5.2 Hz, 1H, H_{7exo}); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.5, 168.7, 134.2, 131.1, 129.7, 128.6, 108.4, 100.7, 100.5, 93.6, 77.9, 70.8, 53.5, 52.5, 41.9, 27.9, 15.6. The triflate carbon signal was not observed. Analysis calculated for $C_{30}H_{35}F_3O_7SRu$: C, 51.64%; H, 5.06%; found: C, 51.62%; H, 4.98%.

[(C_6Me_6)Ru((1:4,5,6,7-η)-4,5-dicarbomethoxy-7-phenylmethanocyclohexa-dienyl)]$^+$OTf$^-$ (184) (characterized from mixture): ^1H NMR (400 MHz, $CDCl_3$): δ 7.70–7.62 (m, 2H, H_{Ph}), 7.51-7.48 (m, 3H, H_{Ph}), 6.06 (s, 1H, H_6), 4.01 (s, 3H, $CO_2\underline{Me}$), 3.75 (s, 3H, $CO_2\underline{Me}$), 3.70 (br s, 1H, H_2), 1.87 (s, 18H, $C_6\underline{Me}_6$), 1.70 (dd, J = 12.6, 2.1 Hz, 1H, H_{3endo}), 1.43-1.39 (m, 2H, H_{1a} and H_{1b}), 1.22 (dt, J = 12.6, 1.6 Hz, 1H, H_{3exo}).



($C_6Me_3H_3$)Ru(η^3-C_3H_5)Cl (190). A 300 mL, oven-dried Schlenk flask was charged with [($C_6Me_3H_3$)$RuCl_2$]$_2$ (1.00 g, 1.71 mmol) and 100 mL of acetonitrile and the resulting red slurry placed under nitrogen. Tetraallyltin (1.20 mL, 5.00 mmol) was added via syringe and the reaction mixture stirred at room temperature for 12 hours, forming an orange solution. Acetonitrile was then removed by rotary evaporation, leaving an oily orange residue. The crude mixture was dried thoroughly under vacuum, then transferred to the

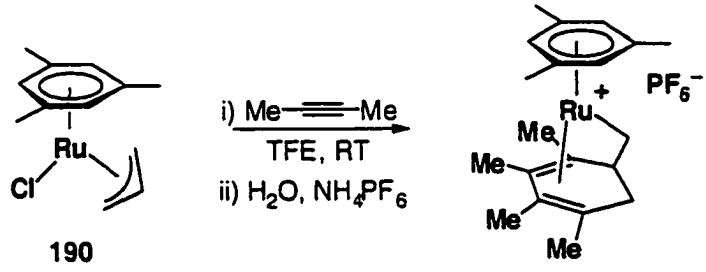
dry box where it was rinsed with several portions of diethyl ether to remove triallyltin chloride and unreacted tetraallyltin. The crude product was then recrystallized from benzene/pentane to give 0.695 g (68%) of orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.02 (s, 3H, $C_6Me_3\underline{H}_3$), 4.10 (tt, J = 11.2, 7.0 Hz, 1H, $H_{central}$), 3.42 (d, J = 7.0 Hz, 2H, H_{syn}), 2.51 (d, J = 11.2 Hz, 2H, H_{anti}), 2.11 (s, 9H, $C_6\underline{Me}_3H_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 101.4, 84.1, 83.9, 56.5, 18.9. Analysis calculated for $C_{12}H_{17}ClRu$: C, 48.40%; H, 5.75%; found: C, 48.12%; H, 5.83%.



190 191

$(C_6Me_3H_3)Ru(\eta^3\text{-}C_3H_5)OTf$ (191). A solution of $Ru(C_6Me_3H_3)(\eta^3\text{-}C_3H_5)Cl$ (0.300 g, 1.01 mmol) in 25 mL acetone was degassed and placed under nitrogen. A solution of AgOTf (0.259 g, 1.0 mmol) in acetone (3 mL) was then added via pipette and a white precipitate was immediately observed. The reaction mixture was allowed to stir at room temperature for one hour. The mixture was quickly filtered through Celite to remove insoluble silver salts and the bright orange solution was concentrated *in vacuo*. The resulting air sensitive solid was transferred to the dry box where it was dissolved in toluene and filtered through Celite again to remove any remaining traces of silver salt. The toluene was removed by evaporation under reduced pressure to give 0.339 g (82%) of an orange solid (pure by ^{1}H NMR spectroscopy), that was kept stored under nitrogen. The solid slowly turns brown on exposure to oxygen. ^{1}H NMR (300 MHz, $CDCl_3$):

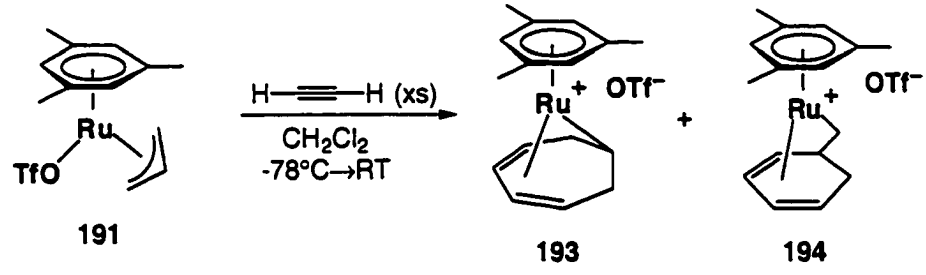
δ 4.34 (s, 3H, $C_6Me_3\underline{H}_3$), 3.54 (d, J = 6.9 Hz, 2H, H_{syn}), 3.26 (tt, J = 11.4, 7.0 Hz, 1H, $H_{central}$), 2.72 (d, J = 11.4 Hz, 2H, H_{anti}), 2.11 (s, 9H, $C_6\underline{Me}_3H_3$); $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ 103.5, 89.1, 84.6, 59.8, 18.6. The triflate carbon signal was not observed.



190 192

[($C_6Me_3H_3$)Ru((1:4,5,6,7-η)-4,5,6,7-tetramethylmethanocyclohexadienyl)]$^+PF_6^-$ (193). A small Schlenk flask equipped with stir-bar and septum was charged with ($C_6Me_3H_3$)Ru(C_3H_5)Cl (0.040 g, 0.134 mmol) and a nitrogen atmosphere was established. Trifluoroethanol (3.0 mL) was added, forming an intense orange solution. With rapid stirring, 2-butyne (0.10 mL, 1.278 mmol) was added by pipette and the reaction flask was sealed. After stirring for 1 hour at room temperature the solvent was removed *in vacuo*, leaving an oily orange residue. This residue was dried under vacuum for several hours before the crude product was extracted into 2 x 3 mL warm distilled water and the aqueous solution was filtered through Celite. Excess NH_4PF_6 (0.050 g, 1.23 mmol) was then added to the filtrate and the yellow precipitate was collected and dried thoroughly. The precipitate was then further purified by recrystallization from acetone/diethyl ether to yield 0.052 g (75%) of pale yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 5.58 (s, 3H, $C_6Me_3\underline{H}_3$), 2.92 (dt, J = 4.5, 2.0 Hz, 1H, H_2), 2.31 (s, 3H, CH_3), 2.15 (s, 9H, $C_6\underline{Me}_3H_3$), 1.64 (s, 3H, CH_3), 1.62 (dt, J = 4.7, 3.4 Hz, partially obscured, 1H, H_{1a}), 1.55 (s, 3H,

CH_3), 0.99 (ddd, J = 11.7, 3.3, 1.9 Hz, 1H, H_{3endo}), 0.98 (d, J = 3.7 Hz, 1H, H_{1b}), 0.89 (dd, J = 11.8, 1.8 Hz, 1H, H_{3exo}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.4 (s, $\underline{C}_6Me_3H_3$), 100.1 (s, C_6), 96.8 (d, $^1J_{CH}$ = 172 Hz, $\underline{C}_6Me_3H_3$), 96.3 (s, C_5), 84.0 (s, C_7), 71.4 (s, C_4), 42.9 (d, $^1J_{CH}$ = 139 Hz, C_2), 31.9 (t, $^1J_{CH}$ = 134 Hz, C_3), 25.1 (q, $^1J_{CH}$ = 127 Hz, CH_3), 19.4 (q, $^1J_{CH}$ = 128 Hz, CH_3), 17.9 (q, $^1J_{CH}$ = 129 Hz, $C_6\underline{Me}_3H_3$), 15.2 (q, $^1J_{CH}$ = 127 Hz, CH_3), 14.2 (q, $^1J_{CH}$ = 129 Hz, CH_3), –3.3 (t, $^1J_{CH}$ = 142 Hz, C_1). Analysis calculated for $C_{20}H_{29}F_6PRu$: C, 46.60%; H, 5.67%; found: C, 46.85%; H, 5.70%.



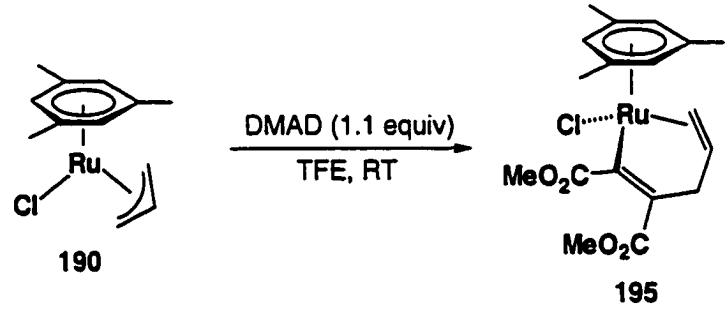
191 193 194

Reaction of $(C_6Me_3H_3)Ru(\eta^3\text{-}C_3H_5)OTf$ (191) with Acetylene. In the dry box, $(C_6Me_3H_3)Ru(C_3H_5)OTf$ (0.030 g, 0.110 mmol) was placed in a Schlenk flask equipped with stir-bar and septum. The flask was removed to the Schlenk line and dichloromethane (3 mL) was added by syringe. The orange solution was cooled to –78°C using a dry ice/acetone bath and the septum was wired on. Acetylene was bubbled through the solution for 5 minutes before slowly warming the reaction mixture. Once the reaction neared room temperature the solvent was immediately removed *in vacuo*, leaving a tan solid. Initial analysis of the crude residue by ^1H NMR spectroscopy indicates compounds **193** and **194** in an approximately 2 : 1 ratio respectively. Stirring at

room temperature for a further 2 days resulted in the conversion of the major product to unidentified products.

$[(C_6Me_3H_3)Ru((1:3,4,5,6-\eta)cycloheptadienyl)]^+OTf^-$ (193). ^1H NMR (400 MHz, $CDCl_3$): δ 6.10 (s, 3H, $C_6Me_3\underline{H}_3$), 5.63-5.60 (m, AA'XX' pattern, 2H, H_4/H_5), 4.39 (br t, J = 6.9 Hz, 2H, H_3/H_6), 2.81 (dt, J = 13.5, 8.5 Hz, 2H, H_{2endo}/H_{7endo}), 2.19 (s, 9H, $C_6\underline{Me}_3H_3$), 2.24 (d, J = 13.8 Hz, 2H, H_{2exo}/H_{7exo}, partially obscured), 0.31 (t, J = 8.4 Hz, 1H, H_1).

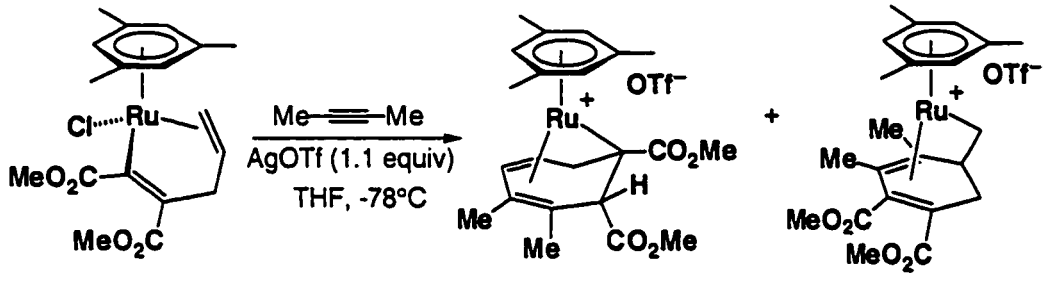
$[(C_6Me_3H_3)Ru((1:4,5,6,7-\eta)methanocyclohexadienyl)]^+OTf^-$ (194). ^1H NMR (400 MHz, $CDCl_3$): δ 6.07 (s, 3H, $C_6Me_3\underline{H}_3$), 6.04 (t, J = 5.6 Hz, 1H, H_5), 5.33 (t, J = 5.5 Hz, 1H, H_5), 4.39 (t, J = 5.5 Hz, 1H, H_7), 3.77 (t, J = 5.5 Hz, 1H, H_4), 3.20 (br s, 1H, H_2), 2.26 (s, 9H, $C_6\underline{Me}_3H_3$), 1.62 (dd, J = 7.3, 3.0 Hz, 1H, H_{1a}), 1.17 (d, J = 3.2 Hz, 1H, H_{1b}), 1.13 (m, 2H, H_{3endo} and H_{3exo}).



190 195

$(C_6Me_3H_3)Ru((1:4,5-\eta)$-1,2-dicarbomethoxypentadienyl)Cl (195). A bright orange solution of $(C_6Me_3H_3)Ru(C_3H_5)Cl$ (0.040 g, 0.134 mmol) in 1 mL trifluoroethanol was placed in a small Schlenk flask under a nitrogen atmosphere. Dimethyl acetylenedicarboxylate (0.020 mL, 0.163 mmol, 1.22 equiv) was added via syringe and the reaction stirred at room temperature, gradually turning dark brown in colour. After 4

hours the solvent was removed *in vacuo*, leaving an oily brown residue. The crude product was then extracted into a minimum of warm toluene and the solution filtered through Celite. Hexane was layered on the filtrate and the mixture cooled to –20°C overnight. The next day the product was filtered off as a brown microcrystalline solid (0.051 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.39 (s, 3H, $C_6Me_3\underline{H}_3$), 5.27-5.17 (m, 1H, H_4), 3.59 (d, 1H, J = 8.9 Hz, H_{5syn}), 3.59 (d, 1H, J = 13.7 Hz, H_{5anti}), 3.66 (s, 3H, CO_2Me), 3.57 (s, 3H, CO_2Me), 3.13-3.10 (m, 2H, H_{3endo} and H_{3exo}), 2.14 (s, 9H, $C_6\underline{Me}_3H_3$).



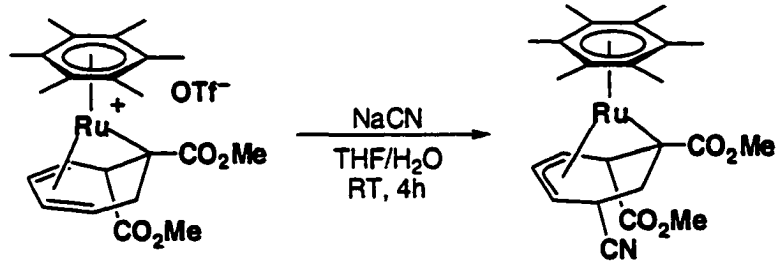
195 196 197

Reaction of ($C_6Me_3H_3$)Ru((1:4,5-η)-1,2-dicarbomethoxypentadienyl)Cl (195) with 2-Butyne. A solution of ($C_6Me_3H_3$)Ru((1:4,5-η)-1,2-dicarbomethoxypentadienyl)Cl (0.030 g, 0.068 mmol) in tetrahydrofuran (6 mL) was cooled to –78°C using a dry ice/acetone bath. 2-Butyne (0.165 mL, 2.11 mmol, 5.0 equiv) was added via syringe, then a solution of AgOTf (0.120 g, 0.467 mmol, 1.12 equiv) in 2 mL tetrahydrofuran was introduced via cannula. The reaction mixture was stirred at –78°C for several hours then gradually allowed to warm to room temperature. After filtration through Celite to remove AgCl, the solvent was evaporated under reduced pressure. ^{1}H NMR

spectroscopic analysis of the crude residue indicated clean formation of compound **196** and compound **197** in a 1.3 to 1 ratio, respectively. These products were not isolated or further characterized.

[($C_6Me_3H_3$)Ru((1:3,4,5,6-η)-1,2-dicarbomethoxy-3,4-dimethylcycloheptadienyl)]$^+$ OTf$^-$ (196). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87(s, 3H, $C_6Me_3\underline{H}_3$), 5.77 (d, J= 8.8 Hz, 1H, H_5), 4.35 (d, J= 1.2 Hz, 1H, H_2), 3.90 (td, 1H, J= 8.7, 2.3 Hz, H_6), 3.89 (s, 3H, $CO_2\underline{Me}$), 3.51 (s, 3H, $CO_2\underline{Me}$), 3.24 (ddd, J= 15.4, 8.7, 1.4 Hz, 1H, H_{7endo}), 2.35 (s, 3H, CH_3), 2.30 (s, 9H, $C_6Me_3\underline{H}_3$), 2.28-2.25 (m, 1H, partially obscured, H_{7exo}), 2.11 (s, 3H, CH_3).

[($C_6Me_3H_3$)Ru((1:4,5,6,7-η)-4,5-dicarbomethoxy-6,7-dimethyl-methanocyclo-hexadienyl)]$^+$OTf$^-$ (197). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 (s, 3H, $C_6Me_3\underline{H}_3$), 3.93 (s, 3H, CO_2Me), 3.72 (s, 3H, CO_2Me), 3.15 (dt, J = 4.4, 2.2 Hz, 1H, H_2), 2.24 (s, 9H, $C_6Me_3\underline{H}_3$), 2.06 (s, 3H, CH_3), 1.96 (dd, J = 4.4, 3.5 Hz, H_{1a}), 1.75 (s, 3H, CH_3), 1.66 (dd, J = 12.2, 1.9 Hz, 1H, H_{3endo}), 1.63 (d, J = 3.5 Hz, 1H, H_{1b}), 0.91 (dt, J = 12.3, 2.1 Hz, 1H, H_{3exo}).

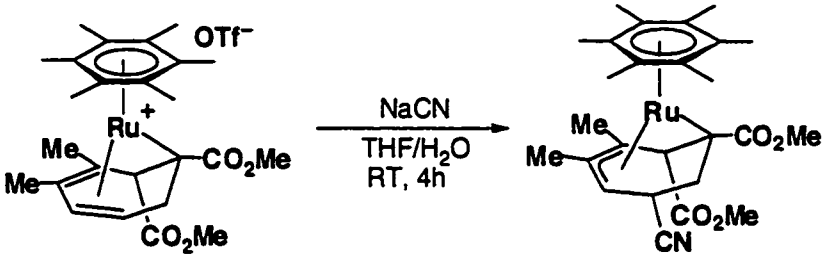


178 **198**

(C_6Me_6)Ru((1:3,4,5-η)-1,2-dicarbomethoxy-6-cyanocycloheptendiyl) (198). A suspension of complex **178** (0.050 g, 0.080 mmol) in tetrahydrofuran (4 mL) was

prepared in a small Schlenk flask and a solution of NaCN (0.012 g, 0.24 mmol) in 0.5 mL distilled water added via syringe. The reaction was then stirred at room temperature for 4 hours. The solvent was evaporated under low pressure and the residue thoroughly dried under vacuum. The crude product was then extracted into 2 x 3 mL toluene and the combined portions filtered through Celite. The yellow filtrate was concentrated to a solid and analytically pure yellow crystals (0.028 g, 70%) were obtained after slow recrystallization from toluene/pentane. ^{1}H NMR (400 MHz, C_6D_6): δ 4.64 (br d, $J_{2\text{-}3}$ = 7.2 Hz, 1H, H_2), 3.73 (s, 3H, $CO_2\underline{Me}$), 3.59 (t, $J_{3\text{-}4} = J_{3\text{-}2}$ = 6.9 Hz, 1H, H_3) 3.48 (s, 3H, $CO_2\underline{Me}$), 3.11 (t, $J_{5\text{-}6} = J_{5\text{-}4}$ = 7.9 Hz, H_5) 2.90 (t, $J_{4\text{-}5} = J_{4\text{-}3}$ = 7.0 Hz, 1H, H_4), 2.79 (dd, $J_{6\text{-}7endo}$ = 10.8 Hz, $J_{6\text{-}5}$ = 8.2 Hz, 1H, H_6), 2.53 (d, $J_{7exo\text{-}7endo}$ = 14.3 Hz, H_{7exo}), 2.23 (dd, $J_{7endo\text{-}7exo}$ = 14.0, $J_{7endo\text{-}6}$ = 11.9 Hz, H_{7endo}), 1.52 (s, 18H, C_6Me_6); ^{13}C NMR (100 MHz, C_6D_6): δ 180.3 (s, $\underline{C}O_2Me$), 172.6 (s, $\underline{C}O_2Me$), 122.5 (s, $\underline{C}N$), 96.5 (s, $C_6\underline{Me}_6$), 86.7 (d, $^1J_{CH}$ = 160 Hz, C_4), 66.8 (d, $^1J_{CH}$ = 154 Hz, C_5), 51.4 (q, $^1J_{CH}$ = 145 Hz, $CO_2\underline{Me}$), 50.6 (q, $^1J_{CH}$ = 145 Hz, $CO_2\underline{Me}$), 50.5 (d, $^1J_{CH}$ = 163 Hz, C_3), 50.1 (d, $^1J_{CH}$ = 161 Hz, C_2), 40.7 (t, $^1J_{CH}$ = 128 Hz, C_7), 29.9 (d, $^1J_{CH}$ = 131 Hz, C_6), 21.7 (s, C_1), 15.1 (q, $^1J_{CH}$ = 126 Hz, $C_6\underline{Me}_6$); HMQC (100 MHz, C_6D_6): δ 86.7 (C_4) ↔ δ 2.90 (H_4); δ 66.8 (C_5) ↔ δ 3.11 (H_5); δ 51.4 (CO_2Me) ↔ δ 3.73 (CO_2Me); δ 50.6 (CO_2Me) ↔ δ 3.48 (CO_2Me); δ 50.5 (C_3) ↔ δ 3.59 (H_3); δ 50.1 (C_2) ↔ δ 4.64 (H_2); δ 40.7 (C_7) ↔ δ 2.23, 2.53 (H_{7endo} and H_{7exo}); δ 29.9 (C_6) ↔ δ 2.79 (H_6); δ 15.1 (C_6Me_6) ↔ δ 1.52 (C_6Me_6); HMBC (100 MHz, C_6D_6): δ 180.3 (CO_2Me) ↔ δ 4.64, 3.48; δ 172.6 (C_5) ↔ δ 4.64, 3.73; δ 122.5 (CN) ↔ δ 2.79, 2.53, 2.23; δ 86.7 (C_4) ↔ δ 4.64, 3.11, 2.79; δ 66.8 (C_5) ↔ δ 3.59, 2.90, 2.53; δ 50.5 (C_3) ↔ δ 4.64, 3.11; δ 50.1 (C_2) ↔ δ 2.90, 2.23; δ 40.7 (C_7) ↔ δ 4.64, 3.11, 2.79; δ 29.9 (C_6) ↔ δ 3.11, 2.90, 2.53, 2.23; δ 21.7 (C_1) ↔ δ 4.64,

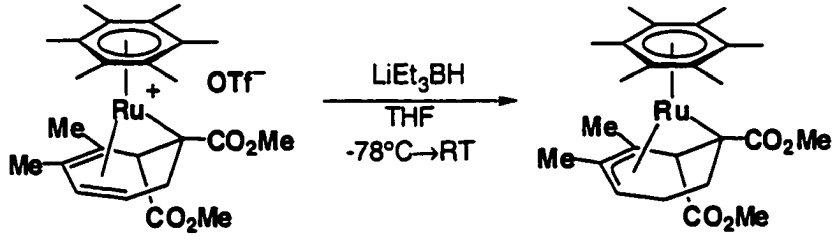
3.59, 2.79, 2.53, 2.23. Analysis calculated for $C_{24}H_{31}NO_4Ru$: C, 57.82%; H, 6.27%; N, 2.81%; found: C, 57.88%; H, 6.19%; N, 2.81%.



173 201

(C_6Me_6)Ru((1:3,4,5-η)-1,2-dicarbomethoxy-3,4-dimethyl-6-cyanocycloheptendiyl) (201). A suspension of complex **173** (0.150 g, 0.231 mmol) in tetrahydrofuran (8 mL) was prepared and a solution of NaCN (0.025 g, 0.51 mmol) in 1.5 mL distilled water added via syringe. The starting material soon dissolved completely and the reaction was stirred at room temperature for a further 4 hours. The solvent was evaporated and the residue thoroughly dried under vacuum. The crude product was then extracted into 2 x 3 mL toluene and the combined portions filtered through Celite. The yellow filtrate was concentrated to approximately 1 mL and pentane was added until the solution became cloudy. Cooling to –20°C overnight resulted in the formation of bright yellow crystals (0.078 g, 64%). ^{1}H NMR (300 MHz, C_6D_6): δ 4.72 (s, 1H, H_2), 3.68 (s, 3H, $CO_2\underline{Me}$), 3.50 (s, 3H, $CO_2\underline{Me}$), 3.05 (d, $J_{5\text{-}6}$ = 8.3 Hz, H_5), 2.79 (ddd, $J_{6\text{-}7endo}$ = 11.8 Hz, $J_{6\text{-}5}$ = 8.3 Hz, $J_{6\text{-}7exo}$ = 1.0 Hz, 1H, H_6), 2.43 (d, $J_{7exo\text{-}7endo}$ = 14.2 Hz, H_{7exo}), 2.11 (dd, $J_{7endo\text{-}7exo}$ = 14.2, $J_{7endo\text{-}6}$ = 11.9 Hz, H_{7endo}), 1.72 (s, 3H, CH_3), 1.52 (s, 18H, $C_6\underline{Me}_6$), 1.31 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 181.1 ($\underline{C}O_2Me$), 172.7 ($\underline{C}O_2Me$), 122.4 ($\underline{C}N$), 96.3 ($\underline{C}_6Me_6$), 95.6 (C_4), 68.1 (C_5), 58.3 (C_2), 55.5 (C_3), 51.3 ($CO_2\underline{Me}$), 50.7 ($CO_2\underline{Me}$),

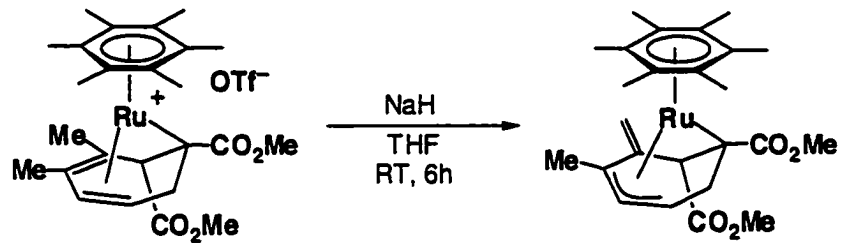
40.0 (C_7), 29.9 (C_6), 23.1 (CH_3), 22.6 (CH_3), 21.8 (C_1), 15.1 ($\underline{C}_6Me_6$); ^1H-^{13}C HETCORR (100 MHz, C_6D_6): δ 68.1 (C_5) ↔ δ 3.05 (H_5); δ 58.3 (C_2) ↔ δ 4.72 (H_2); δ 51.3 ($CO_2\underline{Me}$) ↔ δ 3.69 ($CO_2\underline{Me}$); δ 50.7 ($CO_2\underline{Me}$) ↔ δ 3.50 ($CO_2\underline{Me}$); δ 40.0 (C_7) ↔ δ 2.11 (H_{7endo}) and 2.43 (H_{7exo}); δ 29.9 (C_6) ↔ δ 2.79 (H_6); δ 23.1 (CH_3) ↔ δ 1.31 (CH_3); δ 22.6 (CH_3) ↔ δ 1.72 (CH_3); δ 15.1 ($C_6\underline{Me}_6$) ↔ δ 1.52 ($C_6\underline{Me}_6$). Analysis calculated for $C_{26}H_{35}NO_4Ru$: C, 59.30%; H, 6.70%; N, 2.66%; found: C, 59.46%; H, 6.70%; N, 2.68%.



173 **202**

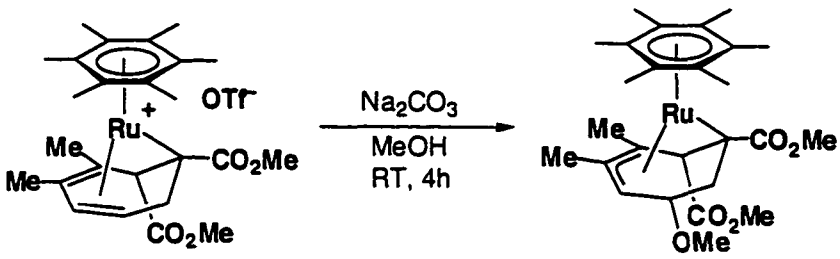
(C_6Me_6)Ru((1:3,4,5-η)-1,2-dicarbomethoxy-3,4-dimethylcycloheptendiyl) (202). A solution of complex **173** (0.021 g, 0.032 mmol) in tetrahydrofuran (4 mL) was prepared in a small Schlenk flask and cooled to –78°C using a dry ice/acetone bath. A solution of $LiEt_3BH$ (1.0 M in THF, 0.034 mL, 0.034 mmol, 1.0 equiv) was added via syringe. The reaction was stirred for 4 hours then the reaction was slowly warmed to room temperature. After stirring a further hour at room temperature the solvent was evaporated and the residue thoroughly dried under vacuum. The flask was then removed to the dry box and crude product was extracted into 2 x 3 mL diethyl ether and the combined portions filtered through Celite. The filtrate was then dried to give 0.013 g (81%) of oily yellow crystals. ^1H NMR (400 MHz, C_6D_6): δ 4.70 (br s, 1H, H_2), 3.67 (s, 3H, $CO_2\underline{Me}$), 3.51 (dd, J = 8.5, 2.3 Hz, H_5), 3.35 (s, 3H, $CO_2\underline{Me}$), 2.03 (dd, J = 11.5, 6.6 Hz, 1H), 1.95-

1.86 (m, 2H), 1.74 (s, 3H, CH_3), 1.69 (s, 18H, $C_6\underline{Me}_6$), 1.68-1.65 (m, partially obscured, 1H), 1.49 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 182.6 ($\underline{C}O_2Me$), 174.8 ($\underline{C}O_2Me$), 97.2 (C_4), 95.5 ($\underline{C}_6Me_6$), 72.1 (C_5), 58.5 (C_2), 50.7 ($CO_2\underline{Me}$), 50.6 (C_3), 50.5 ($CO_2\underline{Me}$), 39.0 (C_7), 26.3 (C_6), 22.8 (CH_3), 22.1 (CH_3), 21.4 (C_1), 15.3 ($\underline{C}_6Me_6$).



173 203

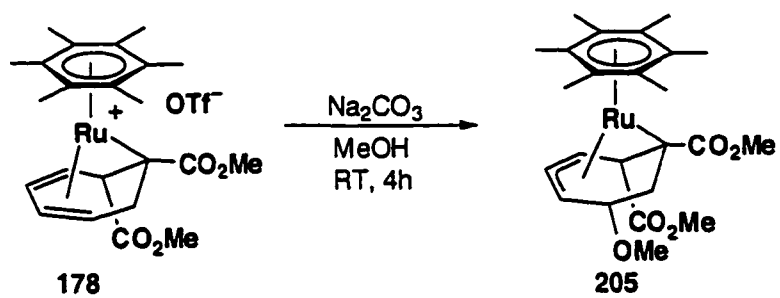
(C_6Me_6)Ru((1:4,5,6-η)-1,2-dicarbomethoxy-4-methyl-3-methylenecycloheptendiyl) (203). In the drybox, a solution of complex **173** (0.020 g, 0.031 mmol) in tetrahydrofuran (3 mL) was prepared in a small Schlenk flask and sodium hydride (0.008 g, 0.33 mmol, 10.7 equiv) added. The suspension was then stirred at room temperature for 6 hours before removing the solvent under reduced pressure. After drying thoroughly, the product was extracted from the residue into 2 x 2 mL pentane and the combined portions filtered through Celite. The filtrate was then dried to yield 0.012 g (77%) of pale yellow crystals. ^1H NMR (300 MHz, C_6D_6): δ 5.42 (dd, J = 2.5, 0.5 Hz, 1H, CH_2), 5.33 (dd, J = 2.3, 0.5 Hz, 1H, CH_2), 4.01 (br t, J = 2.4 Hz, 1H, H_2), 3.55 (s, 3H, $CO_2\underline{Me}$), 3.54 (m, obscured, 1H, H_{7endo}), 3.43 (dd, J = 14.1, 2.5 Hz, 1H, H_{7exo}), 3.39 (s, 3H, $CO_2\underline{Me}$), 3.09 (td, J = 6.0, 2.6 Hz, 1H, H_6), 2.95 (d, J = 6.0 Hz, 1H, H_5), 1.71 (s, 3H, CH_3), 1.61 (s, 18H, C_6Me_6).



