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Titanacyclobutene Synthesis by Free Radical Alkylation of

Titananium(III) Propargyl Complexes and Titanacyclobutene Reactivity

by

Xin Qiu   ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment

of the requirements of the degree of Master of Science

Department of Chemistry

Edmonton, Alberta

Spring, 2000

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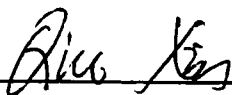
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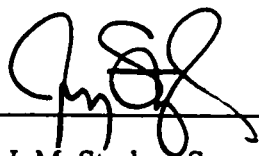
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Titanacyclobutene Synthesis by Free Radical Alkylation of Titananium(III) Propargyl Complexes and Titanacyclobutene Reactivity** submitted by Xin Qiu in partial fulfillment of the requirements for the degree of Master of Science.

Dr. J. M. Stryker, Supervisor

Dr. R. R. Tykwinski

Dr. E. E. Knaus

December 10, 1999

Abstract

The regioselective addition of organic free radicals to titanium(III) propargyl complexes is a general and convenient method for the preparation of β-substituted titanacyclobutenes. This study is focused on extending titanacyclobutene formation to functionalized substitutents to provide more substrates for potential application in synthetic chemistry. Ancillary ligand effects in the radical alkylation are also investigated. We show that electronic effects are more important than steric effects in the free radical addition to η^3-propargyl complexes.

A second part of this work is an investigation into small molecule functionalization of titanacyclobutene complexes. The observed reactivity is quite different from the reactivity of titanacyclobutane complexes. Single insertion of carbon monoxide and isonitriles is obtained. Demetallation of titanacyclobutenes is achieved using dichlorophenylphosphine and dichlorophenylborane, which lead to the forrmation of strained organic heterocycles.

In memory of my Mom

Acknowledgments

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I would like to gratefully acknowledge the technical staff at the University of Alberta for the great service. I truely appreciate the great work done by NMR and MS staff. I especially thank Mr. G. Bigam for the crucial NMR determinations and Dr. R. McDonald for X-ray structure determinations. Your help has been the best!

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Most importantly, I would like to thank my family, especially my wife, Xiaowen Wang, and my daughter, Wenjie Qiu for the continuous support and understanding.

Table of Contents

List of Abbreviations

Å	Angstrom
calcd	calculated
^{t}BuCp	tert-butylcyclopentadienyl
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Et	ethyl
equiv	equivalent
g	grams
h	hour(s)
Hz	hertz
i	iso
IR	infrared
L	liter
M	metal
mL	milliliter
MS	mass spectrometry
n	normal
NMR	nuclear magnetic resonance
Ph	phenyl
Pr	propyl
psig	pounds per square inch gauge pressure
R	alkyl group
THF	tetrahydrofuran
μL	microliter

I. GENERAL INTRODUCTION

A. Background

The reactivity of both nucleophilic and electrophilic reagents toward coordinated ligands has been the focus of the development of many synthetically relevant metal-mediated methodologies.[1,2] However, the reactivity of organic free radicals toward coordinated unsaturated ligands of transition metal complexes, a much less developed area, may become important due to the quite unique selectivity and reactivity that can be obtained.

The central carbon alkylation of neutral d^1 titanocene(III) π-allyl complexes with organic free radicals was reported by Casty and Stryker.[3,4] This study reported that when the allyl complex, $Cp*_2Ti(\eta^3\text{-}C_3H_5)$ 1, is treated with $Cp*_2TiCl$ and an alkyl halide, radical addition takes place exclusively at the central carbon of the allyl ligand, providing a novel entry into β-alkyl titanacyclobutane complexes 2 (Scheme 1, top).

Scheme 1

1 of 97
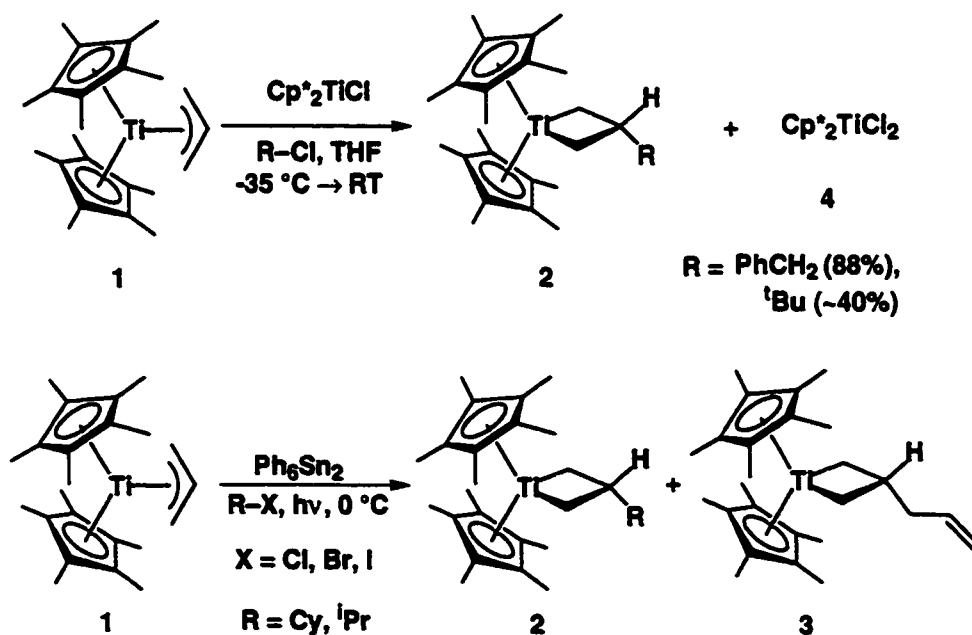
This radical generating strategy, however, is limited to activated organic halides; tert-butyl chloride gave only a low yield of the titanacyclobutane complex. This restriction was attributed to the difficulty associated with generating non-activated radicals using complex $Cp*_2TiCl$. To overcome this restriction, tin-based methodology, the decomposition of (bis)alkyl mercury compounds, and the use of samarium diiodide were investigated to produce the organic free radicals.[5] According to these results, the use of samarium diiodide provides an efficient and convenient method for the preparation of a variety of β-substituted titanacyclobutane complexes. Both stabilized and unstabilized radicals can be added to the allyl complex to form titanacyclobutane complexes and the products are easily separated and purified.[6]

Scheme 2

1   R = PhCH₂, Ph₂CH, Ph(CH₃)CH

R–Cl, SmI₂ (1 equiv)
THF, RT,
1-6 h

2
70 - 95 %

1

R–I, SmI₂ (1 equiv)
THF, 40 °C
0.7-6 h

R = ᵗBu, Cy, ⁱPr, ⁿPr

2
66 - 93 %
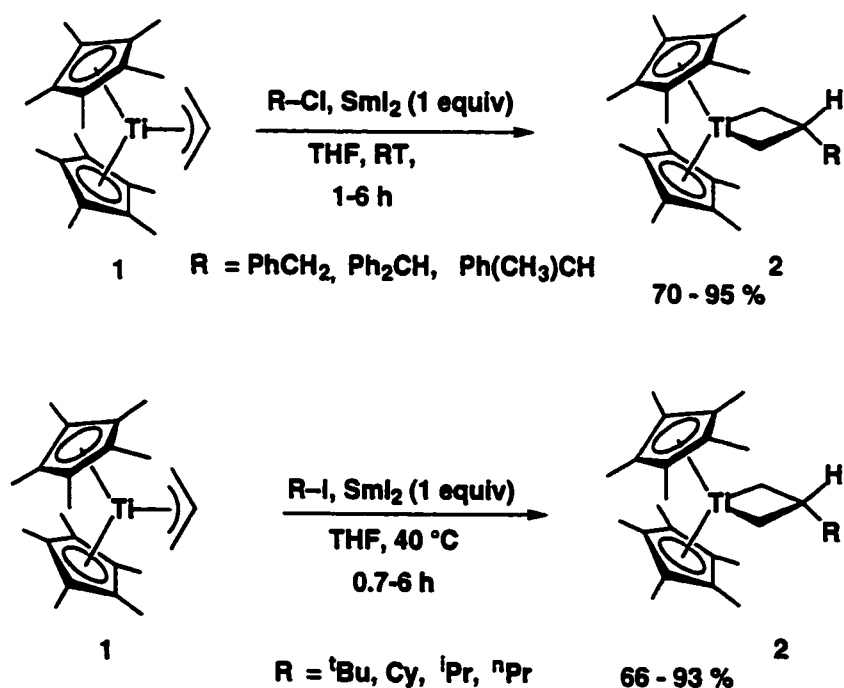
Using this method, many different organic free radicals were generated and added to the central carbon of the η^3-allyl ligand in complex **1**, generating titanacyclobutane complexes in good to excellent yields (**Scheme 2**). For the benzylic cases, the use of low

temperature and the less reactive chloride is necessary to inhibit both SmI_2-induced organic radical dimerization[7, 8] and competitive reaction of the organic halide with the titanocene allyl complex. For simple alkyl halides, the use of the iodide and higher temperature is required to provide central carbon alkylation products efficiently (**Scheme 2**). In all the cases, the crude reaction mixture was triturated with pentane after evaporation of the solvent, separating the Sm(III) byproducts from the product solution, providing a very convenient method for work–up. This central carbon alkylation of neutral d^1 titanocene π-allyl complexes with organic free radicals was also extended to the use of ansa-bridged and aminoindenyl ligands in making the corresponding disubstituted titanacyclobutanes from substituted allyl ligands.[9,10]

The scope of the central carbon radical alkylation has been recently expanded to several titanium(III) η^3-propargyl complexes (*vide infra*).[11] The established method for the preparation of the titanacyclobutene complexes is based on titanium alkylidene/alkyne [2 + 2] cycloaddition, the only other methodology available for preparation of titanacyclobutene complexes.[13,14]

In this work, alkynes are treated with the dimethyltitanocene at elevated temperature, giving corresponding substituted titanacyclobutene complexes. Although this method provides a convenient way for the preparation of some titanacyclobutene complexes, it has limitations, as only a limited number of symmetrical alkynes work well and terminal alkynes do not undergo such a reaction. For example, when dimethyltitanocene is treated with 3-hexyne, a competitive alkyne polymerization reaction occurs. The same problem occurs when 2-butyne is treated with the dimethyltitanocene, gaving irreproducible and variable yields of the dimethyltitanacyclobutene products. For unsymmetrical alkynes, the reaction gives a mixture of two regioisomeric metallacyclobutene products. For example, when (trimethylsilyl)propyne is treated with dimethyltitanocene, the reaction gives a 43 : 57

3
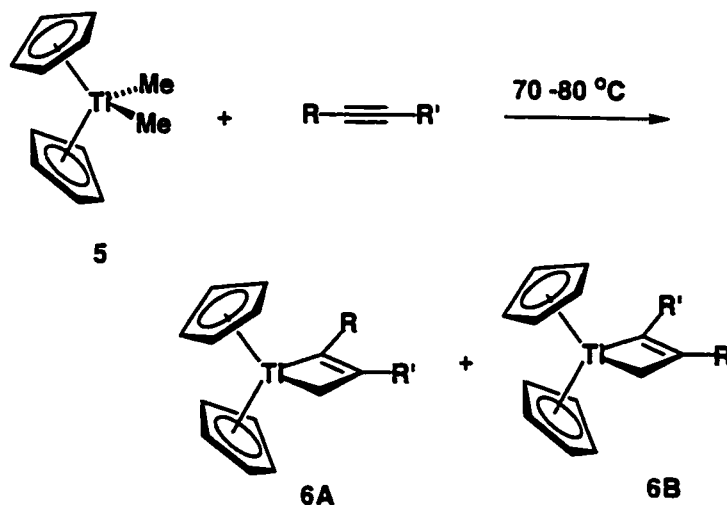
Scheme 3

R	R'	yield (%)		
Me₃Si	Me ₃Si		>95	
Ph	Ph		>95	
Et	Et		70 (+ polymer)	
Me	Me ₃Si	43 %	+	57 %

mixture of the two isomers (**Scheme 3**). The use of Tebbe's reagent instead of complex **7** gives similar mixtures of regioisomers.[15] These results strongly suggest that the two reactions involve the same alkylidene intermediate.

These unfavorable factors limit applications of this method. For developing practical applications of titanacyclobutenes in organic synthesis, our radical methodology needs to be further expanded.

Transition metal allyl complexes have many important applications in organic synthesis.[16,17,18,19-21] The structurally related transition metal propargyl complexes are not yet so popular. Recently, however, metal propargyl complexes have received more

and more attention. Metal propargyl complexes show some similarities to metal allyl complexes, but possess their own unique properties due to the presence of a carbon-carbon triple bond instead of a double bond. For example, η^1-propargyl complexes can undergo a 1,3-shift to form the structurally distinct η^1-allenyl isomers (eq. 1).[22]

eq. 1
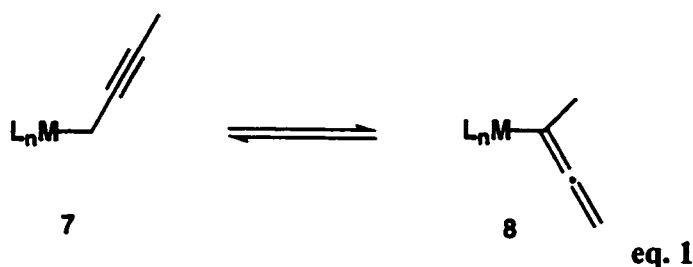
Transition metal η^1-allyl and η^1-propargyl complexes show similar reactivity toward electrophiles.[23-25] For example, both complexes can undergo proton addition at the γ-carbon, forming cationic alkene and allene complexes.

Scheme 4

allyl complex   Propargyl complex
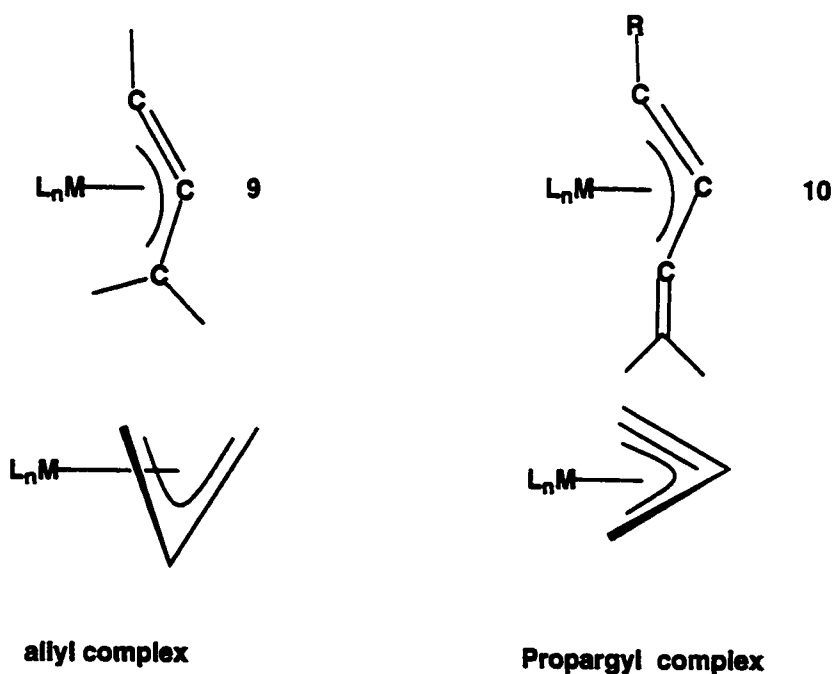
In the η^3-propargyl complexes **9**, a π–bonded propargyl radical acts as a formal

5

three electron donor, which is similar to the π–bonded allyl radical. The coordinated

propargyl ligand is different from free alkyne, however; it is bent instead of straight. The

main structural difference between the allyl complex and the propargyl complex is that

the propargyl ligand carbons and the metal are coplanar, whereas the allyl ligand is side–

on bonded through its π–system (**Scheme 4**). The η^3-propargyl complexes reacts with a

variety of nucleophilies to afford the corresponding metallacyclobutene complexes. The

nucleophilies add exclusively to the central carbon of the η^3-propargyl ligand.[26]

Based on the success of free radical addition to titanium(III) η^3-allyl complexes in

the Stryker group,[27] the group also investigated the same reaction using the previously

unknown titanium(III) η^3-propargyl complexes and developed a new method for the

preparation of titanium(III) η^3-propargyl complexes and titanacyclobutenes.[11]

Scheme 5
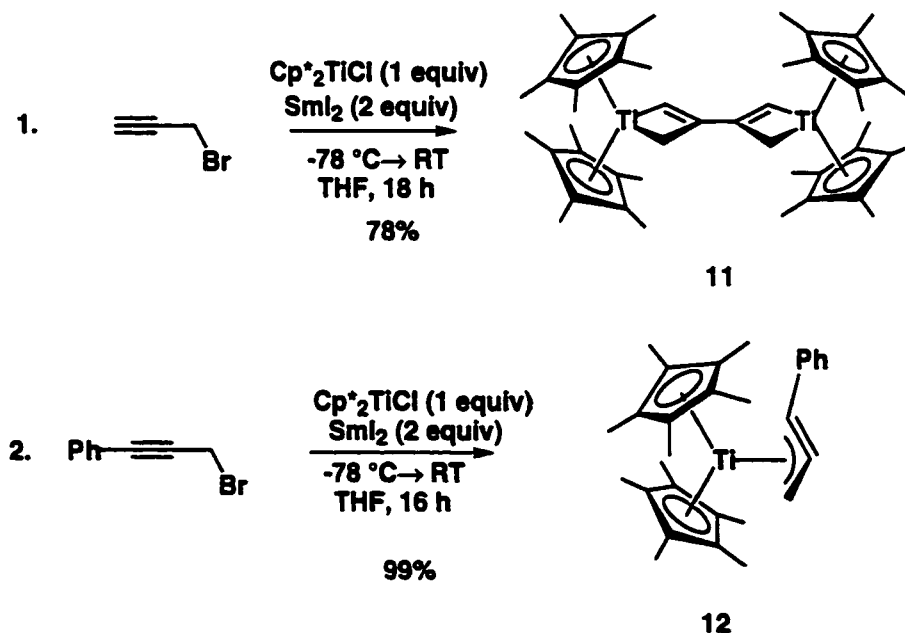
Thus, treatment of Cp*$_2$TiCl with propargyl bromide in the presence of two

equivalents of SmI$_2$ gives dimeric complex **11** in 78 % isolated yield (**Scheme 5, entry 1**).

Under same conditions, the reaction of Cp*$_2$TiCl with 1-phenyl-3-bromopropyne indeed

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gives the titanium (III) η^3-phenylpropargyl complex **12** in quantitative yield (**Scheme 5,** **entry 2**).[11] No dimerization of complex **12** is observed, a reactivity that is not well understood.

Upon further investigation, it was found that titanium(III) η^3-propargyl complexes, even those that dimerize in solution, can also undergo free radical addition

Scheme 6

R = H, CH₃, Ph
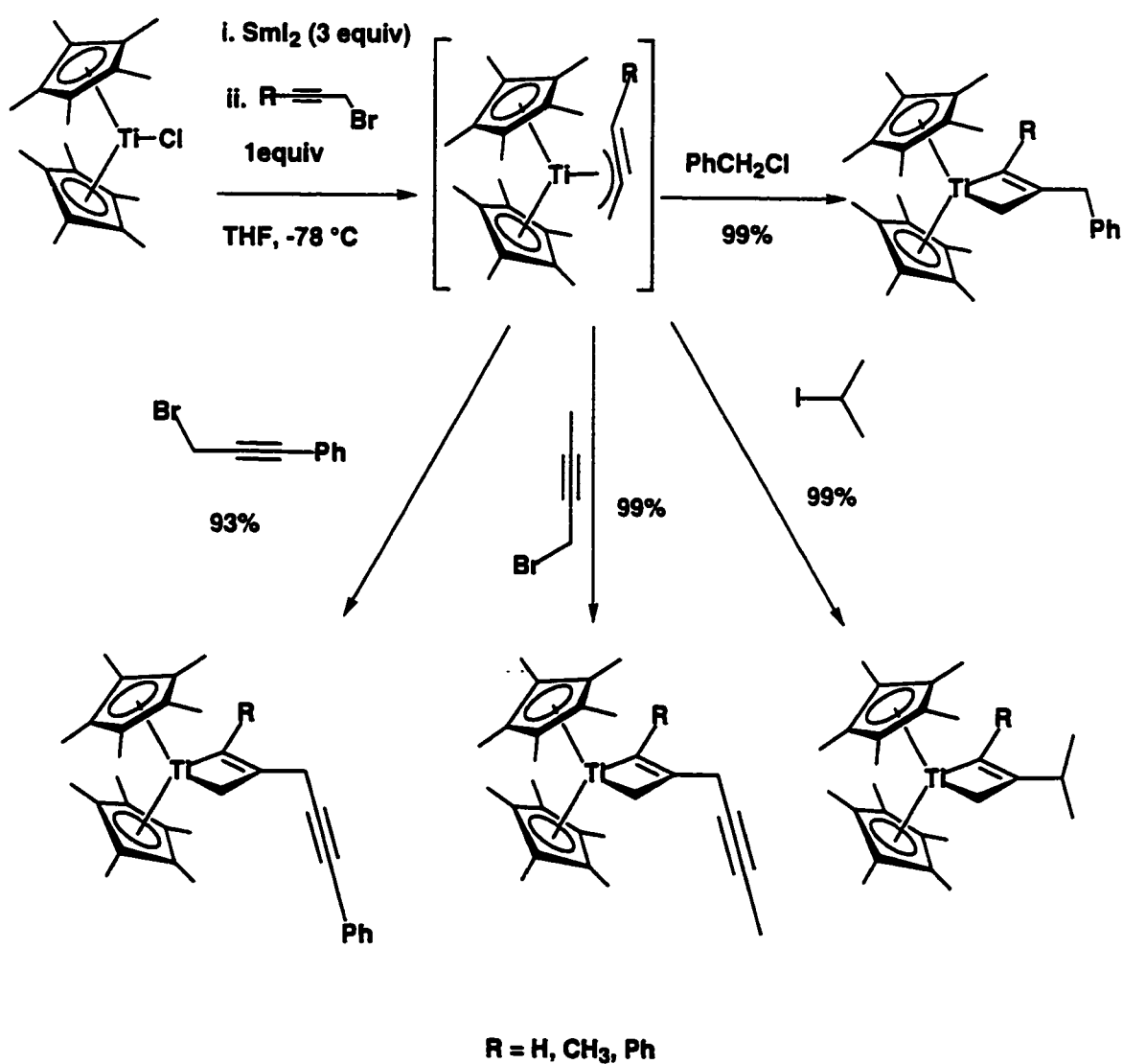
reactions, giving titanacyclobutene complexes (**Scheme 6**).[11] The addition reaction occurs exclusively at the central carbon of the propargyl ligand and provides a convenient and highly regioselective synthetic method for the preparation of disubstituted titanacyclobutene complexes. Thus, a reaction mixture containing Cp^*_2TiCl, three equivalents of SmI_2, 1 equivalent propargyl halide, and one equivalent of an alkyl halide leads to the formation of the corresponding 2,3-disubstituted titanacyclobutene complex in high yield (**Scheme 6**). This synthetic method is also applicable to intramolecular free radical cyclizations reactions (**Scheme 7**) and to the use of different ancillary ligand sets, including TMSCp, ^tBuCp, and Cp itself.[12] Mechanistically, this reaction can be divided into two stages: (1) generation of the propargyltitanium(III) intermediate and (2) alkyl radical formation and addition. Both pathways may proceed at competitive rates, with the partitioning dependent on the nature of the alkyl halide.

Scheme 7

(I) Cp^*_2TiCl (1 equiv)
(II) SmI_2 (3 equiv)

THF, -78 °C→RT,
then 50-60 °C
85-98 %

13

n = 3-6
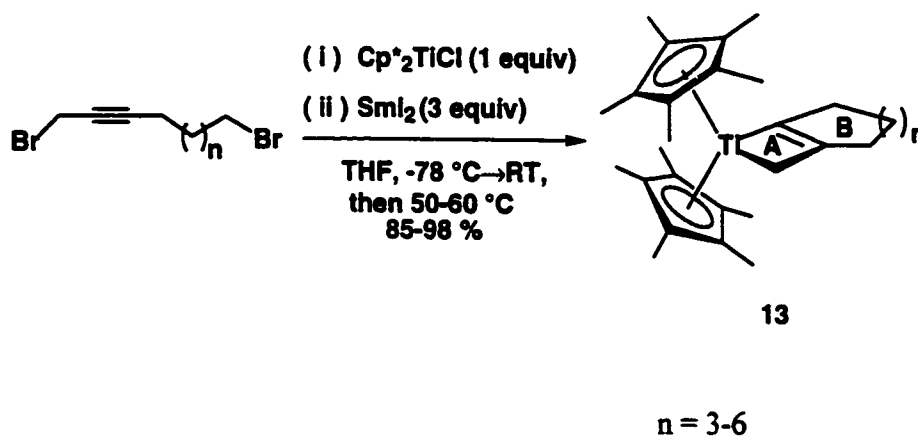
With specially designed bis(propargyl halide) substrates, an intramolecular version of the dimerization reaction yields the dititanacyclobutene complexes **14 and 15** (**Scheme 8**). It is not yet known whether the aromaticity of the product is essential to the success of this reaction.

