# Synthesis and Reactivity of Titanocene Methylene Complexes and Bis($\eta^5$-Cyclopentadienyl) Titanacyclobutenes

Thesis by

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Lastly, I thank my wife, Carol, to whom this thesis is dedicated.

# ABSTRACT

Syntheses of several bis($\eta^5$-cyclopentadienyl) titanium methylene phosphine complexes are reported. The titanium methylene phosphine complexes are generated from themolysis of titanacyclobutanes in the presence of excess phosphine. Spectral data and reactivity are consistent with a methylene phosphine complex rather than an ylide complex.

Bis($\eta^5$-cyclopentadienyl) titanacyclobutenes are readily synthesized by treatment of sources of "$Cp_2TiCH_2$" with disubstituted alkynes. A variety of stable titanacyclobutenes were synthesized containing aryl, alkyl, and etherial substituents. Titanacyclobutenes, unlike the related titanacyclobutanes, do not reform "$Cp_2TiCH_2$" thermally.

Titanacyclobutenes insert carbon monoxide, forming an acyl intermediate which rearranges to a titanocene vinyl ketene complex. A trimethylphosphine adduct of one of the ketene complexes was characterized by x-ray diffraction techniques. The carbonylation mechanism involves insertion of carbon monoxide into the more accessible titanium-carbon bond, followed by intra-molecular attack of the vinyl group to the acyl. Insertion of t-butyl isocyanide into a titanacyclobutene yields a cyclic imino-acyl complex, which was also characterized by x-ray diffraction. The vinyl ketene complexes react with many unsaturated substrates (alkynes, ethylene, and aldehydes) to form new organotitanium species.

Titanacyclobutenes react with ketones and aldehydes *via* 1,2-addition to yield titanium oxacyclohexenes. Aldehydes form both titanium-oxygen and titanium-carbon regioisomers. The organic ligand may be removed from the titanium to give homo-allylic alcohols in good yield. Nitriles also insert into titancyclobutenes to produce titanium imidocyclohexenes.

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# Chapter 1

## Synthesis and Reactivity of Bis($\eta^5$–Cyclopentadienyl) Titanium Methylene Complexes

## Introduction

Transition-metal methylene or carbene complexes are of great experimental and theoretical interest. Metal-methylene complexes are implicated as intermediates in many important reactions, including olefin metathesis, [1] olefin [2] and alkyne polymerization, [3] cyclopropanation of olefins, [4] and methylenation of carbonyl compounds. [5] Surface-bound methylene species have been postulated to be intermediates in Fischer-Tropsch chemistry. [6] As models for these and other reactions, many bridging metal-methlene compounds have been synthesized and studied. [7] Many carbene complexes containing heteroatom substituents ("Fischer" carbenes) have been synthesized; their chemistry is quite different from methylene complexes.[8]

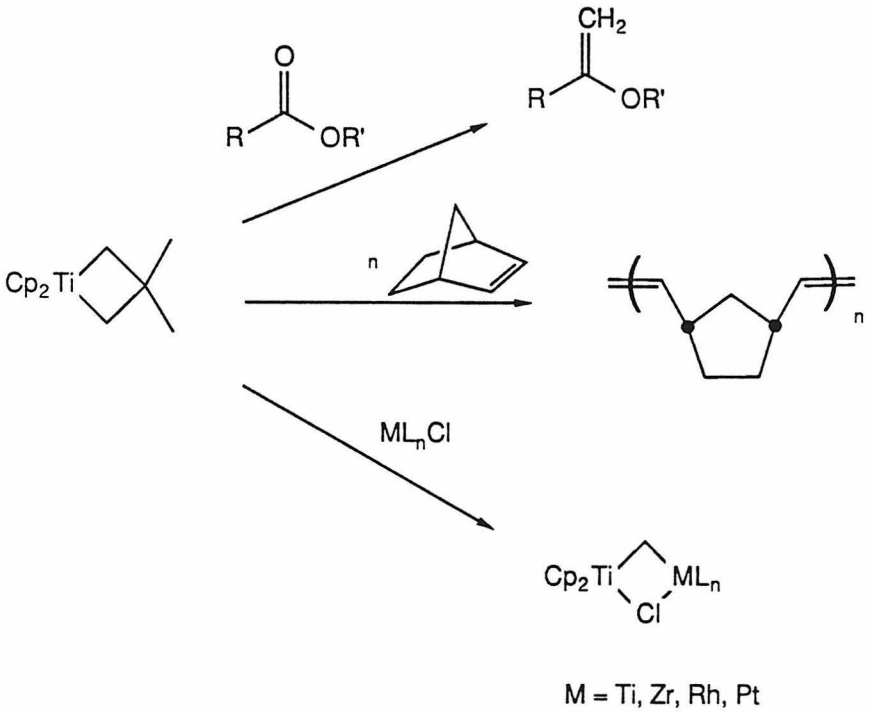
In contrast, the chemistry of terminal methylene and alkylidene complexes is less developed. Terminal methylene complexes appear to be more reactive than their bridging analogues, and a lack of general synthetic methods has made systematic studies difficult. Only a few terminal methylene complexes are well-characterized, the most notable examples being $Cp_2Ta(CH_2)CH_3$ [9], $(W(CH_2)(PMe_3)_4Cl)^+$ $(CF_3SO_5)^-$ [10], $Os(CH_2)Cl(NO)(P\phi_3)_2$ [11], and $Cp_2Ta(CH_2)H$. [12]

Reaction of titanium halides and alkyl aluminum compounds yields an active catalyst for ethylene polymerization. [13] Reinvestigation of this system by Tebbe, utilizing titanocene dichloride and trimethylaluminum, lead to the isolation of a soluble dimethylaluminum chloride-titanocene methylene complex (Tebbe's reagent, **1**). [14] The Tebbe reagent demonstrated activity as a metathesis catalyst with terminal olefins and readily methylenated carbonyl compounds.[15] A titanocene methylene species is implicated as the active species.

From this same system, Grubbs and coworkers successfuly isolated titanacyclobutane species by reaction of **1** with olefins in the presence of Lewis bases.[16]

Titanacyclobutanes transfer methylene groups to carbonyl functionality,[5] ring-open polymerize strained olefins,[2] and form bridging methylene dimers[18] (Scheme 1). The existence of titanocene-methylene or a titanocene methylene-olefin complex is implicated by the reactivity and kinetics of titanacyclobutanes.[17] However, the nature of the methylene complex is not known.

**Scheme 1.** Reactivity of Titanacyclobutanes

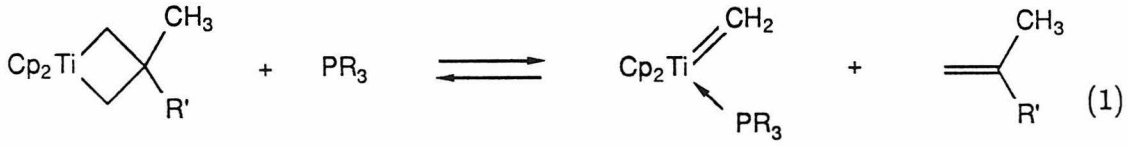



This chapter addresses the formation, isolation, characterization and reactivity of titanocene-methylene phosphine complexes. These compounds provide another entry into titanocene-methylene chemistry and information about transition metal-carbon multiple bonding.

## Results

### Preparation of Titanocene Methylene Phosphine Complexes

Treatment of a solution[16d,20] of $\beta,\beta$–dimethyltitanacyclobutane, **2a**, or $\beta,\beta$–methylpropyltitanacyclobutane, **2b**, with excess trialkylphosphine (trimethyl, dimethylphenyl, or triethylphosphine) at room temperature yields the corresponding titanocene methylene phosphine complex, **3a-c**, in equilibrium with the metallacycle (Equation 1).




(1)

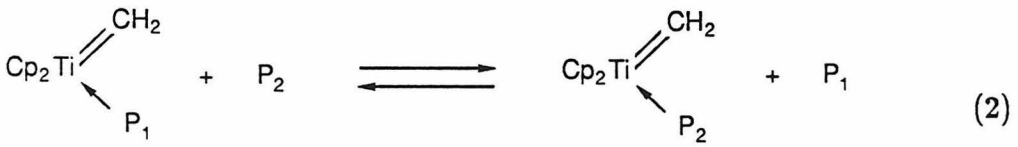
**2a:** R' = $CH_3$
**2b:** R' = $CH_2CH_2CH_3$

**3a:** $PR_3$ = $PMe_3$
**3b:** $PR_3$ = $PMe_2Ph$
**3c:** $PR_3$ = $PEt_3$

If the olefin is removed from the reaction mixture by evacuation, the equilibrium can be shifted entirely to product. The phosphine methylene complexes are isolated as yellow-brown powders, extremely air- and moisture-sensitive. The complexes are quite soluble in aromatic solvents, moderately soluble in diethyl ether, and insoluble in pentane.

The stability of the different phosphine complexes reflects the size of the phosphine.[21] The stability order is $PMe_3 > PMe_2\phi >> PEt_3$. The measured equilibria (Equation 2) for the different complexes is shown in Table 1.

The trimethylphosphine complex is stable as a solid in the drybox at –40 °C for months and in solution at room temperature for hours. The other phosphine complexes, **3b** and **3c**, are much less stable than **3a** in solution.



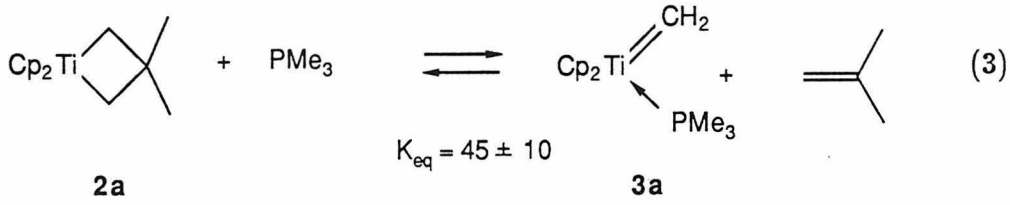

(2)

$P_1 = PMe_3$, $P_2 = PMe_2Ph$
$P_1 = PMe_2Ph$, $P_2 = PEt_3$

**Table 1.** Phosphine Exchange Equilibrium Constants

| Complex | Equilibrium Ratio | Equilibrium Constant ($K_{eq}$) |
|---|---|---|
| **3a⇌3b** | 3.5 ± 0.2 : 1 | 0.13 ± 0.02 |
| **3b⇌3c** | 5.6 ± 0.3 : 1 | 0.03 ± 0.01 |

The equilibrium constant for the initial reaction of phosphine with metallacyclobutane has also been determined ( Equation 3).




$K_{eq} = 45 \pm 10$

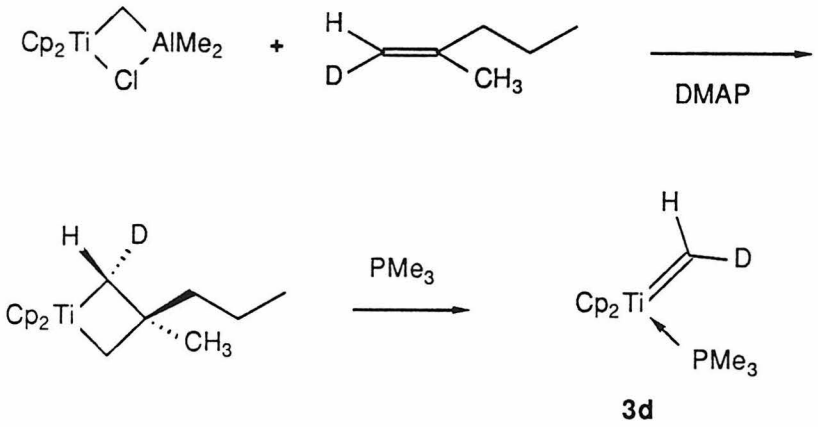
**2a** **3a**

(3)

The phosphine complexes **3a-c** exhibit a characteristic low-field NMR resonance for the $CH_2$ group at $\delta$ 12.0. The $CH_2$ and the $\eta^5$-cyclopentadienyl ligands exhibit $^{31}P$ coupling of 6.8 Hz and 2.0 Hz, respectively. The methylene carbon atom

has a characteristic $^{13}C$ shift of $\delta$ 285 and a $J_{C-P}$ of 30.3 Hz. The $J_{C-H}$ coupling constant of the methylene carbon in **3a** is 127 $\pm$ 1 Hz.

The small $J_{C-H}$ coupling constant of **3a** prompted the synthesis of the H–D labeled methylene–phosphine complex **3d** (Equation 4). The secondary $^2H$ isotope effect on the metallacycle cleavage produces a 2 : 1 mixture of **3a** to **3d**. [19] The NMR of **3d** exhibits an upfield isotopic shift of 5.04 Hz for the methylene proton. No $J_{H-D}$ coupling was observed even with resolution enhancement. Infrared spectral analysis of **3d** revealed a single new peak at 2160 $cm^{-1}$.



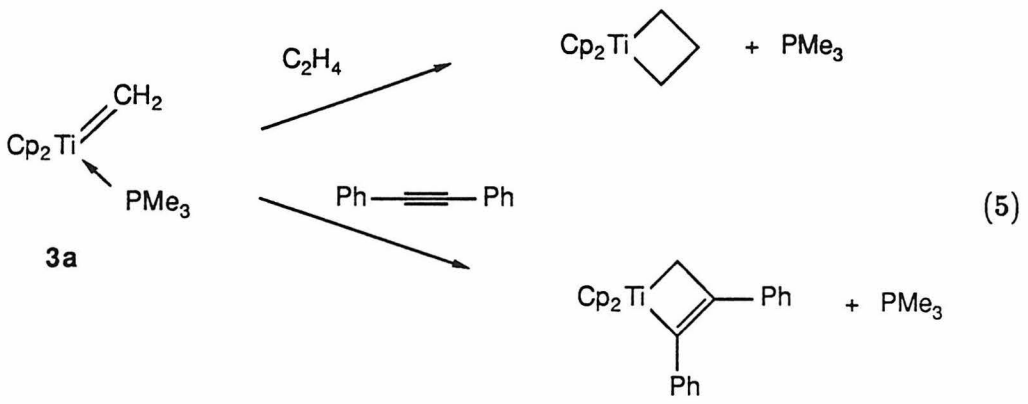

(4)

**3d**

## Reactivity of Titanocene Methylene Phosphine Complexes

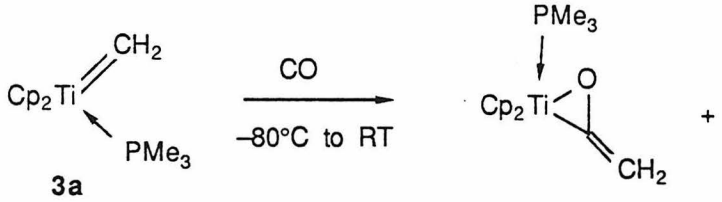
The reaction of several unsaturated substrates with the phosphine-methylene complexes was performed.

The phosphine-methylene complexes react cleanly with olefins to regenerate titanacyclobutanes and with disubstituted acetylenes to form titanacyclobutenes (Equation 5).




(5)

Treatment of a $C_7D_8$ solution of **3a** (Equation 6) with CO yields upon warming from –80 °C to room temperature a mixture of products. Two of the products are $Cp_2Ti(CO)_2$ ($\delta$ 4.58) and $Cp_2Ti(CO)(PMe_3)$ ($\delta$ 4.62 d, $J_{C-P}$ = 2 Hz).[22] A product identified as $Cp_2Ti(CH_2CO)(PMe_3)$ is observed and appears to be the major initial product.[23] The ketene complex decomposes in solution at room temperature; however, no NMR signals attributable to ketene or the ketene dimer are observed. Carbonylation of complex **3b** gives similar results.



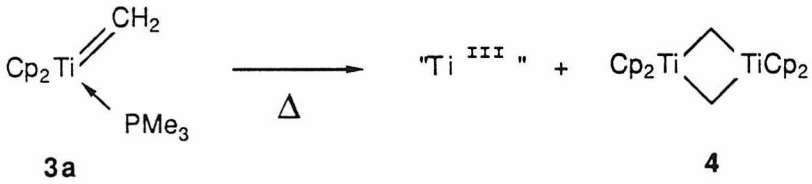

(6)

$Cp_2Ti(CO)_2$ + $Cp_2Ti(CO)(PMe_3)$

Treatment of a $C_7D_8$ solution of **3a** with $CO_2$ results is a rapid reaction at –80°C. The reaction is completed in a few minutes and produces a copious amount of yellow insoluble material, unidentifiable by NMR.

The solutions of phosphine-methylene complexes upon standing at room tem-

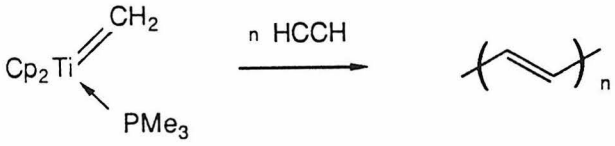
perature yield mostly paramagnetic materials with some methylene dimer **4** (Equation 7). The thermolysis of **3b** has been studied by K. Ott.[24] Thermolysis of the phosphine methylene complexes does not yield the same distribution of hydrocarbons as the titanacyclobutanes, **2**, or the dimer, **4**. While the dimer, **4**, yields primarily methane, the phosphine complex **3b** yields mostly ethane and little methane.




**3a** **4** (7)

Attempts to prepare adducts of $Cp_2TiCH_2$ from other Lewis bases such as pyridine, trimethylphosphite, and triflurophosphine have been unsuccessful.

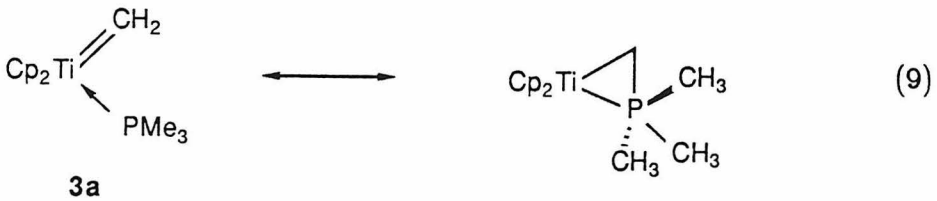
Reaction of the phosphine-methylene complex **3a** with acetylene results in the formation of polyacetylene (Equation 8). No intermediate metallacyclobutenes were observed.




**3a** (8)

## Discussion

Titanacyclobutanes are in equilibrium with either a methylene-olefin complex or free $Cp_2TiCH_2$; either may be trapped by a trialkylphosphine to yield a titanocene methylene phosphine complex **3a-c.** Physical and chemical characterization of the phosphine-methylene complexes suggests the presence of a true methylene phosphine complex rather than an ylide complex (Equation 9).



