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THE UNIVERSITY OF ALBERTA

SYNTHESIS AND REACTIVITY OF CYCLOHEPTATRIENYL-BRIDGED HETEROBIMETALLIC COMPLEXES.

by

STEPHEN THOMAS ASTLEY ©

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA
SPRING, 1990

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Dated 24 November 1989

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The Undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled SYNTHESIS AND REACTIVITY OF CYLCLOHEPTATRIENYL-BRIDGED HETEROBIMETALLIC COMPLEXES submitted by STEPHEN T. ASTLEY in partial fulfillment of the requirements for the degree of Doctor of Philospophy in Chemistry.

Supervisor, J. Takats

M. Cowie

S.W. Wanke

A.D. Hunter

H.J. Liu

T. Bitterwolf
External Examiner

Date November 20, 1989.

Abstract.

The utility of the anionic complexes, $(\eta^3\text{-}C_7H_7)M(CO)_3^-$ (M = Ru, Os) for the preparation of cycloheptatrienyl bridged heterobimetallic compounds has been investigated.

Thus, $(\eta^3\text{-}C_7H_7)Ru(CO)_3^-$ reacts with $[Ir(COD)Cl]_2$ (COD = 1,5 cyclooctadiene) to give *cis*-$(\mu\text{-}\eta^3,\eta^4\text{-}C_7H_7)Ru(CO)_3Ir(COD)$, which contains a Ru-Ir bond with both Ru and Ir bonded to the same face of the seven-membered ring. Displacement of the COD ligand from Ir by CO yielded *cis*-$(\mu\text{-}\eta^3,\eta^4\text{-}C_7H_7)Ru(CO)_3Ir(CO)_2$. The latter compound reacts with dppm to give *cis*-$(\mu\text{-}\eta^3,\eta^4\text{-}C_7H_7)(\mu\text{-dppm})Ru(CO)_2Ir(CO)$, and with PPh_3 via substitution of CO at Ir. This completed a series of complexes, *cis*-$(\mu\text{-}\eta^3,\eta^4\text{-}C_7H_7)M(CO)_3M'(CO)PPh_3$ (M=Fe,Ru; M'=Rh,Ir) in which the rate of intermetallic carbonyl exchange increases upon descending a triad for M and M'.

In contrast to the reactivity of the anionic Ru complex, $(\eta^3\text{-}C_7H_7)Os(CO)_3^-$ reacts with the transition metal electrophiles $[M(COD)Cl]_2$ (M = Rh, Ir) to give initially, the unsaturated trans cycloheptatrienyl bridged heterobimetallic complexes *trans*-$(\mu\text{-}\eta^4,\eta^3\text{-}C_7H_7)Os(CO)_3M(COD)$ in which the two metals are on opposite faces of the C_7H_7 ligand. The trans OsRh complex was isolated and fully characterized. Interestingly it undergoes isomerization to give its coordinatively saturated cis isomer, which contains a metal-metal bond. In addition, the trans OsRh complex reacts rapidly with

dppm to give the cis dppm bridged complex $(\mu-\eta^3,\eta^4-C_7H_7)(\mu-dppm)Os(CO)_2Rh(CO)$.

In order to probe the reasons for the different reactivity of the anionic Ru and Os complexes, $(\eta^3-C_7H_7)M(CO)_3^-$, the solid-state and solution structure (of the $AsPh_4^+$ salt) of the two complexes were investigated. It was found that the ground state structure of both complexes contains an η^3-bonded C_7H_7 ring. This was taken to imply that subtle differences in the metal to $(\eta^3-C_7H_7)$ ligand bonding may account for the observed differences in reactivity.

The reactivity of *cis*-$(\mu-C_7H_7)Ru(CO)_3Rh(CO)_2$ and *cis*-$(\mu-C_7H_7)Ru(CO)_3Ir(CO)_2$ toward alkynes [hexafluoro-2-butyne (HFB), acetylene] was also investigated and proved to be both metal and alkyne dependent. The RuRh complex reacts at room temperature with HFB by addition of one alkyne unit. In contrast, the reaction of the RuIr complex with HFB requires thermal activation and results in CO substitution via the uptake of two HFB molecules. A similar reaction occurs between the RuRh complex and C_2H_2 at room temperature. In all three cases, alkyne insertion between Ru and the C_7H_7 ring occurred.

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List of Abbreviations

AGDP	anisotropic Gaussian displacement parameter
br	broad
Bu	butyl (C_4H_9)
^{t}Bu	tert-butyl [$C(CH_3)_3$]
C.I.	chemical ionization
CHT	cycloheptatriene (C_7H_8)
COD	1,5-cyclooctadiene
COT	cyclooctatetraene (C_8H_8)
Cp	cyclopentadienyl (C_5H_5)
Cp*	pentamethylcyclopentadienyl (C_5Me_5)
Cp'	methylcyclopentadienyl (C_5H_4Me)
d	doublet
dippe	1,2-bis(diisopropylphosphino)ethane
dmad	dimethyl acetylenedicarboxylate [$C_2(CO_2CH_3)_2$]
dppm	bis(diphenylphosphino)methane [$(Ph_2P)_2CH_2$]
E.I.	electron impact
Et	ethyl
FAB	fast atom bombardment
Fv	fulvalene
HFB	hexaflouro-2-butyne
IR	infrared
m	medium (with reference to IR spectra)
m	multiplet (with reference to NMR spectra)
m.p.	melting point

MS	mass spectrometry
Me	methyl
NBD	norbornadiene (C_7H_8)
NMR	nuclear magnetic resonance
Ph	phenyl
PPM	parts per million
PPN	bis(triphenylphosporanylidene)ammonium $[(Ph_3P)_2N]^+$
^{i}Pr	iso-propyl $[CH(CH_3)_2]$
q	quartet
s	strong (with reference to IR spectra)
s	singlet (with reference to NMR spectra)
sp	septet
t	triplet
THF	tetrahydrofuran
TMS	tetramethylsilane $[Si(CH_3)_4]$
w	weak
v	very

Chapter 1

Introduction.

1.1. Background to Dinuclear Transition metal Chemistry.

In the framework of organotransition metal chemistry, bimetallic compounds occupy a central position bridging the chemical properties of mononuclear transition metal compounds and transition metal clusters (and metal surfaces). For this reason, fundamental studies on bimetallic complexes are essential to obtain a global understanding of the bonding, reactivity and applications offered by transition metal organometallic compounds.

Probably the most important industrial application of transition metal compounds today is in catalysis[1]. In this regard, it is hoped that the chemistry of dinuclear complexes may combine the properties of metal-surfaces (used in heterogeneous catalysis) and soluble mononuclear transition metal complexes (widely used as homogeneous catalysts). Hence, the presence of adjacent metal sites coupled with the ability to dissolve in organic solvents may provide special reactivity which is not seen in mononuclear complexes. The ultimate goal of such studies is to provide a smooth and logical progression from the chemistry of mononuclear compounds through bimetallic compounds to metal clusters and ultimately to metal surfaces[2].

Two of the many useful chemical transformations currently known to occur through bimetallic compounds are C-C coupling, and dinuclear reductive elimination of H_2 (equation 1-1)[3]. Additionally, there are

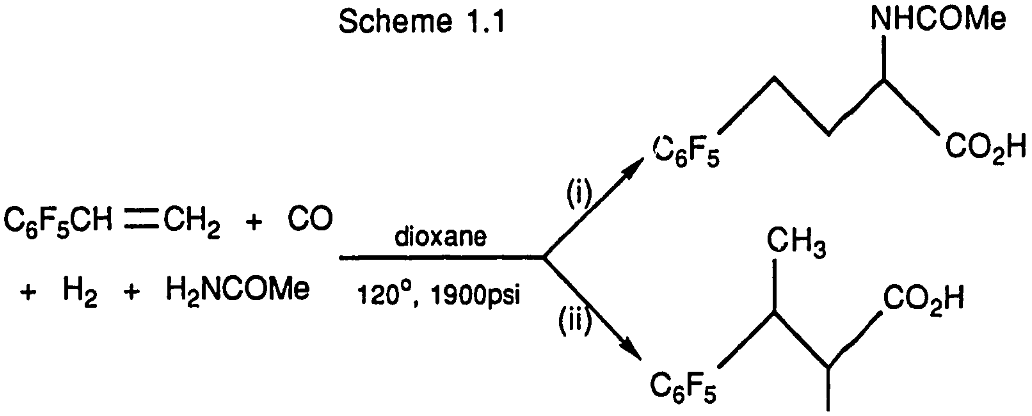
$$\underset{H}{\underset{|}{L_nM}} — \underset{H}{\underset{|}{ML_n}} \longrightarrow \text{"}L_nM — ML_n\text{"} + H_2 \qquad (1\text{-}1)$$

already some examples of homodinuclear compounds which are active in catalytic cycles. For example, dinuclear Rh complexes act as homogenous catalysts for the hydrogenation and hydroformylation of olefins, and the hydrogenation and cyclotrimerization of alkynes[4]. A further benefit of studying dinuclear compounds is that the new chemistry discovered may have applications in organic synthesis[5].

A logical extension of the work centred on homodinuclear compounds is to study the chemistry of heterodinuclear compounds. Heteronuclear (or mixed metal) compounds are particularly interesting as a result of potentially combining the different reactivity properties of the constituent metals. In addition, the nature of the products may provide clues to the adopted reaction pathways, and hence to the role played by the individual metals. Therefore, these complexes are potentially very useful for catalysis, or for modelling catalytic reactions, since every catalytic transformation involves a number of steps and it is unlikely that the maximum selectivity and yield for each step will be obtained from one individual metal[6].

One recent example of a mixed-metal system which proved to have different properties than the constituent homometallic systems is provided by the $Co_2(CO)_8/Rh_6(CO)_{16}$ catalysed hydroformylation-amidocarbonylation of pentafluorostyrene (PFS)[7] (Scheme 1.1):

Scheme 1.1



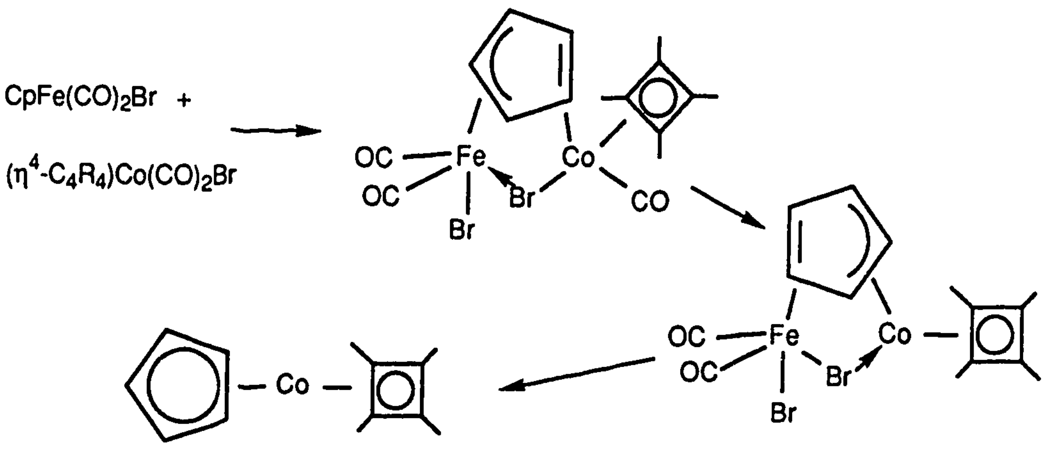
(i) $Co_2(CO)_8$; (ii) $Co_2(CO)_8/Rh_6(CO)_{16} = 50$.

The hydroformylation-amidocarbonylation of PFS using $Co_2(CO)_8/Rh_6(CO)_{16}$ led predominantly to the branched chain product (path ii) with 80 % regioselectivity. In contrast, $Co_2(CO)_8$ catalysis led to the straight chain product (path i) with 90 % regioselectivity. In the mixed-metal system it was determined that the unsaturated heterodinuclear complex $CoRh(CO)_7$ is an active species in the formation of the branched chain product[7].

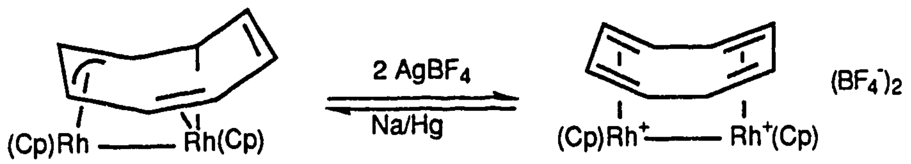
1.2. Bimetallic Compounds containing Cyclic Polyolefinic Bridging Ligands.

There are several benefits to a polyolefinic bridging-ligand system. In addition to holding the two metals in close proximity to one another as a reaction proceeds, polyolefin type bridging units also have the ability to create sites of unsaturation by allowing ring slippage to occur[8]. This property, when combined with rearrangement of the remaining ligands can lead to a variety of possible coordination modes. Hence, the incipient coordinative unsaturation allows associative reaction pathways to occur, and the variable coordination modes accessible to the polyolefinic ligand thus allows a myriad of different reaction pathways. The extreme case of an olefinic bridging ligand changing bonding mode between two metals is provided by complete transfer of a cyclopentadienyl ligand from Fe to Co[9]. The proposed mechanism is shown below.

Scheme 1.2

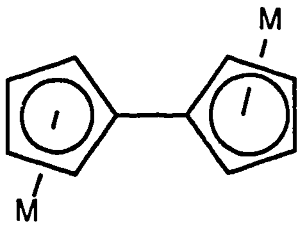


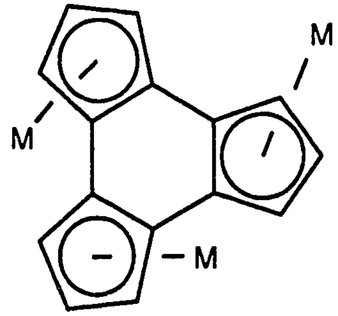
Clearly, depending on the ligand system adopted and the transition metal complexes used a variety of different structural types can be obtained. An interesting example of a bridging ligand adapting its bonding mode to suit the electronic requirements of the two coordinated metals is provided by the redox behaviour of the bis(cyclopentadienyl rhodium) cyclooctatetraene complex[10]:



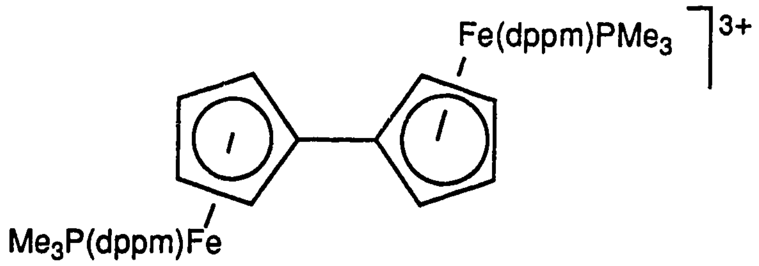
(1-2)

In addition to cyclooctatetraene, there are examples known of dinuclear complexes bridged by cycloheptatrienyl (*vide infra*), benzene[11], and cyclopentadienyl[12] ligands. Ligands which contain more than one unsaturated ring system, either fused[13] or linked by one[14] or more[15] methylene units are also known. The fulvalene (Fv) ligand system which contains two cyclopentadienyl ligands linked by a C-C bond has been studied by several groups[16], and is shown below. One of the more complicated ligand systems being studied which is related to fulvalene is the tridentate trindenyl ligand[17]:

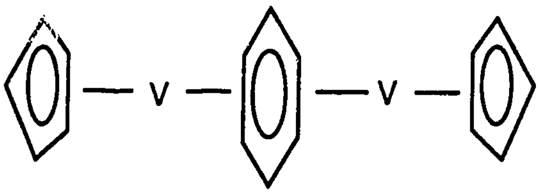




A further useful property of polyolefinic ligands is the ability to stabilise complexes that are coordinatively unsaturated or contain an odd number of electrons[8c,16a-d,18]. This is particularly useful in dinuclear complexes as it enables complexes of mixed oxidation states to be prepared. One example of this is provided by the fulvalene complex, $Fe_2(Fv)(dppm)_2(PMe_3)_2{}^{3+}$ (dppm = bis(diphenylphosphino)methane), which exists as a delocalised mixed valence compound[16a].

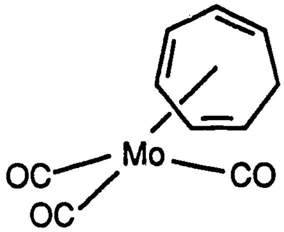


The ability to bind transition metals in a trans fashion where the two metals occupy opposite faces of the ligand is also useful as it affords possible synthetic routes to triple-decker complexes and organometallic polymers[13c,16e,19]. An interesting example of a symmetrical triple decker complex which contains only cyclic hydrocarbon ligands is the vanadium benzene complex shown below[12g].

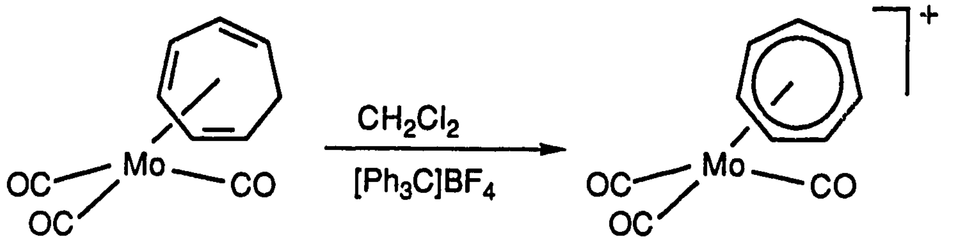


1.3. The Cycloheptatriene (C_7H_8) and Cycloheptatrienyl (C_7H_7) Ligand System.

The first cycloheptatriene metal complex[20], (η^6-C_7H_8)Mo(CO)$_3$ was prepared in 1958 at a time when organometallic chemistry was in its infancy but undergoing a very rapid development[21].



Since that time, a very large number of olefinic and polyolefinic transition metal complexes have been synthesised and studied[22]. Within this category of compounds, although not as widely studied as the cyclopentadienyl ligand[23], cycloheptatriene and related ligands now have an extensive and varied story of their own[24]. Apart from the η^6 coordination mode observed in (η^6-C_7H_8)Mo(CO)$_3$, cycloheptatriene (CHT) is known to coordinate to single metal centres in η^4 and η^2 fashions. In these bonding modes, one and two double bonds are uncoordinated respectively. In addition, cycloheptatriene complexes may be used for the preparation of cycloheptatrienyl (C_7H_7) complexes by the abstraction of a hydride ion from the coordinated cycloheptatriene ligand[25]:



(1-3)

In cationic complexes such as (η-C_7H_7)Mo(CO)$_3^+$ (shown above), the C_7H_7 ligand may best be regarded as a coordinated tropylium ($C_7H_7^+$) ligand. Free tropylium exists in salts such as $C_7H_7^+Br^-$ which are stable solids due to the aromaticity of the seven-membered ring[26]. However, they will react with nucleophiles such as OH^-. For instance, when dissolved in H_2O, C_7H_7Br displays an acidity (Ka = 1.8×10^{-5}) which is close to that of acetic acid[26].

$$C_7H_7^+ + 2H_2O \rightleftharpoons C_7H_7OH + H_3O^+ \qquad (1\text{-}4)$$

This reactivity is not always replicated in cationic transition complexes due to a decrease in electrophilicity of the seven-membered ring[27]. Thus, (C_7H_7)Mo(CO)$_3^+$, is much less reactive with H_2O than is free tropylium[27]. Tropylium salts may, in some cases, be used for the direct preparation of cycloheptatrienyl transition metal compounds[28] (e.g. equation 1.5).

$$CpFe(CO)_2^- + C_7H_7BF_4 \longrightarrow CpFe(CO)(\eta^3\text{-}C_7H_7) + BF_4^- \qquad (1\text{-}5)$$

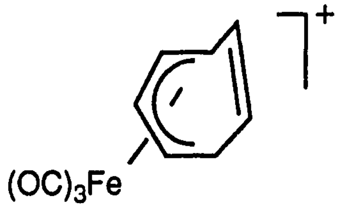
However, in many cases these reactions do not work and instead electron transfer reactions occur leading to the stable ditropyl, $(C_7H_7)_2$. Because of this property, tropylium bromide may be used as an oxidising agent in the preparation of $[CpCr(CO)_3]_2$:[29]

$$Na[CpCr(CO)_3] \quad + \quad C_7H_7Br \quad \text{----->} \quad [CpCr(CO)_3]_2 \quad + \quad NaBr \quad + \quad (C_7H_7)_2 \qquad (1\text{-}6)$$

Cycloheptatrienyl transition metal complexes can also be prepared by removal of a proton from coordinated cycloheptatriene complexes:[30]

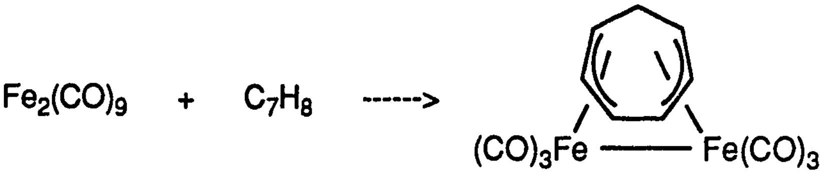
$$(\eta^4\text{-}C_7H_8)Fe(CO)_3 \quad + \quad BuLi \quad \text{------>} \quad Li(\eta^3\text{-}C_7H_7)Fe(CO)_3 \quad + \quad BuH \qquad (1\text{-}7)$$

This contrasts with the known reactivity of cycloheptatriene which has proven difficult to deprotonate[31]. In fact, a satisfactory synthetic route to the cycloheptatrienide anion does not exist[31]. If one considers $(C_7H_7)Fe(CO)_3^-$ to be a coordinated complex of $C_7H_7^-$, this then provides one of the many examples of an organic fragment being stabilised upon coordination to a transition metal centre. Interestingly a related tropylium complex, $[(\eta^5\text{-}C_7H_7)Fe(CO)_3][BF_4^-]$ is also known:[27b]



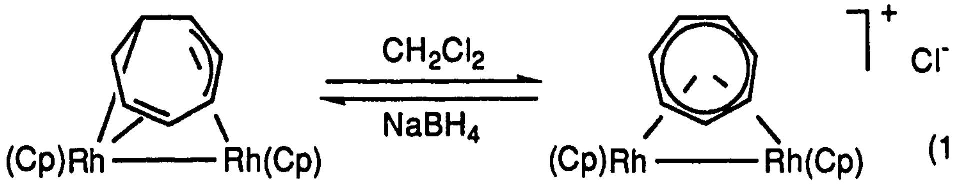
As indicated, in these examples, and in accord with the 18-electron rule[32], the seven-membered ring is not attached to iron via all seven carbon atoms but is bonded in an η^3 and η^5 mode respectively. The different bonding mode represents the ligand's abilty to change its bonding mode according to the electronic requirements of the constituent parts of the molecule and to allow charge delocalization onto the transition metal centre. This charge delocalization is also demonstrated in the average carbonyl stretching frequencies of $(\eta^5\text{-}C_7H_7)Fe(CO)_3^+$, $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ and $(\eta^3\text{-}C_7H_7)Fe(CO)_3^-$ which are 2095, 2025 and 1905 cm^{-1} respectively. The dramatic effect on the carbonyl groups clearly demonstrates that the positive or negative charge in the ionic complexes is not solely residing upon the seven membered ring but that a modest distribution of charge occurs over the entire molecule. Apart from the η^5 and η^3 bonding modes of the C_7H_7 ligand as mentioned above, η^7 and η^1 bonding modes are also known[24].

Dinuclear complexes of CHT or C_7H_7 are also known. However, the first, and still the majority of compounds of this class are homodinuclear complexes. These complexes can be prepared by reaction of the parent ligand with the respective bi- or polymetallic compound[33] (equation 1-8).