8

Scheme 8

14 (83%)

15 (72%)
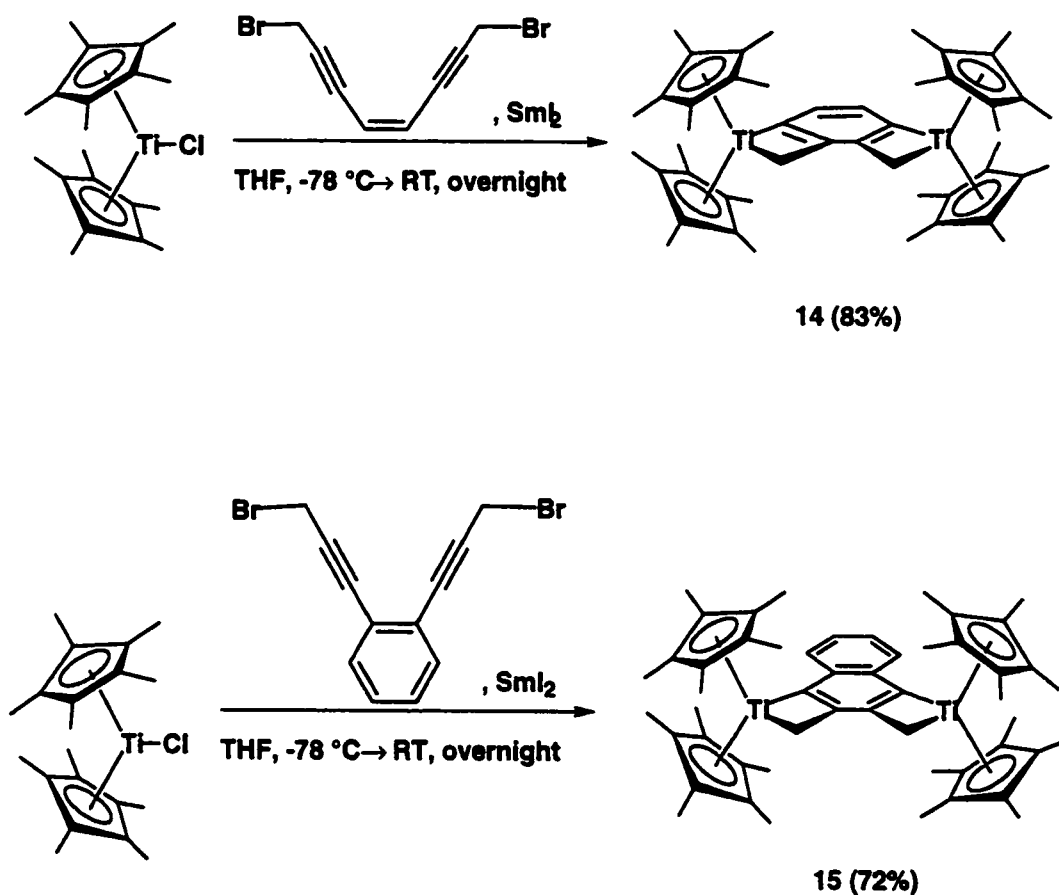
B. General Research Goals

The addition of free radicals to η^3–titanium (III) propargyl complexes provides a highly regioselective method for the preparation of titanacyclobutene complexes. As a result of the new carbon–carbon bond formation, this process has potential applications in synthetic organic chemistry. First, our effort was directed toward extending titanacyclobutene formation to functionalized β-substituents so that the product complexes have extended application in synthetic chemistry. In this effort, the fundamental steric and electronic features of different ancillary ligand sets that support

the addition of organic free radicals to the η^3–propargyl ligand were investigated. Secondly, our goal for this project was to begin an investigation into the functionalization of the titanacyclobutene complexes to give interesting organic products. Here we focused on ring expansion reactions using carbon monoxide and isocyanides. Finally, some effort was made to obtain the demetallation of titanacyclobutenes to produce organic heterocycles.

II. RESULTS AND DISCUSSION

A. Intermolecular Radical Alkylations of Titanium(III) Propargyl Complexes

Typically, the synthesis of titanacyclobutenes involves treating a solution of $Cp*_2TiCl$ and three equivalents of samarium(II) iodide at -78 °C under an inert atmosphere with one equivalent of the propargyl halide, followed by addition of one equivalent of the alkyl halide. The resulting blue solution is simply allowed to warm to room temperature and the yield of the reaction is always very good. Following this procedure, 1,1-bis(pentamethylcyclopentadienyl)-3-(trimethylsilylmethyl)-2-methyltitanacyclobutene **16** was made from the addition of bromomethyltrimethylsilane to the *in situ* prepared η^3-butynyl complex (eq. 2). The complex is isolated by recrystallization from pentane at -35 °C to give a dark red solid in 93% yield.

eq. 2
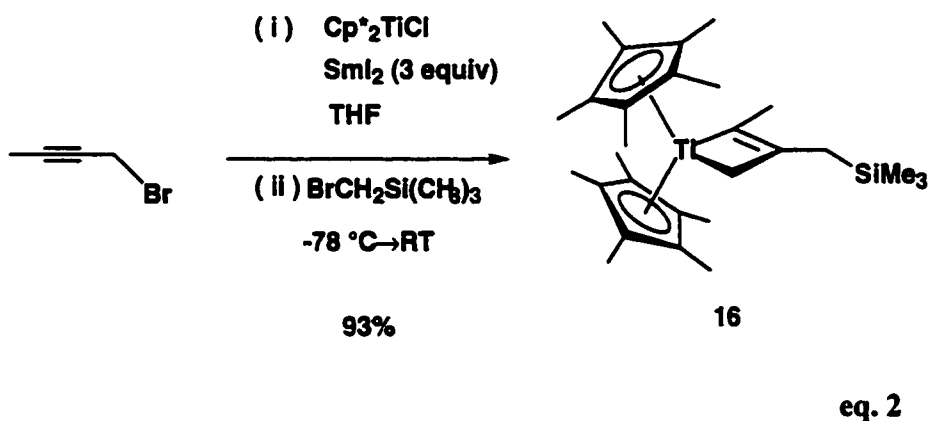
Assignment of the structure of complex **16** is based on analysis of the spectroscopic data and comparision to many analogous compounds.[11] The ^1H NMR spectrum shows a singlet for trimethylsilyl group at δ 0.21. The methylene protons in the titanacyclobutene ring appear as a narrow quartet at δ 2.14 (q, $J = 1.8$ Hz, 2H), due to

11

the small coupling to the methyl protons, as confirmed by the narrow triplet at δ 1.93 (t, J = 1.8 Hz, 3H). The signal for the methylene of the β-substituent appears at δ 1.70. The gated-decoupled ^{13}C NMR spectrum also supports this assignment. The signal for the sp^2 α–carbon of titanacyclobutene ring appears at a typical shift of δ 206.5 and the signal for the β–carbon appears at δ 103.2, also typically observed. The sp^3 α–carbon of the ring appears at δ 78.0 (t, J = 135.6 Hz). The carbon of the substituent appears upfield at δ 20.4 (q, J = 123.3 Hz). In addition, the carbon signal for trimethylsily group appears at δ 0.2 (q, J = 118.4 Hz) and the carbon signal at δ 22.3 (t, J = 117.7 Hz) for the methylene group. The composition of complex **16** is also supported by high resolution mass spectrometry.

An olefinic side chain was installed by addition of cyclopropylmethyl bromide to the *in situ* prepared η^3-propargyl complex, a reaction that also indicates the rate of the cyclopropylmethyl radical rearrangement is faster than the bimolecular radical addition. According to the study of Ingold,[28,29] the isomerization from **17** to **18** is very fast (k = 1.3x10^8, 25 °C). Only below -140 °C, a clean spectrum (EPR) of **17** is obtained. Between -140 °C and -100 °C, both **17** and **18** are observed and above -100 °C, only **18** can be dectected.

Scheme 9

17   18
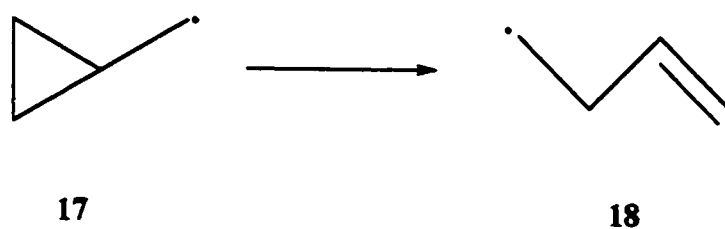
Thus, if cyclopropylmethyl bromide is chosen as a source of free organic radical, it is expected that there will be no β-cyclopropyl methyl titanacyclobutene. To examine

this idea, one equivalent of Cp*$_2$TiCl and three equivalents of samarium(II) iodide at -78 °C were treated with one equivalent of 2-butynyl bromide followed by one equivalent of cyclopropylmethyl bromide, to afford a dark red solid in 97% yield after isolation and purification by recrystallization from pentane at -35 °C (eq. 3).

eq. 3
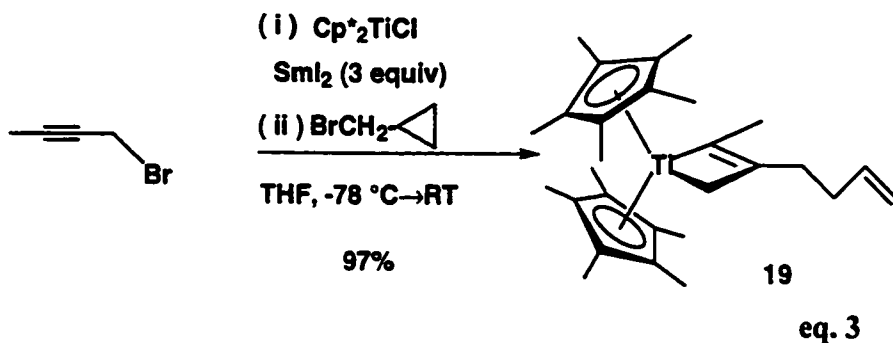
Characterization of complex **19** rests on analysis of its specta and comparision to spectra of analogous complexes. The ^{1}H NMR spectrum shows resonances at δ 1.94 (t, *J* = 2.0 Hz) for the methyl protons, due to the small coupling to the methylene protons of the ring which appear at δ 2.13 (q, *J* = 2.0 Hz). The two chain methylene groups are assigned at from δ 2.29 to δ 2.34 as the multiplets, whereas the signals of the olefinic protons located at δ 6.02, 5.18 and 5.05 are each observed as the expected ddt. Both ^{13}C NMR and mass spectrometry also support this assignment (**Table 1**).

3-Phenylpropargyl bromide was also used to make a similar complex. As a result of Ogoshi's earlier work in this group, bis(pentamethylcyclopentadienyl)(η^3-3-phenylpropargyl)titanium **12** can be separated as a stable compound. Therefore, one equivalent of Cp*$_2$TiCl and two equivalents of samarium(II) iodide at -78 °C were treated with one equivalent of 3-phenylpropargyl bromide, then warmed up to room temperature to give bis(pentamethylcyclopentadienyl)(η^3-3-phenylpropargyl)titanium **12**. To the above solution, one equivalent of samarium(II) iodide was added at at -78 °C, followed by one equivalent of cyclopropylmethyl bromide, to afford a dark green crystalline product **20** (eq. 4). The spectroscopic assignment of complex **20** is similar to

13

complex **19**. The key ^{13}C NMR spectroscopic data for both **19** and **20** are listed in **Table 1.**

Table 1.

^{13}C NMR Resonances of titanacyclobutene complexes 19–20

	19 δ	20 δ
$\underline{C}_5(CH_3)_5$	117.9	119.2
$C_5(\underline{C}H_3)_5$	11.9	12.2
sp^2 α-C	206.8	204.2
sp^3 α-C	75.5	77.9
sp^2 β-C	101.6	111.3
$\underline{C}H=CH_2$	138.7	139.9
CH=$\underline{C}H_2$	114.0	114.1
$(\underline{C}H_2)_2$-	41.1	35.3
	35.6	33.1
α-substituent	19.3	144.3
		129.3
		127.8
		123.8

14

(i) Cp*₂TiCl

Sml₂ (3 equiv)

(ii) BrCH₂◁

THF, -78 °C→RT

91%

20

eq. 4
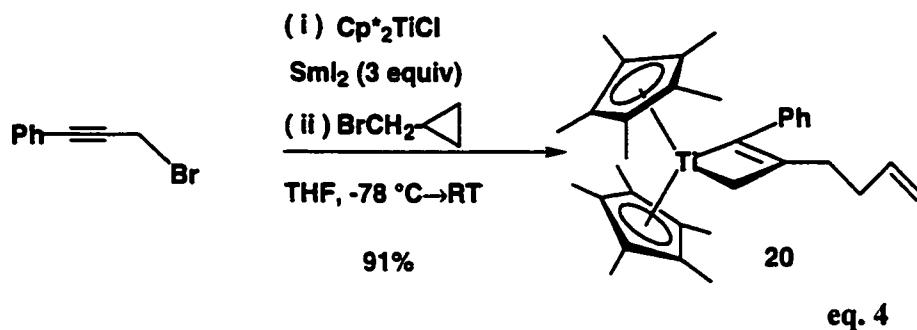
To further introduce a β-functional substitute in titanacyclobutenes, both benzyl chloromethyl ether and 1,2-dibromoethyl ethyl ether were investigated as radical sources. In both cases, however, no desired products were obtained (**Schemes 10 and 12**).

Scheme 10

(i) Cp*₂TiCl

Sml₂ (3 equiv)

(ii) ClCH₂OCH₂Ph

THF, -78 °C→RT

21

65%

22
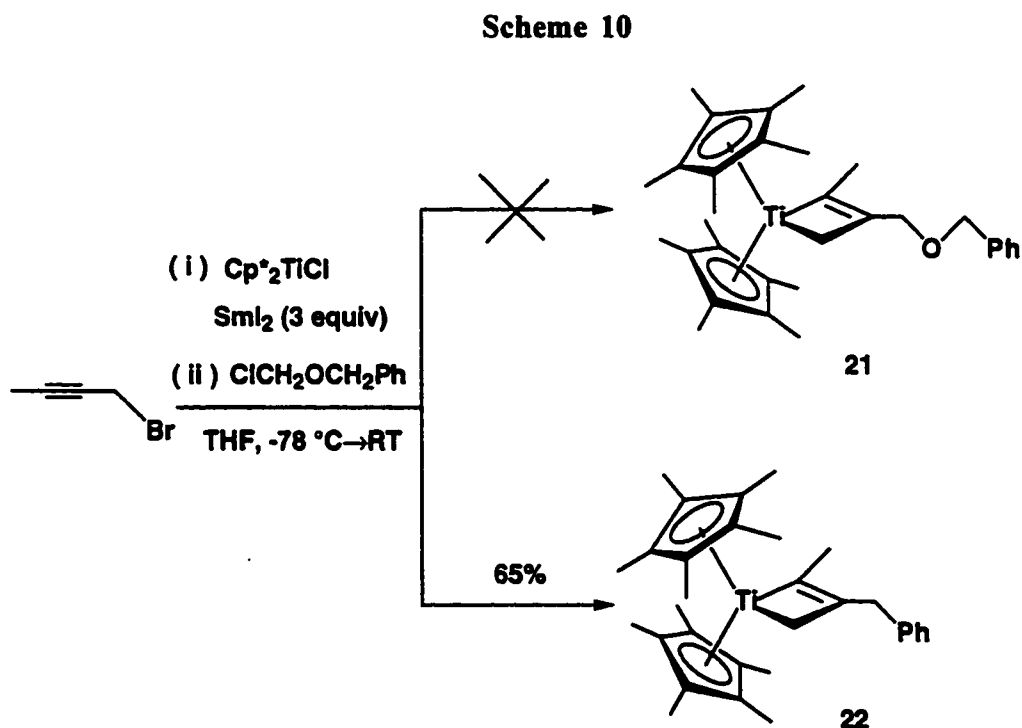
In the case of benzyl chloromethyl ether, the only product isolated was the known β-benzyl titanacyclobutene **22**,[11] obtained in moderate yield (**Scheme 10**). A possible mechanism for the formation of this product is that the initial benzyloxymethyl radical extrudes formaldehyde to give the stabilized benzyl radical, which then attacks the propargyl complex to afford complex **22** (**Scheme 11**).

15
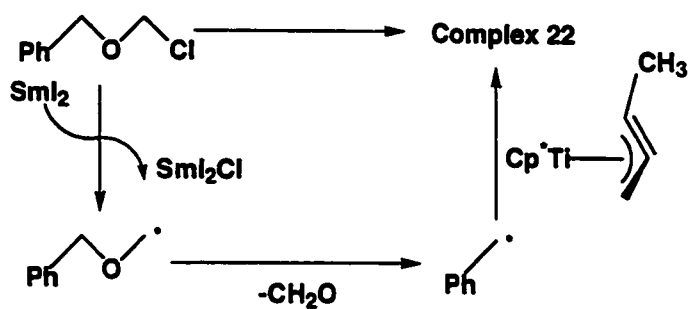
Scheme 11

Scheme 12
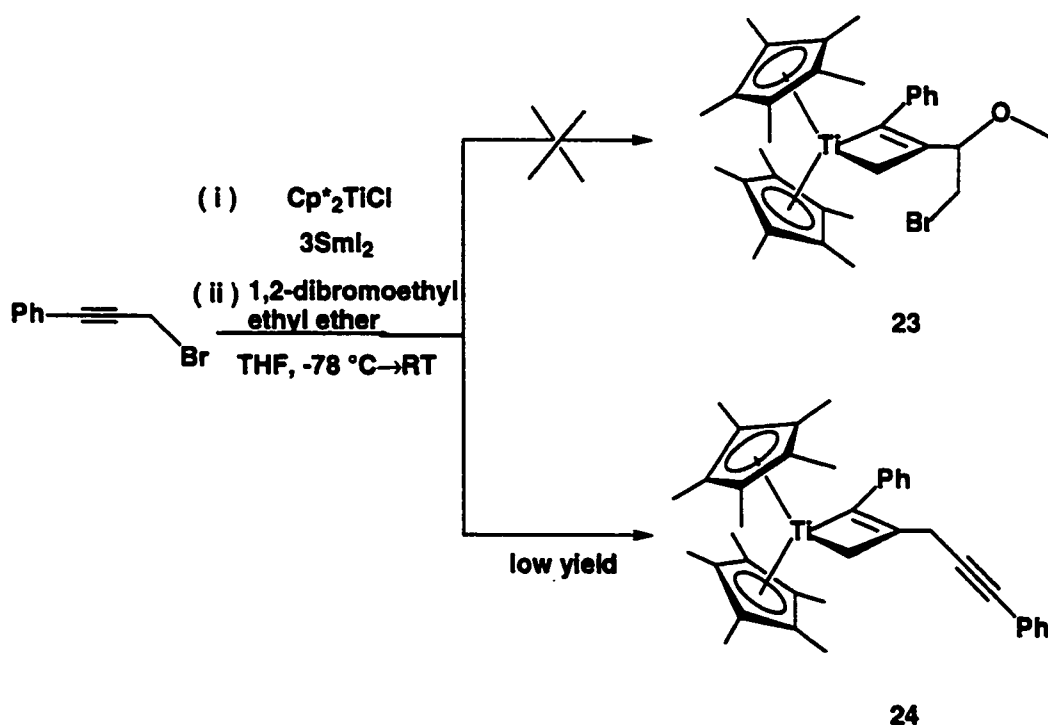
We also tried to add the radical derived from 1,2-dibromoethyl ethyl ether to bis(pentamethylcyclopentadienyl)(η^3-3-phenylpropargyl)titanium **12**, by adding another equivalent of samarium(II) iodide at -78 °C followed by 1,2-dibromoethyl ethyl ether (**Scheme 12**). Quite interestingly, complex **24** was obtained in low yield instead of the expected complex **23**. A possible mechanism is as follows (**Scheme 13**). Characterization of both complexes **22** and **24** is based on analysis and comparision to the known

complexes.[11]

Scheme 13
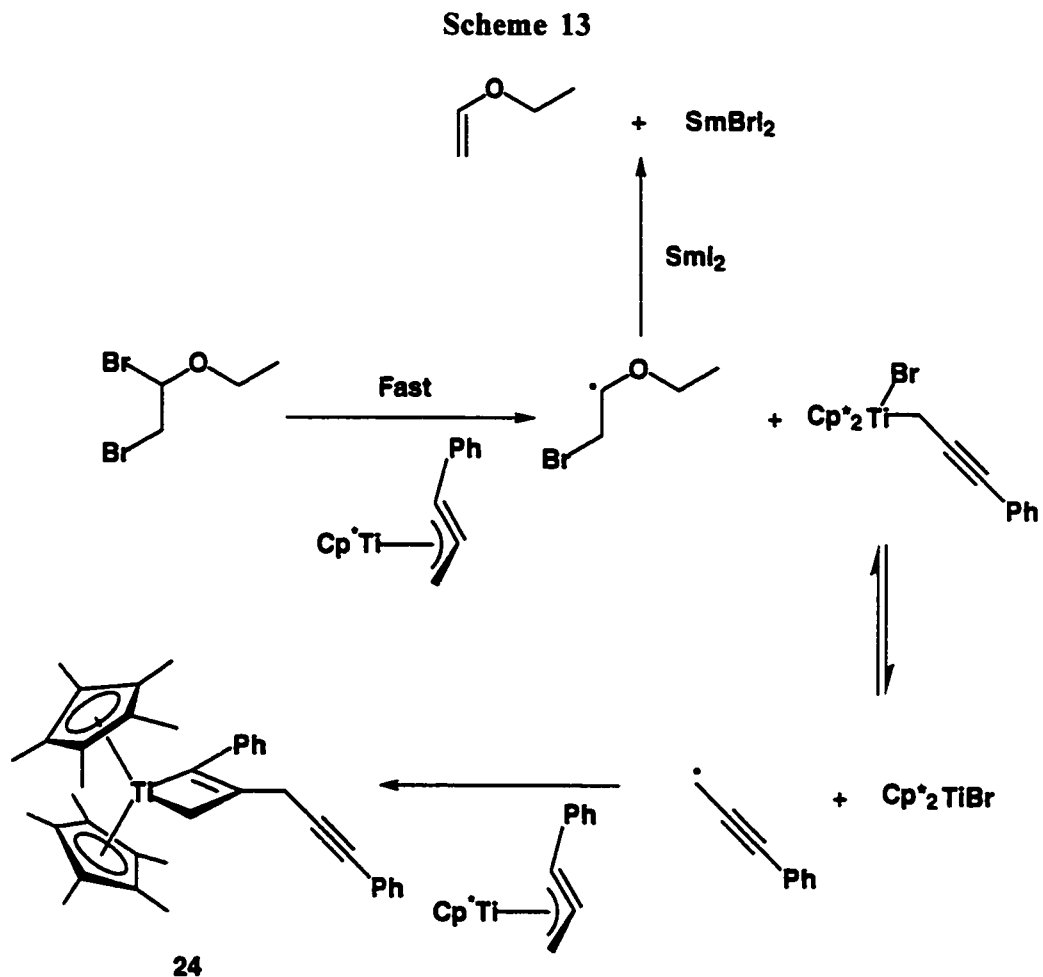
B. Dimerization and Intramolecular Coupling of Titanium(III) Propargyl Complexes

To expand dititanacyclobutene formation by dimerization or intramolecular propargyl coupling, two new ligands were investigated. Compared to 3-phenylpropargyl bromide, we wished to obtain dimerization product by increasing the electronic density of the Ti(III) compound **26**. 3-(4-Methoxyphenyl)propargyl bromide **25** was made using literature procedures with minor experimental modification (eq. 5) [30,31].
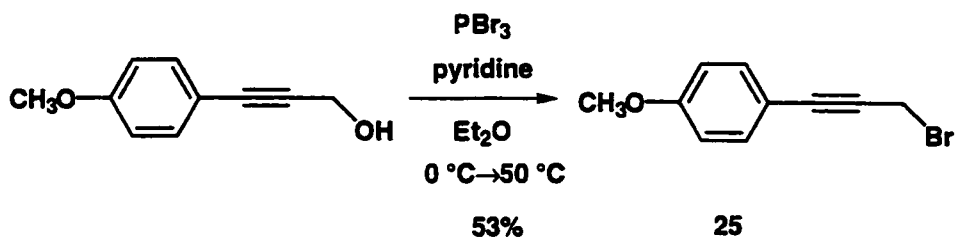
eq. 5

Using a similar procedure to that used to make bis(pentamethylcyclopenta-dienyl)(η^3-3-phenylpropargyl)titanium 12,[11] the preparation of complex 26 was readily accomplished (eq. 6). No dimerization product was observed, despite the increase in electronic density compared to the 3-phenylpropargyl ligand.
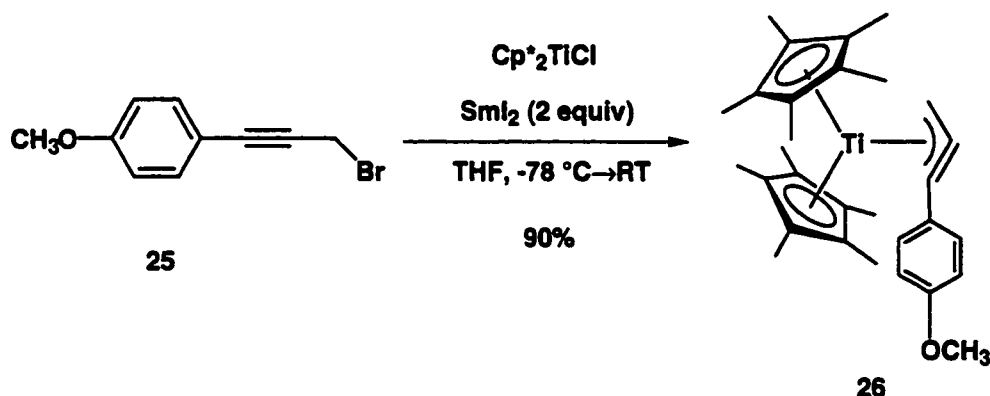
eq. 6

Quite remarkably, the propargyl infrared absorption band for complex 26 is observed at 1958 cm^{-1}, 56 cm^{-1} higher than that for bis(pentamethylcyclopentadie-nyl)(η^3-3-phenylpropargyl)titanium 12, suggesting that the propargyl triple bond of complex 26 is significantly stronger than that in complex 12. Complex 26 is dark green, in contrast to the dark red of complex 12. For both aryl propargyl complexes and the 1-methyl-substituted complex, dimerization does not occur, in contrast to the complex with no substituent at 2 position,[11] for which dimerization is observed even using the less electron rich tert-butylcyclopentadienyl ancillary ligand (Scheme 14). These observations indicate that all propargyl substituents inhibit dimerization.