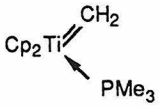
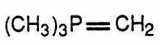
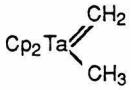
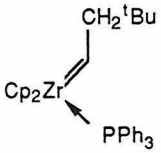
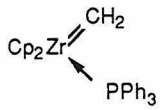
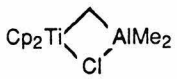
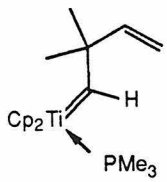

**3a** (9)

The stability of the complexes reflects the size and basicity of the phosphine as expected for a simple dative interaction. The phosphine ligands are quite labile and exchange rapidly in solution at room temperature.

The NMR chemical shifts for the methylene ligand are noteworthy. The strong downfield shift in both the $^1H$ NMR and the $^{13}C$ NMR spectra are characteristic of an early transition metal methylene complex. The carbon-hydrogen coupling constant of the methylene group (127 Hz) is extremely small for a formally $sp^2$ carbon atom. This small coupling may be attributed to an electronic effect caused by bonding to a very electropositive titanium. [25] Schrock has also observed a similar low coupling constant for $CpTa(CH_3)CH_2$ ($J_{C-H}$ = 132 Hz). [9] Pertinent NMR data of various methylene complexes are tabulated in Table 2.

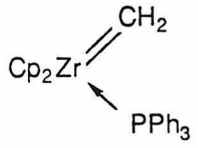
The carbon phosphorous coupling constant of the methylene group in **3a**

**Table 2. NMR Data of Selected Methylene Complexes**

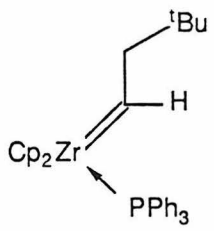
| | $^1H$ | $^{13}C$ | $J_{C-H}$ (Hz) | $J_{P-H}$ (Hz) | $J_{C-P}$ (Hz) |
|---|---|---|---|---|---|
|  | 12.12 | 285.9 | 127 | 6.8 | 31.7 |
|  | 0.78[47] | –1.5 | 149 | 6.5 | 90.5 |
|  | 9.88[46] | 228 | 132 | – | – |
| | –0.22 | –4.0 | 122 | – | – |
|  | 11.71[27] | 270 | – | 4.1 | – |
|  | 11.0[36] | 248 | 121 | 4.8 | 14.6 |
|  | 8.49[16] | 188 | 140 | – | – |
|  | 8.72[18] | 235 | 126 | – | – |
|  | 12.06[28] | 306.9 | 111 | 7.3 | 26.6 |
|  | 2.50[9] | 83.5 | 137 | – | – |

($J_{C-P}$ = 31.7 Hz) is much less than the $CH_2PMe_3$ ylide ($J_{C-P}$ = 90.5 Hz).[26] The magnitude of the coupling constants, together with the chemical reactivity, support our assignment of **3a-c** as phosphine methylene complexes rather than ylide complexes.

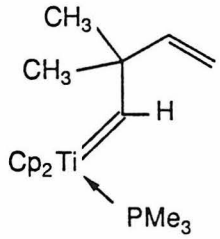
Schwartz has reported[36,27] a bis($\eta^5$-cyclopentadienyl) zirconium methylene–phosphine complex, **5**, and a series of of bis($\eta^5$-cyclopentadienyl)zirconium phosphine–alkylidene complexes, **6**. A substituted titanocene alkylidene–phosphine complex, **7**, has also been isolated.[28] The existence of a substituted "Tebbe" derivative has been inferred from the reactivity of alkenyl aluminum compounds and titanocene dichloride. [20,37] The physical characteristics and reactivity of these alkylidene complexes are consistent with the phosphine-methylene complexes **3a-c**.




**5**




**6**




**7**

The deuterium-labeled methylene complex, **3d**, displayed a C–D stretch at 2160 $cm^{-1}$. The calculated C–H frequency from this C–D stretch is 2944 $cm^{-1}$. This frequency is consistent with normal C–H vibrations. If the C–H bonds were interacting with the metal center, the reduced C–H bond-order would be reflected in the stretching frequency.[38]

The trimethylphosphine–methylene complex, **3a**, reacts with carbon monoxide to yield a titanocene-ketene trimethylphosphine complex (Equation 4). The titanocene ketene complexes are well studied, and the dimethylphenyl phosphine

complex is known.[23] The carbonylation most likely procedes through an unobserved $Cp_2Ti(CH_2)(CO)$ complex or a C,C bound ketene intermediate. The fate of the ketene and other organic fragments when the ketene complex decomposes to $Cp_2Ti(CO)_2$ and $Cp_2Ti(CO)(PMe_3)$ is not known. Straus has observed similar instability of the titanium ketene–phosphine complex.[23] Similar CO insertions into terminal methylene units to yield ketene complexes have also been observed in Mn,[29] Mo,[30] and W[31] systems.

The reaction of carbon dioxide with the phosphine-methylene complex, **3a**, is much more rapid than the carbonylation reaction. The formation of insoluble yellow precipitate is characteristic of titanocene-oxo polymer from methylenation reactions. The product of single methylene transfer to $CO_2$ would be ketene, $CH_2CO$, which likely polymerizes in the presence of the titanocene–oxo product.

The thermolysis data determined by Ott suggest that while the methylene complex usually reacts analogously to titanacyclobutanes, the phosphine ligand may influence the reactivity. The coordination of a phosphine increases electron density at the metal relative to either a titanacyclobutane or a methylene–olefin complex. The thermolysis data suggest that carbon–carbon coupling is a major decomposition path for **3b**.

## Conclusions

A series of titanocene methylene–phosphine complexes has been isolated. The bonding is best described as a methylene–phosphine complex rather than an ylide complex. The complexes are quite reactive toward unsaturated substrates such as alkenes, alkynes, CO, and $CO_2$. The only distinction between the reactivty of methylene–phosphine complexes and titanacyclobutanes is the thermal decomposition. Phosphine–methylene complexes yield mostly $C_2$ products, whereas the titanacyclobutanes or the methylene dimer yield mostly methane. This change in reactivity is attributed to the ability of the phosphine to enhance carbon–carbon coupling by electron donation to the metal.

## Experimental Section

**General Considerations.** All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres glovebox, equipped with an MO-40-1 purification train, DK-3E Dri-Kool conditioner, and Dri-Cold freezer. Flash chromatography was performed by the procedure of Still *et al.*, [33] using silica Woelm 32-63 (32-63 $\mu$m). Thin layer chromatography was performed on EM Reagents 0.25 mm silica gel 60-F plates and visualized with either iodine vapor or phosphomolybdic acid / ethanol spray. All reaction temperatures were measured externally.

**Materials.** Toluene, diethylether, and tetrahydrofuran were stirred over $CaH_2$, then transferred to purple sodium-benzophenone ketyl. Pentane and hexane were stirred over concentrated $H_2SO_4$, washed with $H_2O$, dried over $CaH_2$, then transferred to purple sodium-benzophenone ketyl with tetraglyme. Dichloromethane was stirred over $P_2O_5$ or $CaH_2$ and degassed by evacuation of freeze-pump-thaw cycles. Dried degassed solvents were vacuum-transferred into dry glass vessels equipped with Teflon valve closures and stored under argon. Benzene-$d_6$, toluene-$d_8$, and tetrahydrofuran-$d_8$ (Cambridge Isotopes) were dried and vacuum-transferred from purple sodium-benzophenone ketyl. Dichloromethane-$d_2$ (Cambridge Isotopes and Norell, Inc.) was dried over $CaH_2$ or Na-Pb alloy and degassed by several freeze-pump-thaw cycles. Chloroform-d (Aldrich) was dried over 4 Å molecular sieves.

Tebbe reagent and bis($\eta^5$-cyclopentadienyl) titanacyclobutanes were prepared by the reported procedures. [34] Carbon monoxide (CP) and carbon dioxide (Bone-Dry) were obtained from Matheson Gas Co. Alkyl phosphines were purchased from

Strem Chemical Co. and degassed prior to use.

**Instrumentation.** NMR spectra were recorded on a Varian EM-390 (90 MHz, $^1$H), JEOL FX-90Q (89.60 MHz, $^1$H; 22.53 MHZ, $^{13}$C; 36.27 MHz $^{31}$P), Varian XL-200 (200.3 MHz, $^1$H; 50.1 MHz, $^{13}$C), JEOL GX-400 (399.65 MHz, $^1$H; 100.4 MHz, $^{13}$C), or Brüker WM-500 (500.13 MHz, $^1$H). Chemical shifts are reported in $\delta$ , referenced to residual solvent signals ($^1$H: $C_6D_6$, $\delta$ 7.15; $C_7D_8$, $\delta$ 2.09; THF-$d_8$, $\delta$ 3.58 or 1.73; $CD_2Cl_2$, $\delta$ 5.35; $CDCL_3$, $\delta$ 7.24; $^{13}$C: $C_6D_6$, $\delta$ 128.0; $C_7D_8$, $\delta$ 20.9; THF-$d_8$, $\delta$ 67.4; $CDCL_3$, $\delta$ 77.0). Phosphorous-31 NMR data are referenced externally to 85% $H_3PO_4$ (positive $\delta$, low field). Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad), coupling constant (Hz), integration, and assignment. Difference NOE experiments were performed according to published procedures. [35] Gas chromatography analyses were performed on a Shimatzu GC-Mini-2 equipped with an SE-30 capillary column, flame-ionization detector, and a Hewlett-Packard 3390A integrator. Infrared spectra were recorded on a Beckman 4210, Shimatzu IR-435, or Perkin-Elmer 1310 spectrophotometer. IR data are reported in reciprocal centimeters ($cm^{-1}$) and intensity (s=strong, m=medium, w=weak, sh=shoulder). Combustion analyses (C,H,N) were performed by the California Institute of Technology Analytical Services.

### Preparation of $Cp_2TiCH_2 \cdot PMe_3$, 3a.

Trimethylphosphine (130$\mu$L, 1.27 mmol) was added to a stirred suspension of $\beta,\beta$–dimethyltitanacyclobutane (210 mg, 0.846 mmol) in 5 ml of diethylether at –20°C. The mixture was allowed to warm to room temperature under a partial vacuum. Within 10 minutes, the color changed from red to yellow-orange, and a yellow solid had begun to precipitate. After an additional 15 minutes, the volatiles

were removed to yield a yellow-brown powder, which was dried at –20 °C. The solid (180 mg, 64%) was stored in the drybox at –40 °C. The material was suitable for most uses without further purification. However, the complex may be recrystalized in poor yield from either diethylether or toluene/pentane cooling to –50 °C: $^1$H NMR (90 MHz, $C_7D_8$, –20°C) $\delta$ 12.12 (d, $J_{P-H}$ =6.8 Hz, 2H), 5.30 (d, $J_{P-H}$ =2.0 Hz, 10H), 0.72 (d, $J_{C-P}$ =6.3 Hz, 9H). $^{13}$C{$^1$H} NMR (22.5 MHz, $C_7D_8$, –20°C) $\delta$ 285.9 (d, $J_{C-P}$ =30.3 Hz), 100.6 (s), 20.6 (d, $J_{C-P}$ =18.6 Hz). The $J_{C-H}$ of the resonance at $\delta$ 285.9 was determined to be 127.2 ± 1.9 Hz by polarization transfer techniques.[32] $^{31}$P{$^1$H} NMR (36.3 MHz, $C_7D_8$, –20°C) $\delta$ 11.9 (s). IR (nujol, KBr, cm$^{-1}$) 1420 (m), 1300 (w), 1280 (m), 1125 (m), 1025 (m), 1010 (m), 950 (s), 935 (m.sh), 805 (m), 790 (s), 775 (m.sh), 740 (m), 665 (w). Anal. Calcd. for $C_{14}H_{21}PTi$: C, 62.69; H, 7.89. Found: C, 61.66; H, 7.03.

**Preparation of $Cp_2TiCH_2 \cdot PMe_2\phi$, 3b.**

Dimethylphosphine (64 $\mu$L, 0.46 mmol) was added *via* syringe to a well-stirred solution of $\beta,\beta$–dimethyltitanacyclobutane, **2**, (104 mg, 0.42 mmol) in diethylether at –10°C. The solution was warmed to room temperature in 15 minutes with periodic opening of the flask to vacuum to remove the isobutylene. A color change from red to orange with the formation of a yellow flocculent precipitate was observed. The solvent was removed *in vacuo* to yield a yellow powder, which was washed with cold ( –50°C) pentane (2 x 2 ml) and dried *in vacuo* to yield 107 mg (0.32 mmol, 77%) of **3b**: $^1$H NMR (90 MHz, $C_7D_8$, –20°C) $\delta$ 12.36 (d, $J_{P-H}$ =6.59, 2H), 7.07 (m, 5H), 5.39 (d, $J_{P-H}$ =2.2 Hz, 10H), 1.10 (d, $J_{P-H}$ =6.23 Hz, 6H). $^{13}$C{$^1$H} NMR (22.5 MHz, $C_7D_8$, –20°C) $\delta$ 288.39 (d, $J_{C-P}$ =31.13 Hz), 141.41, 131.49, 131.09, 127.51, 125.48, 101.18, 20.77 (d, $J_{C-P}$ =20.14 Hz). $^{31}$P{$^1$H} NMR (36.3 MHz, $C_7D_8$, –20°C) $\delta$ 25.77. IR (nujol, KBr, cm$^{-1}$) 1310 (m), 1278 (w), 1170 (w),

1157 (w), 1095 (w), 1070 (w), 1020 (m), 1012 (m), 970 (w), 940 (m), 902 (m), 840 (w), 793 (s), 739 (s), 695 (m).

**Preparation of $Cp_2TiCH_2 \cdot PEt_3$, 3c.**

Triethylphosphine (260 $\mu$L, 1.78 mmol) was added *via* syringe to a well-stirred suspension of $\beta,\beta$–dimethyltitanacyclobutane, **2**, (111 mg, 0.45 mmol) in 10 ml of pentane at –10°C. The solution was allowed to warm to room temperature with periodic opening to a vacuum to remove the isobutylene. The color changed from red to orange, and after 15 minutes, the solvent was removed *in vacuo*. The resulting yellow-brown powder was washed with –50°C pentane (2 x 1 ml) and dried *in vacuo* to yield 68 mg (0.22 mmol, 49%) of the desired product contaminated with a small amount of starting material and the dimer, $(Cp_2TiCH_2)_2$. $^1$H NMR (90 MHz, $C_7D_8$, –20°C) $\delta$ 12.13 (d, $J_{P-H}$ =5.13 Hz, 2H), 5.33 (s, 10H), 1.2-0.4 (m, 15H) $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_7D_8$, –20°C) $\delta$ 286.44 (d, $J_{C-P}$ =27.5 Hz), 100.21 (s), 20.44 (d, $J_{C-P}$ =12.82), 8.05 (s). $^{31}P\{^1H\}$ NMR (36.3 MHz, $C_7D_8$, –20°C) $\delta$ 38.97 IR (nujol, KBr, $cm^{-1}$) 1305 (w), 1150 (w), 1035 (w), 1020 (m), 983 (w), 890 (w), 805 (m.sh), 790 (s), 755(m).

**Phosphine Exchange Equilibrium Measurements.**

The samples were prepared in the drybox and capped with a septum. The reactant was dissolved in 400 $\mu$L of $C_6D_6$, and a known amount of the appropriate phosphine added *via* syringe. The equilibrium concentration was determined by both $^1$H and $^{31}$P NMR spectroscopy. The samples were allowed to equilibrate for 15 minutes in the NMR probe before measurement. The $^{31}P\{^1H\}$ NMR data were obtained with inverse gated decoupling to eliminate NOE effects.

**Reaction of $Cp_2TiCH_2 \cdot PMe_3$, 3a, with CO.**

A NMR tube was charged with 8 mg (0.030 mmol) of **3a** in the drybox, attached to a teflon needle valve adapter and evacuated on the vacuum line. Approximately 400 $\mu$L of $C_7D_8$ were condensed into the NMR tube. The NMR tube was cooled to 77 K, 80 torr (0.033 mmol) of CO introduced and the tube sealed. The solvent was thawed at –80°C and the reaction monitored in the NMR probe. As the probe temperature was raised to room temperature, several new signals appeared. These signals corresponded to $Cp_2Ti(CO)_2$ ($\delta$ 4.56), $Cp_2Ti(CO)PMe_3$ ($\delta$ 4.62 (d, $J_{P-H}$ =2.4 Hz)), and $Cp_2Ti(CH_2CO)PMe_3$ ($\delta$ 5.15 (d, $J_{P-H}$ =2.4 Hz, 10H), 5.54 (s, 1H), 3.87 (s, 1H), the $J_{P-H}$ coupling to the $\eta^5$-cyclopentadienyl resonance at $\delta$ 5.15 was observed only below –20°C. Based on integration of the resonances versus the solvent only 50% of the starting phosphine complex resulted in identifiable products. The balance of the material formed a very broad NMR signal from 5 to 6 ppm.

**Reaction of $Cp_2TiCH_2 \cdot PMe_2\phi$, 3b, with CO.**

An NMR tube was loaded with 9 mg (0.027 mmol) of **3b** in the drybox, attached to a teflon needle valve adapter, and evacuated on the vacuum line. Approximately 400 $\mu$L of $C_6D_6$ were condensed into the tube, the tube cooled to 77 K, 300 torr of CO introduced, and the tube sealed. The solvent was thawed at room temperature and the color changed from yellow-brown to red-orange. The sample darkened over several hours at room temperature. NMR analyses revealed the formation of $Cp_2Ti(CO)_2$ ($\delta$ 4.56), $Cp_2Ti(CO)(PMe_2\phi)$ ($\delta$ 4.65 (d, J=2Hz)) and $Cp_2Ti(CH_2CO) \cdot PMe_2\phi$ ($\delta$ 5.26 (s), 4.01 (s); the other vinyl signal was obscured). From integration of the Cp resonances the yield of ketene complex was less than 20%.

**Reaction of $Cp_2TiCH_2 \cdot PMe_3$ , 3a, with $CO_2$.**

An NMR tube was charged in the drybox with 9 mg (0.034 mmol) of **3a**; the tube was attached to a teflon needle valve adapter and evacuated on a vacuum line. Approximately 400 $\mu$L of $C_7D_8$ were condensed into the tube followed by 35 torr (0.037 mmol) of $CO_2$ (dried by sublimation at –78°C) and the tube sealed. As the solvent thawed at –80°C, the yellow solution turned turbid. The NMR spectrum was recorded at –80°C and revealed several Cp resonances, all much smaller than the solvent or trimethylphosphine resonances. The sample was warmed to –40°C and several more resonances appeared, although no resonances attributable to ketene dimer were observed. When the sample was removed from the NMR probe at –40°C, all of the organometallic material had precipitated as flocculent yellow solid, and the solution was pale orange.