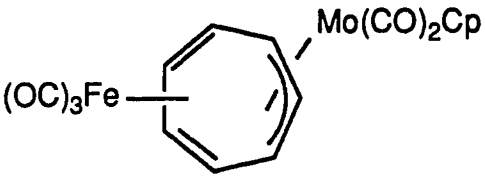
(1-8)

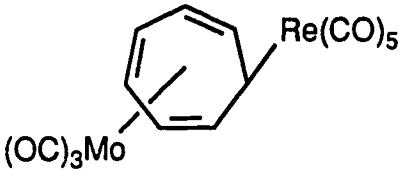
Dinuclear cycloheptatrienyl-bridged complexes may also be prepared via abstraction of a hydride from a coordinated CHT ligand. This reaction is illustrated for a dinuclear Rh complex (equation 1-9)[34].



(1-9)

The most common coordination mode of the μ-C_7H_7 ligand involves coordination of three carbon atoms to one metal centre and four carbon atoms to the second metal centre with both metals being on the same face of the ring (i.e. a cis η^3,η^4- bonding mode). Several examples of this type of coordination are mentioned in Section 1.5. Examples of dinuclear cycloheptatrienyl complexes in which two metals are on the opposite faces of the seven-membered ring in *trans*-(η^3,η^4-)[35] or *trans*-(η^1,η^6-) coordination modes[36] are also known (see below).





1.4. Typical Preparations of Heterobimetallic Compounds.

Of the wide variety of synthetic strategies used to produce heterobimetallic complexes[6a], one of the most commonly used involves a ligand substitution reaction at a mononuclear metal centre. This methodology includes substitution of an anionic ligand by an anionic metal complex (equation 1-10)[37], addition reactions, [where a second neutral metal can take the role of a ligand (equation 1-11)][38], and bridge assisted substitution reactions (equation 1-12)[39].

$$Cp'(OC)_2(SiPh_3)Mn^- \quad + \quad Cp(OC)_2FeI \quad \text{---->} \quad Cp'(SiPh_3)(OC)_2MnFeCp(CO)_4 \qquad (1\text{-}10)$$

$$Os(CO)_4PMe_3 \quad + \quad W(CO)_5THF \quad \text{-------->} \quad (OC)_5WOs(CO)_4PMe_3 \qquad (1\text{-}11)$$

$$Fe(CO)_3(PPh_2H)PPh_2^- \quad + \quad 0.5[Ir(COD)Cl]_2 \quad \text{---->} \quad (OC)_3Fe(\mu\text{-}PPh_2)_2IrH(COD) \qquad (1\text{-}12)$$

In this last strategy a bi- or poly-dentate ligand initially coordinated to only one metal is used to form a bridge in the reaction. The most commonly used bridging ligands are polyphosphines, however the method also works for other ligands including polyolefinic compounds.

One ligand that has played an extensive role in the development of the chemistry of bridged dinuclear complexes is the bridging diphosphine ligand, bis(diphenylphosphino)methane (dppm)[40]. Recently this ligand has also been utilised for the preparation of heterobimetallic compounds. In this effort, the mononuclear iron compound, $Fe(CO)_4(\eta^1\text{-dppm})$ has been used for the preparation of many bimetallic compounds including $(OC)_4Fe(\mu\text{-dppm})RhCl(CO)$[41] (equation 1-13). In our group, the mononuclear compound $Ru(CO)_4(\eta^1\text{-dppm})$ has recently been prepared, and its reaction with $[Rh(CO)_2(solv)_2]^+$ has also been reported[42].

$$Fe(CO)_4(\eta^1\text{-dppm}) \quad + \quad [Rh(CO)_2Cl]_2 \quad \text{------>} \quad (OC)_4Fe(\mu\text{-dppm})RhCl(CO) \qquad (1\text{-}13)$$

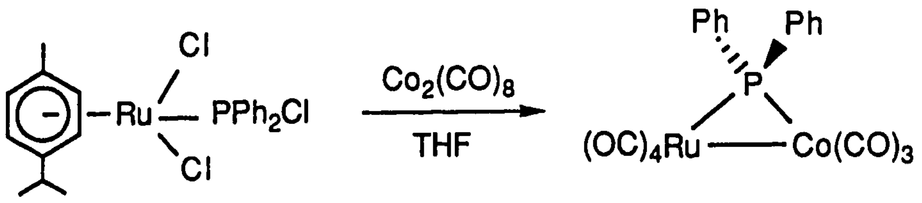
$$\mathrm{Ru(CO)_4(\eta^1\text{-}dppm)} \quad + \quad \mathrm{[Rh(CO)_2(solv)_2]^+} \dashrightarrow \mathrm{(OC)_4Ru(\mu\text{-}dppm)Rh(CO)_2^+} \qquad (1\text{-}14)$$

In related work, Poilblanc has used $RuH_2(dppm)_2$ as a starting material for the synthesis of heterobimetallic compounds. Reaction with $[Rh(COD)Cl]_2$ and $[Ir(COD)Cl]_2$ yielded dinuclear compounds containing bridging and chelating dppm ligands[43] (equation 1-15). A similar chelate ring opening

$$\mathrm{RuH_2(dppm)_2} \; + \; \underset{M = Rh,\, Ir}{\mathrm{[M(COD)Cl]_2}} \dashrightarrow \mathrm{(dppm)HRu(\mu\text{-}dppm)(\mu\text{-}Cl)(\mu\text{-}H)M(COD)} \qquad (1\text{-}15)$$

was seen in the reaction of $OsCl_2(dppm)_2$ with $[Rh(CO)_2Cl]_2$[44] to give $Cl_2Os(\mu\text{-}CO)_2(\mu\text{-}dppm)_2RhCl$. These reactions are surprising due to the general inertness of octahedrally coordinated bis dppm complexes of d^6 transition metals[44] and presumably reflect the thermodynamic driving force of the reaction.

A different phosphorous containing ligand that is commonly used to bridge metal-metal bonds is the phosphido group[6a,39]. In similar fashion to polyolefinic species, this ligand has the ability to adjust its coordination mode as it donates one electron to one metal in a P-M σ-bond and donates two electrons from the lone pair of electrons on P to the second metal in a dative fashion. In one unusual reaction, Dixneuf prepared a dinuclear RuCo complex in 35 % yield[45] (equation 1-16):


(1-16)

1.5. Cycloheptatrienyl Bridged Heterobimetallic Complexes and Scope of the Present Research.

A synthetic route for preparing *cis*-(μ–η^3,η^4-C_7H_7) bridged heterobimetallic complexes has been developed in this group[46]. The initial route to these complexes involved utilization of (η^3-C_7H_7)$Fe(CO)_3^-$ and its reaction with transition metal carbonyl halide complexes such as $[Rh(CO)_2Cl]_2$[46a].

$$(\eta^3\text{-}C_7H_7)Fe(CO)_3^- \ + \ {}^1/_2[Rh(CO)_2Cl]_2 \ \text{--->} \ \underset{(1)}{(\mu\text{-}\eta^3,\eta^4\text{-}C_7H_7)Fe(CO)_3Rh(CO)_2} \qquad (1\text{-}17)$$

This has led to the preparation of a series of metal-metal bonded complexes, (μ–η^3,η^4–C_7H_7)$Fe(CO)_3M'(CO)_n$, (M' = Rh, Ir, Mn, Re)[40a-c] and also more recently, through the use of (η^3-C_7H_7)$Ru(CO)_3^-$ and $[Rh(COD)Cl]_2$, to (μ-η^3,η^4-C_7H_7)$Ru(CO)_3Rh(COD)$[46d]. It was found that the best reactants for the production of these heterobimetallic complexes were the Rh and Ir cyclooctadiene complexes, $[M(COD)Cl]_2$, with the best yield (65%) being for the FeRh combination. Preparation of the FeRh cyclooctadiene complex has also been reported independently by Salzer[34], who noted that the ^{53}Fe and ^{103}Rh NMR indicated that the anionic nature of the Fe centre, and cationic nature of the Rh centre in the starting materials was maintained in the product. The initially produced cyclooctadiene complexes react with CO in hydrocarbon solvents to give the corresponding pentacarbonyl complexes in almost quantitative yield (as shown for the RuRh complex):

$$(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD) \quad + \quad CO \quad \text{-------->} \quad \underset{\mathbf{(2)}}{(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2} \qquad (1\text{-}18)$$

Elementary reactivity studies on the FeRh and RuRh pentacarbonyl complexes, **1** and **2**, showed that rapid phosphine substitution reactions occur at the Rh centre[46b,d]. This and the observed carbonyl scrambling processes known to occur have been attributed to the variable coordination mode of the seven-membered ring and the attendant incipient coordinative unsaturation at the metal centres. Further support for this suggestion came when the reaction of the RuRh pentacarbonyl complex, **2**, with dppm was monitored by low temperature ^{31}P NMR and gave evidence for intermediates where ring slippage has occurred[8b]. The ultimate product in this reaction was a bridging compound caused by substitution of one carbonyl group on each metal (equation 1-19).

$$(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2 \; + \; dppm \quad \text{----->} \quad (\mu\text{-}C_7H_7)(\mu\text{-}dppm)Ru(CO)_2Rh(CO) \qquad (1\text{-}19)$$

An extension of these studies has been provided by Salzer who found that reaction of $(C_7H_7)Fe(CO)_3^-$ with $[(allyl)PdCl]_2$ and

[(2-methylallyl)PdCl]$_2$ afforded fluxional iron-palladium complexes. In the same fashion, (C_7H_7)Co(CO)$_3$ (which is isoelectronic to the Fe anion) reacts with Rh(NBD)$^+$ to give a cycloheptatrienyl bridged cationic CoRh complex[41].

In continuation of these studies and described in this thesis, the related ruthenium-iridium complex, *cis*-(μ-η^3,η^4-C_7H_7)Ru(CO)$_3$Ir(COD) (**3**) has been prepared, and the reactivity of the RuRh and RuIr complexes, **2** and **3** with alkynes has been investigated. Additionally, the synthesis and characterization of the anionic complex (η^3-C_7H_7)Os(CO)$_3^-$ has been accomplished and its reactivity with [M(COD)Cl]$_2$ (M' = Rh, Ir) studied. Surprisingly, the reactivity was different from that of the analogous Fe and Ru anionic complexes. This led to the synthesis and spectroscopic characterization of isomeric cis and trans cycloheptatrienyl bridged OsRh complexes, and of *cis*-(μ-η^3,η^4-C_7H_7)Os(CO)$_3$Ir(COD). Comparisons of the spectroscopic properties of the cis heterobimetallic compounds (μ-η^3,η^4-C_7H_7)M(CO)$_3$M'(COD) (M = Fe, Ru, Os: M' = Rh, Ir) and of the precursor anionic complexes (η^3-C_7H_7)M(CO)$_3^-$ (M = Fe, Ru, Os) are also presented.

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Chapter 2.

Synthesis, Properties, and Reactivity of *cis*-(μ-C_7H_7)Ru(CO)$_3$Ir(L_2) (L_2 = COD, L = CO). Preparation and Fluxional Behaviour of *cis*-(μ-C_7H_7)Ru(CO)$_3$Ir(CO)PPh$_3$.

2.1. Introduction.

As already mentioned in Chapter 1, previous studies in the Takats' group has involved the preparation and investigation of the chemical properties of cis cycloheptatrienyl-bridged heterobimetallic carbonyl complexes of FeRh[2], RuRh[3], and FeIr[4]. As a result of these studies, it has been suggested that the variable bonding capacity, and the incipient coordinative unsaturation of the cycloheptatrienyl ring are responsible for facile CO substitution and carbonyl scrambling processes in these complexes. In this chapter, in an extension of these studies, the preparation and spectroscopic characterization of *cis*-(μ-C_7H_7)Ru(CO)$_3$Ir(L_2) [L_2 = COD (**1**), L = CO (**2**)] (COD = 1,5 cyclooctadiene) are described. Substitution reactions of **2** to give fluxional bimetallic complexes which contain a single phosphine ligand are also reported. The spectroscopic effects of replacing a ligand on the bimetallic unit are discussed, and comparisons with the analogous complexes of FeRh[2], RuRh[3], and FeIr[4] are made when available.

2.2. Results and Discussion

2.2.1. Preparation of (μ-C_7H_7)Ru(CO)$_3$Ir(COD) (1) and (μ-C_7H_7)Ru(CO)$_3$Ir(CO)$_2$ (2).

Addition of K(C_7H_7)Ru(CO)$_3$ to [Ir(1,5-cyclooctadiene)Cl]$_2$ in THF at room temperature, followed by stirring for 12 hours gives a very dark brown solution. Removal of the solvent and extraction in hexane affords (μ-C_7H_7)Ru(CO)$_3$Ir(COD) (**1**, equation 2-1) as the only observed product.

$$\mathrm{K(C_7H_7)Ru(CO)_3} + {}^{1}/_{2}\mathrm{[Ir(COD)Cl]_2} \xrightarrow[\mathrm{RT}]{\mathrm{THF}} \underset{\textbf{(1)}}{(\mu\text{-}\mathrm{C_7H_7)Ru(CO)_3Ir(COD)}} \qquad (2\text{-}1)$$

Chromatographic work up leads to the isolation of complex **1** in 23% yield as yellow, air stable crystals which are freely soluble in common organic solvents. The IR spectrum displays a three band pattern consistent with three carbonyl groups occupying terminal positions on Ru. Whilst the yield of **1** is poor, it is similar to that observed (30 %) for the analogous RuRh complex prepared under similar conditions[5]. On reaction with CO at 100 °C, **1** is quantitatively converted to (μ-C_7H_7)Ru(CO)$_3$Ir(CO)$_2$ (**2**) over a two hour period (equation 2-2).

$$\underset{\textbf{(1)}}{(\mu\text{-}\mathrm{C_7H_7)Ru(CO)_3Ir(COD)}} + \mathrm{CO} \xrightarrow[100^{\circ}\mathrm{C,\ 2hr}]{\mathrm{octane}} \underset{\textbf{(2)}}{(\mu\text{-}\mathrm{C_7H_7)Ru(CO)_3Ir(CO)_2}} \qquad (2\text{-}2)$$

The same thermal conditions (100 °C, 1 atm CO) were required for preparation of the related FeIr complex, (μ-C_7H_7)Fe(CO)$_3$Ir(CO)$_2$. These conditions are significantly more forcing than those required for the carbonylation of the analogous FeRh and RuRh cyclooctadiene complexes, which are both carbonylated in less than an hour at room temperature. Complex **2** is a yellow-orange air stable and thermally robust solid, also soluble in most organic solvents. The IR spectrum shows five peaks in the terminal carbonyl region as has been previously observed for the related FeRh, FeIr, and RuRh complexes.

As expected, the ^1H and ^{13}C NMR data for **1** and **2** give evidence for rapid ring whizzing of the cycloheptatrienyl ligand at ambient temperature. However, as can be seen in Figure 2.1, rotation of the COD ligand in **1** is not observed, there being two sharp resonances for the olefinic hydrogens and carbons in the ^1H and ^{13}C NMR spectra respectively. A similar observation was made in the corresponding FeIr compound[4], but in the analagous RuRh complex[5] rotation of the COD ligand occurs as evidenced by the single olefinic resonance in the room temperature ^1H NMR spectrum. This reflects the well known decrease in metal to ligand bond strength upon ascending a transition metal triad[6]. The observation that the RuIr pentacarbonyl complex, **2**, requires temperatures of 70 °C to give complete enrichment with ^{13}CO is also consistent with this trend. Surprisingly, the variable temperature ^1H NMR spectra of **1** and **2** indicate that the rotation of the μ-C_7H_7 ligand can be frozen out. As shown in Figures 2.2 and 2.3, the low temperature limiting spectra are approached at -100 °C for both complexes. Assignments of the resonances were made by comparison with the related OsIr complexes (Chapter 4) which

Figure 2.1. ^{13}C (a) and ^{1}H (b) NMR spectra of **1** in the C_7H_7 and COD region.

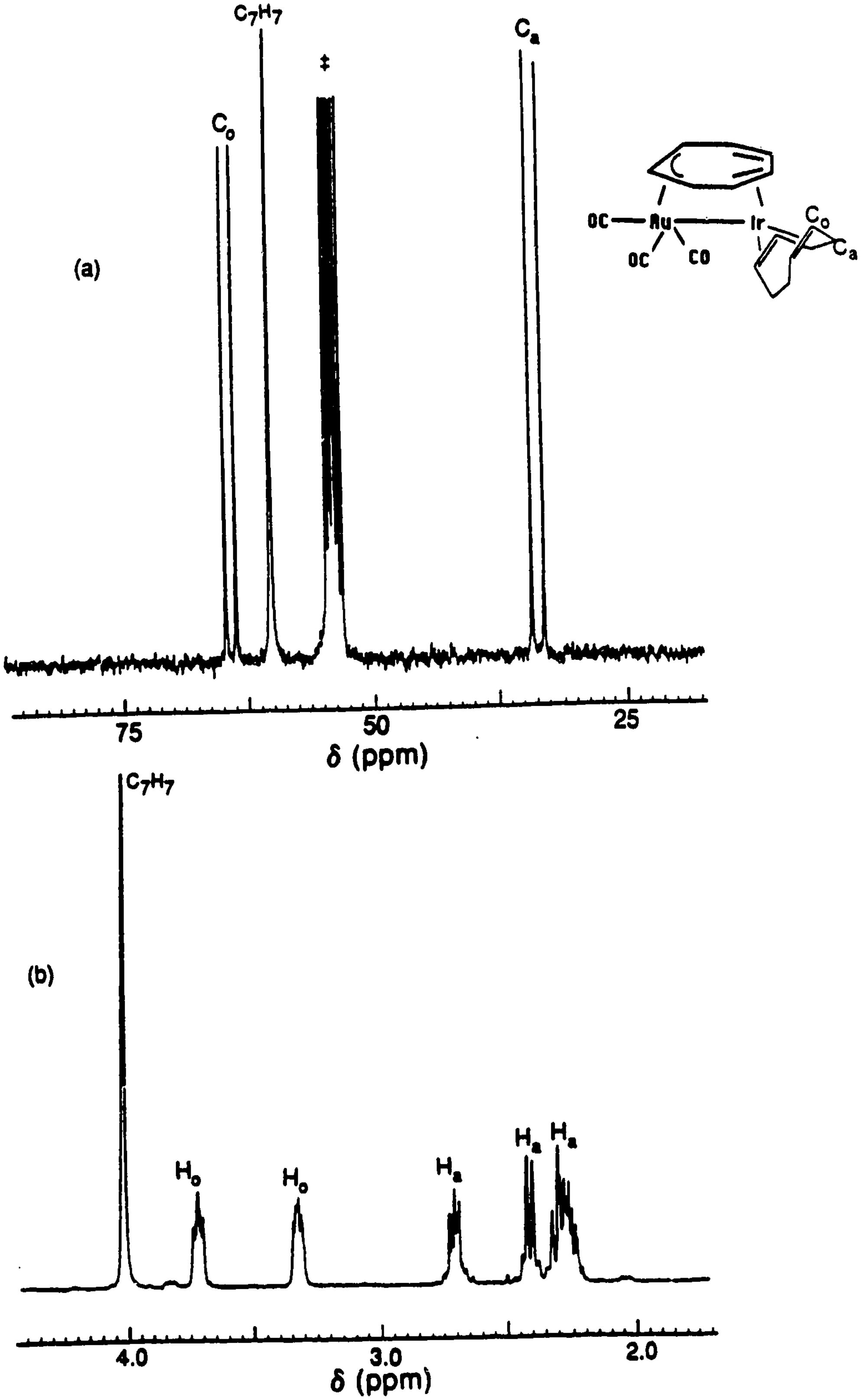


Figure 2.2. Variable Temperature ^1H NMR Spectra of 1.

(a) Spectra recorded in toluene-d8. (b) Spectra recorded in CD_2Cl_2.

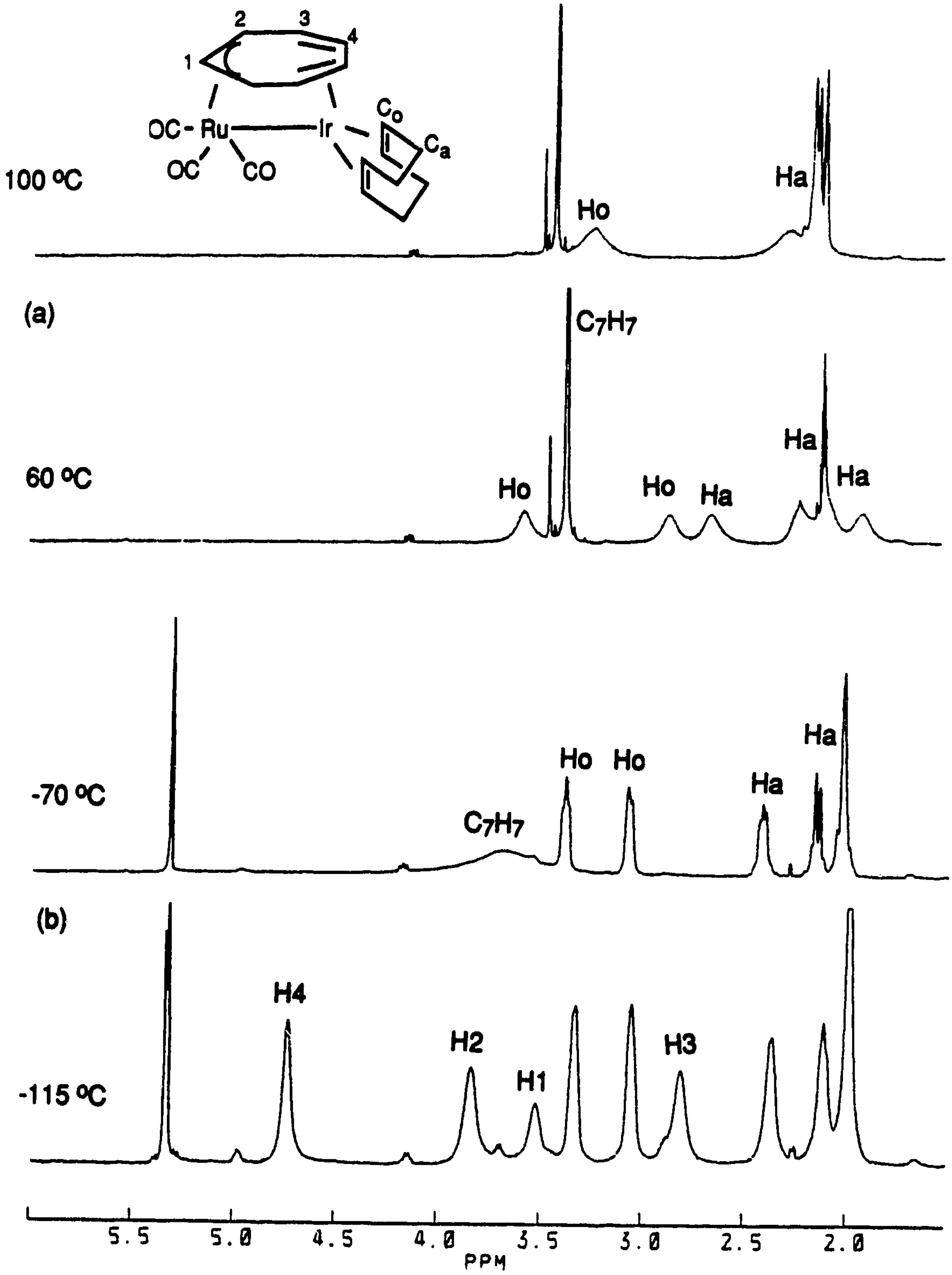
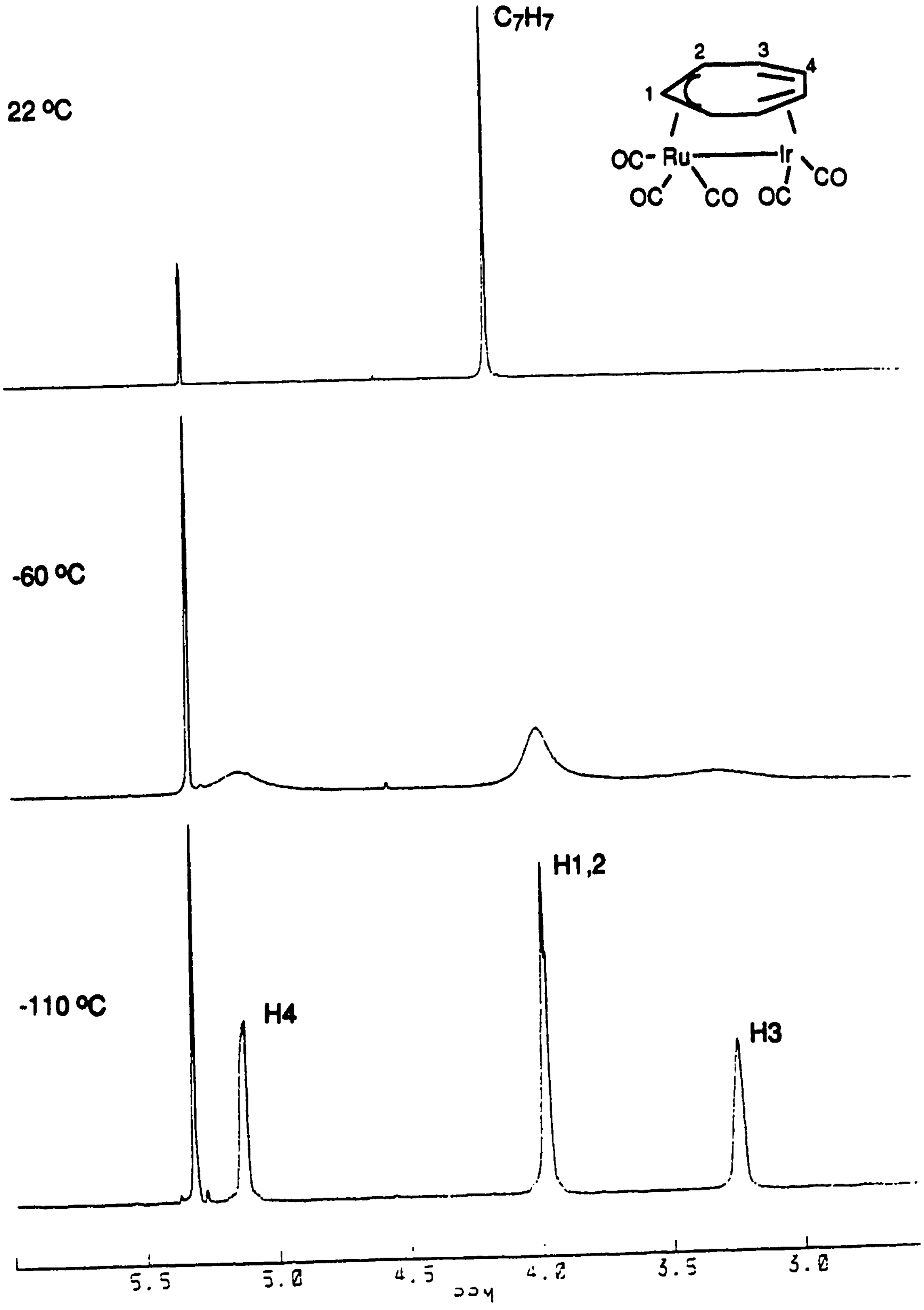