18

Scheme 14

1.
$[^tBuCp_2TiCl]_2$
(0.5 equiv)
SmI_2 (2 equiv)

THF, -78 °C→RT
overnight

10%

27

2.
Cp^*_2TiCl (1 equiv)
SmI_2 (2 equiv)

THF, -78 °C→RT
overnight

78%

11
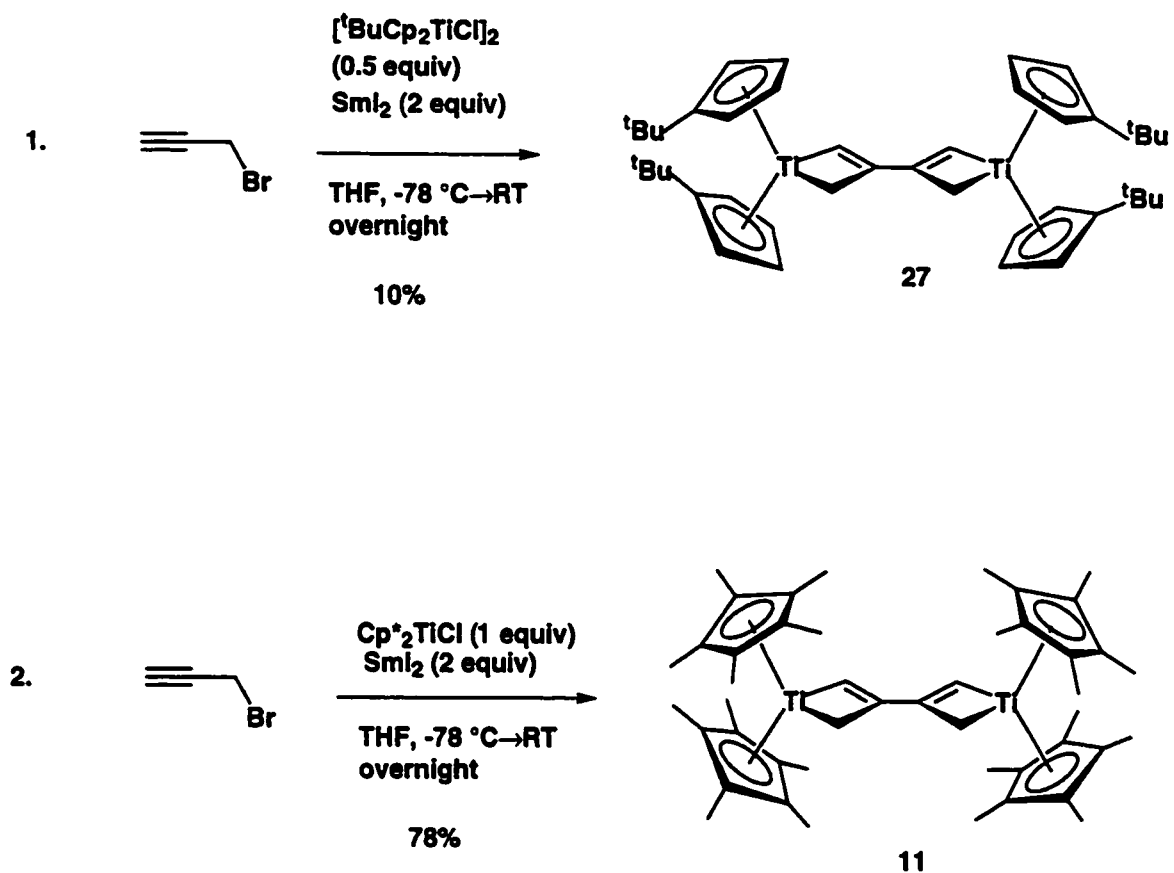
The paramagnetic complex **26** can be efficiently trapped with organic free radicals. To trap bis(pentamethylcyclopentadienyl)[η^3-3-(4-methoxy)phenylpropargyl]titanium **26**, both 2-iodopropane and benzyl chloride were used as radical sources (**eqs. 7, 8**). The spectroscopic data for the product titanacyclobutenes **28** and **29** are quite similar to the corresponding phenyl substituted complexes,[11] except for the signals due to the methoxy group. All the data support the assigned structures.

19

(i) Cp*₂TiCl

SmI₂ (3 equiv)

(ii) 2-iodopropane

THF, -78 °C→RT

93%

25 → **28**   eq. 7

(i) Cp*₂TiCl

SmI₂ (3 equiv)

(ii) benzyl chloride

THF, -78 °C→RT

88%

25 → **29**   eq. 8
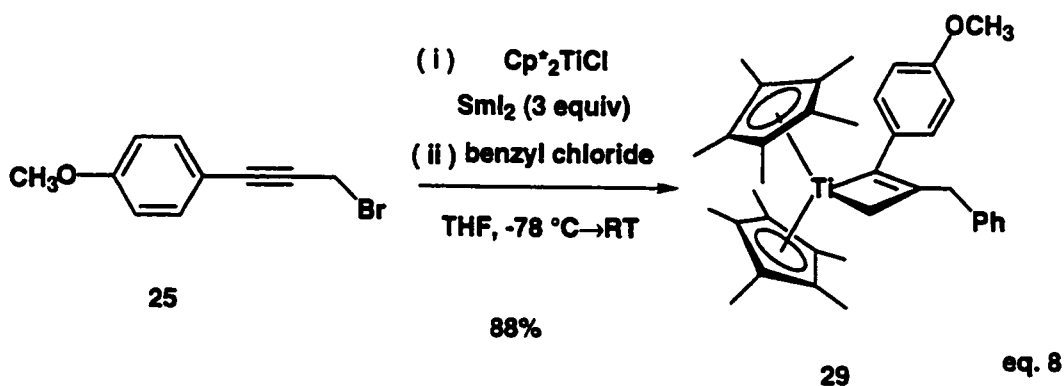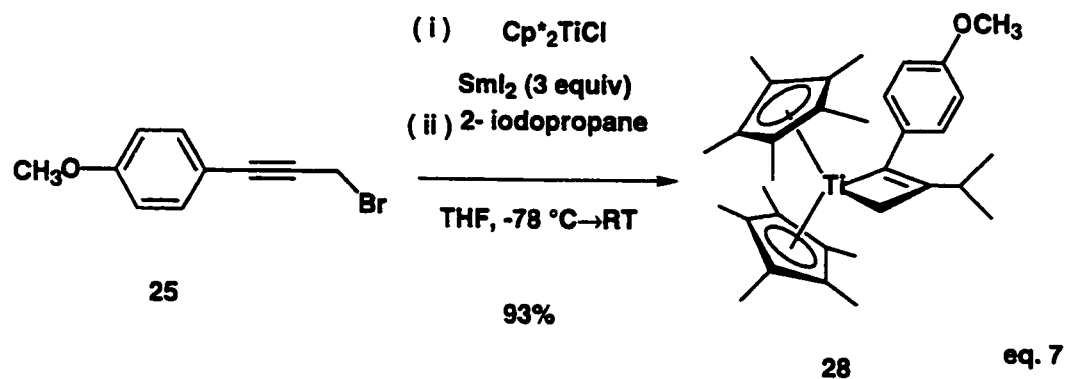
To extend the intramolecular propargyl coupling reactions for dititanacyclobutenes, the synthesis of 1,2,5,6-tetrakis(3-bromopropynyl)benzene **30** was targeted. In the literature, very similar compounds[32-34] have been synthesized. Therefore, 1,2,4,5-tetrabromobenzene was chosen as our starting material. The same procedures or some minor modifications were used for the alkynylation reaction, however, no desired compound was obtained. Alternatively, however, 1,2,4,5-tetraiodobenzene[35] was used as the starting material. Quite surprisingly, the alkynylation reaction was readily accomplished in very good yield and was followed by conversion to 1,2,4,5-tetrakis(3-bromopropynyl)benzene **30** by standard procedures.

Scheme 15

81%

31

31   82%   30
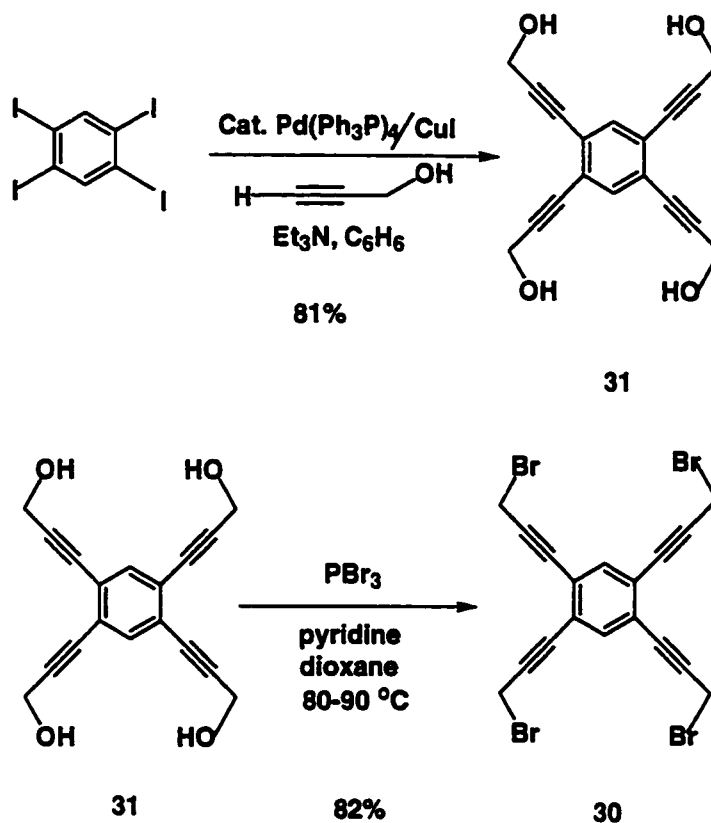
The characterization of these compounds was easily accomplished by ^{1}H NMR spectroscopy, ^{13}C{^{1}H} NMR spectroscopy, elemental analysis, mass spectroscopy and IR spectroscopy. For instance, structural assignment of compound **30** is as follows. The ^{1}H NMR spectrum shows signals for two phenyl hydrogens at δ 7.62 and eight propargyl hydrogens at δ 4.54 as singlets, respectively. In the ^{13}C{^{1}H} NMR spectrum, the signals for the two inequivalent phenyl carbons appear at δ 135.9 and δ 126.2, whereas the triple bond carbons appear at δ 92.3 and δ 83.8. The methylene carbon appears upfield at δ 15.0. Finally, HRMS and elemental analysis also confirm the composition. When this substrate was used for the investigation of the intramolecur coupling reaction (eq. 9), however, we did not obtain the targeted complex using any of the following reagents: Cp*$_2$TiCl, [^{t}BuCp$_2$TiCl]$_2$ or [Cp$_2$TiCl]$_2$. We can not explain the failure of this reaction, especially given the similarity to known reactions (see Scheme 8).

21

Cp^*_2Ti (4 equiv)

SmI_2 (8 equiv)

~~→~~

THF, -78 °C→ RT, 12 h

30

32

eq. 9
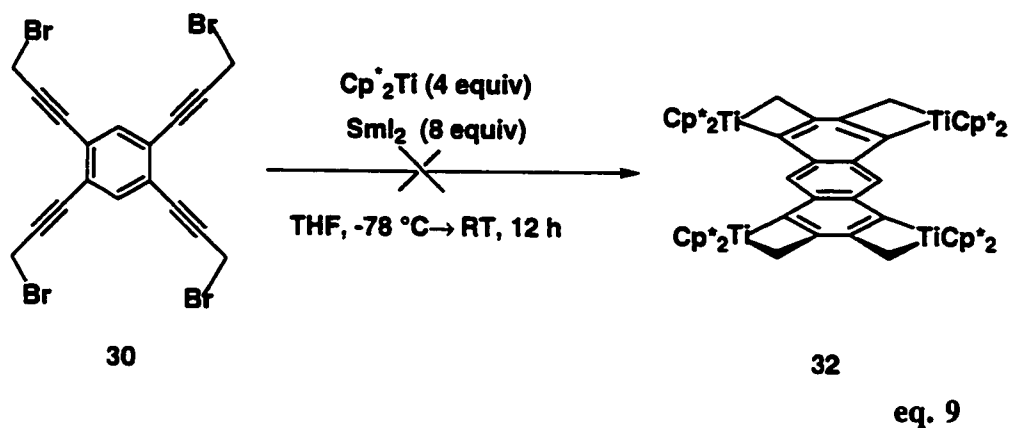
C. Radical Additions of Titanium(III) Propargyl Complexes Using Cp and ^{t}BuCp Templates

To further investigate the steric and electronic features of the ancillary ligand set that affect the addition of organic radicals to the η^3-propargyl ligand, reaction of the *tert*-butylcyclopentadienyl and cyclopentadienyl titanium(III) complexes were investigated. In comparision with Cp* ligand, these ligands are less electron rich and less sterically bulky. Thus, titanacyclobutenes with Cp*, ^{t}BuCp or Cp templates should show different stability and reactivity. For instance, Chen found that 1,1-bis(pentamethylcyclopenta-dienyl)-3-(2-butynyl)-2-methyltitanacyclobutene is very stable in solution, whereas 1,1-bis(*tert*-butylcyclopentadienyl)-3-(2-butynyl)-2-methyl titanacyclobutene survives in solution for only about 10 h and 1,1-bis(cyclopentadienyl)-3-(2-butynyl)-2-methyltitanacyclobutene could not be made[12] (**Figure 1**).
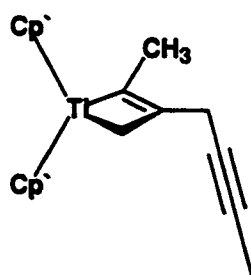
Cp` = Cp*, ^{t}BuCp, Cp   **Figure 1**

Thus, [$^tBuCp_2TiCl$]$_2$ (0.5 equiv.) was treated with three equivalents of samarium(II) iodide at -35 °C, followed by a combined solution of one equivalent of 3-phenyl propargyl bromide and one equivalent of benzyl chloride in THF. The resulting solution was shaken and kept at -35 °C for a short time (1 h) and then allowed to warm to room temperature. After remaining at room temperature for 1 h, complex **33** was obtained as a dark pink solid in 97% yield after standard work–up and isolation (**eq. 10**).

eq. 10
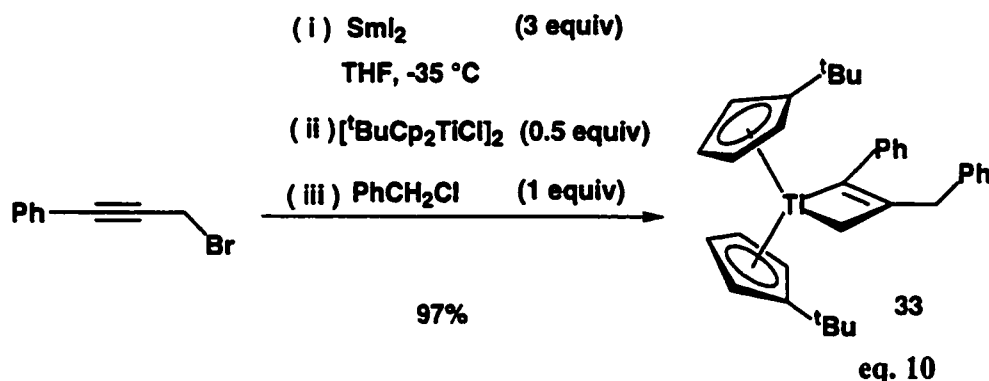
With the exception of the ancillary ligand set, the spectroscopic data of complex **33** are very similar to the previously characterized corresponding Cp* complex.[11] The ^{1}H NMR spectrum indicates the presence of the ^tBuCp ligand set in an unsymetrical environment, with three narrow multiplets at δ 6.12 (m, 2 H), 5.60 (m, 2 H), and 5.33 (m, 4 H), along with a broad singlet at δ 0.99 (s, 18 H). The ^{13}C {^1H} NMR spectrum reveals a typical signal for the sp^2 α-carbon of the titanacyclobutene ring at δ 206.8, identical to the Cp* analogue. The signal for the β-carbon appears at δ 100.0. The sp^3 α-carbon of the titanacyclobutene ring appears at δ 71.9, very close to that of the Cp* analogue. The remaining signals and spectroscopic data are consistent with the assigned structure. Using a similar procedure, the corresponding unsubstituted cyclopentadienyl coordinated complex **34** was also synthesized in 99% isolated yield (**eq. 11**). Structural assignment of complex **34** was accomplished in a manner similar to that of **33**.The product was very similar spectroscopically to the analogous Cp* complex.[11]

(i) SmI_2 (3 equiv)
THF, -35 °C
(ii) $[Cp_2TiCl]_2$ (0.5 equiv)
(iii)$PhCH_2Cl$ (1 equiv)
THF, -35 °C
99%

34

eq. 11
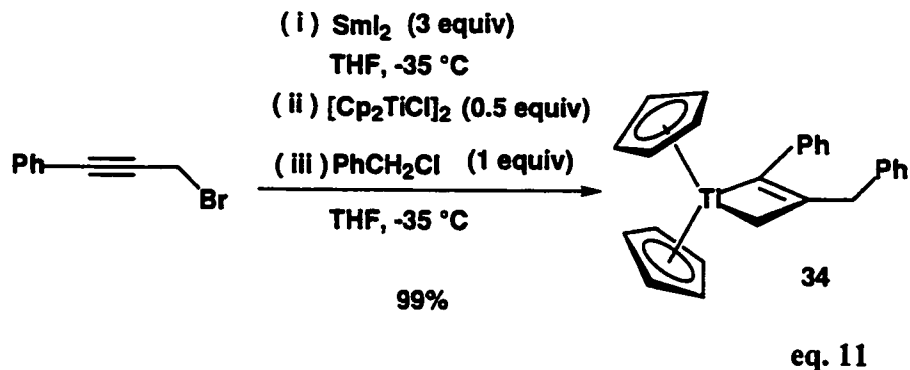
As we had previously tried to obtain dititanacyclobutenes by dimerization, bis(cyclopentadienyl)(η^3–3-phenylpropargyl)titanium **35** was synthesized as shown (eq. 12). Unfortunately, no dimerization is observed in this case either. This paramagnetic

(i) SmI_2 (2equiv)
THF, -35 °C
(ii) $[Cp_2TiCl]_2$ (0.5 equiv)
THF, -35 °C
87%

35

eq. 12
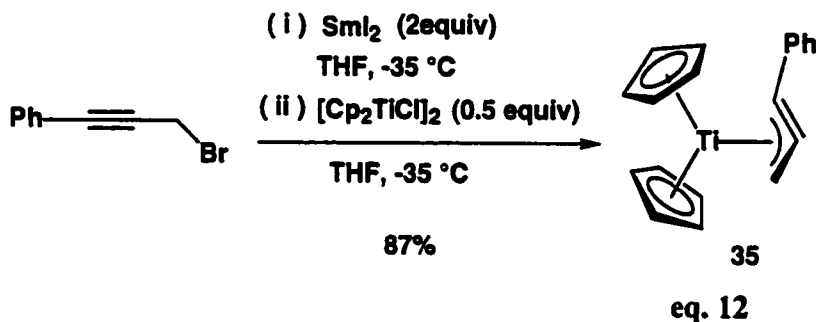
complex **35** was characterized by high resolution mass spectrometry and IR spectroscopy ($v_{C\equiv C}$ 1923 cm^{-1}). Compared to the IR spectrum of bis(pentamethylcyclopentadie-nyl)(η^3-3-phenylpropargyl)titanium **12** ($v_{C\equiv C}$ 1902 cm^{-1}), the absorption of complex **35** appears 21 cm^{-1} higher. This suggests the propargyl triple bond of the complex **35** is significantly stronger than that of the Cp* analogue and indicates that bonding between titanium and propargyl ligand in complex **35** is weaker than that in bis(pentamethylcyclopentadienyl)(η^3-3-phenylpropargyl)titanium **12**, presumably due to the less electron richness of the Cp ligands.

D. The Functionalization of Titanacyclobutene Complexes

1. Introduction

In an effort to develop new methodologies for the efficient synthesis of useful organic molecules, a fundamental study of the functionalization of titanacyclobutene complexes was undertaken using the small unsaturated organic compounds carbon monoxide and various isonitriles.

Hicks and Buchwald previously synthesized iminocyclopentenes from the cyclocondensation of an enyne with an isonitrile, a process that involves the insertion of isonitrile into a substituted titanacyclopropene complex.[36] Berg and Petersen reported simple and multiple insertions of *tert*-butyl isocyanide into a 1–sila–3–zirconacyclobutane complex.[37] There are, however, few reports about the insertions of isonitrile and carbon monoxide into titanacyclobutene complexes. Grubbs reported that bis(pentamethylcyclopentadienyl)-2,3-dimethyltitanacyclobutene upon treatment with *tert*-butyl isocyanide, affords iminoacyl complex 37 (eq. 13).[38] This complex is quite stable and does not react further with CO under the experimental conditions.

eq. 13
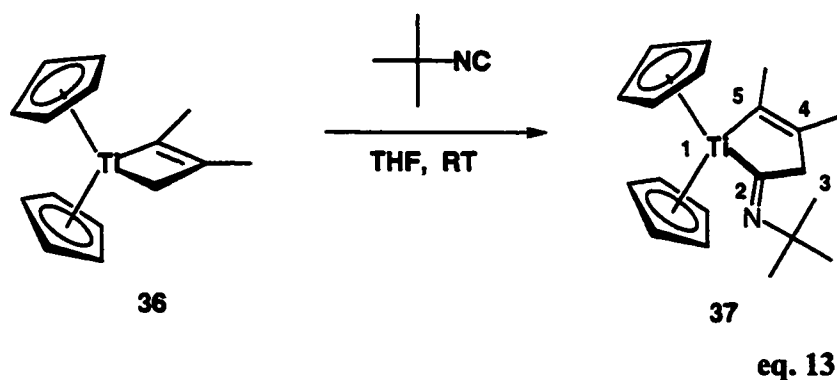
Complex 36 was also treated with carbon monoxide (Scheme 16).[38] In the absence of a Lewis base, the carbonylation proceeds to give a sparingly soluble, oligomeric ketene adduct that may be solubilized by the addition of a ligand such as

trimethylphosphine, pyridine or THF. The likely acyl intermediate **38A**, which is identified by use of low-temperature ^{1}H and ^{13}C NMR spectroscopy, ^{13}CO labeling, and IR studies, was unstable in solution above -30 °C and could not be isolated.[38]

Scheme 16
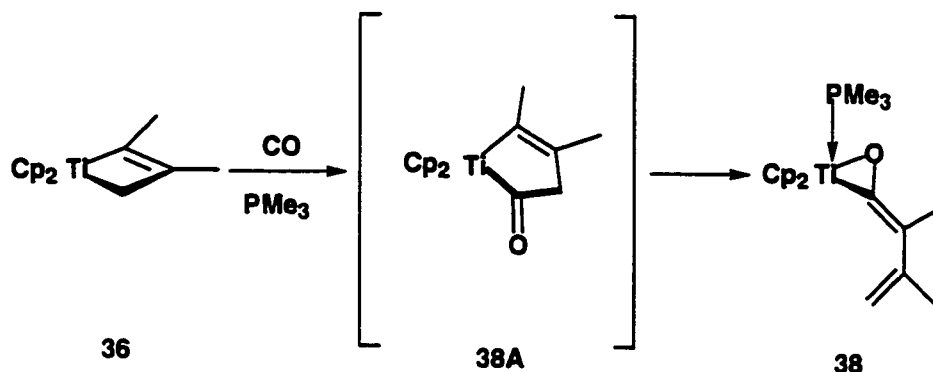
Another reactivity pattern involving titanacyclobutene complexes that we are interested in is direct demetallation to obtain organic molecules. Both Doxsee and others [39-43] have successfully obtained heterocycles from bis(cyclopentadienyl) titanacyclobutene complexes by treatment with electrophilic reagents such as PhPCl$_2$ and PhAsCl$_2$. In the case of the phosphorylation reaction, Doxsee also found that the product depends on the ratio of the reactants (**Scheme 17**).

Scheme 17
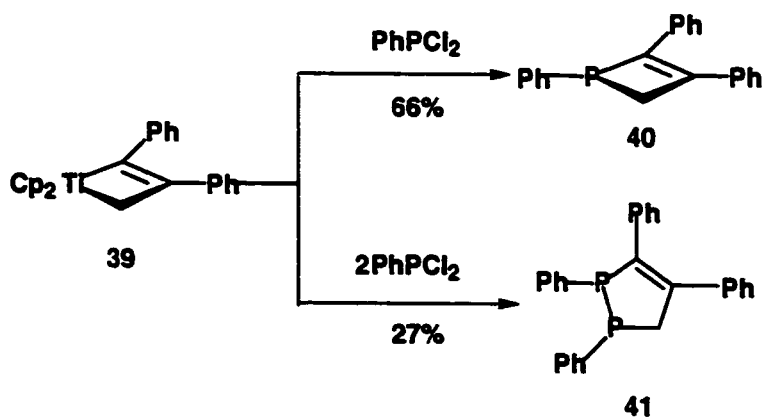
2. Results and Discussion

a. Isonitrile Insertion Reactions of Titanacyclobutenes

The reaction of 2,6-dimethylphenyl isocyanide with titanacyclobutenes occurs efficiently to give iminoacyl complexes. The reaction can be conducted by treatment of the titanacyclobutene **42** or **16** in THF solution with one equivalent of 2,6-dimethylphenyl isocyanide in THF at -35 °C. The resulting solutions were stirred for 1 h and gave iminoacyl insertion products **43** and **44** in good yields (eq. 14).