**Reaction of $Cp_2TiCH_2 \cdot PMe_2\phi$, 3b, with $CO_2$.**

An NMR tube was charged in the drybox with 14 mg (0.042 mmol) of **3b**, the tube attached to a teflon needle valve adapter and evacuated on the vacuum line. Approximately 400 $\mu$L of $C_7D_8$ followed by 100 torr of $CO_2$ were condensed into the tube and the tube sealed. As the solvent thawed at –50°C, the solution changed color to red-brown and a large amount of yellow precipitate formed. NMR analysis at room temperature revealed several small Cp resonances and a very broad signal centered at $\delta$ 6.0. No resonances attributable to ketene dimer were observed.

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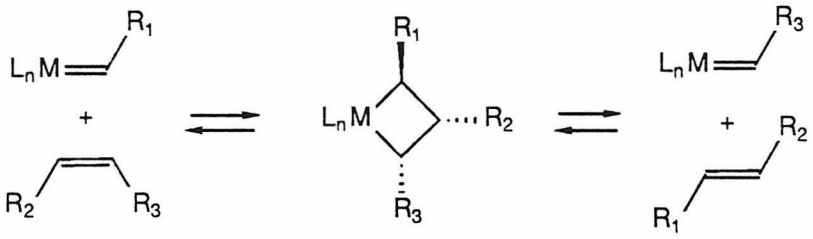
# Chapter 2

## Synthesis of Bis($\eta^5$–Cyclopentadienyl) Titanacyclobutenes

## Introduction

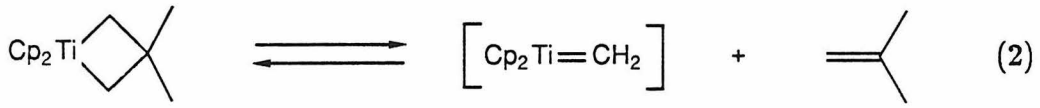
Olefin metathesis, the process whereby the carbon-carbon double bonds of two olefins are exchanged, has been the subject of intense mechanistic investigation in many laboratories. [1] The accepted mechanism, originally proposed by Hérisson and Chauvin, [2] is the interconversion of metal-alkylidenes and metallacyclobutanes (Equation 1).




(1)

Although metallacyclobutanes and transition–metal alkylidenes are required intermediates for olefin metathesis, only recently have derivatives from catalytically active systems been isolated and structurally characterized.[3,4] Metallacyclobutane–alkylidene interconversion has also been studied theoretically. [8]

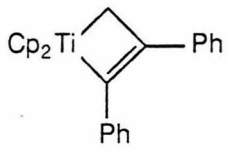
A major advance in this area occurred when Tebbe isolated the dimethylaluminumchloride adduct of a bis(cyclopentadienyl) titanium carbene, [5] now known as "Tebbe reagent," **1**. In the presence of Lewis bases, Tebbe reagent is a catalyst for the degenerate metathesis of terminal olefins. Tebbe reagent also reacts with disubstituted acetylenes to form titanocenecyclobutenes in good yield. [7] Following the discovery of titanacyclobutanes, Howard and Grubbs isolated the elusive titanacyclobutanes, **2**, and demonstrated the existence of the crucial metallacyclobutane-carbene-olefin interconversion (Equation 2). [6]



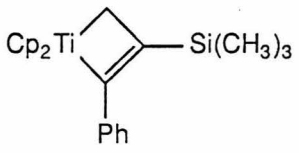

(2)

**2**

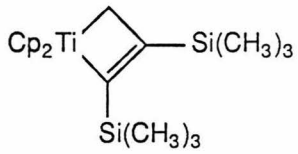
Tebbe and coworkers observed that titanacyclobutenes were not (with the exception of the bis(trimethylsilyl) derivative, **3c**) catalysts for olefin metathesis. [7] Based on x-ray crystal structure analysis of three titanacyclobutenes, **3a-c**, they concluded that **3c** was a catalyst due to a distortion toward a carbene-acetylene complex induced by the bis(trimethylsilyl) substituents. All three titanacyclobutenes which Tebbe characterized have a planar metallacycle ring and well-defined carbon-carbon single and double bonds. The bonding in metallacyclobutenes has been studied theoretically. [7b]




**3a**




**3b**




**3c**

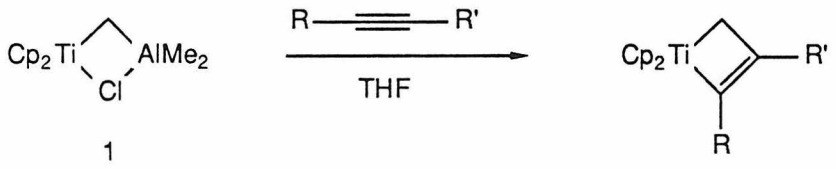
Metallacyclobutenes are a relatively rare class of compounds and are known for Ir[9], Rh[10], Pt[11], Fe[12], Zr[13], and Co[14]. The two most common methods for metallacyclobutene synthesis are 1) addition of alkynes to metal alkylidenes, and

2) addition of unsaturated ligands to metal–alkyne complexes. General synthetic routes to metallacyclobutenes are not available.

Due to the contrasting reactivity of titanacyclobutenes **3a** and **3c**, and the metathesis activity of **1** and **2**, we desired to synthesize other titanacyclobutene derivatives and explore their chemistry.

**Results**

Treatment of **1**, with a stoichiometric amount of an internal acetylene in the presence of tetrahydrofuran yields the corresponding titanacyclobutene **3** in high yield (Equation 3).




1

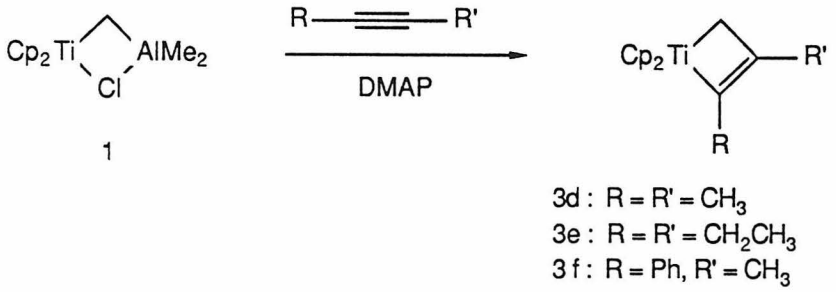
3a : R = R' = Ph
3b : R = Ph, R' = Tms
3c : R = R' = Tms

(3)

Titanacyclobutenes are dark-red or purple crystalline solids with moderate-to-high thermal stability. The diphenyl, **3a**, phenyltrimethylsilyl, **3b**, and bis(trimethylsilyl), **3c**, titanacyclobutenes have been previously isolated and each structurally characterized by Tebbe *et al.*. [7]

Utilizing the titanium metallacyclobutene methodology developed by Howard and Grubbs, [6] the formation of titanacyclobutenes has been extended to more reactive acetylenes. The titanacyclobutenes derived from 2-butyne, **3d**, 3-hexyne, **3e**, 1-phenyl-1-propyne, **3f**, may be isolated in high yield (Equation 4). Titanocenecyclobutene **3f** was isolated as a 10:1 mixture of isomers, the major isomer having the phenyl group $\alpha$ to the metal. The regiochemistry was assigned by acidolysis and analysis of the organic product, NOE experiments, or comparison of NMR chemical shifts.

The regiochemistry of addition of several unsymmetrical alkynes was explored. Addition of 4-methyl-2-pentyne (isopropyl methyl acetylene) to a solution of $\beta,\beta$–

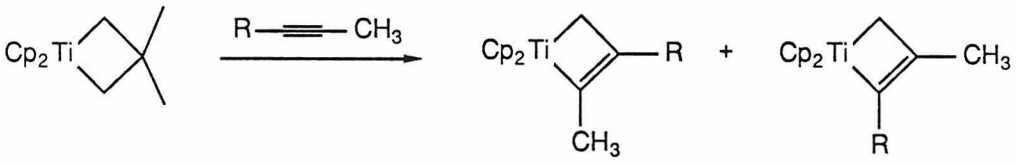



1

(4)

3d : R = R' = $CH_3$
3e : R = R' = $CH_2CH_3$
3 f : R = Ph, R' = $CH_3$

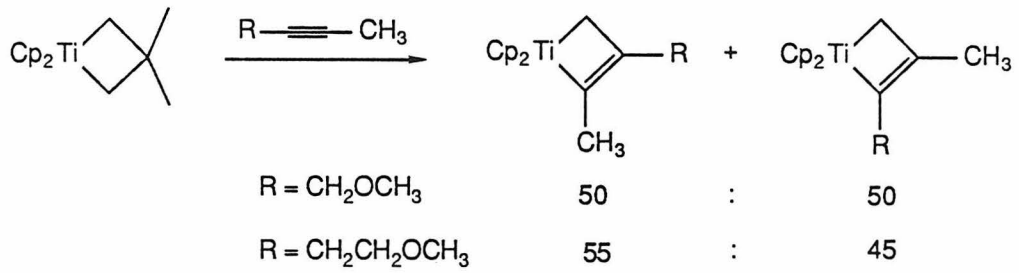
dimethyltitanacyclobutane at room temperature yields two metallacyclobutenes in a 63:37 ratio. The major isomer has the isopropyl group $\beta$ to the titanium. Reaction of 4,4-dimethyl-2-pentyne (t-butyl methyl acetylene) under the same conditions gave a >20:1 ratio of products, the major isomer having the t-butyl group at the $\beta$-position (Equation 5).




(5)

| | | | |
|---|---|---|---|
| R = $CH(CH_3)_2$ | 63 | : | 37 |
| R = $C(CH_3)_3$ | >95 | : | <5 |

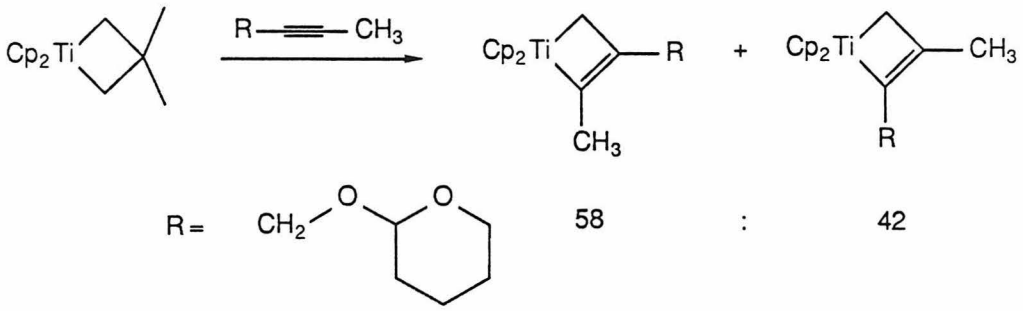
Propargyl and homopropargyl ethers react cleanly with either **1** or **2** to yield the corresponding titanacyclobutene. Treatment of a solution of **2** with 1-methoxy-2-butyne produced an equal mixture of two metallacyclobutenes. Reaction of the same alkyne with **1** was very slow in the absence of added pyridine, and many more by-products were observed. Similarly, treatment of **2** with 1-methoxy-3-pentyne yields two metallacyclobutenes in a 55:45 ratio, the major isomer bearing the larger




(6)

alkyl group at the $\beta$-position (Equation 6).

The tetrahydropyranyl ether of 2-butynol reacts cleanly with **2** to produce two isomeric metallacylobutenes in a 58:42 ratio. Use of **1** also yields the same metallacycles, although the reaction is not as clean (Equation 7).

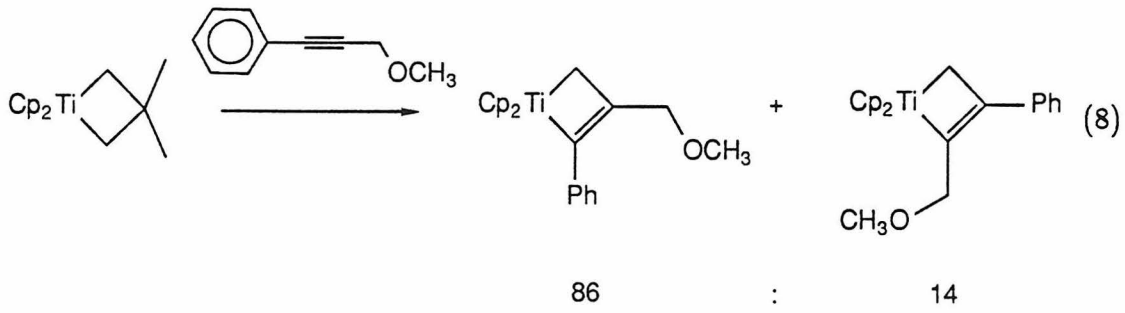



(7)

Treatment of **2** with 1-phenyl-3-methoxy propyne rapidly yields two metallacyclobutenes in a 6:1 ratio. The major isomer has the phenyl group at the $\alpha$–position to the metal. However, these titanacyclobutenes are unstable and decompose in a solution within hours (Equation 8).

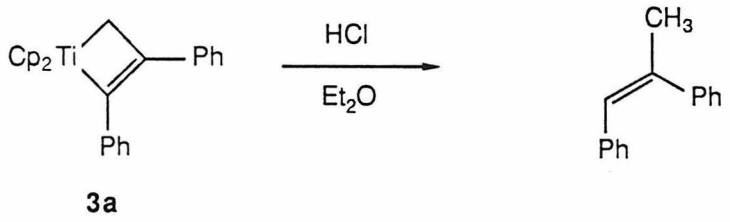
Both 2-butynylacetate and methyl 2-butynoate react with **1** or **2** to yield methylene transfer products and only small amounts of metallacyclobutenes.

The titanacyclobutenes react readily with HCl to yield the corresponding olefin




(8)

with retention of stereochemistry of the double bond. Treatment of a diethylether suspension of **3a** with 2 equivalents of anhydrous HCl produces the hydrocarbon, *cis*-1,2-diphenylpropene, in 58% yield (Equation 9). The geometry was confirmed by difference NOE experiments.

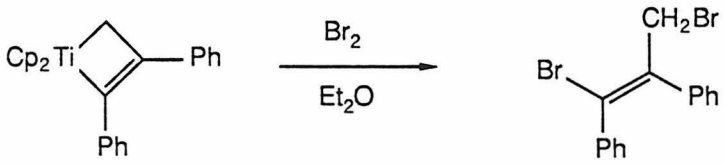



**3a**

(9)

Treatment of titanacyclobutene **3a** with two equivalents of bromine results in the formation of the corresponding 1,3 dibromide (Equation 10).

In contrast to the chemistry of titanacyclobutanes, treatment of titanacyclobutenes (–40°C to room temperature) with iodine does not result in the clean formation of a new organotitanium complex or cyclopropenes. [15] The reaction is rapid, and several products are observed. The major identifiable organotitanium product is $Cp_2TiI_2$.

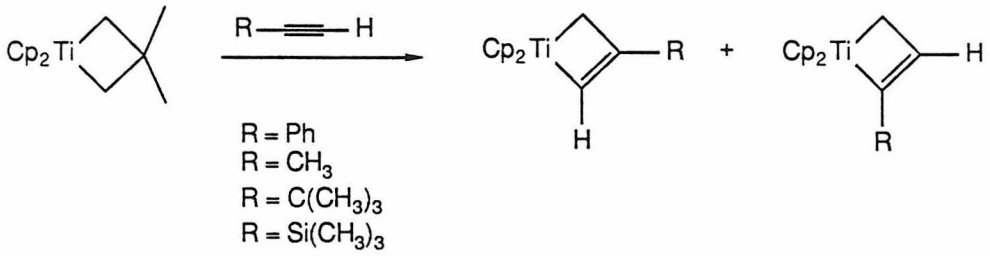



3a (10)

The thermal chemistry of titanacyclobutenes was also examined. Titanacycles **3a, b,** and **f** (all bearing at phenyl group alpha to the metal) are stable for days at 80°C in solution. The bis(trimethylsilyl) titanacyclobutene, **3c**, decomposes on warming to 80 °C, liberating bis(trimethylsilyl) acetylene. Titanacyclobutenes bearing an alkyl group at the $\alpha$-position, **3d** and **e**, are not stable at 80°C and decompose within 12 hours to paramagnetic products. The thermolysis of **3d** was performed in the presence of 2 equivalents of diphenylacetylene to trap any free methylidene or titanocene. After 24 hours at 80°C, the starting metallacycle had decomposed, and no titanacyclopentadiene was detected by NMR. The major organic product was diphenylethane.

Terminal acetylenes react readily with the $\beta,\beta$–dimethyltitanacyclobutane to yield monosubstituted titanacyclobutenes. The monosubstituted titanacyclobutenes are unstable and decompose within several hours at room temperature. Treatment of **2** with phenyl, t-butyl, trimethylsilyl, or methyl acetylene results in the rapid formation of the corresponding metallacyclobutene (Equation 11).

The formation of the monosubstituted titanacyclobutenes is not complete and some of the starting titanacyclobutane remains over when excess alkyne is used. The excess alkyne appears to form polyacetylene, possibly by protonation of the




(11)

metallacycles and the formation of titanocene acetylides. The regiochemistry of alkyne addition was not determined. Addition of olefin (t-butyl ethylene) to stabilize or trap carbene intermediates did not alter the reaction.

## Discussion

Titanacyclobutenes, **3**, are formed rapidly upon treatment of either Tebbe reagent, **1**, or titanacyclobutanes, **2**, with disubstituted alkynes. The formation of titanacyclobutenes is irreversible under normal conditions. The exception is the bis(trimethylsilyl) titanacyclobutene, **3c**, which shows a distortion in the solid state toward carbene-acetylene complex.[7] The basis for this distortion may be steric, as the trimethylsilyl groups are forced to be *cis* on the metallacycle ring. [23] Alternatively, Tebbe *et al.* and have attributed this distortion to an electronic effect induced by the absence of a phenyl ring. [7] However, formation of stable titanacyclobutenes from alkyl-substituted alkynes suggests that steric effects may play a large role.

The presence of a phenyl group does direct the regiochemistry of the alkyne addition. Tebbe *et al.* have attributed this regiochemical control to a polarization of the orbitals of the metallacyclobutene fragment by the phenyl ring. In the crystal structures of titanacyclobutenes **3a** and **3b**, the $\alpha$-phenyl ring is perpendicular to the metallacyclobutene plane, and the orbitals can effectively overlap with the titanium-carbon bond.