173 204

(C_6Me_6)Ru((1:3,4,5-η)-1,2-dicarbomethoxy-3,4-dimethyl-6-methoxycycloheptendiyl) (204). A Schlenk flask was charged with compound **173** (0.200 g, 0.308 mmol), Na_2CO_3, (0.326 g, 3.08 mmol, 10 equiv), then 15 mL of distilled methanol added via syringe. The suspension was stirred at room temperature for 4 hours then the solvent was removed under low pressure. Once the residue was thoroughly dried the flask was removed to the drybox and the residue was triturated with 2 x 4 mL diethyl ether. The combined portions were then filtered through Celite and the filtrate dried to give 0.144 g (88%) of bright yellow crystals. ^{1}H NMR (400 MHz, C_6D_6): δ 4.68 (br s, 1H, H_2), 4.06 (t, $J_{6\text{-}5}$ = $J_{6\text{-}7endo}$ = 7.7 Hz, H_6), 3.57 (s, 3H, $CO_2\underline{Me}$), 3.44 (s, 3H, $CO_2\underline{Me}$), 3.39 (d, $J_{5\text{-}6}$ = 7.6 Hz, H_5), 3.20 (s, 3H, OMe), 2.63 (d, $J_{7exo\text{-}7endo}$ = 14.2 Hz, H_{7exo}), 2.25 (dd, $J_{7endo\text{-}7exo}$ = 13.8, $J_{7endo\text{-}6}$ = 7.8 Hz, H_{7endo}), 1.85 (s, 3H, CH_3), 1.66 (s, 18H, $C_6\underline{Me}_6$), 1.51 (s, 3H, CH_3); ^{13}C NMR (100 MHz, C_6D_6): δ 182.1 (s, $\underline{C}O_2Me$), 173.3 (s, $\underline{C}O_2Me$), 97.1 (s, C_4), 95.6 (s, $\underline{C}_6Me_6$), 83.5 (d, $^1J_{CH}$ = 139 Hz, C_6), 71.1 (d, $^1J_{CH}$ = 141 Hz, C_5), 58.4 (d, $^1J_{CH}$ = 122 Hz, C_2), 56.0 (q, $^1J_{CH}$ = 140 Hz, O$\underline{Me}$), 54.0 (s, C_6), 50.5 (q, $^1J_{CH}$ = 128 Hz, $CO_2\underline{Me}$), 49.9 (q, $^1J_{CH}$ = 128 Hz, $CO_2\underline{Me}$), 43.3 (t, $^1J_{CH}$ = 128 Hz, C_7), 23.6 (q, $^1J_{CH}$ = 125 Hz, CH_3), 22.7 (q, $^1J_{CH}$ = 124 Hz, CH_3), 20.1 (s, C_1), 15.3 (q, $^1J_{CH}$ = 128 Hz, $C_6\underline{Me}_6$); ^{1}H-^{13}C HETCORR (100 MHz, C_6D_6): δ 58.4 (C_2) ↔ δ 4.68 (H_2); δ 83.5 (C_6) ↔ δ 4.06 (H_6); δ 50.5

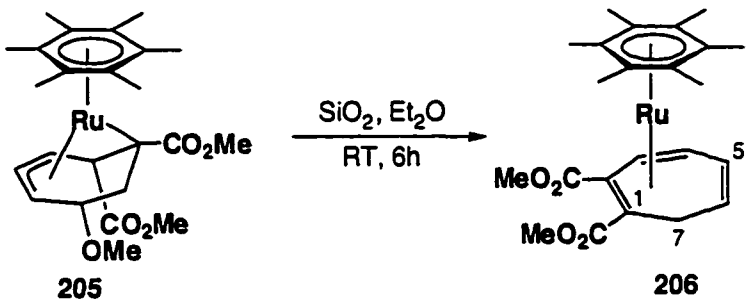
($CO_2\underline{Me}$) ↔ δ 3.57 ($CO_2\underline{Me}$); δ 49.9 ($CO_2\underline{Me}$) ↔ δ 3.44 ($CO_2\underline{Me}$); δ 43.3 (C_7) ↔ δ 2.63 (H_{7exo}) and 2.25 (H_{7endo}); δ 71.1 (C_5) ↔ δ 3.39 (H_5); δ 56.0 (OMe) ↔ δ 3.20 (OMe); δ 23.6 (CH_3) ↔ δ 1.51 (CH_3); δ 22.7 (CH_3) ↔ δ 1.85 (CH_3); δ 15.3 ($C_6\underline{Me}_6$) ↔ δ 1.66 ($C_6\underline{Me}_6$). Analysis calculated for $C_{26}H_{38}O_5Ru$: C, 58.74%; H, 7.20%; found: C, 58.03%; H, 7.06%.



178 205

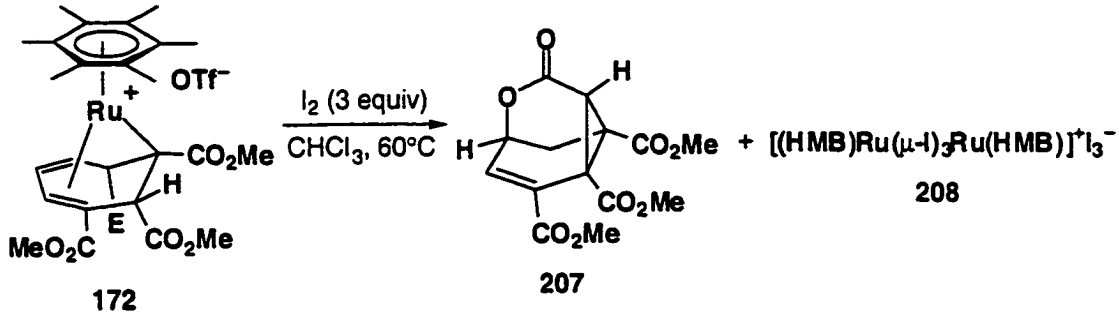
(C_6Me_6)Ru((1:3,4,5-η)-1,2-dicarbomethoxy-6-methoxycycloheptendiyl) (205). A Schlenk flask was charged with complex **178** (0.025 g, 0.040 mmol), Na_2CO_3 (0.025 g, 0.236 mmol, 5.9 equiv) and 3 mL of distilled methanol was added via syringe. The suspension was stirred at room temperature for 4 hours, then the solvent was removed under reduced pressure. Once the residue was thoroughly dried the flask was removed to the drybox and the residue was triturated with 2 x 2 mL diethyl ether. The combined portions were then filtered through Celite and the yellow filtrate dried to give 0.016 g (79%) of bright yellow crystals. ^{1}H NMR (300 MHz, C_6D_6): δ 4.64 (br d, J = 7.3 Hz, 1H, H_2), 4.03 (t, $J_{6\text{-}5} = J_{6\text{-}7endo}$ = 7.3 Hz, H_6), 3.65 (t, $J_{3\text{-}2} = J_{3\text{-}4}$ = 6.9 Hz, H_3), 3.56 (s, 3H, $CO_2\underline{Me}$), 3.47 (t, $J_{5\text{-}4} = J_{5\text{-}6}$ = 7.0 Hz, partially obscured, 1H, H_5), 3.46 (s, 3H, $CO_2\underline{Me}$), 3.23 (s, 3H, OMe), 3.20 (dd, $J_{4\text{-}3}$ = 6.8 Hz, $J_{4\text{-}5}$ = 7.2 Hz, partially obscured, 1H, H_4), 2.72

(d, $J_{7exo\text{-}7endo}$ = 14.2 Hz, H_{7exo}), 2.33 (dd, $J_{7endo\text{-}7exo}$= 14.2, $J_{7endo\text{-}6}$ = 7.6 Hz, H_{7endo}), 1.63 (s, 18H, $C_6\underline{Me}_6$).



205 206

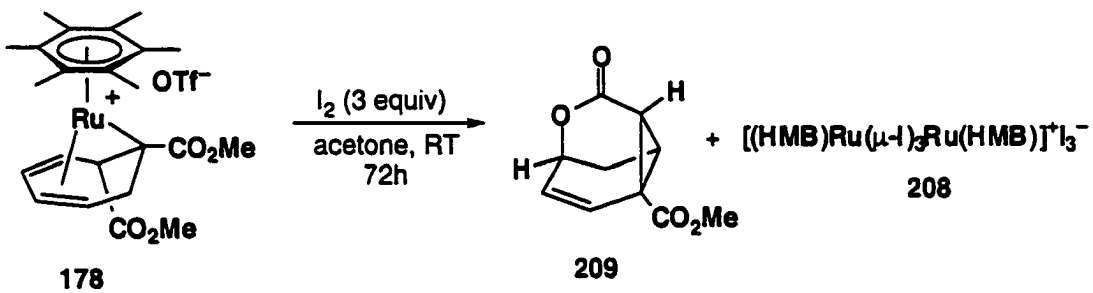
(C_6Me_6)Ru((1-4-η)-1,2-dicarbomethoxycycloheptatriene) (206). A small Schlenk flask was charged with approximately 1.0 g of flash silica gel and a solution of complex **205** (0.016 g, 0.032 mmol) in 3 mL diethyl ether was added via syringe. The suspension was stirred under nitrogen at room temperature for 6 hours, then the reaction mixture was filtered; the silica gel was subsequently rinsed with 2 x 2 mL of diethyl ether. The filtrate was then dried under reduced pressure to yield 0.011 g (73%) of a yellow solid. ^{1}H NMR (300 MHz, C_6D_6): δ 5.96 (dddd, J = 9.8, 7.7, 3.1, 1.8 Hz, 1H, H_5), 5.31(ddd, J = 9.9, 6.0, 2.8 Hz, 1H, H_6), 4.53 (d, J = 7.5 Hz, 1H, H_3), 3.56 (s, 3H, $CO_2\underline{Me}$), 3.48 (s, 3H, $CO_2\underline{Me}$), 3.07 (ddd, J = 20.1, 5.9, 1.6 Hz, 1H, H_{7exo}), 2.62 (t, J = 7.7 Hz, 1H, H_4), 1.86 (s, 18H, $C_6\underline{Me}_6$), 1.49 (dt, J = 20.5, 3.0 Hz, 1H, H_{7endo}).



Iodinolysis of [(C_6Me_6)Ru((1:3,4,5,6-η)-1,2,3,7-tetracarbomethoxycyclo-heptadienyl)]$^+$OTf$^-$ (172). A solution of complex **172** (0.100 g, 0.136 mmol), and iodine (0.110 g, mmol, 3.19 equiv) in 7 mL chloroform was placed in a small glass bomb. The bomb was then sealed and heated to 50°C using an oil bath, without stirring, for 48 hours. After the reaction was cooled to room temperature, black crystals (0.092 g, 88%) of complex **208** were removed by filtration and the brown filtrate was rinsed with a 20% aqueous sodium thiosulfate solution. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography (silica gel, dichloromethane), giving 0.024 g (57%) of yellow oil. IR ($CHCl_3$ cast, cm^{-1}): 2956 (m), 1735 (s), 1438 (m), 1258 (s), 1209 (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18 (dd, $J_{6\text{-}5}$ = 6.9 Hz, $J_{6\text{-}4b}$ = 0.5 Hz, 1H, H_6), 5.02 (ddd, $J_{5\text{-}6}$ = 7.0 Hz, $J_{5\text{-}4a}$ = 4.0 Hz, $J_{5\text{-}4b}$ = 2.0 Hz, 1H, H_5), 3.79 (s, 3H, CO_2Me), 3.77 (s, 3H, CO_2Me), 3.76 (s, 3H, CO_2Me), 3.65 (s, 1H, H_2), 2.27 (dd, $J_{4a\text{-}4b}$ = 15.0 Hz, $J_{4a\text{-}5}$ = 4.0 Hz, 1H, H_{4a}), 1.55 (ddd, $J_{4b\text{-}4a}$ = 14.9 Hz, $J_{4b\text{-}5}$ = 1.9 Hz, $J_{4b\text{-}6}$ = 0.5 Hz, 1H, H_{4b}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1 (s, $\underline{C}O_2Me$), 166.6 (s, $\underline{C}O_2Me$), 164.2 (s, lactone $\underline{C}O_2$-), 164.1 (s, $\underline{C}O_2Me$), 133.7 (d, $^1J_{CH}$ = 174 Hz, C_6), 132.6 (s, C_7), 67.3 (d, $^1J_{CH}$ = 161 Hz, C_5), 53.34 (q, $^1J_{CH}$ = 148 Hz, $CO_2\underline{Me}$), 53.27 (q, $^1J_{CH}$ = 148 Hz, $CO_2\underline{Me}$), 52.9 (q, $^1J_{CH}$ = 148 Hz, $CO_2\underline{Me}$), 39.3 (s, C_1), 35.0 (d, $^1J_{CH}$ = 178 Hz, C_2), 32.3

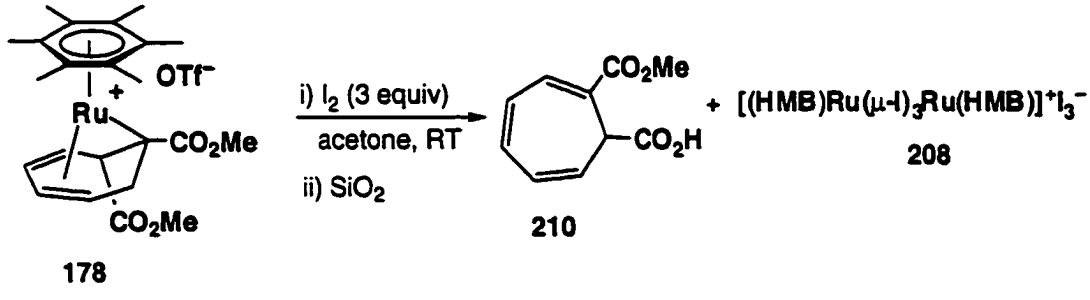
(s, C_3), 21.4 (t, $^1J_{CH}$ = 137 Hz, C_4); ^1H-^{13}C HETCORR (100 MHz, $CDCl_3$): δ 133.7 (C_6) ↔ δ 7.18 (H_6); δ 67.3 (C_5) ↔ δ 5.02 (H_5); δ 53.34 (CO_2Me) ↔ δ 3.76 (CO_2Me); δ 53.27 (CO_2Me) ↔ δ 3.77 (CO_2Me); δ 52.9 (CO_2Me) ↔ δ 3.79 (CO_2Me); δ 35.0 (C_2) ↔ δ 3.65 (H_2); δ 21.4 (C_4) ↔ δ 2.27 (H_{4a}) and 1.55 (H_{4b}); BIRDTRAP (100 MHz, $CDCl_3$): δ 168.1 (CO_2Me) ↔ δ 3.76, 3.65; δ 166.6 (CO_2Me) ↔ δ 3.77, 3.65; δ 164.1 (CO_2Me) ↔ δ 3.79; δ 133.7 (C_6) ↔ δ 2.27; δ 67.3 (C_5) ↔ δ 2.27; δ 53.34 (CO_2Me) ↔ δ 3.76; δ 52.9 (CO_2Me) ↔ δ 3.79; δ 39.3 (C_1) ↔ δ 7.18, 2.27; δ 35.0 (C_2) ↔ δ 3.65, 1.55; δ 32.3 (C_3) ↔ δ 1.55. MS *m/z* calculated for $C_{14}H_{14}O_8$ (M^+): 310.0689; found: 310.0698 (2.26%); calculated for $C_{12}H_{10}O_5$ ($M-C_2H_4O_3$): 234.0528; found: 234.0531 (100.00%).

Complex 208. ^1H NMR (300 MHz, CD_3CN): δ 2.17 (s, 18H, C_6Me_6). Analysis calculated for $C_{12}H_{18}I_4Ru$: C, 18.7%; H, 2.35%; I, 65.84%; found: C, 18.9%; H, 2.00%; I, 65.31%.



Iodinolysis of [(C_6Me_6)Ru((1:3,4,5,6-η)-1,2-dicarbomethoxycycloheptadienyl)]$^+$OTf$^-$ (178). A 4 mL acetone solution of complex **178** (0.100 g, 0.161 mmol) and iodine (0.125 g, 0.491 mmol, 3.05 equiv) were placed in a small Schlenk flask and left at room temperature for 72 hours without stirring. Afterwards, black shiny crystals of complex

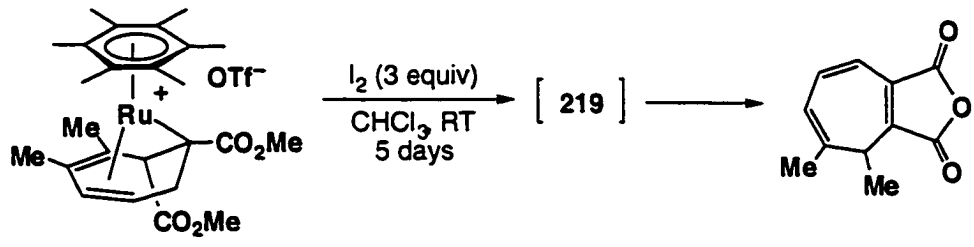
208 were removed by filtration and the brown filtrate dried to a thick black oil. The residue was dissolved in 10 mL chloroform and rinsed with a 20% aqueous sodium thiosulfate solution. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography (silica gel, diethyl ether), giving 0.022 g (70%) of yellow oil. IR ($CHCl_3$ cast, cm^{-1}): 2962 (m), 1728 (s), 1261 (s), 1097 (s), 1084 (s), 1046 (s), 1017 (s), 801.4 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 6.86 (dd, $J_{7\text{-}6}$ = 9.5 Hz, $J_{7\text{-}5}$ = 0.6 Hz, 1H, H_7), 6.18 (dd, $J_{6\text{-}7}$ = 9.5 Hz, $J_{6\text{-}5}$ = 6.5 Hz, 1H, H_6), 4.87- 4.84 (m, 1H, H_5), 3.79 (s, 3H, CO_2Me), 3.06 (d, $J_{2\text{-}3}$ = 7.8 Hz, 1H, H_2), 2.71 (dq, $J_{3\text{-}2}$ = 7.8 Hz, $J_{3\text{-}5} = J_{3\text{-}4a} = J_{3\text{-}4b}$ = 2.6 Hz, 1H, H_3), 2.27 (ddd, $J_{4a\text{-}4b}$ = 14.4 Hz, $J_{4a\text{-}5}$ = 3.9 Hz, $J_{4a\text{-}6}$ = 1.8 Hz, 1H, H_{4a}), 1.55 (dt, $J_{4b\text{-}4a}$ = 14.4 Hz, $J_{4b\text{-}5} = J_{4b\text{-}3}$ = 2.3 Hz, 1H, H_{4b}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6 (s, $\underline{C}O_2Me$), 166.3 (s, $\underline{C}O_2$-), 128.5 (d, $^1J_{CH}$ = 169 Hz, C_6), 124.6 (d, $^1J_{CH}$ = 172 Hz, C_7), 68.3 (d, $^1J_{CH}$ = 154 Hz, C_5), 53.0 (q, $^1J_{CH}$ = 148 Hz, $CO_2\underline{Me}$), 34.5 (d, $^1J_{CH}$ = 176 Hz, C_3), 31.6 (s, C_1), 22.6 (d, $^1J_{CH}$ = 177 Hz, C_2), 20.0 (t, $^1J_{CH}$ = 134 Hz, C_4); MS *m/z* calculated for $C_{10}H_{10}O_4$ (M^+): 194.0579; found: 194.0579 (27.94%); calculated for C_7H_7 ($M\text{-}C_3H_3O_4$): 91.0548; found: 91.0547 (100.00%).



178 210 208

7-carbomethoxycyclohepta-2,7-trienoic acid (210). An acetone (4 mL) solution of complex **178** (0.122 g, 0.196 mmol) and iodine (0.160 g, 0.630 mmol, 3.22 equiv) was

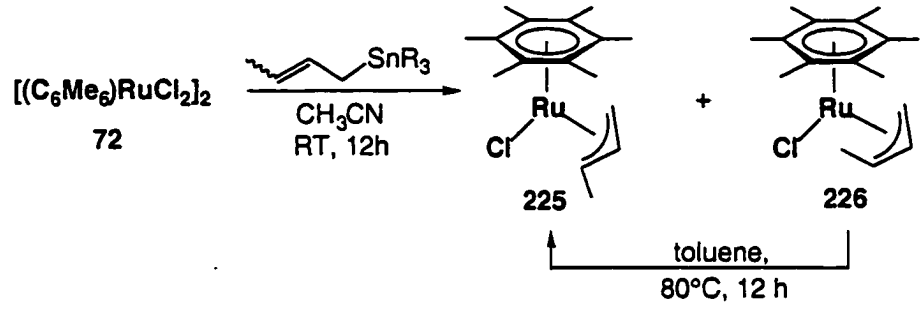
placed in a small Schlenk flask and left at room temperature for 72 hours without stirring. Afterwards, black shiny crystals of complex **208** were removed by filtration and the brown filtrate dried to a thick black oil. The crude residue was dissolved in diethyl ether then filtered through a small plug of silica gel. Analysis of this residue by ^{1}H NMR spectroscopy indicated that the product was the trienoic acid **210**. The acid was further purified by flash chromatography (silica gel, 1% acetic acid in ethyl acetate), giving 0.026 g (68%) of yellow oil. IR ($CHCl_3$ cast, cm^{-1}): 3225 (br), 2960 (m), 1767 (m), 1711 (s), 1437 (m), 1260 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 (d, J = 6.3 Hz, 1H, H_2), 6.83 (dd, J = 11.3, 6.0 Hz, 1H, H_4), 6.66 (ddd, J = 11.3, 6.3, 0.7 Hz, 1H, H_5), 6.44 (ddt, J = 9.6, 6.0, 0.7 Hz, 1H, H_6), 5.85 (t, J = 9.1 Hz, 1H, H_3), 4.37 (dd, J = 8.7, 0.7 Hz, H_7), 3.80 (s, 3H, CO_2Me); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8 (s, CO_2H), 166.0 (s, CO_2Me), 134.9 (d, $^1J_{CH}$ = 152 Hz, C_3), 133.4 (d, $^1J_{CH}$ = 165 Hz, C_4), 128.7 (d, $^1J_{CH}$ = 155 Hz, C_2), 127.8 (d, $^1J_{CH}$ = 158 Hz, C_5), 123.8 (d, $^1J_{CH}$ = 166 Hz, C_6), 122.1 (s, C_1), 52.4 (d, $^1J_{CH}$ = 148 Hz, $CO_2\underline{Me}$), 42.5 (d, $^1J_{CH}$ = 128 Hz, C_7). MS *m/z* calculated for $C_{10}H_{10}O_4$ (M^+): 194.0579; found: 194.0570 (3.09%); calculated for $C_9H_9O_2$(M-CHO_2): 91.0548; found: 91.0547 (100.00%).



173 220

Iodinolysis of [(C_6Me_6)Ru((1:3,4,5,6-η)-1,2-dicarbomethoxy-3,4-dimethylcyclohepta-dienyl)]$^+$OTf$^-$ (173). A solution of complex **173** (0.050 g, 0.077 mmol) in 3 mL chloroform was placed in a small round-bottom flask and iodine (0.060 g, 0.236 mmol, 3.07 equiv) was added. The flask was then sealed and allowed to stand at room temperature. After 5 days the black crystals of complex **208** were removed by filtration (0.052 g, 88%) and the solvent removed *in vacuo* from the black filtrate. Spectroscopic analysis of the crude residue indicates one major organic product, compound **219** [^{1}H NMR (300 MHz, $CDCl_3$, partial data only): δ 6.97-6.75 (very br s, 1H), 6.72-6.54 (m, 1H), 6.10 (d, J = 7.0 Hz, 1H), 3.82 (br s, 3H), 3.80 (s, 3H), 1.97 (br s, 3H)]. The residue was redissolved in chloroform (3 mL) and the reaction mixture allowed to stand at room temperature for a further 5 days before removing the solvent under reduced pressure. Subsequent ^{1}H NMR analysis of the crude residue indicates a mixture of compound **219** and compound **220**. The second product was isolated by room temperature sublimation on the Schlenk line from the crude residue, giving 0.010 g (68%) of a waxy yellow solid. IR ($CHCl_3$ cast, cm^{-1}): 1843 (s), 1767 (s), 1250 (m), 906 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (dd, J = 11.0, 7.0 Hz, 1H, H_4), 6.68 (d, J = 11.0 Hz, 1H, H_3), 6.20 (d, J = 7.2 Hz, 1H, H_5), 3.50 (qd, J = 7.1, 1.1 Hz, 1H, H_7), 2.10 (s, 3H, CH_3), 0.98 (d, J = 7.1 Hz,

3H, CH_3); $^{13}C\{APT\}$ NMR (75 MHz, $CDCl_3$): δ 165.2 (C_{quat}), 164.5 (C_{quat}), 145.2 (C_{quat}), 138.9 (CH), 136.3 (C_{quat}), 132.0 (C_{quat}), 123.6 (CH), 116.9 (CH), 33.6 (CH), 26.2 (CH_3), 13.4 (CH_3). MS *m/z* calculated for $C_{11}H_{10}O_3$ (M^+): 190.0630; found: 190.0627 (22.30%); calculated for $C_{10}H_7O_3$ (M-CH_3): 175.0395; found: 175.0393 (100.00%). Analysis calculated for $C_{11}H_{10}O_3$: C, 69.45%; H, 5.30%; found: C, 68.76%; H, 5.39%.



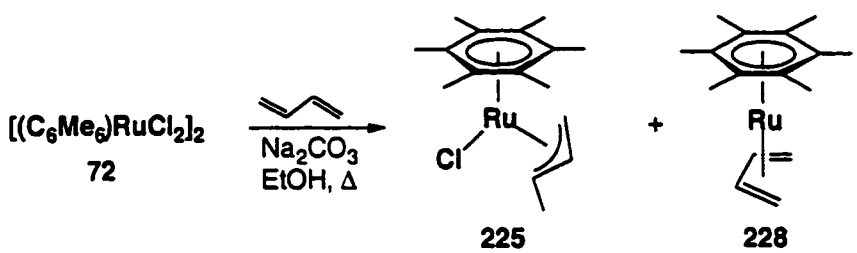
Synthesis of (η^6-C_6Me_6)Ru(η^3-1-MeC_3H_4)Cl (225).

Method A. A 100 mL, oven-dried Schlenk flask was charged with $[(C_6Me_6)RuCl_2]_2$ (0.200 g, 0.598 mmol/Ru) and 40 mL of acetonitrile and the resulting red slurry placed under nitrogen. Freshly prepared 2-butenyltributylstannane (0.28 g, 0.811 mmol, 1.35 equiv) (a mixture of both *cis* and *trans* isomers) was added via syringe and the reaction mixture was stirred at room temperature for 9 hours, forming a clear yellow solution. Acetonitrile was removed by rotary evaporation to leave an oily orange residue. This crude mixture was dried under vacuum, then transferred to the dry box where it was rinsed with several portions of pentane (10-12 mL) to remove the tin compounds. Spectroscopic analysis (^{1}H NMR) of the resultant residue indicated a mixture of *exo*, *syn* and *exo*, *anti* crotyl complexes **225** and **226**, in an approximate ratio of 1 : 1. Trace quantities of an unidentified third isomer were also present. The crude product mixture was then dissolved in 15 mL toluene and the solution placed in a Kontes flask, which was sealed and transferred to a oil bath heated to 80°C. After 12 hours the toluene solution was cooled and the solvent removed under reduced pressure. The residue was then dissolved in a minimum of dichloromethane and the solution was filtered through a small

plug of flash silica gel. The isolated product was then recrystallized from toluene/pentane to give 0.134 g (63 %) of orange crystals.

(η^6-C_6Me_6)Ru(η^3-*exo,anti*-1-MeC_3H_4)Cl (226). ^{1}H NMR (300 MHz, C_6D_6): δ 3.53 (sextet, J = 6.5 Hz, 1H, H_{1syn}), 3.12 (d, J = 6.6 Hz, 1H, H_{3syn}), 3.08 (d, J = 11.9 Hz, 1H, H_{3anti}), 3.05 (dt, J = 11.9, 6.6 Hz, 1H, H_2), 1.58 (s, 18H, C_6Me_6), 1.41 (d, J = 6.4 Hz, 3H, CH_3).

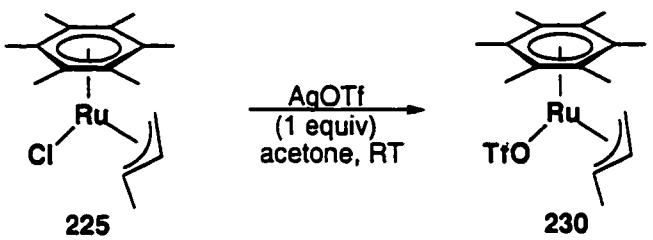
(η^6-C_6Me_6)Ru(η^3-*exo,syn*-1-MeC_3H_4)Cl (225). ^{1}H NMR (300 MHz, C_6D_6): δ 3.57 (dq, J = 10.3, 6.4 Hz, 1H, H_{1anti}), 3.05 (td, J = 10.3, 6.6 Hz, 1H, H_2), 2.93 (d, J = 6.6 Hz, 1H, H_{3syn}), 2.76 (d, J = 10.4 Hz, 1H, H_{3anti}), 1.62 (s, 18H, C_6Me_6), 1.43 (d, J = 6.4 Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 95.5, 89.9, 67.3, 51.7, 17.9, 15.1. Analysis calculated for $C_{16}H_{25}ClRu$: C, 54.30%; H, 7.12%; found: C, 54.41%; H, 6.89%.



Method B. A small Kontes flask equipped with a stir-bar was charged with [(η^6-C_6Me_6)$RuCl_2$]$_2$ (0.200 g, 0.598 mmol/Ru) and Na_2CO_3 (0.200 g, 1.89 mmol, 3.16 equiv), then 10 mL anhydrous ethanol was added. The reaction mixture was rigorously degassed with three freeze-pump-thaw cycles before adding 1,3-butadiene (1.20 g, 22.18 mmol, 37.1 equiv) via vacuum transfer. The flask was then sealed and placed in an oil bath heated to 80°C. The dark red suspension gradually faded to a light orange solution with white precipitate. After 3 hours the reaction was cooled to room temperature before

removing solvent and excess butadiene *in vacuo*. The bomb was then transferred to the drybox where the orange residue was triturated with 2 x 3 mL toluene and the combined portions filtered through Celite, then dried to an orange solid. Rinsing this solid with 2-3 mL pentane removes the small amount of air-sensitive $(C_6Me_6)Ru(\eta^4\text{-butadiene})$ (**228**) (~ 4% as measured by ^1H NMR spectroscopy) and organic byproducts. The remaining air stable product was recrystallized from toluene/pentane to give 0.176 g (83%) of orange crystals.

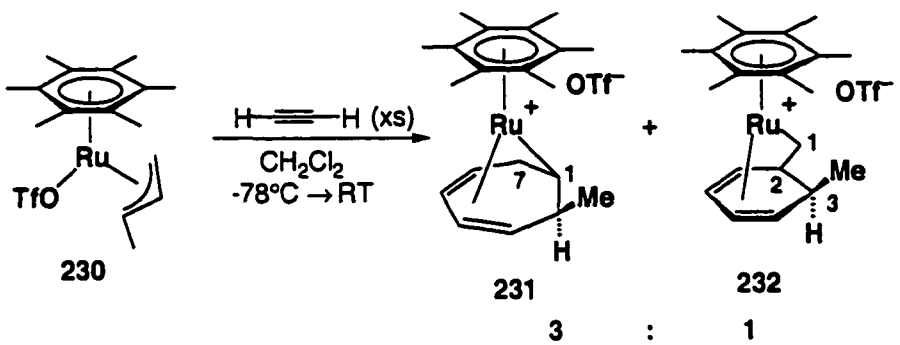
$(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4H_6)$ (228). ^1H NMR (300 MHz, C_6D_6): δ 4.31-4.27 (m, second-order pattern, 2H, $H_{2/3}$), 1.96 (s, 18H, C_6Me_6), 1.44-1.40 (m, 2H, $H_{1syn/4syn}$), 0.23-0.20 (m, 2H, $H_{1anti/4anti}$).