42	R = ^{i}Pr	**43**	R = ^{i}Pr (88%)
16	R = CH$_2$Si(CH$_3$)$_3$	**44**	R = CH$_2$Si(CH$_3$)$_3$ (85%)

eq. 14
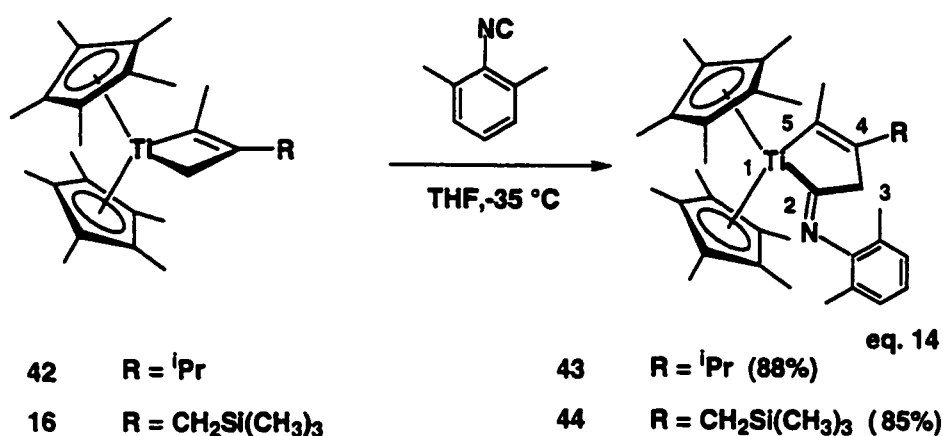
The structural assignment of complex **43** is based on a comprehensive analysis of the spectroscopic data. The ^{1}H NMR spectrum shows signals at δ 7.07 (d, 2H, J = 7.4 Hz), 6.89 (t, 3H, J = 7.4 Hz) and 2.44 (s, 6H), assigned to the phenyl and methyl protons of the imine substituent. The resonances for the isopropyl group appear at δ 0.88 (d, 6H, J = 6.9 Hz) and δ 2.52 (sept, 1H, J = 6.9 Hz). The methylene protons in the titanacyclobutene ring appear as a quartet at δ 2.62, owing to the small coupling constant to the methyl protons, as confirmed by the triplet at δ 0.93 (t, 3H, J = 1.9 Hz). In the ^{13}C NMR spectrum, the signal for the iminoacyl carbon appears at δ 244.8, a highly deshielded carbon resonance typical of this functionality.[44-52] The signal for the C-3 methylene carbon is observed upfield at δ 41.0, whereas the metal-bound sp^2-carbon (C-5)

appears at δ 195.4. The signal for C-4 of the five member ring is deshielded and observed at δ 152.0. Confirmation of this structure was obtained by single crystal X-ray analysis (see experimental section). The structure reveals some interesting features: the carbon-nitrogen bond is a typical double bond (1.283 Å), and the distance between the Ti and N atoms (3.16 Å) indicates there is no bonding, thus the stucture is drawn as an η^1-iminoacyl complex. The infrared absorption band at 1537 cm^{-1} is tentatively assigned to the C=N bond. We do not understand why it is about 210 cm^{-1} lower than that for the tert-butyl insertion products (*vide infra*).

The ^{1}H and ^{13}C NMR spectra of the iminoacyl complex **44** show similar resonances for the five-membered iminoacyl moiety. All the spectroscopic data fully support the structural assignment of complex **44**.

When various substituted bis(pentamethylcyclopentadienyl)titanacyclobutenes were treated with tert-butyl, cyclohexyl or benzyl isonitrile, only mixtures of products were obtained which could not be separated or fully characterized. Considering the differences among Cp*, ^{t}BuCp and Cp ligands, isonitrile insertion was attempted using the ^{t}BuCp and Cp analogues. Thus, the treatment of complex **45** with one equivalent of either 2,6-dimethylphenyl or tert-butyl isonitrile at -35 °C affords the corresponding iminoacyl complexes in high yield (eq. 15).

eq. 15

| 45 | 46 | R= 2,6-dimethylphenyl (87%) |
| | 47 | R= ^{t}Bu (84%) |

28

The structural assignment of iminoacyl complex **46** follows from analysis of the spectroscopic data and comparison to complexes **43** and **44** The ^{1}H NMR spectrum reveals the presence of the ^{t}BuCp ligand set, with the characteristic four narrow multiplets at δ 6.67 (m, 2 H), 6.61 (m, 2 H), 6.42 (m, 2 H), and 6.24 (m, 2 H), along with a singlet at δ 1.03, integrating to 18 protons. The signals for the benzyl group appear at δ 7.19–7.16 (m, 2H), 7.06 (m, 3H) and 2.96 (s, 2H). The ^{13}C {^{1}H} NMR spectrum reveals a typical signal for the iminoacyl carbon (C–2) at δ 235.6 and a signal for the metal-bound sp^{2}carbon (C–5) at δ 189.2. The sp^2 ring carbon (C–4) appears at δ 111.9 and the signal for the C-3 methylene carbon is observed at δ 47.9. The remaining signals and spectroscopic data are consistent with the assigned structure.

The ^{1}H and ^{13}C NMR spectra of the iminoacyl complex **47** show similar resonances for the five-membered iminoacyl moiety to complex **46**, along with the additional signals for the tert-butyl substituent. The remaining signals in the ^{1}H NMR spectrum are, along with the ^{13}C NMR data, fully consistent with the assigned structue of complex **47**. It is not clear why tert-butyl isocyanide works here and not in the Cp* case, although it maybe a simple steric effect.

eq. 16
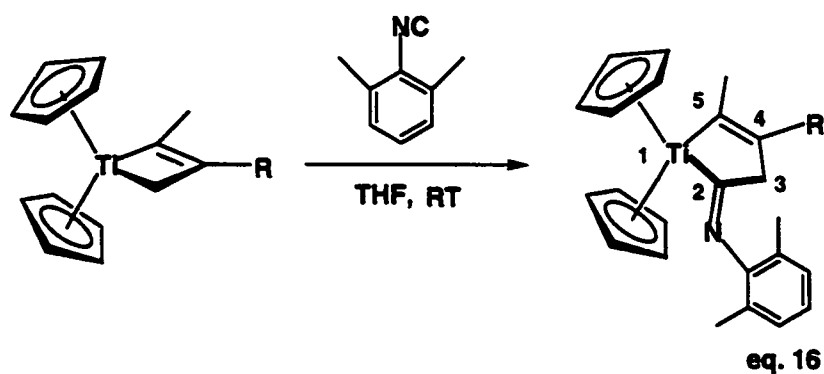
48	R = benzyl		**50**	R = benzyl (84%)
49	R = ^{i}Pr		**51**	R = ^{i}Pro (81%)

The unsubstituted cyclopentadienyl ligand is one of the most important ligands in organometallic chemistry. Complexes of this ligand also have important applications in organic synthesis.[53-58] It is highly desirable to extend the isonitrile insertion to titanacyclobutenes of the cyclopentadienyl series. Both complex **48** and **49** were thus treated with one equivalent of 2,6-dimethylphenyl isocyanide in THF at room temperature. The resulting solutions were stirred for 1 h and gave iminoacyl i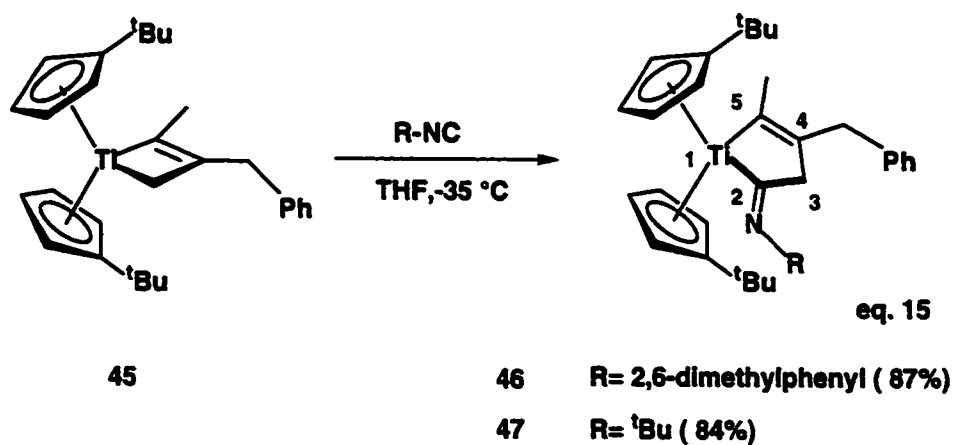nsertion products **50** and **51** in good yields (eq. 16). The structural assignments of complex **50** and **51** follows from analysis of the spectroscopic data and comparison to complexes **43**, **44**, **46** and **47**. For instance, the Cp moiety in complex **50** was identified by a singlet at δ 6.09 in the ^{1}H NMR spectrum. The ^{13}C $\{^1$H$\}$ NMR spectrum reveals a typical signal for the iminoacyl carbon (C–2) at δ 234.0 and a signal for the metal-bound sp^2 carbon (C–5) at δ 188.5. The other sp^2 carbon (C–4) appears at δ 152.3 and the signal for the C-3 methylene carbon is observed at δ 47.7. The remaining signals and spectroscopic data are consistent with the assigned structure and quite close to the data for complex **46**. The ^{1}H and ^{13}C NMR spectra of the iminoacyl complex **51** show quite similar resonances to complex **50**, along with the additional signals for the isopropyl substituent. The remaining signals in the ^{1}H NMR spectrum are, along with the ^{13}C NMR data, fully consistent with the assigned structue of complex **51**.

48   88%   52
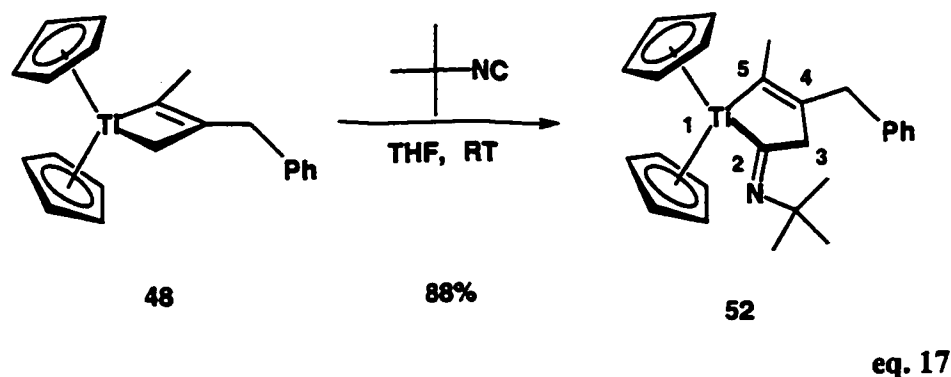
eq. 17

When complex **48** is treated with one equivalent of tert-butyl isocyanide in THF at room temperature, followed by the regular workup, iminoacyl insertion product **52** is

formed in 85% yield (eq. 17). The structural assignment of complex 52 follows from analysis of the spectroscopic data and comparison to similar complexes.[58, 36]

In summary, the ᵗBuCp and Cp titanacyclobutene complexes are even more general than the Cp* ligand for the isonitrile insertion reaction. Further investigation is needed to figure out the mixtures of products obtained by treatment of bis(pentamethylcyclopentadienyl)titanacyclobutenes with tert-butyl, cyclohexyl, or benzyl isonitrile, and to find conditions for reductive coupling of the iminoacyl complexes to give synthetically valuable cyclobutenimines.

b. Carbon Monoxide Insertion Reaction of Titanacyclobutenes

Carbon monoxide, the isoelectronic analogue of isonitriles, also undergoes single insertion reactions. Hence, subjecting the bis(pentamethylcyclopentadienyl)titana-cyclobutenes at -78 °C to CO under low pressure yields dark green acyl complexes 54 and 55 (eq. 18) in high isolated yields.

53 R = 2-butynyl   **54 R = 2-butynyl (84%)**
42 R = ⁱPr   **55 R = ⁱPr (99%)**
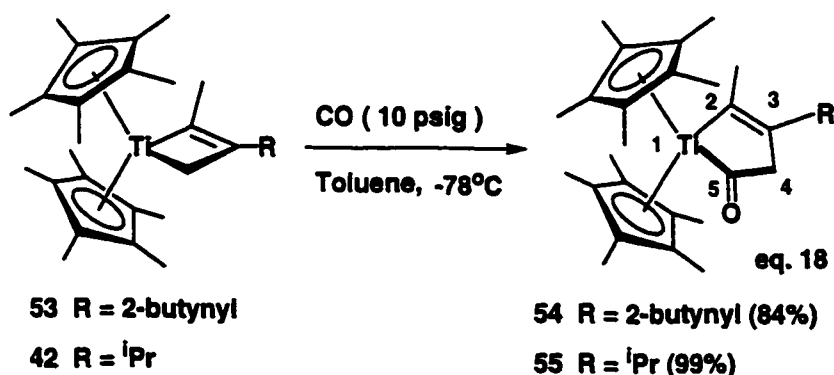
The structural assignment of complex 54 was based on a comprehensive analysis of the spectroscopic data, which are analgous to those obtained from iminoacyl complex 43 and 44. The ¹H NMR spectrum indicates a signal for the methylene protons in the acyl ring, which appears as a narrow quartet at δ 2.81, owing to the persistent small homoallylic coupling constant to the methyl attached to C-2, as confirmed by the narrow

31

triplet at δ 1.64. The methylene protons of the butynyl substituent are observed as narrow quartet at δ 2.67, a result of long rang coupling from its own methyl protons, which is confirmed by the triplet resonance at δ 0.92. The $^{13}C\{^1H\}$ NMR spectrum reveals the signal for the acyl carbon at δ 302.5, a characteristically deshielded carbon resonance.[38] The infrared absorption band at 1614 cm^{-1} is consistent with a similar Cp-coordinated complex.[34] The remaining signals and spectroscopic data are fully consistent with the assigned structure. An analytical sample of complex **54** suitable for X-ray crystallography was prepared from toluene/pentane at -35 °C. The structure was confirmed by single crystal X-ray analysis (see experimental section), which shows no bonding between Ti and O (3.07Å). This is consistent with the intense infrared absorption at 1614 cm^{-1}, indicative of an acyl ligand with little η^2–character.[59, 60] This complex is unstable in solution at room temperature, which we do not know what happens, but the solid is stable for a long time without any change. This insertion was also acomplished by reaction in pentane under 40 psig of CO at -78 °C to give the identical product **54**.

The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of complex **55** show similar resonances for the five-membered acyl moiety, along with the additional signals for the isopropyl group. The resonances for the isopropyl protons appear δ 2.55 (sept, 1H, J = 6.7 Hz) and δ 2.55 (d, 6H, J = 6.7 Hz) respectively, while the resonance for the methylene protons in the five-membered ring is observed at δ 2.36 (q, 2H, J = 1.9 Hz) owing to the small coupling constant to the methyl attached to C-2, as confirmed by the narrow triplet at δ 0.79. The remaining signals and spectroscopic data are fully consistent with the assigned structure. When this insertion reaction is conducted in THF solution, a slightly higher pressure of CO (20 psig) is required due to the different solubility of CO in THF and toluene.[61]

The ^tBuCp coordinated complex **45** also undergoes clean carbon monoxide

insertion. Thus, treatment of complex **45** with 60 psi of CO in THF at -78°C gives the corresponding acyl complex **56** in 92% isolated yield (**eq. 19**).
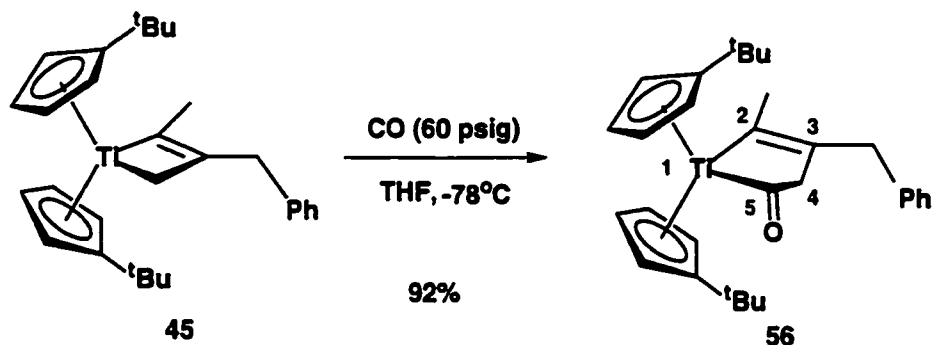
eq. 19

With the exception of the ancillary ligand set and benzyl substitute, the spectroscopic data for the complex **56** are very similar to the Cp* coordinated complexes **54** and **55**. The ^{1}H NMR spectrum further indicates the presence of the ^{t}BuCp ligand set, with three narrow multiplets at δ 6.58 (m, 2H), 6.30 (m, 2H) and 6.25 (m, 4H). The characteristic signal for the tert-butyl group appears as a singlet at δ 1.06, with an integral of 18 protons. The resonances for the benzyl group appear as multiplets at δ 7.26, 7.15 and a singlet at δ 3.08. The remaining signals in the ^{1}H NMR spectrum are, along with the ^{13}C{^{1}H} NMR data, fully consistent with the assigned structure. Complex **56** is also unstable in solution at room temperature.

Future work will be focused on preparing additional titanacyclopentenone complexes with different substituents and ancillary ligands and discovering conditions for reductive coupling of the acyl complexes to give very valuable organic cyclobutenones.

c. Demetallation of Titanacyclobutenes

After the successful functionalization of titanacyclobutenes with carbon monoxide and isonitriles, some effort was made toward transmetalation using $PhPCl_2$ and $PhBCl_2$ to

provide heterocyclic organic products.[39-43] Thus, treatment of complex **34** with one one equivalent of dichlorophenylphosphine in benzene solution at room temperature affords the corresponding dihydrophosphete **57** in 60% yield (eq. 20).

$$\text{Cp}_2\text{Ti} \quad \xrightarrow[\text{benzene, RT, 3 h}]{\text{PhPCl}_2\text{ (1 equiv)}} \quad \text{Ph—P}$$

34   60%   **57**   eq. 20
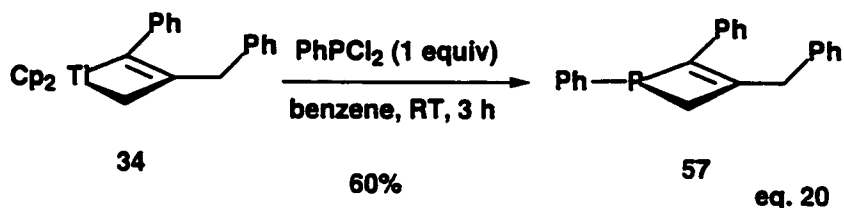
The structural assignment of compound **57** follows from analysis of the spectroscopic data and comparison to similar complexes reposted in the literature.[41,42] The ^{1}H NMR spectrum reveals the presence of the methylene group of the benzyl substituent with the AB doublets at δ 3.68 and 3.52, owing to the geminal coupling caused by the chirality at phosphous. The two protons of the methylene group in the four-membered ring are also stereochemically inequivalent and observed at 2.46 (dd, 1H, $^2J_{HH}$ = 14.8 Hz, $^2J_{PH}$ = 9.8 Hz) and 1.98 (dd, 1H, $^2J_{HH}$ = 14.8 Hz, $^2J_{PH}$ = 9.8 Hz), respectively. The ^{13}C{^{1}H} NMR spectrum reveals the sp^3 α-carbon of the dihydrophosphete **57**, which appears at δ 28.6 (d, $^1J_{CP}$ = 7.4 Hz), very close to that in a similar known dihydrophosphete.[38] The signal for the methylene carbon of the benzyl group is observed at δ 39.7 (d, $^3J_{CP}$ = 2.5 Hz). The ^{31}P {^{1}H} NMR spectrum clearly shows a single resonance at δ -12.8. The remaining signals and spectroscopic data are fully consistent with the assigned structure. A similar result was obtained in the reaction of 1,1-bis(*tert*-butylcyclopentadienyl)-3-benzyl-2-phenyltitanacyclobutene **33** with dichlorophenyl-phosphine, which gave **57** in 40% yield (eq. 21). This low yield is due to the fact that complex **33** is more stable than the corresponding complex **34**.

$$\text{}^t\text{BuCp}_2\text{Ti} \quad \xrightarrow[\text{hexane, RT, 1 h}]{\text{PhPCl}_2\text{ (1 equiv)}} \quad \text{Ph—P}$$

33   40%   **57**   eq. 21

34
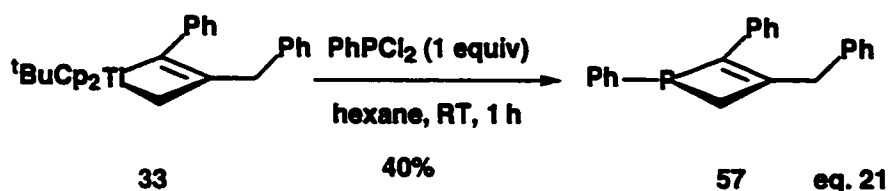
The addition of two equivalents of dichlorophenylphosphine directly to the solution of bis(cyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene **48** or bis(*tert*-butylcyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene **45** in benzene at room temperature yields the expected 1,2-diphosphacyclopentene **58** in yields of 33% and 28% respectively (**eqs. 22, 23**).
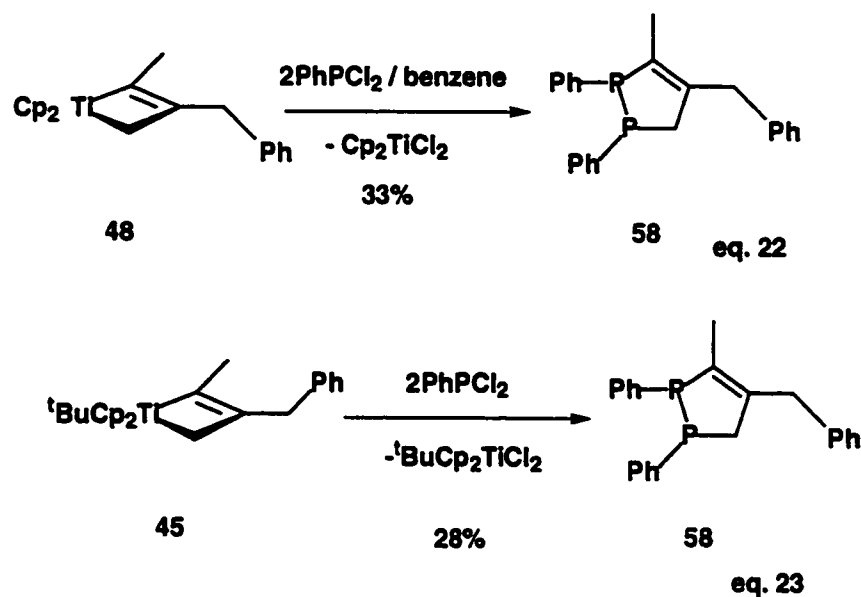
The structural assignment of compound **58** follows from analysis of the spectroscopic data and comparison to analogous complexes prepared by Doxsee.[41] The $^{31}P\{^1H\}$ NMR spectrum clearly indicates the presence of two inequivalent phosphorus atoms with a 220 Hz coupling constant, consistent with the presence of a direct P-P bond.[41] The chemically inequivalent protons of the methylene group in the five-membered ring appear as multiplets at δ 3.17 ("t", 1H, $^2J_{HH} \sim {}^2J_{PH} \sim 18$ Hz, $^3J_{PH} \sim 0$ Hz) and 2.89 ("d", 1H, $^2J_{HH} \sim 18$ Hz, $^2J_{HH} \sim 2$ Hz, $^2J_{PH} \sim {}^3J_{PH} \sim 2$ Hz) which are quite similar to the literature.[41] The methyl protons are observed as a triplet of doublets at δ 1.92 due to coupling to one phosphorus and the protons of the methylene of the ring. The two protons of the benzyl methylene group are also chemically inequivalent and appear as AB doublets at δ 3.51 and δ 3.25 due to geminal coupling ($^2J_{HH} = 14.1$ Hz). The remaining

signals in the ^{1}H NMR spectrum and ^{13}C{^{1}H} NMR data are, along with high resolution mass spectrometry, fully consistent with the assigned structure.