Titanacyclobutenes do not react in a Wittig sense with carbonyl compounds as do titanacyclobutanes (the bis(trimethylsilyl) titanacyclobutene is the exception). The irreversible nature of titanacyclobutene formation from titanocene-methylene and an internal acetylene as compared to titanacyclobutanes is primarily due to the difference in bond strength between the first and second carbon-carbon $\pi$-bond. The incremental bond strength of the first carbon-carbon $\pi$-bond is 67 kcal $mol^{-1}$ and the second carbon-carbon $\pi$-bond is 46 kcal $mol^{-1}$. [16] Thus, the titanacyclobutene is stabilized by $\sim$21 kcal $mol^{-1}$ relative to a titanacyclobutane. This comparison is a rough approximation assuming similar electronic and steric environments. Be-

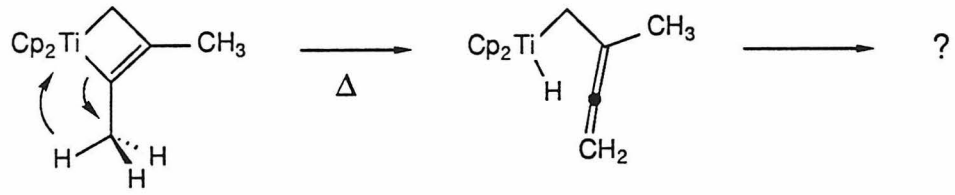
cause titanacyclobutanes are very sensitive to steric interactions, the actual energy difference may be different.[6] However, this calculated stabilization is consistent with the observed reactivity.

Thermolysis of titanacyclobutenes does not result in formation of titanocene methylene except for the bis(trimethylsilyl) derivative. The presence of a phenyl group at the $\alpha$-position enhances the thermal stability of the metallacycle. The $\alpha$–$CH_2$ group of the metallacycle does not appear to participate in the thermal chemistry even though it is allylic. If $\beta$-hydrogens are present, as in metallacycles **3d** and **e**, the compounds decompose at elevated temperatures. The products of the decomposition are presumably paramagnetic, low valent titanocene species due to the lack of NMR signals. Attempts to trap the titanocene or titanocene hydrides as titanacyclopentadienes were unsuccessful. [17] The hydrogenation reactivity of the thermolysis products is consistent with titanocene or titanium hydrides. [18]

The mechanism of the decomposition probably occurs *via* a bond homolysis or exo-cyclic $\beta$-hydrogen elimination. Exo-cyclic $\beta$-elimination (Equation 12) would initially yield an allene titanocene hydride, which would be expected to decompose or react rapidly with another titanium center. Titanium-carbon bond homolysis could yield similar products. The marked thermal stability of **3a** suggests that bond homolysis is not a dominant path because the phenyl substitutent is oriented to stablize the resulting radical. Exo-cyclic $\beta$-eliminations have been proposed in other systems [19].

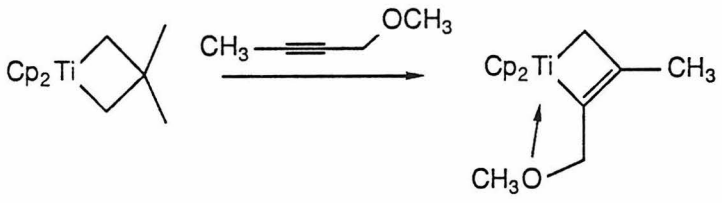
Simple disubstituted alkynes display the anticipated steric bias, placing the largest group at the $\beta$–position of the metallacycle. Both isopropyl methyl and t-butyl methyl acetylene preferentially place the larger alkyl group at the $\beta$–position.

Propargyl and homo-propargyl ethers did not display any large regiochemical bias. The coordination of an oxygen atom to the titanium-methylene might direct




(12)

the alkyne regiochemistry (Equation 13). However, no exceptional selectivity was observed. The small amount of selectivity that was obtained is attributed to steric effects. Possible reasons for the lack of selectivity are 1) the alkyne is a much better donor than the ether and consequently, the ether does not direct the addition; 2) the geometry is not favorable for ether coordination; 3) prior coordination of ligands does not occur.

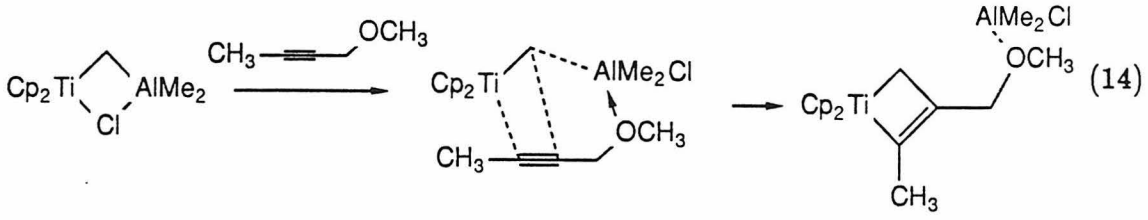



(13)

The titanium-methylene intermediate has formally 16–electron configuration. Addition of a 2–electron donor, either the alkyne or ether, achieves an 18–electron configuration. However, the coordination of both an alkyne and an ether would result in a 20–electron complex. The titanacyclobutene has a 16–electron configuration and could potentially coordinate another ligand. The titanium–methylene

species is a very high-energy species and has never been observed in its free state. Because of the exothermicity and irreversible nature of the reaction, the formation of titanacyclobutenes may have a very early transition state resulting in low selectivity.

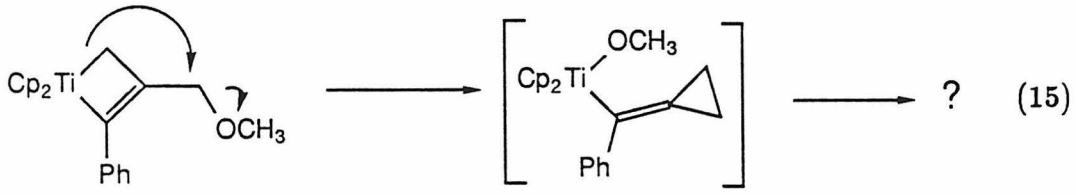
Similar results were found when the same reactions were performed starting from **1**. If there is a strong interaction between the ether and the dimethylaluminum chloride fragment, some regioselectivity might be attained (Equation 14). The reactions with **1** were quite slow in the absence of pyridine or DMAP, several by-products were observed, and no regio-selectivity was noted. It is known from Tebbe's work that tetrahydrofuran is a sufficiently strong Lewis base to activate **1** by complexing the dimethylaluminum chloride. It appears that progargyl and tetrahydropyranyl ethers are not as reactive as THF toward **1**.



(14)

The instability of the phenyl methoxymethyl titanacyclobutene was unexpected. One possible reason for its instability is the methoxy group $\beta$ to the titanium–carbon bond. A $\beta$–elimination (Equation 15) could form an intermediate containing both a titanium–oxygen bond and a methylene cyclopropane derivative. The elimination could also be bimolecular involving two titanium centers. The formation of a titanium–oxygen bond could provide a sufficient driving force for such an

elimination, and intermediates containing a methylene cyclopropane moiety would not be expected to be long-lived. $\beta$–elimination of halides has been observed in other titanocene systems.[22]

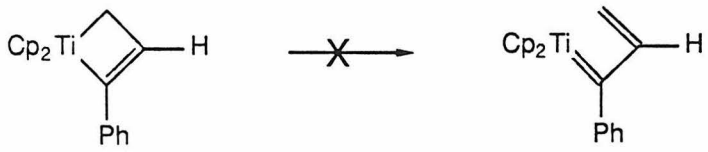



(15)

The reaction of terminal alkynes with titanocene methylene to form monosubstituted titanacyclobutenes was straightforward; however, the instability of the products was not expected. One possible explanation of the reactivity is to invoke a metallacyclobutene – vinyl carbene electrocyclic opening (Equation 16). This mechanism is proposed to occur in reactions of Group VI carbene complexes with alkynes[20] and some acetylene polymerizations.[21] However, this 2 + 2 electrocyclic ring opening has never been observed in titanocene systems. Alternatively, the alkyne could inititate the decomposition/polymerization *via* protonation of the metallacycle. It is also possible that the monosubstituted metallacyclobutenes are less stable because they are less sterically encumbered.

The oxidative cleavage of the titanacyclobutenes with either HCl or bromine results in the formation of either the hydrocarbon or dibromide. The cleavage proceeds with retention of the double-bond stereochemistry as determined by NMR analysis. This is consistent with direct protonation of the titanium-carbon bonds.

In contrast to titanacyclobutanes, neither titanocene alkenyl iodides or cyclo-




(16)

propenes were observed upon treatment with iodine, yet several organotitanium products were observed. No cyclopropene was detected by NMR, and it is unlikely that it would be stable in the presence of iodine. Although the two different titanium-carbon bonds of the titanacyclobutanes might cleave at different rates, no differentiation was observed upon reaction with one equivalent of iodine at low temperature. The iodine may attack the double bond of the metallacyclobutene ring.

## Conclusions

Several new bis($\eta^5$-cyclopentadienyl)titanacyclobutenes have been isolated. The regiochemistry of alkyne addition is related to both steric and electronic factors. The larger substituent on the alkyne prefers to occupy the $\beta$–position of the metallacycle, and aromatic substituents prefer to bond to the $\alpha$–position when present. Placement of ether functionality on the alkyne did not inhibit formation of titanacyclobutenes; however, control of the metallacyle regiochemistry was not observed.

Titanacyclobutenes containing aliphatic substituents on the metallacycle were thermally unstable, decomposing *via* $\beta$–elimination to titanium hydrides. Similar titanacycles possessing aromatic groups were very thermally stable.

## Experimental Section

See Chapter 1 for General Experimental Considerations and Instrumentation.

**Materials.** Tebbe reagent, **1**, titanacyclobutanes, **2**, and titanacyclobutenes, **3a, b,** and **c**, were synthesized by published procedures.[6] Diphenyl acetylene and bis(trimethylsilyl) acetylene were obtained from Aldrich Chemical Co. Other alkynes were obtained from Farchan Laboratories. Alkyne derivatives were synthesized by standard procedures.[24]

### Preparation of Dimethyltitanocenecyclobutene, 3d.

To a well-stirred solution of Tebbe reagent (5.00 g (90%), 15.8 mmol) in 20 ml of $CH_2Cl_2$ cooled to –20°C was added 2-butyne (2.0 ml, 25.5 mmol) followed by 4-dimethylaminopyridine (DMAP) (2.15 g., 17.6 mmol). The mixture was stirred at –20°C for 15 minutes, and then warmed to 0°C for 15 minutes. The solution was added dropwise *via* cannula to 200 ml of stirred pentane at 0°C. The dimethylaluminumchloride – DMAP adduct was removed by schlenk filtration and the filtrate concentrated *in vacuo* at room temperature to yield a red solid.

The material was dissolved in the minimum volumes of ether (30 ml) at room temperature, filtered and crystallized at –50°C. The mother liquor was removed *via* cannula, the crystals washed with cold pentane and dried *in vacuo* to yield 2.4 g (9.74 mmol, 62%) of the product. Although the metallacycle appeared to be quite stable at room temperature, it was stored in a –40°C freezer: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 5.49 (s, 10H); 3.21 (q of d, J=0.7, 2.1 Hz, 2H); 2.13 (t of d, J=0.7, 2.1 Hz, 3H); 1.51 (d of d, J=0.7, 0.7 Hz, 3H) $^1$H NMR (90 MHz, THF-$d_8$) $\delta$ 5.71 (s, 10H); 3.01 (br s, 2H); 2.12 (br s, 3H); 1.34 (br s, 3H). $^{13}$C{$^1$H} NMR (22.5 MHz, $C_6D_6$) $\delta$ 213.3, 110.2 (Cp), 88.1, 79.8 ($CH_2$), 21.7 ($CH_3$), 14.2 ($CH_3$). IR (KBr, $cm^{-1}$) 3100 (w), 3075 (w), 2940 (m), 2900 (m), 1440 (m), 1362 (m), 1050 (s), 802 (s). Anal.

Calcd. for $C_{15}H_{18}Ti$: C, 73.18; H, 7.37. Found: C, 72.99; H, 7.18.

**Preparation of Diethyltitanocenecyclobutene, 3e.**

To a well-stirred solution of Tebbe reagent, **1**, (3.00 g (~93%), 9.8 mmol) in 15 ml of $CH_2Cl_2$ at –20°C was added 3-hexyne (1.1 ml, 10.0 mmol) followed by DMAP (1.29 g, 10.5 mmol). The mixture was stirred at –20°C for 10 minutes, warmed to room temperature over the course of 20 minutes, and then cooled to –20°C. The mixture was added dropwise to 150 ml of stirred pentane at –20°C. The precipitate was removed by schlenk filtration and the filtrate concentrated *in vacuo* to yield a sticky red solid. The solid was extracted with 20 ml of pentane, the extract filtered and cooled to –50°C to deposit the product as dark red crystals. The product was isolated by removal of the mother liquor at –50°C and dried *in vacuo* to yield 1.22 g (4.45 mmol, 45%): $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 5.53 (s, 10H); 3.30 (t, J=1.9 Hz, 2H); 2.53 (q of t, J=7.5, 1.9 Hz, 2H); 2.00 (q, J=7.5, 2H); 1.04 (t, J=7.5, 3H); 0.92 (t, 7.5, 3H). Difference NOE experiments at 500 MHz: irradiation of $\delta$ 3.30 enhances $\delta$ 2.00 , 0.92; irradiation of $\delta$ 2.53 enhances $\delta$ 2.00, 1.04; irradiation of $\delta$ 2.53 enhances $\delta$ 2.00, 1.04, but not $\delta$ 3.30. $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 220.88, 109.93 (Cp), 92.00, 77.57, 29.35, 22.46, 16.03, 12.58. IR (KBr, $cm^{-1}$) 3100 (w), 2900 (w), 2850 (w), 1440 (m), 1360 (m), 1008 (s). Anal. Calcd. for $C_{17}H_{22}Ti$: C, 74.45; H, 8.08. Found: C, 73.86; H, 7.88.

**Preparation of 2-phenyl-3-methyl titanocenecyclobutene, 3f.**

To a well-stirred solution of Tebbe reagent, **1** (3.00 g (~93%), 9.8 mmol) in 15 ml $CH_2Cl_2$ at –20°C was added 1-phenylpropyne (1.2 ml, 9.8 mmol) followed by DMAP (1.29 g., 10.5 mmol). The mixture was stirred at –20°C for 15 minutes, warmed to 0°C for 15 minutes, then added dropwise *via* cannula to 150 ml of stirred pentane at –20°C. The precipitate was removed by schlenk filtration and the filtrate

concentrated *in vacuo* to yield a soft, dark solid. The solid was extracted with 60 ml of hexane, the extract filtered and cooled to –50°C to yield 1.62 g (5.25 kmmol, 55%) of the product as a dark red powder.

Alternatively, the filtrate may be extracted with diethylether (8 ml), the extract filtered, layered with an equal volume of pentane and cooled to –50°C to yield 1.85 g (6.00 mmol, 63%) of the product as a soft, dark-red solid. $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.15 (m, 5H), 5.58 (s, 10H), 3.28 (s, 2H), 1.60 (s, 3H). Occasionally, a small amount of the other regioisomer was observed: $^1$H NMR (90 MHz, $C_6D_6$7.15 (m, 5H), 5.56 (s, 10H), 3.39 (q, J=2.0 Hz, 2H), 2.22 (t, J=2.0 Hz, 3H). Major isomer: $^{13}$C{$^1$H} NMR (50 MHz, $C_6D_6$) $\delta$) $\delta$ 210.18, 147.63, 128.27 125.75, 124.44, 111.33, 94.35, 79.95, 16.80. IR (KBr, cm$^{-1}$) 3050 (w), 2920 (m), 2870 (s), 1594 (s), 1472 (m), 1010 (s), 798 (s).

**Reaction of $\beta,\beta$–dimethyltitanacyclobutane with 4-methyl-2-pentyne.**

To a solution of $\beta,\beta$–dimethyltitanacyclobutane (26 mg, 0.105 mmol) dissolved in 400 $\mu$L of $C_6D_6$ in an NMR tube was added 4-methyl-2-pentyne (12 $\mu$L, 0.105 mmol) *via* syringe. The solution was allowed to warm to room temperature and the NMR spectrum recorded. Two isomeric titanacyclobutenes were formed in a 63:37 ratio. Major product:$^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 5.491 (s, 10H), 3.095 (br q, J=1.95 Hz, 2H), 2.741 (septet, J=6.8 Hz, 1H), 2.101 (t, J=1.95 Hz, 3H), 0.887 (d, J=6.8 Hz, 6H). Minor product:$^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 5.554 (s, 10H), 3.306 (s, 3H), 2.932 (septet, J=6.8 Hz, 1H), 1.517 (s, 3H), 1.045 (d, J=6.8 Hz, 6H).

**Reaction of $\beta,\beta$–dimethyltitanacyclobutane with 4,4-dimethyl-2-pentyne.**

To a solution of $\beta,\beta$–dimethyltitanacyclobutane (26 mg, 0.105 mmol) dissolved in 400 $\mu$L of $C_6D_6$ in an NMR tube was added 4,4-dimethyl-2-pentyne (14 $\mu$L, 0.105

mmol) *via* syringe. The solution was allowed to warm to room temperature and the NMR spectrum recorded. Only one titanacyclobutene was formed. $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 5.544 (s, 10H), 3.088 (q, J=1.95 Hz, 2H), 2.158 (t, J=1.95, 3H), 1.087 (s, 9H).

**Reaction of $\beta,\beta$–dimethyltitanacyclobutane with 1-methoxy-2-butyne.**

To a solution of $\beta,\beta$–dimethyltitanacyclobutane (20 mg, 0.081 mmol) dissolved in 400 $\mu$L of $C_6D_6$ in an NMR tube was added 1-methoxy-2-butyne (10 $\mu$L, 0.087 mmol) *via* syringe. The solution was warmed to room temperature and the NMR spectrum recorded. Two isomeric titanacylobutenes were formed in nearly equal amounts. 2-Methyl isomer $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 5.67 (s, 10H), 4.24 (br s, 2H), 3.38 (br s, 2H), 3.18 (s, 3H), 1.47 (s, 3H); 3-methyl isomer $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 5.49 (s, 10H), 3.89 (s, 2H), 3.10 (s, 3H), 3.05 (br s, 2H), 2.19 (br s, 3H).

**Reaction of $\beta,\beta$–dimethyltitanacyclobutane with 1-methoxy-3-pentyne.**

To a solution of $\beta,\beta$–dimethyltitanacyclobutane (42 mg, 0.169 mmol) dissolved in 400 $\mu$L of $C_6D_6$ in an NMR tube was added 1-methoxy-3-pentyne *via* syringe. The solution was warmed to room temperature and the NMR spectrum recorded. Two isomeric titanacyclobutenes were found in nearly equal amounts; however, complete assignment of the spectrum was not possible due to overlapping peaks. Partial NMR data : $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 5.55 (s, 5H, Cp), 5.53 (s, 5H, Cp), 3.29 (m), 3.19, 3.13 (s, 3H, $OCH_3$), 2.81 (m), 2.26 (m), 2.14 (t, 3H, $CH_3$), 1.48 (s, 3H, $CH_3$)

**Reaction of $\beta,\beta$–dimethyltitanacyclobutane with tetrahydropyranyl 2-butynyl ether.**

To a solution of $\beta,\beta$–dimethyltitanacyclobutane (32 mg, 0.123 mmol) dissolved

in 400 $\mu$L of $C_6D_6$ in an NMR tube was added tetrahydropyranyl ether of 2-butynol (22 $\mu$L, 0.128 mmol) *via* syringe. The solution was warmed to room temperature and the NMR spectrum recorded. Two metallacyclobutenes were formed in a 58:42 ratio; however, the spectrum was not assigned due to overlapping resonances. Partial NMR data: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 5.70, 5.68, (major Cp), 5.52, 5.50 (minor Cp), 4.25 (m), 4.20 (m), 3.73 (m), 3.29 (m), 3.05 (br s), 2.25 (t), 1.47 (s), 1.29 (br m), 0.73 (s).