225 230

$(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}1\text{-}MeC_3H_4)OTf$ (230). A solution of $(C_6Me_6)Ru(\eta^3\text{-}1\text{-}MeC_3H_4)Cl$ (0.100 g, 0.283 mmol) in 10 mL acetone was degassed and placed under nitrogen atmosphere. A solution of AgOTf (0.077 g, 0.296 mmol, 1.05 equiv) in acetone (2 mL) was added via syringe, followed by the immediate formation of a white precipitate. The reaction mixture was stirred at room temperature for a further 30 min. The mixture was quickly filtered through Celite to remove insoluble AgCl and the bright orange solution was concentrated *in vacuo*. The resulting solid was transferred to the drybox where it was dissolved in benzene and filtered through Celite to remove any remaining AgCl. The

benzene was then removed by lyophilization to give 0.119 g (90%) of an orange powder, which was pure by ^{1}H NMR spectroscopy, and kept stored under nitrogen. The solid slowly turns brown on exposure to air. ^{1}H NMR (300 MHz, C_6D_6): δ 3.29 (d, J = 6.7 Hz, 1H, H_{3syn}), 3.28 (dq, J = 10.5, 6.2 Hz, 1H, H_{1anti}, partially obscured), 2.87 (td, J = 10.5, 6.8 Hz, 1H, H_2), 2.70 (d, J = 10.6 Hz, 1H, H_{3anti}), 1.56 (s, 18H, C_6Me_6), 1.51 (d, J = 6.2 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 95.3, 92.4, 72.4, 55.3, 17.5, 15.1. Triflate carbon was not observed.

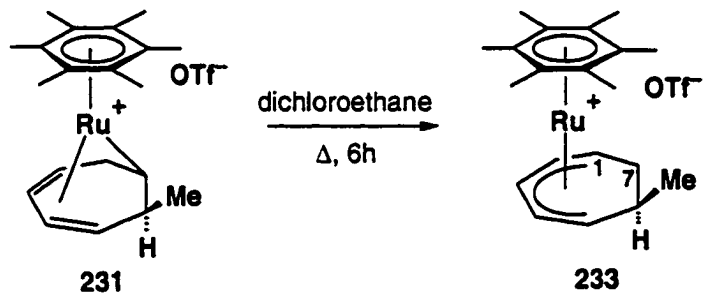


Reaction of (η^6-C_6Me_6)Ru(η^3-1-MeC_3H_4)OTf (230) with Acetylene. A solution of (C_6Me_6)Ru(η^3-1-MeC_3H_4)OTf (0.050 g, 0.107 mmol) in 3 mL dichloromethane was cooled to –78°C using a dry ice/acetone bath. Acetylene was bubbled through the solution for 3 minutes, then the flask sealed, the cold bath removed, and the reaction warmed to room temperature. After 10 minutes at room temperature the solvent was removed *in vacuo,* leaving a tan solid. The ^{1}H NMR spectrum of the crude reaction residue indicates two products, **231** and **232**, in a ratio of 3 : 1, respectively.

[(η^6-C_6Me_6)Ru((1:3,4,5,6-η)-2-methylcycloheptadienyl)]$^+$OTf$^-$ (231).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25 (ap dt, J = 6.5 Hz, AB pattern, 2H, H_4 and H_5), 3.44 (br t, J = 7.2 Hz, 1H, H_6), 3.16 (br d, J = 5.8 Hz, 1H, H_3), 2.73 (dt, J = 14.0, 8.4 Hz, 1H, H_{7endo}), 2.23 (s, 18H, C_6Me_6), 1.00 (d, J = 7.1 Hz, 3H, CH_3), –0.55 (d, J = 8.5 Hz, 1H, H_1). H_2 and H_{7exo} obscured. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 107.7, 97.6, 96.0, 51.2, 44.3, 41.8, 35.4, 20.4, 16.4, –29.1. Triflate carbon was not observed.

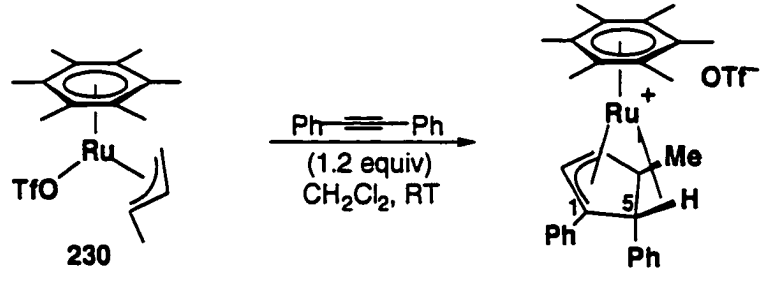
[(C_6Me_6)Ru((1:4,5,6,7-η)-3-methylmethanocyclohexadienyl)]$^+$OTf$^-$ (232) (characterized as a mixture with complex **231**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13 (t, J = 5.4 Hz, 1H, H_5), 5.09 (t, J = 5.7 Hz, 1H, H_6), 4.00 (t, J = 4.9 Hz, 1H, H_4), 3.39 (t, J = 5.6 Hz, 1H, H_7), 2.94 (br s, 1H, H_2), 2.21 (s, 18H, C_6Me_6), 1.04 (m, 1H, H_{3exo}), 0.87 (d, J = 3.1 Hz, 1H, H_{1b}), 0.78 (d, J = 6.8 Hz, 3H, CH_3). H_{1a} was obscured.



231 233

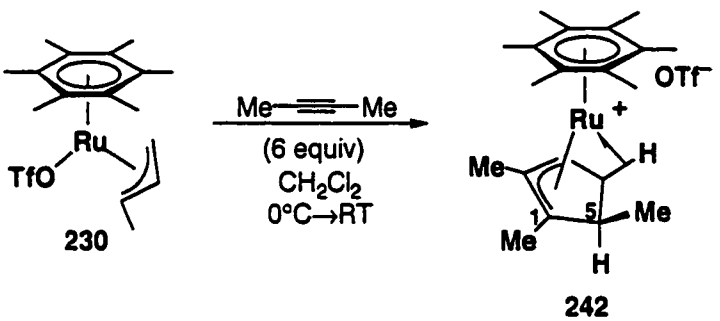
[(η^6-C_6Me_6)Ru(η^5-6-methylcycloheptadienyl)]$^+$OTf$^-$ (233). The crude reaction mixture containing complex **231** and complex **232** from the previous reaction was dissolved in 4 mL dichloroethane and the solution placed into a 25 mL two-necked round-bottom flask equipped with condenser and nitrogen inlet. The yellow solution was heated to reflux for 6 hours then the solvent removed *in vacuo*. Subsequent ^{1}H NMR spectroscopic analysis of the mixture showed clean conversion of **231** to η^5-6-methylcycloheptadienyl complex **233**, accompanied by conversion of **232** to an unidentified product. Some decomposition

of this minor thermodynamic product was also noted. Analytically pure η^5-6-methylcycloheptadienyl complex **233** was isolated after recrystallization from dichloromethane/diethyl ether, giving 0.027 g (39 %) of an off-white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (t, J = 5.9 Hz, 1H, H_3), 4.80 (dd, J = 7.9, 5.9 Hz, 1H, H_4), 4.74 (dd, J = 8.2, 6.1 Hz, 1H, H_2), 3.78 (ddd, J = 8.2, 4.7, 3.0 Hz, 1H, H_1), 2.30 (s, 18H, C_6Me_6), 1.74 (ddd, J = 14.4, 5.7, 3.0 Hz, 1H, H_{7a}), 1.60 (dt, J = 14.5, 6.1 Hz, 1H, H_{7b}), 1.46 (sext d, J = 6.6, 2.8 Hz, 1H, H_6), 0.98 (d, J = 6.9 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 104.1, 96.1, 91.0, 89.5, 84.0, 76.4, 44.0, 38.2, 23.2, 16.6. Triflate carbon was not observed. Analysis calculated for $C_{21}H_{29}F_3O_3RuS$: C, 48.54%; H, 5.63%; found: C, 48.38%; H, 5.74%.



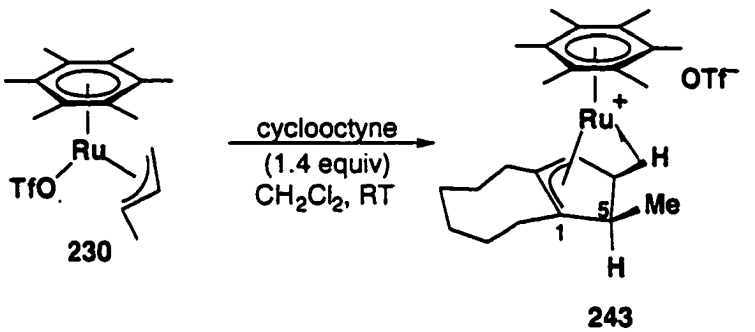
[(η^6-C_6Me_6)Ru(η^3-$C_5H_4MePh_2$)]$^+$OTf$^-$ (234). A solution of (C_6Me_6)Ru(η^3-1-MeC_3H_4)OTf (0.040 g, 0.113 mmol) in 5 mL acetone was placed in a small Schlenk flask equipped with a stir-bar and a septum. Diphenylacetylene (0.024 g, 0.136 mmol, 1.20 equiv) was then added and the reaction stirred at room temperature for 30 minutes. The solvent was subsequently removed under low pressure, leaving a light orange solid. Analytically pure orange crystals (0.068 g, 93%) were obtained by recrystallization in the drybox using anhydrous tetrahydrofuran/diethyl ether. ^{1}H NMR (300 MHz, $CDCl_3$):

δ 7.30-7.23 (m, 6H, H_{Ph}), 7.09-7.04 (m, 2H, H_{Ph}), 6.87-6.84 (m, 2H, H_{Ph}), 5.79 (d, J = 3.2 Hz, 1H, H_2), 3.83 (dq, J = 12.6, 6.4 Hz, 1H, H_{4exo}), 3.65 (d, J = 3.2 Hz, 1H, H_3), 2.12 (s, 18H, C_6Me_6), 0.93 (d, J = 6.4 Hz, 3H, CH_3), –9.45 (d, J = 12.7 Hz, 1H, H_{ag}); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 134.1(s, C_{Ph}), 132.7(s, C_{Ph}), 129.5 (m, C_{Ph}), 128.9 (m, C_{Ph}), 128.4 (m, C_{Ph}), 127.4 (m, C_{Ph}), 100.1 (s, $\underline{C}_6Me_6$), 89.3 (s, C_1), 87.1 (d, $^1J_{CH}$ = 175 Hz, C_2), 66.8 (d, $^1J_{CH}$ = 170 Hz, C_3), 64.5 (d, $^1J_{CH}$ = 133 Hz, C_4), 41.2 (d, $^1J_{CH}$ = 78 Hz, C_5), 16.6 (d, $^1J_{CH}$ = 128 Hz, CH_3), 16.4 (d, $^1J_{CH}$ = 129 Hz, $C_6\underline{Me}_6$). Triflate carbon was not observed. Analysis calculated for $C_{31}H_{35}F_3O_3RuS$: C, 57.66%; H, 5.46%; found: C, 57.35%; H, 5.41%.



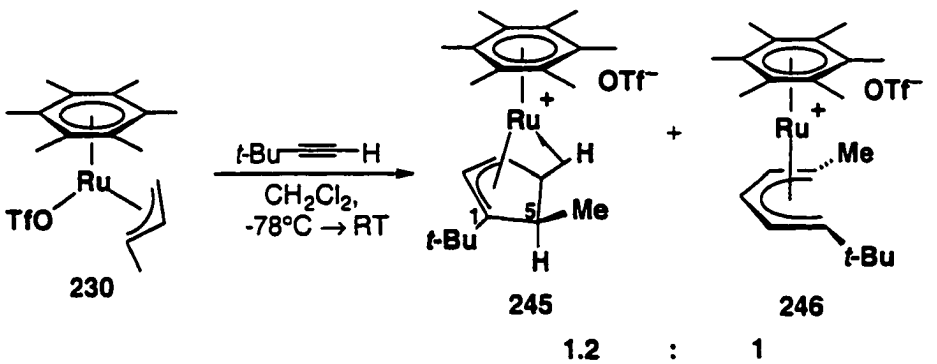
[(η^6-C_6Me_6)Ru(η^3-$C_5H_4Me_3$)]$^+$OTf$^-$ (242). A solution of (C_6Me_6)Ru(η^3-1-MeC_3H_4)OTf (0.030 g, 0.064 mmol) in 3 mL acetone was cooled to 0 °C using an ice bath. 2-Butyne (0.060 mL, 0.77 mmol, 12.0 equiv) was then added via microliter syringe and the cold solution stirred for another hour. The solvent was subsequently removed under reduced pressure, leaving a yellow solid. Dissolving this residue in a minimum of acetone and adding diethyl ether precipitated the product as a yellow powder (0.029 g, 87%); an attempt at a slower recrystallization resulted in a mixture of the agostic complex **242** and cyclopentadienyl products. ^1H NMR (400 MHz, CD_2Cl_2): δ 5.19 (d, J = 3.1 Hz, 1H, H_3),

3.34 (dqd, J = 12.5, 6.4, 2.8 Hz, 1H, H_5), 2.24 (s, 18H, C_6Me_6), 2.20 (dt, J = 11.9, 2.9 Hz, 1H, H_{4exo}), 1.98 (s, 3H, CH_3), 1.10 (d, J = 1.8 Hz, 3H, CH_3), 0.98 (d, J = 6.2 Hz, 3H, CH_3), −11.11 (td, J = 12.4, 1.5 Hz, 1H, H_{ag}); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 121.4 (q, J = 318 Hz, $O_3S\underline{C}F_3$), 99.6 (s, $\underline{C}_6Me_6$), 97.8 (s, C_2), 79.4 (d, J = 182 Hz, C_3), 60.3 (d, J = 135 Hz, C_5), 58.2 (s, C_1), 36.3 (coupling not observed above baseline), 17.0 (q, J = 126 Hz, CH_3), 16.9 (q, J = 129 Hz, $C_6\underline{Me}_6$), 13.0 (q, J = 128 Hz, CH_3), 10.9 (q, J = 128 Hz, CH_3).



[(η^6-C_6Me_6)Ru(η^3-$C_5H_4(CH_2)_6$)]$^+$OTf$^-$ (243). A solution of (η^6-C_6Me_6)Ru(η^3-MeC_3H_4)OTf (0.030 g, 0.064 mmol) in 5 mL acetone was prepared in a small Schlenk flask equipped with a rubber septum and placed under a nitrogen atmosphere. Freshly distilled cyclooctyne (0.012 mL, 0.090 mmol, 1.4 equiv) was introduced via microliter syringe. The reaction mixture was allowed to stir at room temperature for 30 minutes before removing the solvent *in vacuo*, leaving an oily yellow residue. This residue was rinsed with several small portions of diethyl ether then dried thoroughly to yield 0.028 g (78%) of yellow foam. ^1H NMR (300 MHz, $CDCl_3$): δ 5.41 (d, J = 3.1 Hz, 1H, H_3), 3.48 (dqd, J = 12.5, 6.2, 2.8 Hz, 1H, H_5), 2.51 (ddd, J = 15.2, 3.6, 2.5 Hz, 1H, H_{4exo}), 2.24 (s,

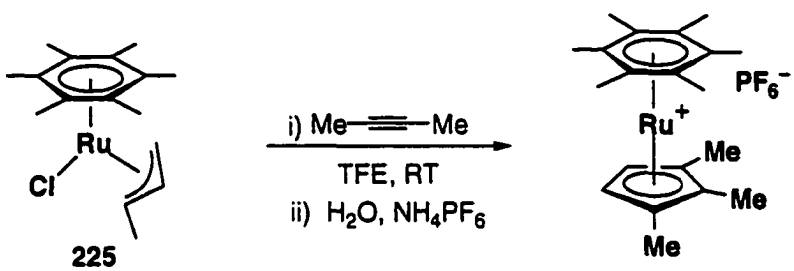
18H, C_6Me_6), 2.15-2.08 (m, 1H, cyclooctyl ring), 2.03-1.91(m, 1H, cyclooctyl ring), 1.87-1.62 (m, 4H, cyclooctyl ring), 1.50-1.30 (m, 5H, cyclooctyl ring), 1.28-1.15 (m, 1H, cyclooctyl ring), 0.98 (d, J = 6.2 Hz, 3H, CH_3), –11.12 (dd, J = 15.7, 13.1 Hz, 1H, H_{ag}); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 104.9, 99.1, 74.7, 69.1, 55.9, 32.5, 26.6, 26.2, 25.7, 25.4, 24.7, 23.3, 16.8, 16.6. Triflate carbon was not observed.



Reaction of $(C_6Me_6)Ru(\eta^3\text{-}1\text{-}MeC_3H_4)OTf$ (230) with 3,3-dimethyl-1-butyne. A solution of $(C_6Me_6)Ru(\eta^3\text{-}1\text{-}MeC_3H_4)OTf$ (0.020 g, 0.043 mmol) in 5 mL acetone was placed in a small Schlenk flask equipped with a stir-bar and a septum. The reaction was then cooled to –78°C using a dry ice/acetone bath and 3,3-dimethyl-1-butyne (0.021 mL, 0.171 mmol, 3.97 equiv) added via microliter syringe and the reaction stirred at –78°C for one hour. The cold bath was then removed and the reaction allowed to quickly warm to room temperature, then stirred for a further hour. The solvent was subsequently removed under reduced pressure, leaving a yellow solid. Subsequent ^1H NMR spectroscopic analysis of the crude residue revealed a mixture of the agostic complex **245** and the acyclic η^5-pentadienyl complex **246**, in a ratio of 1.2 : 1, respectively.

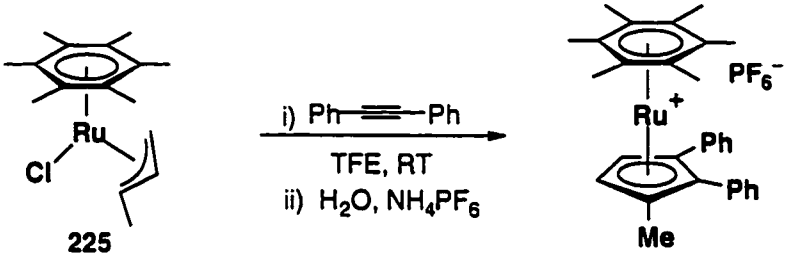
[(η^6-C_6Me_6)Ru(η^3-1-*t*-butyl-5-methylcyclopentenyl)]$^+$OTf$^-$ (245). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.90 (d, J = 3.1 Hz, 1H, H_2), 3.36 (dqd, J = 12.6, 6.5, 2.8 Hz, 1H, H_5), 3.04 (dd, J = 3.1, 1.6 Hz, 1H, H_3), 2.24 (s, 18H, C_6Me_6), 1.63 (ddd, J = 19.7, 2.9, 1.6 Hz, 1H, H_{4exo}), 1.30 (s, 9H, *t*-butyl), 1.06 (d, J = 6.5 Hz, 3H, CH_3), −11.20 (dd, J = 19.8, 12.6 Hz, 1H, H_{ag}).

[(η^6-C_6Me_6)Ru(η^5-1-*t*-butyl-5-methylpentadienyl)]$^+$OTf$^-$ (246). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.90 (t, J = 6.4 Hz, 1H, H_3), 4.66 (dd, J = 9.9, 6.5 Hz, 1H, H_4), 3.89 (dd, J = 9.5, 6.5 Hz, 1H, H_2), 3.14 (d, J = 9.5 Hz, 1H, H_1), 2.65 (dq, J = 9.9, 6.4 Hz, 1H, H_3), 2.30 (s, 18H, C_6Me_6), 1.53 (d, J = 6.4 Hz, 3H, CH_3), 0.87 (s, 9H, *t*-butyl).



[(C_6Me_6)Ru(η^5-$C_5H_2Me_3$)]$^+$$PF_6^-$. A small Schlenk flask equipped with a stir-bar and a septum was charged with (C_6Me_6)Ru(η^3-1-MeC_3H_4)Cl (0.030 g, 0.085 mmol) and 2.0 mL trifluoroethanol added to form an orange solution. 2-Butyne (0.020 mL, mmol, 3.01 equiv) was then added via microliter syringe. After stirring for 4 hours the solvent was removed *in vacuo*, leaving an oily yellow residue. This residue was dried under vacuum for several hours before the crude product was extracted into 5 mL warm distilled water, and the aqueous solution filtered through Celite. Excess NH_4PF_6 (0.100 g, 0.61 mmol, 6.1 equiv) was then added to the yellow filtrate and the precipitate collected and dried

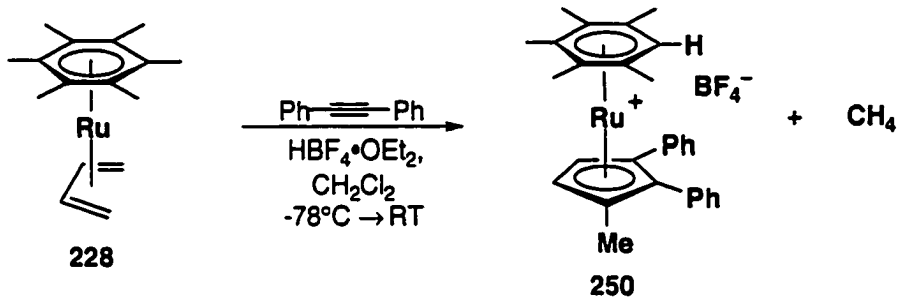
thoroughly, giving 0.031 g (71%) of white powder. Recrystallization from dichloromethane/diethyl ether yields analytically pure white crystals. ^{1}H NMR (300 MHz, acetone-d_6): δ 4.83 (s, 2H, $C_5\underline{H}_2Me_3$), 2.30 (s, 18H, C_6Me_6), 1.80 (s, 6H, $C_5H_2\underline{Me}_3$), 1.73 (s, 3H, $C_5H_2\underline{Me}_3$); ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 99.7, 95.6, 93.8, 81.4, 16.3, 10.6, 8.2. Analysis calculated for $C_{20}H_{29}F_6PRu$: C, 46.60%; H, 5.67%; found: C, 47.01%; H, 5.54%.



225 236

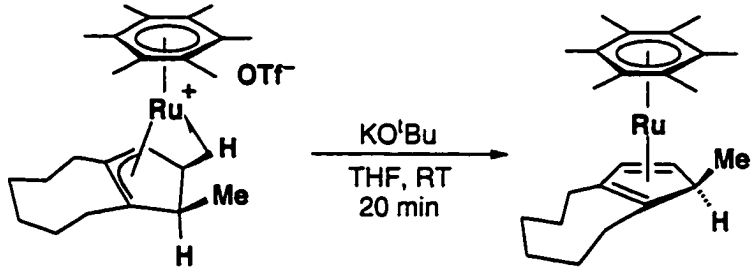
[(C_6Me_6)Ru(η^5-$C_5H_2MePh_2$)]$^+PF_6^-$ (236). A small Schlenk flask equipped with stir-bar and a septum was charged with (C_6Me_6)Ru(η^3-1-MeC_3H_4)Cl (0.030 g, 0.085 mmol) and diphenylacetylene (0.017 g, 0.095 mmol, 1.12 equiv) and 2.5 mL trifluoroethanol added to form an orange solution. After stirring for 4 hours the solvent was removed *in vacuo*, leaving an oily yellow residue. This residue was dried under vacuum for several hours before the crude product was extracted into 5 mL warm distilled water, then the aqueous solution filtered through Celite. Excess NH_4PF_6 (0.100 g, 0.61 mmol, 6.1 equiv) was then added to the yellow filtrate and the precipitate collected and dried thoroughly, giving 0.036 g (66%) of white powder. Recrystallization from dichloromethane/diethyl ether yields analytically pure white crystals. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.43-7.39 (m, 6H, H_{Ph}), 7.32-7.24 (m, 6H, H_{Ph}), 7.10-7.04 (m, 4H, H_{Ph}), 7.01-6.97 (m, 4H, H_{Ph}), 5.15

(d, J = 2.6 Hz, 1H, $C_5\underline{H}_2MePh_2$), 4.89 (d, J = 2.5 Hz, 1H, $C_5\underline{H}_2MePh_2$), 2.14 (s, 18H, C_6Me_6), 1.81 (s, 3H, $C_5H_2\underline{Me}Ph_2$); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 130.7, 130.6, 129.2, 129.3, 128.6, 100.1, 99.5, 97.5, 96.2, 82.3, 79.3, 16.7, 11.5. Analysis calculated for $C_{30}H_{33}F_6PRu$: C, 56.33%; H, 5.20%; found: C, 55.98%; H, 5.18%.



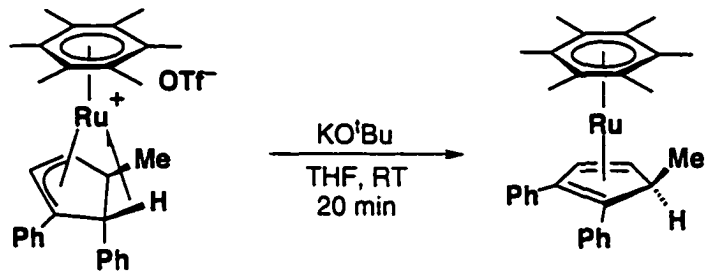
[(η^6-C_6Me_5H)Ru(η^5-$C_5H_2MePh_2$)]$^+PF_6^-$ (250). In the drybox a small Schlenk flask equipped with a stir-bar and a septum was charged with (C_6Me_6)Ru(η^4-butadiene) (0.020, 0.063 mmol) and diphenylacetylene (0.015 g, 0.084 mmol, 1.3 equiv), and the sealed flask removed to the Schlenk line. Dichloromethane (2 mL) was added by syringe, followed by tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) (0.013 mL, 0.075 mmol, 1.2 equiv) via microliter syringe. The reaction mixture was stirred at room temperature for 3 hours before the solvent was removed under reduced pressure. The residue was then dissolved in approximately 5 mL warm distilled water and the yellow aqueous solution filtered through Celite. Excess NH_4PF_6 (0.100 g, 0.61 mmol, 9.7 equiv) was added to precipitate the product, which was collected and dried under vacuum to yield 0.016 g (41%) of white powder. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.43-7.40 (m, 6H, H_{Ph}), 7.32-7.23 (m, 6H, H_{Ph}), 7.20-7.13 (m, 4H, H_{Ph}), 7.03-6.96 (m, 4H, H_{Ph}), 5.88 (s, 1H, $C_6Me_5\underline{H}$) 5.24 (d, J = 2.6 Hz, 1H, $C_5\underline{H}_2MePh_2$), 4.98 (d, J = 2.6 Hz, 1H,

$C_5H_2C_5H_2MePh_2$), 2.23 (s, 3H, C_6Me_5H), 2.17 (s, 3H, C_6Me_5H), 2.13 (s, 3H, C_6Me_5H), 2.00 (s, 3H, C_6Me_5H), 1.95 (s, 3H, C_6Me_5H), 1.83 (s, 3H, $C_5H_2MePh_2$).



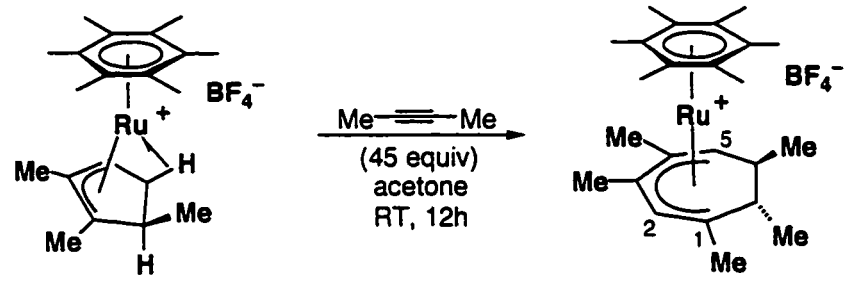
243 254

(η^6-C_6Me_6)Ru(η^4-$C_5H_3(CH_2)_6$) (254). In the drybox a solution of [(η^6-C_6Me_6)Ru(η^3-$C_5H_4Me(CH_2)_6$)]$^+$OTf$^-$ (0.025 g, 0.043 mmol) in 5 mL of tetrahydrofuran was placed in a small Schlenk flask, potassium *t*-butoxide (0.015 g, 0.134 mmol, 3.1 equiv) was added and the reaction stirred at room temperature for 20 minutes. The resulting brown solution was evaporated under reduced pressure, then the residue triturated with several portions of diethyl ether. The combined ether extracts were filtered through Celite and the yellow filtrate concentrated to an oily solid. After thorough drying *in vacuo* the crude product was dissolved in pentane and filtered through a plug of alumina (5% H_2O). The filtrate was then evaporated under reduced pressure to give 0.015 g (82%) of a yellow foam. ^{1}H NMR (400 MHz, C_6D_6): δ 4.19 (d, J = 2.6 Hz, 1H, H_3), 3.77 (q, J = 6.3 Hz, 1H, H_5), 2.24 (dt, J = 13.6, 3.5 Hz, 1H, cyclooctyl ring), 1.94 (s, 18H, C_6Me_6), 1.93 (d, J = 2.9 Hz, 1H, H_4), 1.85-1.23 (series of overlapping multiplets, 11H, cyclooctyl ring), 1.30 (d, J = 6.3 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 91.6, 91.5, 73.5, 54.2, 52.2, 46.4, 33.7, 29.5, 26.8, 26.7, 25.3, 24.9, 19.2, 17.0.



234 255

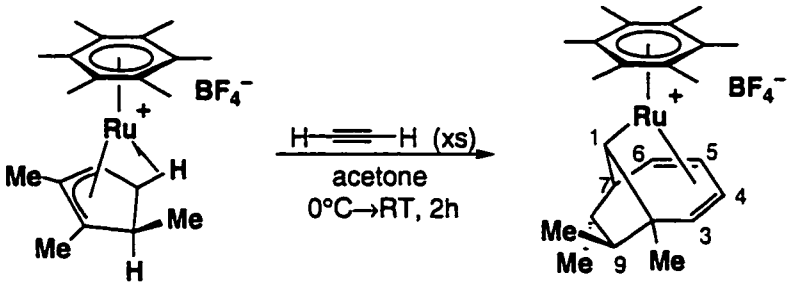
(η^6-C_6Me_6)Ru(η^4-$C_5H_3MePh_2$) (255). In the drybox a solution of [(η^6-C_6Me_6)Ru(η^3-$C_5H_4MePh_2$)]$^+$OTf$^-$ (0.020 g, 0.031 mmol) in 4 mL of tetrahydrofuran was placed in a small Schlenk flask, potassium *t*-butoxide (0.010 g, 0.089 mmol, 2.87 equiv) was added and the reaction stirred at room temperature for 20 minutes. The resulting brown solution was then evaporated under reduced pressure and the residue triturated with several portions of diethyl ether. The combined ether extracts were filtered through Celite and the yellow filtrate concentrated to a solid. After thorough drying *in vacuo* the yellow solid was dissolved in pentane and filtered through a plug of alumina (5% H_2O). The filtrate was then evaporated under low pressure to give 0.012 g (78%) of yellow crystals. ^{1}H NMR (300 MHz, C_6D_6): δ 7.27-6.91 (m, 10H, H_{Ph}), 4.61 (d, J = 2.5 Hz, 1H, H_3), 4.22 (q, J = 6.2 Hz, 1H, H_5), 2.06 (d, J = 2.5 Hz, 1H, H_4), 1.81 (s, 18H, C_6Me_6), 1.42 (d, J = 6.2 Hz, 3H, CH_3).