Simple borocyclobutenes look very useful synthetically as both an allyborane and a vinylborane reagent. Despite the unsuccessful transmetalation reactions of Cp* titanacyclobutenes with dichlorophenylphosphine, treatment of 1,1-bis(pentamethyl-cyclopentadienyl)-3-benzyl-2-(4-methoxyphenyl)titanacyclobutene 29 with one equivalent of the more electrophilic dichlorophenyl borane in toluene at -35 °C followed by workup and recrystallization from hexane at -35 °C gives a white solid product, along with a red solid of Cp*$_2$TiCl$_2$ (eq. 24). Although the separation was not complete, partial characterization of the borocyclobutene was obtained by spectroscopic methods. The ^{1}H NMR spectrum indicates the signal for the boron-bound methylene group as a singlet at δ 2.24. The methyl of benzyl group appears as a singlet at δ 3.47, while the methyoxy protons are observed at δ 3.47. High resolution mass spectrometry also supports the assigned structure.

eq. 24
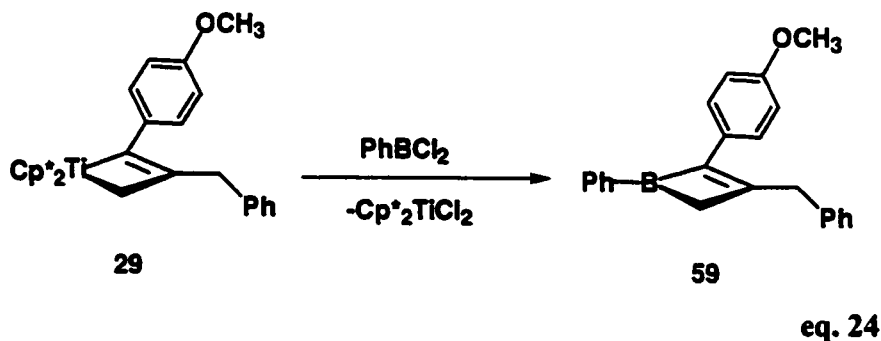
Further work on transmetallaton to boron is continuing toward obtaining fully characteratized borocyclobutenes and development of a general isolation method.

36

III. CONCLUSIONS

We have investigated the synthesis of titanium(III) propargyl complexes and titanacyclobutene formation by regioselective addition of free radicals. We found that the thermal stability and reactivity of titanacyclobutene complexes are strongly dependent on the ancillary ligands. Our results show that bis(Cp*) ligand set forms more stable titanacyclobutene complexes with various substituents, whereas less electron rich bis(^{t}BuCp) and bis(Cp) ligand sets gives less stable complexes, but still afford synthetically useful yields. These observations indicate that relatively electron-rich ancillary ligand sets facilitate radical addition and provide more thermostable complexes. In the functionalization reactions using isonitriles and carbon monoxide, we found that titanacyclobutene complexes undergo only single insertion reactions, in contrast to titanacyclobutane complexes, which can undergo both single and double insertion reactions.[10] We have also extended the demetallation reactions of titanacyclobutenes using phenyldichlorophosphine to the ^{t}BuCp coordinated complexes, which may provide more accessibles substrates for the synthesis of small-ring phosphorus heterocycles.

Continuing work in this area will be focused on demetallation of the titanacyclopentenones and iminotitanacyclopentenes to give valuable cyclobutenone derivatives and preparing more phosphacyclobutenes and 1,2-dihydrophosphetes to provide practical utility for organic synthesis. Finally, a general strategy to isolate the potentially important borocyclobutenes needs to be developed.

IV. EXPERIMENTAL SECTION

General: All air-sensitive manipulations were conducted under a nitrogen atmosphere using standard Schlenk techniques or drybox techniques. The high vacuum line ($<10^{-5}$ torr) was used to add solvent and reagents to reaction mixtures via vacuum transfer and to remove volatile compounds from reaction mixtures.

Infrared (IR) spectra were recorded on Perkin-Elmer 1420, 298, and 283, Pye Unicam PU9522, and Nicolet 7199 Fourier transform spectrophotometers, and are reported in reciprocal wave numbers (cm^{-1}) calibrated to the 1601 cm^{-1} absorption of polystyrene. Infrared determinations were done on compounds applied as a film on KBr or KCl salt plates and are referred to as a "cast". Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AM-200, Bruker AM-300, Bruker AM-360, and Bruker AM-400 [400 MHz (^{1}H) and 100 MHz (^{13}C)] spectrometers. Chemical shifts are reported in parts per million (ppm, δ) relative to TMS (^{1}H and ^{13}C) and coupling constants are reported in hertz (Hz). Unless stated otherwise, NMR spectra were obtained at 23 °C, and coupling constants reported as J refer to J_{HH} for ^{1}H NMR spectra and J_{CH} for ^{13}C NMR spectra or could not be unambiguously assigned due to the presence of multiple spin active atoms in close proximity. Coupling constants are reported to 0.1 hertz, which is within the limits of instrumental precision, but these values are normally accurate only to within ± 0.5 Hz. Multiplicities are reported as observed. X-ray crystallographic analyses were done on a Siemans P4/RA X-ray diffractometer. Mass spectra were obtained on a Kratos MS-80 spectrometer operating at 40 eV. Combustion analyses were performed by the University of Alberta Microanalysis Laboratory. All air-sensitive compounds (~3.0 mg) were wrapped in strips of pre-weighed tin foil and kept in nitrogen-filled one-dram vials immediately prior to analysis.

All carbonylation reactions above atmospheric pressure were done in a Fisher & Porter medium pressure glass bottle (Andrews Glass Co.).

Flash column chromatographic separations[69] were performed on silica gel 60 (0.040-0.063 mm, E. Merck). Celite filtrations were performed using a plug of Hyflo Super Cel (Fisher) over glass wool in disposable pipets or alone on sintered glass funnels under vacuum. Cylindrical medium-walled Pyrex vessels equipped with Kontes k-826510 Teflon vacuum stopcocks are referred to as glass bombs.

Materials: Unless indicated otherwise, solvents and reagents were purchased from commercial vendors, distilled or passed down a plug of neutral alumina, and degassed prior to use by repeated freeze-pump-thaw cycles on a vacuum line. Benzene, hexanes, pentane, tetrahydrofuran, and diethyl ether were purified by distillation from sodium or potassium benzophenone ketyl.

The following complexes were prepared according to published procedures: C_5Me_5H,[62] Cp^*_2TiCl, [63,64] $[Cp_2TiCl]_2$,[65] $[(^tBuCp)_2TiCl]_2$,[66,67,64] $Pd(Ph_3P)_4$,[68] Complexes **42** and **53**, [11] Complexes **45**, **48** and **49**.[12]

A. Intermolecular Radical Alkylations of Titanium(III) Propargyl Complexes

1,1-Bis(pentamethylcyclopentadienyl)-3-(trimethylsilylmethyl)-2-methyltitana-cyclobutene 16.

16
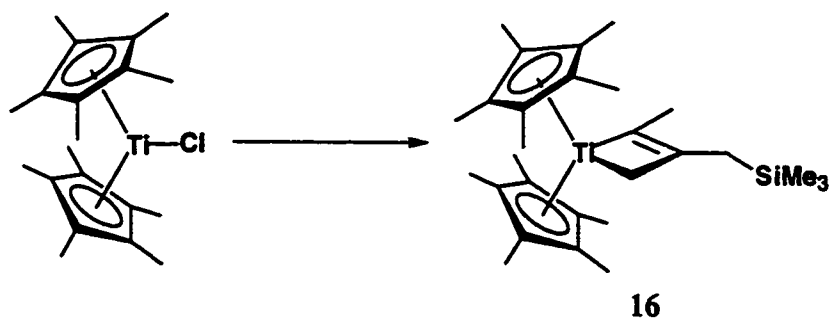
To a cold (-78 °C) solution of Cp*$_2$TiCl (53.1 mg, 0.150 mmol) and SmI$_2$ (0.1 M in THF, 4.5 mL, 0.45 mmol) in dry THF (5 mL) was added a solution of 2-butynyl bromide (19.9 mg, 0.150 mmol) in dry THF (1 mL) at -78 °C. After 30 min, a solution of bromomethyltrimethylsilane (25.1 mg, 0.150 mmol) in dry THF(1 mL) was added at -78 °C. The mixture was allowed to warm to room temperature overnight. During that time the colour of the solution changed from blue to brown. The solvent was evaporated *in vacuo* and the residue was triturated with pentane. The combined extracts were filtered through a short column of celite followed by concentration to give 1,1-bis(pentamethylcyclopentadienyl)-3-(trimethylsilylmethyl)-2-methyltitanacyclobutene **16** as a red solid (63.3 mg, 93%). An analytical sample was prepared by recrystallization from pentane at -35 °C. In general experiments, the butynyl derived titanacyclobutenes were very soluble, so recrystallization gives poor recovery. Spectroscopic data for complex **16**: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 2.14 (q, 2H, J = 1.8 Hz), 1.93 (t, 3H, J = 1.8 Hz), 1.72 (s, 30H), 1.68 (s, 2H), 0.21 (s, 9H); ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$, gated decoupled) δ 206.5 (s), 117.9 (s), 103.2 (s), 78.0 (t, J = 135.6 Hz), 22.3 (t, J = 117.7 Hz), 20.4 (q, J = 123.3 Hz), 12.9 (q, J = 125.4 Hz) 0.2 (q, J = 118.4 Hz); HRMS calcd. *m/z* for C$_{28}$H$_{46}$TiSi 458.28482, found 458.28334.

40

1,1-Bis(pentamethylcyclopentadienyl)-2-methyl-3-(1-butenyl)titanacyclobutene 19.

19
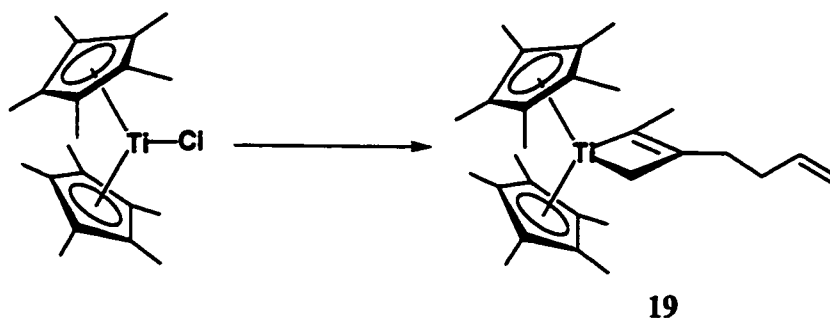
To a solution of Cp*$_2$TiCl (36.9 mg, 0.104 mmol) and SmI$_2$ (0.1 M in THF, 3.2 mL, 0.32 mmol) in dry THF (1 mL) was added a solution of 2-butynyl bromide (13.9mg, 0.104 mmol) in dry THF (1 mL) at -35 °C. After 10 min, a solution of cyclopropyl-methyl bromide (14.1 mg, 0.104 mmol) in dry THF(1 mL) was added at -35 °C. The mixture was allowed to warm to room temperature overnight. During that time the colour of the solution changed from blue to dark red. The solvent was evaporated *in vacuo* and the residue was triturated with pentane. The combined extracts were filtered through a short column of celite followed by concentration to give 1,1-bis(pentamethylcyclopentadienyl)-2-methyl-3-(1-butenyl)titanacyclobutene **19** as a dark red oil (43.0 mg, 97%). An analytical sample was prepared by recrystallization from pentane at -35 °C to give a red solid. Spectroscopic data for complex **19**: ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 6.02 (ddt, 1H, C**H**=CH$_2$, J = 17.0, 11.0, 6.1 Hz), 5.18 (ddt, 1H, CH=C**H**$_2$, J = 17.0, 2.0, 1.2 Hz), 5.05 (ddt,1H, CH=C**H**$_2$, J = 11.0, 2.0, 1.1 Hz), 2.34-2.29 (m, 4H, CH$_2$CH$_2$), 2.13 (q, 2H, TiCH$_2$, J = 2.0 Hz), 1.94 (t, 3H, CH$_3$, J = 2.0 Hz), 1.75 (s, 30H, C$_5$(CH$_3$)$_5$); ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$, APT) δ 206.8 (p), 138.7 (a), 117.9 (p), 114.0 (p), 101.6 (p), 75.5 (p), 41.1 (p), 35.6 (p), 19.3 (a), 11.9 (a); HRMS calcd. *m/z* for C$_{28}$H$_{42}$Ti 426.27661, found 426.27637.

1,1-Bis(pentamethylcyclopentadienyl)-2-phenyl-3-(1-butenyl)titanacyclobutene 20.

20

To a solution of Cp*$_2$TiCl (57.5 mg, 0.162 mmol) and SmI$_2$ (0.1 M in THF, 5.4 mL, 0.54 mmol) in dry THF (5 mL) was added a solution of 3-phenylpropargyl bromide (31.7 mg, 0.162 mmol) in dry THF (1 mL) at -78 °C. After 30 min, a solution of cyclopropylmethyl bromide (22.0 mg, 0.162 mmol) in dry THF(1 mL) was added at -78 °C. The mixture was allowed to warm to room temperature overnight. During that time the colour of the solution changed from blue to brown. The solvent was evaporated *in vacuo* and the residue was triturated with pentane. The combined extracts were filtered through a short column of celite followed by concentration and recrystallization from pentane at -35 °C to give 1,1-bis(pentamethylcyclopentadienyl)-2-phenyl-3-(1-butenyl)titanacyclobutene **20** as a dark green solid (72.0 mg, 91%). Spectroscopic data for complex **20**: ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 7.25 (m, 2H, ArH), 7.00 (m, 1H, ArH), 6.91 (m, 2H, ArH), 6.07 (ddt, 1H, C$\underline{H}$=CH$_2$, J = 17.0, 10.1, 6.2 Hz), 5.24 (ddt, 1H, CH=C$\underline{H}_2$, J = 17.0, 2.0, 1.2 Hz), 5.09 (ddt,1H, CH=C$\underline{H}_2$, J = 10.1, 2.0, 1.1 Hz), 2.62-2.41 (m, 4H, CH$_2$CH$_2$), 2.33 (s, 2H, TiCH$_2$), 1.69 (s, 30H, C$_5$(CH$_3$)$_5$); ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$) δ 204.2, 144.3, 139.9, 129.3, 127.8, 123.8, 119.2, 114.1, 111.3, 77.9, 35.3, 33.1, 12.2; HRMS calcd. *m/z* for C$_{33}$H$_{44}$Ti 488.29224, found 488.29271.

1,1-Bis(pentamethylcyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene 22.
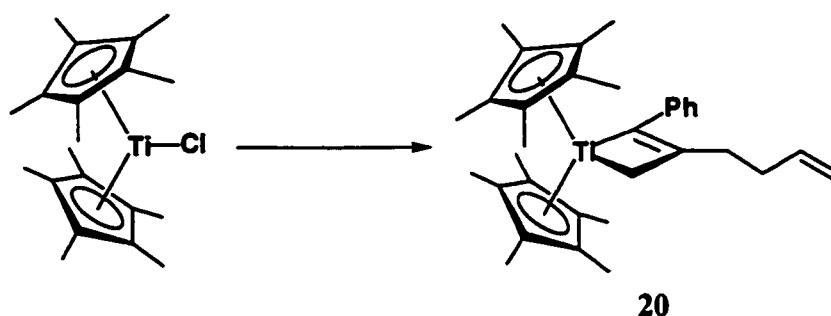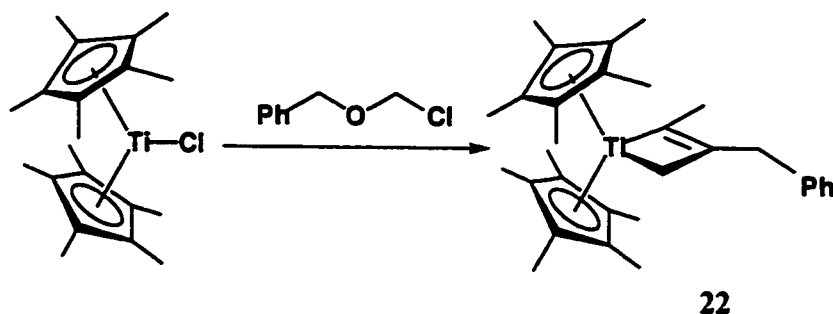

To a solution of Cp*$_2$TiCl (53.1 mg, 0.150 mmol) and SmI$_2$ (0.1 M in THF, 5.0 mL, 0.50 mmol) in dry THF (5 mL) at -78 °C was added a solution of 2-butynyl bromide (19.9 mg, 0.150 mmol) in dry THF (1 mL). After 30 min, a solution of benzyl chloromethyl ether (23.5 mg, 0.150 mmol) in dry THF (1 mL) was added at -78 °C. The mixture was allowed to warm to room temperature overnight. During that time the colour of the solution changed from blue to dark red. The solvent was evaporated *in vacuo* and the residue was triturated with pentane. The combined extracts were filtered through a short column of celite followed by concentration and recrystallization from pentane at -35 °C to give a dark red solid (45.5 mg, 65%). Analysis and comparision of spectroscopic data for the complex found that the known 1,1-bis(pentamethylcyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene 22[11] was obtained instead of the expected 1,1-bis(pentamethylcyclopentadienyl)-3-(benzyloxymethyl)-2-methyltitanacyclobutene 21.

**1,1-Bis(pentamethylcyclopentadienyl)-2-phenyl-3-(1-phenylpropargyl)titana-cyclobutene 24.**
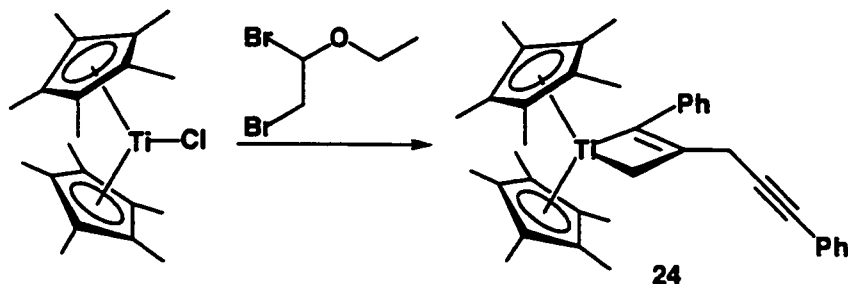
To a solution of Cp*$_2$TiCl (53.8 mg, 0.152 mmol) and SmI$_2$ (0.1 M in THF, 4.6 mL, 0.46 mmol) in dry THF (5 mL) was added a solution of 2-phenylpropargyl bromide (29.7 mg, 0.152 mmol) in dry THF (1 mL) at -78 °C. The mixture was allowed to warm to room temperature overnight. Then a solution of 1,2-dibromoethyl ethyl ether (35.1 mg, 0.152 mmol) in dry THF (1 mL) was added at -78 °C. The mixture was slowly warmed to room temperature. The solvent was evaporated *in vacuo* and the residue was triturated with pentane. The combined extracts were filtered through a short column of celite followed by concentration and recrystallization from pentane at -35 °C to give a dark red solid. Analysis and comparision of spectroscopic data for the complex found the known 1,1-bis(pentamethylcyclopentadienyl)-2-phenyl-3-(1-phenylpropargyl)titanacyclobutene 24[11] was obtained in low yield instead of the expected 1,1-bis(pentamethylcyclopen-tadienyl)-2-phenyl-3-(1-ethoxy-2-bromoethyl)titanacyclobutene 23.

B. Dimerazation and Intramolecular coupling of Titanium(III) Propargyl Complexes

Synthesis of 3-(4-methoxyphenyl)propargyl bromide 25.

25

To a mixture of 3-(4-methoxyphenyl)-2-propyn-1-ol (810 mg, 5.00 mmol) in 6mL Et_2O and 0.4 mL pyridine was added dropwise PBr_3 (0.60 mL, 6.3 mmol) at 0 °C. When the addition of PBr_3 was complete, the mixture was heated for 3 h at 50 °C. The cooled mixture was added to 40 mL ice water and the aqueous layer was extracted with ether. The combined organic layer was washed with a $NaHCO_3$ solution, water, brine, and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (silical gel, Ethyl acetate/Hexane, 3%) to give the desired product (595 mg, 53%) as a pale yellow oil. Spectroscopic data for compound **25**: IR (neat) 3003 (w), 2958 (w), 2934 (w), 2836 (w), 2217 (m), 1606 (m), 1509 (s), 1249 (s), 1032 (m), 986 (m), 799 (m) cm^{-1}; ^1H NMR (200 MHz, CDCl$_3$) δ 7.39 (d, 2H, J = 18 Hz), 6.85 (d, 2H, J = 18 Hz), 4.17 (s, 2H), 3.80 (s, 3H, CH$_3$); ^{13}C {^1H} NMR (50 MHz, CDCl$_3$, APT) δ 160.1 (p), 133.4 (a), 114.0 (a), 86.9 (p), 83.0 (p), 55.3 (a), 15.9 (p); HRMS calcd. m/z for C$_{10}$H$_9$BrO 225.98163, found 225.98209.

**Bis(pentamethylcyclopentadienyl)[η³-3-(4-methoxyphenyl)-propargyl]titanium 26.**

26
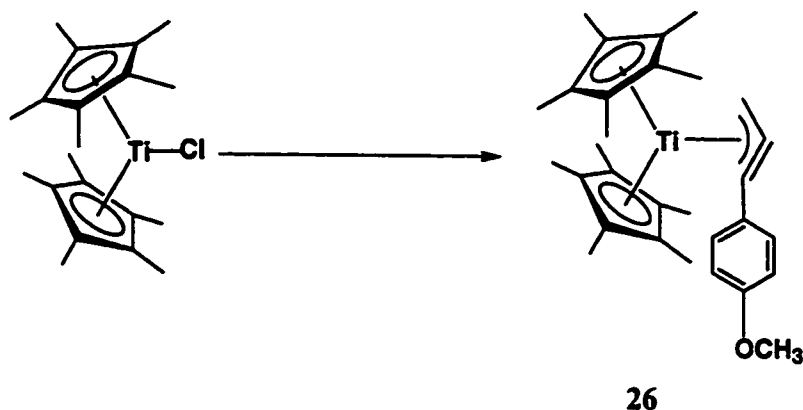
To a solution of Cp*₂TiCl (53.1 mg, 0.150 mmol) and SmI₂ (0.1 M in THF, 3.3 mL, 0.33 mmol) in dry THF (4 mL) was added a solution of 3-(4-methoxyphenyl)-propargyl bromide (33.8 mg, 0.150 mmol) in dry THF (2 mL) at -78 °C. The mixture was allowed to warm to room temperature overnight. The solvent was evaporated *in vacuo* and the residue was triturated with pentane. The combined extracts were filtered through a short column of celite followed by concentration to give the highly air-sensitive bis(pentamethylcyclopentadienyl)[η³-3-(4-methoxyphenyl)propargyl]titanium **26** as a dark green solid (62.0 mg, 90%). A crystalline sample was prepared by crystallization from toluene at -35 °C. Spectroscopic data for complex **26**: IR (ether, cast) 2980 (w), 2903 (m), 2850 (w), 1958 (w), 1505 (s), 1439 (m), 1242 (s), 1067 (m), 1039 (s), 831 (m), cm⁻¹; HRMS calcd. *m/z* for C₃₀H₃₉TiO 463.24805, found 463.24803; Anal. Calcd for C₃₀H₃₉TiO: C, 77.74; H, 8.48; Found: C, 77.11; H, 8.20.

1,1-Bis(pentamethylcyclopentadienyl)-3-isopropyl-2-(4-methoxyphenyl)titana-cyclobutene 28.
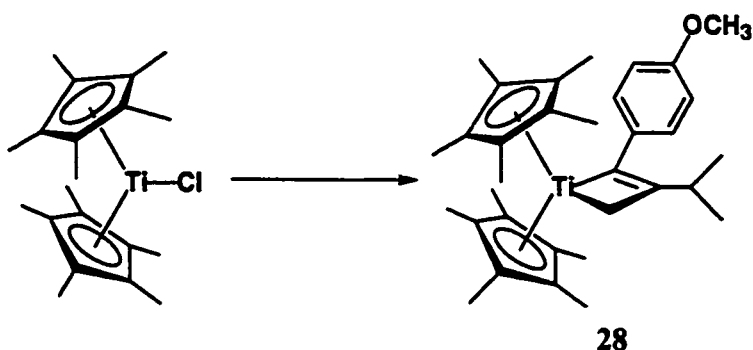
To a solution of Cp*$_2$TiCl (35.4 mg, 0.100 mmol) and SmI$_2$ (0.1 M in THF, 3.5 mL, 0.35 mmol) in dry THF (5 mL) was added a solution of 3-(4-methoxyphenyl)-bromide (22.5 mg, 0.100 mmol) in dry THF (1 mL) at -78 °C. After 30 min, a solution of 2-iodopropane (17.0 mg, 0.1 mmol) in dry THF(1 mL) was added at -78 °C. The mixture was allowed to warm to room temperature overnight. During that time the colour of the solution changed from blue to brown. The solvent was evaporated *in vacuo* and the residue was triturated with pentane. The combined extracts were filtered through a short column of celite followed by concentration and recrystallization from pentane at -35 °C to give 1,1-bis(pentamethylcyclopentadienyl)-3-isopropyl-2-(4-methoxyphenyl)-titanacyclobutene **28** as a dark brown solid (47.0 mg, 93%). Spectroscopic data for complex **28**: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 6.99–6.94 (m, 4H, ArH), 3.42 (sept, 1H, J = 6.5 Hz), 3.41 (s, 3H, OCH$_3$), 2.21 (s, 2H, CH$_2$), 1.73 (s, 30H, C$_5$(CH$_3$)$_5$), 1.22 (d, 6H, CH(CH$_3$)$_2$, J = 6.5 Hz); ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$, APT) δ 202.8 (p), 156.7 (p), 137.7 (p), 130.1 (a), 119.1 (p), 114.3 (p), 113.4 (a), 68.8 (p), 54.7 (a), 28.4 (a), 23.6 (a), 12.3 (a); HRMS calcd. m/z for C$_{33}$H$_{46}$TiO 506.30194, found 506.30283.

1,1-Bis(pentamethylcyclopentadienyl)-3-benzyl-2-(4-methoxyphenyl)titanacyclo-butene 29.