**Acidolysis of metallacyclobutene 2a.**

To a stirred suspension of diphenyl metallacyclobutene (205 mg, 0.554 mmol) in 5 ml of ether cooled to 0°C was added anhydrous HCl gas (30 ml, 1.4 mmol) *via* syringe. Immediate precipitation of $Cp_2TiCl_2$ was observed and the mixture was warmed to room temperature. The mixture was filtered through a frit and the filtrate concentrated at reduced pressure to yield 112 mg of an oil. The material was flashed through a 1-inch plug of silica gel with petroleum ether to yield 62.5 mg (58%) of cis-1,2-diphenyl propene as a white crystalline solid. $^1$H NMR (400 MHz, $CDCL_3$) $\delta$ 7.25 (m, 3H), 7.19 (m, 2H), 7.07 (m, 3H), 6.94 (m, 2H), 6.47 (br s, 1H), 2.20 (d, J=1.5 Hz, 3H). Different NOE experiments: irradiation of $\delta$ 6.47 enhances $\delta$ 2.20, 6.94; irradiation of $\delta$ 2.20 enhances $\delta$ 6.47.

**Bromination of metallacycle 2a.**

To a stirred suspension of diphenyltitanacyclobutene, **3a** (200 mg, 0.540 mmol) in 2 ml of diethyl ether cooled to 0°C was added bromine (56 $\mu$L, 1.09 mmol) *via* syringe. The mixture warmed to room temperature, filtered through a 1-inch plug with silica gel with pet ether, and the filtrate concentrated at reduced pressure to yield 121 mg of a clear oil. $^1$H NMR (90 MHz, $CDCL_3$) $\delta$ 7.41-7.07 (m, 10H), 4.60 (s, 2H). Some of the monobromides were also observed, $\delta$ 5.95 and 2.40, due to HBr

contamination of the $Br_2$. The material turned black after several days at room temperature even when protected from light.

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# Chapter 3

## Carbonylation of Bis($\eta^5$-Cyclopentadienyl) Titanacyclobutenes. Synthesis and Reactivity of Titanocene Vinyl Ketene Complexes

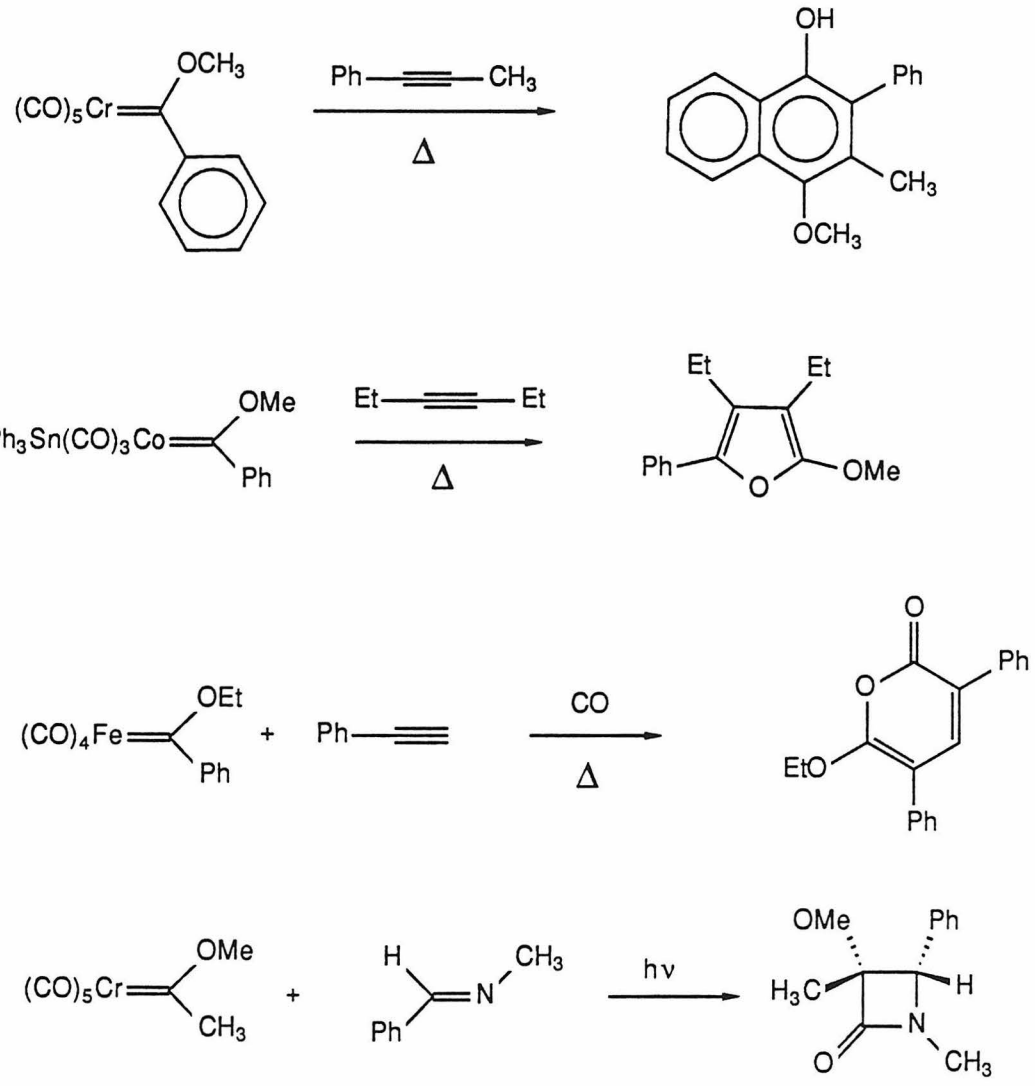
## Introduction

Mediation of complex organic transformations by organometallic catalysts and reagents is an important area of organic chemistry. Incorporation of small organic molecules by organometallic catalysts into larger more complex structures has prompted a great deal of study. [1] Potential regio- and stereoselectivity by the appropriate metal-ligand combinations has also attracted the interest of both organic and inorganic chemists. In particular, "Fischer" carbene complexes of Cr and Fe react with a variety of alkynes and carbon monoxide to form hydroquinones, [2] napthols, [2] napthoquinones, [3] or pyrones [4] and with imines to yield $\beta$-lactams [5] (Scheme 1).

The mechanism of these complex tranformations have yet to be determined, and further understanding will provide better insight into the scope and limitations of this reaction. Several proposed mechanisms suggest the formation of a metallacyclobutene complex derived from the carbene and the alkyne, followed by carbon monoxide insertion and rearrangement. [2,4] However, no metallacyclobutenes or acyl complexes have been isolated and characterized from these systems. One report of trapping experiments suggests vinyl ketenes are intermediates, [6] and a vinyl ketene has been isolated and structurally characterized as a Cr arene complex. [7]

In light of the complexity and potential utility of these annulation reactions, and our long-standing interest in titanocene-methylene chemistry, carbonylation of the titanacyclobutene system has been investigated.[26]

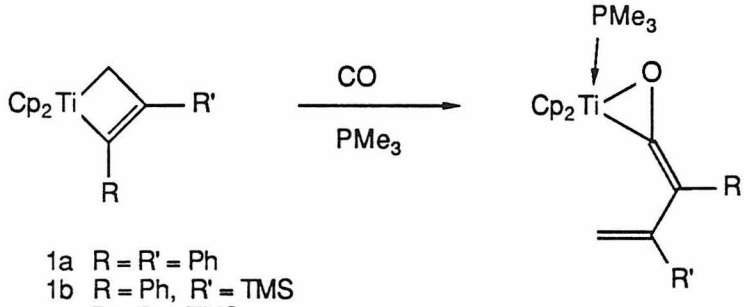
**Scheme 1.** Reactivity of Fischer Carbenes and Alkynes



## Results

### Synthesis of Titanocene Vinyl Ketene Complexes

Treatment of a toluene solution of titanacyclobutene, **1**, with carbon monoxide in the presence of 1 equivalent of trimethylphosphine (Equation 1) produces [9] the titanium vinyl ketene complex, **2**.




(1)

1a R = R' = Ph
1b R = Ph, R' = TMS
1c R = R' = TMS
1d R = R' = $CH_3$
1e R = R' = $CH_2CH_3$

The carbonylation proceeds with a variety of titanacyclobutenes to yield the corresponding ketene complex in good yield, Table 1. The bis(trimethylsilyl) titanacyclobutene, **1f**, does not react to yield an analogous product even under forcing conditions (80 °C, 3 days). [10] The use of $^{13}C$-enriched CO (90% $^{13}C$), followed by $^{13}C$ NMR analysis shows exclusive incorporation of the $^{13}C$ label at the metal-bound ketene carbon. In the absence of a Lewis base, the carbonylation proceeds to produce a sparingly soluble, oligomeric ketene adduct, **3**, which may be dissolved by the addition of a ligand such as trimethylphosphine, pyridine, or THF. [9b] The carbonylation and rearrangement is not reversible on prolonged heating. Exhaustive carbonylation at room temperature leads to the formation of paramagnetic products and a small amount of free vinyl ketene.

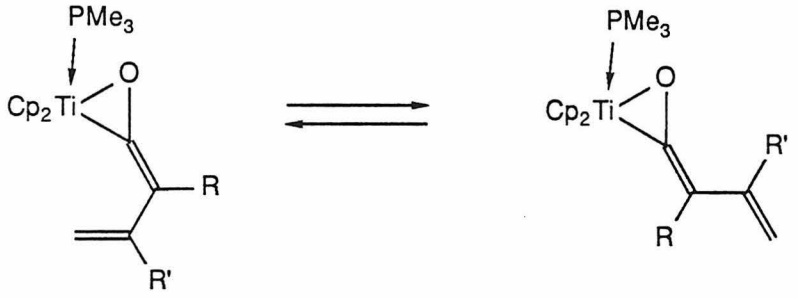
Crystals of **2b** suitable for an x-ray diffraction analysis were obtained and the refined structure is shown in Figures 1 and 2. [11] Details of the data collection and

**Table 1.** Titanocene – Vinyl Ketene Trimethylphosphine Complexes

| Compound | R | R′ | Yield (%) |
|---|---|---|---|
| **2a** | $\phi$ | $\phi$ | 82 |
| **2b** | $\phi$ | TMS | 92 |
| **2c** | $\phi$ | $CH_3$ | 80 |
| **2d** | $CH_3$ | $CH_3$ | 77 |
| **2e** | $CH_2CH_3$ | $CH_2CH_3$ | 70 |

refinement are in Appendix 1.

Ketene complexes **2c**, **2d**, and **2e** exist in two isomeric forms. Based on NMR nuclear Overhauser experiments, the isomerization occurs about the carbon-carbon double bond of the ketene (Equation 2).




R = $CH_3$, $CH_2CH_3$, Ph
R' = $CH_3$, $CH_2CH_3$

(2)

Addition of trimethylphosphine to a suspension of the oligomeric ketene complex (*vide supra*) initially yields one isomer of the complex ($^1$H NMR), but over several hours at room temperature an equilibrium between isomers is established. Monitoring the isomerization by NMR yields a forward rate constant, $k_1 = 6.8 \pm 1.0 \times 10^3$ min$^{-1}$ and a reverse rate constant, $k_{-1} = 4.1 \pm 0.6 \times 10^3$ min$^{-1}$

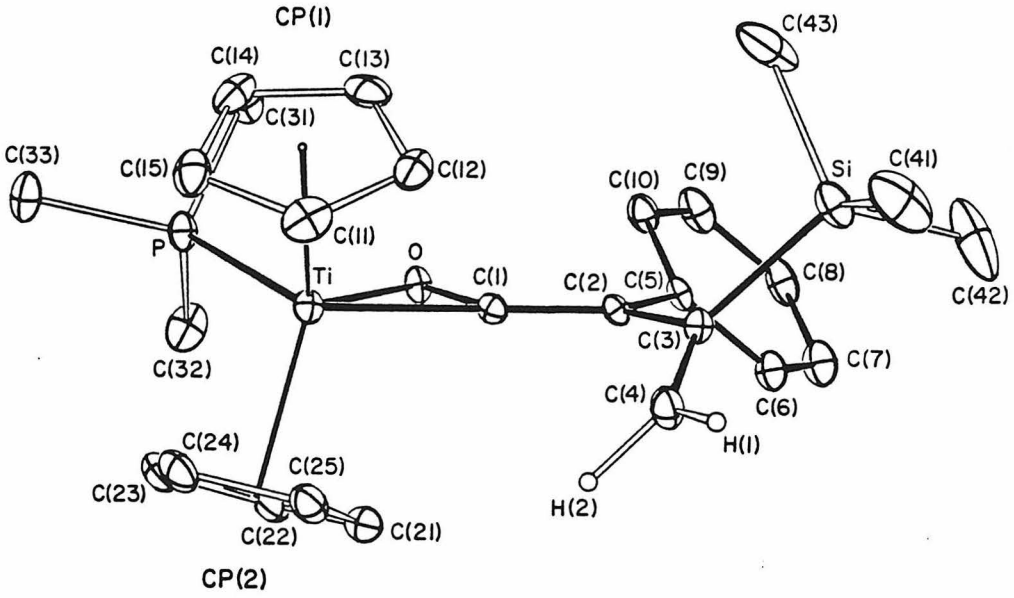



**Figure 1.** ORTEP Drawing of **2b** with Atom Labeling.

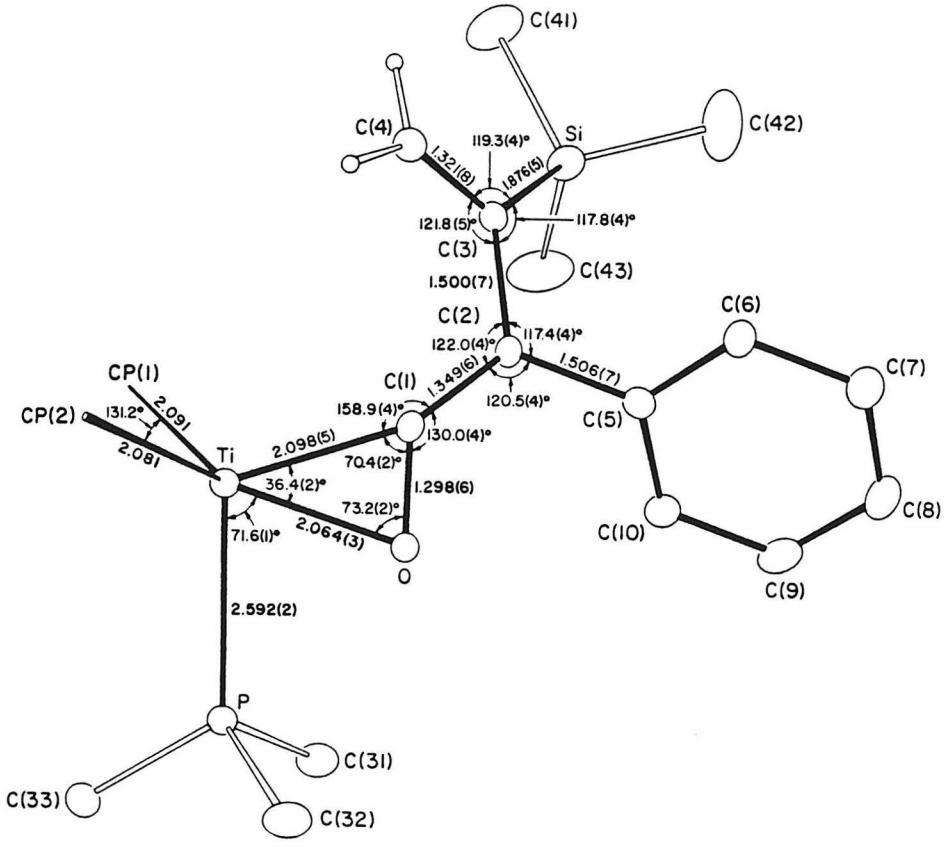
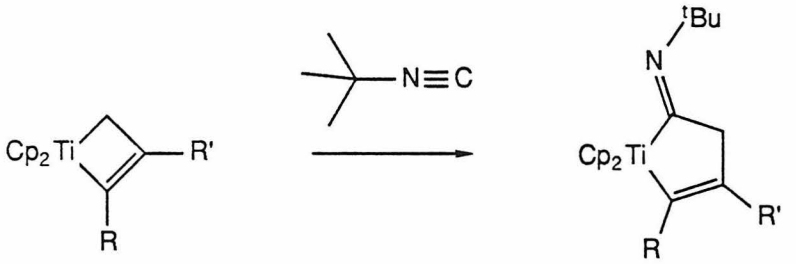



**Figure 2.** ORTEP Drawing of **2b** with Selected Bond Lengths and Angles.

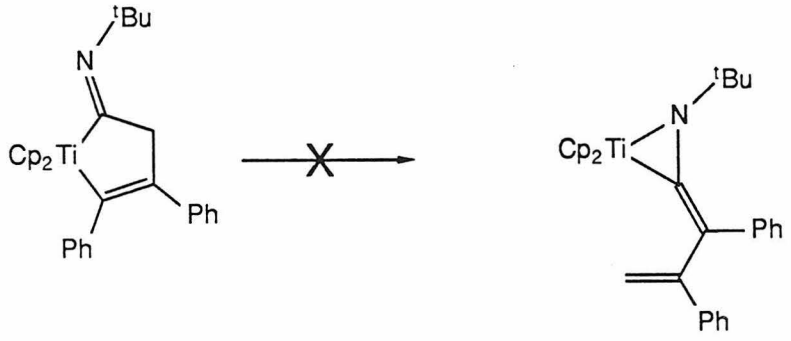
at 303 K.

Titanacyclobutenes also readily insert molecules, which are isoelectronic with CO, such as isocyanides (Equation 3). Treatment of a solution of titanacyclobutene **2a** with one equivalent of t-butylisocyanide yields the iminoacyl complex , **4**, quantitatively by NMR.[26] The iminoacyl complexes are orange, crystalline compounds and exhibit IR stretches at $\sim 1700\ cm^{-1}$. The compounds are thermally stable and do not rearrange to an aza-ketene (Equation 4).




(3)

4a R = R' = Ph
4b R = Ph, R' = TMS
4c R = Ph, R' = $CH_3$
4d R = R' = $CH_3$




(4)

Crystals of **4a** suitable for x-ray diffraction analysis were obtained from toluene solution and the refined structure is shown in Figure 3. Details of the data collection and structure refinement are in Appendix 2.