242 256

[(η^6-C_6Me_6)Ru(η^5-1,3,4,6,7-pentamethylcycloheptadienyl)]$^+PF_6^-$ (256). A solution of (C_6Me_6)Ru(η^3-1-MeC_3H_4)Cl (0.050 g, 0.141 mmol) in 1.5 mL acetone was prepared in a small Schlenk flask, then silver tetrafluoroborate (0.028 g, 0.087 mmol, 1.02 equiv) added. A large excess of 2-butyne (0.50 mL, 6.39 mmol, 45.3 equiv) was added by pipette and the reaction stirred at room temperature for a further 10 hours. Afterwards, the reaction mixture was filtered through Celite to remove the AgCl precipitate and the filtrate evaporated under reduced pressure, leaving a yellow solid. The crude product was purified by chromatography on silica gel, (5% ethanol/dichloromethane), to obtain 0.054 g (74%) of light yellow powder. Analytically pure material was obtained by dissolving the product in a minimum of warm distilled water and adding excess NH_4PF_6 (0.100 g, 0.614 mmol) to precipitate the hexafluorophosphate product, followed by recrystallization from acetone/diethyl ether. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.76 (s, 1H, H_2), 3.43 (d, J = 4.0 Hz, 1H, H_5), 2.16 (s, 18H, C_6Me_6), 2.06 (s, 3H, CH_3), 2.01-1.94 (m, 1H, H_{6exo}), 1.72 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 0.84 (d, J = 6.9 Hz, 3H, CH_3), 0.79 (d, J = 6.7 Hz, 3H, CH_3), 0.47 (dq, J = 13.5, 6.8 Hz, 1H, H_{7endo}); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 103.9, 103.6, 96.4, 93.1, 91.0, 80.7, 55.4, 43.2, 23.8, 22.5, 21.3, 18.8, 17.6, 15.9. Analysis calculated for $C_{24}H_{37}F_6PRu$: C, 50.43%; H, 6.52%; found: C, 50.13%;

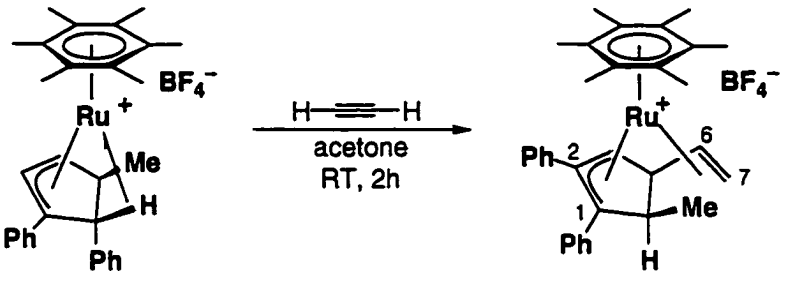
H, 6.44%.



242 259

[(C_6Me_6)Ru((1:3,4,5,6-η)-2,8,9-trimethylbicyclo[4.2.1]nonadienyl)]$^+BF_4^-$ (259). A solution of (C_6Me_6)Ru(η^3-1-MeC_3H_4)Cl (0.050 g, 0.141 mmol) in 4 mL acetone was cooled to 0 °C using an ice bath and silver tetrafluoroborate (0.030 g, 0.154 mmol, 1.09 equiv) added. 2-Butyne (0.100 mL, 1.28 mmol, 9.06 equiv) was then added by microliter syringe and the reaction stirred at 0 °C for 40 minutes. Acetylene was subsequently bubbled through the solution for approximately 3 minutes, turning the reaction mixture black, then the flask was sealed and the reaction stirred at room temperature for a further 2 hours. Afterwards, the reaction mixture was filtered through Celite to remove the AgCl precipitate, then the filtrate was evaporated under reduced pressure, to leave a solid yellow residue. Recrystallization from tetrahydrofuran/diethyl ether results in the formation of 0.053 g (73%) of tan needles. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.09 (dd, J = 8.5, 6.7 Hz, 1H, H_5), 4.89 (t, J = 7.0 Hz, 1H, H_4), 3.51 (d, J = 7.6 Hz, 1H, H_3), 3.34 (td, J = 8.3, 0.6 Hz, 1H, H_6), 2.72 (q, J = 8.0 Hz, 1H, H_7), 2.24 (s, 18H, C_6Me_6), 0.92 (quint., partially obscured, 1H, H_8), 0.90 (s, 3H, CH_3), 0.68 (d, J = 6.7 Hz, 3H, CH_3), 0.61 (br s, 3H, CH_3), 0.63-0.59 (m, obscured, 1H, H_9), –0.20 (d, J = 6.9 Hz, 1H, H_1);

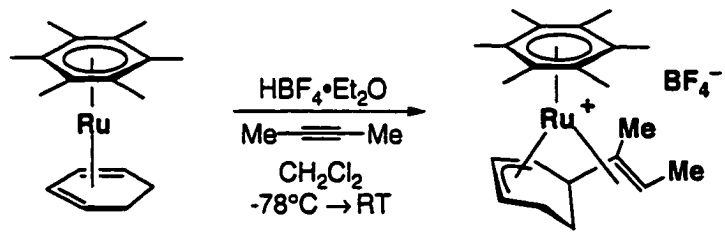
^{1}H-^{1}H GCOSY (300 MHz, $CDCl_3$): (each correlation only listed once) δ 5.09 (H_5) ↔ 4.89, 3.34; δ 4.89 (H_4) ↔ 3.51; δ 3.51 (H_3)↔ –0.20; δ 3.34 (H_6) ↔ 2.72, –0.20; δ 2.72 (H_7) ↔ 0.93, 0.68, –0.20; δ 0.92 (CH_3) ↔ 0.68, 0.61; δ 0.90 (CH_3) ↔ 0.61; ^{13}C NMR (100 MHz, $CDCl_3$): δ 107.8 (s, $\underline{C}_6Me_6$), 97.0 (d, $^1J_{CH}$ = 167 Hz, C_5), 91.9 (d, $^1J_{CH}$ = 169 Hz, C_4), 62.7 (d, $^1J_{CH}$ = 160 Hz, C_3), 55.6 (d, $^1J_{CH}$ = 141 Hz, C_9), 51.3 (d, $^1J_{CH}$ = 148 Hz, C_8), 49.6 (d, $^1J_{CH}$ = 155 Hz, C_6), 48.3 (s, C_2), 48.2 (d, $^1J_{CH}$ = 131 Hz, C_7), 22.2 (q, $^1J_{CH}$ = 126 Hz, CH_3), 16.7 (q, $^1J_{CH}$ = 127 Hz, $C_6\underline{Me}_6$), 14.5 (q, $^1J_{CH}$ = 126 Hz, CH_3), 10.5 (q, $^1J_{CH}$ = 128 Hz, CH_3), –20.1 (d, $^1J_{CH}$ = 150 Hz, C_1); HMQC (300 MHz, CD_2Cl_2): δ 97.0 (C_5) ↔ δ 5.09 (H_5); δ 91.9 (C_4) ↔ δ 4.89 (H_4); δ 62.7 (C_3) ↔ δ 3.51 (H_3); δ 55.6 (C_9) ↔ δ 0.60 (H_9); δ 51.3 (C_8) ↔ δ 0.92 (H_8); δ 49.6 (C_6) ↔ δ 3.34 (H_6); δ 48.2 (C_7) ↔ δ 2.72 (H_7); δ 22.2 (CH_3) ↔ δ 0.90 (CH_3); δ 16.7 (C_6Me_6) ↔ δ 2.24 (C_6Me_6); δ 14.5 (CH_3) ↔ δ 0.61 (CH_3); δ 10.5 (CH_3) ↔ δ 0.68 (CH_3); δ –20.1 (C_1) ↔ δ –0.20 (H_1); HMBC (300 MHz, $CDCl_3$): δ 97.0 (C_5) ↔ δ 4.89 (weak), 3.51, 2.72; δ 91.9 (C_4) ↔ δ 3.34; δ 62.7 (C_3) ↔ δ 5.09, 4.89, 0.90; δ 55.6 (C_9) ↔ δ 3.51 (weak), 2.72, 0.68, 0.61; δ 51.3 (C_8) ↔ δ 0.68, 0.60; δ 49.6 (C_6) ↔ δ 5.09 (weak), 4.98, 2.72, –0.20; δ 48.3 (C_2) ↔ δ 4.89, 3.51, 0.68; δ 48.2 (C_7) ↔ δ 5.09, 3.34, 2.72; δ 22.2 (CH_3) ↔ δ 3.51, –0.20; δ –20.1 (C_1) ↔ δ 3.34, 2.72, 0.90. Analysis calculated for $C_{25}H_{35}F_3O_3RuS$: C, 52.34%; H, 6.15%; found: C, 52.03%; H, 6.04%.



234 265

[(η^6-C_6Me_6)Ru((1,2,3:6,7-η)-1,2-diphenyl-5-methyl-4-vinylcyclopentenyl)]$^+BF_4^-$ (265). A solution of (C_6Me_6)Ru(η^3-1-MeC_3H_4)Cl (0.030 g, 0.085 mmol) and diphenylacetylene (0.016 g, 0.090 mmol, 1.05 equiv) in 3 mL acetone was cooled to 0°C using an ice bath, then a solution of silver tetrafluoroborate (0.017 g, 0.087 mmol, 1.03 equiv) in 2 mL acetone was added by syringe. After stirring for 20 minutes, the cold bath was removed and acetylene was bubbled through the solution for approximately 3 minutes, turning the reaction mixture black. The flask was then sealed and the reaction stirred at room temperature for a further 2 hours. Afterwards the reaction mixture was filtered through Celite to remove the AgCl precipitate, then the filtrate evaporated under reduced pressure to leave a yellow solid as residue. The crude product was then purified by chromatography on silica gel, (5% ethanol/dichloromethane), followed by recrystallization from dichloromethane/diethyl ether to obtain 0.032 g (62 %) of bright yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.37 (m, 4H, H_{Ph}), 7.26-7.24 (m, 3H, H_{Ph}), 7.19-7.06 (m, 3H, H_{Ph}), 4.16 (d, J = 3.8 Hz, 1H, H_3), 3.56 (d, J = 12.6 Hz, 1H, H_{7anti}), 3.53 (q, J = 4.2 Hz, partially overlapping, 1H, H_4), 2.93 (ddd, J = 12.7, 8.3, 4.2 Hz, 1H, H_6), 2.33 (d, J = 8.1 Hz, 1H, H_{7syn}), 1.92 (s, 18H, C_6Me_6), 1.87 (dq, J = 7.4, 4.2 Hz, partially obscured, 1H, H_5), 0.54 (d, J = 7.4 Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz,

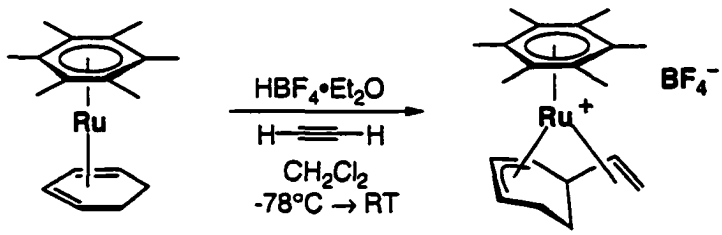
$CDCl_3$): δ 139.2, 132.0, 130.5, 129.3, 128.5, 128.2, 127.8, 106.8, 92.8, 82.7, 48.5, 47.1, 42.0, 36.5, 29.7, 16.2, 12.4. Analysis calculated for $C_{32}H_{34}BF_4Ru$: C, 63.37%; H, 5.65%; found: C, 63.05%; H, 5.70%.



227 267

[(η⁶-C_6Me_6)Ru(1,2,3:7,8-η)-4-dimethylvinylcyclohexenyl)]⁺BF_4^- (267). A pale yellow solution of (C_6Me_6)Ru(η⁴-cyclohexadiene) (0.069 g, 0.201 mmol) in 3 mL dichloromethane was placed in a small Schlenk flask and the reaction cooled to 0 °C using an ice bath. Tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) (0.033 mL, 0.221 mmol, 1.1 equiv) was then added by microliter syringe. The solution immediately turned dark yellow and, after stirring for 5 minutes, 2-butyne (0.16 mL, 10 equiv) was added. The flask was then sealed and the reaction warmed to room temperature. The solution was allowed to warm slowly to room temperature. The solvent was reduced to 5 mL and the product was precipitated by the addition of diethyl ether to afford 0.059 g (60%) of a yellow powder. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 4.05 (m, ddt, $J_{1\text{-}2}$ = 7.1 Hz, $J_{1\text{-}6exo}$ = 4.3 Hz, $J_{1\text{-}3}$ = $J_{1\text{-}5exo}$ = 1.4 Hz, 1H, H_1), 3.96 (q, J = 6.4 Hz, 1H, H_8), 3.74 (dddt, $J_{3\text{-}2}$ = 7.0 Hz, $J_{3\text{-}5exo}$ = 5.6 Hz, $J_{3\text{-}1}$ = 1.4 Hz, $J_{3\text{-}5endo}$ = $J_{3\text{-}4}$ = 0.5 Hz, 1H, H_3), 3.35 (ddd, $J_{2\text{-}1}$ = 7.1 Hz, $J_{2\text{-}3}$ = 6.7 Hz, $J_{2\text{-}6exo}$ = 0.8 Hz, 1H, H_2), 2.45 (ddt, $J_{6exo\text{-}6endo}$ = 14.1 Hz, $J_{6exo\text{-}1}$ = 3.6 Hz, $J_{6exo\text{-}5exo}$ = $J_{6exo\text{-}5endo}$ = 1.7 Hz, 1H, H_{6exo}), 2.13 (s, 18H,

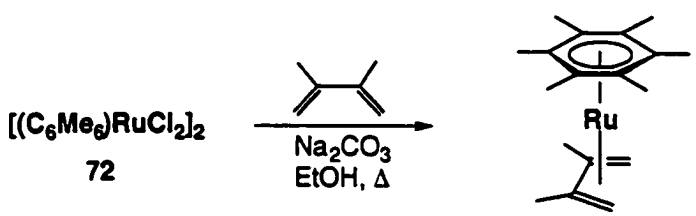
$C_6\underline{Me_6}$), 1.87 (br m, overlap with δ 1.85, 1H, H_4), 1.85 (m, 1H, H_{6endo}), 1.82 (d, J = 6.4 Hz, 3H, Me), 1.69 (s, 3H, Me), 1.03 (m, 1H, H_{5exo}), 0.92 (br d, J= 14.7 Hz, 1H, H_{5endo}); ^{1}H-^{1}H COSY (400 MHz, CD_2Cl_2): δ 4.05 (H_1) ↔ δ 3.74 (H_3), δ 3.35 (H_2), δ 2.45 (H_{6exo}), δ 1.85 (H_{6endo}); δ 3.96 (H_8) ↔ δ 1.82 (Me); δ 3.74 (H_3) ↔ δ 3.35 (H_2), δ 1.03 (H_{5exo}), δ 0.92 (H_{5endo}); δ 2.45 (H_{6exo}) ↔ δ 1.85 (H_{endo}); δ 1.86 (H_4 and H_{6endo}) ↔ δ 1.03 (H_{5exo}), δ 0.92 (H_{5endo}); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 106.5 (s, $\underline{C}_6Me_6$), 100.8 (s, C_7), 81.9 (d, $^1J_{CH}$ = 166 Hz, C_2), 74.0 (d, $^1J_{CH}$ = 154 Hz, C_1), 73.2 (d, $^1J_{CH}$ = 155 Hz, C_8), 66.2 (d, $^1J_{CH}$ = 170 Hz, C_3), 43.6 (d, $^1J_{CH}$ = 130 Hz, C_4), 36.2 (t, $^1J_{CH}$ = 127 Hz, C_6), 23.5 (t, $^1J_{CH}$ = 130 Hz, C_5), 18.0 (q, $^1J_{CH}$ = 125 Hz, Me), 16.7 (q, $^1J_{CH}$ = 129 Hz, $C_6\underline{Me_6}$), 16.69 (q, $^1J_{CH}$ = 129 Hz, Me); HMBC (400 MHz, CD_2Cl_2): δ 81.9 (C_2) ↔ δ 3.35 (H_2); δ 74.0 (C_1) ↔ δ 4.05 (H_1); δ 66.2 (C_3) ↔ δ 3.74 (H_3); δ 43.6 (C_4) ↔ δ 1.87 (H_4); δ 36.2 (C_6) ↔ δ 2.45 (H_{6exo}), δ 1.85 (H_{6endo}); δ 23.5 (C_5) ↔ δ 1.03 (H_{5exo}), 0.92 (H_{5endo}); δ 18.0 (Me) ↔ δ 1.82 (Me); δ 16.70 (C_6Me_6) ↔ δ 2.13 (C_6Me_6); δ 16.69 (Me) ↔ δ 1.69 (Me).



227 268

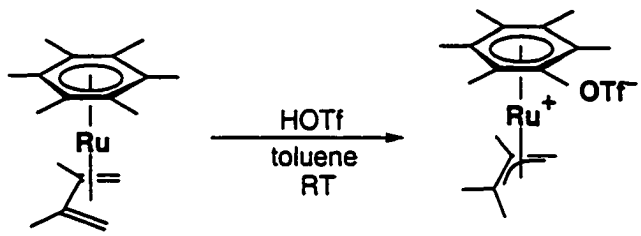
[(η^6-C_6Me_6)Ru(1,2,3:7,8-η)-4-vinylcyclohexenyl)]$^+BF_4^-$ (268). A pale yellow solution of (C_6Me_6)Ru(η^4-cyclohexadiene) (0.030 g, 0.087 mmol) in 3 mL dichloromethane was placed in a small Schlenk flask and the reaction was cooled to 0 °C using an ice bath. Tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) (0.018 mL, 0.104

mmol, 1.19 equiv) was then added by microliter syringe. The solution immediately turned dark yellow and, after stirring for 5 minutes, acetylene was bubbled through the cold reaction mixture for a further 3 minutes. The flask was then sealed and the reaction warmed to room temperature. After 2 hours stirring at room temperature the solvent was removed *in vacuo*, leaving a solid yellow residue. The product was then recrystallized from acetone/diethyl ether to give 0.028 g (70%) of bright yellow needles. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.59-3.48 (m, 3H, H_1, H_2, and H_3), 3.21-3.13 (m, 1H, H_4), 2.87 (ddd, J = 12.7, 9.0, 5.9 Hz, 1H, H_7), 2.55 (d, J = 8.5 Hz, 1H, H_{8syn}), 2.18 (s, 18H, C_6Me_6), 1.87 (d, J = 12.8 Hz, 1H, H_{8anti}), 1.83-1.71 (m, 1H, H_{6a}), 1.21-0.94 (m, 3H, H_{5a}, H_{5b}, and H_{6b}); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 103.4, 81.2, 58.5, 57.0, 42.1, 37.5, 27.2, 23.3, 19.0, 16.0. Analysis calculated for $C_{20}H_{29}BF_4Ru$: C, 52.53%; H, 6.39%; found: C, 52.88%; H, 6.12%.



(η^6-C_6Me_6)Ru(η^4-2,3-dimethylbutadiene) (229). A small Kontes flask was charged with $[(C_6Me_6)RuCl_2]_2$, (0.100 g, 0.299 mmol/Ru), sodium carbonate (0.150 g, 1.42 mmol, 4.73 equiv) and 5 mL anhydrous ethanol. 2,3-Dimethylbutadiene (0.50 mL, 4.42 mmol, 15 equiv) was added and the flask sealed. The flask was placed in an oil bath heated to 85°C; the red suspension gradually faded to a peach coloured solution with white precipitate. After 3 hours the reaction was cooled to room temperature and the solvent

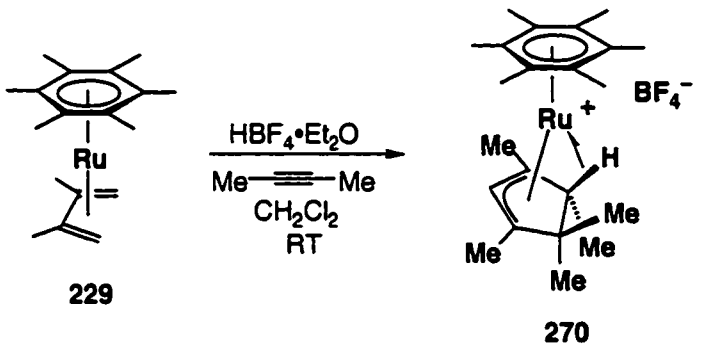
and excess diene removed under vacuum. Once the residue was dried thoroughly, the flask was removed to the drybox and the crude product extracted into 2 x 3 mL diethyl ether. The combined portions were filtered through Celite and the orange filtrate dried to an oily solid. This residue was then dissolved into pentane and the solution filtered through a small plug of alumina (5% H_2O) and concentrated to yield 0.083 g (80%) of air-sensitive, pale yellow crystals. ^1H NMR (300 MHz, C_6D_6): δ 1.96 (s, 18H, C_6Me_6), 1.82 (s, 6H, CH_3), 1.28 (s, 2H, H_{syn}), 0.22 (s, 2H, H_{anti}); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 91.4, 85.3, 38.4, 19.4, 16.8. MS *m/z* calculated for $C_{18}H_{28}{}^{102}Ru(M^+)$: 346.1234; found: 346.1235 (100.00%); calculated for $C_{17}H_{23}{}^{102}Ru(M\text{-}CH_5)$: 329.0843; found: 329.0838 (23.55%).



229 **269**

$[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}1,1,3\text{-}Me_3C_3H_2)]^+OTf^-$ (269). In the drybox a light yellow solution of $(C_6Me_6)Ru(\eta^4$-2,3-dimethylbutadiene) (0.033 g, 0.096 mmol) in 2 mL toluene was placed in a small Schlenk flask equipped with a stir-bar and septum. With rapid stirring of the solution, triflic acid (0.009 mL, 0.102 mmol, 1.06 equiv) was added by microliter syringe, causing the reaction to immediately darken in colour. Within a few minutes a bright yellow precipitate began to form and the reaction was stirred for another 30 minutes at room temperature, before adding 3 mL diethyl ether to the suspension. The

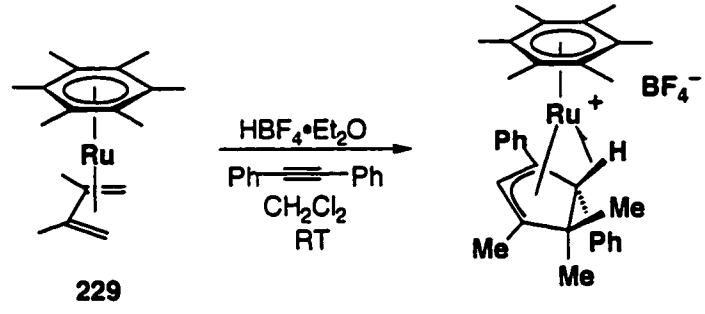
precipitate was then filtered off and rinsed with cold diethyl ether to give 0.029 g (61 %) of a yellow powder. ^{1}H NMR (400 MHz, acetone-d_6): δ 2.66 (s, 2H), 2.32 (s, 18H, C_6Me_6), 2.00 (s, 6H), −1.60 (br s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ 99.7, 91.2, 25.4, 17.7, 16.6. Triflate carbon was not observed.



229 270

[(η^6-C_6Me_6)Ru(η^3-1,3,4,4,5-pentamethylcyclopentenyl)]$^+BF_4^-$ (270). A solution of (C_6Me_6)Ru(η^4-2,3-dimethylbutadiene) (0.025 g, 0.072 mmol) in 3 mL dichloromethane was placed in a small Schlenk flask and the solution stirred vigorously. Tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) (0.013 mL, 0.075 mmol, 1.04 equiv) was added via microliter syringe, causing the reaction to turn dark yellow. After stirring for 20 minutes, 2-butyne (0.100 mL, 1.28 mmol, 17.8 equiv) was added by pipette and the reaction stirred for a further 2 hours. The solvent and excess 2-butyne was then evaporated under reduced pressure, leaving a solid yellow residue. This residue was dissolved in a minimum of acetone and the product precipitated by the addition of diethyl ether, giving 0.022 g (63%) of bright yellow powder. Attempts at a slower recrystallization resulted in some decomposition of the product. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.61 (s, 1H, H_2), 2.22 (s, 18H, C_6Me_6), 2.03 (s, 3H, CH_3), 1.17 (s, 3H, CH_3),

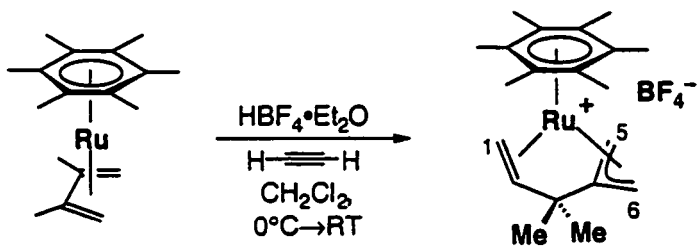
1.05 (d, J = 4.0 Hz, 3H, CH_3), 0.95 (s, 3H, CH_3), 0.57 (s, 3H, CH_3), –11.22 (q, J = 3.9 Hz, 1H, H_{ag}); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 100.2 (s, $\underline{C}_6Me_6$), 86.8 (s, C_3), 86.2 (d, $^1J_{CH}$ = 179 Hz, C_2), 75.4 (s, C_1), 67.5 (s, C_4), 45.4 (d, $^1J_{CH}$ = 65 Hz, C_5), 26.3 (q, $^1J_{CH}$ = 127 Hz, CH_3), 23.2 (q, $^1J_{CH}$ = 126 Hz, CH_3), 16.7 (q, $^1J_{CH}$ = 129 Hz, $C_6\underline{Me}_6$), 14.0 (q, $^1J_{CH}$ = 128 Hz, CH_3), 10.8 (q, $^1J_{CH}$ = 126 Hz, CH_3), 6.9 (q, $^1J_{CH}$ = 129 Hz, CH_3).



229 271

[(C_6Me_6)Ru(η^3-1,5-diphenyl-3,4,4-trimethylcyclopentenyl)]$^+BF_4^-$ (271). A solution of (C_6Me_6)Ru(η^4-2,3-dimethylbutadiene) (0.025 g, 0.072 mmol) and diphenylacetylene (0.015 g, 0.084 mmol, 1.169 equiv) in 3 mL dichloromethane was placed in a small Schlenk flask and the solution stirred vigorously. The addition of tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) (0.013 mL, 0.075 mmol, 1.04 equiv) via microliter syringe turned the reaction dark yellow and the reaction was stirred for a further 3 days at room temperature. The solvent was then removed under reduced pressure, leaving an orange solid. This residue was dissolved in a minimum of acetone and the product precipitated by the addition of diethyl ether, giving 0.033 g (75%) of orange powder. Analytically pure orange crystals were obtained by recrystallization in the drybox using anhydrous tetrahydrofuran/diethyl ether. ^1H NMR (300 MHz, acetone-

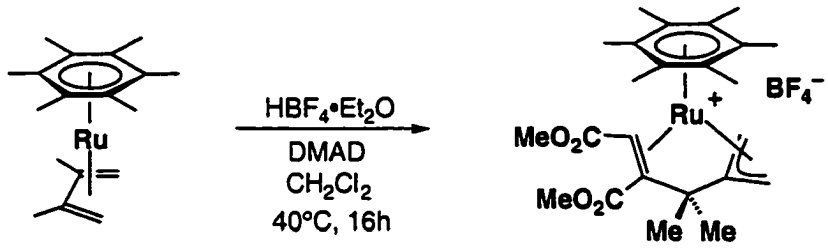
d_6): δ 7.35-7.30 (m, 6H, H_{Ph}), 7.15-7.03 (m, 4H, H_{Ph}), 5.78 (s, 1H, $C_5Me_3Ph_2\underline{H_2}$), 2.14 (s, 18H, C_6Me_6), 1.50 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 0.65 (s, 3H, CH_3), –9.32 (s, 1H, H_{ag}); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 134.5, 130.8, 129.2, 129.1, 128.2, 100.8, 86.4, 85.2, 83.7, 70.1 47.7, 27.9, 23.6, 16.4, 12.0. Analysis calculated for $C_{32}H_{39}BF_4Ru$: C, 62.85%; H, 6.43%; found: C, 63.22%; H, 6.57%.



229 272

[(η^6-C_6Me_6)Ru(η^3:η^2-C_8H_{13})]$^+BF_4^-$ (272). A solution of (C_6Me_6)Ru(η^4-2,3-dimethylbutadiene) (0.020 g, 0.058 mmol) in 3 mL dichloromethane was cooled to 0°C using an ice bath. Upon addition of tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) (0.009 mL, 0.061 mmol, 1.05 equiv) by microliter syringe the solution turned dark yellow; acetylene was then bubbled through the cold solution for 5 min. The cold bath was removed and the reaction warmed to room temperature and stirred for another hour. The solvent was then removed *in vacuo*, leaving a yellow solid that was subsequently recrystallized from dichloromethane/diethyl ether. Bright yellow crystals were collected, giving 0.022 g (83%) of analytically pure product. Slower recrystallization using dichloromethane/diethyl ether resulted in diffractable crystals. ^1H NMR (300 MHz, $CDCl_3$): δ 4.04 (d, J = 3.9 Hz, 1H, H_{6syn}), 2.46 (dd, J = 11.5, 1.6 Hz, 1H, H_{1anti}), 2.34 (dd, J = 11.5, 7.2 Hz, 1H, H_2), 2.28 (dd, J = 3.9, 2.0 Hz, 1H, H_{5syn}), 2.22

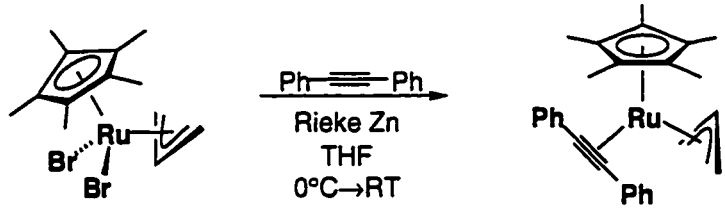
(s, 18H, C_6Me_6), 1.83 (dd, J = 7.3, 1.5 Hz, 1H, H_{1syn}), 1.49 (s, 1H, H_{6anti}), 1.09 (s, 3H, CH_3), 0.76 (s, 3H, CH_3), 0.72 (d, J = 1.9 Hz, 1H, H_{5anti}); ^1H-^1H GCOSY (300 MHz, $CDCl_3$) (each correlation only listed once): δ 4.04 (H_{6syn}) ↔ 2.28, 1.49; δ 2.46 (H_{1anti}) ↔ 2.34, 1.83; δ 2.34 (H_2) ↔ 1.83; δ 2.28 (H_{5syn}) ↔ 0.72; δ 1.49 (H_{6anti}) ↔ 0.72; δ 1.09 (CH_3) ↔ 0.76, 0.72; δ 0.76 (CH_3) ↔ 0.72; ^{13}C NMR (75 MHz, $CDCl_3$): δ 105.7 (s, $\underline{C}_6Me_6$), 92.1 (s, C_4), 59.6 (t, $^1J_{CH}$ = 161 Hz, C_6), 51.5 (t, $^1J_{CH}$ = 157 Hz, C_1), 50.4 (d, $^1J_{CH}$ = 167 Hz, C_2), 47.5 (t, $^1J_{CH}$ = 160 Hz, C_5), 30.9 (s, C_3), 26.3 (q, $^1J_{CH}$ = 127 Hz, CH_3), 25.5 (q, $^1J_{CH}$ = 129 Hz, CH_3), 16.9 (q, $^1J_{CH}$ = 128 Hz, $C_6\underline{Me}_6$); HMQC (300 MHz, $CDCl_3$): δ 59.6 (C_6) ↔ δ 4.04, 1.49 (H_{6syn} and H_{6anti}); δ 51.5 (C_1) ↔ δ 2.46, 1.83 (H_{1syn} and H_{1anti}); δ 50.4 (C_2) ↔ δ 2.34 (H_2); δ 47.5 (C_5) ↔ δ 2.28, 0.72 (H_{5syn} and H_{5anti}); δ 26.3 (CH_3) ↔ δ 1.09 (CH_3); δ 25.5 (CH_3) ↔ δ 0.76 (CH_3); δ 16.9 (C_6Me_6) ↔ δ 2.22 (C_6Me_6); HMBC (300 MHz, $CDCl_3$): δ 92.1 (C_4) ↔ δ 4.04, 1.09, 0.76; δ 59.6 (C_6) ↔ δ 0.72; δ 50.4 (C_2) ↔ δ 1.09, 0.76; δ 47.5 (C_5) ↔ δ 4.04, 1.49; δ 30.9 (C_3) ↔ δ 4.04, 2.46, 2.34, 1.49, 1.09, 0.76, 0.72; δ 26.3 (CH_3) ↔ δ 0.76; δ 25.5 (CH_3) ↔ δ 1.09. Analysis calculated for $C_{32}H_{39}BF_4Ru$: C, 52.30%; H, 6.80%; found: C, 52.28%; H, 6.76%.