Figure 2.3. Variable Temperature ^1H NMR Spectra of **2**.



have been determined by a series of decoupling experiments. Another noteworthy observation is that high temperature ^{1}H NMR spectra of the RuIr cyclooctadiene complex, **1**, (60 °C, 100 °C, Figure 2.2) give evidence for rotation of the COD ligand. The fluxional processes involving the COD and C_7H_7 ligand, and complementary results in related Os complexes, will be commented upon more fully in Chapter 4 and in Chapter 7.

In their ^{13}C NMR spectra, both complexes **1** and **2** display a sharp singlet for the three CO ligands on Ru due to rapid scrambling of the CO groups on one metal centre. Intermetallic CO exchange is not observed in **2** at ambient temperature; there being two sharp resonances at δ 196 ppm (CO_{Ru}) and δ 175 ppm (CO_{Ir}), easily distinguishable on the basis of their chemical shifts[7]. These signals remain sharp until 70 °C when slight broadening is noticed. Coalescence of the two signals was not observed upon heating an NMR sample of **2** in dodecane/toluene-d^8 (ca. 10:1) to 120 °C. At these temperatures some decomposition of the sample occurs. Intermetallic CO scrambling was also not observed at elevated temperatures for the analogous FeRh, FeIr, and RuRh pentacarbonyl complexes. The variable temperature ^{13}C NMR spectra of the pentacarbonyl complex **2** are shown in Figure 2.4. Although heating **2** failed to give evidence of global carbonyl scrambling, the low temperature NMR spectrum recorded at -80 °C (Figure 2.4) showed halting of the local carbonyl scrambling at the Ru centre. Thus two signals for the $Ru(CO)_3$ carbonyls are observed at δ 199.9 (2C) and δ 189.3 (1C). Of course, at

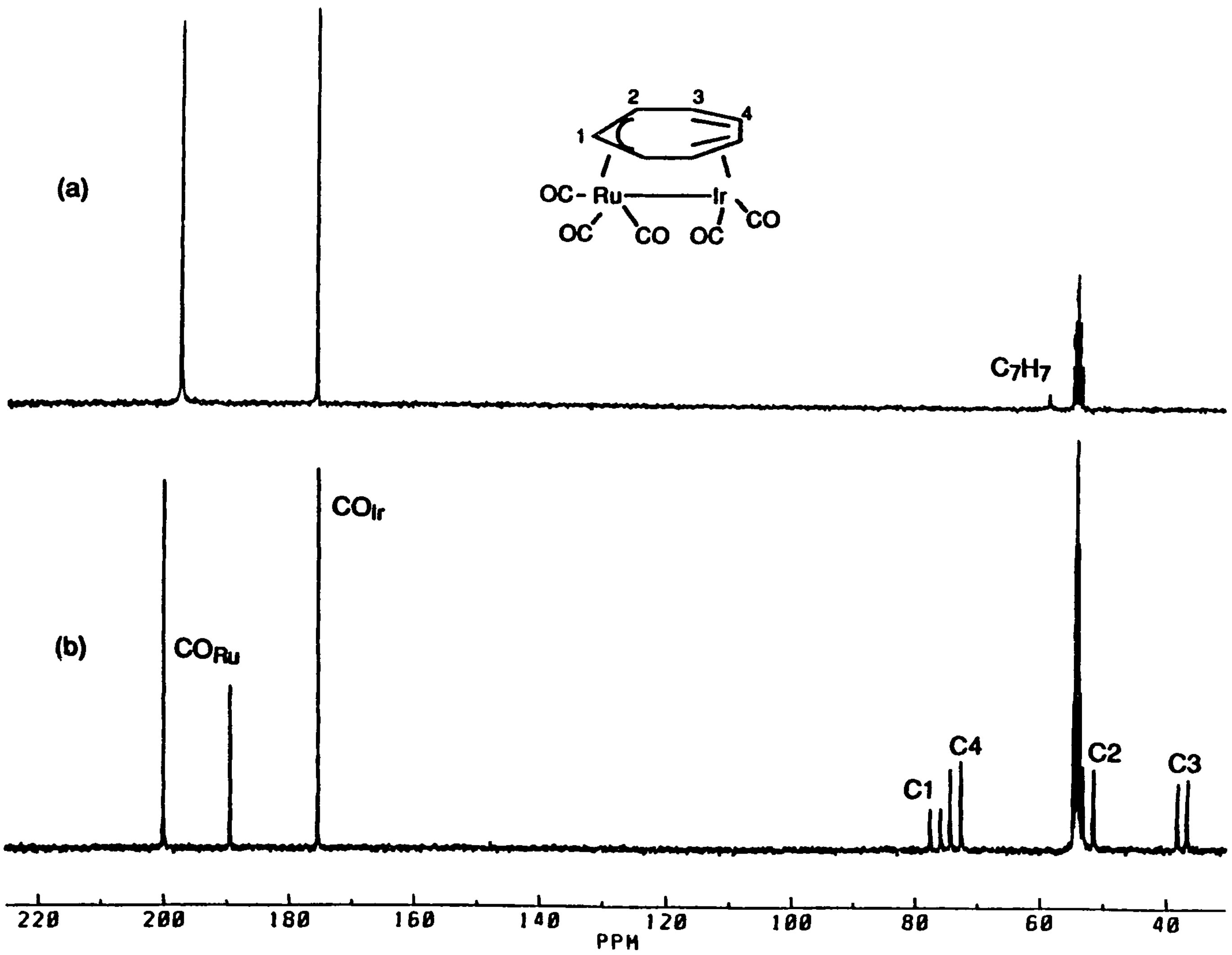


Figure 2.4. (a) Room Temperature {^1H} ^{13}C NMR Spectrum of **2** (enriched with ^{13}CO).

(b) Low Temperature (proton coupled) ^{13}C NMR of **2** (^{13}CO in natural abudance).

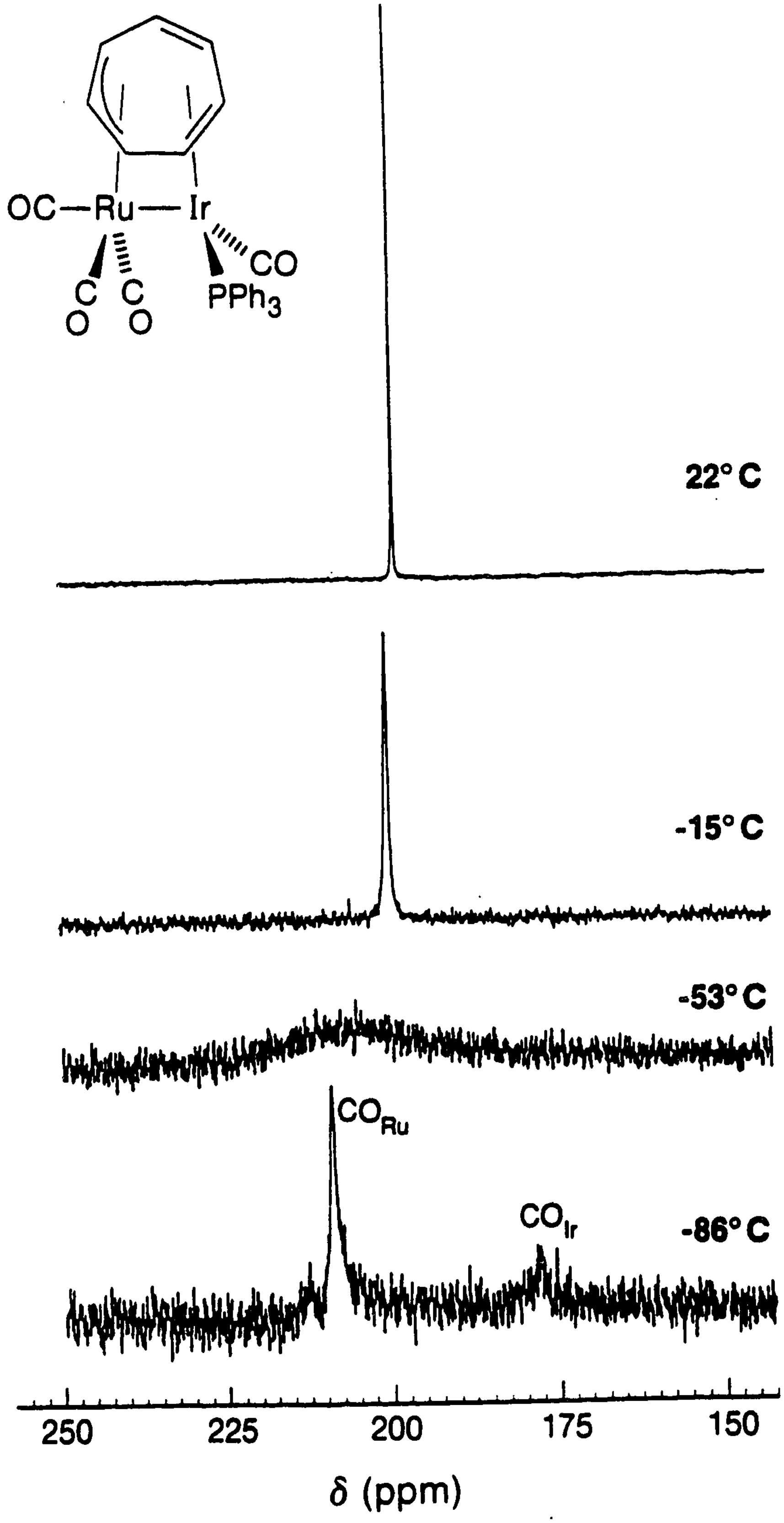
this temperature the rotation of the seven-membered ring is also frozen out.

2.2.2. Preparation of (μ-C_7H_7)Ru(CO)$_3$Ir(CO)(PPh$_3$) (3).

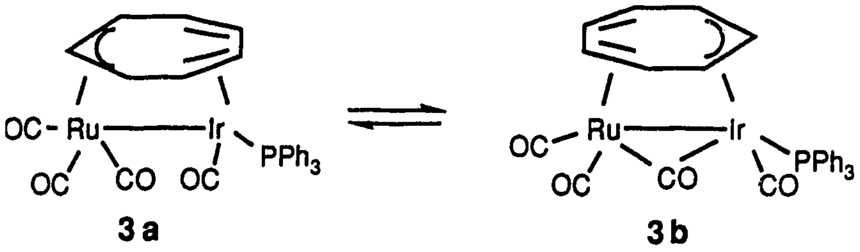
Although the carbonylation experiments had required thermal activation, it was observed that **2** reacted with one equivalent of PPh$_3$ cleanly at room temperature giving substitution of one CO ligand. The ^{31}P NMR spectrum of the product shows one singlet at δ 5.2 ppm. The variable temperature ^{13}C NMR spectra are shown in Figure 2.5. The ^{13}C NMR spectrum in the carbonyl region displays one sharp singlet at room temperature indicating rapid intermetallic CO exchange. As seen in Figure 2.5, upon decreasing the temperature the signal broadens and coalescence is observed at -53 °C. At -85 °C intermetallic CO exchange is not completely frozen out, however, it can be seen that there are two resonances at δ 210 ppm and δ 179 ppm in a 3:1 ratio. These signals therefore indicate that phosphine substitution has occurred at Ir and that at - 85 °C, there is local carbonyl scrambling within the Ru(CO)$_3$ group. At this temperature there is also one signal for the C_7H_7 ligand indicating that the seven-membered ring is also involved in a form of fluxional behaviour. Both of these processes are close to being frozen out at this temperature for **1** and **2**, indicating that the presence of PPh$_3$ significantly enhances the fluxional behaviour of the bimetallic complexes. The site of attack in the formation of **3** is presumably determined by the more pronounced tendency of Ir to produce 16 electron species via ring dissociation[8].

Figure 2.5.

Variable Temperature ^{13}C NMR Spectra of **3** in the carbonyl region.



The IR spectrum of compound **3** is complicated due to the presence of both all terminal, (**3a**) and carbonyl bridged (**3b**) isomers, as has been previously noticed in the related FeRh[2] and FeIr[4] complexes. The isomerization involves a change in the bonding mode of the (μ-C_7H_7) moiety between the two metals as shown below. Rapid equilibrium

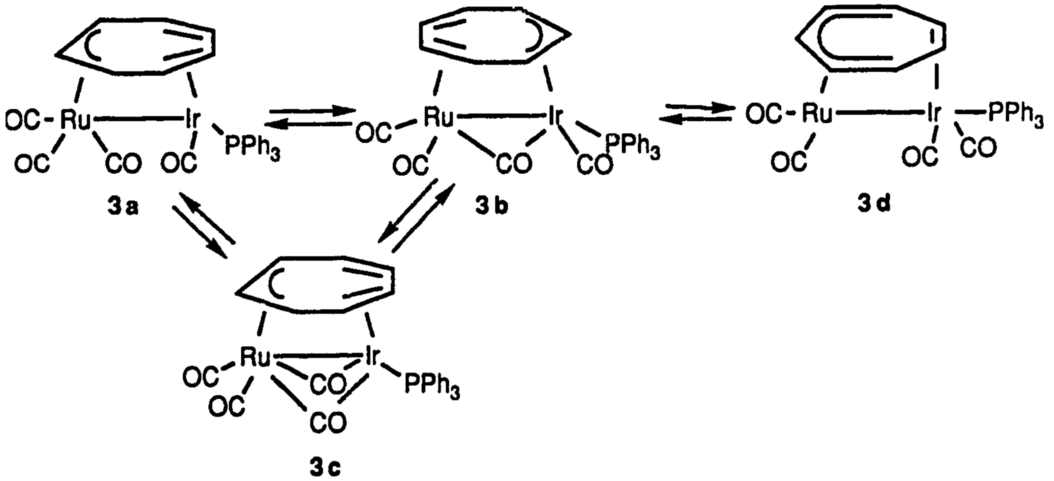


between these isomers would lead to interchange of carbonyl groups on Ru and hence explains the low temperature ^{13}C NMR spectrum. Clearly there is a very low activation energy for this process.

The free energy of activation for intermetallic carbonyl exchange in **3** calculated at the coalescence temperature[9] is 9.0 kcal/mole. This can be compared with the analogous complexes of RuRh (11.0 kcal/mole), FeIr (10.3 kcal/mole) and FeRh (15.4 kcal/mole). Of the several plausible intermediates available for this process, we have previously favoured the doubly bridged species **3c** (Scheme 2.1). The rationale behind our choice was that **3c** is easily achieved from both isomeric **3a** and **3b** while maintaining the μ-η^4,η^3 bonding functionality of the cycloheptatrienyl ring. However the surprising and unexpected trend of increasing facility for carbonyl group migration (Ru > Fe and Ir > Rh) is difficult to reconcile with this postulate since it is contrary to the well known greater reluctance of transition metals to accomodate bridging carbonyl groups upon descending a triad[10].

It now seems possible that an alternative intermediate (**3d**) which contains only terminal carbonyl ligands may also be involved in this process and may gain importance upon descending a triad. The necessary change in bonding mode of the cycloheptatrienyl ring to μ–η^5,η^2 may in this case dominate the energetics for global carbonyl scrambling, and account for the observed trend.

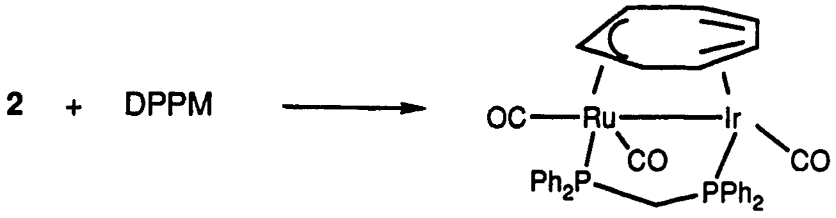
Scheme 2.1



2.2.3. Reaction of (μ-C_7H_7)$Ru(CO)_3Ir(CO)_2$ with dppm.

The reaction of **2** with bis(diphenylphosphino)methane (dppm) was carried out under conditions similar to the reaction with PPh_3, but this time the displacement of two CO groups was observed. The IR spectrum of the product shows three bands, all in the terminal carbonyl stretching region at

1980, 1936, and 1914 cm^{-1}. Two doublets were observed in the ^{31}P NMR spectrum at δ 65.3 ppm (Ru) and δ 25.0 ppm (Ir) with P-P coupling constants of 125 Hz, typical of μ-dppm complexes[11]. The ^{13}C NMR in the carbonyl region now shows three resonances at room temperature at δ 208 ppm (Ru), δ 196 ppm (Ru) and δ 183 ppm (Ir).



4

(2-3)

These data are characteristic[2,3] of the expected product (μ-C_7H_7)(μ-DPPM)Ru(CO)$_2$Ir(CO), **4**. The reaction was followed at room temperature by IR and ^{31}P NMR spectroscopies, but these studies failed to give evidence for any intermediates. A reasonable explanation for this would be that the reaction proceeds via slow initial substitution at Ir, in a fashion similar to the PPh$_3$ reaction and this is followed by rapid substitution of a second carbonyl group at Ru leading to product formation (i.e. the chelate effect[12]). Unfortunately, crystallization failed to eliminate various phosphorus containing minor impurities which appeared erratically in the ^{31}P NMR spectrum. In addition, **4** appears less thermally stable and is considerably more air sensitive than **3**, which renders purification more difficult. The decrease in stability upon addition of phosphorus donor ligands is probably electronic in origin and perhaps opens new channels for competing reaction pathways leading to the unexpected minor byproducts. Due to these difficulties, complex **4** was not further investigated.

2.3. Conclusion.

The synthesis of the series of complexes (μ-C_7H_7)MM`$(CO)_4$L (M=Fe,Ru and M`=Rh,Ir: L=CO,PPh_3) has been completed. For L=PPh_3 a decrease in activation energy for intermetallic CO exchange is noticed on going from Fe to Ru and from Rh to Ir. Due to the necessary involvement of bridging carbonyl groups in this process, this is a surprising result in view of the greater tendency to accomodate bridging carbonyls for 1st row transition metals. It has however been noticed that substitution by phosphines increases the tendency for carbonyl groups to occupy bridging positions, and also the facility for carbonyl group migration[13]. This effect is dramatically demonstrated in our observation that intermetallic CO scrambling is facile for the phosphine complex **3**, but it is not observed in the pentacarbonyl complex **2**.

2.4. Experimental.

2.4.1. General Techniques.

Reactions and manipulations were carried out under purified nitrogen using standard Schlenk and canula techniques[14] and carefully dried solvents. N_2 was purified by passage through a heated column (100 °C), containing BASF (Cu-based) catalyst R3-11 to remove oxygen and a column of Malinkrodt Aquasorb (P_2O_5 on an inert base) to remove water. Solvents were dried by refluxing and distilling from the appropriate drying agent under N_2 (Table 2.1).

Table 2.1 Drying Agents used in the Distillation of Solvents.

Solvent	Drying Agent
Pentane	CaH_2
Hexane	Potassium metal
Benzene	Potassium metal
Toluene	Sodium metal
THF	Potassium metal/benzophenone
CH_2Cl_2	P_2O_5.

Pentane and hexane were preconditioned before refluxing and distillation by washing with H_2SO_4 and water and drying over Na_2SO_4 in order to remove alkenes. All deuterated solvents were dried over molecular sieves except THF-d_8 which was distilled from Na-benzophenone prior to use. Glassware was cleaned by treatment with KOH-ethanol solution and was oven-dried at 100 °C. Separation and purification of compounds was done by crystallization or by silica gel column chromatography (using.Merck Kieselgel 60 PF_{254} silica gel) unless otherwise stated.

2.4.2.Physical Measurements.

Reactions were monitored by infrared spectroscopy with the aid of a Nicolet MX-1 Fourier Transform Interferometer over the range 2200 - 1600 cm^{-1}. Solution samples were held between KBr or KCl (0.1 mm) plates. Mass spectra and NMR spectra were recorded by the staff of the respective laboratories. Mass spectra were recorded an A.E.I. MS-12 spectrometer operating at 70 eV or 16 eV. The mass number of the molecular ion refers to the most abundant isotope combination. NMR spectra were recorded on a Bruker WH 200, Bruker AM 400 or Bruker AM 300 spectrometer. Variable temperature spectra were recorded on the Bruker AM 400 with samples which were either sealed under vacuum or by wrapping the plastic cap with parafilm. Solvent resonances (vs. TMS) were used as internal standards for ^{1}H and ^{13}C NMR spectra. H_3PO_4 was used as a calculated external standard for ^{31}P spectra (downfield being positive). Melting points were obtained on a Thomas Hoover apparatus in open capillaries and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of this department.