29
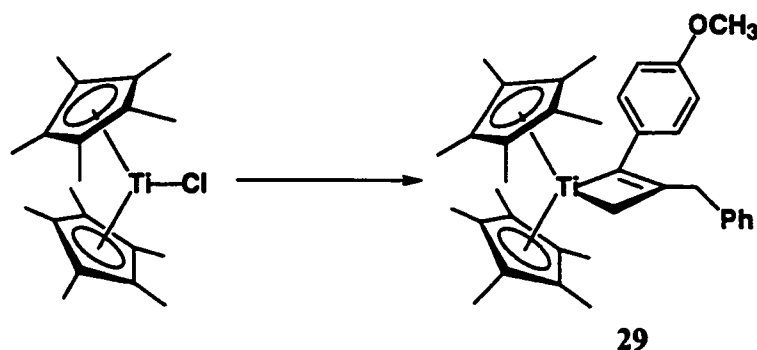
To a solution of Cp*$_2$TiCl (141.6 mg, 0.4000 mmol) and SmI$_2$ (0.1 M in THF, 14 mL, 1.4 mmol) in dry THF (15 mL) was added a solution of 3-(4-methoxyphenyl)-bromide (90.0 mg, 0.400 mmol) in dry THF (2 mL) at -78 °C. After 30 min, a solution of benzyl chloride (50.2 mg, 0.400 mmol) in dry THF (2 mL) was added at -78 °C. The mixture was allowed to warm to room temperature overnight. The solvent was evaporated *in vacuo* and the residue was triturated with pentane. The combined extracts were filtered through a short column of celite followed by concentration to give 1,1-bis(pentamethylcyclopentadienyl)-3-benzyl-2-(4-methoxyphenyl)titanacyclobutene **29** as a dark green solid (195.2 mg, 88%). Recrystallization from THF at -35 °C gave a dark brown crystalline product. Spectroscopic data for complex **29**: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 7.47–7.39 (m, 2H, ArH), 7.30–7.22 (m, 3H, ArH), 7.05–6.99 (m, 2H, ArH), 6.95–6.87 (m, 2H, ArH), 3.84 (s, 2H, PhCH$_2$), 3.42 (s, 3H, OCH$_3$), 2.31 (s, 2H, TiCH$_2$), 1.66 (s, 30H, C$_5$(CH$_3$)$_5$); ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$, APT) δ 204.0 (p), 157.0 (p), 142.6 (p), 137.2 (p),130.4 (a), 130.3 (a), 128.5 (a), 128.2 (a), 119.3 (p), 113.4 (a), 108.6 (p), 77.3 (p), 54.8 (a), 39.1 (p), 12.2 (a); HRMS calcd. *m/z* for C$_{37}$H$_{46}$TiO 554.30280, found 554.30146

Attempted synthesis of complex 32 from 1,2,4,5-tetrakis(3-bromopropynyl)benzene 30.

I. 1,2,4,5-tetrakis(3-hydroxypropynyl)benzene 31.

31
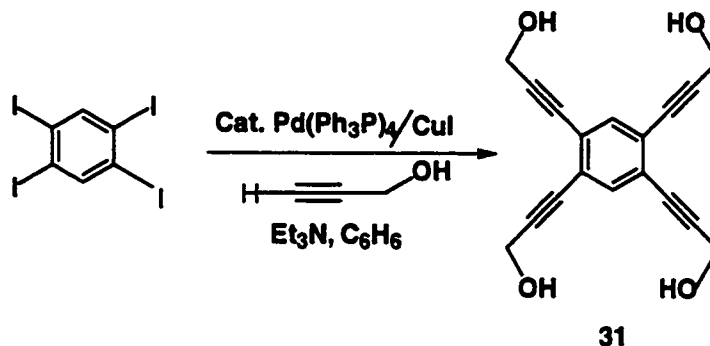
Under N_2, a mixture of $Pd(Ph_3P)_4$ (1.11 g, 0.961 mmol), CuI (1.88 g, 9.87 mmol), 1,2,4,5-tetraiodobenzene[35] (5.63 g, 9.68 mmol), and freshly distilled propargyl alcohol (4.45 g, 80.0 mL) in a mixed solvent of Et_3N (310 mL) and benzene (110 mL) was stirred at room temperature for 2 days. The solution was filtered and concentrated under reduced pressure. The yellow residue was carefully washed with acetone followed by recrystallization from CH_3OH to give a pale yellow crystalline material (2.32 g, 81%). Spectroscopic data for complex **31**: IR (KBr, cast) 3260 (s), 2918 (w), 1488 (m), 1424 (m), 1393 (m), 1352 (m), 1221 (w), 1029 (s), 978 (m) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 7.47 (s, 2H, ArH), 5.37 (t, 4H, OH, J = 6.0 Hz), 4.34 (d, 8H, CH_2, J = 6.0 Hz); ^{13}C {^1H} NMR (75 MHz, DMSO-d_6) δ 134.7, 124.6, 96.0, 80.9, 49.5; HRMS calcd. m/z for $C_{18}H_{14}O_4$ 294.08920, found 294.08922.

II. 1,2,4,5-tetrakis(3-bromopropynyl)benzene 30.
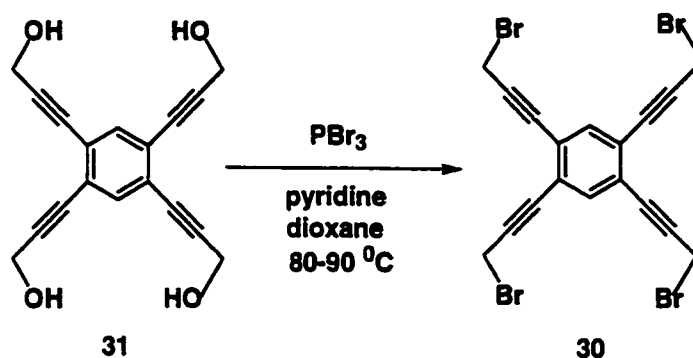
A mixture of 1,2,4,5-tetrakis(3-hydroxypropynyl)benzene **31** (0.430 g, 1.45 mmol), dioxane (50.0 mL) and pyridine (0.3 mL) was placed in 100 mL flask. PBr₃ (2.00 g, 7.37 mmol) was added dropwise over 15 min at room temperature. The reaction mixture was stirred for 3 h between 80 °C and 90 °C until all the solid dissolved. The solution was cooled to room temperature and ethyl acetate (ca. 50 mL) was added. The mixture was then washed with water, brine and dried over MgSO₄, followed by evaporation *in vacuo* to give a pale yellow crystalline solid (0.65 g, 82%). Spectroscopic data for complex **30**: IR (KBr, cast) 3003 (m), 2952 (w), 2234 (w), 1490 (s), 1415 (m), 1395 (m), 1234 (m), 1196 (s), 898 (w), 856 (m), 607 (s) cm⁻¹; ¹H NMR (300 MHz, THF-d₈) δ 7.55 (s, 2H, ArH), 4.37 (s, 8H); ¹³C {¹H} NMR (75 MHz, THF-d₈) δ 135.9, 126.2, 92.4, 83.8, 15.0; HRMS calcd. *m/z* for $C_{18}H_{10}Br_4$ 545.74750, found 545.74815; Anal. Calcd for $C_{18}H_{10}Br_4$: C, 39.60; H, 1.84; Found: C, 39.43; H, 1.73.

III. Attempted synthesis of complex 32.

50
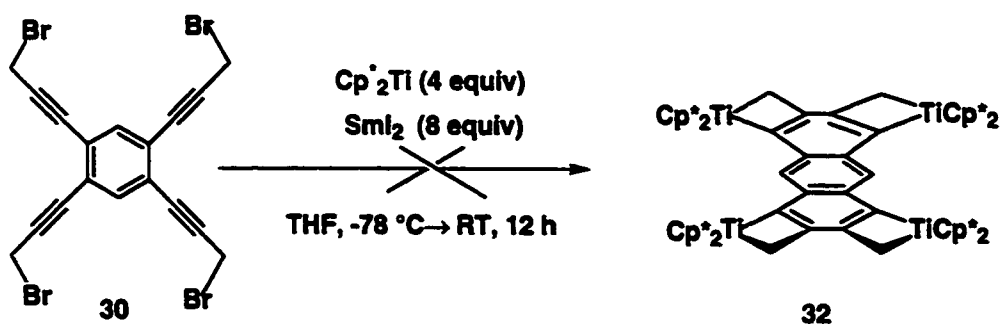
To a solution of Cp*$_2$TiCl (70.8 mg, 0.200 mmol) and SmI$_2$ (0.1 M in THF, 16 mL, 1.6 mmol) in dry THF (5 mL) was added a solution of 1,2,4,5-tetrakis(3-bromopropynyl)benzene **30** (11.3 mg, 0.0500 mmol) in dry THF (1 mL) at -78 °C. The mixture was allowed to warm to room temperature overnight. During that time the colour of the solution changed from blue to dark red. The solvent was evaporated *in vacuo* and the residue was triturated with pentane. The combined extracts were filtered through a short column of celite followed by concentration to give a dark red solid . The ^{1}H NMR spectrum and HRMS (ESI) showed the residue is a complex mixture and no desired compound was observed.

C. Radical Additions of Titanium(III) Propargyl Complexes Using Cp and ^{t}BuCp Templates

1,1-bis(*tert*-butylcyclopentadienyl)-3-benzyl-2-phenyltitanacyclobutene 33.
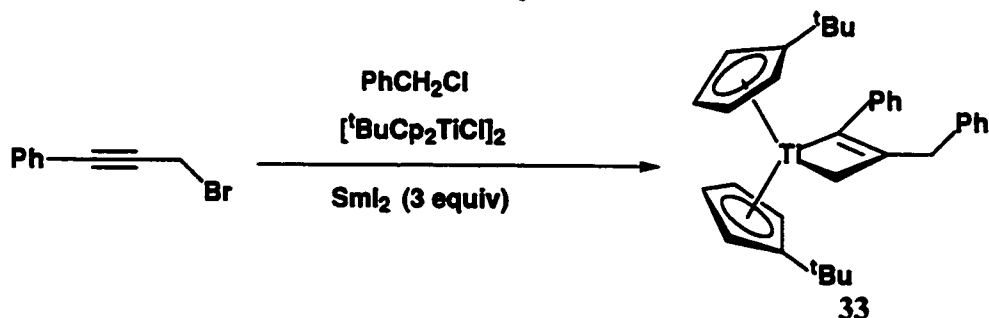
In the drybox, to a solution of [(^{t}BuCp)$_2$TiCl]$_2$ (71.1 mg, 0.109 mmol) and SmI$_2$ (0.1 M in THF, 6.6 mL, 0.66 mmol) in THF (2 mL) at -35 °C was added a solution of 3-phenylpropargyl bromide (42.5 mg, 0.218 mmol) and benzyl chloride (27.7 mg, 0.218 mmol) in THF (1 mL) at -35 °C. After shaking occasionally for 1 h at -35 °C, the solution was warmed to room temperature, during which time the color changed gradually from dark blue to dark red. The reaction mixture was maintained at room temperature for 1 h. The volatiles were removed *in vacuo* and the residue was triturated with pentane and filtered through a plug of celite. Evaporation of the solvent under reduced pressure

gave 1,1-bis(*tert*-butylcyclopentadienyl)-3-benzyl-2-phenyltitanacyclobutene **33** (105.0 mg, 97%) as a dark pink solid. A pure crystalline solid was obtained from pentane at -35°C. Spectroscopic data for complex **33**: ^{1}H NMR (300 MHz, C_6D_6) δ 7.40–7.01 (m, 10H, 2ArH), 6.12 (q, 2H, J = 2.8 Hz), 5.60 (q, 2H, J = 2.8 Hz), 5.53 (q, 4H, J = 2.8 Hz), 3.38 (s, 2H, PhCH$_2$), 3.13 (s, 2H, TiCH$_2$), 0.99 (s, 18 H, C(CH$_3$)$_3$); ^{13}C {^{1}H} NMR (75 MHz, C_6D_6, APT) δ 206.8 (p), 148.1 (p), 141.0 (p), 140.3 (p), 129.7 (a), 128.5 (a), 126.1 (a), 125.9 (a), 124.4 (a), 111.4 (a), 110.7 (a), 108.0 (a), 100.6 (p), 71.9 (p), 37.5 (p), 32.9 (p), 31.5 (a); HRMS calcd. *m/z* for $C_{34}H_{40}Ti$ 496.26096, found 496.25982.

1,1-Bis(cyclopentadienyl)-3-benzyl-2-phenyltitanacyclobutene 34.

34
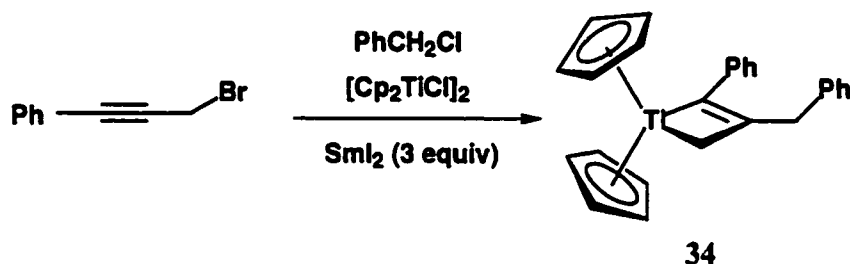
In the drybox, to a solution of [Cp$_2$TiCl]$_2$ (39.4 mg, 0.0925 mmol) and SmI$_2$ (0.1 M in THF, 5.7 mL, 0.57 mmol) in THF (2 mL) at -35 °C was added a solution of 3-phenylpropargyl bromide (36.0 mg, 0.185 mmol) and benzyl chloride (23.5 mg, 0.185 mmol) at -35 °C. The reaction mixture was warmed to room temperature and maintained at room temperature for 1 h until the solution turned dark red. The volatiles were removed *in vacuo* and the residue was triturated with pentane and filtered through a plug of celite. Evaporation of solvent from the filtrate under reduced pressure gave 1,1-bis(cyclopentadienyl)-3-benzyl-2-phenyltitanacyclobutene **34** (71.0 mg, 99%) as a dark-red solid. An analytical sample was recrystallized from pentane at -35 °C. Spectroscopic data for complex **34**: ^{1}H NMR (360 MHz, C_6D_6) δ 7.30–7.04 (m, 10H, 2ArH, obscured by C_6D_6), 5.54 (s, 10 H, C$_5$H$_5$), 3.25 (s, 2H, PhCH$_2$), 3.13 (s, 2H, TiCH$_2$); ^{13}C {^{1}H} NMR (75 MHz, C_6D_6) δ 209.9, 148.2, 140.9, 129.5, 128.6, 128.4, 126.0,

125.3, 124.5, 111.5, 96.3, 75.5, 37.1; HRMS calcd. *m/z* for $C_{26}H_{24}Ti$ 384.13574, found 384.13490.

Bis(cyclopentadienyl) (η^3-3-phenylpropargyl)titanium 35.
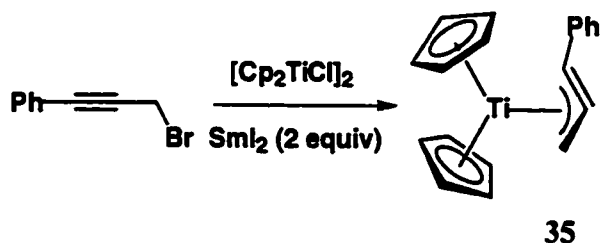
In the drybox, to a solution of $[Cp_2TiCl]_2$ (27.8 mg, 0.00653 mmol) and SmI_2 (0.1 M in THF, 2.7 mL, 0.27 mmol) in THF (2 mL) was added a solution of 3-phenyl-propargyl bromide (25.4 mg, 0.131 mmol) in THF (1 mL) at -35 °C. The reaction mixture was warmed to room temperature and maintained at room temperature for 1 h until the solution turned dark green. The volatiles were removed *in vacuo* and the residue was triturated with pentane and filtered through a plug of celite. Evaporation of solvent from the filtrate under reduced pressure gave bis(cyclopentadienyl)(η^3-3-phenyl-propargyl)titanium 35 (33.3 mg, 87%) as a dark green oil. An analytical sample was crystallized from ether at -35 °C, which was a dark green solid at room temperature. Spectroscopic data for complex 35: IR (pentane,cast) 3073 (w), 2916 (w), 1923 (w), 1592 (m), 1568 (m), 1487 (m), 1440 (m), 1015 (s), 760 (s) cm^{-1}; HRMS calcd. *m/z* for $C_{19}H_{17}Ti$ 293.08096, found 293.08105.

D. Functionalization of Metallacycloutene Complexes

1. Isocyanide Insertion Reactions of Titanacyclobutene complexes.

1,1-Bis(pentamethylcyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-isopropyl-5-methyltitanacyclopentene 43.

42   43
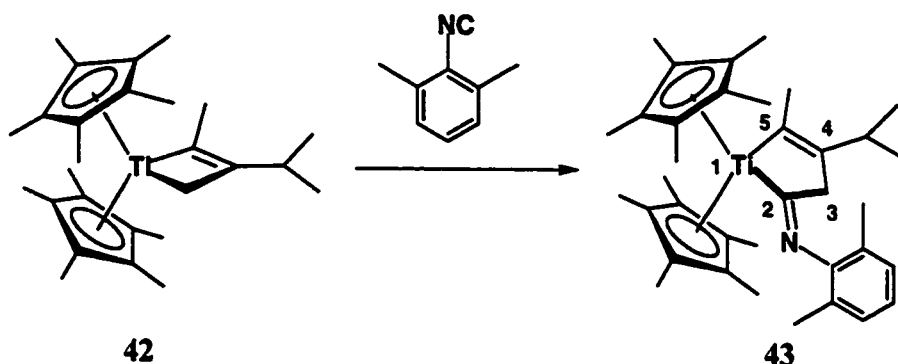
In the drybox, a solution of 1,1-bis(pentamethylcyclopentadienyl)-3-isopropyl-2-methyltitanacyclobutene **42** (92.4 mg, 0.223 mmol) in dry THF (2 mL) at -35 °C was treated with a solution of 2,6-dimethylphenyl isocyanide (29.2 mg, 0.223 mmol) in THF at -35 °C. The resulting solution was warmed slowly to room temperature and stirred for 3 h. The solvent was removed *in vacuo* and the residue was extracted with hexane. The combined extracts were filtered through a short column of celite followed by concentration and recrystallization from hexane at -35 °C to give dark brown crystals (103.0 mg, 85%). Spectroscopic data for complex **43**: IR (pentane, cast) 1537 cm^{-1}; ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 7.07 (d, 2H, J = 7.4 Hz), 6.89 (t, 1H, J = 7.4 Hz), 2.62 (q, 2H, J = 1.9 Hz), 2.52 (sept, 1H, J = 6.9 Hz), 2.44 (s, 6H), 1.80 (s, 30H), 0.93 (t, 3H, J = 1.9 Hz), 0.88 (d, 6H, J = 6.9 Hz); ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$, APT) δ 244.8 (p), 195.4 (p), 152.0 (p), 133.0 (p), 129.2 (a), 126.3 (p), 123.1 (p), 121.8 (a), 41.0 (p), 29.3 (a), 21.8 (a), 21.3 (a), 19.7 (a), 12.9 (a); HRMS calcd. *m/z* for C$_{35}$H$_{51}$NTi 545.35010, found 545.34895. Selected X-ray crystallographic data for compex **43** are listed at the end of experimental section (p.69) .

1,1-Bis(pentamethylcyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-(methyl-trimethylsilyl)-5-methyltitanacyclopentene 44.
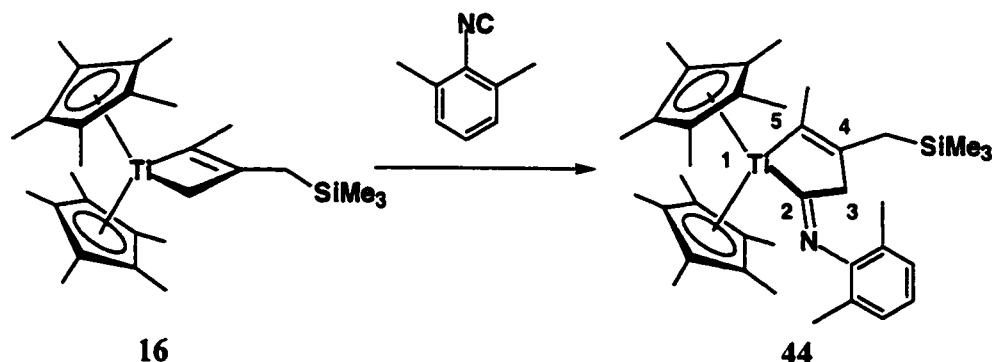
16   44

In the drybox, a solution of 1,1-bis(pentamethylcyclopentadienyl)-3-(trimethyl-silylmethyl)-2-methyltitanacyclobutene **16** (29.6 mg, 0.0646 mmol) in dry THF (1 mL) at -35 °C was treated with a solution of 2,6-dimethylphenyl isocyanide (8.5 mg, 0.065 mmol) in THF at -35 °C. The resulting solution was warmed to room temperature and stirred for 2 h. The solvent was removed *in vacuo* and the residue was extracted with hexane. The combined extracts were filtered through a short column of celite followed by concentration to give dark brown solid (33.5 mg, 88%). An analytical sample was prepared by recrystallization from pentane at -35 °C. Spectroscopic data for complex **44**: IR (pentane, cast) 1529 cm^{-1}; ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 7.06 (d, 2H, J = 7.4 Hz), 6.89 (t, 1H, J = 7.4 Hz), 2.55 (q, 2H, J = 1.8 Hz), 2.47 (s, 6H), 1.82 (s, 30H), 1.30 (s, 2H), 0.97 (t, 3H, J = 1.8 Hz), 0.06 (s, 9H); ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$, APT) δ 246.4 (p), 193.5 (p), 152.5 (p), 129.2 (a), 126.4 (p), 125.0 (p), 123.2 (p), 121.8 (a), 53.8 (p), 49.9 (p), 22.0 (a), 21.8 (a), 13.0 (a), 0.4 (a); HRMS (ESI) calcd. *m/z* for C$_{37}$H$_{55}$NTiSi 589.35832, found 589.35832

55

1,1-Bis(*tert*-butylcyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-benzyl-5-methyltitanacyclopentene 46.

In the drybox, a solution of 1,1-bis(*tert*-butylcyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene **45** (60.0 mg, 0.138 mmol) in dry THF (1 mL) at -35 °C was treated with a solution of 2,6-dimethylphenyl isocyanide (18.1 mg, 0.138 mmol) in THF at -35 °C. The resulting solution was warmed to room temperature and stirred for 1 h. The solvent was removed *in vacuo* and the residue was extracted with hexane. The combined extracts were filtered through a short column of celite followed by concentration to give a dark brown solid (68.0 mg, 87%), which was not further purified. Spectroscopic data for complex **46**: IR (pentane, cast) 1562 cm^{-1}; ^{1}H NMR (360 MHz, C_6D_6) δ 7.19–7.16 (m, 1H), 7.06 (m, 3H), 6.96 (m, 2H), 6.82 (m, 1H), 6.67 (m, 2H), 6.61 (m, 2H), 6.42 (m, 2H), 6.24 (m, 2H), 2.96 (s, 2H), 2.62 (q, 2H, J = 1.8 Hz), 2.20 (s, 6H), 1.14 (t, 3H, J = 1.8 Hz), 1.03 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz C_6D_6, APT) δ 235.6 (p), 189.2 (p), 152.7 (p), 141.7 (p), 141.3 (p), 128.6 (a), 128.5 (a), 128.4 (a), 128.3 (a), 125.7 (a), 125.1 (p), 124.3 (p), 121.7 (a), 121.3 (a), 113.0 (a), 112.2 (a), 111.9 (a), 47.9 (p), 38.1 (p), 33.2 (p), 31.9 (a), 20.6 (a), 19.1 (a); HRMS calcd. *m/z* for $C_{36}H_{50}NTi$ 544.34229, found 544.34375.

1,1-Bis(*tert*-butylcyclopentadienyl)-2-(*tert*-butylimino)-4-benzyl-5-methyltitanacy-clopentene 47.
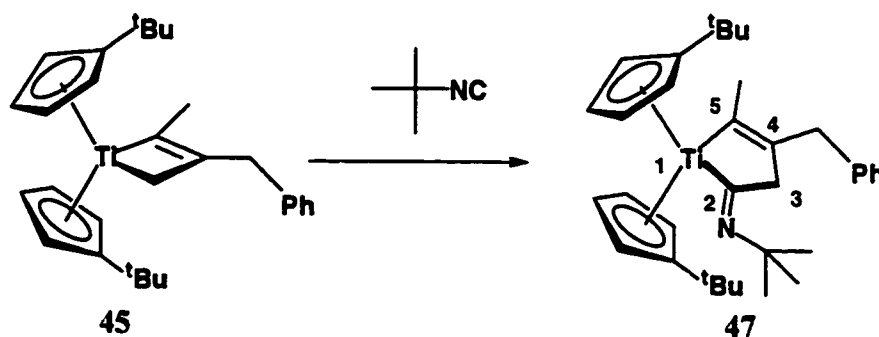
In the drybox, a solution of 1,1-bis(*tert*-butylcyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene **45** (43.4 mg, 0.100 mmol) in dry THF (1 mL) at -35 °C was treated with a solution of tert-butyl isocyanide (8.3 mg, 0.10 mmol) in THF at -35 °C. The resulting solution was warmed to room temperature and stirred for 2 h. The solvent was removed *in vacuo* and the residue was extracted with hexane. The combined extracts were filtered through a short column of celite followed by concentration to give a dark green solid (43.6 mg, 84%), which was not further purified. Spectroscopic data for complex **47**: IR (pentane, cast) 1754 cm^{-1}; ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 7.37 (m, 2H), 7.28 (m, 2H), 7.09 (m, 1H), 5.80 (m, 2H), 5.58 (m, 2H), 5.17 (m, 2H), 5.06 (m, 2H), 3.63 (s, 2H), 3.56 (q, 2H, J = 1.8 Hz), 2.20 (t, 3H, J = 1.8 Hz), 1.13 (s, 18H), 0.95 (s, 9H); ^{13}C {^{1}H} NMR (75 MHzC$_6$D$_6$, APT) δ 227.5 (p), 186.7 (p), 142.6 (p), 137.8 (p), 134.3 (p), 128.9 (a), 128.7 (a), 125.7 (a), 106.2 (a), 106.0 (a), 103.9 (a), 103.3 (a), 59.5 (p), 51.3 (p), 37.1 (p), 33.0 (p), 31.6 (a), 29.6 (a), 27.7 (a); HRMS calcd. *m/z* for C$_{34}$H$_{47}$NTi 517.31879, found 517.31870.