229 276

[(η^6-C_6Me_6)Ru(η^3:η^2-$(CO_2Me)_2C_8H_{11}$)]$^+BF_4^-$ (276). A solution of (C_6Me_6)Ru(η^4-2,3-dimethylbutadiene) (0.025 g, 0.072 mmol) in 2 mL dichloromethane and DMAD (0.022 mL, 0.179 mmol, 2.49 equiv) were placed in a small Kontes flask and the solution stirred vigorously. Addition of tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) (0.013 mL, 0.075 mmol, 1.04 equiv) via microliter syringe rapidly turned the reaction dark yellow; the flask was then sealed and placed in an oil bath at 40°C for 16 hours. Afterwards the solvent was removed under reduced pressure, leaving an orange solid. This residue was dissolved in a minimum of acetone and the product precipitated by the addition of diethyl ether to give 0.031 g (75%) of orange powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.56 (d, J = 3.7 Hz, 1H, H_{6syn}), 3.75 (s, 3H, CO_2Me), 3.63 (s, 3H, CO_2Me), 2.79 (s, 1H, H_1), 2.63 (dd, J = 3.6, 2.0 Hz, 1H, H_{5syn}), 2.19 (s, 18H, C_6Me_6), 1.94 (s, 1H, H_{6anti}), 1.36 (d, J = 1.8 Hz, 1H, H_{5anti}), 1.14 (s, 3H, CH_3), 0.91(s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.4, 167.8, 111.5, 101.5, 94.0, 64.0, 53.9, 52.5, 51.9, 43.2, 34.3, 26.1, 23.5, 16.7.

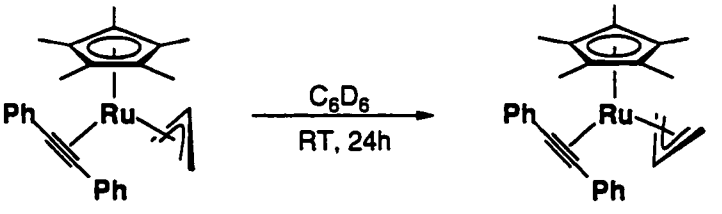
Chapter 5 Experimental



281 **282-*exo***

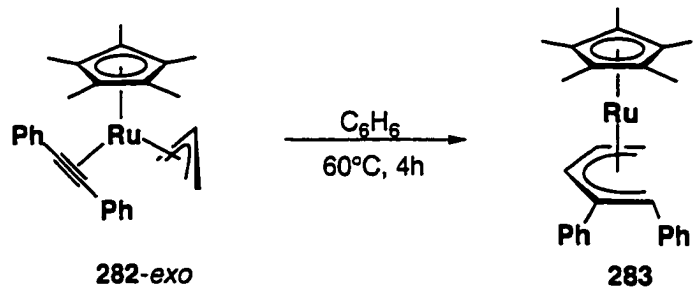
$(C_5Me_5)Ru(\eta^3$-*exo*-$C_3H_5)(\eta^2$-PhC≡CPh) (282-*exo*). In the drybox, a small Schlenk flask equipped with a stir-bar and a septum was charged with $(C_5Me_5)Ru(C_3H_5)Br_2$ (0.200 g, 0.457 mmol), diphenylacetylene (0.090 g, 0.505 mmol, 1.10 equiv) and Rieke Zn (0.300 g, 4.6 mmol, 10 equiv). The sealed flask was removed to the Schlenk line and cooled to 0°C using an ice bath. Cold, distilled tetrahydrofuran (6 mL) was then introduced via cannula and the reaction mixture stirred for two hours at 0°C, then warmed to room temperature for another hour. Then solvent was then removed *in vacuo*, leaving a black residue. This residue was triturated with several portions of pentane (4 x 3 mL) or until the pentane washes became colourless. The combined pentane extracts were then filtered through Celite and the yellow filtrate concentrated to approximately 1 mL before being filtered through a small plug of alumina (5% H_2O). The filtrate was then dried to give a bright orange solid that was further purified by recrystallization from cold pentane, yielding 0.159 g (76%) of orange needles. ^{1}H NMR (300 MHz, C_6D_6): δ 8.01 (dt, J = 8.2, 1.5 Hz, 4H, H_{Ph}), 7.29 (t, J = 8.4 Hz, 4H, H_{Ph}), 7.10 (tt, J = 6.9, 1.5 Hz, 2H, H_{Ph}), 3.12 (tt, J = 9.5, 6.4 Hz, 1H, $H_{central}$), 2.85 (d, J = 6.4 Hz, 2H, H_{syn}), 1.47 (s, 15 H, C_5Me_5), 0.44 (d, J = 9.5 Hz, 2H, H_{anti}); NOE (^{1}H difference spectrum, 400 MHz,

C_6D_6): irradiation of δ 3.12 ($H_{central}$) ↔ enhancement of signals at δ 2.85 (H_{syn}, 8%), δ 1.47 (C_5Me_5, 14%), δ 0.44 (H_{anti}, 4%); irradiation of δ 1.47 (C_5Me_5) ↔ enhancement of signal at δ 3.12 ($H_{central}$, 10%); irradiation of δ 0.44 (H_{anti}) ↔ enhancement of signal at δ 2.85 (H_{syn}, 36%); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 132.5, 132.3, 128.3, 126.3, 98.1, 94.1, 79.6, 44.8, 9.7. Analysis calculated for $C_{27}H_{30}Ru$: C, 71.18%; H, 6.64%; found: C, 70.89%; H, 6.68%.



282-*exo* **282**-*endo*

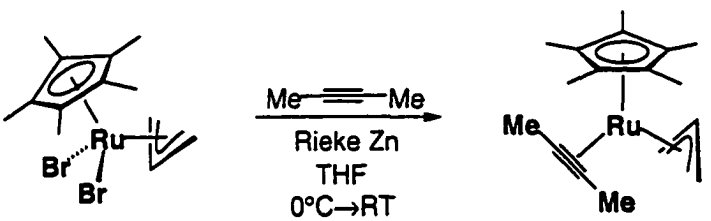
(C_5Me_5)Ru(η^3-*endo*-C_3H_5)(η^2-PhC≡CPh) (282-*endo*). A solution of complex **282**-*exo* (0.020 g, 0.044 mmol) in 0.5 mL benzene-d_6 was placed in a NMR tube and left standing at room temperature for 24 hours. After this time ^1H NMR analysis indicates approximately 30% conversion of **282a** to the *endo*-isomer **282b**. ^1H NMR (300 MHz, C_6D_6): δ 7.89 (dd, J = 7.8, 0.7 Hz, 4H, H_{Ph}), 7.31-7.00 (m, 6H, H_{Ph}), 3.27 (d, J = 6.6 Hz, 2H, H_{syn}), 2.37 (tt, J = 10.5, 6.5 Hz, 1H, $H_{central}$), 1.52 (s, 15 H, C_5Me_5), 1.17 (d, J = 10.4 Hz, 2H, H_{anti}).



282-*exo* 283

(C_5Me_5)Ru(η^5-1,2-diphenylpentadienyl) (283). In the drybox a solution of diphenylacetylene complex **282**-*exo* (0.040 g, 0.088 mmol) in 2 mL benzene was placed in a small Kontes flask and the reaction flask was sealed. The flask was then removed to a 60°C oil bath and the reaction heated for four hours. Afterwards the solvent was evaporated under low pressure, leaving a yellow solid. This residue was dissolved in pentane and filtered through a plug of alumina (5% H_2O), and the filtrate was then concentrated under reduced pressure to yield 0.038 g (95%) of bright yellow crystalline material. Analytically pure material was obtained by recrystallization from cold pentane. ^{1}H NMR (300 MHz, C_6D_6): δ 7.91 (dd, J = 8.3, 1.3 Hz, 2H, H_{Ph}), 7.05-7.40 (m, 3H, H_{Ph}), 6.95 (td, J = 6.1, 1.4 Hz, 2H, H_{Ph}), 6.85 (d, J = 7.4 Hz, 1H, H_{Ph}), 6.74 (dd, J = 8.3, 1.3 Hz, 2H, H_{Ph}), 5.19 (d, J = 5.9 Hz, 1H, H_3), 3.78 (td, J = 8.8, 5.9 Hz, 1H, H_4), 2.46 (dd, J = 8.6, 2.8 Hz, 1H, H_{5syn}), 1.44 (s, 15H, C_5Me_5), 1.31 (dd, J = 9.0, 2.9 Hz, 1H, H_{5anti}), 1.23 (s, 1H, H_1); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 145.2 (s, C_{ipso}), 141.9 (s, C_{ipso}), 131.0 (d, $^1J_{CH}$ = 157 Hz, C_{Ph}), 128.6 (d, $^1J_{CH}$ = 163 Hz, C_{Ph}), 128.2 (d, $^1J_{CH}$ = 161 Hz, C_{Ph}), 127.5 (d, $^1J_{CH}$ = 155 Hz, C_{Ph}), 126.9 (d, $^1J_{CH}$ = 154 Hz, C_{Ph}), 122.5 (d, $^1J_{CH}$ = 160 Hz, C_{Ph}), 98.4 (s, C_2), 94.6 (d, $^1J_{CH}$ = 164 Hz, C_3), 90.7 (s, $\underline{C}_5Me_5$), 82.9 (d, $^1J_{CH}$ = 163 Hz, C_4), 56.4 (d, $^1J_{CH}$ = 156 Hz, C_1), 47.1 (t, $^1J_{CH}$ = 153 Hz, C_5), 9.8 (q, $^1J_{CH}$ = 128 Hz, $C_5\underline{Me}_5$); HMQC (300 MHz, C_6D_6): δ 131.0 (C_{Ph}) ↔ δ 7.22 (H_{Ph}); δ 128.6 (C_{Ph})

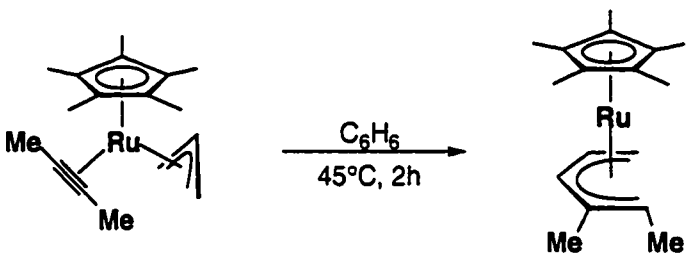
↔ δ 6.74 (H_{Ph}); δ 128.2 (C_{Ph}) ↔ δ 7.91 (H_{Ph}); δ 127.5 (C_{Ph}) ↔ δ 6.95 (H_{Ph}); δ 122.5 (C_{Ph}) ↔ δ 6.85 (H_{Ph}); δ 94.6 (C_3) ↔ δ 5.19 (H_3); δ 82.9 (C_4) ↔ δ 3.78 (H_4); δ 56.4 (C_1) ↔ δ 1.23 (H_1); δ 47.1 (C_5) ↔ δ 2.46, 1.31 (H_{5syn} and H_{5anti}); δ 9.8 ($C_5\underline{Me}_5$) ↔ δ 1.44 ($C_5\underline{Me}_5$). Analysis calculated for $C_{27}H_{30}Ru$: C, 71.18%; H, 6.64%; found: C, 70.76%; H, 6.74%.



281 **284**

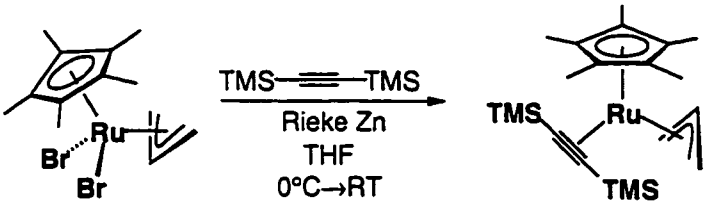
$(C_5Me_5)Ru(\eta^3$-*exo*-$C_3H_5)(\eta^2$-$CH_3C{\equiv}CCH_3)$ (284). In the drybox, a small Schlenk flask equipped with a stir-bar and a septum was charged with $(C_5Me_5)Ru(\eta^3$-$C_3H_5)Br_2$ (0.200 g, 0.457 mmol), and Rieke Zn (0.300 g, 4.6 mmol, 10 equiv). The flask was then removed to the Schlenk line and the flask was cooled to 0°C using an ice bath. A cold solution of 2-butyne (0.20 mL, 2.56 mmol, 5.6 equiv) in 5 mL tetrahydrofuran was then introduced via cannula. The reaction mixture was stirred at 0°C for two hours, then the solvent was removed under reduced pressure, without allowing the reaction mixture to warm to room temperature. The crude product was then extracted from the reaction residue with several portions of pentane (3 x 3 mL) and the pentane fractions filtered through Celite. The yellow filtrate was concentrated and then further filtered through a small plug of alumina (5% H_2O) and dried to yield 0.136 g (90%) of a dark yellow crystalline material. This thermally unstable compound was stored under nitrogen in the freezer to prevent decomposition. ^{1}H NMR (300 MHz, C_6D_6): δ 3.08 (tt, J = 9.0, 6.2 Hz,

1H, $H_{central}$), 2.58 (d, J = 6.2 Hz, 2H, H_{syn}), 2.18 (s, 6H, CH_3), 1.52 (s, 15 H, $C_5\underline{Me_5}$), –0.04 (d, J = 9.0 Hz, 2H, H_{anti}); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 92.5 (C_5Me_5), 77.0 ($C_{central}$), 74.0 (C_{quat}), 43.2 ($C_{terminal}$), 14.2 (CH_3), 9.5 ($C_5\underline{Me_5}$).



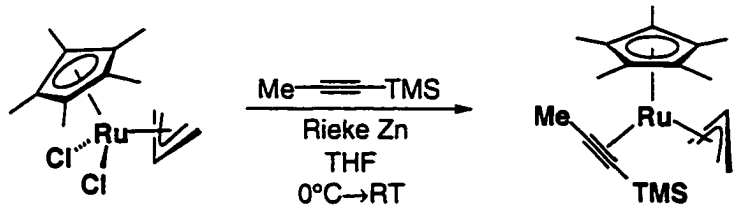
284 **285**

(C_5Me_5)Ru(η^5-1,2-dimethylpentadienyl) (285). In the drybox a solution of 2-butyne complex **284** (0.030 g, 0.091 mmol) in 2 mL benzene was placed in a small Kontes flask and the reaction flask was sealed. The flask was then removed to an oil bath and the reaction stirred at 45°C for a period of two hours. Afterwards the solvent was evaporated under low pressure, leaving a yellow solid. This residue was dissolved in pentane and filtered through a plug of alumina (5% H_2O), and the filtrate was then concentrated under low pressure to yield 0.026 g (87%) of yellow crystalline material. ^1H NMR (300 MHz, C_6D_6): δ 4.71 (d, J = 5.8 Hz, 1H, H_3), 3.74 (td, J = 8.6, 5.8 Hz, 1H, H_4), 2.22 (dd, J = 8.5, 2.6 Hz, 1H, H_{5syn}), 1.73 (s, 3H, CH_3) 1.68 (s, 15H, C_5Me_5), 1.44 (d, J = 6.1 Hz, 3H, CH_3), 0.67 (dd, J = 8.7, 2.6 Hz, 1H, H_{5anti}), 0.24 (q, J = 6.2 Hz, 1H, H_1); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 93.9, 91.4, 89.0, 82.3, 51.4, 45.1, 18.9, 16.7, 10.4.



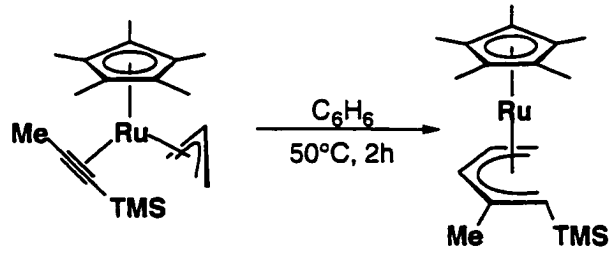
281 286

(C_5Me_5)Ru(η^3-*exo*-C_3H_5)(η^2-TMSC≡CTMS) (286). In the drybox, a small Schlenk flask equipped with a stir-bar and a septum was charged with (C_5Me_5)Ru(η^3-C_3H_5)Br_2 (0.060 g, 0.137 mmol), and Rieke Zn (0.110 g, 1.7 mmol, 12 equiv). The flask was then removed to the Schlenk line and a solution of BTMSA (0.093 mL, 4.1 mmol, 3.0 equiv) in 3 mL tetrahydrofuran was then introduced via cannula. The reaction mixture was stirred at room temperature for 30 min, then the solvent was removed under reduced pressure. The flask was transferred to the drybox, where the crude product was then extracted from the reaction residue with several portions of pentane (3 x 2 mL) and the combined pentane fractions filtered through Celite. The yellow filtrate was concentrated and then further filtered through a small plug of alumina (5% H_2O), then dried to yield 0.045 g (73%) of a dark yellow solid. ^{1}H NMR (400 MHz, C_6D_6): δ 3.00 (tt, J = 9.5, 6.3 Hz, 1H, $H_{central}$), 2.60 (d, J = 6.3 Hz, 2H, H_{syn}), 1.48 (s, 15H, C_5Me_5), 0.32 (s, 18H, TMS), –0.73 (d, J = 9.5 Hz, 2H, H_{anti}); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 111.7, 92.0, 79.3, 44.0, 9.7, 2.8.



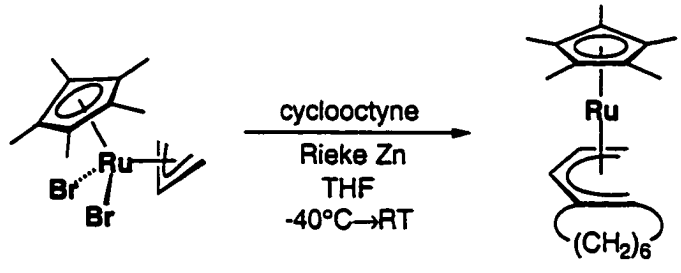
281 287

$(C_5Me_5)Ru(\eta^3\text{-}exo\text{-}C_3H_5)(\eta^2\text{-}CH_3C{\equiv}CTMS)$ (287). In the drybox a small Schlenk flask equipped with a stir-bar and a septum was charged with $(C_5Me_5)Ru(\eta^3\text{-}C_3H_5)Cl_2$ (0.055 g, 0.158 mmol) and Rieke Zn (0.150 g, 2.3 mmol, 14.5 equiv). The sealed flask was then removed to the Schlenk line and the flask was cooled to 0°C using an ice bath. A cold solution of 1-(trimethylsilyl)propyne (0.090 mL, 0.061 mmol, 3.8 equiv) in 4 mL tetrahydrofuran was then introduced via cannula. The reaction mixture was stirred at 0°C for one hour, then the solvent was removed under reduced pressure. The flask was transferred to the drybox, where the crude product was extracted from the reaction residue with several portions of pentane (3 x 2 mL). The combined pentane fractions were then filtered through Celite. The yellow filtrate was concentrated and filtered through a small plug of alumina (5% H_2O), then dried to yield 0.056 g (92%) of a dark yellow foam. ^1H NMR (300 MHz, C_6D_6): δ 3.00 (tt, J = 9.2, 6.2 Hz, 1H, $H_{central}$), 2.66 (dd, J = 6.1, 2.0 Hz, 1H, H_{syn}), 2.47 (dd, J = 6.2, 2.1 Hz, 1H, H_{syn}), 2.35 (s, 3H, CH_3), 1.49 (s, 15H, C_5Me_5), 0.31 (s, 9H, $SiMe_3$), 0.18 (d, J = 9.3 Hz, 1H, H_{anti}), –0.29 (d, J = 9.2 Hz, 1H, H_{anti}); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 92.3, 89.0, 78.1, 70.3, 45.0, 42.5, 9.6, 2.6. MS *m/z* calculated for $C_{19}H_{32}{}^{102}RuSi$ (M^+): 390.1234; found: 390.1265 (24.17%); calculated for $C_{13}H_{20}{}^{102}Ru$ (M-$C_6H_{12}Si$): 278.0609; found: 278.0599 (100.00%); calculated for $C_{10}H_{14}{}^{102}Ru$ (M-$C_8H_{14}Si$): 236.0139; found: 236.0137 (41.80%).



287 288

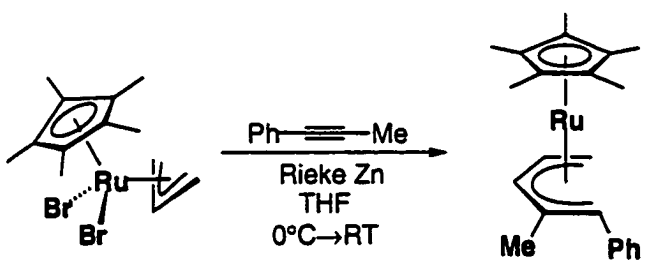
(C_5Me_5)Ru(η^5-1-trimethylsilyl-2-methylpentadienyl) (288). In the drybox a solution of 1-(trimethylsilyl)propyne complex **287** (0.030 g, 0.077 mmol) in 2 mL benzene was placed in a small Kontes flask and the reaction flask was sealed. The flask was then placed in an oil bath and the solution warmed to 50°C for a period of two hours. Afterwards the solvent was evaporated under low pressure, leaving a yellow solid. This residue was dissolved in pentane and filtered through a plug of alumina (5% H_2O), and the filtrate was then concentrated under low pressure to yield 0.025 g (83%) of yellow crystalline material. ^{1}H NMR (300 MHz, C_6D_6): δ 4.61 (d, J = 6.1 Hz, 1H, H_3), 3.62 (td, J = 8.9, 6.1 Hz, 1H, H_4), 2.25 (dd, J = 8.8, 2.9 Hz, 1H, H_{5syn}), 1.85 (s, 3H, CH_3), 1.67 (s, 15H, C_5Me_5), 1.12 (dd, J = 8.9, 3.0 Hz, 1H, H_{5anti}), 0.26 (s, 9H, TMS), −1.27 (s, 1H, H_1).



281 289

(C_5Me_5)Ru(η^5-1,2-(cyclooctyl)pentadienyl) (289). In the drybox, a small Schlenk flask equipped with a stir-bar and a septum was charged with (C_5Me_5)Ru(η^3-C_3H_5)Br_2 (0.025 g, 0.057 mmol) and Rieke Zn (0.050 g, 0.76 mmol, 13 equiv)). The sealed flask was

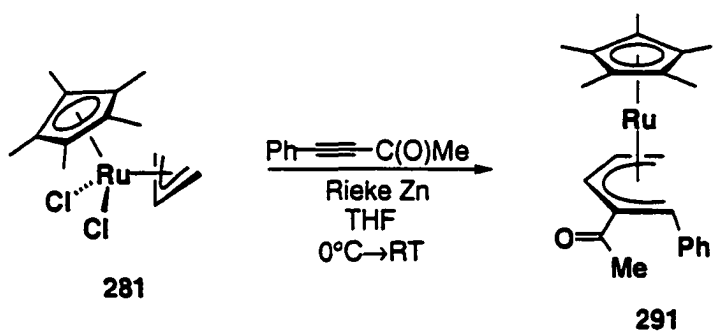
then removed to the Schlenk line and the flask was cooled to -40°C using a cold bath of dry ice/acetonitrile. A cold solution of cyclooctyne (0.046 mL, 0.340 mmol, 6.0 equiv) in 4 mL tetrahydrofuran was then introduced via cannula. The reaction mixture was stirred at -40°C for four hours, then the cold bath was removed and the reaction warmed to room temperature for approximately 20 minutes. Afterwards the solvent was removed under reduced pressure. The crude product was then extracted from the reaction residue with several portions of pentane (3 x 2 mL) and the combined pentane fractions filtered through Celite. The yellow filtrate was concentrated and then further filtered through a small plug of alumina (5% H_2O), then dried to yield 0.017 g (77%) of a yellow powder. ^{1}H NMR (300 MHz, C_6D_6): δ 4.59 (d, J = 6.0 Hz, 1H, H_3), 3.77 (td, J = 8.7, 5.9 Hz, 1H, H_4), 2.25 (dd, J = 8.6, 2.6 Hz, 1H, H_{5syn}), 2.20-2.11 (m, 4H, cyclooctyl ring), 1.79-1.20 (m, 8H, cyclooctyl ring), 1.70 (s, 15H, C_5Me_5), 0.76 (dd, J = 8.6, 2.6 Hz, 1H, H_{5anti}), 0.12 (dd, J = 11.0, 3.7 Hz, 1H, H_1).



281 290

(C_5Me_5)Ru(η^5-1-phenyl-2-methylpentadienyl) (290). In the drybox, a small Schlenk flask equipped with a stir-bar and a septum was charged with (C_5Me_5)Ru(η^3-C_3H_5)Br_2 (0.086 g, 0.197 mmol) and Rieke Zn (0.110 g, 1.7 mmol, 8.5 equiv). The flask was then removed to the Schlenk line and cooled to 0°C using an ice bath. A cold solution of 1-

phenyl-propyne (0.030 mL, 0.28 mmol, 1.4 equiv) in 3 mL tetrahydrofuran was then introduced via cannula. The reaction mixture was stirred at 0°C for one hour, then the solvent was removed under reduced pressure, without allowing the reaction mixture to warm to room temperature. The crude product was then extracted from the reaction residue with several portions of pentane (3 x 2 mL) and the combined pentane fractions filtered through Celite. The yellow filtrate was concentrated and further filtered through a small plug of alumina (5% H_2O), then dried to yield 0.066 g (85%) of a thick yellow oil. ^{1}H NMR (300 MHz, C_6D_6): δ 7.30-6.95 (m, 5H, H_{Ph}), 4.74 (d, J = 6.0 Hz, 1H, H_3), 3.72 (td, J = 9.0, 5.9 Hz, 1H, H_4), 2.39 (dd, J = 8.8, 2.8 Hz, 1H, H_{5syn}), 1.48 (s, 15H, C_5Me_5), 1.25 (dd, J = 9.0, 2.7 Hz, 1H, H_{5anti}), 0.99 (s, 1H, H_1).

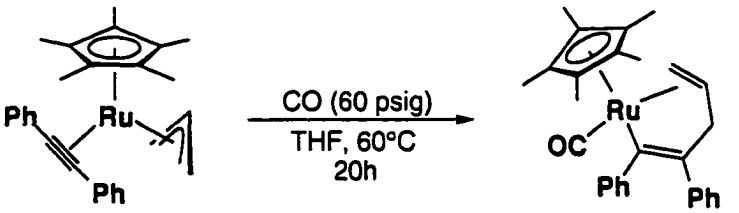


281 291

(C_5Me_5)Ru(η^5-2-acetyl-1-phenylpentadienyl) (291). In the drybox a small Schlenk flask equipped with a stir-bar and a septum was charged with (C_5Me_5)Ru(η^3-C_3H_5)Cl_2 (0.060 g, 0.172 mmol), and Rieke Zn (0.110 g, 1.7 mmol, 9.8 equiv)). The flask was then removed to the Schlenk line and cooled to 0°C using an ice bath. A cold solution of 4-phenyl-3-butyn-2-one (0.120 mL, 0.824 mmol, 4.8 equiv) in 3 mL tetrahydrofuran was then introduced via cannula. The reaction mixture was stirred at 0°C for one hour, then the reaction was warmed to room temperature before evaporating the solvent under

reduced pressure. The crude product was extracted from the reaction residue with several portions of pentane (3 x 2 mL) and the combined pentane fractions were filtered through Celite. The yellow filtrate was concentrated and further filtered through a small plug of alumina (5% H_2O), then dried under vacuum to yield 0.068 g (94%) of a yellow solid. ^1H NMR (400 MHz, C_6D_6): δ 7.16-7.12 (m, obscured, 1H, H_{Ph}), 7.09-7.05 (m, 2H, H_{Ph}), 6.95-6.90 (m, 2H, H_{Ph}), 5.11 (d, J = 5.8 Hz, 1H, H_3), 3.74 (td, J = 8.7, 5.8 Hz, 1H, H_4), 2.43 (dd, J = 8.7, 3.0 Hz, 1H, H_{5syn}), 2.18 (s, 3H, CH_3), 1.49 (s, 15H, $C_5\underline{Me_5}$), 1.11 (dd, J = 8.7, 3.0 Hz, 1H, H_{5anti}), 1.05 (s, 1H, H_1); ^{13}C NMR (75 MHz, C_6D_6): δ 206.5 (s, $\underline{C}(O)CH_3$), 145.3 (s, C_{ipso}), 130.4 (d, $^1J_{CH}$ = 154 Hz, C_{Ph}), 128.7 (d, $^1J_{CH}$ = 152 Hz, C_{Ph}), 128.4 (d, $^1J_{CH}$ = 163 Hz, C_{Ph}), 127.3 (d, $^1J_{CH}$ = 162 Hz, C_{Ph}), 123.4 (d, $^1J_{CH}$ = 159 Hz, C_{Ph}), 100.0 (s, C_2), 92.4 (d, $^1J_{CH}$ = 163 Hz, C_3), 91.4 (s, $\underline{C_5}Me_5$), 83.5 (d, $^1J_{CH}$ = 160 Hz, C_4), 53.7 (d, $^1J_{CH}$ = 161 Hz, C_1), 46.8 (t, $^1J_{CH}$ = 158 Hz, C_5), 31.5 (q, $^1J_{CH}$ = 128 Hz, $C(O)\underline{C}H_3$), 9.6 (q, $^1J_{CH}$ = 125 Hz, $C_5\underline{Me_5}$); HMQC (300 MHz, C_6D_6): δ 130.4 (C_{Ph}) ↔ δ 7.14 (H_{Ph}); δ 128.7 (C_{Ph}) ↔ δ 7.07 (H_{Ph}); δ 128.4 (C_{Ph}) ↔ δ 7.07 (H_{Ph}); δ 127.3 (C_{Ph}) ↔ δ 6.93 (H_{Ph}); δ 123.4 (C_{Ph}) ↔ δ 6.93 (H_{Ph}); δ 92.4 (C_3) ↔ δ 5.11 (H_3); δ 83.5 (C_4) ↔ δ 3.74 (H_4); δ 53.7 (C_1) ↔ δ 1.05 (H_1); δ 46.8 (C_5) ↔ δ 2.43, 1.11 (H_{5syn} and H_{5anti}); δ 31.5 ($C(O)\underline{C}H_3$) ↔ δ 2.18 ($C(O)\underline{CH_3}$); δ 9.6 ($C_5\underline{Me_5}$) ↔ δ 1.54 ($C_5\underline{Me_5}$); HMBC (300 MHz, C_6D_6): δ 206.5 ($\underline{C}(O)CH_3$) ↔ δ 5.11 (H_3), 2.18 ($C(O)\underline{CH_3}$), 1.05 (H_1); δ 145.3 (C_{ipso}) ↔ δ 7.07 (H_{Ph}); δ 130.4 (C_{Ph}) ↔ δ 6.93 (H_{Ph}); δ 128.4 (C_{Ph}) ↔ δ 7.07 (H_{Ph}); δ 128.3 (C_{Ph}) ↔ δ 7.14 (H_{Ph}); δ 127.3 (C_{Ph}) ↔ δ 6.93 (H_{Ph}), 1.05 (H_1); δ 123.4 (C_{Ph}) ↔ δ 6.93 (H_{Ph}); δ 100.0 ($\underline{C_5}Me_5$) ↔ δ 5.11 (H_3), 3.74 (H_4); δ 92.4 (C_3) ↔ δ 3.74 (H_4), 2.43 (H_{5syn}), 1.11 (H_{5anti}), 1.05 (H_1); δ 83.5 (C_4) ↔ δ 5.11 (H_3), 2.43 (H_{5syn}); δ 53.7 (C_1) ↔ δ 6.93 (H_{Ph}), 5.11 (H_3); δ 46.8 (C_5) ↔ δ 5.11 (H_3). MS *m/z*

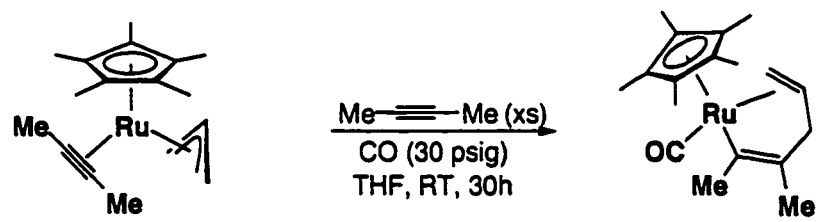
calculated for $C_{23}H_{28}O^{102}Ru$ (M^+): 422.1184; found: 422.1204 (68.83%); calculated for $C_{21}H_{25}{}^{102}Ru$ ($M-C_2H_3O$): 379.1000; found: 379.1002 (100.00%).