2.4.3. Reagents for Chapter 2.

Bis(diphenylphosphino)methane (DPPM) was purchased from Pressure Chemical Company and triphenylphosphine, dodecane, and 1,5-cyclooctadiene (COD) from Aldrich, these materials were used as received. Ammonium hexachloroiridate (IV) was obtained from Engelhard. Potassium tertiarybutoxide (KO^tBu) was purchased from Aldrich and sublimed prior to use (150 °C, 10^{-3} mmHg). $[Ir(COD)Cl]_2$[15] and $(C_7H_8)Ru(CO)_3$[5] were prepared according to literature methods. Octane was obtained from Terochem Laboratories Ltd. and degassed by three freeze-pump-thaw cycles before use.

2.4.4. $(\mu\text{-}C_7H_7)Ru(CO)_3Ir(COD)$, (1).

$K(C_7H_7)Ru(CO)_3$ (4.60 mmol, 1.45 g) was prepared by the addition of equimolar quantities of KO^tBu in THF (20 ml) to $(C_7H_8)Ru(CO)_3$ in THF (40 ml) at -78 °C. The anion was transferred to a jacketed dropping funnel which was cooled by dry-ice and was then added dropwise to a solution of $[Ir(COD)Cl]_2$ (2.30 mmol, 1.54 g) in THF (40 ml) at room temperature. The dark solution was stirred for 12 hours at room temperature and evaporated to dryness. The brown residue was extracted with 2 aliquots of toluene (20 ml) and chromatographed on a 16 x 2.5 cm silica gel column (Merck, Kieselgel 60 mesh). Elution with hexane produced a large red band which was collected under nitrogen. The solvent was removed from the eluate and the residue was redissolved in hexane (20 ml) and cooled at -78 °C for 12 hours to obtain yellow crystals (0.462 g, 17%). Concentration of the mother liquor to 2ml yielded a final crop (0.140 g, 23% overall) mp 139 °C (dec).

Anal. Calcd for $C_{18}H_{19}IrO_3Ru$: C, 37.49; H, 3.32. Found: C, 37.66; H, 3.40.

Mass spectrum (70 eV, 90 °C); M^+, M^+-nCO (n = 1-3).

IR (hexane): υ_{CO} 2038(s), 1977(s), 1970(s) cm^{-1}.

^1H NMR (25 °C, CD_2Cl_2): δ 3.82 (s,7H,C_7H_7), 3.52 (m,2H,CH_{COD}), 3.16 (m,2H,CH_{COD}), 2.54 (m,2H,$CH_{2\,COD}$), 2.24 (m,2H,$CH_{2\,COD}$), 2.12 (m,4H,$CH_{2\,COD}$).

(-100 °C): δ 2.80 (br,2H,C_7H_7), 3.54 (br,1H,C_7H_7), 3.76 (br,2H,C_7H_7), 4.72 (br,2H,C_7H_7).

^{13}C {1H} NMR (25 °C,CD_2Cl_2): δ 33.5 (s,$CH_{2\,COD}$), 34.7 (s,$CH_{2\,COD}$), 60.0 (s,C_7H_7), 63.4 (s,CH_{COD}), 64.4 (s,CH_{COD}), 196.8 (s,CO_{Ru}).

2.4.5. (μ-C_7H_7)Ru(CO)$_3$Ir(CO)$_2$, (2).

(μ-C_7H_7)Ru(CO)$_3$Ir(COD) (90 mg,0.16 mmol) was dissolved in octane (30 ml). The solution was degassed by two freeze-pump-thaw cycles. An atmosphere of CO was introduced to the reaction vessel, which was then heated at 100 °C for 2 hours and then evaporated to dryness in vacuo. The residue was redissolved in hexane (5 ml), concentrated to 0.5 ml, and then cooled to -78 °C over 12 hours to give yellow-orange crystals of **2** (72 mg, 73%) mp 126-127 ° C.

Anal. Calcd for $C_{12}H_7IrO_5Ru$: C, 27.48; H, 1.35. Found: C, 27.94; H, 1.42.

Mass spectrum (70 eV, 110 °C): M^+, M^+-nCO (n = 1-5).

IR (hexane) υ_{CO}: 2066(s), 2019(s), 2005(s), 1984(m), 1973(w) cm^{-1}

^1H NMR (25 °C, CD_2Cl_2): δ 4.16 (s,7H,C_7H_7); (-100°C): δ 3.24 (br,2H,C_7H_7), 4.00 (br,2H +1H,C_7H_7), 5.24 (br,2H,C_7H_7).

$^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2): δ 58.4 (s,C_7H_7), 175.4 (s,CO_{Ir}), 196.8 (s,CO_{Ru}).

2.4.6. Synthesis of ^{13}CO enriched sample.

^{13}CO (99.1%) was purchased from Isotech Inc. Compound **2** was enriched in ^{13}CO by stirring an octane solution of **2** under 1 atm of ^{13}CO at 70 °C for 1 hour. The enrichment was 94% as determined from the mass spectrum of the compound.

2.4.7. (μ-C_7H_7)Ru(CO)$_3$Ir(CO)PPh$_3$ (3).

(μ-C_7H_7)Ru(CO)$_3$Ir(CO)$_2$ (31 mg,0.059 mmol) was dissolved in C_6H_6 (15 ml), and the solution was degassed. PPh_3 (15.5 mg,0.059 mmol) was added as a solid and the solution was stirred for 3 hours, and then evaporated to dryness. The orange residue was washed once with hexane and then recrystallised from CH_2Cl_2/hexane at -78 °C to give orange red crystals of **3** (34 mg, 76%) mp 138 - 139 °C (dec).

Anal. Calcd for $C_{29}H_{22}IrO_4PRu$: C, 45.91; H, 2.92. Found: C, 45.82; H, 2.98.

Mass Spectrum (70 eV, 180 °C): M^+, M^+-*n*CO (*n* = 1-4).

IR (C_6H_6) υ_{CO}: 2034(w), 2004(m), 1970(s,br), 1935(br), 1785(w,br) cm^{-1}

^1H NMR (25 °C, C_6D_6): δ 7.6 (m,2H,Ph,*o*), 7.1 (m,2H,Ph,*m*), 7.0 (m,1H,Ph,*p*), 3.56 (s,7H,C_7H_7).

$^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2): δ 60.5 (s,C_7H_7), 128.6 (d,J_{P-C}=10.5Hz,Ph,*m*), 130.6 (s,Ph,*p*), 135.6 (d,J_{P-C}=11.4Hz,Ph,*o*), 136.0 (d,J_{P-}

$_{C}$=40Hz,Ph,*ipso*), 199.7 (s,CO,averaged); (-86 °C): δ 209.6 (s,CO_{Ru}), 179.3 (s,CO_{Ir}).

^{31}P {^{1}H} NMR (25 °C, C_6D_6): δ 5.15 (s,PPh_3).

2.4.8. (μ-C_7H_7)Ru$(CO)_2$Ir(CO)(μ-DPPM), (4).

(μ-C_7H_7)Ru$(CO)_3$Ir$(CO)_2$ (25 mg, 0.048 mmol) was dissolved in toluene (15 ml) and the solution was degassed. DPPM (18.3 mg, 0.048 mmol) was added as a solid. The solution was stirred for 3 hours during which time starting material was consumed and **4** was formed as monitored by IR spectroscopy. The solution was then concentrated to 0.5 ml and layered with hexane (2 ml). The vessel was then cooled at -78 °C to give a bright orange air sensitive solid, **4** which was analysed immediately by NMR spectroscopy mp 75 °C (dec).

Anal. Calcd for $C_{35}H_{29}IrO_3P_2Ru$: C, 49.29; H, 3.43. Found: C, 47.88; H, 3.86.

Mass Spectrum (70 eV, 200 °C): M^+, M^+-*n*CO, (*n* = 1-3).

IR (benzene) υ_{CO}: 1980(s), 1936(s), 1914(m) cm^{-1}.

^{1}H NMR (25 °C, C_6D_6): δ 7.7-6.8 (m,20H,Ph), 3.82 (dt,1H,J_{H-H}=14Hz, J_{H-P}=12Hz,CH_2), 3.65 (s,7H,C_7H_7), 2.11 (dt,1H,J_{H-H}=14Hz,J_{H-P}=8Hz,CH_2).

^{13}C {^{1}H} NMR (25 °C,toluene d_8): δ 208.2 (s,CO_{Ru}), 195.7 (d,J_{P-C}=9Hz,CO_{Ru}), 182.7 (d,J_{P-C}=9Hz,CO_{Ir}), 138.2-129.3 (Ph), 57.2 (C_7H_7), 42.2 (dd,J_{H-P}=24,41Hz,CH_2).

^{31}P {^{1}H} NMR (25 °C, C_6D_6): δ 65.3 (d,J_{P-P}=125Hz,Ru-P), 25.0 (d,J_{P-P}=125Hz,Ir-P).

2.5. References.

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Chapter 3.

Preparation, properties and reactivity of $(\eta^4\text{-}C_7H_8)Os(CO)_3$. Synthesis of $(\eta^3\text{-}C_7H_7)Os(CO)_3^-$ and $(\eta^5\text{-}C_7H_9)Os(CO)_2[C(O)Bu]$.

3.1. Introduction.

Complexes of formula (diene)$Fe(CO)_3$ compose one of the earliest studied family of transition metal organometallic complexes[1], and twenty five years later many applications of these compounds are still being studied[2]. It is therefore not surprising that the synthesis and some properties of the (η^4-cycloheptatriene)$M(CO)_3$ complexes (M = Fe; **1a**, Ru; **1b**) have for a long time been known[3].

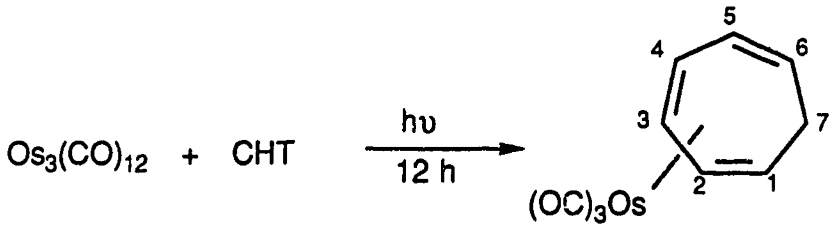
The synthesis of these compounds can be achieved by either thermal, or photochemical reaction of the appropriate binary metal carbonyl complex with cycloheptatriene, or by substitution of a labile ligand in a $LM(CO)_3$ complex such as (BDA)$Fe(CO)_3$ or (COD)$Ru(CO)_3$ (BDA = benzylidene acetone, COD = 1,5 cyclooctadiene)[3]. In our studies here, we have found the photochemical route to the Ru complex the most convenient[4], and hence a similar approach was used for the synthesis of the corresponding Os complex (**1c**).

As the related Fe and Ru complexes (**1a, 1b**) are known to be deprotonated by strong bases[4-6], the isolation of $(\eta^4\text{-}C_7H_8)Os(CO)_3$ (**1c**) provides a route to the anionic complex, $(\eta^3\text{-}C_7H_7)Os(CO)_3^-$ (**2c**). Some chemistry of the group of compounds $(\eta^3\text{-}C_7H_7)M(CO)_3^-$ [M = Fe (**2a**), M = Ru, (**2b**), M = Os, (**2c**)] has already been explored. In the case of Fe, these findings have provided some useful methodology for the synthesis of natural products containing seven-membered rings[5]. Additionally, these complexes react readily with inorganic electrophiles to produce metal-metal bonded complexes[6] or to add substituents to the seven membered ring[7]. Reactions with the transition metal electrophiles $[M(COD)Cl]_2$ (M = Rh, Ir), in an attempt to produce cycloheptatrienyl bridged OsRh and OsIr complexes, will be described in a later chapter. In this chapter, the preparation, and some elementary reactions of $(\eta^4\text{-}C_7H_8)Os(CO)_3$ are described.

3.2. Results.

3.2.1. Preparation of $(\eta^4\text{-}C_7H_8)Os(CO)_3$.

At the start of this work, the synthesis of $(\eta^4\text{-}C_7H_8)Os(CO)_3$ (**1c**) had been accomplished in 80% yield starting from $Os(CO)_5$ and cycloheptatriene (CHT)[8]. This procedure however, requires the preparation of $Os(CO)_5$ from $Os_3(CO)_{12}$ and hence a more convenient synthesis of **1c** directly from $Os_3(CO)_{12}$ was sought. It was found that an overnight photolysis of $Os_3(CO)_{12}$ and CHT in benzene gave a yellow solution. The IR spectrum of this solution indicated that the required $(\eta^4\text{-}C_7H_8)Os(CO)_3$ was the major product.

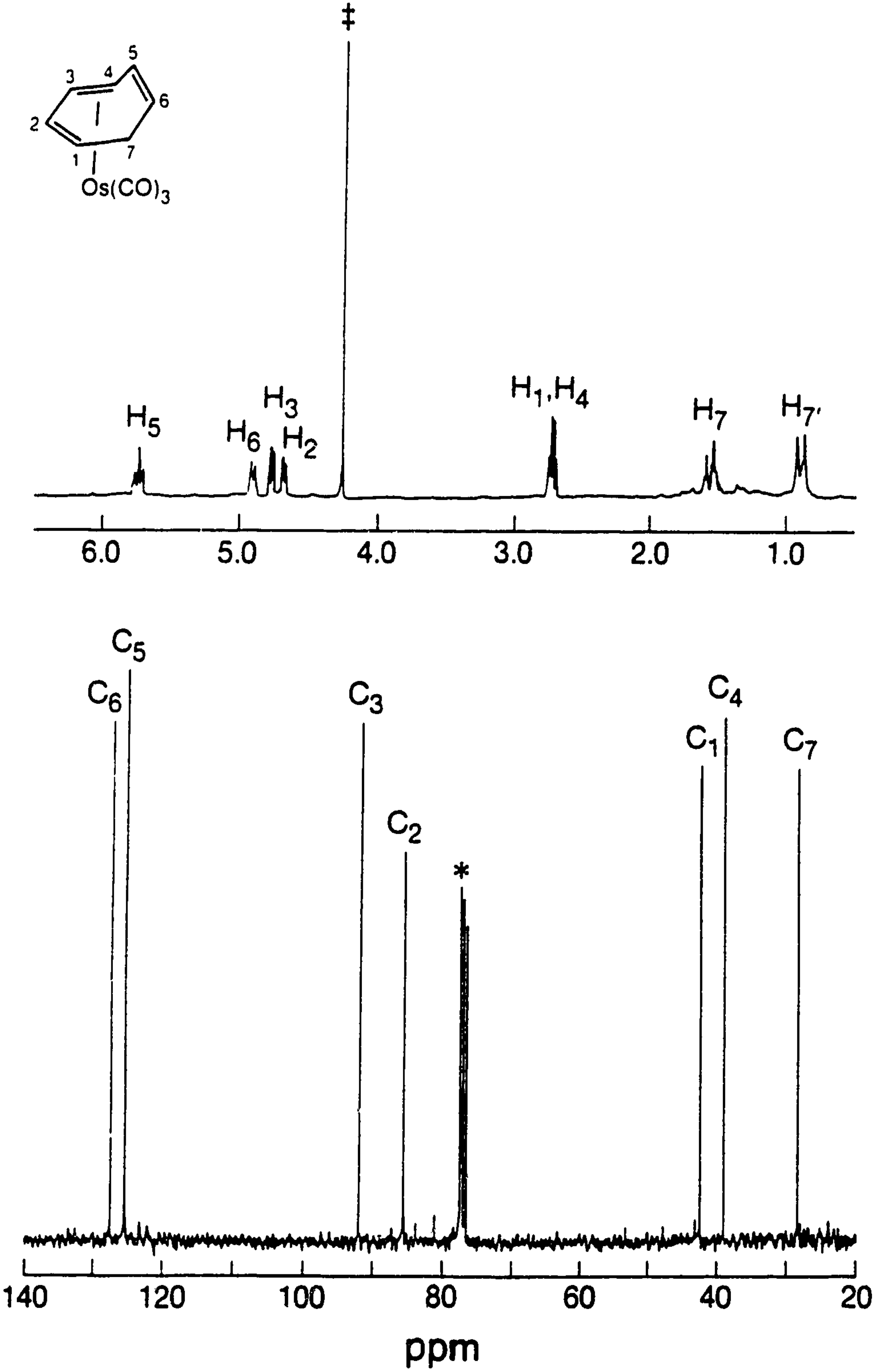


(3-1)

The reaction was cleanest when efficient cooling of the benzene solution was allowed in order to avoid reflux. This was accomplished by stirring the solution in a reaction vessel with a large surface area for the volume of solvent and placing the lamp inside a water-cooled quartz immersion well at least 10 cm from the reaction vessel. This method allows dissolution of $Os_3(CO)_{12}$ and hinders competitive thermal reaction pathways. The drawback of this procedure is that it limits the quantity of solvent that can be used. This, combined with the low solubility of $Os_3(CO)_{12}$ in benzene limits the amount of $Os_3(CO)_{12}$ to about 0.3 g in 100 ml solvent. Under these conditions, most of the starting material has dissolved after about three hours photolysis, probably due to the unavoidable warming of the solution from the absorbed irradiation. After 12 hours the reaction is essentially complete. Solvent removal gives a yellow brown oil which can be purified by chromatography. When this is carried out, two bands become visible; the first band is pale yellow in colour, and this is followed directly by an orange band. The pale yellow band, which corresponds to the desired product, was eluted with pentane. The following band is thought to be a mixture of trinuclear compounds. Mixtures of polynuclear compounds have been observed in the thermal reaction between CHT and $Ru_3(CO)_{12}$[9]. However, when one monitors the eluted solvent by IR spectroscopy, it becomes apparent that in the colourless solvent prior to the first visible band there are small amounts of carbonyl containing compounds. Again, by analogy to the types of compounds obtained from the thermal reaction between CHT and $Ru_3(CO)_{12}$, it is thought that these are due to a mixture of $(\eta^4\text{-}C_7H_8)Os(CO)_3$ and $(\eta^4\text{-}C_7H_{10})Os(CO)_3$. No attempt was made to isolate and identify the by-products.

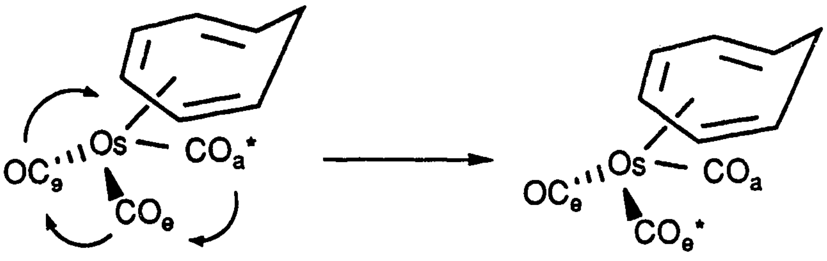
Removal of the pentane solvent from the desired fraction gave a pale yellow-green oil which was purified further by vacuum distillation at room temperature to a dry-ice cooled probe. This procedure eliminates the baseline impurities which are often visible in the IR spectrum of the compound after chromatography, and gives the pure product in about 60% yield. The IR spectrum of (**1c**) as expected gives three bands in hexane at 2066, 1994, 1984 cm^{-1}. The ^1H and ^{13}C NMR spectra in the cycloheptatrienyl region are shown in Figure 1[11]. The spectra display signals due to a rigid seven-membered ring in similar fashion to those reported for the related Fe and Ru complexes[9,10]. There is also a weak, broad signal in the ^{13}C NMR spectrum at 176.3 ppm due to the CO groups on Os. This indicates that the $Os(CO)_3$ group is rotating whilst the seven-membered ring is static (see Scheme 3.1). This feature of the compound is expected from the known fluxional behaviour of related $(diene)Fe(CO)_3$ compounds[12].

Figure 3.1. ^1H and ^{13}C NMR spectra of $(\eta^4\text{-}C_7H_8)Os(CO)_3$.[a]



a ^1H NMR recorded in C_6D_6; ^{13}C NMR recorded in $CDCl_3$
‡ = residual CH_2Cl_2; * = solvent.

Scheme 3.1



3.2.2. Reactivity of (η^4-C_7H_8)Os(CO)$_3$ with bases. Preparation of K(η^3-C_7H_7)Os(CO)$_3$.

Prior to this work the preparation of (η^3-C_7H_7)Os(CO)$_3^-$ had been accomplished from (η^4-C_7H_8)Os(CO)$_3$ (**1c**) and KO^{t}Bu. In order to further study the chemistry of **1c** and to possibly find more convenient deprotonating agents, **1c** has been reacted with several alternative bases. It was found that **1c** was not as acidic as the analogous Fe and Ru complexes. For instance, in contrast to Fe and Ru, no reaction occurred when a toluene solution of **1c** was stirred with Na[($Me_3Si)_2N$] at room temperature over 24 hours. Additionally, no carbonyl containing products were observed in the room temperature reaction of **1c** with KH in THF solution[13]. The attempted deprotonation of **1c** using BuLi is discussed later in this chapter. Consequently, as in the case of Ru, the most convenient base was found to be KO^{t}Bu. Upon addition of one equivalent of KO^{t}Bu to (η^4-C_7H_8)Os(CO)$_3$ at room temperature, the yellow-green THF solution rapidly turns to a bright orange colour.

$$(\eta^4\text{-}C_7H_8)Os(CO)_3 + KO^tBu \text{ ---> } K(C_7H_7)Os(CO)_3 + HO^tBu \qquad (3\text{-}2)$$

The IR spectrum of the bright orange solution [1961 (s), 1884 (s), 1863 (sh)] shows the expected shift to lower energy from the starting material. As shown in Figure 3.2, the room temperature ^1H NMR spectrum shows a single peak for the C_7H_7 ligand. This is expected for rapid rotation of the seven membered ring. This process, which is stopped at -100 °C, will be commented upon more fully in Chapter 5. In the room temperature ^{13}C NMR spectrum, there is a single peak for the C_7H_7 ligand, and one sharp resonance for all three CO groups on the Os centre.