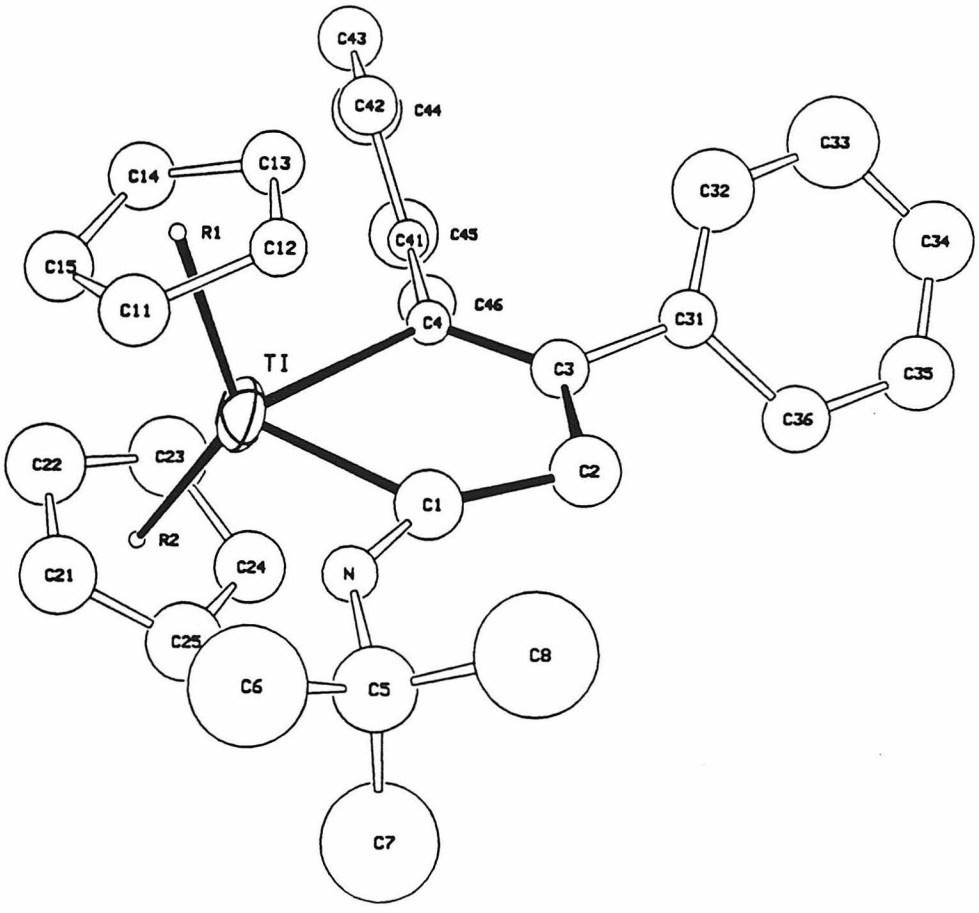



**Figure 3.** ORTEP Drawing of **4a**.

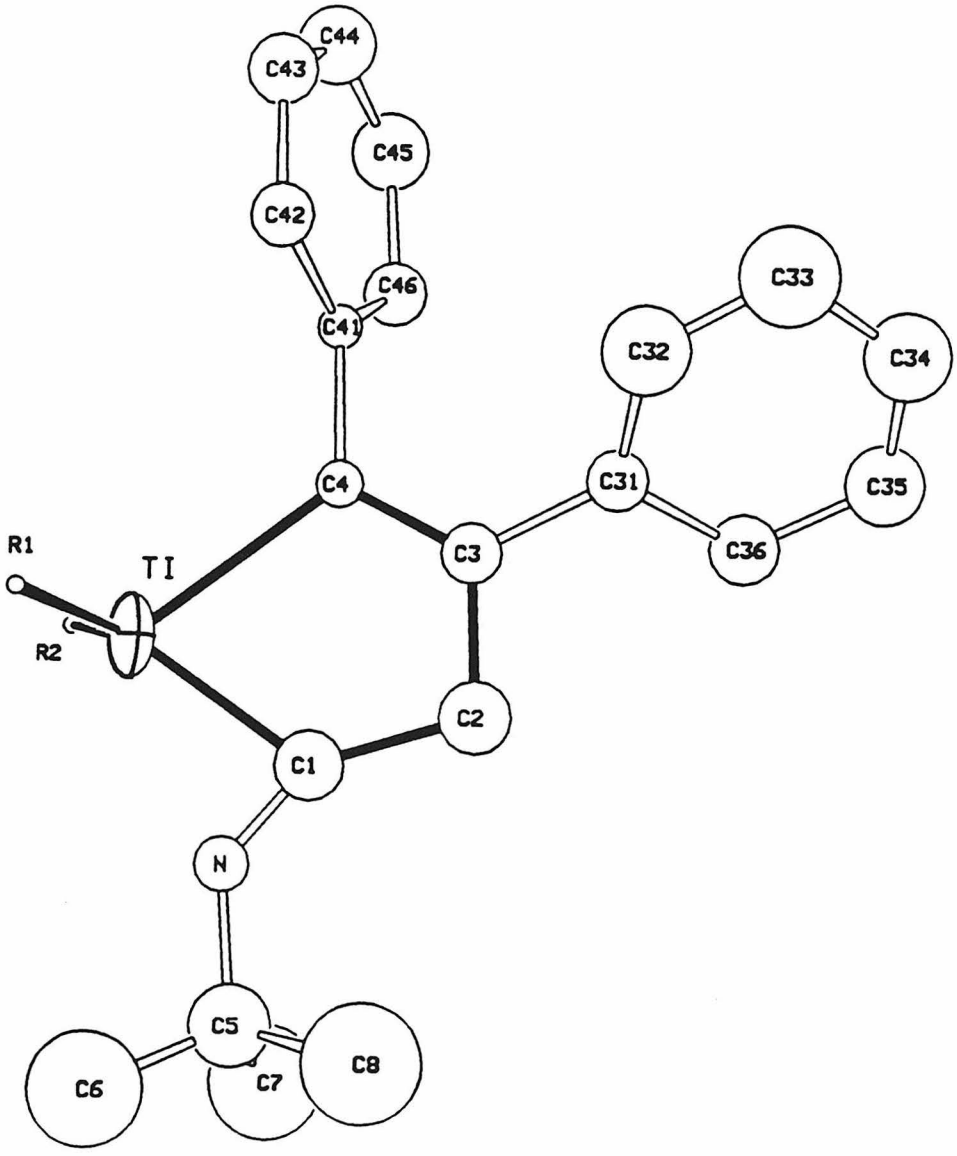
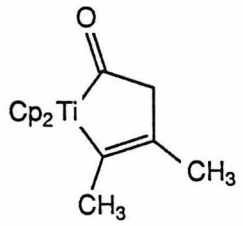



**Figure 4.** ORTEP View of the Metallacycle Plane of **4a**.

## Mechanism of Titanacyclobutane Carbonylation

During the carbonylation of **1d**, a transient green color was observed. By use of low-temperature $^{1}H$ and $^{13}C$ NMR, $^{13}CO$ labeling and IR, the intermediate was identified as the titanocene acyl complex **5**. Only titanacyclobutene **1d** gives an observable acyl intermediate, although a transient green or brown color is observed during the carbonylation of **1c** and **1e**.



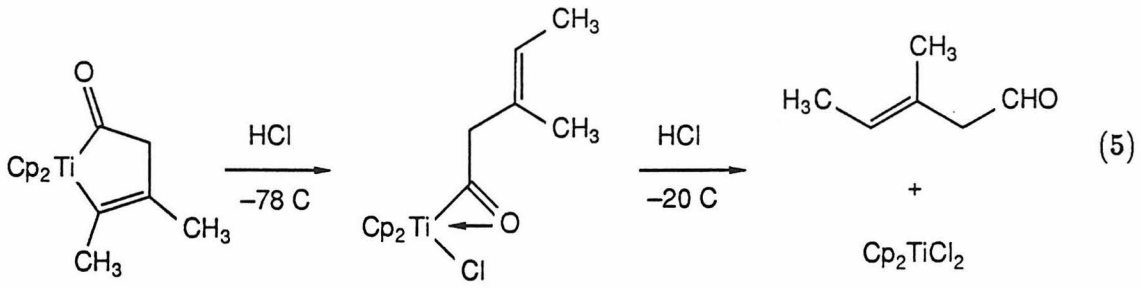

5

The intermediate is unstable in solution above –30 °C but is moderately stable in the solid state at room temperature. The IR shows an intense absorption at 1615 $cm^{-1}$, indicative of an acyl with little $\eta^2$–character. [14,15] In order to establish which side of the metallacycle the CO inserts, the acyl intermediate was synthesized with $^{13}CO$ and the $^{13}C-^{13}C$ coupling constants determined from the $^{13}C\{^{1}H\}$ NMR. The $^{13}C$ NMR signal for the acyl carbon is $\delta$ 294. The $^{13}C-^{13}C$ coupling constant from the acyl carbon to the methylene carbon was 11.9 ± 0.9 Hz, but neither of the $^{13}C$ couplings to the olefinic carbons was larger than 5.5 ± 0.9 Hz. The 11.9 Hz coupling is small for a one-bond $^{13}C$-$^{13}C$ coupling, [16] but it is consistent with other titanocene acyls. [17]

To test for the possibility of a reversible carbonylation of the metallacycle, a toluene solution of the acyl **5** was prepared with $^{13}CO$ (90% $^{13}C$) and immediately cooled to –78 °C. The $^{13}CO$ atmosphere was replaced with natural abundance $^{12}CO$

at 100 psi and the solution warmed to –30 °C to effect the rearrangement. NMR analysis of the ketene complex revealed complete loss of the $^{13}C$ label. The high pressure of CO is necessary to obtain 1 equivalent of CO in solution, due to the low solubility of CO in toluene. [18] The loss of the $^{13}C$ label was observed regardless of solvent (toluene, diethylether, THF), or the addition of trimethylphosphine.

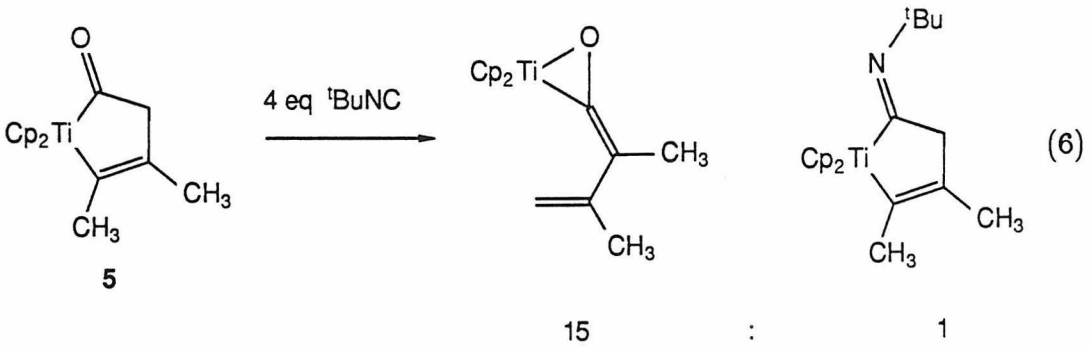
Attempts to identify the acyl species by decomposition of the intermediate **5** with either trifluoracetic acid or HCl were unsuccessful due to the apparent rapid decarbonylation of the acyl in the absence of excess carbon monoxide.[27] However, if a solution of the acyl in diethyl ether under 100 psi of CO is treated with excess anhydrous HCl at –78 °C, the corresponding titanocene acyl chloride **6** may be obtained (Equation 5). The $^1H$ NMR confirms the predicted structure of the acyl chloride derived from titanium-vinyl bond cleavage by one equivalent of HCl. If the reaction mixture is warmed to –20 °C in the presence of excess HCl, the products are titanocene dichloride and 3-methyl-3-pentenal. The aldehyde was very difficult to isolate, so it was transformed to the 2,4-dinitrophenylhydrazone (DNP) derivative. NMR analysis of the DNP derivative showed that the $\beta - \gamma$ double bond had migrated into conjugation with the hydrazone.




**5** (5)

In order to determine if the acyl complex **5** is on the reaction path to ketene

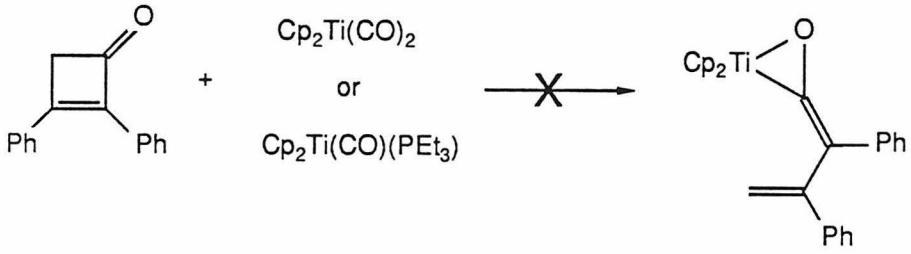
product, a solution of **5**, was treated with t–butylisocyanide. The t–butyl isocyanide traps any free metallacyclobutene formed from decarbonylation of **5**. Both the metallacyclobutene **1d** and the vinyl ketene complexes **2d** and **3d** react with t-butyl isocyanide to give observable products. [19] Treatment of the ketene complex with t-butylisocyanide gives a mixture of products; however, the ratio of the products is reproducible. Treatment of metallacyclobutene **1d** with one equivalent of t-butylisocyanide yields quantatively the iminoacyl complex **4d** (*vide supra*). To determine the relative rates of the insertion of t-butylisocyanide versus CO into the metallacyclobutene, a solution with equimolar concentrations of t-butylisocyanide and CO was reacted with the metallacycle. Within the detection limits of the NMR, only the formation of **4d** was observed. This result demonstrates that if any **1d** were formed during the rearrangement of **5** to **2d**, it would be rapidly trapped by the t-butylisocyanide. The iminoacyl complex **4d** does not react with CO under the experimental conditions. Treatment of **5** in the absence of CO at –78 °C with four equivalents of t-butylisocyanide, followed by warming to room temperature, results in a 15:1 ratio of vinyl ketene products to **4d** (Equation 6).




Attempts to determine accurately the kinetic parameters of the carbonylation were thwarted by several factors. The observed rate of rearrangement of **5** is de-

pendent on the concentration of $PMe_3$ and the partial pressure of CO. An increased concentration of $PMe_3$ slows the rearrangement, and an increase of CO presence accelerates the rate of reaction. However, neither trimethylphosphine nor excess CO is necessary for conversion of the metallacycle to ketene complex.

In efforts to demonstrate the cyclobutenone complex as a viable intermediate, a sample of 1,3-diphenylcyclobut-2-ene-1-one was prepared [21] and treated with titanocene dicarbonyl and titanocene carbonyl triethylphosphine complex [22] (Equation 7). However, in neither case was a titanocene ketene product observed.

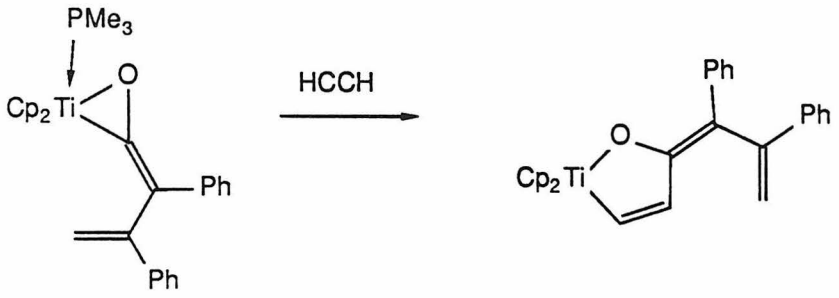



(7)

## Reactivity of Titanocene Vinyl Ketene Complexes

Titanocene vinyl ketene complexes react with several unsaturated organic substrates. Ketene complex **2a** reacts rapidly with acetylene (Equation 8) to yield the corresponding green titanaoxacyclopentene **7a** in high yield. The reaction works equally well with the ketene oligomer **3a**. The reaction is faster in coordinating solvents that solubilize the ketene oligomer. The resulting titanaoxacyclopentenes are thermally stable.

Ketene complex **2d** or the oligomer **3d** also inserts acetylene to yield a titanaoxacyclopentene; however, the initial oxacyclopentene isomerizes to an equilibrium mixture of two oxacyclopentenes, **7b** and **7c** (Equation 9). Both isomers have

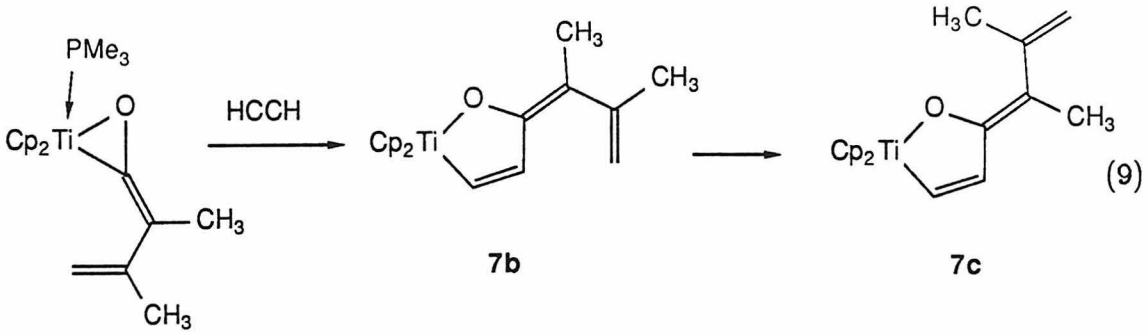



2a or 3a

7a

(8)

very similar NMR spectra and color. Based on the NMR spectra, the isomerization occurs about the exo-cyclic double bond. The titanaoxacyclopentenes did not react with methyl iodide.