57

1,1-Bis(cyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-benzyl-5-methyltitana-cyclopentene 50.

In the drybox, a solution of 1,1-bis(cyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene **48** (37.7 mg, 0.117 mmol) in dry THF (1 mL) at -35 °C was treated with a solution of 2,6-dimethylphenyl isocyanide (15.3 mg, 0.117 mmol) in THF at -35 °C. The resulting solution was warmed to room temperature and stirred for 1 h. The solvent was removed *in vacuo* and the residue was extracted with hexane. The combined extracts were filtered through a short column of celite followed by concentration to give a dark brown solid (44.3 mg, 84%), which was not further purified. Spectroscopic data for complex **50**: IR (ether, cast) 1577 cm^{-1}; ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 7.18 (m, 2H, obscured by C$_6$D$_6$), 7.03 (m, 3H), 6.89 (m, 2H), 6.82 (m, 1H), 6.09 (s, 10H), 2.93 (s, 2H), 2.54 (q, 2H, J = 1.8 Hz), 2.14 (s, 6H), 0.88 (t, 3H, J = 1.8 Hz); ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$, APT) δ 234.4 (p), 188.5 (p), 152.4 (p), 141.5 (p), 128.4 (a), 128.3 (a), 128.2 (a), 125.8 (p), 125.2 (p), 124.9 (p), 121.8 (a), 115.0 (a), 47.7 (p), 37.8 (p), 18.9 (a), 18.8 (a); HRMS calcd. *m/z* for C$_{36}$H$_{50}$NTi 544.34229, found 544.34375.

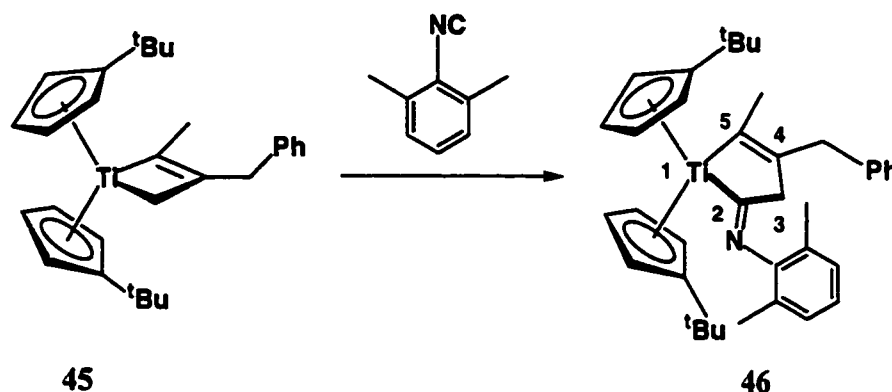**1,1-Bis(cyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-isopropyl-5-methyl-titanacyclopentene 51.**
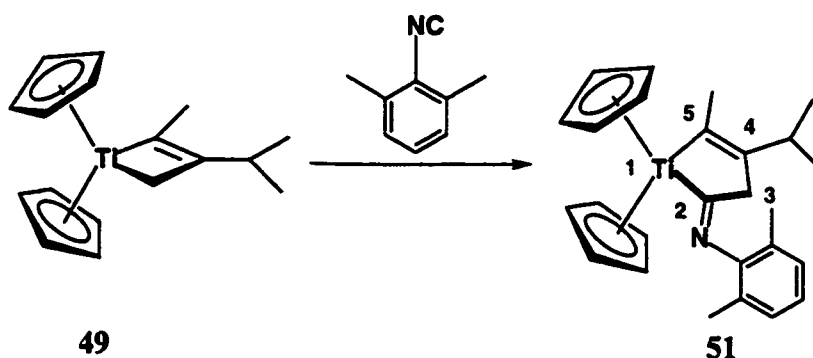
In the drybox, a solution of 1,1-bis(cyclopentadienyl)-3-isopropyl-2-methyltitanacyclobutene **49** (55.2 mg, 0.201 mmol) in dry THF (1 mL) was treated with a solution of 2,6-dimethylphenyl isocyanide (26.4 mg, 0.201 mmol) in THF at room temperature. The resulting solution was stirred for 1 h. The solvent was removed *in vacuo* and the residue was extracted with hexane. The combined extracts were filtered through a short column of celite followed by concentration to give a dark brown solid (66.0 mg, 81%), which was not further purified. Spectroscopic data for complex **51**: IR (pentane, cast) 1565 cm^{-1}; ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 7.01 (d, 2H, J = 7.5 Hz), 6.89 (t, 1H, J=7.5Hz), 6.09 (s, 10H), 2.60 (q, 2H, J = 1.8 Hz), 2.37 (sept, 1H, J = 6.8 Hz), 2.26 (s, 6H), 0.75 (t, 3H, J = 1.8 Hz), 0.72 (d, 6H, J = 6.8 Hz); ^{13}C {^{1}H} NMR (75 MHz, C$_6$D$_6$) δ 234.2, 185.3, 152.5, 132.2, 128.5, 124.9, 121.8, 114.9, 42.3, 28.8, 20.4, 19.1, 16.9; HRMS calcd.*m/z* for C$_{26}$H$_{31}$NTi 405.19360, found 405.19259.

1,1-Bis(butylcyclopentadienyl)-2-(*tert*-butylimino)-4-benzyl-5-methyltitanacyclo-pentene 52.
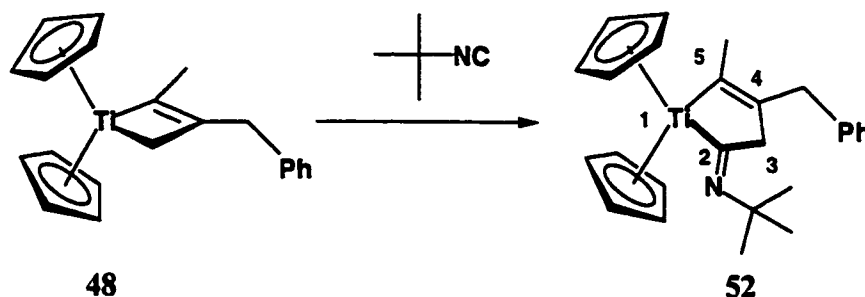
48   52
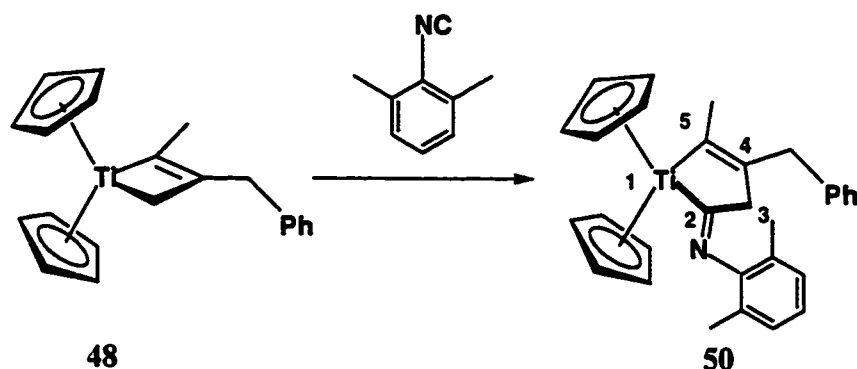
In the drybox, a solution of 1,1-bis(cyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene **48** (43.1 mg, 0.134 mmol) in dry THF (1 mL) was treated with a solution of excess tert-butyl isocyanide (33.4 mg, 0.402 mmol) in THF at room temperature. The resulting solution was stirred for 1 h. The solvent was removed *in vacuo* and the residue was extracted with hexane. The combined extracts were filtered through a short column of celite followed by concentration to give a dark green solid (46.0 mg, 85%), which was not further purified. Spectroscopic data for complex **52**: IR (ether, cast) 1763 cm^{-1}; ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 7.36 (d, 2H, J = 7.5 Hz), 7.26 (t, 2H, J = 7.5 Hz), 7.09 (t, 1H, J = 7.5 Hz), 5.24 (s, 10H), 3.73 (s, 2H), 3.58 (q, 2H, J = 1.9 Hz), 2.22 (t, 3H, J = 1.9 Hz), 0.82 (s, 9H); ^{13}C {^{1}H} NMR (75 MHz, THF-d$_8$, APT) δ 224.6 (a), 183.5 (a), 142.6 (a), 138.2 (a), 128.3 (p), 128.2 (p), 125.1 (p), 104.9 (p), 50.1 (a), 35.9 (a), 29.0 (p); HRMS calcd. *m/z* for C$_{26}$H$_{31}$NTi 405.19360, found 405.19326.

2. Carbonylation of Titanacyclobutene complexes.

1,1-Bis(pentamethylcyclopentadienyl)-3-(2-butynyl)-2-methyltitanacyclopent-2-en-5-one 54.
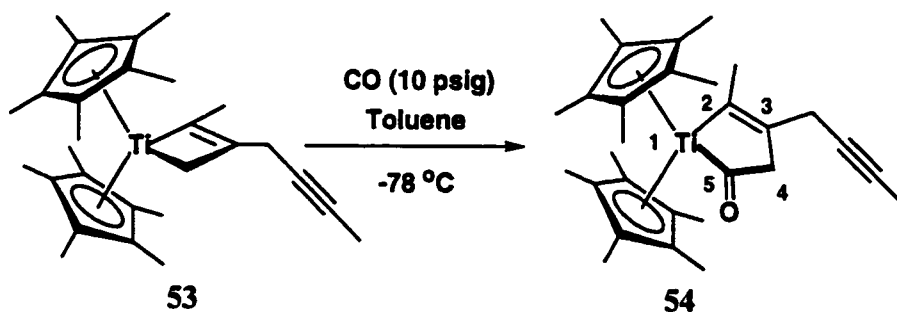
In the drybox, a solution of 1,1-bis(pentamethylcyclopentadienyl)-3-(2-butynyl)-2-methyl titanacyclobutene **53** (28.0 mg, 0.0660 mmol) in toluene-d_8 (0.6 mL) was transferred into a Fischer-Porter bottle fitted with a stirbar. The bottle was removed from the drybox and cooled to -78 °C, then flushed the N_2 out of the bottle and pressurized with carbon monoxide (10 psig). The solution was carefully warmed from -78 °C with stirring. When the temperature reached approximately between -22 °C and -15 °C, a color change from red to green was observed. The solution was immediately cooled down to -78 °C and rapidly transferred into a precooled NMR tube via cannula for collecting data. Later, the solvent was rapidly removed *in vacuo* to give a dark green solid (25.0 mg, 84%). A suitable sample for X-ray crystallography was prepared from toluene/pentane at -35 °C. Spectroscopic data for complex **54**: IR (ether, cast) 1614 m^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 2.81 (q, 2H, J = 2.7 Hz), 2.61 (q, 2H, J = 2.1 Hz), 1.64 (t, 3H, J = 2.7 Hz), 1.66 (s, 30H), 0.92 (t, 3H, J = 2.1 Hz); ^{13}C{^{1}H} NMR (75 MHz, toluene-d_8, -30 °C) δ 302.5, 195.9, 122.2, 120.5, 78.6, 74.7, 56.1, 22.0, 18.8, 12.0, 3.5; HRMS (ESI) calcd. *m/z* for $C_{29}H_{40}TiO$ 452.25586, found 452.25576. Selected X-ray crystallographic data for compex **54** are listed at the end of experimental section (p.76) .

1,1-Bis(pentamethylcyclopentadienyl)-3-isopropyl-2-methyltitanacyclopent-2-en-5-one 55.
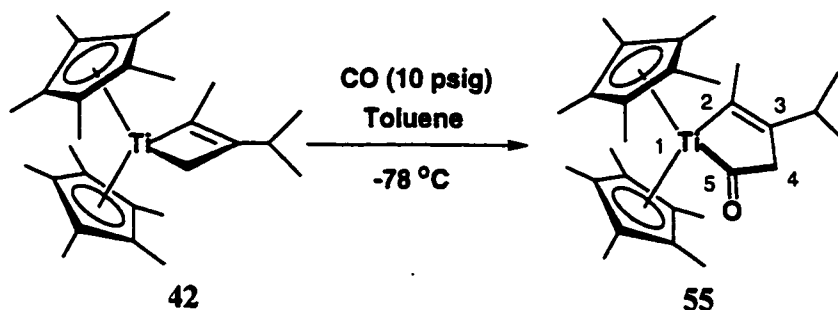
In the drybox, a solution of 1,1-bis(pentamethylcyclopentadienyl)-3-isopropyl-2-methyl titanacyclobutene **42** (27.4 mg, 0.0661 mmol) in toluene-d_8 (0.6 mL) was transferred into Fischer-Porter bottle fitted with a stirbar. The bottle was removed from the drybox and cooled to -78 °C, then flushed the N_2 out of the bottle and pressurized with carbon monoxide (10 psig). The solution was carefully warmed from -78 °C with stirring. When the temperature reached approximately betwwen -78 °C and -70 °C, a color change from red to green was observed. The solution was immediately cooled down to -78 °C and rapidly transferred into a precooled NMR tube via cannula for collecting data. Later, the solvent was rapidly removed *in vacuo* to give a dark green solid (28.9 mg, 99%). Spectroscopic data for complex **55**: IR (ether, cast) 1611 cm^{-1}; ^{1}H NMR (360 MHz, toluene-d_8) δ 2.55 (sept, 1H, J = 6.7 Hz), 2.36 (q, 2H, J = 1.9 Hz), 1.68 (s, 30H), 1.00 (q, 6H, J = 6.7 Hz), 0.79 (t, 3H, J = 1.9 Hz); ^{13}C{^{1}H} NMR (100 MHz, toluene-d_8, -25 °C) δ 302.1, 194.4, 131.9, 122.0, 51.6, 29.1, 21.5, 17.4, 12.0; HRMS (ESI) calcd. *m/z* for $C_{28}H_{42}TiO$ 442.27151, found 442.27172.

1,1-Bis(*tert*-butylcyclopentadienyl)-3-benzyl-2-methyltitanacyclopent-2-en-5-one 57.
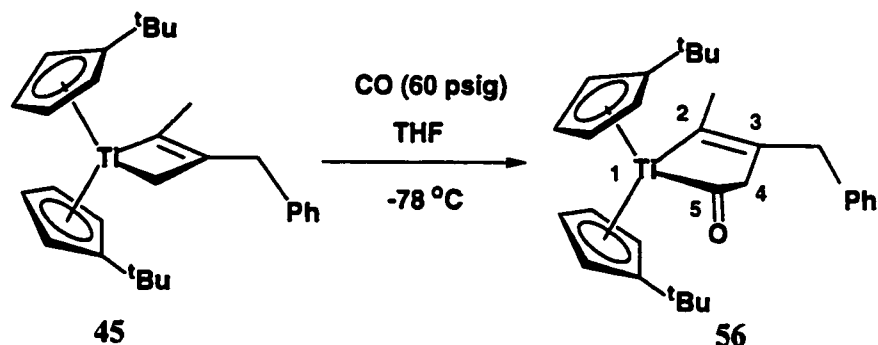
In the drybox, a solution of 1,1-bis(*tert*-butylcyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene **45** (32.0 mg, 0.0737 mmol) in THF-d$_8$ (0.6 mL) was transferred into Fischer-Porter bottle fitted with a stirbar. The bottle was removed from the drybox and cooled to -78 °C, then flushed the N$_2$ out of the bottle and pressurized with carbon monoxide (60 psig). The solution was carefully warmed from -78 °C with stirring. When the temperature reached approximately betwwen 0 °C and 10 °C, a color change from red to green was observed. The solution was immediately cooled down to -78 °C and rapidly transferred into a precooled NMR tube via cannula for collecting data. Later, the solvent was rapidly removed *in vacuo* to give a dark green solid (31.5 mg, 92%). Spectroscopic data for complex **56**: IR (ether, cast) 1625 cm^{-1}; ^{1}H NMR (400 MHz, THF-d$_8$, -25 °C) δ 7.26 (m, 2H), 7.15 (m, 3H), 6.58 (m, 2H), 6.30 (m, 2H), 6.25 (m, 4H), 3.08 (s, 2H), 2.31 (q, 2H, *J* = 2.0 Hz), 1.11 (t, 3H, *J* = 2.0 Hz), 1.06 (s, 18H);^{13}C{^{1}H} NMR (100 MHz, THF-d$_8$, -25 °C) δ 293.3, 188.0, 142.6, 142.3, 129.2, 129.0, 126.1, 124.7, 120.8, 113.1, 112.3, 111.5, 59.0, 38.6, 33.8, 31.4, 19.1; HRMS (ESI) calcd. *m/z* for C$_{30}$H$_{38}$TiO 462.24021, found 462.24045.

3. Demetallization of Titanacyclobutene complexes.

3-Benzyl-1,2-diphenylphosphacyclobutene 58.

I. Synthesis of compound 57 from 1,1-bis(cyclopentadienyl)-3-benzyl-2-phenyl-titanacyclobutene 34.
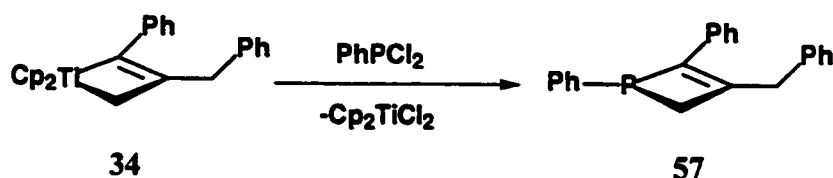
Under N_2, to a solution of 1,1-bis(cyclopentadienyl)-3-benzyl-2-phenyltitanacyclobutene **34** (154.8 mg, 0.4030 mmol) in benzene (4.5 mL) was added dichlorophenylphosphine (72.2 mg, 0.403 mmol) via syringe at room temperature. A color change from red to brick red and precipitation of a red solid (Cp_2TiCl_2) were observed. The reaction mixture was stirred for 3 h, then filtered through a plug of celite. The red solution was evaporated *in vacuo* and the residue was suspended in a minimum of ether and passed through a short column of basic alumina (Brockman Activity I, 150 mesh), eluting with ether. Organometallic byproducts were left at the top of the column. Evaporation of solvent under reduced pressure followed by recrystallization from pentane at -35 °C gave 3-benzyl-1,2-diphenylphosphacyclobutene **57** (76.7 mg, 60%) as a white solid. Spectroscopic data for complex **57**: ^1H NMR (400 MHz, C_6D_6) δ 7.68 (m, 2H, ArH), 7.54 (m, 2H, ArH), 7.16 (m, 11H, ArH, obscured by C_6D_6), 3.68 (d, 1H, $^2J_{HH} = 15.4$ Hz), 3.52 (d, 1H, $^2J_{HH} = 15.4$ Hz), 2.46 (dd, 1H, $^2J_{HH} = 14.8$ Hz, $^2J_{PH} = 9.8$ Hz), 1.98 (dd, 1H, $^2J_{HH} = 14.8$ Hz, $^2J_{PH} = 9.8$ Hz); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, APT) δ 146.5 (d, $J_{CP} = 6.3$ Hz, p), 143.6 (s, p), 139.2 (d, $J_{CP} = 33.9$ Hz), 137.9 (s, p), 135.8 (d, $J_{CP} = 10.2$ Hz), 132.9 (d, $J_{CP} = 18.8$ Hz), 129.2 (s, a), 128.9 (s, a), 128.7-127.1 (m, obscured by C_6D_6, a), 126.3 (s, a), 39.7 (d, $^3J_{CP} = 2.5$ Hz), 28.6 (d, $^1J_{CP} = 7.4$ Hz); $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6) δ -12.8; HRMS (ESI) calcd. *m/z* for $C_{22}H_{19}P$

314.12244, found 314.12243.

II. Synthesis of compound 57 from 1,1-bis(*tert*-butylcyclopentadienyl)-3-benzyl-2-phenyltitanacyclobutene 33.

$$\text{33} \xrightarrow[\text{-}^tBuCp_2TiCl_2]{\text{PhPCl}_2} \text{57}$$

Under N_2, to a solution of 1,1-bis(*tert*-butylcyclopentadienyl)-3-benzyl-2-phenyltitanacyclobutene 33 (201.5 mg, 0.4060 mmol) in hexane (8 mL) was added dichlorophenylphosphine (72.7 mg, 0.406 mmol) via syringe at room temperature. A color change from red to brick red and precipitation of a red solid ($^tBuCp_2TiCl_2$) were observed. The reaction mixture was stirred for 1 h, then filtered through a plug of celite. The red solution was evaporated *in vacuo* and the residue was suspended in a minimum of ether and passed through a short column of basic alumina (Brockman Activity I, 150 mesh), eluting with ether. Organometallic byproducts were left at the top of the column. Evaporation of solvent under reduced pressure followed by recrystallization from pentane at -35 °C gave a product identical to 58 (51.2 mg, 40%).

4-Benzyl-1,2-diphenyl-3-methyl-1,2-diphosphacyclopent-3-ene 58.

I. Synthesis of compound 58 from 1,1-bis(cyclopentadienyl)-3-benzyl-2-methyl-titanacyclobutene 48.

$$\text{48} \xrightarrow[\text{-}Cp_2TiCl_2]{\text{2PhPCl}_2} \text{58}$$

Under N_2, to a solution of 1,1-bis(cyclopentadienyl)-3-benzyl-2-

methyltitanacyclobutene **48** (40.8 mg, 0.127 mmol) in benzene (2 mL) was added dichlorophenylphosphine (22.7 mg, 0.262 mmol) via syringe at room temperature. A color change from red to brick red and precipitation of a red solid (Cp_2TiCl_2) were observed. The reaction mixture was stirred for 2 h, then filtered through a plug of celite. The red solution was evaporated *in vacuo* and the residue was suspended in a minimum of ether and passed through a short column of basic alumina (Brockman Activity I, 150 mesh), eluting with ether. Organometallic byproducts were left at the top of the column. Evaporation of solvent under reduced pressure followed by recrystallization from pentane at -35 °C gave 3-benzyl-1,2-diphenyl-3-methyl-1,2-diphosphacyclopent-3-ene **58** (15.2 mg, 33%) as a off-white solid. The same result was obtained when one equivalent of dichlorophenylphosphine was used. Spectroscopic data for complex **59**: ^1H NMR (400 MHz, C_6D_6) δ 7.63 (m, 2H, ArH), 7.48 (m, 2H, ArH), 7.27–7.05 (m, 11H, ArH, obscured by C_6D_6), 3.51 (d, 1H, $^2J_{HH} = 14.1$ Hz), 3.25 (d, 1H, $^2J_{HH} = 14.1$ Hz), 3.17 ("t", 1H, $^2J_{HH}$~$^2J_{PH}$~18 Hz, $^3J_{PH}$~0 Hz), 2.89 ("d", 1H, $^2J_{HH}$~18 Hz, $^5J_{HH} = 2.0$ Hz, $^2J_{PH}$~$^3J_{PH}$~2 Hz), 1.92 (dt, 3H, $^5J_{HH} = 2.0$ Hz, $J_{PH} = 10.9$ Hz); ^{13}C {^1H} NMR (100.6 MHz, C_6D_6, APT) δ 147.5 (d, $J_{CP} = 5.6$ Hz, p), 139.5 (s, p), 139.4 (m, p), 137.1 (m, p), 133.3-132.0 (m, a), 130.9 (m, p), 128.9-128.1 (m, a), 126.3 (s, a), 40.4 (d, $J_{CP} = 25$ Hz, p), 38.5 (d, $J_{CP} = 2.6$ Hz, p), 16.6 (d, $J_{CP} = 29.6$ Hz, a); ^{31}P {^1H} NMR (161.9 MHz, C_6D_6) δ 25.9 (d, $J_{PP} = 220$ Hz), 30.4 (d, $J_{PP} = 220$ Hz); HRMS calcd. m/z for $C_{23}H_{22}P_2$ 360.11969, found 360.12019.

II. Synthesis of compound 58 from 1,1-(*tert*-butylcyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene 45.
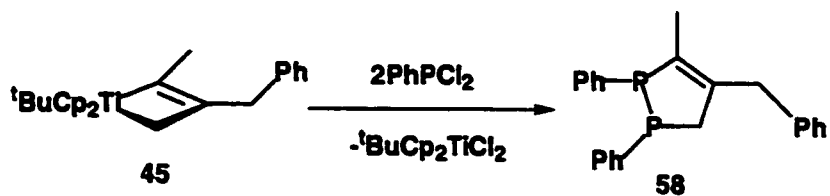
Under N$_2$, to a solution of 1,1-bis(cyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene **45** (56.8 mg, 0.131 mmol) in benzene (2 mL) was added dichlorophenylphosphine (46.9 mg, 0.262 mmol) via syringe at room temperature. A color change from red to brick red and precipitation of a red solid (^{t}BuCp$_2$TiCl$_2$) were observed. The reaction mixture was stirred for 2 h, then filtered through a plug of celite. The red solution was evaporated *in vacuo* and the residue was suspended in a minimum of ether and passed through a short column of basic alumina (Brockman Activity I, 150 mesh), eluting with ether. Organometallic byproducts were left at the top of the column. Evaporation of solvent under reduced pressure followed by recrystallization from pentane at -35 °C gave a off-white solid identical to **58** (13.1 mg, 28%).