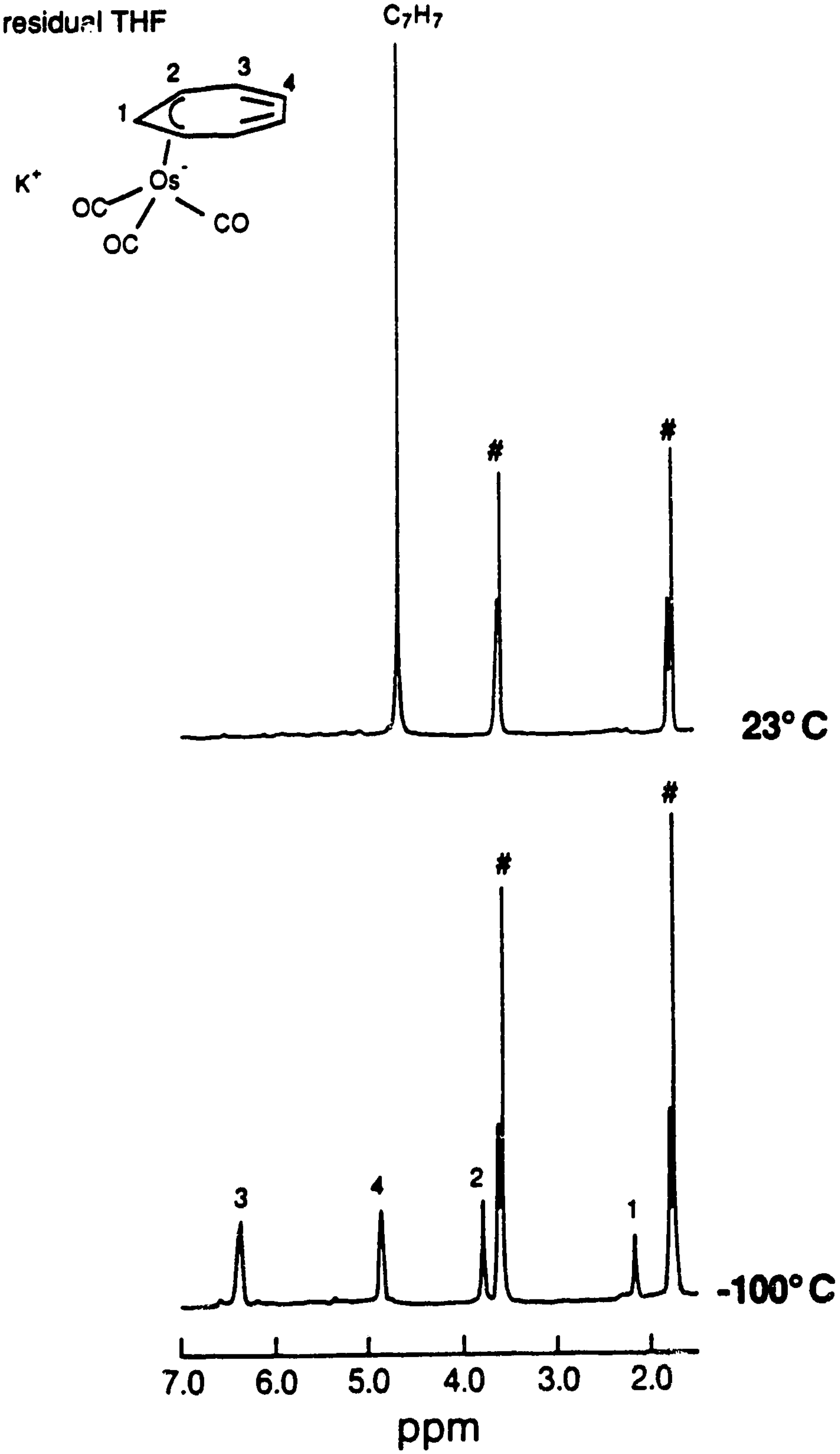
One surprising observation about this reaction was that it was found to be temperature dependent: Thus, when a dark orange solution of $K(\eta^3\text{-}C_7H_7)Os(CO)_3$ (**2c**), prepared from reaction of **1c** with KO^tBu at room temperature, is allowed to stir at -78 °C the solution will regain the original pale yellow-green colour and IR spectroscopy indicates substantial reformation of $(\eta^4\text{-}C_7H_8)Os(CO)_3$ (equation 3-3). This led to

$$K[(\eta^3\text{-}C_7H_7)Os(CO)_3] + HO^tBu \rightleftharpoons (\eta^4\text{-}C_7H_8)Os(CO)_3 + KO^tBu \qquad (3\text{-}3)$$

complications in some reactions of **2c**, as a minor pathway was often reprotonation to give back **1c**. For this reason, in certain instances it was deemed desirable to isolate the anion in the solid state in the absence of HO^tBu, and hence the preparation and isolation of $[Ph_4As][(\eta^3\text{-}C_7H_7)Os(CO)_3]$ was carried out.

Figure 3.2. Room Temperature and -100 °C ^{1}H NMR Spectra of **2c**.

= residual THF



3.2.3. Preparation of $[Ph_4As][(\eta^3\text{-}C_7H_7)Os(CO)_3]$.

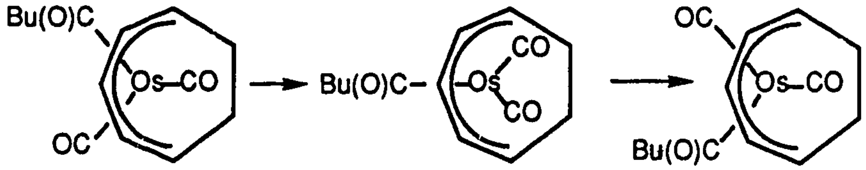
Crystals of the $AsPh_4^+$ salt of the Os anion, were prepared by reaction of a freshly made THF solution of $K(\eta^3\text{-}C_7H_7)Os(CO)_3$ with $AsPh_4Cl$. Upon addition of the anionic solution to a slurry of $AsPh_4Cl$ in THF at room temperature, most of the suspension dissolves to give a dark red solution of $[Ph_4As][(C_7H_7)Os(CO)_3]$ and a precipitate of KCl. The IR spectrum of the supernatant solution [1963 (s), 1883 (s), 1864 (s)] indicates complete cation exchange by the much sharper bands for the carbonyl stretching vibrations[14]. Separation of the supernatant solution followed by filtration and rapid crystallization from THF/toluene gives dark red crystals of $[Ph_4As][(C_7H_7)Os(CO)_3]\cdot THF$. The maximum yield obtained as crystals is about 40 % as the compound has a tendency to form an oil in the presence of any slight impurities such as $(\eta^4\text{-}C_7H_8)Os(CO)_3$.

3.2.4. Reaction of $(\eta^4\text{-}C_7H_8)Os(CO)_3$ with BuLi.

Addition of one equivalent of BuLi to a THF solution of **1c** gave a colour change from pale yellow-green to yellow-orange as expected for formation of an anionic complex. Surprisingly the IR showed only two sharp bands at 1955 and 1883 cm^{-1} which contrasts with $K(\eta^3\text{-}C_7H_7)Os(CO)_3$ [1961 (s), 1884 (s), 1863(sh)]. Addition of this anion to $[Ir(COD)Cl]_2$ failed to give a clean reaction. Following this experiment, the ^1H NMR spectrum of the anionic complex was run. Instead of the expected single peak for $Li(C_7H_7)Os(CO)_3$, a very complicated spectrum was obtained indicating that a different product had been formed. This was verified when hydrolysis of the anion followed by work-up gave a light green oil (**3c**) which was determined not to be (η^4-C_7H_8)Os(CO)$_3$. The ^{1}H and ^{13}C NMR spectra of **3c** are shown in Figure 3.3. It can be seen that there are too many peaks to be assigned to a single C_7H_7 ring. The structure as depicted in the figure was deduced from homonuclear decoupling experiments. Assignments of the ^{13}C signals were according to literature reports of cycloheptadienyl[15] and acyl[16] compounds.

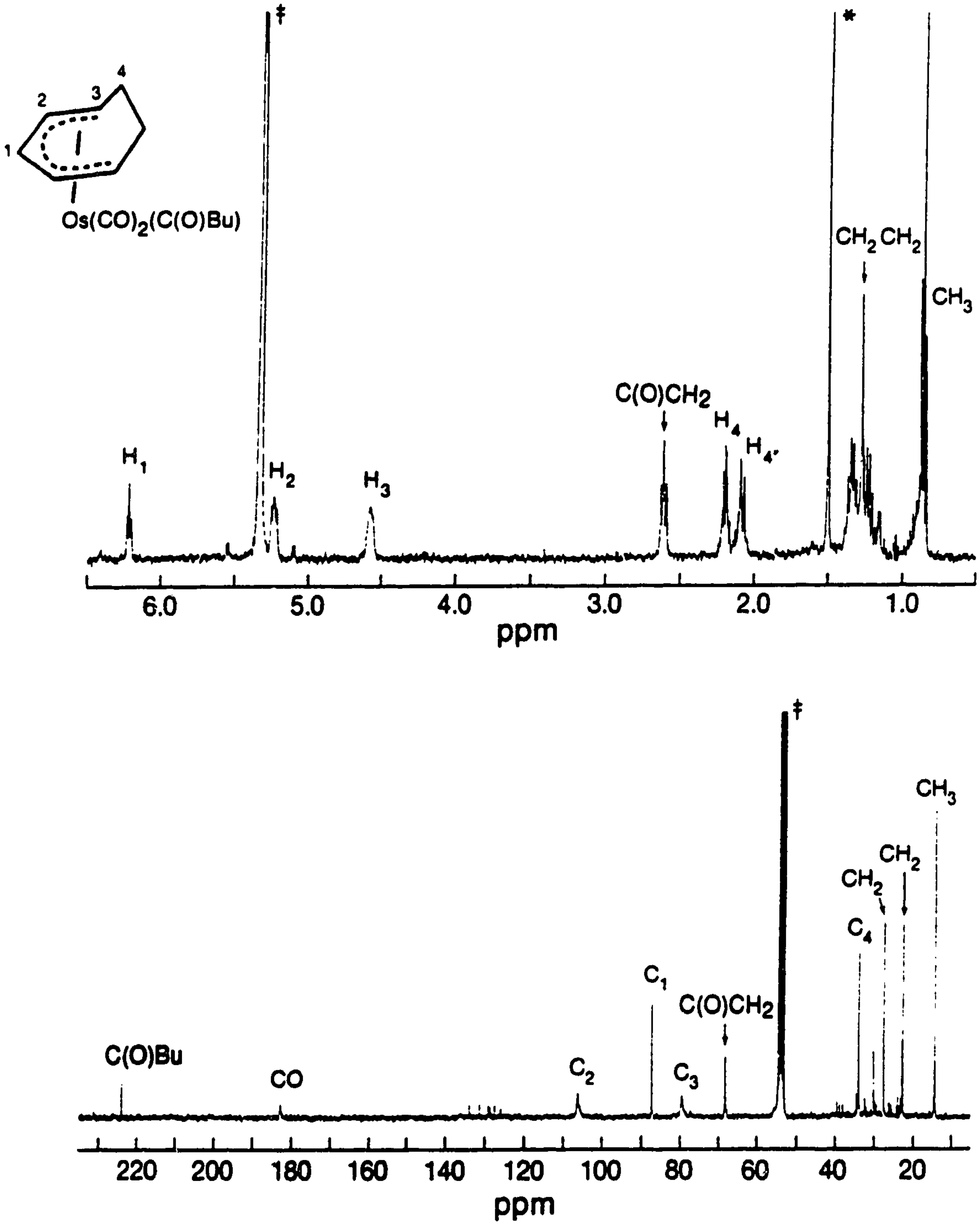
It can be seen from the figure that two of the ring signals (H_2 and H_3) have a slightly broad nature. This is also reflected in the ^{13}C NMR spectrum of the respective signals. The broad nature of two of the signals can be explained by interconversion of the two enantiomeric forms of the asymmetric isomer. This is accomplished by rotation of the Os(CO)$_2$[C(O)Bu] group with respect to the C_7H_9 ligand (Scheme 3.2)[15]. Consistent with this postulate, the CO resonance is also broad due to the exchange of two distinct resonances. In the symmetric isomer, only one sharp resonance would be expected.

Scheme 3.2



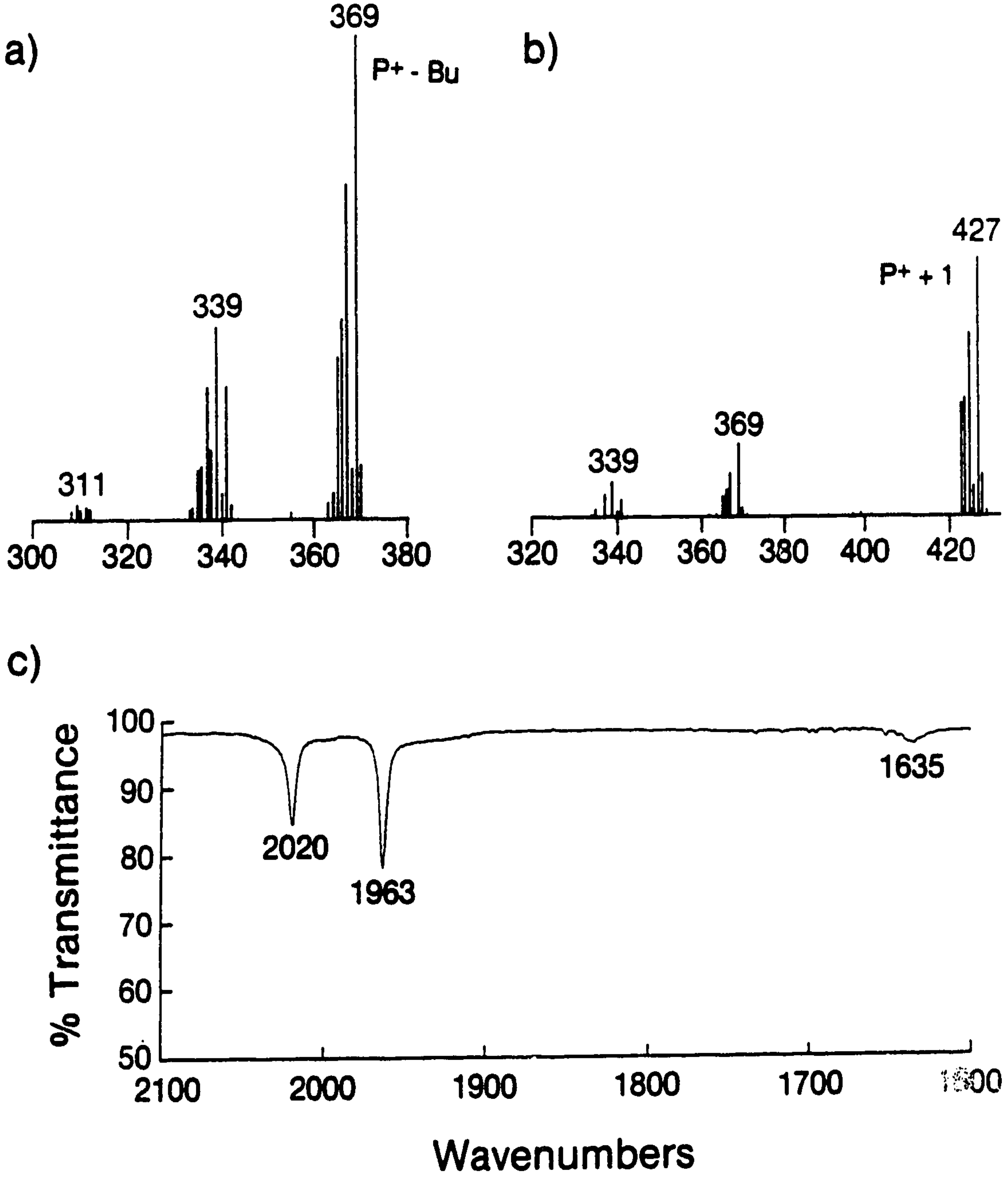
The IR spectrum for **3c** (Figure 3.4) shows two strong bands in the terminal CO stretching region at 2020 and 1963 cm^{-1} (hexane).

Figure 3-3 ^{1}H and ^{13}C NMR Spectra of $(\eta^5\text{-}C_7H_9)Os(CO)_2[C(O)Bu]^a$



[a] Spectra recorded in CD_2Cl_2; ‡ = solvent * = unidentified impurity.

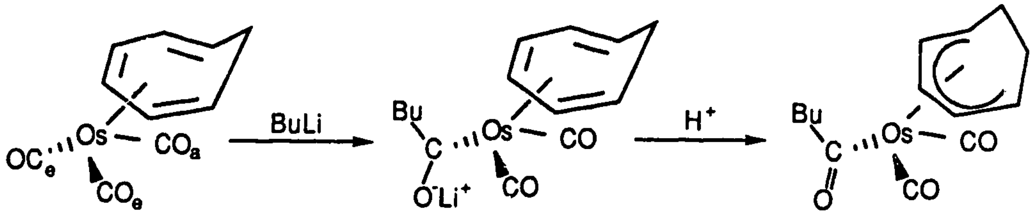
Figure 3.4. Mass Spectra (a,b) and IR spectrum in the carbonyl region (c) of $(\eta^5\text{-}C_7H_9)Os(CO)_2[C(O)Bu]$.



a) electron impact (16 eV, 100 °C), b) chemical ionisation (NH_3)

A weak band outside the terminal CO stretching region due to the acyl CO group can also be observed at 1635 cm^{-1}. The observation of only two strong bands in hexane solution at very similar frequencies has also been seen for several closely related acyl compounds $Cp(OC)_2Fe(C(O)R)$ (R = aryl)[17]. The electon impact and chemical ionization mass spectra of **3c** are also shown in Figure 3.4. The electron impact mass spectra has large peaks due to (P^+ - Bu) (most intense peak = 369). In addition the cluster of peaks centred at 339 is due to (P^+ - Bu - CO) (most intense peak = 341) and (P^+ - Bu - CO - H_2) (most intense peak = 339). The ready loss of alkyl groups on acyl substituents has previously been observed[16]. In addition, strong peaks due to (M^+ - CO - H_2) are typical of exo substituted cyclohexadiene compounds[18]. Using chemical ionization (NH_3) as the ionization method, the cluster of peaks due to the parent ion at 427 (P^+ +1)[19] is observed. The MS data were simulated using a locally available program. The mechanism of formation of this compound, which is discussed further in the next section, is most likely nucleophilic attack at the carbonyl ligand, followed by protonation at the C_7H_8 ligand as shown below.

Scheme 3.3



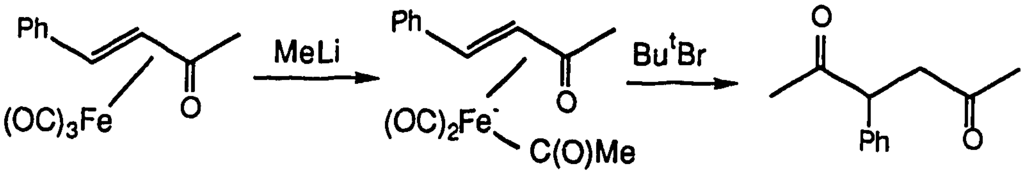
3.3. Discussion

It may appear surprising that the reaction of **1c** with BuLi is different from that observed for the analogous Fe and Ru compounds. However, it has previously been observed in (dienyl)$M(CO)_3$ cations that nucleophilic attack at CO is more prone for M = Os than for M = Fe[20]. One possible reason for this, is that in the case of Os there is more negative charge delocalised onto the CHT ligand than onto the carbonyl ligands, making nucleophilic attack at CO more amenable. Nucleophilic attack of BuLi on carbonyl groups of both Os and Ru cluster compounds leading to stable acyl anions has been previously observed[21]. In addition, nucleophilic attack by aryl lithium compounds has been seen on $(\eta^4\text{-}C_7H_8)Fe(CO)_3$[22]:

$$\text{(CHT)Fe(CO)}_3 \quad + \quad \text{Li}\mathit{o}\text{-CH}_3\text{C}_6\text{H}_4 \quad \text{----->} \quad \text{(CHT)(CO)}_2\text{FeC(OLi)}\mathit{o}\text{-CH}_3\text{C}_6\text{H}_4 \qquad (3\text{-}4)$$

A series of acylate iron complexes has been prepared in this fashion. This, of course, contrasts to the deprotonation which occurs when BuLi is used in place of Lio-$CH_3C_6H_4$[23]. In addition, and also very recently, butyl lithium has been observed to react in similar fashion with related tricarbonyl iron complexes of α,β-unsaturated ketones[24]. Rearrangement of the resultant acylate compounds upon reaction with Bu^tBr ultimately gives products useful in organic synthesis.

Scheme 3.4.



The second step in the formation of **3c** is the hydrolysis of (η^4-C_7H_8)Os(CO)$_2$C(OLi)Bu. In this reaction, protonation occurs at the seven-membered ring instead of the acylate group. This is consistent with the known reactivity of (cyclooctatetraene)Fe(CO)$_2$(C(OLi)(aryl))[25] where, upon reaction with [Et_3O][BF_4] in H_2O at 0 °C (or in CH_2Cl_2 at -30 °C), protonation at the ring is the favoured pathway.

The complexes **2c**, **1c**, and **3c**; (η^3-C_7H_7)Os(CO)$_3^-$, (η^4-C_7H_8)Os(CO)$_3$, and (η^5-C_7H_9)Os(CO)$_2$(C(O)Bu) provide an interesting series of complexes with increasing coordination to an unsaturated seven-membered ring. The variable temperature ^1H and ^{13}C NMR spectra of these complexes thus affords information about the changing interaction between the metal centre and the seven-membered ring within this series. As already mentioned, and as expected[26], very rapid fluxional behaviour of the C_7H_7 ring and Os(CO)$_3$ group is observed for **2c**. This will be discussed more fully in Chapter 5. Complexes **1c** and **3c**, again as expected, show decreased fluxional behaviour. No ring movement is observed for **1c**. A net 1,3 shift motion is possible[27] however, it is not expected to occur at room temperature[28]. No such process is available for

3c due to the lack of uncoordinated sites of unsaturation in the seven-membered ring. Interestingly, both **1c** and **3c** display a broad signal in their ^{13}C NMR spectra for the CO resonances at room temperature indicating both are undergoing a rotation of the $Os(CO)_2L$ group with respect to the seven membered ring at close to the same rate. In the related complex, $(\eta^4\text{-}C_7H_8)M(CO)_3$ (M = Ru) a very similar observation was made[29]. However, for the analogous iron complex (M = Fe), a fairly sharp singlet for the three carbonyl groups was observed which broadens only when the sample is cooled below 0 °C[12]. This indicates that the process may be slightly more facile for Fe, which, of course, is in accord with the well-known increase in metal-ligand bond strengths[30] as a transition metal triad is descended.

3.4. Experimental.

3.4.1. General Techniques and Reagents, Chapter 3.

$Os_3(CO)_{12}$ was prepared according to the literature[31]. Cycloheptatriene and tetraphenylarsonium chloride hydrate were purchased from Aldrich Chemical Company. Cycloheptatriene was distilled prior to use, and tetraphenylarsonium chloride hydrate was dehydrated by evacuation (10^{-3} mm Hg) at 110 °C for 24 hours, or until no further weight loss was observed. Butyl lithium was bought from Aldrich Chemical Company as a 1.6 M solution in hexanes. Elemental analyses on oils **1c** and **3c** were not attempted due to difficulties in separation from solvents.

3.4.2. Typical Synthesis of $(\eta^4\text{-}C_7H_8)Os(CO)_3$, 1c.

$Os_3(CO)_{12}$ (0.28 g), cycloheptatriene (6 ml) and C_6H_6 (90 ml) were placed in a pyrex 3 x 18 cm Schlenk tube which was purged with N_2 for 10 minutes and then fitted with a water cooled condenser. The pale green solution was placed 11 cm from a 450 W high pressure Hanovia mercury lamp and the solution was then irradiated for 12 hours with shielding of the lamp and vessel by aluminium foil on only one side. The solvent was removed from the resultant yellow solution to leave a yellow brown residue which was chromatographed on a silica gel column (3 cm x 5 cm, Merck, Kieselgel 60, 230 - 400 mesh) with pentane. A pale yellow-green band due to $(\eta^4\text{-}C_7H_8)Os(CO)_3$ was easily visible. This band was followed by a slow moving orange band. The eluent was collected from the beginning of the pale yellow-green band until the beginning of the orange band. The solvent was then removed to obtain a pale yellow-green oil (0.18 g, 62%). Further purification could be accomplished by distillation under vacuum at room temperature to a dry-ice cooled probe. The solid could then be washed from the probe with pentane into a separate flask. Removal of the solvent afforded $(\eta^4\text{-}C_7H_8)Os(CO)_3$ as a pale yellow-green oil (0.16 g, *ca.* 55%).

IR ν_{CO} (hexane) 2066, 1994, 1982 cm^{-1}.

^1H NMR: (22 °C, CD_2Cl_2); δ 5.74 (1H,m,H_5) 4.91 (1H,m,H_6), 4.77 (1H,m,H_3), 4.68 (1H,m,H_2), 2.72 (2H,m,H_1+H_4), 1.56 (m,$H_{7'}$), 0.89 (m,H_7). For numbering scheme see text.

3.4.3. Synthesis of $[AsPh_4][(\eta^3\text{-}C_7H_7)Os(CO)_3]$, 2c.

$K[(\eta^3\text{-}C_7H_7)Os(CO)_3]$ in THF (15 ml) was made directly from $(\eta^4\text{-}C_7H_8)Os(CO)_3$ (85 mg, 0.23 mmoles) and KO^tBu (26 mg, 0.23 mmoles)[8]. The dark red solution was transferred under nitrogen to a separate flask containing a slurry of $AsPh_4Cl$ (97 mg, 0.23 mmoles) in THF (15 ml). The solution was filtered and then the solvent was removed to leave a dark orange residue which was redissolved in THF and cystallised rapidly at room temperature by addition of toluene to give dark red crystals of $[AsPh_4][(\eta^3\text{-}C_7H_7)Os(CO)_3]\cdot$THF (70 mg, 41%). The inclusion of one molecule of THF was determined from integration of the ^1H NMR spectrum in CD_2Cl_2.