2a

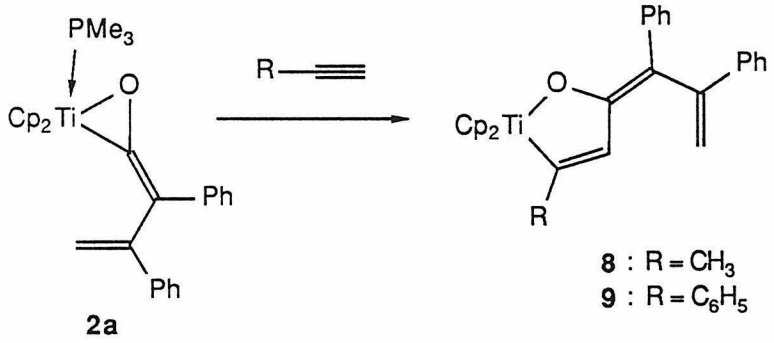
7b

7c

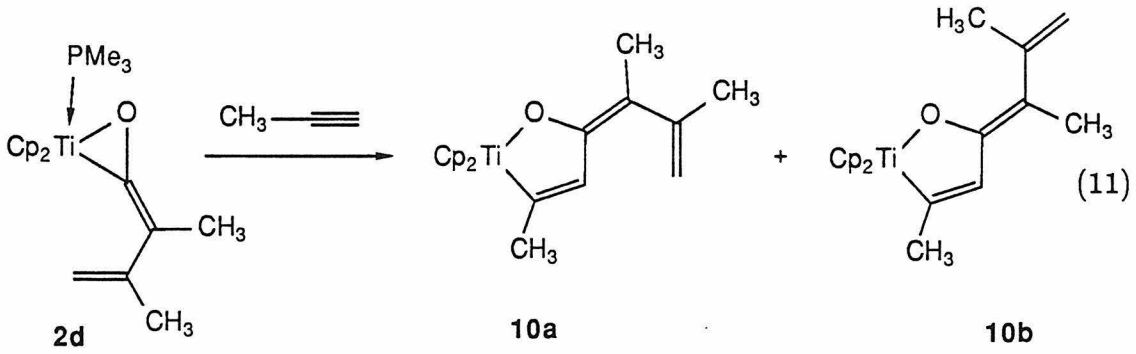
(9)

Terminal alkynes also insert into the vinylketene complexes. Propyne and phenyl acetylene react with **3a** to yield substituted titanaoxacyclopentenes **8** and **9**, respectively. Analysis of the products shows only one regioisomer. NMR analysis and NOE experiments indicate that the substituent is located at the $\alpha$–position of the metallacyclic ring (Equation 10). Internal alkynes do not react with the ketene complexes.

Ketene complex **3d** also reacts with propyne to form an analogous titanaoxacyclopentene **10b**. As was found with the acetylene insertion, the kinetic isomer,




(10)




(11)

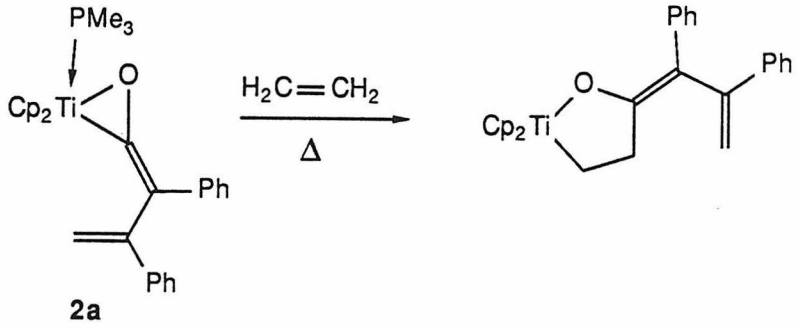
**10b**, equilibrated to a mixture of isomers, **10b** and **10c** (Equation 11).

In contrast to alkynes, nitriles did not insert into **3a**. NMR spectra did confirm that the nitrile was coordinated to the ketene complex, yet no reaction was observed.

Ketene complex **2a** will insert ethylene under moderately vigorous conditions (80 °C, 12 hrs) to yield a purple titanaoxacyclopentane (Equation 12). Substituted alkenes are unreactive toward insertion.

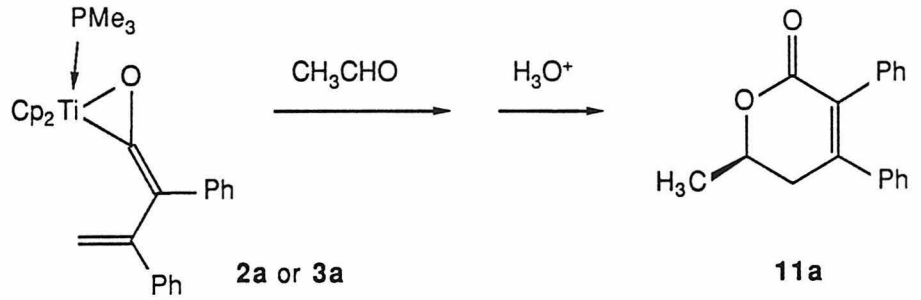
The vinyl ketene complex **3a** did not appear to be nucleophilic. The complex did not react with methyl iodide at room temperature.

Treatment of the vinyl ketene complexes at room temperature with aldehydes results in the immediate formation of a new purple complex. The $^1$H NMR shows inequivalent $\eta^5$-cyclopentadienyl resonances and absence of the terminal vinyl $CH_2$

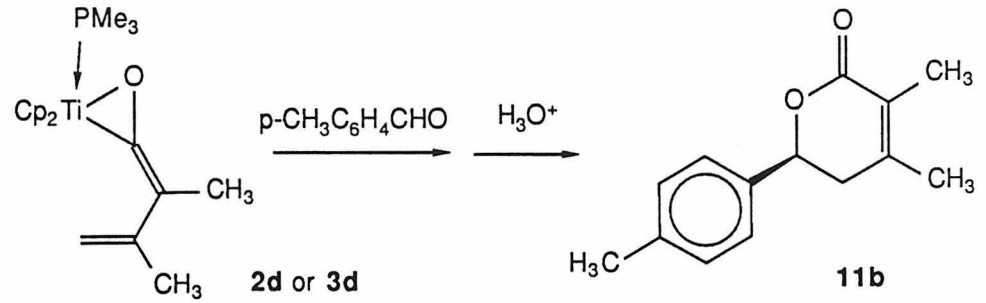



2a (12)

resonances. The complex is unstable and decomposes over several hours to paramagnetic products. Quenching of the reaction mixture followed by normal organic work-up and flash chromatography yields the lactones **11a** and **11b** (Equation 13) in 44% and 25% yield, respectively. Attempts to increase the yield by adding reagents such as diphenylacetylene to trap the titanium by-products were unsuccessful.




**2a** or **3a** **11a**

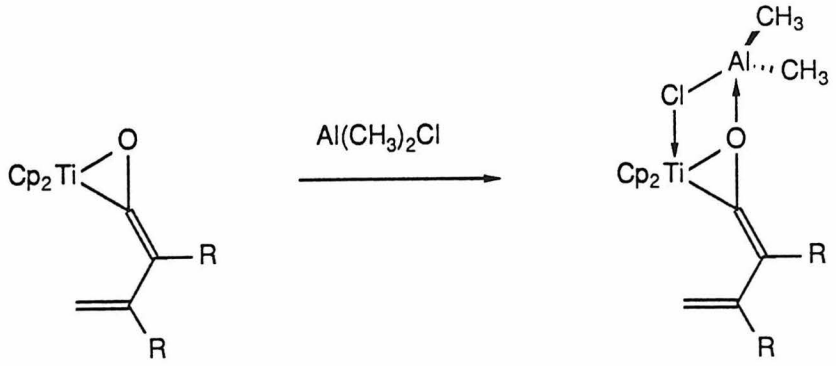



**2d** or **3d** **11b** (13)

Examination of the initial aldehyde reaction by $^{13}C$ NMR with $^{13}C$-enriched ketene complex (derived from $^{13}CO$), revealed a new resonance at $\delta$ 276.2. The IR spectrum of the reaction solution also revealed a band at 1595 $cm^{-1}$, which shifted

to 1560 $cm^{-1}$ when the starting ketene complex was labeled with $^{13}CO$. Ketones (acetone, acetophenone) did not react.

The vinyl ketene complexes also react rapidly with alkyl aluminum reagents. Addition of one equivalent of dimethylaluminum chloride to a suspension of the ketene oligomer in $C_6D_6$ at room temperature results in the immediate formation of a new ketene complex. The NMR spectra suggest that the new complex is a 1:1 adduct, in which the aluminum is complexed to the ketene oxygen (Equation 14). An analogous, but less stable, complex is also formed from trimethylaluminum. The complexation does not activate the ketene complexes toward olefin insertion.

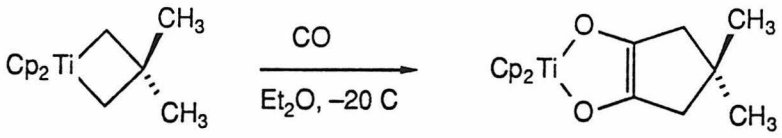



(14)

**3a** R = Ph
**3d** R = $CH_3$

## Discussion

Titanacyclobutenes carbonylate to yield vinyl ketene complexes, **2**, in high yield. This reactivity is in contrast to titanacyclobutanes, which carbonylate to yield titanocene ene-diolate complexes (Equation 15).[28] The formation of ene-diolate complexes presumably arises from rapid interception of the initially formed acyl species by a second equivalent CO. Cyclobutanones can be isolated in low yield from the carbonylation under conditions of limited CO. Carbonylation of titanacyclobutenes shows no evidence for the formation of either cyclobutenes or ene-diolates.




(15)

The difference in reactivity could arise from two factors. The coordination and insertion of the second CO molecule may be hindered by the substituent on the metallacyclobutene ring. All titanacyclobutenes in this study have a substituent at the $\alpha$–position. A second possibility may be that the intramolecular migration of the vinyl group to the acyl is faster than alkyl group migration. No data on the relative rates of alkyl vs. vinyl migration are available. Substituent effects on the migration of benzyl groups in $CpMo(CO)_3$(benzyl) indicate that electron donation accelerates the migratory insertion.[29]

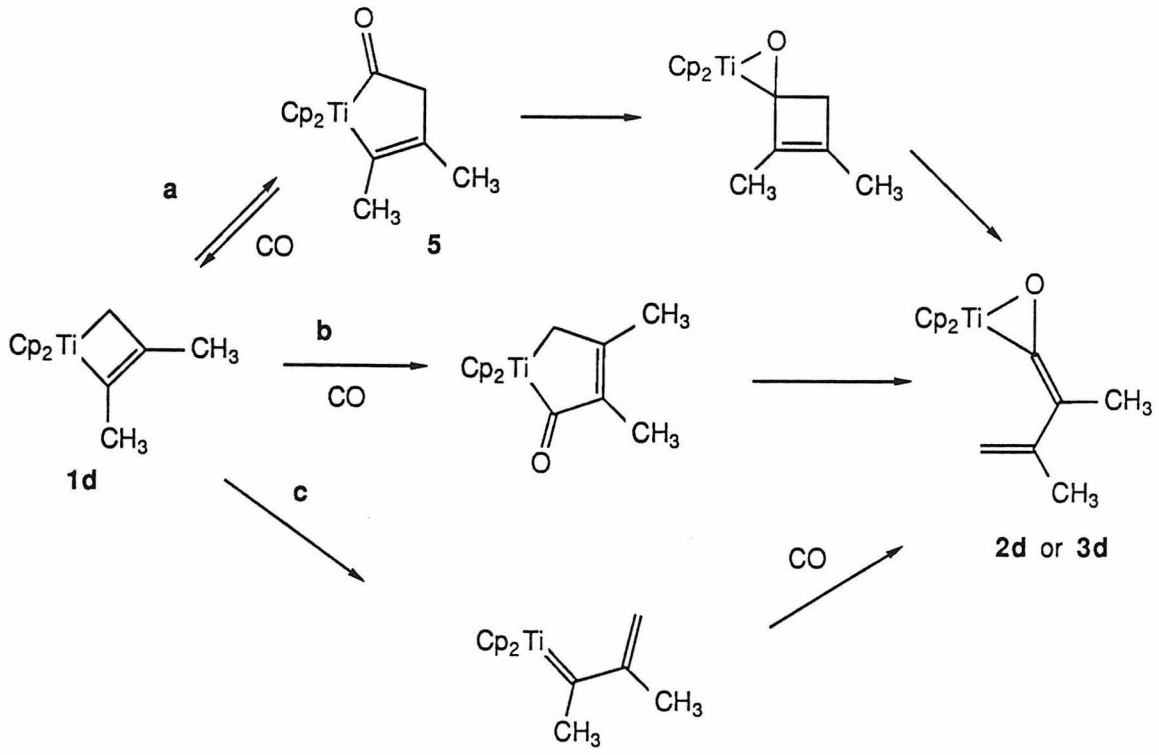
Although the isolation and characterization of the acyl complex **5** is inter-

esting, it does not provide sufficient evidence to distinguish among other possible mechanisms leading to vinyl ketene formation. Three reasonable mechanisms for the carbonylation and formation of ketene complexes are shown in Scheme 2. The metallacyclobutenes have two different titanium–carbon bonds and carbonylation of either bond could lead to the observed product (Scheme 2). It must be determined if 1) the isolated acyl complex **5** leads directly to ketene product (Scheme 2, path **a**), or 2) it is the kinetic product of carbonylation into the more sterically accessible titanium-carbon bond which, in a subsequent step, decarbonylates, and the reaction occurs *via* carbonylation of the titanium-vinyl bond (Scheme 2, path **b**). The methyl group at the $\alpha$–position of the metallacycle could hinder the insertion of CO into the Ti–vinyl bond and result in the kinetic formation of **5**. The loss of the $^{13}C$ label proves that the acyl intermediate, **5**, carbonylates reversibly. However, it does not distinguish between paths **a** or **b**.

An alternative mechanism involves the ring opening of the titanocenecyclobutene to a titanocene vinyl alkylidene complex (Scheme 2, path **c**). [24] Carbonylation of the alkylidene could yield the ketene complex.[2,30] This mechanism is unlikely for several reasons: the observation and isolation of the acyl intermediate, **3**, the results of the isocyanide trapping experiments, and the lack of alkylidene transfer reactions of the titanocenecyclobutenes with ketones. In contrast to the reactivity of titanocenecyclobutanes, which is dominated by titanocene-methylene chemistry,[20] the titanocenecyclobutenes exhibit reactivity similar to that observed for titanocene alkyl complexes. [19]

The intermediate acyl complex has a relatively high IR stretch at 1615 $cm^{-1}$. Transition metal acyl complexes containing an $\eta^2$–acyl usually display IR stretches at *ca.* 1500 $cm^{-1}$.[31] The high IR stretch suggests that **5** has considerable $\eta^1$–acyl character. The $^{13}C$ NMR shift of $\delta$ 285 is consistent with both $\eta^1$- and $\eta^2$-

**Scheme 2.** Mechanism of Carbonylation of **2d**




transition-metal acyl complexes.[32]

Acidolysis of **5** yielded the expected aldehyde. It was necessary to perform the acidolysis under a high pressure of CO to prevent decarbonylation. Although the aldehyde double bond had shifted into conjugation with the carbonyl, only CO insertion into the $sp^3$ titanium–carbon bond can result in the observed product. The differentiation of the cleavage of the cyclic acyl species, **5**, is interesting. The titanium–carbon bond is cleaved by HCl at –78°C, but the remaining titanium acyl bond does not react rapidly until approximately –20°C. These observations firmly establish that CO inserts into the Ti–C($sp^3$) bond in the initial carbonylation step.

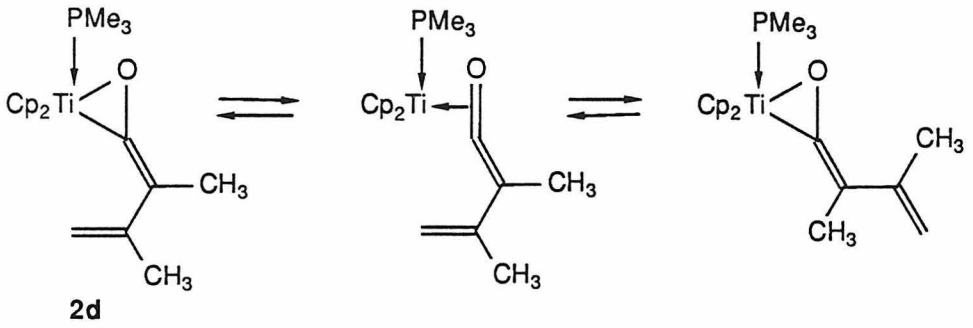
The competitive trapping of **5** with t-butylisocyanide demonstrates that it is not necessary for the acyl complex to decarbonylate during the reaction. If any of

the metallacycle were formed, it would be trapped as **4**. In order for the two acyl species to equilibrate, the CO must migrate to the other side of the metallacycle. Although a bi-molecular mechanism cannot be ruled out, migration of the CO to the opposite side of the metallacycle without trapping by the t-butyl isocyanide is unlikely. Therefore, the reaction proceeds *via* carbonylation of the $sp^2$ bond of the metallacycle.

Given the experimental data, path **a** of Scheme 2 is the most likely mechanism. The intramolecular attack of a coordinated, cyclic acyl to form a ketone complex in a Zr system has been postulated. [15] Carbonylation of hafnocene metallacyclobutanes yields a dimer containing both cyclobutanone and ene-diolate complexes.[33] Cyclobuteneones have been isolated from the reaction of Fischer carbene complexes with alkynes. [25] The lack of $\eta^2$–acyl character in **5** and the formation of a Ti–O bond in the ketene provide a driving force for the reaction.

To confirm that a cyclobuteneone complex is a viable intermediate, diphenyl cyclobuteneone was treated with $Ti^{II}$ precursors, $Cp_2Ti(CO)_2$ and $Cp_2Ti(CO)(PEt_3)$. No ketene products were observed in either case. A ketene complex was not formed due to the difficulty of displacing the ligands already on the titanium and the propensity of low-valent titanium derivatives to reduce ketones. [23]

The isomerization of the ketene complexes was unexpected. Previously isolated Group IV ketene complexes did not display any evidence for isomerization or liberation of ketene. The rate of isomerization and the equilibrium ratio is not influenced by excess trimethylphosphine. The mechanism for isomerization may involve a $\pi$–bound ketene intermediate. [12,13] The ketene complexes **2a** and **2b** have bulkier substituents on the ketene skeleton that apparently prevent the isomerization. The intermediacy of a $\pi$–bound ketene complex could explain the formation of a small amount of free vinyl ketene during prolonged carbonylation




(16)

The crystal structure of **2b** displays some interesting features. The $\eta_2$–coordination of the ketene group places the six atoms Ti, O, C(1), C(3), and C(5) in a plane (maximum deviation from Ti-O-C(1) plane 0.13 Å). The vinyl ketene moiety adopts an *s-cis* conformation to reduce the steric interaction between the trimethylsilyl group and the cyclopentadienyl ligands. The terminal double bond and the phenyl rings were expected to be coplanar to maximize electronic overlap. However, the substituents are twisted relative to the ketene plane by 38.5(8)°and 42.7(7)°, respectively. The absence of a planar vinyl ketene has been observed for an arene–coordinated Cr vinyl ketene complex and is attributed to the steric repulsions prevailing over the electronic effects. [7] The trimethylphosphine ligand is slightly (0.42 Å) out of the plane defined by the Ti, O, and C(1). The ketene complex, **2b**, retains the relative connectivity of the carbon skeleton found in the starting titanacyclobutene, **2a**. [8b]

The only other structurally characterized titanocene ketene complex is a bridged diphenyl ketene dimer. [9c] A closely related ketene complex of permethylzirconocene has been structurally characterized as the pyridine adduct. [9a] All three crystal structures exhibit similar $\eta_2$–bonding of the ketene fragment. Pertinent bond lengths and angles are in Table 2.