282 **294**

(C_5Me_5)Ru((1:4,5-η)-1,2-diphenylpentadienyl)(CO)) (294). A solution of diphenylacetylene complex **282a** (0.132 g, 0.290 mmol) in 4 mL tetrahydrofuran was placed in a Fisher-Porter bottle equipped with a stir-bar and the apparatus flushed three times with carbon monoxide. The Fisher-Porter bottle was pressurized with carbon monoxide to 60 psig, then placed in a hot water bath (60°C) for approximately 20 hours. Afterwards the carbon monoxide pressure was carefully released and the yellow solution evaporated under reduced pressure. The solid residue was dissolved in diethyl ether and filtered through a plug of alumina (5% H_2O) before being concentrated to a yellow crystalline material. Bright yellow crystals (0.113 g, 81%) were obtained after recystallization from diethyl ether/methanol. IR ($CHCl_3$ cast): 1933 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.27 (dd, J = 8.1, 1.2 Hz, 2H, H_{Ph}), 7.13 (dd, J = 9.5, 1.2 Hz, 2H, H_{Ph}), 7.06 (t, J = 7.6 Hz, 2H, H_{Ph}), 6.97 (t, J = 7.6 Hz, 2H, H_{Ph}), 6.92-6.84 (m, 2H, H_{Ph}), 3.88 (dd, J = 16.4, 6.4 Hz, 1H, H_{3a}), 3.61 (dddd, J = 12.0, 8.0, 7.5, 6.2 Hz, 1H, H_4), 3.03 (d, J = 11.7 Hz, 1H, H_{5anti}), 2.59 (d, J = 16.4, 7.3 Hz, 1H, H_{3b}), 2.11 (d, J = 8.0 Hz, 1H, H_{5syn}), 1.22 (s, 15H, C_5Me_5); ^{13}C NMR (75 MHz, C_6D_6): δ 211.0 (s, CO), 152.0 (s, C_1), 151.7 (s, C_2), 151.4 (s, C_{ipso}), 142.4 (s, C_{ipso}), 130.0 (d, $^1J_{CH}$ = 158 Hz, C_{Ph}), 129.2 (d, $^1J_{CH}$

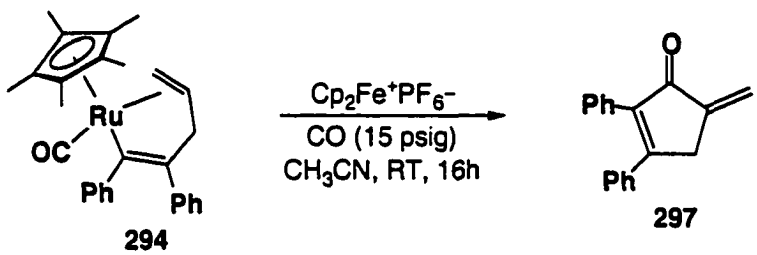
= 147 Hz, C_{Ph}), 128.3 (d, $^1J_{CH}$ = 155 Hz, C_{Ph}), 127.5 (d, $^1J_{CH}$ = 139 Hz, partially obscured, C_{Ph}), 125.0 (d, $^1J_{CH}$ = 160 Hz, C_{Ph}), 123.9 (d, $^1J_{CH}$ = 160 Hz, C_{Ph}), 98.3 (s, $\underline{C}_5Me_5$), 72.7 (d, $^1J_{CH}$ = 152 Hz, C_4), 48.8 (t, $^1J_{CH}$ = 158 Hz, C_5), 47.8 (t, $^1J_{CH}$ = 124 Hz, C_3), 8.9 (q, $^1J_{CH}$ = 127 Hz, $C_5\underline{Me}_5$); ^1H-^{13}C HETCORR (100 MHz, C_6D_6): δ 130.0 (C_{Ph}) ↔ δ 7.13 (H_{Ph}); δ 129.2 (C_{Ph}) ↔ δ 7.27 (H_{Ph}); δ 128.3 (C_{Ph}) ↔ δ 6.97 (H_{Ph}); δ 127.5 (C_{Ph}) ↔ δ 7.06 (H_{Ph}); δ 125.0 (C_{Ph}) ↔ δ 6.88 (H_{Ph}); δ 123.9 (C_{Ph}) ↔ δ 6.88 (H_{Ph}); δ 72.7 (C_4) ↔ δ 3.61 (H_4); δ 48.8 (C_5) ↔ δ 3.03 (H_{5anti}), 2.11 (H_{5syn}); δ 47.8 (C_3) ↔ δ 3.88 (H_{3a}), 2.59 (H_{3b}); δ 8.9 ($C_5\underline{Me}_5$) ↔ δ 1.22 ($C_5\underline{Me}_5$). Analysis calculated for $C_{28}H_{30}ORu$: C, 69.54%; H, 6.25%; found: C, 69.45%; H, 6.30%.



284 **295**

(C_5Me_5)Ru((1:4,5-η)-1,2-dimethylpentadienyl)(CO)) (295). A solution of 2-butyne complex **284** (0.090 g, 0.272 mmol) and 2-butyne (0.064 mL, 0.82 mmol, 3.0 equiv) in 3 mL tetrahydrofuran was placed in the Fisher-Porter bottle and the apparatus flushed three times with carbon monoxide. The Fisher-Porter bottle was pressurized with carbon monoxide to 30 psig, then the reaction was stirred at room temperature for approximately 30 hours. Afterwards, the carbon monoxide pressure was carefully released and the yellow solution evaporated under reduced pressure. The solid residue was dissolved in diethyl ether and filtered through a plug of alumina (5% H_2O) before being concentrated to a yellow crystalline material. Recystallization from diethyl ether/methanol resulted in 0.047 g (48%) of pale yellow crystals. IR ($CHCl_3$ cast): 1938 (s) cm^{-1}. ^1H NMR (300

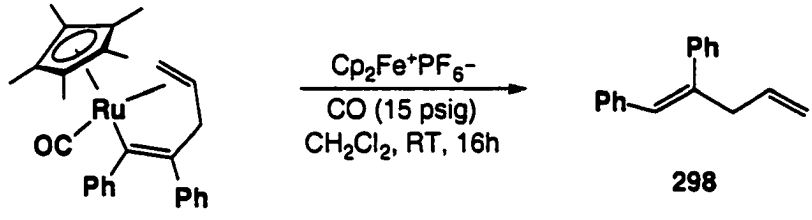
MHz, CD_2Cl_2): δ 3.36 (dddd, J = 12.0, 8.3, 6.7, 6.0 Hz, 1H, H_4), 2.87 (br dd, J = 16.0, 6.7 Hz, 1H, H_{3a}), 2.61 (d, J = 11.9 Hz, 1H, H_{5anti}), 2.15 (d, J = 8.3 Hz, 1H, H_{5syn}), 2.04 (br dd, J = 15.9, 7.5 Hz, 1H, H_{3b}), 1.88 (s, 3H, CH_3), 1.75 (s, 15H, C_5Me_5), 1.53 (s, 3H, CH_3); ^1H-^1H GCOSY (300 MHz, CD_2Cl_2, each correlation only listed once): δ 3.36 (H_4) ↔ 2.87 (H_{3a}), 2.61 (H_{5anti}), 2.15 (H_{5syn}), 2.04 (H_{3b}); δ 2.87 (H_{3a}) ↔ 2.04 (H_{3b}), 1.88 (CH_3), 1.53 (CH_3); δ 2.04 (H_{3b}) ↔ 1.88 (CH_3), 1.53 (CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 211.5, 142.1, 142.0, 98.0, 72.7, 47.5, 46.0, 27.3, 15.8, 9.9. Analysis calculated for $C_{18}H_{26}ORu$: C, 60.14%; H, 7.29%; found: C, 60.34%; H, 7.28%.



One-electron Oxidation of (C_5Me_5)Ru((1:4,5-η)-1,2-diphenylpentadienyl)(CO)) (294) in Acetonitrile. A solution of diphenylacetylene derivative **294** (0.040 g, 0.083 mmol) in 4 mL acetonitrile was placed in a Fisher-Porter bottle equipped with a stir-bar and $Cp_2Fe^+PF_6^-$ (0.032 g, 0.097 mmol, 1.16 equiv) was then added. The apparatus was flushed twice with carbon monoxide before a carbon monoxide pressure of 15 psig was established. The reaction was then stirred at room temperature for 16 hours before venting the carbon monoxide pressure. Excess zinc dust (0.050 g) was then added to the reaction mixture (to reduce any remaining $Cp_2Fe^+PF_6^-$) and the reaction mixture was stirred for 5 minutes, before filtering the reaction mixture through Celite. The yellow filtrate was concentrated *in vacuo* and the residue was triturated with dichloromethane (3 x 2 mL). The combined dichloromethane fractions were chromatographed on silica gel

using dichloromethane as eluent. The first fraction from the column consisted of Cp_2Fe along with a trace of 1,2-diphenyl-1,4-pentadiene **298** (~1%). The second fraction was the organic product **297**, which when dried *in vacuo* yields 0.020 g (98%) of white crystalline material.

2,3-Diphenyl-5-methylenecyclopent-2-en-1-one (297). IR ($CHCl_3$ cast, cm^{-1}): 1692 (s), 1357 (m), 1357 (m). ^1H NMR (300 MHz, $CDCl_3$): δ 7.37- 7.25 (overlapping m's, 10H, H_{Ph}), 6.28 (td, J = 2.0, 1.0 Hz, 1H, H_{6a}), 5.58 (td, J = 1.5, 1.0 Hz, 1H, H_{6a}), 3.68 (t, J = 1.7 Hz, 2H, H_{4a} and H_{4b}); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 194.2, 162.0, 141.5, 135.1, 132.5, 130.0, 129.5, 128.5, 128.3, 128.0, 117.1, 35.2. MS *m/z* calculated for $C_{18}H_{14}O$ (M^+): 246.1045; found: 246.1032 (100.00%); calculated for $C_{18}H_{13}O$ (M-H): 245.0966; found: 245.0959 (64.71%).

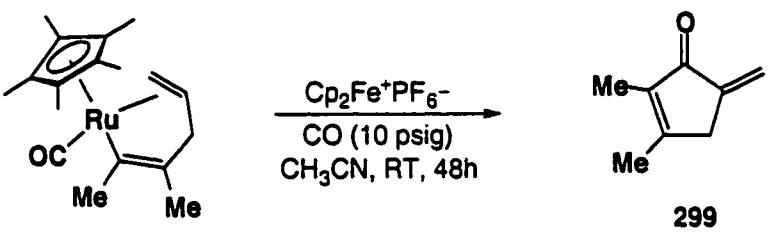


294 **298**

One-electron Oxidation of (C_5Me_5)Ru((1:4,5-η)-1,2-diphenylpentadienyl)(CO)) (294) in Dichloromethane. A similar procedure to that described above was used except that dichloromethane was used in the place of acetonitrile. A solution of carbonyl complex **294** (0.020 g, 0.041 mmol) and $Cp_2Fe^+PF_6^-$ (0.016 g, 0.048 mmol, 1.2 equiv) in 3 mL dichloromethane was placed in the Fisher-Porter bottle under 15 psig of carbon monoxide and stirred at room temperature for 16 hours. The reaction mixture was treated with excess Zn dust (0.030 g) then filtered through Celite and the yellow filtrate

concentrated *in vacuo*. The residue was then chromatographed on silica gel using 10% diethyl ether/dichloromethane as the eluent. The first fraction from the column consisted of Cp_2Fe, while the second fraction was organic compound **298**, isolated as 0.008 g (88 %) of a colourless oily solid. No trace of compound **297** was detected in any of the fractions.

1,2-Diphenyl-1,4-pentadiene (298). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30- 6.90 (complicated m's, 10H, H_{Ph}), 6.45 (s, 1H, H_1), 5.87 (ddt, J = 17.0, 10.1, 6.9 Hz, 1H, H_4), 5.10 (ddd, J = 17.0, 2.0, 1.2 Hz, 1H, H_{5anti}), 5.06 (ddd, J = 10.0, 2.0, 1.3 Hz, 1H, H_{5syn}), 3.23 (dq, J = 6.8, 1.3 Hz, 2H, H_{3a}/H_{3b}). MS *m/z* calculated for $C_{17}H_{16}$ (M^+): 220.1252; found: 220.1249 (100.00%).

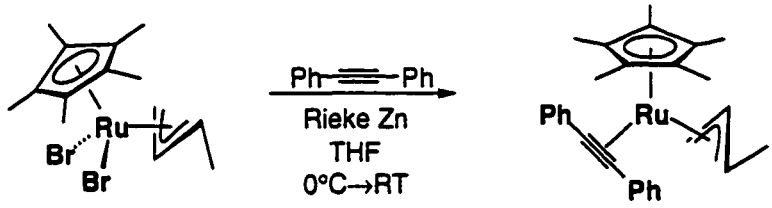


295 **299**

One-electron Oxidation of (C_5Me_5)Ru((1:4,5-η)-1,2-dimethylpentadienyl)(CO)) (295) in Acetonitrile. A solution of 2-butyne derivative **295** (0.044 g, 0.122 mmol) in 4 mL acetonitrile was placed in a Fisher-Porter bottle equipped with a stir-bar and $Cp_2Fe^+PF_6^-$ (0.050 g, 0.151 mmol, 1.24 equiv) was then added. The apparatus was flushed twice with carbon monoxide before a carbon monoxide pressure of 10 psig was established. The reaction was then stirred at room temperature for 48 hours before venting the carbon monoxide pressure. Excess zinc dust (0.050 g) was then added to the reaction mixture (to reduce any remaining $Cp_2Fe^+PF_6^-$) and the reaction was stirred for 5

minutes, before filtering the reaction mixture through Celite. The yellow filtrate was concentrated *in vacuo* and the residue was triturated with dichloromethane (3 x 2 mL). The combined dichloromethane fractions were then chromatographed on silica gel using dichloromethane as the eluent. The first fraction from the column was Cp_2Fe, while the second fraction was the organic product, which was dried *in vacuo* to yield 0.012 g (80%) of a colourless oil, which is spectroscopically identical to the literature compound.[140] The residue that was not soluble in dichloromethane was dissolved in acetonitrile, filtered through Celite and diethyl ether was then added to precipitate the $(C_5Me_5)Ru$ byproducts $[(C_5Me_5)Ru(CH_3CN)_2L]^+PF_6^-$ (L = CO and CH_3CN) as a yellow crystalline material.

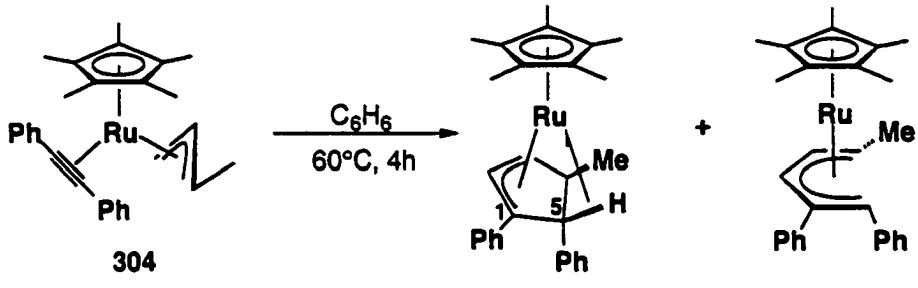
2,3-Dimethyl-5-methylenecyclopent-2-en-1-one (299). ^1H NMR (300 MHz, $CDCl_3$): δ 6.03 (br s, 1H), 5.33 (br s, 1H), 3.07 (br s, 2H), 2.07 (br s, 3H, CH_3), 1.77 (br s, 3H, CH_3).



303 **304**

$(C_5Me_5)Ru(\eta^3$-*exo,syn*-1-$MeC_3H_4)(\eta^2$-PhC≡CPh) (304). In the drybox a small Schlenk flask equipped with stir-bar and septum was charged with $(C_5Me_5)Ru(1\text{-}MeC_3H_4)Br_2$ (0.080 g, 0.177 mmol), diphenylacetylene (0.035 g, 0.196 mmol, 1.11 equiv) and Rieke Zn (0.120 g, 1.8 mmol, 10 equiv). The sealed flask was removed to the Schlenk line and cooled to 0°C using an ice bath. Cold, distilled tetrahydrofuran (4 mL) was then introduced via cannula and the reaction mixture stirred for 30 minutes at 0°C, then warmed to room temperature for another hour of stirring. Then solvent was then

removed *in vacuo*, leaving a black residue. This residue was triturated with several portions of pentane (3 x 2 mL) until the pentane washes became colourless. The combined pentane extracts were then filtered through Celite and the yellow filtrate concentrated to approximately 1 mL before being filtered through a small plug of alumina (5% H_2O). The filtrate was then dried to give a bright orange solid that was further purified by recrystallization from cold pentane, yielding 0.054 g (65%) of orange crystals. ^{1}H NMR (400 MHz, C_6D_6): δ 7.99 (dd, J = 5.6, 1.1 Hz, 4H, H_{Ph}), 7.28 (q, J = 5.6 Hz, 4H, H_{Ph}), 7.15-7.06 (m, 2H, H_{Ph}), 3.04 (td, J = 9.1, 6.5 Hz, 1H, $H_{central}$), 2.73 (dd, J = 6.5, 0.9 Hz, 1H, H_{syn}), 1.72 (d, J = 6.1 Hz, CH_3), 1.50 (s, 15 H, C_5Me_5), 0.68 (dq, J = 9.0, 6.1 Hz, 1H, H_{anti}), 0.53 (d, J = 9.3 Hz, 1H, H_{anti}); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 133.0, 132.3, 132.1, 126.2, 126.4, 98.2, 97.9, 93.9, 83.4, 57.3, 44.6, 19.0, 10.0. MS *m/z* calculated for $C_{28}H_{32}{}^{102}Ru$ (M^+): 470.1548; found: 470.1505 (100.00%); calculated for $C_{27}H_{29}{}^{102}Ru$ ($M-CH_3$): 455.1313; found: 455.1304 (70.63%); calculated for $C_{14}H_{22}{}^{102}Ru$ ($M-C_{14}H_{10}$): 292.0765; found: 292.0708 (44.45%).

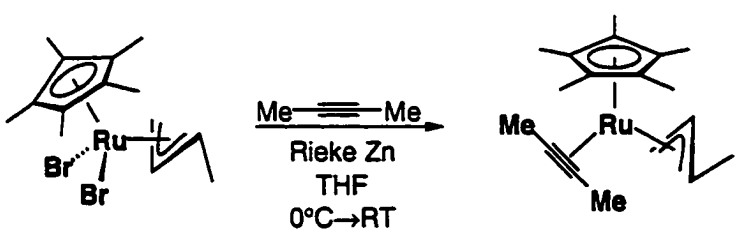


Thermolysis of $(C_5Me_5)Ru(\eta^3$-*exo,syn*-1-$MeC_3H_4)(\eta^2$-PhC≡CPh). In the drybox a solution of diphenylacetylene complex **304** (0.020 g, 0.043 mmol) in 2 mL benzene was

placed in a small Kontes flask equipped with a stir-bar and the reaction flask was then sealed. The flask was removed to an oil bath (60°C) and the reaction stirred for a period of twelve hours. The solvent was then evaporated under low pressure, and the reaction flask returned to the drybox. The yellow residue was dissolved in pentane and filtered through a plug of alumina (5% H_2O), and this filtrate was then concentrated under low pressure to yield 0.036 g (84%) of yellow powder. Analysis by ^1H NMR spectroscopy of this material indicates a mixture of two products, **305** and **306**, in a ratio of 2.2 : 1, respectively.

$(C_5Me_5)Ru(\eta^3\text{-}C_5H_4MePh_2)$ (305). ^1H NMR (360 MHz, C_6D_6): δ 7.27-7.67 (m, 10H, H_{Ph}), 4.67 (d, J = 3.5 Hz, 1H, H_2), 3.74 (dq, J = 11.8, 5.9 Hz, 1H, H_{4exo}), 2.94 (d, J = 3.7 Hz, 1H, H_3), 1.59 (s, 15H, C_5Me_5), 1.31 (d, J = 5.9 Hz, 3H, CH_3), –4.89 (d, J = 11.9 Hz, 1H, H_{ag}).

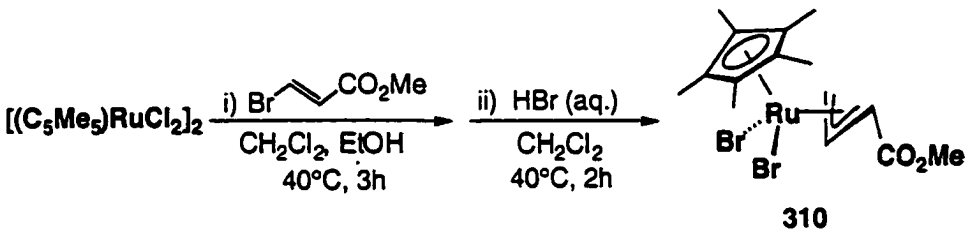
$(C_5Me_5)Ru(\eta^5$-1,2-diphenyl-5-methylpentadienyl) (306). ^1H NMR (360 MHz, C_6D_6): δ 7.48-7.64 (m, 10H, H_{Ph}), 5.12 (d, J = 5.9 Hz, 1H, H_3), 2.73 (dd, J = 8.6, 6.0 Hz, 1H, H_4), 1.74 (dq, J = 8.4, 6.0 Hz, 1H, H_5), 1.52 (d, J = 6.0 Hz, 3H, CH_3), 1.45 (s, 15H, C_5Me_5), 1.18 (s, 1H, H_1).



303 **309**

$(C_5Me_5)Ru(\eta^3\text{-}exo,syn\text{-}1\text{-}MeC_3H_4)(\eta^2\text{-}CH_3C{\equiv}CCH_3)$ (309). In the drybox a small Schlenk flask equipped with a stir-bar and a septum was charged with $(C_5Me_5)Ru(\eta^3$-1-

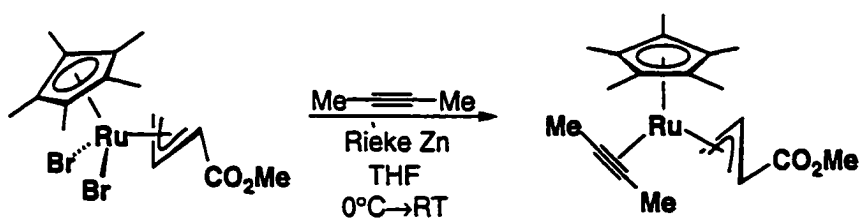
$MeC_3H_4)Br_2$ (0.030 g, 0.066 mmol) and Rieke Zn (0.050 g, 0.8 mmol, 12 equiv). The flask was then removed to the Schlenk line and the flask cooled to 0°C using an ice bath. A cold solution of 2-butyne (0.060 mL, 0.77 mmol, 11.6 equiv) in 3 mL tetrahydrofuran was then introduced via cannula. The reaction mixture was stirred at 0°C for 30 minutes, then the solvent was removed under reduced pressure without allowing the reaction mixture to warm to room temperature. The crude product was then extracted from the reaction residue with several portions of pentane (3 x 2 mL) and the combined pentane fractions filtered through Celite. The yellow filtrate was concentrated and further filtered through a small plug of alumina (5% H_2O), then dried to yield 0.019 g (83%) of a dull yellow solid. ^1H NMR (400 MHz, C_6D_6): δ 3.05 (td, J = 8.5, 6.2 Hz, 1H, $H_{central}$), 2.40 (d, J = 6.1 Hz, 1H, H_{syn}), 2.20 (q, J = 1.6 Hz, 3H, CH_3), 2.12 (q, J = 1.6 Hz, 3H, CH_3), 1.69 (d, J = 6.3 Hz, 3H, CH_3), 1.53 (s, 15 H, $C_5\underline{Me_5}$), 0.11 (dq, J = 8.3, 6.3 Hz, 1H, H_{anti}), 0.03 (d, J = 8.6 Hz, 1H, H_{anti}); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 92.3, 80.2, 75.0, 73.5, 57.4, 41.6, 18.8, 10.3, 10.2, 9.5. MS *m/z* calculated for $C_{18}H_{28}{}^{102}Ru$ (M^+): 346.1234; found: 346.1173 (30.48%); calculated for $C_{14}H_{20}{}^{102}Ru$ ($M-C_4H_8$): 290.0609; found: 290.0646 (100.00%); calculated for $C_{10}H_{14}{}^{102}Ru$ ($M-C_8H_{14}$): 236.0139; found: 236.0137 (89.59%).



310

$(C_5Me_5)Ru(\eta^3\text{-}1\text{-}(CO_2Me)C_3H_4)Br_2$ (310). $[(C_5Me_5)RuCl_2]_2$ (0.150 g, 0.488 mmol) was dissolved in 15 mL dichloromethane containing a mixture of ethanol and water (95:1, 0.3

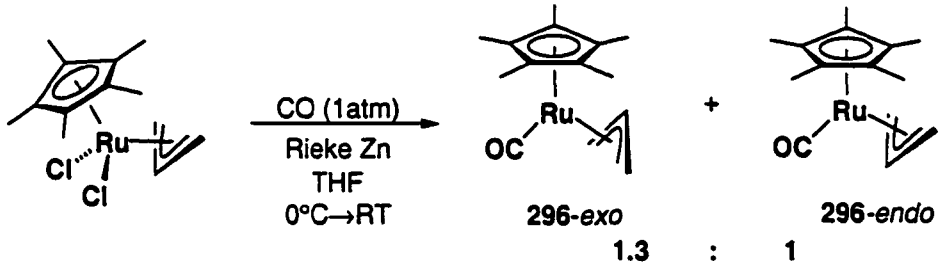
mL) under a nitrogen atmosphere. Methyl 4-bromocrotonate (0.172 mL, 1.46 mmol, 3 equiv) was added to the solution via microliter syringe, and the resulting dark brown solution was stirred at 40°C for 3 hours. Afterwards the solvent was evaporated under reduced pressure and the residue was dried. The residue was then dissolved in 10 mL dichloromethane and an aqueous solution of HBr (47%, 2.0 mL) was added to the solution. The mixture was heated to 40°C for 2 hours, then 15 mL water was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane, then the combined organic layers were washed with brine and dried over $MgSO_4$. After concentration, the product was purified by passing the residue through a short silica gel column using dichloromethane as eluent. The product was then recrystallized from dichloromethane/diethyl ether to afford 0.093 g (38%) of a red powder. ^1H NMR (400 MHz, $CDCl_3$): δ 5.77 (td, J = 9.8, 6.3 Hz, 1H, $H_{central}$), 4.29 (d, J = 6.3 Hz, 1H, H_{syn}), 3.73 (s, 3H, CO_2Me), 2.76 (d, J = 9.7 Hz, 1H, H_{anti}), 2.21 (d, J = 9.9 Hz, 1H, H_{anti}), 1.77 (s, 15 H, $C_5\underline{Me_5}$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 105.7, 96.0, 66.1, 62.7, 51.2, 10.2. Analysis calculated for $C_{15}H_{22}Br_2O_2Ru$: C, 36.38%; H, 4.48%; found: C, 36.04%; H, 4.31%.



310 **311**

$(C_5Me_5)Ru(\eta^3$-*exo,syn*-1-$(CO_2Me)C_3H_4)(\eta^2$-$CH_3C{\equiv}CCH_3)$ (311). In the drybox a small Schlenk flask equipped with a stir-bar and a septum was charged with

$(C_5Me_5)Ru(\eta^3\text{-}1\text{-}(CO_2Me)C_3H_4)Br_2$ (0.020 g, 0.040 mmol) and Rieke Zn (0.040 g, 0.6 mmol, 15 equiv). The flask was then removed to the Schlenk line and the flask cooled to 0°C using an ice bath. A cold solution of 2-butyne (0.060 mL, 0.77 mmol, 19 equiv) in 3 mL tetrahydrofuran was then introduced via cannula. The reaction mixture was stirred at 0°C for 30 minutes, then the solvent was removed under reduced pressure without allowing the reaction mixture to warm to room temperature. The crude product was then extracted from the reaction residue with several portions of pentane (3 x 2 mL) and the combined pentane fractions filtered through Celite. The yellow filtrate was concentrated and filtered through a small plug of alumina (5% H_2O) using diethyl ether as eluent, then dried to yield 0.014 g (89%) of a bright yellow solid. ^{1}H NMR (300 MHz, C_6D_6): δ 4.32 (td, J = 8.1, 6.4 Hz, 1H, $H_{central}$), 3.56 (s, 3H, CO_2Me), 2.52 (d, J = 6.4 Hz, 1H, H_{syn}), 2.37 (q, J = 1.6 Hz, 3H, CH_3), 2.01 (q, J = 1.6 Hz, 3H, CH_3), 1.50 (s, 15 H, $C_5\underline{Me_5}$), 1.28 (d, J = 8.1 Hz, 1H, H_{anti}), 0.64 (d, J = 8.1 Hz, 1H, H_{anti}).



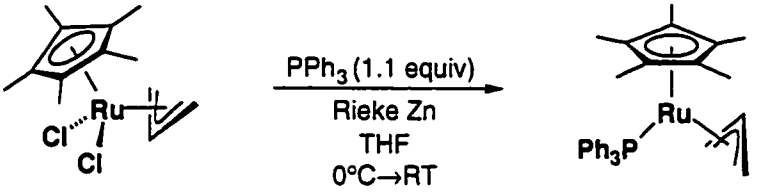
$(C_5Me_5)Ru(\eta^3\text{-}C_3H_5)(CO)$ (296). In the drybox a small Schlenk flask equipped with a stir-bar and septum was charged with $(C_5Me_5)Ru(\eta^3\text{-}C_3H_5)Cl_2$ (0.050 g, 0.144 mmol) and Rieke Zn (0.100 g, 1.5 mmol, 10.6 equiv). The sealed flask was removed to the Schlenk line where a carbon monoxide atmosphere was established by three successive evacuations and backfills. Distilled tetrahydrofuran (3 mL) was added via syringe, then

carbon monoxide was bubbled through the reaction mixture for a further 5 minutes. The flask was sealed and stirred at room temperature for 30 minutes. The solvent was subsequently evaporated under reduced pressure and the crude product was extracted from the residue with several portions (3 x 2 mL) of pentane. The combined fractions were filtered through Celite, concentrated under reduced pressure, then filtered again through a small plug of alumina (5% H_2O). The filtrate was dried to yield 0.032 g (72%) of a pale yellow crystalline material. Spectroscopic analysis by ^1H NMR of this material indicates that a mixture of *exo* and *endo* isomers is present in a ratio of 1.3 : 1, respectively. This crystalline material was dissolved in 2 mL benzene and placed in a small Kontes flask equipped with a stir-bar. The flask was then sealed and transferred to a 80°C oil bath where the solution was stirred for 24 hours. Afterwards the solvent was evaporated under reduced pressure, leaving a yellow solid. This residue was dissolved in pentane and filtered through a plug of alumina (5% H_2O), and the filtrate was then dried to yield 0.028 g of a white crystalline material. Spectroscopic analysis by ^1H NMR of this material indicates this product is exclusively the *endo* isomer.

(C_5Me_5)Ru(η^3-*exo*-C_3H_5)(CO) (296-*exo*). ^1H NMR (300 MHz, C_6D_6): δ 4.03 (tt, J = 10.9, 6.5 Hz, 1H, $H_{central}$), 3.04 (d, J = 6.5 Hz, 2H, H_{syn}), 1.65 (s, 15 H, $C_5\underline{Me_5}$), 0.63 (d, J = 10.9 Hz, 2H, H_{anti}); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 209.2, 94.8, 89.9, 39.8, 10.8.