Anal. Calcd for $C_{38}H_{35}AsO_4Os$: C, 55.55, H, 4.29. Found: C, 55.80; H, 4.38.

IR (THF) υ_{CO}: 1963(s), 1883(s), 1864(s) cm^{-1}.

^{1}H NMR (25 ^{o}C, THF-d_8): δ 7.7 - 7.9 (20H,Ph) 4.66 (s,7H,C_7H_7); (-115 ^{o}C): 6.42 (m,2H,H_3), 4.87 (dd,$J_{H3\text{-}H4}$=8.3, 3,7 Hz, 2H,H_4), 3.83 (dd,$J_{H2\text{-}H3}$=7.5 Hz; $J_{H1\text{-}H2}$=7.5 Hz, 2H,H_2), 2.19 (t,$J_{H1\text{-}H2}$=4.5 Hz,1H,H_1).

^{13}C {^{1}H} NMR (25^{o}C, THF-d_8): δ 191.9 (s,CO), 135.3 (s,Ph,*p*) 134.4 (s,Ph), 131.8 (s,Ph), 89.2 (s,C_7H_7); (-110^{o}C): 142.0 (s,C_7H_7,C_3) 111.9 (s,C_7H_7,C_4), 37.9 (s,C_7H_7,C_1+C_2).

3.4.4. Reaction of (η^4-C_7H_8)Os(CO)$_3$ with Butyl Lithium and Subsequent Hydrolysis.

1c (130 mg, 0.36 mmoles) was dissolved in a 100 ml reaction vessel in THF (15 ml) under nitrogen. To this pale green solution was added 0.25 ml of 1.6 M butyl lithium solution in hexane (0.40 mmoles) from a new bottle . This gave a yellow-orange solution to which was added three drops of water. The solution lightened and was then extracted in hexane and dried over Na_2SO_4. The solvent was removed to give a yellow-brown residue which was chromatographed on silica gel (CH_2Cl_2/acetone; 25:1) and then vacuum distilled to give a pale green oil (60 mg, 40%).

IR (hexane) υ_{CO}: 2020 (s), 1963 (s), 1635 (w) cm^{-1}.

^{1}H NMR: (22 ^{o}C, CD_2Cl_2) δ 6.22 (1H,t,J=6Hz,H_1), 5.24 (2H,br,m,$H_{2/2'}$), 4.58 (2H,br,m,$H_{3/3'}$), 2.62 (2H,m,C(O)CH_2), 2.20 (2H,m,H_4), 2.08 (2H,m,$H_{4'}$), 1.34 (2H,m,CH_2), 1.25 (2H,m,CH_2), 0.88 (3H,m,CH_3).

^{13}C NMR: (22 ^{o}C, CD_2Cl_2) δ 224 (C(O)Bu), 183 (br,CO), 106.2 (br,$C_{2/2'}$), 87.3 (C_1) 79.2 (br,$C_{3/3'}$), 68.1 (C(O)CH_2), 34.0 ($C_{4/4'}$), 27.4, 22.6 (CH_2), 14.2 (CH_3).

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Chapter 4.

Reaction of $(\eta^3\text{-}C_7H_7)Os(CO)_3^-$ with $[M(COD)Cl]_2$ (M = Rh, Ir). Formation, Characterization and Derivatization of Isomeric *cis*- and *trans*-$(\mu\text{-}C_7H_7)Os(CO)_3M(COD)$ Complexes.

4.1 Introduction.

Of the many useful synthetic reactions available to anionic carbonyl complexes of the transition metals, a particularly important and currently topical application is the ability to produce heterobimetallic complexes upon reaction with suitable electrophilic transition metal substrates[1]. As already mentioned in this thesis, we have for some time been involved in the chemistry of the ambident organometallic nucleophiles $(\eta^3\text{-}C_7H_7)M(CO)_3^-$ (M = Fe, **1a**, Ru, **1b**). Thus reaction of **1a** with group 14 electrophiles R_3SiCl and R_3GeBr gives ring substituted complexes[2], whereas reaction of **1a** and **1b** with $[M'(COD)Cl]_2$ (M' = Rh, Ir)[3] leads to the formation of cycloheptatrienyl bridged heterobimetallic complexes; *cis*-$(\mu\text{-}C_7H_7)M(CO)_3M'(COD)$ (M-M') (M' = Rh, Ir; COD = 1,5-cyclooctadiene), in which both metals are situated on the same side of the seven-membered ring.

As described in Chapter 2, the synthesis of the anionic osmium complex $(\eta^3\text{-}C_7H_7)Os(CO)_3^-$ (**1c**) has been accomplished and its structure is compared to that of the analogous Fe and Ru derivatives in

Chapter 5[4]. In brief, it was found that in the solid state all three compounds contain an η^3-bound cycloheptatrienyl moiety and it is believed that the $(\eta^3\text{-}C_7H_7)M(CO)_3^-$ formulation is maintained in solution as well. Accordingly, **1c** reacts with Ph_3SnCl to give the anticipated product, $(\eta^3\text{-}C_7H_7)Os(CO)_3SnPh_3$[5] containing an Os-Sn bond. However, unexpectedly and in contrast to Fe and Ru, the reaction of the osmium anion with $[M'(COD)Cl]_2$ (M' = Rh, Ir) gives heterobimetallic complexes where the two metal fragments occupy opposite faces of the bridging cycloheptatrienyl moiety, *trans*-$(\mu\text{-}C_7H_7)Os(CO)_3M'(COD)$ (M' = Rh, **2a**, Ir, **3a**) as the initial product. Subsequent isomerization yields the thermodynamically more stable, and ubiquitous product of previous reactions, *cis*-$(\mu\text{-}C_7H_7)Os(CO)_3M'(COD)$ (M' = Rh, **2b**, Ir, **3b**). In this chapter, the synthesis, characterization, and structure of complexes **2** and **3**, are described, and a detailed triad comparison of the fluxional solution behaviour of the thermodynamically more stable *cis*-$(\mu\text{-}C_7H_7)M(CO)_3M'(COD)$ compounds (M = Fe, Ru, Os; M' = Rh, Ir) is also given.

4.2 Results

4.2.1 Reaction of $K(\eta^3\text{-}C_7H_7)Os(CO)_3^-$ with $[Rh(COD)Cl]_2$.

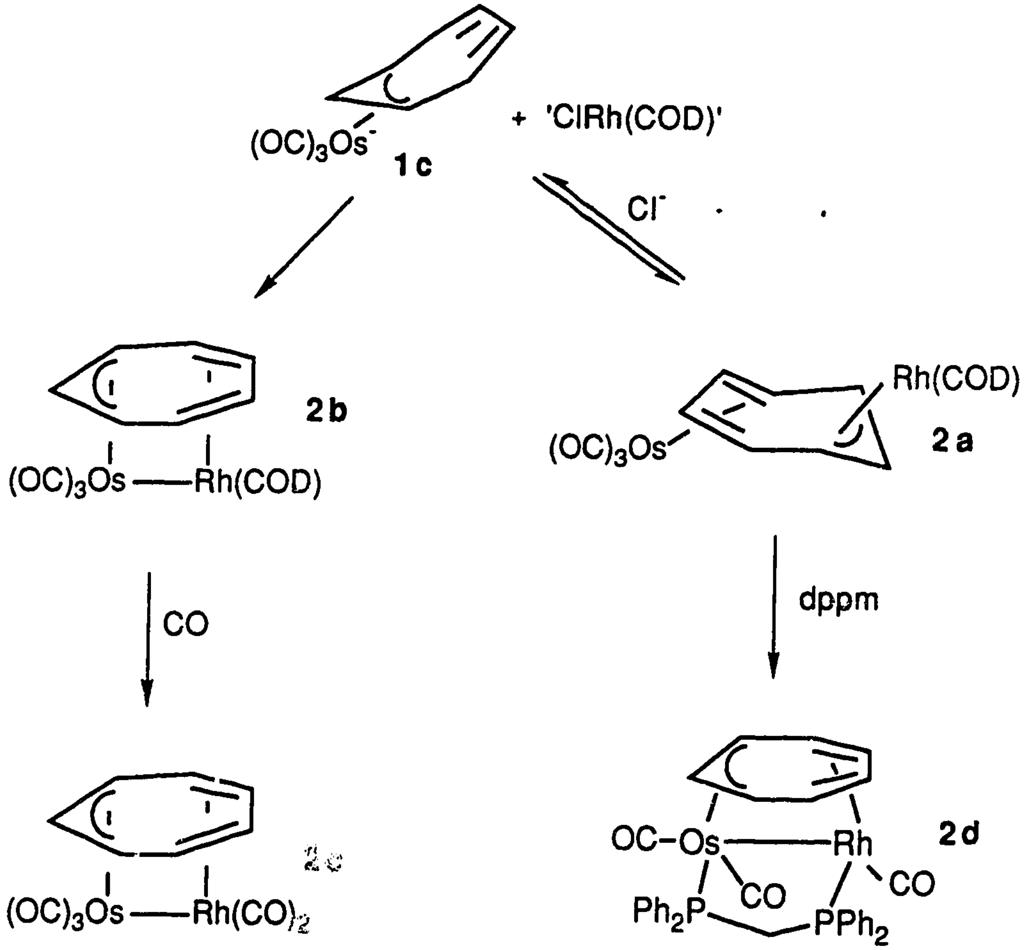
The reaction of $K[(C_7H_7)Os(CO)_3]$ (**1c**) with $[Rh(COD)Cl]_2$ at -78 °C in THF solution followed by solvent removal at room temperature leads to the isolation of two new products, in addition to a small amount of the reformed starting material, $(\eta^4\text{-}C_7H_8)Os(CO)_3$. The mass spectra and elemental analyses of these new compounds, separated by fractional crystallization, identified them as two isomers of the expected product; (μ-C_7H_7)Os(CO)$_3$Rh(COD) (**2**).

K(C_7H_7)Os(CO)$_3$ + $^1/_2$ [Rh(COD)Cl]$_2$ --> (μ-C_7H_7)Os(CO)$_3$Rh(COD) (4-1)
(**1**) [**2a**(11%) + **2b**(5%)]

The IR spectrum of one of these compounds (**2b**) (2030, 1962, 1957 cm^{-1}) is very close to the expected spectrum for *cis*-(μ-C_7H_7)Os(CO)$_3$Rh(COD). Compound **2b** is a bright orange, air stable solid which can be purified further by chromatography. In contrast the larger yield product (11%, **2a**) is more sensitive to air or trace impurities and does not survive chromatography. This product was crystallised from CH_2Cl_2/hexane over 12 hours at -40 °C and was obtained as a tan-yellow microcrystalline solid which can be stored for several days in the solid state under inert atmosphere without noticeable decomposition. Darkening of the compound does occur at room temperature after more prolonged periods. The IR spectrum of this compound in the carbonyl region (2060, 1991, 1979 cm^{-1}) is very close to that observed for (η^4-C_7H_8)Os(CO)$_3$, (2066, 1994, 1982 cm^{-1}). On the basis of these observations this compound (**2a**) was assigned to be *trans*-(μ-C_7H_7)Os(CO)$_3$Rh(COD) and **2b** was assigned to be its cis isomer.

When the reaction was repeated in diethyl ether and the reaction mixture was not allowed to warm above -10 °C the yield of **2a** was doubled. In this reaction, only a trace amount of **2b** was formed implying that the cis compound may have been formed via isomerization of **2a** during attempted work up. When the reaction was carried out using the Ph_4As^+ salt of **1** instead of K^+ the reaction followed a different path. Again the initial product appeared to be **2a**, based on IR spectroscopy. However, upon warming to room temperature, work up of the orange residue did not give any **2a**, but yielded 25% of cis compound **2b** in addition to a small amount of $(\eta^4\text{-}C_7H_8)Os(CO)_3$. This indicated that in this reaction the isomerization of **2b** to **2a** had been much cleaner presumably due to the presence of $AsPh_4Cl$ in solution. To account for this, and the significant increase in yield we suggest that the increased concentration of chloride ion in solution can act as a catalyst in this process as shown in Scheme 4.1. This hypotheses was strengthened when the reaction of **2a** with 0.5 equivalents of PPNCl was carried out. The THF solution darkened from yellow to orange-brown and complete consumption of starting material had occured after stirring for 15 minutes at room temperature. Although the reaction was not clean, the major product (25%) was **2b**, with a small amount of $(\eta^4\text{-}C_7H_8)Os(CO)_3$ also visible in the IR spectrum of the hexane extract. There were apparently no other carbonyl containing products formed. The variable temperature ^1H and ^{13}C NMR spectra of compounds **2** (*vide infra*) were consistent with these assignments however in view of the unexpected results it was deemed necessary to confirm the assignments by X-ray structural characterization.

Scheme 4.1 Preparation of OsRh Heterobimetallic Compounds.



4.2.2. Solid State Structure of 2a.

X-ray quality crystals of **2a** were obtained by crystallization from CH_2Cl_2/hexane (1:1) at -40 °C for 2 days under inert atmosphere. This produced a small amount of thin yellow plates. The molecular structure of **2a** was determined from one of the thickest crystals by Dr. B. D. Santarsiero of the Structure Determination Laboratory of this department. The structure is shown in Figures 4.1 and 4.2. Selected interatomic bond lengths and angles are given in Tables 4.1 and 4.2. As can be seen from Figure 4.1, the central seven-membered ring is separated into an allylic portion bonded to Rh, and a diene unit bonded to Os. The two parts of the C_7H_7 ring are separated by relatively long C-C bonds. The orientation of the ring can be referred to as being in a chair conformation. This conformation was also observed in the *trans*-(μ–η^3,η^4-C_7H_7) complex, $Cp(OC)_2Mo(\mu\text{-}C_7H_7)Fe(CO)_3$[6]. The main features of the seven-membered ring are very similar in both cases. Thus the allylic C-C bond lengths are typical at ca. 1.40 Å and the terminal allylic carbons are bonded to the outer diene carbons by long bonds of ca. 1.50 Å. Within the diene section of the seven membered ring the central bond is relatively short at 1.391 (18) Å. The two remaining outer diene C-C bonds are intermediate at ca. 1.45 Å. The $Os(CO)_3$ group is bonded to the diene fragment in a close to symmetric fashion with distances to the outer diene carbons of 2.252 (10) (C3) and 2.232 (10) (C6) Å. The Os to inner carbon bond distances are shorter and approximately identical at ca. 2.18 Å. The Os centre thus can be thought of as having an approximate square-

Figure 4.1 Molecular Structure of **2a** (Front View).

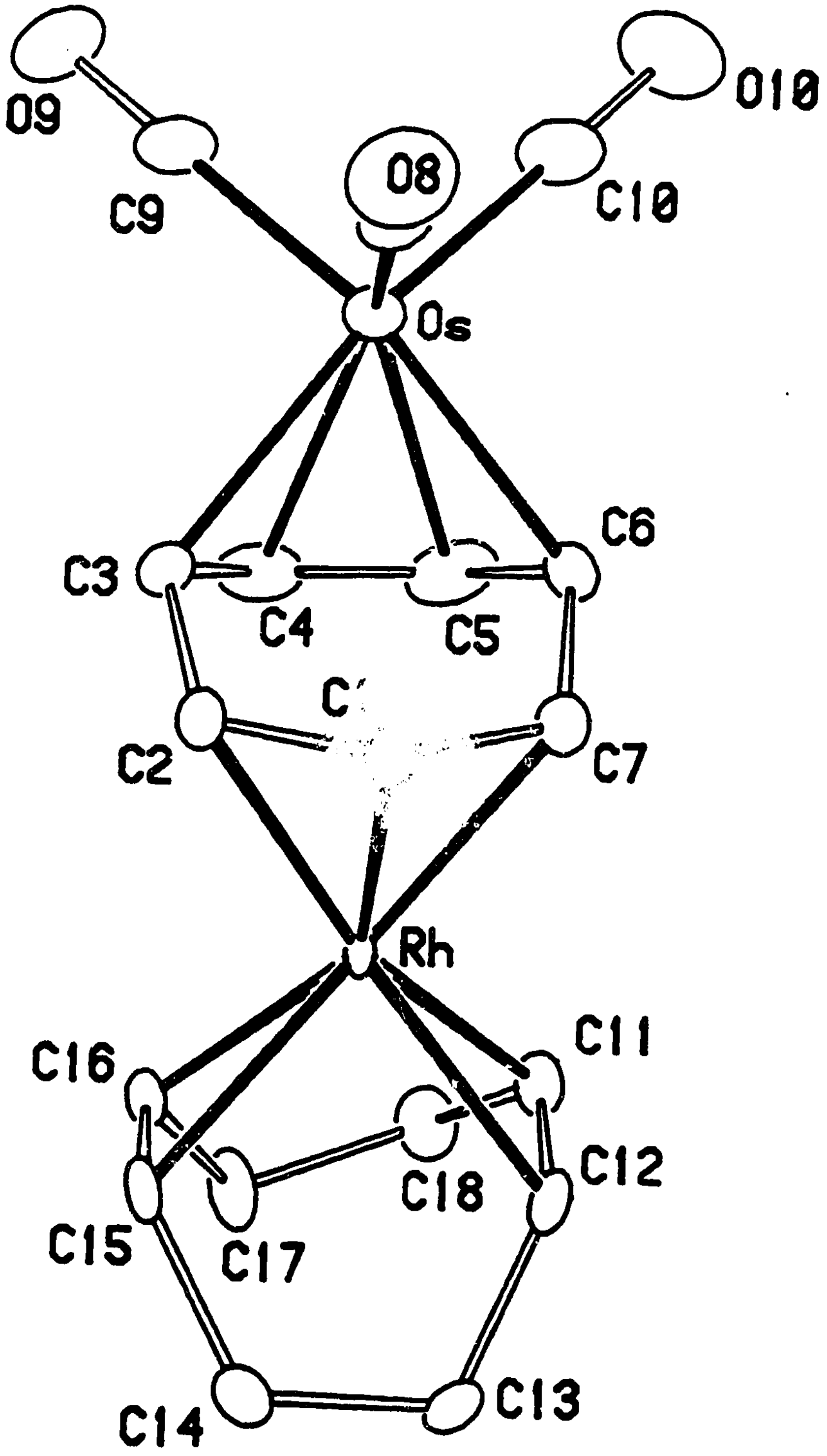
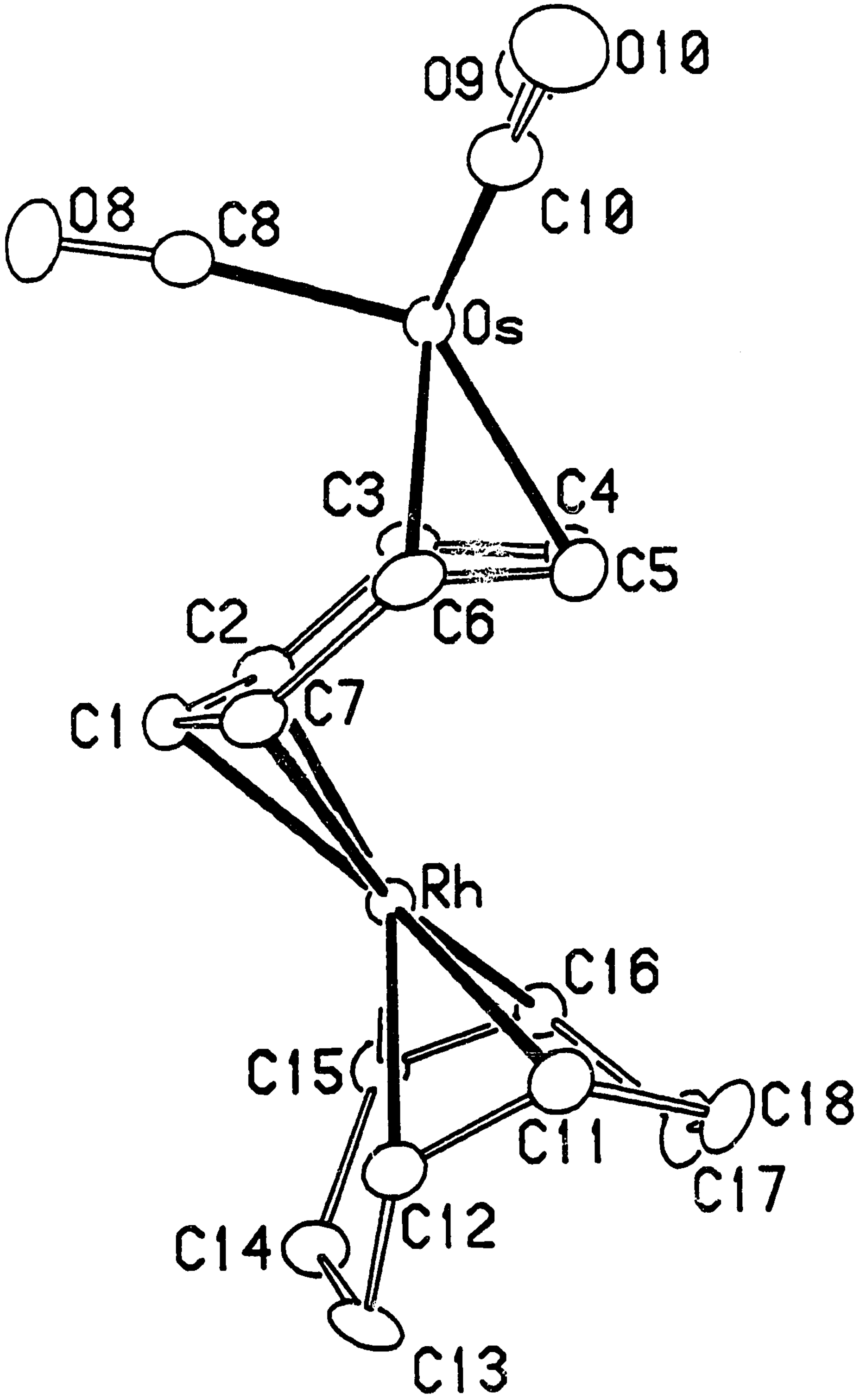


Figure 4.2.

Molecular Structure of **2a** showing chair conformation of C_7H_7 ring.



33.2 ppm) in the ^{13}C NMR spectrum which was previously assigned to a saturated carbon atom. Hence **4a** is the preferred structure.

Consistent with the above structure are the known coupling constants and chemical shifts of related bridging allylidene functionalities. There have been complexes reported in the literature which contain CF_3 groups on similar allylic functions as **4a** and which show coupling constants in the range of 14 - 16 Hz[17]. The fourth CF_3 group is out of the plane of the pseudo metallacyclopentadiene fragment due to the sp^3 hybridization of C11. This CF_3 group is staggered with respect to the CF_3 group on the adjacent carbon, and the observed F-F coupling between these two groups is 9 Hz. This can be compared to F-F coupling between staggered CF_3 groups on an η^2-vinyl moiety of ca. 5 Hz in $[Cp(HFB)(SC_6H_4Me\text{-}4)W\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}$, reported by Davidson[18]. The ^{13}C chemical shifts of complexes containing similar bridging allylidene and the very closely related "three alkyne flyover" functionalities are also consistent with this assignmnent[19]. Other support for the proposed geometry include the 2 Hz coupling between a ^{13}CO group on Ir to H5 (see Figure 6.4) and the 4 Hz coupling between $CF_3(9)$ and H7. Both of these through space interactions could easily occur for **4a**. Additionally, in **4a** one could expect hindrance of the $CF_3(8)$ group with a CO group on Ru and it is unlikely that any of the other three CF_3 groups would undergo restricted rotation. In summary, for the following reasons we favour structure **4a** to be the accurate description of the geometry of the bis alkyne moiety in **4**:

(a) The ^{13}C chemical shifts of the α, β, γ, and δ, carbons are in the expected range for bridging allylidene carbons and an alkyl carbon respectively.