3-Benzyl-2-(4-methoxyphenyl)-1-phenylborocyclobutene 59.
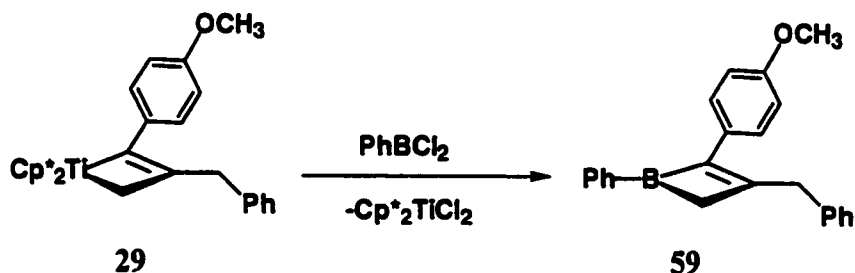
Under N$_2$, to a solution of 1,1-bis(pentamethylcyclopentadienyl)-3-benzyl-2-(4-methoxyphenyl)titanacyclobutene **29** (141.2 mg, 0.2550 mmol) in toluene (5 mL) was added dichlorophenylboron (40.4 mg, 0.255 mmol) via syringe at -35 °C. A color change from red to brick red and precipitation of a red solid (Cp*$_2$TiCl$_2$) were observed. The reaction mixture was stirred for 3 days, then the red solution was decanted. The red solution was evaporated *in vacuo* and the residue was extracted with hexane followed by concentration and recrystallization from hexane at -35 °C to give both red and white crystals. Further purifications were unsuccessful. The red residue was determined to be CpTiCl by comparision to an authentic compound. Spectroscopic data for compound **60**: ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 8.03–6.85 (m, 14H, ArH, obscured by C$_6$D$_6$), 3.47 (s,

2H, PhCH$_2$), 3.34 (s, 3H, OCH$_3$), 2.24 (s, 2H, BCH$_2$); HRMs calcd. *m/z* for C$_{23}$H$_{21}$BO 324.16855, found 324.16867.

SELECTED CRYSTALLOGRAPHIC DATA FOR COMPLEXES 43 AND 54

Selected X-Ray Crystallographic data for 1,1-Bis(pentamethylcyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-isopropyl-5-methyltitanacyclopentene 43.

Additional information (including structure factors, etc.) can be obtain directly from Dr. Robert McDonald at the University of Alberta Molecular Structure Center, Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2 Canada. Request report # *jms9903*.

Table 4.1. Crystallographic Experimental Details of Complex **43**

A. Crystal Data

formula	$C_{36}H_{51}NTi$
formula weight	545.68
crystal dimensions (mm)	$0.41 \times 0.20 \times 0.20$
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters^a	
a (Å)	15.1007 (9)
b (Å)	11.2716 (6)
c (Å)	19.0911 (11)
β (deg)	107.7050 (10)
V (Å^3)	3095.6 (3)
Z	4
ρ_{calcd} (g cm^{-3})	1.171
μ (mm^{-1})	0.300

B. Data Collection and Refinement Conditions

diffractometer	Bruker P4/RA/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ϕ rotations (0.3) / ω scans (0.3) (20 s exposures)
data collection 2θ limit (deg)	51.50
total data collected	16317 (-18 h 17, -13 k 13, -23 l 23)
independent reflections	5885
number of observations (*NO*)	4130 [F_o^2 2$\sigma(F_o^2)$]
structure solution method	Patterson interpretation (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d])
absorption correction method	*SADABS*
range of transmission factors	0.9562–0.7450
data/restraints/parameters	5885 [F_o^2 –3$\sigma(F_o^2)$] / 0 / 356
goodness-of-fit (*S*)[e]	0.983 [F_o^2 –3$\sigma(F_o^2)$]
final *R* indices[f]	
R_1 [F_o^2 2$\sigma(F_o^2)$]	0.0434
wR_2 [F_o^2 –3$\sigma(F_o^2)$]	0.1181
largest difference peak and hole	0.301 and –0.324 e Å^{-3}

[a]Obtained from least-squares refinement of 5044 centered reflections.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

Table 4.1. Crystallographic Experimental Details of Complex **43** (continued)

[d]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having F_o^2 -$3\sigma(F_o^2)$). Weighted R-factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional R-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. R-factors based on F_o^2 are statistically about twice as large as those based on F_o, and R-factors based on ALL data will be even larger.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0634P)^2]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Figure 2. ORTEP for Complex **43** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS 9903.

Table 4.2. Selected Interatomic Distances (Å) of Complex **43**

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ti	C1	2.165(2)	C13	C14	1.369(3)
Ti	C4	2.214(2)	C14	C15	1.375(3)
Ti	C20	2.442(2)	C15	C16	1.391(3)
Ti	C21	2.424(2)	C16	C18	1.499(3)
Ti	C22	2.420(2)	C20	C21	1.409(3)
Ti	C23	2.465(2)	C20	C24	1.418(3)
Ti	C24	2.435(2)	C20	C25	1.502(3)
Ti	C30	2.467(2)	C21	C22	1.420(3)
Ti	C31	2.474(2)	C21	C26	1.507(3)
Ti	C32	2.461(2)	C22	C23	1.411(3)
Ti	C33	2.460(2)	C22	C27	1.499(3)
Ti	C34	2.428(2)	C23	C24	1.420(3)
N	C4	1.283(3)	C23	C28	1.509(3)
N	C11	1.438(2)	C24	C29	1.513(3)
C1	C2	1.342(3)	C30	C31	1.416(3)
C1	C5	1.513(3)	C30	C34	1.424(3)
C2	C3	1.497(3)	C30	C35	1.496(3)
C2	C6	1.541(3)	C31	C32	1.430(3)
C3	C4	1.523(3)	C31	C36	1.493(3)
C6	C7	1.520(4)	C32	C33	1.407(3)
C6	C8	1.510(4)	C32	C37	1.501(3)
C11	C12	1.409(3)	C33	C34	1.410(3)
C11	C16	1.406(3)	C33	C38	1.513(3)
C12	C13	1.397(3)	C34	C39	1.498(3)
C12	C17	1.506(3)			

Table 4.3. Selected Interatomic Angles (deg) of Complex **43**

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	Ti	C4	78.85(8)	C22	Ti	C30	121.19(8)
C1	Ti	C20	75.11(8)	C22	Ti	C31	153.38(8)
C1	Ti	C21	91.97(8)	C22	Ti	C32	139.25(8)
C1	Ti	C22	125.86(8)	C22	Ti	C33	107.44(8)
C1	Ti	C23	128.56(8)	C22	Ti	C34	98.10(8)
C1	Ti	C24	96.09(8)	C23	Ti	C24	33.68(8)
C1	Ti	C30	107.77(8)	C23	Ti	C30	121.48(7)
C1	Ti	C31	80.03(8)	C23	Ti	C31	137.25(7)
C1	Ti	C32	86.77(8)	C23	Ti	C32	108.49(8)
C1	Ti	C33	119.17(8)	C23	Ti	C33	81.63(8)
C1	Ti	C34	136.00(8)	C23	Ti	C34	88.37(7)
C4	Ti	C20	102.29(7)	C24	Ti	C30	144.39(7)
C4	Ti	C21	77.30(7)	C24	Ti	C31	134.86(7)
C4	Ti	C22	89.01(7)	C24	Ti	C32	101.57(8)
C4	Ti	C23	122.52(8)	C24	Ti	C33	90.10(7)
C4	Ti	C24	133.11(7)	C24	Ti	C34	112.00(7)
C4	Ti	C30	78.52(7)	C30	Ti	C31	33.31(7)
C4	Ti	C31	90.64(7)	C30	Ti	C32	55.30(7)
C4	Ti	C32	124.29(8)	C30	Ti	C33	55.37(7)
C4	Ti	C33	133.30(8)	C30	Ti	C34	33.82(7)
C4	Ti	C34	102.45(7)	C31	Ti	C32	33.68(7)
C20	Ti	C21	33.65(8)	C31	Ti	C33	55.63(8)
C20	Ti	C22	56.19(8)	C31	Ti	C34	56.07(8)
C20	Ti	C23	55.73(7)	C32	Ti	C33	33.24(8)
C20	Ti	C24	33.80(7)	C32	Ti	C34	55.70(8)
C20	Ti	C30	177.11(7)	C33	Ti	C34	33.53(7)
C20	Ti	C31	148.99(8)	C4	N	C11	123.82(17)
C20	Ti	C32	125.46(8)	Ti	C1	C2	115.50(16)
C20	Ti	C33	123.40(7)	Ti	C1	C5	123.45(16)
C20	Ti	C34	143.61(7)	C2	C1	C5	121.0(2)
C21	Ti	C22	34.08(7)	C1	C2	C3	120.27(19)
C21	Ti	C23	55.84(7)	C1	C2	C6	124.8(2)
C21	Ti	C24	56.15(7)	C3	C2	C6	114.89(18)
C21	Ti	C30	144.96(7)	C2	C3	C4	112.64(17)
C21	Ti	C31	166.69(7)	Ti	C4	N	127.51(15)
C21	Ti	C32	157.46(7)	Ti	C4	C3	110.73(14)
C21	Ti	C33	137.44(8)	N	C4	C3	121.74(18)
C21	Ti	C34	131.64(8)	C2	C6	C7	112.7(2)
C22	Ti	C23	33.56(7)	C2	C6	C8	111.9(2)
C22	Ti	C24	56.26(8)	C7	C6	C8	108.5(2)

Table 4.3. Selected Interatomic Angles (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
N	C11	C12	122.77(18)	Ti	C24	C20	73.34(12)
N	C11	C16	117.60(18)	Ti	C24	C23	74.29(12)
C12	C11	C16	119.24(18)	Ti	C24	C29	126.21(16)
C11	C12	C13	118.5(2)	C20	C24	C23	107.8(2)
C11	C12	C17	124.33(18)	C20	C24	C29	125.0(2)
C13	C12	C17	117.11(19)	C23	C24	C29	126.4(2)
C12	C13	C14	122.1(2)	Ti	C30	C31	73.64(12)
C13	C14	C15	119.2(2)	Ti	C30	C34	71.61(12)
C14	C15	C16	121.3(2)	Ti	C30	C35	133.23(14)
C11	C16	C15	119.5(2)	C31	C30	C34	108.47(19)
C11	C16	C18	121.48(18)	C31	C30	C35	127.31(19)
C15	C16	C18	119.0(2)	C34	C30	C35	122.22(19)
Ti	C20	C21	72.51(12)	Ti	C31	C30	73.05(12)
Ti	C20	C24	72.87(12)	Ti	C31	C32	72.64(13)
Ti	C20	C25	131.18(16)	Ti	C31	C36	125.71(15)
C21	C20	C24	108.0(2)	C30	C31	C32	106.94(19)
C21	C20	C25	124.9(2)	C30	C31	C36	125.20(19)
C24	C20	C25	125.6(2)	C32	C31	C36	127.4(2)
Ti	C21	C20	73.84(12)	Ti	C32	C31	73.69(12)
Ti	C21	C22	72.79(12)	Ti	C32	C33	73.34(13)
Ti	C21	C26	131.21(15)	Ti	C32	C37	129.24(16)
C20	C21	C22	108.12(19)	C31	C32	C33	108.5(2)
C20	C21	C26	124.5(2)	C31	C32	C37	126.6(2)
C22	C21	C26	125.6(2)	C33	C32	C37	123.6(2)
Ti	C22	C21	73.13(12)	Ti	C33	C32	73.42(13)
Ti	C22	C23	74.96(13)	Ti	C33	C34	72.01(12)
Ti	C22	C27	123.05(16)	Ti	C33	C38	132.99(16)
C21	C22	C23	108.0(2)	C32	C33	C34	108.32(19)
C21	C22	C27	126.0(2)	C32	C33	C38	122.9(2)
C23	C22	C27	125.6(2)	C34	C33	C38	126.8(2)
Ti	C23	C22	71.48(12)	Ti	C34	C30	74.57(12)
Ti	C23	C24	72.02(12)	Ti	C34	C33	74.45(13)
Ti	C23	C28	135.09(16)	Ti	C34	C39	126.12(16)
C22	C23	C24	107.92(19)	C30	C34	C33	107.7(2)
C22	C23	C28	123.5(2)	C30	C34	C39	123.0(2)
C24	C23	C28	126.4(2)	C33	C34	C39	128.2(2)

Selected X-Ray Crystallographic data for 1,1-Bis(pentamethylcyclopentadienyl)-3-(2-butynyl)-2-methyltitanacyclopent-2-en-5-one 54.

Additional information (including structure factors, etc.) can be obtain directly from Dr. Robert McDonald at the University of Alberta Molecular Structure Center, Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2 Canada. Request report # *jms9911*.

Table 4.4. Crystallographic Experimental Details of Complex **54**

A. Crystal Data

formula	$C_{29}H_{40}OTi$
formula weight	452.51
crystal dimensions (mm)	$0.33 \times 0.23 \times 0.18$
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters^a	
a (Å)	16.3004 (10)
b (Å)	14.6471 (8)
c (Å)	10.9482 (6)
β (deg)	105.6000 (10)
V (Å^3)	2517.6 (2)
Z	4
ρ_{calcd} (g cm^{-3})	1.194
μ (mm^{-1})	0.358

B. Data Collection and Refinement Conditions

diffractometer	Bruker P4/RA/SMART 1000 CCD^b
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)

temperature (°C)	−80
scan type	ϕ rotations (0.3) / ω scans (0.3) (20 s exposures)
data collection 2θ limit (deg)	51.50
total data collected	16749 (-19 h 19, -17 k 17, -13 l 13)
independent reflections	4795
number of observations (NO)	3491 [F_o^2 2$\sigma(F_o^2)$]
structure solution method	direct methods/fragment search ($DIRDIF$-96[c])
refinement method	full-matrix least-squares on F^2 ($SHELXL$-93[d])
absorption correction method	$SADABS$
range of transmission factors	0.9280–0.6650
data/restraints/parameters	4795 [F_o^2 −3$\sigma(F_o^2)$] / 0 / 292
goodness-of-fit (S)[e]	1.065 [F_o^2 −3$\sigma(F_o^2)$]
final R indices[f]	
R_1 [F_o^2 2$\sigma(F_o^2)$]	0.0539
wR_2 [F_o^2 −3$\sigma(F_o^2)$]	0.1700
largest difference peak and hole	0.644 and −0.433 e Å^{-3}

[a]Obtained from least-squares refinement of 6217 centered reflections.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

Table 4.4. Crystallographic Experimental Details of Complex **54** (continued)

[c]Beurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Garcia Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. (1996). The *DIRDIF-96* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

[d]Sheldrick, G. M. *SHELXL-93.* Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having F_o^2 -3$\sigma(F_o^2)$). Weighted R-factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional R-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. R-factors based on F_o^2 are statistically about twice as large as those based on F_o, and R-factors based on ALL data will be even larger.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.1038P)^2 + 0.3078P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Figure 3. ORTEP for Complex **54** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS 9911.
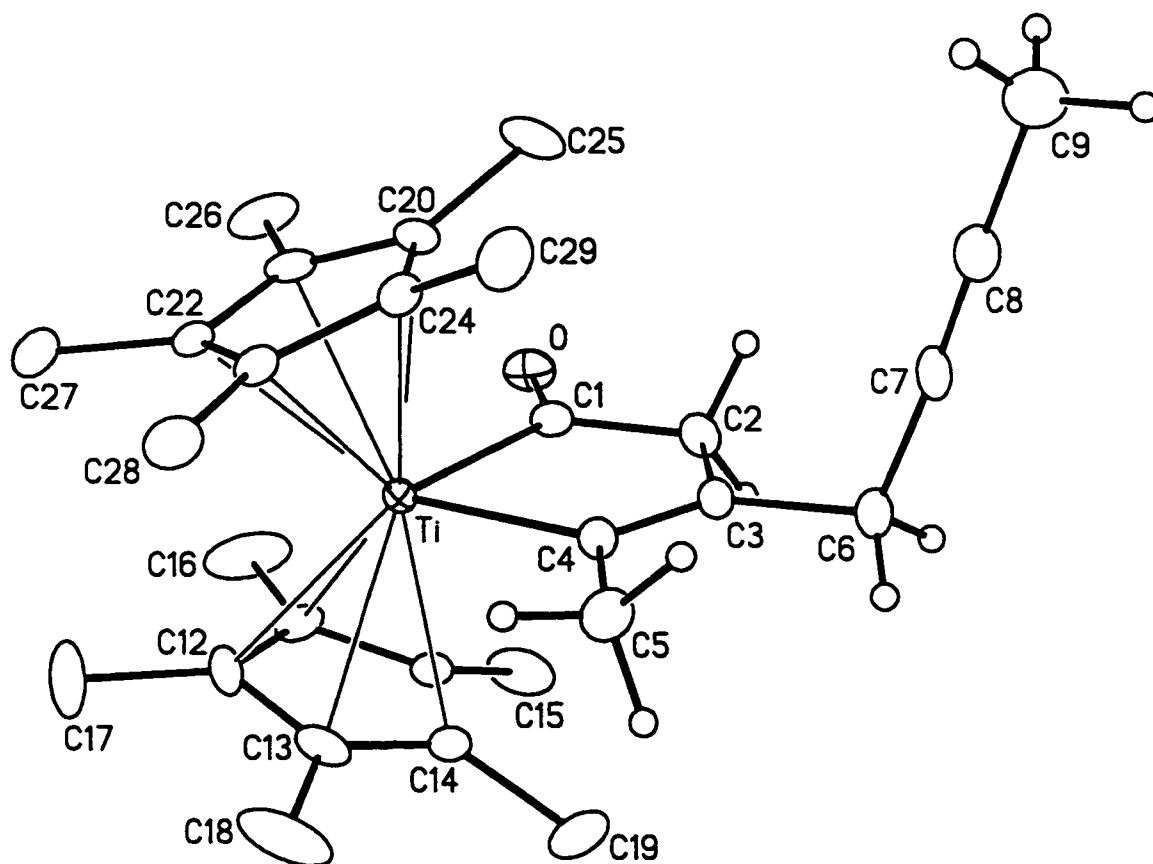
Table 4.5. Selected Interatomic Distances (Å) of Complex **54**

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ti	C1	2.171(3)	C10	C11	1.406(4)
Ti	C4	2.160(3)	C10	C14	1.382(4)
Ti	C10	2.409(3)	C10	C15	1.513(5)
Ti	C11	2.400(3)	C11	C12	1.415(5)
Ti	C12	2.420(3)	C11	C16	1.492(5)
Ti	C13	2.426(3)	C12	C13	1.425(6)
Ti	C14	2.442(3)	C12	C17	1.502(5)
Ti	C20	2.422(3)	C13	C14	1.383(5)
Ti	C21	2.430(3)	C13	C18	1.506(5)
Ti	C22	2.440(3)	C14	C19	1.511(5)
Ti	C23	2.393(3)	C20	C21	1.415(5)
Ti	C24	2.417(3)	C20	C24	1.423(4)
O	C1	1.219(3)	C20	C25	1.487(4)
C1	C2	1.531(4)	C21	C22	1.383(4)
C2	C3	1.504(5)	C21	C26	1.520(5)
C3	C4	1.332(4)	C22	C23	1.416(4)
C3	C6	1.527(4)	C22	C27	1.515(5)
C4	C5	1.519(4)	C23	C24	1.413(4)
C6	C7	1.467(5)	C23	C28	1.505(4)
C7	C8	1.172(5)	C24	C29	1.506(4)
C8	C9	1.469(5)			

Table 4.6. Selected Interatomic Angles (deg) of Complex **54**

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	Ti	C4	79.19(11)	C12	Ti	C20	139.04(12)
C1	Ti	C10	73.70(10)	C12	Ti	C21	106.19(12)
C1	Ti	C11	90.23(12)	C12	Ti	C22	84.77(11)
C1	Ti	C12	124.04(13)	C12	Ti	C23	97.69(11)
C1	Ti	C13	126.68(11)	C12	Ti	C24	131.80(11)
C1	Ti	C14	94.67(11)	C13	Ti	C14	33.01(11)
C1	Ti	C20	73.19(10)	C13	Ti	C20	160.12(11)
C1	Ti	C21	84.17(11)	C13	Ti	C21	137.36(13)
C1	Ti	C22	117.05(11)	C13	Ti	C22	108.24(12)
C1	Ti	C23	129.97(11)	C13	Ti	C23	103.30(11)
C1	Ti	C24	100.14(11)	C13	Ti	C24	128.86(11)
C4	Ti	C10	97.14(10)	C14	Ti	C20	164.80(11)
C4	Ti	C11	130.12(11)	C14	Ti	C21	156.62(10)
C4	Ti	C12	125.58(13)	C14	Ti	C22	139.37(11)
C4	Ti	C13	91.48(12)	C14	Ti	C23	134.04(11)
C4	Ti	C14	76.17(10)	C14	Ti	C24	146.08(10)
C4	Ti	C20	92.27(11)	C20	Ti	C21	33.90(11)
C4	Ti	C21	126.11(11)	C20	Ti	C22	55.83(10)
C4	Ti	C22	131.53(11)	C20	Ti	C23	56.83(10)
C4	Ti	C23	99.31(11)	C20	Ti	C24	34.21(11)
C4	Ti	C24	76.89(10)	C21	Ti	C22	32.99(11)
C10	Ti	C11	34.00(10)	C21	Ti	C23	56.18(10)
C10	Ti	C12	55.71(11)	C21	Ti	C24	56.19(10)
C10	Ti	C13	55.39(10)	C22	Ti	C23	34.04(11)
C10	Ti	C14	33.08(10)	C22	Ti	C24	56.04(10)
C10	Ti	C20	143.09(10)	C23	Ti	C24	34.15(11)
C10	Ti	C21	126.43(10)	Ti	C1	O	127.7(2)
C10	Ti	C22	130.71(11)	Ti	C1	C2	112.7(2)
C10	Ti	C23	153.40(11)	O	C1	C2	119.6(3)
C10	Ti	C24	172.29(10)	C1	C2	C3	111.8(2)
C11	Ti	C12	34.14(13)	C2	C3	C4	120.4(3)
C11	Ti	C13	56.83(12)	C2	C3	C6	114.5(3)
C11	Ti	C14	56.09(10)	C4	C3	C6	125.2(3)
C11	Ti	C20	131.16(11)	Ti	C4	C3	115.8(2)
C11	Ti	C21	100.53(10)	Ti	C4	C5	122.9(2)
C11	Ti	C22	96.78(11)	C3	C4	C5	121.2(3)
C11	Ti	C23	123.23(12)	C3	C6	C7	112.0(3)
C11	Ti	C24	152.73(11)	C6	C7	C8	177.0(4)
C12	Ti	C13	34.20(13)	C7	C8	C9	179.0(4)
C12	Ti	C14	55.51(11)	Ti	C10	C11	72.64(16)

Table 4.6. Selected Interatomic Angles (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Ti	C10	C14	74.78(17)	Ti	C20	C24	72.70(17)
Ti	C10	C15	131.8(2)	Ti	C20	C25	130.0(2)
C11	C10	C14	109.5(3)	C21	C20	C24	107.1(3)
C11	C10	C15	122.7(3)	C21	C20	C25	127.7(4)
C14	C10	C15	125.8(3)	C24	C20	C25	123.8(3)
Ti	C11	C10	73.36(17)	Ti	C21	C20	72.75(17)
Ti	C11	C12	73.70(18)	Ti	C21	C22	73.90(17)
Ti	C11	C16	122.6(2)	Ti	C21	C26	124.5(2)
C10	C11	C12	106.2(3)	C20	C21	C22	108.9(3)
C10	C11	C16	125.1(4)	C20	C21	C26	125.3(3)
C12	C11	C16	128.4(4)	C22	C21	C26	125.5(3)
Ti	C12	C11	72.15(18)	Ti	C22	C21	73.11(17)
Ti	C12	C13	73.14(18)	Ti	C22	C23	71.15(16)
Ti	C12	C17	131.6(3)	Ti	C22	C27	133.4(2)
C11	C12	C13	107.9(3)	C21	C22	C23	108.5(3)
C11	C12	C17	127.5(5)	C21	C22	C27	122.4(3)
C13	C12	C17	123.0(5)	C23	C22	C27	127.4(3)
Ti	C13	C12	72.66(18)	Ti	C23	C22	74.81(17)
Ti	C13	C14	74.14(18)	Ti	C23	C24	73.87(17)
Ti	C13	C18	125.9(2)	Ti	C23	C28	123.2(2)
C12	C13	C14	107.5(3)	C22	C23	C24	107.6(3)
C12	C13	C18	125.7(4)	C22	C23	C28	125.0(3)
C14	C13	C18	126.2(4)	C24	C23	C28	127.0(3)
Ti	C14	C10	72.13(17)	Ti	C24	C20	73.09(16)
Ti	C14	C13	72.85(18)	Ti	C24	C23	71.98(17)
Ti	C14	C19	130.2(2)	Ti	C24	C29	130.3(2)
C10	C14	C13	108.7(3)	C20	C24	C23	107.8(3)
C10	C14	C19	123.4(3)	C20	C24	C29	125.2(3)
C13	C14	C19	126.8(3)	C23	C24	C29	125.8(3)
Ti	C20	C21	73.35(17)				

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