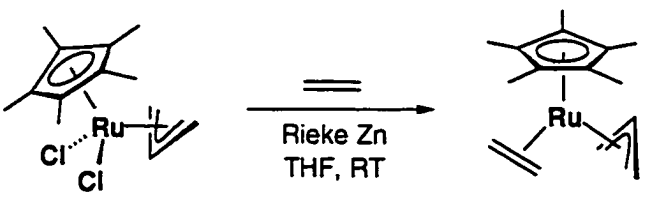
(C_5Me_5)Ru(η^3-*endo*-C_3H_5)(CO) (296-*endo*). ^1H NMR (300 MHz, C_6D_6): δ 2.90 (tt, J = 10.5, 6.7 Hz, 1H, $H_{central}$), 2.19 (dt, J = 6.7, 1.1 Hz, 2H, H_{syn}), 1.64 (dt, J = 10.5, 1.1 Hz, 2H, H_{anti}, partially obscured), 1.62 (s, 15 H, $C_5\underline{Me_5}$); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 209.9, 93.8, 77.3, 35.4, 10.3. NOE difference experiments (400 MHz, C_6D_6): irradiation of δ 2.90 ($H_{central}$) ↔ 9.1% enhancement of signal at δ 2.19 (H_{syn}); irradiation

of δ 1.62 ($C_5\underline{Me_5}$) ↔ 2.3% enhancement of signal at δ 2.19 (H_{syn}). MS *m/z* calculated for $C_{14}H_{20}{}^{102}RuO$ (M^+): 306.0558; found: 306.0543 (34.67%); calculated for $C_{13}H_{20}{}^{102}Ru$ (M-CO): 278.0609; found: 278.0569 (68.15%); calculated for $C_{10}H_{14}{}^{102}Ru$ (M-C_4H_6O): 236.0139; found: 236.0131 (100.00%).



281 **312**

(C_5Me_5)Ru(η^3-*exo*-C_3H_5)(PPh_3) (312). In the drybox a small Schlenk flask equipped with a stir-bar and a septum was charged with (C_5Me_5)Ru(η^3-C_3H_5)Cl_2 (0.020 g, 0.057 mmol), triphenylphosphine (0.017 g, 0.065 mmol, 1.1 equiv) and Rieke Zn (0.050 g, 0.76 mmol, 13 equiv). Tetrahydrofuran (3 mL) was then added via pipette and the reaction mixture was stirred at room temperature for 30 minutes, then the solvent was evaporated under reduced pressure. The crude product was extracted from the reaction residue with several portions of diethyl ether (3 x 2 mL) and the combined pentane fractions filtered through Celite. The yellow filtrate was concentrated and then further filtered through a small plug of alumina (5% H_2O). This was then dried to yield 0.026 g (85%) of a yellow crystalline solid. ^{1}H NMR (300 MHz, C_6D_6): δ 7.11-6.98 (overlapping multiplets, 15H, H_{Ph}), 2.89 (tt, J = 10.3, 6.8, Hz, 1H, $H_{central}$), 2.14 (d, J = 6.9 Hz, 2H, H_{syn}), 1.43 (s, 15 H, $C_5\underline{Me_5}$), 0.63 (dd, J = 16.5, 9.8 Hz, 2H, H_{anti}).

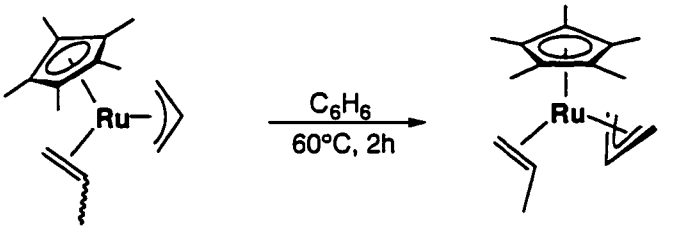


313

$(C_5Me_5)Ru(\eta^3\text{-}exo\text{-}C_3H_5)(\eta^2\text{-}C_2H_4)$ (313). In the drybox a small Schlenk flask equipped with a stir-bar and septum was charged with $(C_5Me_5)Ru(\eta^3\text{-}C_3H_5)Cl_2$ (0.050 g, 0.144 mmol) and Rieke Zn (0.100 g, 1.5 mmol, 10.6 equiv). The sealed flask was removed to the Schlenk line where an ethylene atmosphere was established by three successive evacuations and backfills. Distilled tetrahydrofuran (3 mL) was added via syringe, then ethylene was bubbled through the reaction mixture for a further 5 minutes. The flask was sealed and stirred at room temperature for 30 minutes. The solvent was subsequently evaporated under reduced pressure and the crude product was extracted from the residue with several portions (3 x 2 mL) of pentane. The combined pentane fractions were filtered through Celite, concentrated under reduced pressure, then filtered again through a small plug of alumina (5% H_2O). The filtrate was dried to yield 0.036 g (82%) of a pale yellow crystalline material, which could be further purified by recrystallization using diethyl ether/methanol. Spectroscopic analysis by ^1H NMR of this material indicates a small amount (~8%) of the product is the *endo* isomer. ^1H NMR (300 MHz, C_6D_6): δ 2.99 (tt, J = 10.0, 7.3 Hz, 1H, $H_{central}$), 2.63 (d, J = 7.3 Hz, 2H, H_{syn}), 2.27 (br d, J = 11.4 Hz, 2H, C_2H_4), 1.44 (br d, J = 11.3 Hz, 2H, C_2H_4), 1.39 (s, 15H, $C_5\underline{Me_5}$), 0.39 (d, J = 9.9 Hz, 2H, H_{anti}); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 91.7, 80.4, 45.3, 42.2, 8.8.

280
(mixture of isomers)

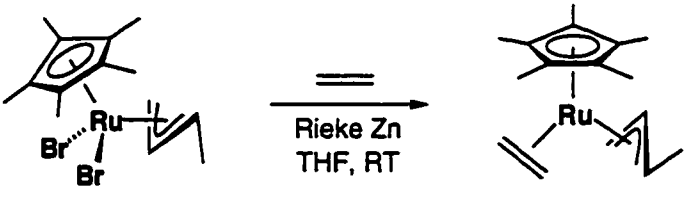
$(C_5Me_5)Ru(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_7)$ (280). In the drybox a small Schlenk flask equipped with a stir-bar and septum was charged with $(C_5Me_5)Ru(\eta^3\text{-}C_3H_5)Cl_2$ (0.150 g, 0.431 mmol) and Rieke Zn (0.200 g, 3.0 mmol, 7 equiv). The sealed flask was removed to the Schlenk line where a propene atmosphere was established by three successive evacuations and backfills. Distilled tetrahydrofuran (4 mL) was added via syringe, and propene was bubbled through the reaction mixture for a further 5 minutes, then the flask was sealed and the reaction stirred at room temperature for 30 minutes. The solvent was evaporated under reduced pressure and the sealed flask was returned to the drybox. The crude product was then extracted from the residue with several portions (3 x 2 mL) of pentane. The combined pentane fractions were filtered through Celite, concentrated under reduced pressure, then filtered again through a small plug of alumina (5% H_2O). The filtrate was dried to yield 0.112 g (81%) of a pale yellow crystalline material. Spectroscopic analysis by ^1H NMR of this material indicates this material is a complex mixture of isomers. ^1H NMR (300 MHz, C_6D_6, selected data only): δ 3.10-2.35 (series of overlapping multiplets), 2.08 (br d, J = 11.7 Hz), 1.79 (d, J = 6.9 Hz), 1.43 (s, C_5Me_5), 1.37 (s, C_5Me_5), 0.31 (br d, J = 9.9 Hz), –0.81 (br d, J = 11.0 Hz). MS *m/z* calculated for $C_{16}H_{26}{}^{102}Ru$ (M^+): 320.1078; found: 320.1078 (34.67%); calculated for $C_{13}H_{20}{}^{102}Ru$ (M-C_3H_6): 278.0609; found: 278.0590 (100.00%).



280 (mixture of isomers)

280-*endo*

Thermolysis of $(C_5Me_5)Ru(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_7)$ (280). A solution of $(C_5Me_5)Ru(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_7)$ (mixture of isomers) (0.020 g, 0.063 mmol) in 1.5 mL benzene was placed in a small Kontes flask and a propene atmosphere established before sealing the flask. The flask was then transferred to a 60°C oil bath and the solution heated for a period of 2 hours. Afterwards the solvent was evaporated under low pressure, leaving a yellow residue that was dissolved in pentane and filtered through a plug of alumina (5% H_2O). The filtrate was dried to yield 0.018 g (90%) of a pale yellow crystalline material, which was spectroscopically identical to $(C_5Me_5)Ru(\eta^3\text{-}endo\text{-}C_3H_5)(\eta^2\text{-}C_3H_7)$ (**280-*endo***) reported by Koelle.[134]

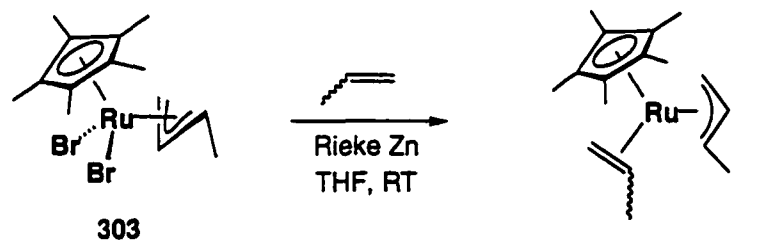


303

279-*exo*

$(C_5Me_5)Ru(\eta^3\text{-}exo\text{-}1\text{-}MeC_3H_4)(\eta^2\text{-}C_2H_4)$ (279-*exo*). In the drybox a small Schlenk flask equipped with a stir-bar and septum was charged with $(C_5Me_5)Ru(\eta^3\text{-}1\text{-}MeC_3H_4)Br_2$ (0.050 g, 0.111 mmol) and Rieke Zn (0.080 g, 1.2 mmol, 11 equiv). The sealed flask was removed to the Schlenk line where an ethylene atmosphere was established by three

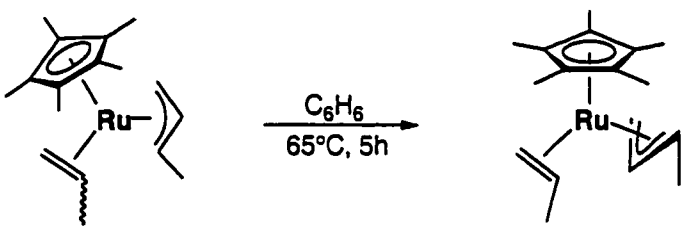
successive evacuations and backfills. Distilled tetrahydrofuran (3 mL) was added via syringe, then ethylene was bubbled through the reaction mixture for a further 5 minutes. The flask was sealed and stirred at room temperature for 1 hour. The solvent was then evaporated under reduced pressure and the crude product was extracted from the residue with several portions (3 x 2 mL) of pentane. The combined pentane fractions were filtered through Celite, concentrated under reduced pressure, then filtered again through a small plug of alumina (5% H_2O). The filtrate was dried to yield 0.030 g (85%) of a pale yellow crystalline material that was spectroscopically identical to the $(C_5Me_5)Ru(\eta^3$-*exo*-1-$MeC_3H_4)(\eta^2$-$C_2H_4)$ reported by Koelle.[134]



303 **314** (mixture of isomers)

$(C_5Me_5)Ru(\eta^3$-1-$MeC_3H_4)(\eta^2$-$C_3H_7)$ (314). In the drybox a small Schlenk flask equipped with a stir-bar and septum was charged with $(C_5Me_5)Ru(\eta^3$-1-$MeC_3H_5)Cl_2$ (0.140 g, 0.386 mmol) and Rieke Zn (0.200 g, 3.0 mmol, 7.9 equiv). The sealed flask was removed to the Schlenk line where a propene atmosphere was established by three successive evacuations and backfills. Distilled tetrahydrofuran (4 mL) was added via syringe and propene was bubbled through the reaction mixture for a further 5 minutes, then the flask was sealed and the reaction stirred at room temperature for 30 minutes. The solvent was then evaporated under reduced pressure and the sealed flask was

returned to the drybox. The crude product was extracted from the residue using several portions (3 x 2 mL) of pentane. The combined pentane fractions were filtered through Celite, concentrated under reduced pressure, then filtered again through a small plug of alumina (5% H_2O). The filtrate was dried to yield 0.121 g (93%) of a pale yellow crystalline material. Spectroscopic analysis by ^1H NMR of this material indicates this material is a complex mixture of isomers. ^1H NMR (300 MHz, C_6D_6, select data only): δ 3.10 - 2.45 (series of overlapping multiplets), 2.09 (d, J = 11.1 Hz), 1.76 (d, J = 6.3 Hz), 1.66 (d, J = 6.2 Hz), 1.60 (d, J = 6.3 Hz), 1.44 (s, C_5Me_5), 1.39 (s, C_5Me_5), 1.37 (s, C_5Me_5), 1.05 (d, J = 6.3 Hz), –0.43 (dq, J = 11.0, 6.3 Hz). MS *m/z* calculated for $C_{17}H_{28}{}^{102}Ru$ (M^+): 334.1234; found: 334.1238 (34.67%); calculated for $C_{14}H_{20}{}^{102}Ru$ (M-C_3H_8): 290.0609; found: 290.0649 (100.00%).

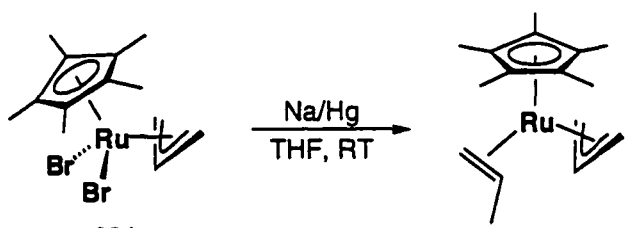


314
(mixture of isomers)

314-*endo*

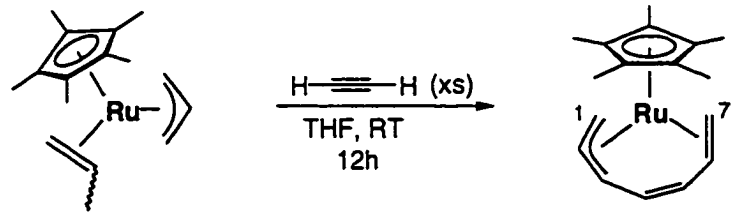
Thermolysis of (C_5Me_5)Ru(η^3-1-MeC_3H_4)(η^2-C_3H_7) (314). A solution of (C_5Me_5)Ru(η^3-1-MeC_3H_4)(η^2-C_3H_7) (mixture of isomers) (0.020 g, 0.060 mmol) in 2.0 mL benzene was placed in a small Kontes flask and a propene atmospherewas established before sealing the flask. The flask was then transferred to a 65°C oil bath and the solution heated for a period of 5 hours. Afterwards the solvent was evaporated under low pressure, leaving a yellow residue that was dissolved in pentane and filtered through a

plug of alumina (5% H_2O). The filtrate was dried to yield 0.017 g (85%) of a pale yellow crystalline material. ^1H NMR (300 MHz, C_6D_6): δ 2.38 (d, J = 6.4 Hz, 1H, H_{syn}), 2.25 (td, J = 7.9, 6.3 Hz, 1H, $H_{central}$), 2.20 (q, J = 1.6 Hz, 3H, CH_3), 2.12 (q, J = 1.6 Hz, 3H, CH_3), 1.70 (d, J = 6.1 Hz, 3H, CH_3), 1.54-1.45 (overlapping multiplets, 2H), 1.40 (s, 15 H, $C_5\underline{Me_5}$), 1.22 (d, J = 6.1 Hz, 3H, CH_3), 1.15 (dd, J = 8.4, 1.1 Hz, 1H), 0.80 (dd, J = 10.2, 1.3 Hz, 1H, H_{anti}), 0.67 (d, J = 9.6 Hz, 1H, H_{anti}); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 93.2, 90.7, 56.7, 43.0, 42.0, 40.0, 17.3, 16.3, 9.2.



281 **280-*endo***

Na/Hg Reduction of $(C_5Me_5)Ru(\eta^3\text{-}C_3H_5)Br_2$. In the drybox a small Schlenk flask equipped with stir-bar and septum was charged with a solution of $(C_5Me_5)Ru(C_3H_5)Br_2$ (0.030 g, 0.069 mmol) in 5 mL tetrahydrofuran. Sodium amalgam (0.69%, 1.0 g, 0.30 mmol, 4.3 equiv) was added by pipette while the solution was stirring rapidly. The flask was sealed and the reaction was stirred at room temperature for a further 40 minutes before evaporating the solvent under reduced pressure. The solid residue was rinsed with several portions of pentane (3 x 2 mL) and the combined pentane washes filtered over Celite. The red filtrate was concentrated to form 0.010 g of a red oily solid. Analysis of this residue by ^1H NMR spectroscopy indicates that the only pentamethyl-cyclopentadienyl product is $(C_5Me_5)Ru(\eta^3\text{-}endo\text{-}C_3H_5)(\eta^2\text{-}C_3H_7)$ (**280-*endo***), formed in approximately 40% yield.

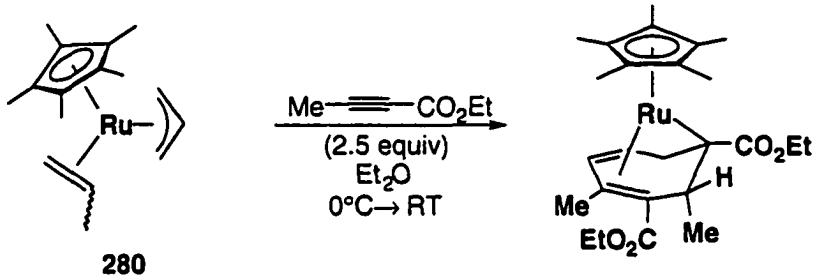


280
(mixture of isomers)

316

(C_5Me_5)Ru((1,2,3:6,7-η)heptatrienyl) (316). A small Schlenk flask equipped with a stir-bar and septum was charged with a solution of $(C_5Me_5)Ru(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_6)$ (0.110 g, 0.344 mmol) in 5 mL tetrahydrofuran. Acetylene was slowly bubbled through the solution for 20 minutes, then the flask was sealed and stirred at room temperature. A significant amount of black precipitate was formed, suggesting decomposition to ruthenium powder or polyacetylene. After 12 hours of stirring the solvent was evaporated under reduced pressure. The solid residue was rinsed with several portions of pentane (3 x 2 mL) and the combined pentane washes filtered over Celite. The yellow filtrate was concentrated and then further filtered through a small plug of alumina (5% H_2O), then dried to give a yellow solid residue. Recrystallization of this material from diethyl ether/methanol resulted in the formation of 0.020 g (18%) of bright yellow crystals. ^1H NMR (400 MHz, C_6D_6): δ 5.83 (dd, J = 5.5, 0.9 Hz, 1H, H_5), 5.40 (dd, J = 5.5, 2.3 Hz, 1H, H_4), 4.35 (br d, J = 7.1 Hz, 1H, H_3), 3.84 (ddq, J = 10.9, 9.0, 1.8 Hz, 1H, H_6), 3.20 (dt, J = 9.7, 7.0 Hz, 1H, H_2), 2.82 (dd, J = 6.8, 2.5 Hz, 1H, H_{1syn}), 2.39 (d, J = 9.1 Hz, 1H, H_{7syn}), 2.18 (d, J = 11.0 Hz, 1H, H_{7anti}), 1.43 (s, 15H, C_5Me_5), 0.65 (d, J = 9.7 Hz, 1H, H_{1anti}); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 137.3 (C_5), 132.1 (C_4), 92.0 ($\underline{C}_5Me_5$), 81.5 (C_2), 72.5 (C_3), 71.3 (C_6), 48.7 (C_7), 45.1 (C_1), 8.9 ($C_5\underline{Me}_5$); ^1H-^{13}C HETCORR (100 MHz, C_6D_6): δ 137.3 (C_5) ↔ δ 5.83 (H_5); δ 132.1 (C_4) ↔ δ 5.40

(H_4); δ 81.5 (C_2) ↔ δ 3.20 (H_2); δ 72.5 (C_3) ↔ δ 4.35 (H_3); δ 71.3 (C_6) ↔ δ 3.84 (H_6); δ 48.7 (C_7) ↔ δ 2.39, 2.18 (H_{7syn} and H_{7anti}); δ 45.1 (C_1) ↔ δ 2.82, 0.65 (H_{1syn} and H_{1anti}); δ 8.5 ($\underline{C}_5Me_5$)↔ δ 1.64, ($C_5\underline{Me}_5$). Analysis calculated for $C_{17}H_{24}Ru$: C, 61.98%; H, 7.34%; found: C, 61.90%; H, 7.33%.

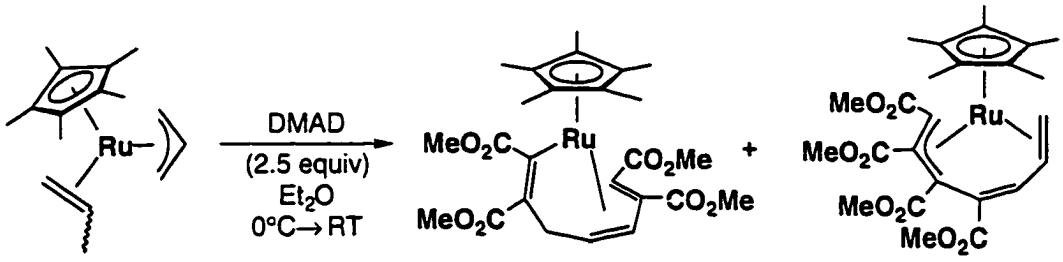


280
(mixture of isomers)

317

(C_5Me_5)Ru((1:3,4,5,6-η)-1,3-dicarboethoxy-2,4-dimethylcycloheptadienyl) (317). A small Schlenk flask equipped with a stir-bar and septum was charged with a solution of (C_5Me_5)Ru(η^3-C_3H_5)(η^2-C_3H_6) (0.052 g, 0.163 mmol) in 3 mL diethyl ether and the reaction flask cooled to 0°C in an ice bath. Ethyl 2-butynoate (0.047 mL, 0.404 mmol, 2.5 equiv) was then added via microliter syringe. After 2 hours of stirring at 0°C the ice bath was removed and the reaction stirred at room temperature for a further 5 hours, before evaporating the solvent under reduced pressure. The residue was then chromatographed on silica gel using 15% pentane/diethyl ether as eluent, which resulted in the isolation of the major product as 0.046 g (56%) of a bright yellow crystalline material. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.30 (d, J = 8.5 Hz, 1H, H_5), 4.16 (2 overlapping quartets, diastereotopic, 2H, $CO_2C\underline{H}_2CH_3$), 4.09 (q, J = 7.2 Hz, 1H, partially obscured, H_2), 4.05 (q, J = 7.1 Hz, 2H, $CO_2C\underline{H}_2CH_3$), 3.18 (dd, J = 13.6, 8.0 Hz, 1H, H_{7exo}), 3.11 (td, J = 8.2, 1.4 Hz, 1H, H_6), 2.99 (dd, J = 13.8, 1.2 Hz, 1H, H_{7endo}), 2.29 (s,

3H, CH_3), 1.51 (s, 15H, C_5Me_5), 1.32 (t, J = 7.1 Hz, 3H, $CO_2CH_2C\underline{H}_3$), 1.24 (t, J = 7.1 Hz, 3H, $CO_2CH_2C\underline{H}_3$), 0.45 (d, J = 7.2 Hz, 3H, CH_3); ^{1}H-^{1}H GCOSY (300 MHz, $CDCl_3$, each correlation only listed once): δ 4.30 (H_5) ↔ 3.11 (H_6), 2.99 (H_{7endo}); δ 4.16 ($CO_2C\underline{H}_2CH_3$) ↔ 1.32 ($CO_2CH_2C\underline{H}_3$); δ 4.09 (H_2) ↔ 0.45 (CH_3); δ 4.05 ($CO_2C\underline{H}_2CH_3$) ↔ 1.24 ($CO_2CH_2C\underline{H}_3$); δ 3.18 (H_{7exo}) ↔ 3.11 (H_6), 2.99 (H_{7endo}); δ 3.11(H_6) ↔ 2.99 (H_{7endo}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8 (s, $\underline{C}O_2CH_2CH_3$), 174.3 (s, $\underline{C}O_2CH_2CH_3$), 104.3 (s, C_4), 97.3 (d, J_{CH} = 156 Hz, C_5), 93.7 (s, $\underline{C}_5Me_5$), 59.8 (t, $^1J_{CH}$ = 141 Hz, $CO_2\underline{C}H_2CH_3$), 59.1 (t, $^1J_{CH}$ = 143 Hz, $CO_2\underline{C}H_2CH_3$), 40.6 (d, $^1J_{CH}$ = 157 Hz, C_6), 38.9 (d, $^1J_{CH}$ = 135 Hz, C_2), 38.3 (s, C_3), 28.8 (t, $^1J_{CH}$ = 130 Hz, C_7), 23.5 (q, $^1J_{CH}$ = 133 Hz, CH_3), 21.8 (q, $^1J_{CH}$ = 126 Hz, CH_3), 14.5 (q, $^1J_{CH}$ = 128 Hz, 2 x $CO_2CH_2\underline{C}H_3$), 8.4 (q, $^1J_{CH}$ = 126 Hz, $C_5\underline{Me}_5$), –32.9 (s, C_1); HMQC (300 MHz, $CDCl_3$): δ 97.3 (C_5) ↔ δ 4.30 (H_5); δ 59.8 ($CO_2\underline{C}H_2CH_3$) ↔ δ 4.16 ($CO_2C\underline{H}_2CH_3$); δ 59.1 ($CO_2\underline{C}H_2CH_3$) ↔ δ 4.05 ($CO_2C\underline{H}_2CH_3$); δ 40.6 (C_6) ↔ δ 3.11 (H_6); δ 38.9 (C_2) ↔ δ 4.09 (H_2); δ 28.8 (C_7) ↔ δ 3.18 (H_{7exo}), 2.99 (H_{7endo}); δ 23.5 (CH_3) ↔ δ 2.29 (CH_3); δ 21.8 (CH_3) ↔ δ 0.45 (CH_3); δ 14.5 ($CO_2CH_2\underline{C}H_3$) ↔ δ 1.32 and 1.24 ($CO_2CH_2C\underline{H}_3$); δ 8.4 ($C_5\underline{Me}_5$) ↔ δ 1.51 ($C_5\underline{Me}_5$); HMBC (300 MHz, $CDCl_3$): δ 180.8 ($\underline{C}O_2CH_2CH_3$) ↔ δ 4.09 (H_2), 3.18 (H_{7exo}); δ 174.3 ($\underline{C}O_2CH_2CH_3$) ↔ δ 4.09 (H_2); δ 104.3 (C_4) ↔ δ 4.09 (H_2), 3.11 (H_6), 2.29 (CH_3); δ 97.3 (C_5) ↔ δ 3.18 (H_{7exo}), 2.99 (H_{7endo}), 2.29 (CH_3); δ 59.8 ($CO_2\underline{C}H_2CH_3$) ↔ δ 1.32 ($CO_2CH_2C\underline{H}_3$); δ 59.1 ($CO_2\underline{C}H_2CH_3$) ↔ δ 1.24 ($CO_2CH_2C\underline{H}_3$); δ 40.6 (C_6) ↔ δ 3.18 (H_{7exo}), 2.99 (H_{7endo}); δ 38.9 (C_2) ↔ δ 3.18 (H_{7exo}), 2.99 (H_{7endo}), 0.45 (CH_3); δ 38.3 (C_3)↔ δ 4.30 (H_5), 4.09 (H_2), 2.29 (CH_3), 0.45 (CH_3); δ 28.8 (C_7) ↔ δ 4.30 (H_5), 4.09 (H_2); δ 23.5 (CH_3) ↔ δ 4.30 (H_5); δ 21.8 (CH_3) ↔ δ 4.09 (H_2); δ –32.9 (C_1) ↔ δ 4.09 (H_2), 3.18 (H_{7exo}), 3.11 (H_6), 2.99 (H_{7endo}), 0.45 (CH_3).



280
(mixture of isomers)

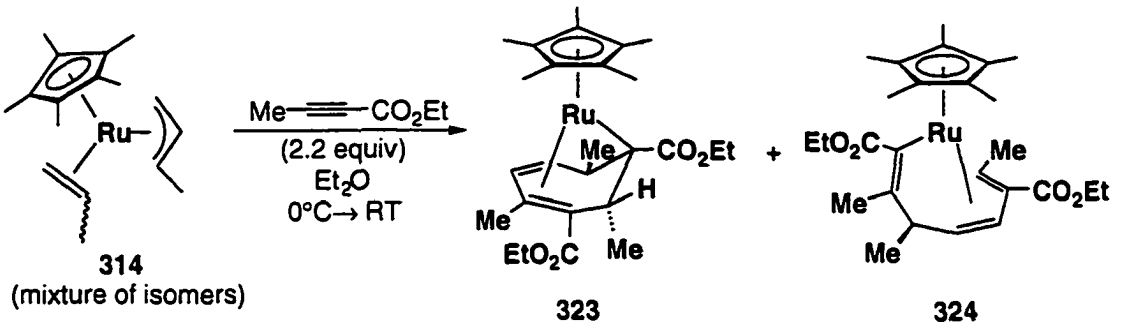
318

319

(C_5Me_5)Ru((1:4,5,6,7-η)-1,2,6,7-tetracarbomethoxyheptatrienyl) (318). A small Schlenk flask equipped with a stir-bar and septum was charged with a solution of (C_5Me_5)Ru(η^3-C_3H_5)(η^2-C_3H_6) (0.052 g, 0.163 mmol) in 3 mL diethyl ether and the reaction flask was cooled to 0°C in an ice bath. DMAD (0.050 mL, 0.407 mmol, 2.5 equiv) was then added via microliter syringe. After 2 hours of stirring at 0°C the ice bath was removed and the reaction was stirred at room temperature for a further 6 hours, before evaporating the solvent under reduced pressure. The residue was then chromatographed on silica gel using 15% pentane/diethyl ether as eluent, which resulted in the isolation of the major product **318** as 0.056 g (61%) of an orange crystalline material. Analytically pure crystals of this product were obtained by recrystallization using methanol/water. The second, minor product **319** was also isolated from chromatography, yielding 0.011 g (12%) of yellow crystalline material. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.86 (d, J = 8.6 Hz, 1H, H_5), 4.04 (dt, J = 9.5, 7.7 Hz, 1H, H_4), 3.82 (s, 3H, CO_2Me), 3.72 (s, 3H, CO_2Me), 3.67 (s, 3H, CO_2Me), 3.56 (s, 3H, CO_2Me), 3.31 (dd, J = 17.7, 9.7 Hz, 1H, H_{3endo}), 1.95 (dd, J = 17.7, 6.2 Hz, 1H, H_{3exo}), 1.91 (d, J = 0.8 Hz, 1H, H_7), 1.64 (s, 15H, C_5Me_5); ^{1}H-^{1}H GCOSY (300 MHz, $CDCl_3$, each correlation only

listed once): δ 4.86 (H_5) ↔ 4.04 (H_4), 1.91(H_7); δ 4.04 (H_4) ↔ 3.31 (H_{3endo}), 1.95 (H_{3exo}); δ 3.31 (H_{3a}) ↔ 1.95 (H_{3b}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.7 (s, C_1), 175.1 (s, $\underline{C}O_2Me$), 172.4 (s, $\underline{C}O_2Me$), 169.5 (s, $\underline{C}O_2Me$), 161.9 (s, $\underline{C}O_2Me$), 139.7 (s, C_2), 99.1 (s, $\underline{C}_5Me_5$), 92.3 (s, C_6), 88.6 (d, $^1J_{CH}$ = 168 Hz, C_5), 72.5 (d, $^1J_{CH}$ = 153 Hz, C_4), 56.9 (d, $^1J_{CH}$ = 168 Hz, C_7), 52.5 (q, $^1J_{CH}$ = 146 Hz, $CO_2\underline{Me}$), 51.6 (q, $^1J_{CH}$ = 143 Hz, $CO_2\underline{Me}$), 51.1 (q, $^1J_{CH}$ = 144 Hz, $CO_2\underline{Me}$), 50.8 (q, $^1J_{CH}$ = 143 Hz, $CO_2\underline{Me}$), 35.4 (t, $^1J_{CH}$ = 129 Hz, C_3), 8.5 (q, $^1J_{CH}$ = 128 Hz, $C_5\underline{Me}_5$); HMQC (300 MHz, $CDCl_3$): δ 88.6 (C_5) ↔ δ 4.86 (H_5); δ 72.5 (C_4) ↔ δ 4.04 (H_4); δ 56.9 (C_7) ↔ δ 1.91 (H_7); δ 52.5 ($CO_2\underline{Me}$)↔ δ 3.82 ($CO_2\underline{Me}$); δ 51.6 ($CO_2\underline{Me}$) ↔ δ 3.72 ($CO_2\underline{Me}$); δ 51.1 ($CO_2\underline{Me}$)↔ δ 3.67 ($CO_2\underline{Me}$); δ 50.8 ($CO_2\underline{Me}$) ↔ δ 3.56 ($CO_2\underline{Me}$); δ 35.4 (C_3) ↔ δ 3.31, 1.95 (H_{3endo} and H_{3exo}); δ 8.5 ($C_5\underline{Me}_5$) ↔ δ 1.64 ($C_5\underline{Me}_5$); HMBC (300 MHz, $CDCl_3$): δ 179.7 (C_1) ↔ δ 3.31 (H_{3endo}), 1.95 (H_{3exo}); δ 169.5 ($\underline{C}O_2Me$) ↔ δ 4.86 (H_5), 1.91 (H_7); δ 139.7 (C_2) ↔ δ 3.31 (H_{3endo}), 1.95 (H_{3exo}), 1.91 (H_7); δ 92.3 (C_6) ↔ δ 4.04 (H_4); δ 88.6 (C_5) ↔ δ 3.31 (H_{3endo}), 1.95 (H_{3exo}), 1.91 (H_7); δ 72.5 (C_4) ↔ δ 4.86 (H_5), 3.31 (H_{3endo}), 1.95 (H_{3exo}); δ 56.9 (C_7) ↔ δ 4.86 (H_5); δ 35.4 (C_3) ↔ δ 4.86 (H_5). Analysis calculated for $C_{25}H_{32}O_8Ru$: C, 53.47%; H, 5.74%; found: C, 53.53%; H, 5.70%.