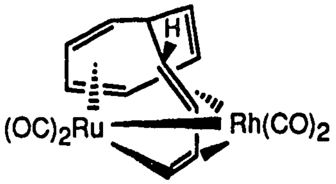
(b) The $^{5}J_{F\text{-}F}$ coupling constants indicate a cis relationship of the α, β, and γ CF_3 groups, and a staggered relationship of the γ and δ CF_3 groups.

(c) The through space interactions of the δ CF_3 group with CO_{Ru} and of the γ CF_3 group with H_7 are easily explained by this structure.

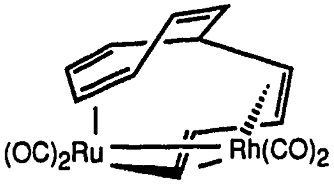
(d) The high field resonance of C5 suggests that the bonding mode of the ring is more appropriately represented by **4a** than by **4b**.

6.3.3. Reaction of (μ-C_7H_7)Ru(CO)$_3$Rh(CO)$_2$ with C_2H_2.

The reaction of **1** with the acetylene, C_2H_2 is much slower than that observed with the electron poor acetylene, HFB. Due to difficulties in isolation, this product was investigated only by its IR and NMR spectra, however, these proved quite informative. According to the IR spectrum (Figure 6-8), a product closely related to complex **4** [(C_7H_7)(HFB)$_2$Ru(CO)$_2$Ir(CO)$_2$] is obtained. The ^{13}C NMR spectrum clearly showed that only two of the three double bonds of the seven-membered ring were coordinated to a metal. A series of homonuclear proton decoupling experiments showed clearly that two acetylene units had coupled and inserted between the seven-membered ring, and a metal centre. It is assumed that this metal centre is Ru due to the absence of Rh coupling to the terminal hydrogen atom (H11). The chemical shifts of carbons 11, 10 and 9 are again close to those observed in **4** and in the related bridging allylidene and flyover complexes. However there are several features in the spectra of **5** not consistent with those of **4** (see Table 6.2). For instance, all four of the carbons of the linked alkyne unit show Rh-C coupling. Also, the carbon atoms C4 and C8 which were at 33.2 and 10.0 ppm respectively in **4** are at much lower field in **5** (75.2 and 65.6 respectively). This suggests these carbons are best represented as coordinated olefinic carbons rather than sp^3 hybridized saturated carbon atoms. In order to satisfy these requirements two likely alternative structures (**5c** and **5d**) could be envisioned:



5c



5d

Structure **5c** contains a μ–σ–η^4-butadiene fragment. This type of bonding of a butadienyl fragment to a dinuclear compound has been previously observed and structurally characterized in $[(dippe)Rh]_2(\mu$–η^4-σ-$C_4H_5)(\mu$-$H)$[20] [dippe = 1,2-bis(diisopropylphosphino)ethane]. The construction of **5c** is based on that structure. In this case the four carbons of the diene fragment are close to being planar and occupy an s-cis configuration. An alternative structure (**5d**) can also be imagined where the diene occupies an s-trans configuration. Apart from the configuration of the diene unit, the other main difference between **5c** and **5d** is that the hydrogen atoms on the double bonds between C11 and C10 and between C9 and C8 are in a cis-trans arrangement in **5c** but are trans-cis in **5d**. Structures containing a cis-cis relationship or a trans-trans relationship were ruled out as neither would meet the requirements set by the ^{13}C NMR spectrum. In order to elucidate which structural alternative (**5c** or **5d**) may most accurately describe the bonding in **5**, a survey of H-H coupling constants in coordinated diene systems was carried out.

Both configurations of the diene unit (s-cis and s-trans) have been noted previously in Cp_2Zr(butadiene)[21], CpMo(NO)(butadiene)[22] and $CpMo(CO)_2(butadiene)^+$ complexes[23]. Typical H-H coupling constants in these complexes (where α and δ represent the terminal atoms) are s-cis: $J_{H\alpha\text{-}H\beta} = J_{H\gamma\text{-}H\delta}$ = 8-10.5 (cis-H), 10.5 - 12.5 (trans-H), $J_{H\beta\text{-}H\gamma}$ = 6-11; s-trans: $J_{H\alpha\text{-}H\beta} = J_{H\gamma\text{-}H\delta}$ = 6-8 (cis-H), 7-16.5 (trans-H), $J_{H\beta\text{-}H\gamma}$ = 7-16. The magnitude of the coupling constants is very dependent on the system and the bonding of the diene fragment to the transition metal. For example, the Hβ-Hγ coupling constant is much larger for Cp_2Zr(butadiene) complexes than for $CpMo(CO)_2(butadiene)^+$ complexes, possibly due to an increased double bond character of the central Cβ-Cγ bond in the former complexes.[24] The observed coupling constants for **5** ($J_{H\alpha\text{-}H\beta} = J_{H\gamma\text{-}H\delta}$ = 11, $J_{H\beta\text{-}H\gamma}$ = 8) are therefore consistent with the formulation of a diene unit containing two separate double bonds with little double bond character between them. This may be expected as the structure is probably twisted due to the coordination requirements and may be better viewed as two olefinic units rather than a conjugated diene functionality. Apart from this observation, however it is difficult to make any further predictions. On the basis of a precedential compound structurally related to **5c** we very tentatively favour **5c** over **5d**.

In summary, **5** clearly has a structure related to **4**, where two acetylene units have coupled and inserted between Ru and the C_7H_7 ring, however for this complex we tentatively suggest that the adopted structure is closer to **5c** than to **4a** for the following reasons:

(a) The observation of Rh-C coupling constants of 8, 3, 8, and 8 Hz for carbons 11 - 8 and no Rh coupling to carbons of the seven-membered ring.

(b) In the ^{13}C NMR spectrum, the resonances for C11 and C10 are close to those expected for **4a** or **4b**. However, the resonance for C9 and especially that for C8 are at much lower field than in **4**, and are more characteristic of a coordinated olefin[10b]. Similarly the H9 and H8 resonances are more consistent with a coordinated olefin[14a,b] than a bridging allylidene unit[17].

(c) The H-H coupling constants of the C_4 fragment suggest a diene unit with not much double bond character of the central C10-C9 bond.

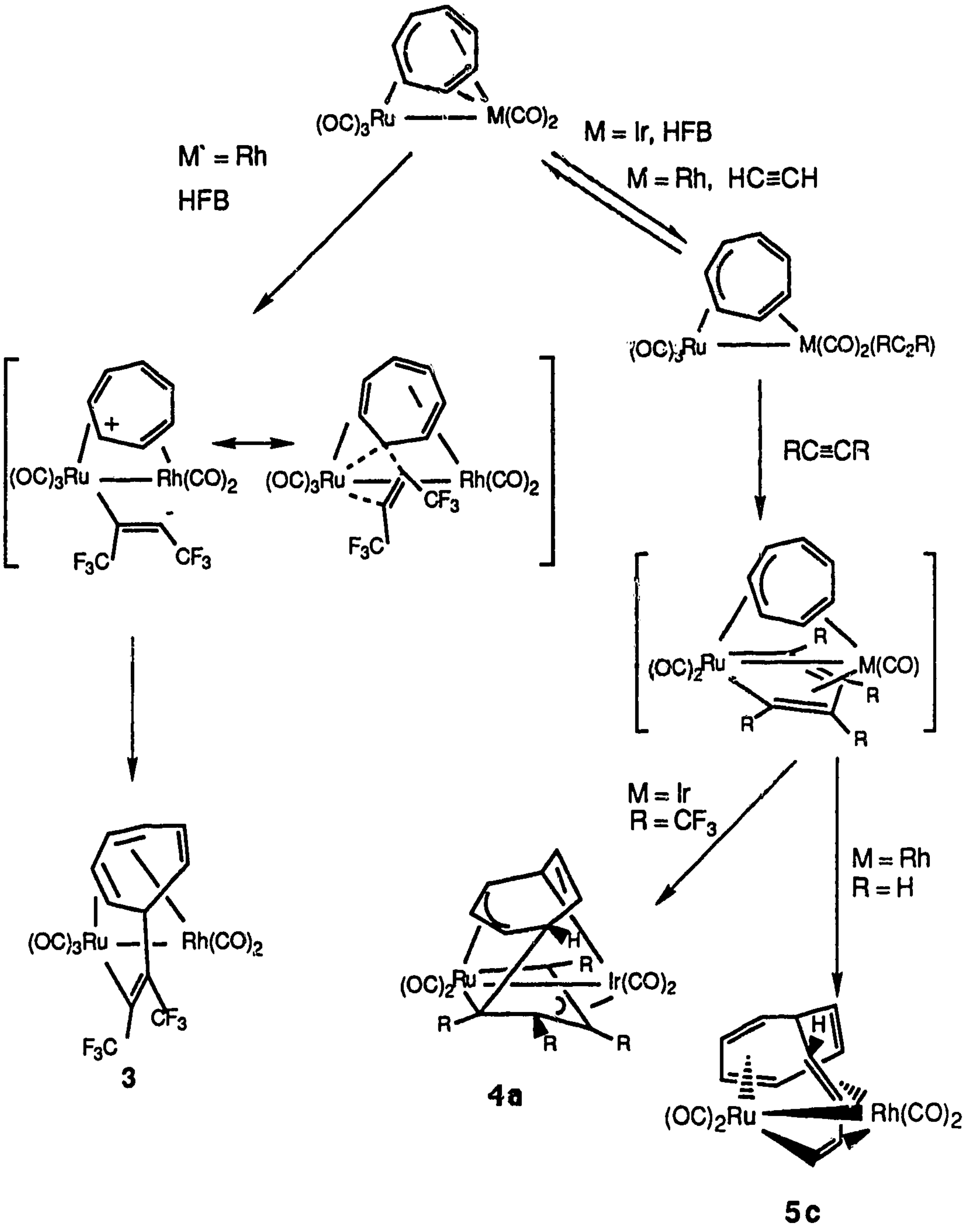
(d) There are few similarities in the ^1H and ^{13}C NMR spectra of the C_7H_7 ring between **4** and **5**. In particular, the chemical shifts of the outer carbons of the diene fragment coordinated to Ru show large differences (**5**; C1; 52.1, C4; 75.2. **4**; C1; 61.1, C4; 33.2). Other noteworthy features of **5** which are not reflected in the spectra of **4** are the surprisingly high field shifts of H1 (0.84) and the uncoordinated olefinic proton H6 (2.84).

6.3.4. Possible Explanation for the Observed Reactivity.

The rapid reaction of **1** with HFB can be explained by rapid electrophilic attack of the HFB moiety at the electron rich Ru centre, Scheme 6.1. The insertion could occur via an ionic intermediate or by a concerted pathway. This reaction is closely related to the insertion of HFB into a Ru-Cp bond observed by Stone[25].

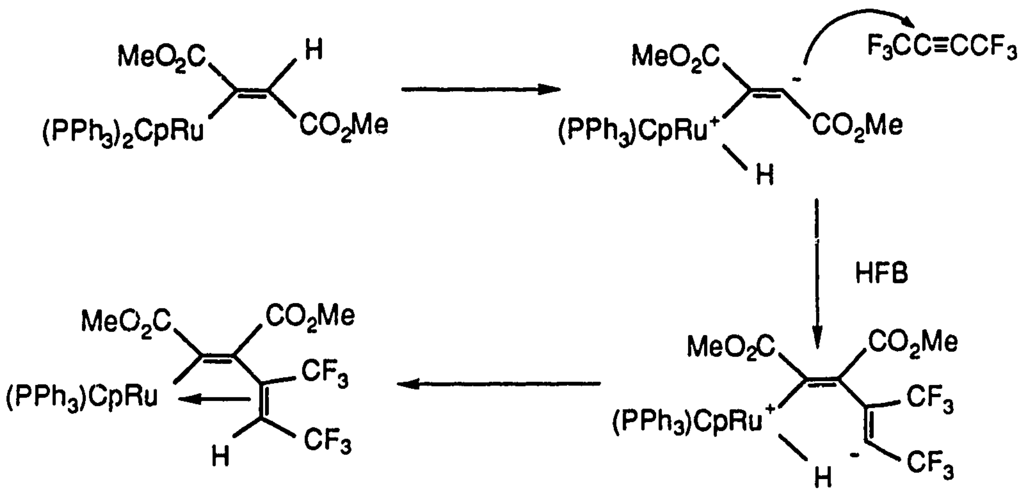
In contrast, the analogous RuIr complex (**2**) requires thermal activation of 100 °C to enable a reaction to occur. The presence of an Ir centre instead of the 2nd row Rh centre clearly leads to the increased inertness. The most logical initial step in the RuIr reaction at 100 °C is coordination of an HFB unit to one of the metal centres. Due to the lack of a product analogous to **3** $[(C_7H_7)(C_4F_6)Ru(CO)_3Rh(CO)_2]$ and the inability of **3** to insert cleanly one more equivalent of HFB upon heating, the next step is apparently not insertion of the alkyne moiety between Ru and the seven-membered ring. Instead upon subsequent approach of a second HFB moiety to the dinuclear complex, coupling between the two alkynes and insertion between Ru and the seven-membered ring must occur to obtain

Scheme 6.1. Possible reactivity of alkynes with **3** and **4**.



the observed product. Clearly the formation of the RuIr complex (**4**) is far more complicated than the path followed in the RuRh reaction. One obvious contender for the formation of **4a** involves a metallacyclopentadiene complex as shown in the scheme. Numerous examples of similar complexes are known, and further insertion reactions of these complexes with extra alkynes are well documented[5,13a,28]. Hence the observed C-C bond formation in our complex is easily envisioned.

The reaction between **1** $[(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2]$ and HC_2H follows a similar path to the reaction between RuIr and HFB although the geometry of the final product appears to be different. This is probably a consequence of the different steric requirements of the alkynes in the coupling step. The effects of the very different electronic demands of HFB and C2H2 cannot be entirely ruled out, however. A very similar reaction was observed between the cyclooctadiene complex **1b** and HC_2H although the final product in this reaction maintained the COD moiety. Thus these reactions are alkyne dependent as well as metal dependent. The decrease in the observed rate of reaction, and reversal of reactivity going from HFB to C_2H_2 suggests that the path followed for the reaction of **1** with HFB reaction is heavily favoured for alkynes with electron withdrawing substituents. This is consistent with the ionic intermediate shown in the scheme. Zwitterionic intermediates have been previously proposed in related C-C bond forming reactions[26]. In one related example, such an intermediate is proposed to undergo addition to an HFB ligand[27]:



6.4. Summary.

(μ-C_7H_7)Ru(CO)$_3$Rh(CO)$_2$ (**1**) undergoes a rapid addition reaction with the activated alkyne HFB. However the analogous reaction of (μ-C_7H_7)Ru(CO)$_3$Rh(COD) (**1b**) produces no such product. Clearly replacement of two CO groups on Rh with the bulky COD ligand blocks the reaction pathway. Alternatively, (μ-C_7H_7)Ru(CO)$_3$Ir(CO)$_2$ reacts with HFB under thermal conditions with loss of 1 CO ligand to give the complicated product **4**. In this case substitution of two CO groups on Ir with the COD ligand in the starting material has little effect on the reactivity and the same product (**4**) is produced in lower yield. Thus the first step in the reactions of the RuIr complexes with HFB may be substitution of a ligand at the Ir centre. Also consistent with this proposal was the observation that no product analogous to **4** is produced when **3** is heated in the presence of HFB. Thus implies that insertion of one HFB moiety between Ru as the first step in these reactions followed by a second insertion is not likely. These observations suggest that replacement of Rh with Ir in the starting pentacarbonyl compounds $(\mu\text{-}C_7H_7)Ru(CO)_3M(CO)_2$ decreases the nucleophilicity of the Ru centre and hence alters the reaction pathway.

6.5. Experimental.

6.5.1. General Techniques and Reagents, Chapter 6.

Hexafluorobut-2-yne (HFB) was bought from S. C. M. Speciality Chemicals. Acetylene was purchased from Matheson Gas Products Canada, and passed through a cold trap at -78 °C to remove small amounts of acetone. For ^{19}F NMR, $CFCl_3$ was used as a calculated external standard. $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ (**1**) was made according to the literature[2a]. The preparation of $(\mu\text{-}C_7H_7)Ru(CO)_3Ir(CO)_2$ (**2**) is described in Chapter 2. The complete solid-state structural determination of compound **3** was carried out by Dr. R. G. Ball of the Structure Determination Laboratory of this department. Some relevant information from the structure report is included in this thesis. Further information including listings of observed and calculated structure factors may be obtained from Dr. J. Takats of this department.

6.5.2. Preparation of $(\mu\text{-}C_7H_7)(\mu\text{-}C_4F_6)Ru(CO)_3Rh(CO)_2$ (3).

$(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ (25 mg) was dissolved in hexane (10 ml) and freeze-thaw degassed. A slow stream of HFB was then bubbled through the reaction mixture for 1 minute. The red-brown solution was then stirred for 5 minutes with no colour change. The solvent was then removed to leave a brown residue which was chromatographed on a silica gel column (3 cm x 1.5 cm) eluting with hexane. The major band which is an orange colour is collected and crystallized from hexane to leave yellow-orange crystals of **3** (16 mg, 45 %).

Anal. Calcd. for $C_{16}H_{7}F_{6}O_{5}RhRu$: C; 32.18, H; 1.35. Found: C; 32.35, H; 1.22.

M. S. (90 °C, 16 eV, 70 eV) P^{+} = 598, P^{+} -n(CO), n = 0 - 5.

IR (υ_{CO}, hexane); 2089 (m), 2056 (s), 2035 (m), 2015 (m).

^{1}H NMR (22 °C, CD_2Cl_2) δ 3.66 (1H,t,H7,$J_{H7\text{-}H1}$=$J_{H6\text{-}H7}$=7), 4.12 (^{1}H,t,H1,$J_{H1\text{-}H2}$=$J_{H7\text{-}H1}$=7), 4.96 (1H,dd,H3,$J_{H2\text{-}H3}$=5.5,$J_{H3\text{-}H4}$=9.5), 5.10 (1H,dd,H2,$J_{H1\text{-}H2}$=7$J_{H2\text{-}H3}$=5.5), 5.96 (1H,dd,H4,$J_{H3\text{-}H4}$=9.5,$J_{H4\text{-}H5}$=6.5) 6.04 (1H,dd,H6,$J_{H5\text{-}H6}$=9.5,$J_{H6\text{-}H7}$=7), 6.48 (1H,dd,H5,$J_{H4\text{-}H5}$=6.5,$J_{H5\text{-}H6}$=9.5).

^{13}C NMR (22 °C, CD_2Cl_2) δ 42.0 (C7), 73.2 (C3), 77.9 (C1), 80.1 (C2), 83.5 (C4), 127.2 (C5), 138.3 (C6), 101.1 (m,Cβ), 125.5 (q,$J_{C\text{-}F}$=220Hz,C($CF_3\beta$)), 129.0 (q,$J_{C\text{-}F}$=220Hz,C($CF_3\alpha$)), 157.6 (m,Cα), 188.8 (d,CO_{Rh},$J_{Rh\text{-}C}$=80 Hz), 189.6 (d,CO_{Rh},$J_{Rh\text{-}C}$=70 Hz), 192.6 (s,CO_{Ru}), 195.4 (s,CO_{Ru}), 197.7 (s,CO_{Ru})

^{19}F NMR (22 °C, CD_2Cl_2) δ -61.1 (3F,q,$J_{F\text{-}F}$=14Hz,$CF_3\beta$), -40.2 (3F,dq,$J_{F\text{-}F}$=14Hz,$J_{Rh\text{-}F}$=3Hz,$CF_3\alpha$).

6.5.3. Solid-State Structure Determination of 3.

The structure determination was carried out by Dr. R. G. Ball of the Structure Determination Laboratory of this department. The following information was extracted from SDL report number SR: 200111-03-87. A yellow crystal of **3** was mounted on an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed using MoKα radiation with a graphite crystal, incident beam monochromator. The automatic peak search and reflection indexing programs in conjunction with a cell reduction program showed the crystal to be monoclinic and from the systematic absences of h0l, h + l odd; 0k0, k odd the space group was determined to be $P2_1/n$, (an alternative setting of $P2_1/c$). Cell constants were obtained from a least-squares refinement of the setting angles of 24 reflections in the range $14 < 2\theta < 28^\circ$. The various crystal parameters are given in Table 6.3. The structure was solved using the direct methods program MITHRIL[29] which gave the positional parameters for the Rh and Ru atoms. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis[30]. An empirical absorption correction was applied, using the Fourier filter scheme of Walker and Stuart[31]. The positional and thermal parameters of the non-hydrogen atoms are given in Table 6.4.

Table 6.3. Crystallographic Data for Compound **3**.

		3
empirical formula		$C_{16}H_7F_6O_5RhRu$
colour of crystal		yellow
crystal dimensions (mm)		0.20 x 0.24 x 0.43
space group		$P2_1/n$
cell dimensions	a (Å)	9.875(2)
	b (Å)	13.583(2)
	c (Å)	13.636(4)
	β (°)	102.09(2)
Z (Molecules/cell)		4
V (Å^3)		1788
d (calcd), (g/cm^3)		2.218
wavelength (Å)		0.71069
mol wt		597.20
linear abs coeff (cm^{-1})		18.22
detector to sample dist (cm)		20.5
scan type		ω-2θ
scan rate (deg/min)		10.1 - 2.6
scan width (deg)		0.70 + 0.35tan(θ)
data collection 2θ limit(deg)		55.00
aperture size (mm)		2.40 x 4.0
total no. of reflctns collected		4518
no. of unique intensities		4232
no. with $I > 3.0\sigma(I)$		3369
observations/variables ratio		3369/262
R1		0.023
R2		0.033
goodness of fit for the last cycle		1.22
corrections applied		absorption correction
data collection index range		h,k,±l

Table 6.4. Positional (x 10^4) and Thermal (x 10^2) Parameters for **3**.

Atom	x	y	z	U,Å^2
Rh	6333.8(2)	2603.7(2)	7865.3(1)	3.168(6)
Ru	3759.0(2)	1983.2(2)	7966.5(2)	3.436(6)
O12	3232(3)	3815(2)	9104(2)	8.05(9)
O13	3839(3)	829(2)	9920(2)	8.27(9)
O14	718(3)	1666(3)	6992(3)	8.6(1)
O15	8985(3)	3520(2)	7489(3)	8.2(1)
O16	6682(3)	3471(3)	9942(2)	10.4(1)
C12	3426(3)	3139(2)	8669(2)	5.1(1)
C13	3772(3)	1242(3)	9201(2)	5.31(9)
C14	1843(3)	1755(3)	7373(3)	5.3(1)
C15	7979(3)	3192(2)	7606(3)	4.73(9)
C16	6572(4)	3117(3)	9179(2)	5.7(1)
C2	5075(3)	581(2)	7800(2)	4.02(8)
C3	6474(3)	904(2)	8237(2)	4.00(8)
C4	7505(3)	984(2)	7708(2)	4.40(9)
C5	7384(3)	686(2)	6674(2)	4.58(9)
C6	6248(3)	760(2)	5948(2)	4.50(9)
C7	4993(3)	1316(2)	6075(2)	3.81(8)
C1	4352(3)	791(2)	6852(2)	3.87(8)
C9	4370(3)	2878(2)	6886(2)	3.47(7)
C11	3693(3)	3864(2)	6602(2)	5.1(1)
C8	5265(3)	2411(2)	6344(2)	3.49(7)
C10	5828(4)	2941(3)	5538(2)	5.3(1)
F1	3395(3)	4022(2)	5619(2)	8.85(9)
F2	2479(2)	3959(2)	6866(2)	8.76(8)
F3	4410(3)	4638(2)	6995(2)	9.3(1)
F4	6073(2)	3895(1)	5710(1)	6.47(7)
F5	7039(2)	2572(2)	5416(2)	7.17(7)
F6	4985(3)	2865(2)	4632(2)	8.9(1)

The equivalent isotropic thermal parameter is given by: $U = 1/3\sum r_i^2$ where r_i are the root-mean-square amplitudes of vibration.