(C_5Me_5)Ru((1,2,3:6,7-η)-1,2,3,4-tetracarbomethoxyheptatrienyl) (319). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96 (d, J = 2.0 Hz, 1H, H_5), 4.04 (td, J = 10.0, 2.0 Hz, 1H, H_6), 3.87 (s, 3H, CO_2Me), 3.70 (s, 3H, CO_2Me), 3.62 (s, 3H, CO_2Me), 3.61 (s, 3H, CO_2Me), 2.76 (d, J = 12.3 Hz, 1H, H_{7anti}), 2.70 (dd, J = 10.0, 1.5 Hz, 1H, H_{7syn}), 1.56 (s, 15H, C_5Me_5), 0.88 (s, 1H, H_1).



314
(mixture of isomers)

323

324

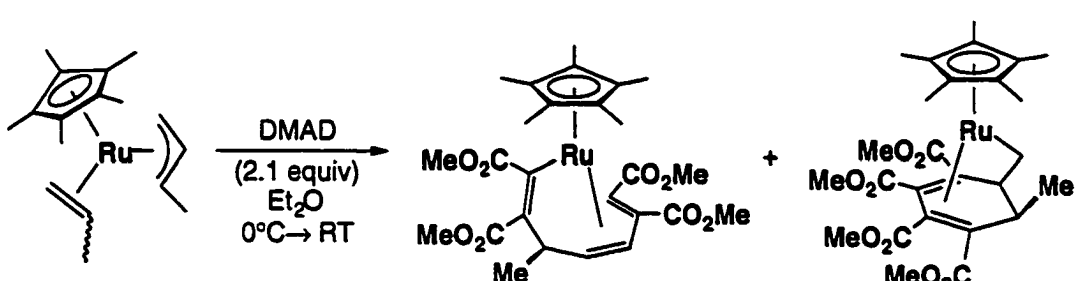
Reaction of $(C_5Me_5)Ru(\eta^3\text{-}1\text{-}MeC_3H_5)(\eta^2\text{-}C_3H_6)$ (314) with Ethyl 2-Butynoate. A small Schlenk flask equipped with a stir-bar and septum was charged with a solution of $(C_5Me_5)Ru(\eta^3\text{-}1\text{-}MeC_3H_5)(\eta^2\text{-}C_3H_6)$ (0.061 g, 0.183 mmol) in 3 mL diethyl ether and the reaction flask cooled to 0°C in an ice bath. Ethyl 2-butynoate (0.047 mL, 0.404 mmol, 2.2 equiv) was then added via microliter syringe. After 2 hours of stirring at 0°C the ice bath was removed and the reaction stirred at room temperature for a further 12 hours, before evaporating the solvent under reduced pressure. The residue was then chromatographed on silica gel using 8% diethyl ether/hexane as eluent, which resulted in the isolation of the minor product **324** as 0.015 g (16%) of an orange crystalline material and of the major product **323** as 0.045 g (48%) of a bright yellow crystalline material.

$(C_5Me_5)Ru$((1:3,4,5,6-η)-1,3-dicarboethoxy-2,4,7-trimethylcycloheptadienyl) (323). (Major Product) ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27 (q, J = 7.2 Hz, 1H, H_2), 4.16 (q, J = 7.1 Hz, 2H, $CO_2C\underline{H}_2CH_3$), 4.155 (d, J = 8.9 Hz, 1H, H_5), 4.00 (2 overlapping quartets, diastereotopic, 2H, $CO_2C\underline{H}_2CH_3$), 3.23 (qd, J = 7.2, 1.8 Hz, 1H, H_{7exo}), 2.62 (dd, J = 8.6, 2.0 Hz, 1H, H_6), 2.27 (s, 3H, CH_3), 1.52 (s, 15H, $C_5\underline{Me}_5$), 1.39 (d, J = 7.2 Hz, 3H, CH_3), 1.31 (t, J = 7.1 Hz, 3H, $CO_2CH_2C\underline{H}_3$), 1.22 (t, J = 7.1 Hz, 3H, $CO_2CH_2C\underline{H}_3$), 0.49 (d, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3 (s, $\underline{C}O_2CH_2CH_3$),

174.5 (s, $\underline{C}O_2CH_2CH_3$), 104.1 (s, C_4), 94.8 (d, J_{CH} = 159 Hz, C_5), 93.9 (s, $\underline{C}_5Me_5$), 59.8 (t, $^1J_{CH}$ = 147 Hz, $CO_2\underline{C}H_2CH_3$), 58.5 (t, $^1J_{CH}$ = 145 Hz, $CO_2\underline{C}H_2CH_3$), 46.9 (d, $^1J_{CH}$ = 156 Hz, C_6), 40.4 (d, $^1J_{CH}$ = 134 Hz, C_2), 37.3 (s, C_3), 34.7 (d, $^1J_{CH}$ = 136 Hz, C_7), 23.3 (q, $^1J_{CH}$ = 127 Hz, CH_3), 22.4 (q, $^1J_{CH}$ = 125 Hz, CH_3), 21.1 (q, $^1J_{CH}$ = 127 Hz, CH_3), 14.55 (q, $^1J_{CH}$ = 126 Hz, $CO_2CH_2\underline{C}H_3$), 14.5 (q, $^1J_{CH}$ = 126 Hz, $CO_2CH_2\underline{C}H_3$), 8.6 (q, $^1J_{CH}$ = 125 Hz, $C_5\underline{Me}_5$), –32.6 (s, C_1); HMQC (300 MHz, $CDCl_3$): δ 94.8 (C_5) ↔ δ 4.155 (H_5); δ 59.8 ($CO_2\underline{C}H_2CH_3$) ↔ δ 4.16 ($CO_2C\underline{H}_2CH_3$); δ 58.5 ($CO_2\underline{C}H_2CH_3$) ↔ δ 4.00 ($CO_2C\underline{H}_2CH_3$); δ 46.9 (C_6) ↔ δ 2.62 (H_6); δ 40.4 (C_2) ↔ δ 4.27 (H_2); δ 34.7 (C_7) ↔ δ 3.23 (H_7); δ 23.3 (CH_3) ↔ δ 2.27 (CH_3); δ 22.4 (CH_3) ↔ δ 0.49 (CH_3); δ 21.1 (CH_3) ↔ δ 1.39 (CH_3); δ 14.55 ($CO_2CH_2\underline{C}H_3$) ↔ δ 1.31 ($CO_2CH_2C\underline{H}_3$); δ 14.5 ($CO_2CH_2\underline{C}H_3$) ↔ δ 1.22 ($CO_2CH_2C\underline{H}_3$); δ 8.6 ($C_5\underline{Me}_5$) ↔ δ 1.52 ($C_5\underline{Me}_5$); MS *m/z* calculated for $C_{26}H_{38}O_4{}^{102}Ru$ (M^+): 516.1813; found: 516.1832 (26.56%); calculated for $C_{23}H_{33}O_2{}^{102}Ru$ (M-$C_3H_5O_2$): 443.1524; found: 443.1517 (100.00%).

(C_5Me_5)Ru((1:4,5,6,7-η)-1,6-dicarboethoxy-2,3,7-trimethylheptatrienyl) (324). ^1H NMR (400 MHz, $CDCl_3$): δ 4.64 (d, *J* = 8.5 Hz, 1H, H_5), 4.26 (q, *J* = 7.1 Hz, 2H, $CO_2C\underline{H}_2CH_3$), 4.22 (2 overlapping quartets, diastereotopic, 2H, $CO_2C\underline{H}_2CH_3$), 3.28 (dd, *J* = 8.5, 6.0 Hz, 1H, H_4), 2.08 (q, *J* = 6.7 Hz, 1H, H_7), 1.73 (d, *J* = 6.7 Hz, 3H, CH_3), 1.69 (qdq, *J* = 7.0, 6.0, 1.1 Hz, 1H, H_3), 1.54 (s, 15H, C_5Me_5), 1.51 (d, *J* = 1.1 Hz, 3H, CH_3), 1.38 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2C\underline{H}_3$), 1.35 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2C\underline{H}_3$), 1.03 (d, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6 (s, $\underline{C}O_2CH_2CH_3$), 171.1 (s, $\underline{C}O_2CH_2CH_3$), 147.2 (s, C_2), 145.9 (s, C_1), 95.1 (s, $\underline{C}_5Me_5$), 90.5 (s, C_6), 83.8 (d, $^1J_{CH}$ = 166 Hz, C_5), 81.0 (d, $^1J_{CH}$ = 150 Hz, C_4), 63.0 (d, $^1J_{CH}$ = 161 Hz, C_3), 60.7 (t, $^1J_{CH}$ = 147 Hz, $CO_2\underline{C}H_2CH_3$), 58.8 (t, $^1J_{CH}$ = 148 Hz, $CO_2\underline{C}H_2CH_3$), 45.0 (d, $^1J_{CH}$ = 129 Hz, C_7), 23.0

(q, $^1J_{CH}$ = 125 Hz, CH_3), 19.2 (q, $^1J_{CH}$ = 127 Hz, CH_3), 16.7 (q, $^1J_{CH}$ = 126 Hz, CH_3), 14.6 (q, $^1J_{CH}$ = 126 Hz, $CO_2CH_2\underline{C}H_3$), 14.3 (q, $^1J_{CH}$ = 126 Hz, $CO_2CH_2\underline{C}H_3$), 8.5 (q, $^1J_{CH}$ = 125 Hz, $C_5\underline{Me}_5$); HMQC (300 MHz, $CDCl_3$): δ 83.8 (C_5) ↔ δ 4.64 (H_5); δ 81.0 (C_6) ↔ δ 3.28 (H_4); δ 63.0 (C_2) ↔ δ 2.08 (H_3); δ 60.7 ($CO_2\underline{C}H_2CH_3$) ↔ δ 4.26 ($CO_2C\underline{H}_2CH_3$); δ 58.8 ($CO_2\underline{C}H_2CH_3$) ↔ δ 4.22 ($CO_2C\underline{H}_2CH_3$); δ 45.0 (C_7) ↔ δ 1.69 (H_7); δ 23.0 (CH_3) ↔ δ 1.03 (CH_3); δ 19.2 (CH_3) ↔ δ 1.51 (CH_3); δ 16.7 (CH_3) ↔ δ 1.73 (CH_3); δ 14.6 ($CO_2CH_2\underline{C}H_3$) ↔ δ 1.35 ($CO_2CH_2C\underline{H}_3$); δ 14.3 ($CO_2CH_2\underline{C}H_3$) ↔ δ 1.38 ($CO_2CH_2C\underline{H}_3$); δ 8.5 ($C_5\underline{Me}_5$) ↔ δ 1.54 ($C_5\underline{Me}_5$); HMBC (300 MHz, $CDCl_3$): δ 176.6 ($\underline{C}O_2CH_2CH_3$) ↔ δ 4.22 ($CO_2CH_2\underline{C}H_3$); δ 171.1 ($\underline{C}O_2CH_2CH_3$) ↔ δ 4.64 (H_5), 4.26 ($CO_2\underline{C}H_2CH_3$), 2.08 (H_3); δ 90.5 (C_6) ↔ δ 3.28 (H_4), 2.08 (H_3), 1.73 (CH_3); δ 83.8 (C_5) ↔ δ 2.08 (H_3); δ 81.0 (C_6) ↔ δ 1.03 (CH_3); δ 63.0 (C_2) ↔ δ 4.64 (H_5), 1.73 (CH_3); δ 60.7 ($CO_2\underline{C}H_2CH_3$) ↔ δ 1.38 ($CO_2CH_2C\underline{H}_3$); δ 58.8 ($CO_2\underline{C}H_2CH_3$) ↔ δ 1.35 ($CO_2CH_2C\underline{H}_3$); δ 45.0 (C_7) ↔ δ 4.64 (H_5), 1.03 (CH_3), 1.51 (CH_3); δ 23.0 (CH_3) ↔ δ 3.28 (H_4), 1.69 (H_7), 1.51 (CH_3); δ 14.3 ($CO_2CH_2\underline{C}H_3$) ↔ δ 4.26 ($CO_2CH_2C\underline{H}_3$).



314 (mixture of isomers) **325** **326**

Reaction of $(C_5Me_5)Ru(\eta^3\text{-}1\text{-}MeC_3H_5)(\eta^2\text{-}C_3H_6)$ (314) with DMAD. A small Schlenk flask equipped with a stir-bar and septum was charged with a solution of $(C_5Me_5)Ru(\eta^3\text{-}1\text{-}MeC_3H_4)(\eta^2\text{-}C_3H_6)$ (0.115 g, 0.345 mmol) in 3 mL diethyl ether and the reaction flask

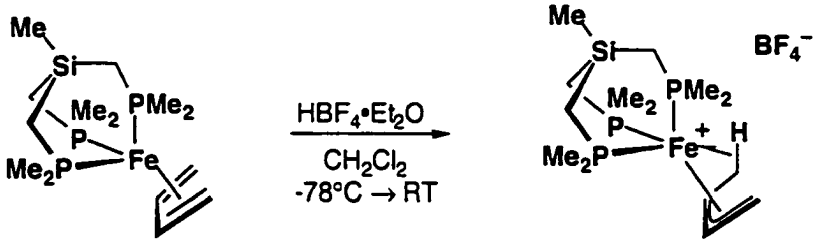
cooled to 0°C in an ice bath. DMAD (0.089 mL, 0.724 mmol, 2.1 equiv) was then added via microliter syringe. After 2 hours of stirring at 0°C the ice bath was removed and the reaction was stirred at room temperature for a further 5 hours, before evaporating the solvent under reduced pressure. The residue was then chromatographed on silica gel using 15% pentane/diethyl ether as eluent, which resulted in the isolation of the major product **325** as 0.163 g (82%) of an orange crystalline material. Analytically pure crystals of this product were obtained by recrystallization using dichloromethane/pentane. The second, minor product **326** was also isolated by chromatography, yielding 0.021 g (11%) of yellow crystalline material.

(C_5Me_5)Ru((1:4,5,6,7-η)-3-methyl-1,2,6,7-tetracarbomethoxyheptatrienyl) (325). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.83 (d, J = 8.7 Hz, 1H, H_5), 3.80 (s, 3H, CO_2CH_3), 3.66 (s, 3H, $CO_2C\underline{H}_3$), 3.65 (s, 3H, $CO_2C\underline{H}_3$), 3.56 (s, 3H, $CO_2C\underline{H}_3$), 3.45 (dd, J = 8.8, 5.1 Hz, 1H, H_4), 2.30 (qd, J = 6.7, 5.2 Hz, 1H, H_3), 1.70 (d, J = 0.7 Hz, 1H, H_7), 1.64 (s, 15H, C_5Me_5), 1.24 (d, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6 (s, C_1), 175.1 (s, $\underline{C}O_2CH_3$), 172.3 (s, $\underline{C}O_2CH_3$), 169.3 (s, $\underline{C}O_2CH_3$), 163.0 (s, $\underline{C}O_2CH_3$), 144.1 (s, C_2), 99.1 (s, $\underline{C}_5Me_5$), 92.7 (s, C_6), 87.0 (d, $^1J_{CH}$ = 167 Hz, C_5), 80.7 (d, $^1J_{CH}$ = 146 Hz, C_4), 58.4 (d, $^1J_{CH}$ = 169 Hz, C_7), 52.5 (q, $^1J_{CH}$ = 145 Hz, $CO_2\underline{Me}$), 51.5 (q, $^1J_{CH}$ = 144 Hz, $CO_2\underline{Me}$), 51.0 (q, $^1J_{CH}$ = 145 Hz, $CO_2\underline{Me}$), 50.7 (q, $^1J_{CH}$ = 146 Hz, $CO_2\underline{Me}$), 41.4 (d, $^1J_{CH}$ = 129 Hz, C_3), 24.3 (q, $^1J_{CH}$ = 128 Hz, C_5), 8.5 (q, $^1J_{CH}$ = 128 Hz, $C_5\underline{Me}_5$); HMQC (300 MHz, $CDCl_3$): δ 87.0 (C_5) ↔ δ 4.83 (H_5); δ 80.7 (C_4) ↔ δ 3.45 (H_4); δ 58.4 (C_7) ↔ δ 1.70 (H_7); δ 52.5 (CO_2Me) ↔ δ 3.80 (CO_2Me); δ 51.5 (CO_2Me) ↔ δ 3.65 (CO_2Me); δ 51.0 (CO_2Me) ↔ δ 3.56 (CO_2Me); δ 50.7 (CO_2Me) ↔ δ 3.66 (CO_2Me); δ 41.4 (C_3) ↔ δ 2.30 (H_3); δ 24.3 (CH_3) ↔ δ 1.24 (CH_3); δ 8.5 (C_5Me_5) ↔ δ 1.64

(C_5Me_5); HMBC (300 MHz, $CDCl_3$): δ 176.6 (C_1) ↔ δ 2.30 (H_3); δ 175.1 ($\underline{C}O_2Me$) ↔ δ 3.66 ($CO_2\underline{Me}$); δ 172.3 ($\underline{C}O_2Me$) ↔ δ 3.65 ($CO_2\underline{Me}$); δ 169.3 ($\underline{C}O_2Me$) ↔ δ 4.83(H_5), 3.80 ($CO_2\underline{Me}$), 1.70 (H_7); δ 163.0 ($\underline{C}O_2Me$) ↔ δ 3.56 (CO_2Me); δ 144.1 (C_2) ↔ δ 2.30 (H_3), 1.24 (CH_3); δ 92.7 (C_6) ↔ δ 3.45 (H_4); δ 87.0 (C_5) ↔ δ 2.30 (H_3), 1.70 (H_7); δ 80.7 (C_4) ↔ δ 4.83 (H_5), 2.30 (H_3), 1.24 (CH_3); δ 58.4 (C_7) ↔ δ 4.83 (H_5); δ 41.4 (C_3) ↔ δ 4.83 (H_5), 1.24 (CH_3); δ 24.3 (CH_3) ↔ δ 3.45 (H_4), 2.30 (H_3). Analysis calculated for $C_{26}H_{34}O_8Ru$: C, 54.25%; H, 5.95%; found: C, 54.31%; H, 5.99%.

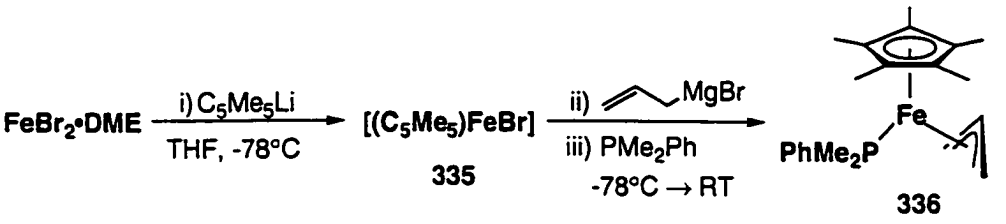
(C_5Me_5)Ru((1:4,5,6,7-η)-3-methyl-4,5,6,7-tetracarbomethoxymethanocyclo-hexadienyl) (326). ^1H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 3H, CO_2Me), 3.77 (s, 3H, CO_2Me), 3.68 (s, 3H, CO_2Me), 3.64 (dd, J = 4.7, 1.9 Hz, 1H, H_2), 3.60 (s, 3H, CO_2Me), 2.25 (qd, J = 6.7, 2.0 Hz, 1H, H_3), 1.56 (s, 15H, C_5Me_5), 1.19 (dd, J = 4.9, 2.8 Hz, 1H, H_{1a}), 0.98 (d, J = 2.8 Hz, 1H, H_{1b}), 0.78 (d, J = 6.7 Hz, 3H, CH_3); ^1H-^1H GCOSY (300 MHz, $CDCl_3$, each correlation only listed once): δ 3.64 (H_2) ↔ 2.25 (H_3), 1.19 (H_{1a}); δ 2.25 (H_3) ↔ 0.78 (CH_3); δ 1.19 (H_{1a}) ↔ 0.98 (H_{1b}); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.5 ($\underline{C}O_2Me$), 171.2 ($\underline{C}O_2Me$), 169.2 ($\underline{C}O_2Me$), 167.6 ($\underline{C}O_2Me$), 97.6 ($\underline{C}_5Me_5$), 97.1 (C_6), 85.6 (C_5), 60.8 (C_4), 52.7 ($CO_2\underline{Me}$), 52.5 ($CO_2\underline{Me}$), 51.6 ($CO_2\underline{Me}$), 51.2 ($CO_2\underline{Me}$), 49.3 (C_2), 34.8 (C_7), 31.6 (C_3), 17.9 (CH_3), 8.9 ($C_5\underline{Me}_5$), –2.8 (C_1); HMQC (300 MHz, $CDCl_3$): δ 52.7 (CO_2Me) ↔ δ 3.77 (CO_2Me); δ 52.5 (CO_2Me) ↔ δ 3.80 (CO_2Me); δ 51.6 (CO_2Me)↔ δ 3.68 (CO_2Me); δ 51.2 (CO_2Me) ↔ δ 3.60 (CO_2Me); δ 49.3 (C_2) ↔ δ 3.64 (H_2); δ 31.6 (C_3) ↔ δ 2.25 (H_3); δ 17.9 (CH_3) ↔ δ 0.78 (CH_3); δ 8.9 (C_5Me_5) ↔ δ 1.56 (C_5Me_5); δ –2.8 (C_1) ↔ δ 1.19, 0.98 (H_{1a} and H_{1b}); HMBC (300 MHz, $CDCl_3$): δ 172.5 ($\underline{C}O_2Me$) ↔ δ 3.60 ($CO_2\underline{Me}$), 2.25 (H_3); δ

171.2 ($\underline{C}O_2Me$) ↔ δ 3.68 ($CO_2\underline{Me}$); δ 169.2 ($\underline{C}O_2Me$) ↔ δ 3.80 ($CO_2\underline{Me}$); δ 167.6 ($\underline{C}O_2Me$) ↔ δ 3.77 ($CO_2\underline{Me}$); δ 85.6 (C_5) ↔ δ 2.25 (H_3); δ 60.8 (C_4) ↔ δ 0.78 (CH_3), 2.25 (H_3); δ 49.3 (C_2) ↔ δ 0.78 (CH_3), 2.25 (H_3); δ 34.8 (C_7) ↔ δ 2.25 (H_3), 1.19 (H_{1a}), 0.98 (H_{1b}); δ 31.6 (C_3) ↔ δ 0.78 (CH_3), 1.19 (H_{1a}), 0.98 (H_{1b}); δ 17.9 (CH_3) ↔ δ 2.25 (H_3); δ –2.8 (C_1) ↔ δ 2.25 (H_3).

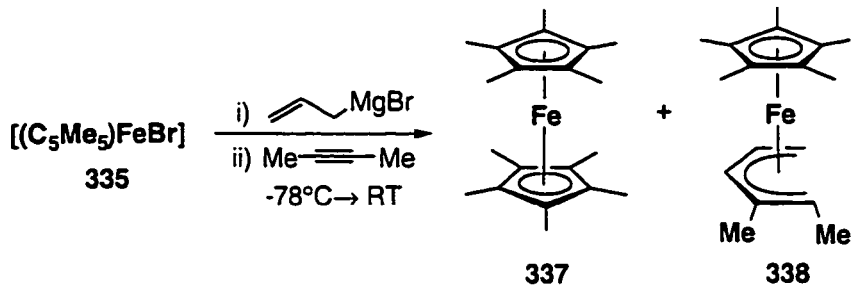


333 334

[(MeSi(CH$_2$PMe$_2$)$_3$)Fe(η^3-1-MeC$_3$H$_4$)]$^+$BF$_4^-$ (334). A yellow solution of (MeSi(CH$_2$PMe$_2$)$_3$)Fe(η^4-1,3-butadiene) (0.020 g, 0.053 mmol) in 3.0 mL anhydrous dichloromethane was placed in a small Schlenk flask equipped with a stir-bar and a septum and the reaction cooled to –78°C using a dry ice/acetone bath. Tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) was then added via microliter syringe (0.005 mL, 0.056 mmol). The reaction was then slowly warmed to room temperature, during which time the reaction mixture turned deep red in colour. After stirring at room temperature for another 30 minutes, the solvent was removed under reduced pressure to provide a red solid residue. The flask was removed to the drybox where the residue was broken up, rinsed with diethyl ether, then filtered to collect 0.021 g (85%) of red powder. The crude product was used without further purification. ^{1}H NMR (300 MHz, acetone-d$_6$): δ 5.33 (br s, 2H), 2.10-1.48 (br m, 20H), 1.38-1.20 (br m, 6H), 0.72 (br d, J = 14.4 Hz, 2H, -C<u>H$_2$</u>PMe$_2$), 0.26 (s, 3H, -Si<u>Me</u>), –6.07 (br s, 3H, Me$_{ag}$).

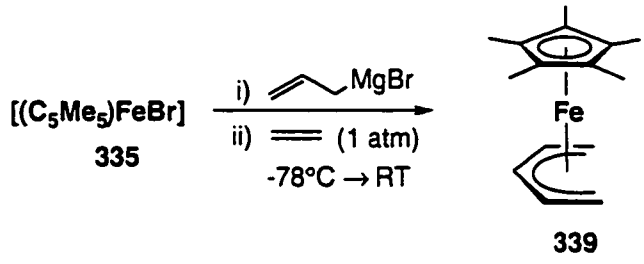


$(C_5Me_5)Fe(\eta^3\text{-}C_3H_5)(PMe_2Ph)$ (336). A suspension of C_5Me_5Li (0.070 g, 0.492 mmol, equiv) in 3 mL THF was placed in a small Schlenk flask equipped with a stir-bar and septum and rapidly stirred at room temperature for 20 minutes. A solution of $FeBr_2$•DME (0.150 g, 0.491 mmol) in 10 mL THF was prepared in a second Schlenk flask and both flasks were then cooled to –78°C using a dry ice/acetone bath. The C_5Me_5Li suspension was slowly transferred via cannula to the cold iron solution and stirred for another 20 minutes at –78°C before adding allylmagnesium bromide (2.0 M in THF, 0.27 mL, 0.54 mmol, 1.1 equiv) via microliter syringe. After stirring for 10 minutes dimethylphenylphosphine (0.075 mL, 0.53 mmol, 1.07 equiv) was added by microliter syringe and the reaction was slowly warmed to room temperature. The reaction mixture was stirred at room temperature for a one hour (turning dark orange) before removing the solvent *in vacuo*. In the drybox the residue was triturated with 3 x 3 mL pentane and the combined pentane extracts filtered through Celite and dried to an orange oil. The crude product was then redissolved in pentane and filtered through a plug of alumina (5% H_2O). After evaporation of pentane the known[151a] complex **336** was obtained as an orange solid (0.131 g, 72%).



(C_5Me_5)Fe(η^5-1,2-dimethylpentadienyl) (338). A suspension of C_5Me_5Li (0.070 g, 0.492 mmol, 1.0 equiv) in 3 mL THF was placed in a small Schlenk flask equipped with a stir-bar and septum and rapidly stirred at room temperature for 20 minutes. A solution of $FeBr_2$•DME (0.150 g, 0.491 mmol) in 10 mL THF was prepared in a second Schlenk flask and both flasks were then cooled to –78°C using a dry ice/acetone bath. The C_5Me_5Li suspension was slowly transferred via cannula to the cold iron solution and stirred for 20 minutes at –78°C. 2-Butyne (0.30 mL, 3.8 mmol, 7.8 equiv) was then added via microliter syringe and the reaction mixture stirred for 40 minutes before adding allylmagnesium bromide (2.0 M in THF, 0.27 mL, 0.54 mmol, 1.1 equiv) by syringe. The reaction was slowly warmed to room temperature and stirred for one hour before removing the solvent *in vacuo*. In the drybox the residue was triturated with 3 x 3 mL pentane and the pentane extracts filtered through Celite and dried to an orange oil. The crude product was then redissolved in pentane and filtered through a plug of alumina (5% H_2O). The filtrate was dried to yield an orange solid; analysis of this crude material by ^1H NMR spectroscopy indicates a mixture of decamethylferrocene **337** and complex **338** in a ratio of approximately 2 : 1. No further attempt was made to separate the products. ^1H NMR (300 MHz, C_6D_6): δ 4.68 (d, J = 5.6 Hz, 1H, H_3), 3.58 (td, J = 8.9, 5.7 Hz, 1H, H_4), 2.14 (dd, J = 9.0, 3.0 Hz, 1H, H_{5syn}), 1.86 (s, 3H, CH_3) 1.57 (s, 15H, C_5Me_5), 0.58 (d,

J = 5.9 Hz, 3H, CH_3), –0.06 (dd, J = 9.0, 3.0 Hz, 1H, H_{5anti}), –0.93 (q, J = 6.1 Hz, 1H, H_1).



339

(C_5Me_5)Fe(η^5-pentadienyl) (339). A suspension of C_5Me_5Li (0.070 g, 0.492 mmol, 1.0 equiv) in 3 mL THF was placed in a small Schlenk flask equipped with a stir-bar and septum and rapidly stirred at room temperature for 20 minutes. A solution of $FeBr_2$•DME (0.150 g, 0.491 mmol) in 10 mL THF was prepared in a second Schlenk flask and both flasks were then cooled to –78°C using a dry ice/acetone bath. The C_5Me_5Li suspension was slowly transferred via cannula to the iron solution and stirred for 20 minutes at –78°C. Ethylene was then bubbled through the solution for 5 minutes and the reaction stirred at –78°C for 40 minutes, before adding allylmagnesium bromide (2.0 M in THF, 0.27 mL, 0.54 mmol, 1.1 equiv) by syringe. The reaction was slowly warmed to room temperature and stirred for 3 hours before removing the solvent *in vacuo*. In the drybox the residue was triturated with 3 x 3 mL pentane and the pentane extracts filtered through Celite and dried to an red oil. The crude product was then redissolved in pentane and filtered through a plug of alumina (5% H_2O) and the filtrate dried to yield an oily red solid. Analysis of this crude material by ^1H NMR spectroscopy indicates it primarily consists of complex **339** with traces of decamethylferrocene. No further purification was attempted. ^1H NMR (300 MHz, C_6D_6): δ 4.73 (t, J = 5.7 Hz, 1H,

H_3), 3.82 (td, J = 9.8, 5.8 Hz, 2H, $H_{2/4}$), 2.13 (dd, J = 9.6, 2.8 Hz, 2H, $H_{1syn/5syn}$), 1.26 (s, 15H, $C_5\underline{Me}_5$), –0.42 (dd, J = 10.1, 3.0 Hz, 2H, $H_{1anti/5anti}$).

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