6.5.4. Preparation of (μ-C_7H_7)(C_4F_6)$_2$RuIr(CO)$_4$ (4).

(μ-C_7H_7)Ru(CO)$_3$Ir(CO)$_2$ (50 mg) was dissolved in octane (10 ml) and freeze-thaw degassed. One atmosphere of HFB gas was then introduced to the frozen solution which was warmed to 100 °C and stirred for 2 hours. The solvent was removed from the dark orange solution to leave an orange-brown residue which was washed with hexane (4 ml) and chromatographed on a silica gel column (9 cm x 1.5 cm) eluting with 40 % CH_2Cl_2/hexane. There appeared to be two major bands. The first band is yellow, which is followed by a green band, however the IR and NMR spectra of the two bands showed few differences. Both fractions were combined, and the solvent was removed to leave a cream solid which was recrystallized from CH_2Cl_2/hexane to give pale yellow-green crystals of **4** (40 mg, 51 %).

Anal. Calcd. for $C_{19}H_7F_{12}OIrRu$: C; 27.81, H, 0.85, Found, C, 27.74, H, 0.84.

M. S, (FAB), $P^+ = 822$, P^+ -n(CO), n = 0 - 4.

IR (υ_{CO}, hexane); 2095 (m), 2055 (s), 2049 (w), 2005 (m).

^{1}H NMR (22 °C, acetone d_6); δ 3.13 (1H,dd,H4,$J_{H3\text{-}H4}$=7.5,$J_{H4\text{-}H5}$=9), 4.08 (1H,t,$J_{H1\text{-}H2}$=$J_{H7\text{-}H1}$=7.5), 4.94 (1H,t,H3,$J_{H2\text{-}H3}$=$J_{H3\text{-}H4}$=7.5), 5.14 (1H,t,H2,$J_{H1\text{-}H2}$=$J_{H2\text{-}H3}$=7.5), 5.38 (1H,m,H7), 6.23 (1H,t,H5,$J_{H4\text{-}H5}$=$J_{H5\text{-}H6}$=9), 6.62 (1H,dd,H6,$J_{H5\text{-}H6}$=9,$J_{H6\text{-}H7}$=6)

^{13}C NMR (22 °C, acetone-d_6); δ 10.0 (q,C8,$J_{C\text{-}F}$=30), 25.9 (s,C7), 33.2 (s,C4), 48.5 (m,C9), 61.1 (s,C1), 64.1 (s,C3), 71.1 (s,C2), 98.6 (m,C10), 124.0 (q,CF_3,$J_{C\text{-}F}$=280), 124.5 (q,CF_3,$J_{C\text{-}F}$=280), 129.5 (q,CF_3,$J_{C\text{-}F}$=275), 130.0 (q,CF_3,J_{C-F}=280), 133.7 (s,C6), 136.3 (s,C5), 159.8 (s,CO_{Ru}), 166.2 (s,CO_{Ru}), 191.4 (s,CO_{Ir}), 195.3 (s,CO_{Ir}).

^{19}F NMR (22 °C, acetone-d_6); δ -67.0 (br,$CF_3\delta$), -55.4(sp,J=16Hz,$CF_3\beta$), -51.2 (qqd,J_{F-F}=14,9Hz,J_{H7-F}=4Hz,$CF_3\gamma$), -45.5 (q,J=16Hz,$CF_3\alpha$). (-95 °C); -72.3 (t,J_{F-F}=115), -70.3 (qt, $^2J_{F-F}$=115, $^5J_{F-F}$=25), -58.9 (t,J_{F-F}=115).

6.5.5. Reaction of (μ-C_7H_7)$Ru(CO)_3$Rh(COD) with HFB.

(μ-C_7H_7)$Ru(CO)_3$Rh(COD) (**1b**) (10 mg) was dissolved in hexane (10 ml) to give an orange solution. The solution was degassed and then introduced to 1 atmosphere of HFB gas. The solution was then stirred for 12 hours at room temperature with no colour change. An IR spectrum of the reaction mixture at this point showed approximately half of the starting material had been consumed. The solvent was removed and the residue was redissolved in hexane (5 ml) and rapidly cooled to -78 °C for 15 minutes. The supernatant solution was then transferred to a separate vessel. An IR spectrum of this solution showed only bands due to the starting RuRh(COD). Extraction of the residue in hexane gave no carbonyl containing compounds. The residue did dissolve in CH_2Cl_2 however the IR spectrum showed several bands all of very low intensity.

6.5.6. Reaction of (μ-C_7H_7)$Ru(CO)_3$Ir(COD) with HFB.

(μ-C_7H_7)$Ru(CO)_3$Ir(COD) (**2b**) (30 mg, 0.052 mmoles) was dissolved in toluene (5 ml) and freeze-thaw degassed. The frozen solution was then introduced to one atmosphere of HFB gas and the closed reaction vessel was placed in an oil bath which was heated to 118 °C. The solution was stirred for 1 hour, cooled and then the solvent was removed. The residue was dissolved in hexane and filtered to a separate reaction vessel. An IR spectrum of the extract showed primarily **4**. Chromatography and crystallization of 4 as described above yielded 7 mg (14 %) of **4**.

6.5.7. Preparation of $(\mu\text{-}C_7H_7)(C_2H_2)_2RuRh(CO)_4$ (5).

$(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ (30 mg) was dissolved in toluene (5 ml) and freeze-thaw degassed three times. The frozen red solution was then put under 1 atmosphere of HC_2H and warmed to room temperature. The solution was then stirred for 2 hours to give a black solution. The solvent was then removed and the dark residue was evacuated for 1 further minute before it was reintroduced to an acetylene atmosphere. Toluene d_8 (0.6 ml) was then added to the reaction vessel. The dark black solution was then filtered by canula into an NMR tube under acetylene pressure.

IR (υ_{CO}, hexane); 2055 (m), 2014 (s), 2004 (w), 1958 (m).

^{1}H NMR (22 ^{o}C, toluene-d_8); δ 0.84 (dd,H1,$J_{H1\text{-}H2}$=8,$J_{H1\text{-}H3}$=1.5), 1.78 (d,H7,$J_{H7\text{-}H8}$=8), 2.84 (d,H6,$J_{H5\text{-}H6}$=8), 3.88 (t,H4,$J_{H3\text{-}H4}$=$J_{H4\text{-}H5}$=8), 4.38 (dd,H2,$J_{H1\text{-}H2}$=8,$J_{H2\text{-}H3}$=5), 4.64 (ddd,H3,$J_{H1\text{-}H3}$=1.5,$J_{H2\text{-}H3}$=5,$J_{H3\text{-}H4}$=8), 5.32 (dd,H8,$J_{H7\text{-}H8}$=8, $J_{H8\text{-}H9}$=11), 5.42 (t,H5,$J_{H4\text{-}H5}$=$J_{H5\text{-}H6}$=8), 6.08 (dd,H9,$J_{H8\text{-}H9}$=11,$J_{H9\text{-}H10}$=7), 7.66 (ddd,H10,$J_{H9\text{-}H10}$=7,$J_{H10\text{-}H11}$=11,$J_{H10\text{-}Rh}$=2), 9.78 (d,H11,$J_{H10\text{-}H11}$=11).

^{13}C NMR (22 ^{o}C, toluene-d_8); δ 34.8 (s,C7), 52.1 (s,C1), 65.6 (d,C8,$J_{C8\text{-}Rh}$=7), 68.2 (s,C3), 75.2 (s,C4), 77.5 (d,C9,JC9-Rh=8), 82.6 (s,C2), 110.6 (d,C2,$J_{C2\text{-}Rh}$=2.4), 130.0 (s,C6), 133.4 (s,C5), 150.5 (d,C11,$J_{C11\text{-}Rh}$=8), 186.4 (d,CO_{Rh},$J_{C\text{-}Rh}$=61), 190.4 (d,CO_{Rh},$J_{C\text{-}Rh}$=73), 194.7 (s,CO_{Ru}), 196.6 (s,CO_{Ru}).

6.5.8. Reaction of (μ-C_7H_7)Ru(CO)$_3$Rh(COD) with C_2H_2.

(μ-C_7H_7)Ru(CO)$_3$Rh(COD) (26 mg) was dissolved in hexane (18 ml) and placed in a 100 ml 'pop-bottle' which was connected to a vacuum line and an acetylene tank. The red solution was then freeze-thaw degassed and introduced to 15 psi above atmospheric of HC_2H. The solution was then stirred for 24 hours before the pressure was released. The solution was then filtered, concentrated to 3 ml and cooled to -78 °C for 16 hours. The orange supernatant solution was then separated from the brown residue and crystallized from hexane/$(Me_3SiO)_2$ at -30 °C to give an orange-red residue which was used for the NMR sample.

IR (ν_{CO}, hexane); 2004 (s) 1941 (s) cm^{-1}.

^1H NMR (22 °C, toluene-d_8); δ 1.08 (dd,H1,$J_{H1\text{-}H2}$=8,$J_{H1\text{-}H3}$=1.5), 1.96 (m,2H,COD), 2.01 (1H,m,H6), 2.08 (d,H7,$J_{H7\text{-}H8}$=8), 2.10 (m,2H,COD) 2.56 (m,2H,COD), 2.76 (m,1H,COD), 2.94 (m,2H,COD), 3.62 (m,1H,COD), 4.20 (m,1H,COD), 4.28 (t,H4,$J_{H3\text{-}H4}$=$J_{H4\text{-}H5}$=8), 4.70 (m,2H,COD), 4.82 (dd,H2,$J_{H1\text{-}H2}$=8, $J_{H2\text{-}H3}$=5), 5.22 (dd,H3,$J_{H1\text{-}H3}$=1.5,$J_{H2\text{-}H3}$=5,$J_{H3\text{-}H4}$=8), 5.46 (dd,H8,$J_{H7\text{-}H8}$=8,$J_{H8\text{-}H9}$=11), 5.84 (t,H5,$J_{H4\text{-}H5}$=$J_{H5\text{-}H6}$=8), 6.29 (dd,H9,$J_{H8\text{-}H9}$=11), 7.70 (dd,H10,$J_{H9\text{-}H10}$=7,$J_{H10\text{-}H11}$=11), 10.26 (d,H11,$J_{H10\text{-}H11}$=11).

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Chapter 7.

Fluxional Processes and Trends in Properties within a Series of Cycloheptatrienyl Bridged Heterobimetallic Complexes.

7.1. Properties of the Cyclooctadiene Complexes, $(\mu\text{-}C_7H_7)M(CO)_3M'(COD)$.

As a result of the studies reported in this thesis, the series of cis heterobimetallic complexes $(\mu\text{-}C_7H_7)M(CO)_3M'(COD)$ (M = Fe, Ru, Os; M' = Rh, Ir) is complete. Within this series of complexes, the inertness of the isolated complexes increases as either metal triad is descended. One way that this can be demonstrated is by looking at the substitution reaction of the COD ligand at the group 9 metal centres. For example carbonylation of the RuIr[1] and FeIr[2] cyclooctadiene complexes occurs only upon thermal heating whereas this reaction occurs readily at room temperature for the related RuRh[3] and FeRh[4] complexes. More interesting was the observation that the same effect, albeit less dramatic, was seen when the group 8 metal was changed. For example, reaction times for the FeRh[4], RuRh[3] and OsRh[5] complexes at room temperature are 5 mins, 90 mins, and 150 minutes respectively. The net effect thus appears to be a greater amount of electron donation from the $M(CO)_3$ to the M'(COD) fragment as the M triad is descended.

A more quantitive method of comparing the strengths of the M'-COD interaction is by comparing the free energies of activation for rotation of the COD group. This process, which is shown diagramatically in Scheme 7.1 involves change in geometry at the M' centre from square pyramidal to trigonal bipyramidal[4] and back to the original ground state structure.

Scheme 7.1

The free energies of activation for COD rotation were obtained from the approximate expression, equation 7.1, which relates the free energy of activation, $\Delta G^{\ddagger}$, coalescence temperature, Tc, and chemical shift separation $\Delta\upsilon$ (Hz) for a pair of equal singlets undergoing exchange[6].

$$\Delta G^{\ddagger} = 4.57Tc[9.97 + \log(Tc/\Delta\upsilon)] \qquad (7\text{-}1)$$

The coalescence temperature and chemical shift separation between exchanging pairs of olefinic or aliphatic carbon/hydrogen signals were obtained from variable temperature NMR studies. Although it is recognized that approximating the ^{1}H NMR signals as singlets is strictly not correct, the errors introduced by neglecting H-H coupling are less than the error due to the uncertainties in Tc (±5 K). Beside, in view of the approximations, we have much more reliance on the trends exhibited by

$\Delta G^{\ddagger}$ than the absolute values obtained for a specific compound. The resultant free energies of activation are listed in Table 7.1. As expected, when one replaces Rh(COD) with Ir(COD) there is a considerable stabilization of the metal-olefin bonding as evidenced by an increase of 4 kcal/mole in $\Delta G^{\ddagger}$. What is more interesting and pleasing to see is the effect of the non-participating metal. When the spectator metal is changed from Fe to Ru to Os there is a sequential increase in $\Delta G^{\ddagger}$ of 1 kcal/mole. This trend parallels the observed trend in the average ^{13}C chemical shift of the olefinic carbon atoms resonance to higher field upon descending the triad. Shifts to higher fields in the ^{13}C NMR spectrum of coordinated olefinic ligands have been associated with enhanced metal to ligand back-bonding[7] and hence stronger metal-olefin bonds.

The other two fluxional processes occurring in these complexes involve the metal tricarbonyl unit, and the seven membered ring. As mentioned in Chapter 4, these processes appear to be related and are explained in Scheme 7.2.

Scheme 7.2

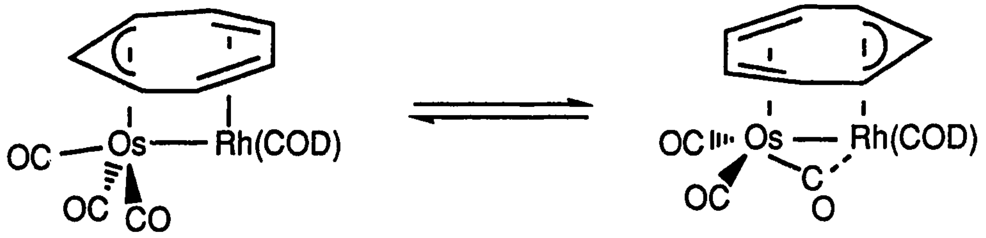

Table 7.1. ^{13}C NMR Data and $\Delta G^{\ddagger}$ for COD rotation in *cis*-(μ-C_7H_7)M$(CO)_3$M'(COD) compounds (M = Fe, Ru, Os; M' = Rh, Ir).

M-M'	δC_0 ave	Tc/°C[a]	$\Delta\delta$/Hz	$\Delta G^{\ddagger}$/kcal/mole[b]
Os-Ir	63.3	95 (Ha)	130	18
Ru-Ir	64.7	80 (Ca)	180	17
Fe-Ir	68.0	60 (Co)	80	16
Os-Rh	75.2	15 (Co)	100	14
Ru-Rh	80.9	0 (Ca)	100	13
Fe-Rh	84.2	-30 (Ha)	140	12

a Coalescence of: Ha; aliphatic hydogens, Ca; aliphatic carbons, Co; olefinic carbons, of COD ligand.

b Errors in $\Delta G^{\ddagger}$ are approximately 1 kcal/mole.

The carbonyl scrambling process is best considered as a trigonal twist of the octahedral M$(CO)_3$ group. In the trigonal prismatic intermediate involved in this process, one of the CO ligands comes into close proximity of the second metal centre thus allowing the formation of a bridging intermediate. This would also involve concommitant change in bonding mode of the C_7H_7 ring. In this mechanism, the two exchange processes are coupled and hence each is influenced by the nature of both metal centres. Thus on going from complex **3** (c-OsIr) to **2** (c-OsRh), a dramatic effect on the carbonyl scrambling in Os$(CO)_3$ is observed (see Chapter 4). In contrast the local carbonyl scrambling in both complexes **1** (c-RuIr) and

2 (c-OsRh) is frozen out at about - 80 °C, despite the fact that one is considering a Ru(CO)$_3$ group in **1** (see Chapter 2) versus an Os(CO)$_3$ group in **2**.

7.2. Rotation of the C_7H_7 ring in dinuclear (μ-η^3,η^4-C_7H_7) complexes.

In this thesis the preparation of the cis-cycloheptatrienyl bridged heterobimetallic compounds (μ-C_7H_7)M(CO)$_3$M'(COD) [MM' = RuIr (**1**), OsRh (**2**), OsIr (**3**)] have been described. In all three cases, the low temperature ^{1}H and ^{13}C NMR spectra have displayed signals for the static molecule. This was quite surprising as the number of examples of bimetallic compounds which contain a *cis*-(μ-η^3,η^4-cycloheptatrienyl) ring in which freezing out of metal migration around the ring is observed is still quite limited. Table 7.2 gives the chemical shifts of the ring hydrogens in those bimetallic compounds where the slow limiting spectrum has been attained. Apart from the series of complexes prepared in our group a cis-CoCr complex, Cp*Co(μ–η^3,η^4-C_7H_7)(μ-H)Cr(CO)$_3$ (**4**), and a trans-FeMo complex, (OC)$_3$Fe(μ–η^3,η^4-C_7H_7)Mo(CO)$_2$Cp (**5**) are also included in the table. Whilst the data set is still limited, there are three trends which can be found:

a) For both trans complexes, the slow limiting spectrum is obtained relatively easily. Also, the average chemical shift for the ring hydrogens is at lower field in the trans compounds than in the cis complexes.

Table 7.2. ^{1}H and ^{13}C NMR data for bimetallic (μ-η^3-η^4-C_7H_7) Complexes.

Compound	T[a]	ΔG‡	δH1	δH2	δH3	δH4	δHave	δCave
3 (c-OsIr)	-30	14[b]	3.07	3.30	2.03	3.81	3.34	-
2b (c-OsRh)	-100	10[c]	4.10	3.56	2.54	4.50	3.68	80.8
1 (c-RuIr)	-100	8.4[c]	3.54	3.76	2.80.	4.72	3.82	60.0
4 (c-CoCr)[d]	-73	-	1.55	2.58	2.68	4.07	2.92	68.2
5 (t-FeMo)[d]	-71	13[c]	4.82	4.37	3.77	5.37	4.57	-
2a (t-OsRh)	-50	12[b]	4.90	4.24	3.88	4.74	4.43	-
6 (c-FeRh)	-	-	-	-	-	-	3.76	-
7 (c-RuRh)	-	-	-	-	-	-	3.75	-
8 (c-FeIr)	-	-	-	-	-	-	3.82	-

a Temperature at which the slow limiting spectrum was recorded.

b ΔG‡ (for C_7H_7 rotation) obtained from spin inversion experiments (see Chapter 4)

c ΔG‡ obtained from simulation of spectral data [± 1 kcal/mole (approx)].

d **4** is $Cp^*Co(\mu-\eta^3,\eta^4-C_7H_7)(\mu-H)Cr(CO)_3$[8]; **5** is $(OC)_3Fe(\mu-\eta^3,\eta^4-C_7H_7)Mo(CO)_2Cp$[9]; Spectrum in $CDCl_3$/ toluene-d_8 (4:1).

e **6** is $(\mu-C_7H_7)Fe(CO)_3Rh(COD)$[3], **7** is $(\mu-C_7H_7)Ru(CO)_3Rh(COD)$[4], **8** is $(\mu-C_7H_7)Fe(CO)_3Ir(COD)$[2].

b) For cis complexes **3** and **4** in which the limiting spectrum has been obtained relatively easily, δH_{ave} is at relatively high field.

c) For complexes containing identical ligands, the activation energy for ring rotation increases as the metal triad is descended. In the cis-cycloheptatrienyl bridged complexes of FeRh, FeIr, and RuRh, complexes ring rotation has not been frozen out upon cooling, and values of δH_{ave} are close to 3.8.

A possible explanation for these observations is that for cis complexes of the lower transition series there is increased back-bonding from the metal into antibonding molecular orbitals of the C_7H_7 ligand. This should result in increasing the metal-ligand bond strength and consequently decreasing fluxional behaviour. This is likely as increases in metal-ligand bond strengths upon descending a triad are well known[10]. The CoCr complex **4** is an exception to this rule. This may be the result of different electronic contributions to the seven-membered ring as a consequence of the bridging hydrogen atom. Alternatively the presence of the highly electron donating ligand, Cp^* may allow strong back-bonding to the seven-membered ring such that its rotation may be stopped. The high field shift of the ring hydrogens in complexes **3** and **4** is consistent with this proposal as an increase in backbonding from the metals to the seven-membered ring should lead to an increase in sp^3 character of the ring hydrogens. There is some precedent to these claims as both olefin rotation barriers have been shown to increase[11], and the bond order of unsaturated organic substrates coordinated to a transition metal, have been shown to decrease upon descending a transition metal triad[12].

7.3. General Conclusions.

As discussed in this chapter, both metals appear to have an effect on the local and global fluxional behaviour of the complexes ($(\mu$-$C_7H_7)M(CO)_3M'(COD)$ (M = Fe, Ru, Os; M' = Rh, Ir). This effect is also extended to the chemical properties of these complexes. Thus, in Chapter 6 it was observed that the reactivity of $(\mu$-$C_7H_7)Ru(CO)_3Rh(CO)_2$ with HFB at the Ru centre was not replicated when Rh was replaced by Ir, almost certainly due to electronic reasons. Substitution of COD with carbonyl groups appeared to have little effect on the fluxional behaviour of the bimetallic compounds (see Chapter 2), although a dramatic effect in the reactivity of $(\mu$-$C_7H_7)Ru(CO)_3Rh(COD)$ with HFB was observed. This was presumably due to steric reasons. Upon coordination of a PPh_3 ligand to the group 9 metal centre a change in the electronic properties of the bimetallic complexes occurs such that the expected compounds, $(\mu$-$C_7H_7)M(CO)_3M'(CO)PPh_3$ exist in equilbrium with the carbonyl bridged compounds, $(\mu$-$C_7H_7)(\mu$-$CO)M(CO)_2M'(CO)(PPh_3)$ in which there is a reversal of the bonding mode of the C_7H_7 ligand. In these phosphine substituted complexes, (M = Fe, Ru, M' = Rh, Ir), the fluxional behaviour is greater than the parent pentacarbonyl complexes as evidenced by the appearance of relatively facile global carbonyl scrambling. However, a more surprising result is the trend in free energies of activation (Fe > Ru and Rh > Ir) for the intermetallic carbonyl scrambling process. A possible explanation for this phenomenon was offered in Chapter 2.

7.4. Experimental.

The synthesis, NMR Data and deduction of activation parameters for complexes **2a**, **2b**, and **3** were described in Chapter 4. The synthesis of **1** was described in Chapter 2. The values of the activation parameters for **1** were calculated by the method which was described in Chapter 4. The observed and calculated rate constants for **1** are given in Table 7.3, and the deduced activation parameters are given below.

Table 7.3. Observed and Calculated Rate Constants for the 1,2-metal migration around the seven-membered ring in **1**.

Temperature	Rate Constant	
	Observed	Calculated
213	15000	16353.71
203	7000	6436.10
183	800	740.32
173	250	109.13
163	50	50.77
158	20	23.42

Activation Parameters for **1** $\Delta H^{\ddagger}$; 7.60 (0.53) kcal/mol, $\Delta S^{\ddagger}$; -2.92 (2.90) cal/mol K (standard deviation in parenthesis). This gives a calculated vaue of $\Delta G^{\ddagger}$ of 8.5 kcal/mole.

7.5. References for Chapter 7.

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