**Table 2. Selected Bond Lengths (Å) and Angles (°) of 2b.**

| | |
|---|---|
| Ti – O | 2.064(3) |
| Ti – C(1) | 2.098(5) |
| Ti – Cp(1)* | 2.091 |
| Ti – Cp(2)* | 2.081 |
| Ti – P | 2.592(2) |
| C(1) – O | 1.298(6) |
| C(1) – C(2) | 1.349(6) |
| C(2) – C(3) | 1.500(7) |
| C(3) – C(4) | 1.321(8) |
| | |
| C(1) – Ti – O | 36.4(2) |
| Ti – C(1) – O | 70.4(2) |
| C(1) – O – Ti | 73.2(2) |
| O – Ti – P | 71.6(1) |
| Ti – C(1) – C(2) | 158.9(4) |
| O – C(1) – C(2) | 130.0(4) |
| Cp(1) – Ti – Cp(2)* | 131.2 |

* Cp(1) and Cp(2) are the $\eta^5$-cyclopentadienyl ring centroids.

The crystal structure of iminoacyl complex **4a** has some strong similarities with the structures of the titanacyclobutenes **3a-c**. Due to decomposition of the crystal in the x-ray beam, the errors in the atomic positions are moderate; however, the structure contains some interesting features. Pertinent bond lengths and angles are in Table 3. The metallacycle ring is flat, containing well-defined carbon-carbon double and single bonds. The $\alpha$–phenyl ring is oriented perpendicular to the metallacycle plane. The Ti–N distance is 2.23(2)Å, and the Ti–(C1)–N and C(2)–C(1)–N angles are 83(2)°and 147(3)°, respectively. The Ti–C(1) distance of 2.02(3)Å is substantially less than the Ti–C(4) distance 2.34(3)Å. The Ti–C(4) distance is exceptionally long for a Ti–C bond and thus may reflect distortion prior

to migration of the vinyl ligand. In contrast, the titanacyclobutene metallacycle structures contain nearly equal $sp^2$ and $sp^3$ Ti–C bond lengths.

The iminoacyl group is correctly positioned relative to the titanocene fragment to interact with the empty LUMO on the metal. The iminoacyl complex is formally a 16 electron complex and could accommodate imido-coordination. The coordination could also contribute to lengthening of the Ti–C(4) bond. The Ti–N distance is 2.23(3)Å, a reasonable distance for interaction. The intense stretch at 1772 $cm^{-1}$ is more consistent with $\eta^1$–bonding of the iminoacyl group. Zirconocene $\eta^2$–iminoacyl complexes exhibit infrared stretches ca. 1520-1580 $cm^{-1}$.[34] Structurally characterized $\eta^1$–iminoacyl complexes of Pt have infrared stretches ca. 1620 $cm^{-1}$.[35] Organic secondary imines have a band at 1650 $cm^{-1}$.[36]

The vinyl ketene complexes **3a - e** insert terminal alkynes to form titanaoxacyclopentenes, **8-10**. The yield of insertion products is high; however, some poly-alkyne is formed. The insertion works well for the ketene oligomers, even in non-coordinating solvents. The alkyne may act as a Lewis base and solubilize the oligomer. Terminal alkynes insert regiospecifically, the substituent placed at the $\alpha$–position. The $\alpha$–position may appear to be the more sterically crowded regioisomer, but analysis of the $\beta$–isomer reveals a severe 1,3 allylic interaction with the exo–methylene substituent (Equation 17).[37] The titanacycle ring is quite flat, due to the three adjacent $sp^2$ carbons, and the $\alpha$–substituent is held in the plane of the metallacycle, minimizing steric interactions with the $\eta^5$-cyclopentadienyl rings. Similar additions across transition metal ketene and ketone complexes have been observed previously for titanium and zirconium.[9a,38] Similar oxacyclopentenes have been synthesized by addition of ketones and aldehydes to alkyne and alkene complexes.[39]

The isomerization of titanaoxacyclopentenes **7b** and **7c** is surprising. The mechanism of isomerization could proceed through a zwitterionic enolate resonance,

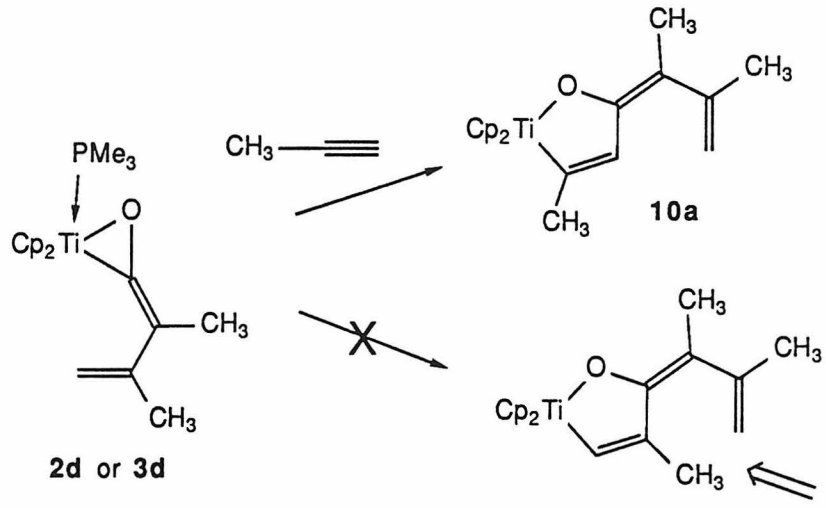
**Table 3. Selected Bond Lengths (Å) and Angles (°) for 4a.**

| | |
|---|---|
| Ti – C(1) | 2.02(3) |
| Ti – C(4) | 2.34(3) |
| Ti – N | 2.23(2) |
| C(1) – N | 1.19(4) |
| C(1) – C(2) | 1.57(4) |
| C(2) – C(3) | 1.49(4) |
| C(3) – C(4) | 1.36(4) |
| Ti – R(1)* | 2.11 |
| Ti – R(2)* | 2.08 |
| | |
| C(1) – Ti – C(4) | 71(1) |
| Ti – C(1) – C(2) | 128(2) |
| C(1) – C(2) – C(3) | 103(2) |
| C(2) – C(3) – C(4) | 119(2) |
| C(3) – C(4) – Ti | 116(2) |
| Ti – C(1) – N | 83(2) |
| N – C(1) – C(2) | 147(3) |
| C(5) – N – C(1) | 134(2) |
| R(1) – Ti – R(2)* | 134.4 |

* R(1) and R(2) are the $\eta^5$-cyclopentadienyl ring centroids.

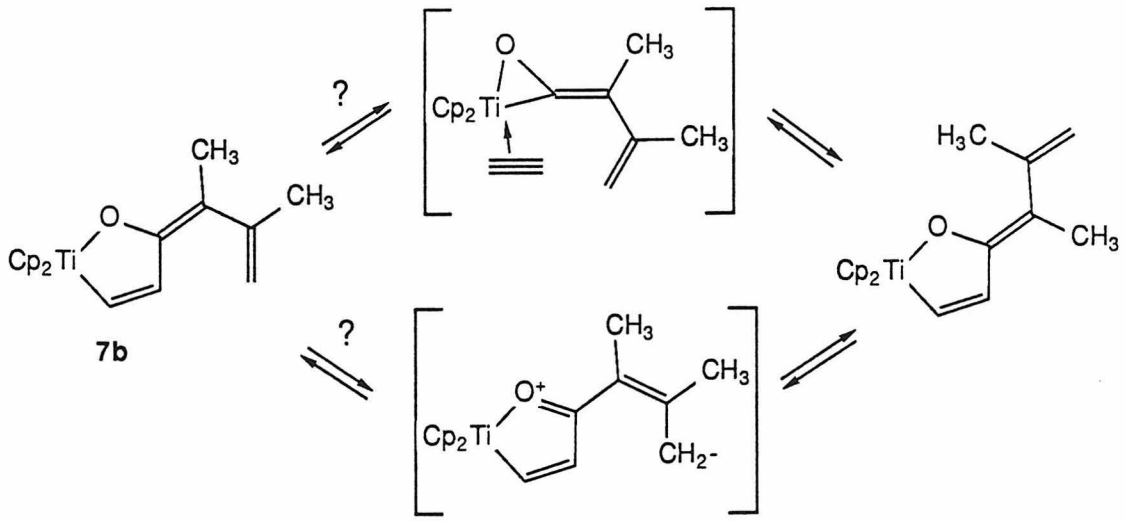
followed by bond rotation of the intermediate (Scheme 3). Alternatively, alkyne insertion may be reversible to form a ketene–alkyne complex, which isomerizes by a mechanism similar to the ketene–phosphine complex, **2a**. As was found with the ketene–phosphine complexes; the diphenyl isomer, **2a**, does not isomerize, whereas the dimethyl complex, **2d**, isomerizes to a more stable complex. The lack of reactivity of **7b** with methyl iodide suggests that the titanaoxacyclopentenes are not strong nucleophiles, and zwitterionic intermediates are not involved.

The only alkene that inserts into the vinyl ketene complexes **2a** or **3a** is




(17)

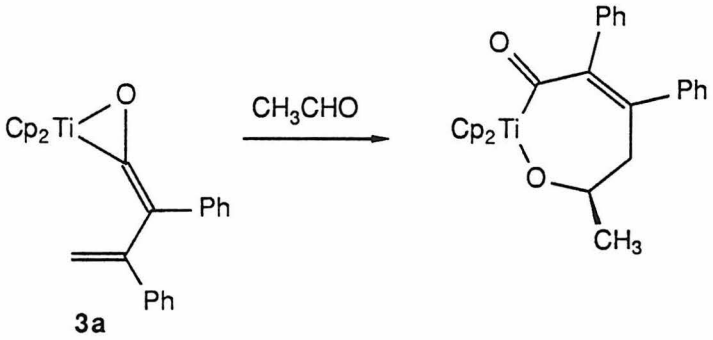
**Scheme 3.** Isomerization Mechanism of **7b**




ethylene. Substituted alkenes do not react due to steric interactions with the $\eta^5$-cyclopentadienyl rings.

Based on the reactivity of alkynes, the insertion of aldehydes into ketene complexes **3a** and **3d** was anticipated; however, the products were unexpected. We had expected aldehydes should insert to yield a titanocene diolate complex; however, spectral data of the intial product are inconsistent with a titanocene diolate complex. Spectral data suggest the formation of a titanocene acyl alkoxide complex.

Formation of an acyl alkoxide requires reaction of the ketene complex from the dieneolate manifold and a 1,2–addition across the aldehyde (Equation 18). The $^{13}C$ NMR resonance at $\delta$ 276.2 and the isotopic shift of the infrared stretch at 1595 $cm^{-1}$ are characteristic of Group IV acyl complex.[31]




3a (18)

The acyl alkoxide reductively eliminates to yield the lactone **11**, but the overall yield is low (25-44%). Possible explanations for the low yield are decompostion initated by the titanocene fragment or decarbonylation of the acyl alkoxide to a titanoxacyclopentane. No other products were observed in the reaction mixture; however, the signals were severely broadened by paramagnetic decomposition. Rapid hydrolysis of the acyl alkoxide intermediate may produce higher yields of lactone. Ketones do not react with the ketene complexes, reflecting the steric constraints of the titanocene system.

Lewis acids are cocatalysts of many organometallic reactions. Organoaluminum reagents readily react with zirconocene ketene oligomers to form novel compounds.[40] Titanocene vinyl ketene oligomers, **3a** and **3d**, form stable 1:1 adducts with either trimethylaluminum or dimethylaluminum chloride. The complex is probably monomeric, but a molecular weight determination has not been performed. A simple Lewis acid-Lewis base interaction of the titanium and alu-

minum species is consistent with the NMR data. The aluminum complexation did not enhance the reactivity of the ketene complex toward olefin insertion.

## Conclusions

We have demonstrated that carbonylations of titanocenecyclobutene complexes yield titanocene vinyl ketene complexes. The mechanism appears to involve several steps and one of the intermediates has been isolated. This reaction may provide insight into the mechanism of Fischer carbene annulation reactions of carbon monoxide and alkynes as well as the carbonylation of metal alkyl complexes. In particular, the observed products could be derived from the opening of the metallacyclobutene to a vinyl alkylidene, though this is not a viable mechanism in our system. Our findings shed some doubt on the use of a metallacyclobutene opening to a vinyl alkylidene in mechanisms of related reactions [24] and suggest that such reactions may also occur by direct insertion into the metal-carbon single bonds of intermediates.

The structure of a titanocene vinyl ketene complex has been determined by x-ray diffraction and is the first structurally characterized example of a monomeric titanium ketene complex. Isocyanides insert into titanacyclobutenes to yield iminoacyl complexes, analogous to the acyl intermediate, **5**. The structure of the iminoacyl compound shows an $\eta^2$–coordination of the imino group, and a very long titanium–carbon bond across from the iminoacyl ligand. The structure may provide an indication of the bonding in the titanium acyl intermediate as it proceeds toward the transition-state to product.

The vinyl ketene complexes also react with unsaturated molecules such as alkynes and aldehydes. Addition of alkynes occurs across the titanium–carbon bond to yield titanaoxacyclopentenes. With aldehydes, the ketene complexes act as dieneolates and form a titanium acyl alkoxide intermediate, which reductively eliminates to form a lactone.

## Experimental Section

**General Considerations.** All manipulations were performed with the use of standard Schlenk techniques under argon or in a Vacuum Atmospheres Co. glovebox under nitrogen. Argon was purified by passage through columns of BASF R3-11 (Chemalog) and Linde 4 Å molecular sieves. Carbonylations were performed in Lab-Glass pressure bottles (60 or 100 mL) fitted with two inlet valves and a pressure gauge. Toluene, benzene, THF, and diethyl ether were vacuum-transferred from sodium benzophenone ketyl and stored in teflon-valve sealed vessels under argon. Pentane and hexane were stirred over concentrated $H_2SO_4$, dried, vacuum-transferred from sodium benzophenone ketyl and stored in teflon-valve sealed vessels under argon. Methylene chloride was vacuum-transferred from $P_2O_5$ or $CaH_2$ and stored under argon. Benzene–$d_6$, toluene–$d_8$, and THF–$d_8$ were vacuum-transferred from sodium benzophenone ketyl. Carbon monoxide (CP) was obtained from Matheson. $^{13}C$-enriched carbon monoxide (90% $^{13}C$) was obtained from Monsanto-Mound Laboratories. Trimethylphosphine was obtained from Strem Chemicals. Acetylenes were obtained from Aldrich, Farchan Laboratory, or Wiley Organics and dried or distilled before use.

**Instrumentation.** Infrared spectra were recorded on either a Beckman 4240, Shimatzu IR-435, or Perkin-Elmer 1310 spectrophotometer. $^1H$ NMR were recorded on a Varian EM-390, JEOL FX-90Q, Varian XL-200, JEOL GX-400, or Brüker WM-500 and referenced to residual solvent ($C_6D_6$, $\delta$ 7.15; $C_7D_8$, $\delta$ 2.09; THF-$d_8$, $\delta$ 3.58 or 1.73; $CDCL_3$, $\delta$ 7.24). $^{31}P\{^1H\}$ NMR were recorded on a JEOL FX-90Q and referenced to external 85% $H_3PO_4$ (positive $\delta$, lower field). $^{13}C\{^1H\}$ NMR were recorded on a JEOL FX-90Q, Varian XL-200, or JEOL GX-400. Difference NOE spectra were recorded on a JEOL GX-400 or a Brüker WM-500 at the Southern California Regional NMR Facility located at the California Institute of

Technology. Reaction kinetics were performed on the JEOL FX-90Q using an automated routine. Elemental analyses were performed by Dornis and Kolbe, Mulheim, West Germany, and the analytical facility of the California Institute of Technology.

**$\eta^2$-(C,O)-2,3-Diphenyl Vinyl Ketene Titanocene Trimethylphosphine, 2a.**

A solution of 2,3-diphenyl titanacyclobutene (150 mg, 0.405 mmol) and trimethylphosphine(45 $\mu$L, 0.444 mmol) in 2 mL of toluene was transferred into a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The transfer cannula and schlenk flask were rinsed twice with 0.5 mL portions of toluene. The pressure bottle was partially evacuated, and CO (20 psi) was introduced with stirring. After 10 min the color had changed from dark-red to yellow and the CO was vented . The solution was transferred into a schlenk flask and the pressure bottle rinsed twice with 0.5 mL portions of toluene. The volatiles were removed *in vacuo* to yield a yellow solid, which was washed twice with 2 mL portions of pentane and dried *in vacuo* to yield the product as a yellow powder (158 mg, 0.333 mmol, 82%). $^1$H NMR (200 MHz, $C_6D_6$) $\delta$ 8.20 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 7.0 Hz, 2H), 7.35 (t, J = 7.6 Hz , 2H), 7.2-7.0 (m, 4H), 5.89 (d, J = 2.7 Hz, 1H), 5.72 (d, J = 2.7 Hz, 1H), 5.10 (s, 10H), 0.73 (d, J = 6.3 Hz, 9H); $^{31}$P{$^1$H} NMR (36.3 MHz, THF-$d_8$, -20°C) $\delta$ 5.72 (s); $^{13}$C{$^1$H} NMR (22.5 MHz, THF-$d_8$, -20 °C) $\delta$ 193.6 (d, $J_{C-P}$ = 11.0 Hz), 152.7, 145.4, 143.4, 128.6, 128.2, 127.6, 127.2, 126.6, 121.1, 112.4, 104.8, 102.3 (d, $J_{C-P}$ = 3.7 Hz), 14.2 (d, $J_{C-P}$ = 14.6 Hz); IR (nujol, cm$^{-1}$) KBr 1590 (m), 1565 (m), 1540 (s), 1487 ( s), 1425 (m), 1305 (m), 1282 (m), 1265 (m), 1155 (m), 1072 (m), 1045 (m), 1028 (m), 1018 (m), 952 (s), 918 (w), 895 (w), 805 (s). The band at 1540 cm$^{-1}$ shifts to 1512 cm$^{-1}$ upon the use of $^{13}$CO. Anal. Calcd. for $C_{29}H_{31}OPTi$: C, 73.42; H, 6.59. Found: C, 73.21; H, 6.68.

**$\eta^2$-(C,O)-2-Phenyl-3-Trimethylsilyl Vinyl Ketene Titanocene Trimethylphosphine, 2b.**

A solution of 2-phenyl-3-trimethylsilyl titanocenecyclobutene (500 mg, 1.36 mmol) and trimethylphosphine (150 $\mu$L, 1.48 mmol) in 8 mL of THF was transferred into a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The transfer cannula and schlenk flask were rinsed twice with 1 mL portions of THF. The pressure bottle was charged with 60 psi of CO. The solution was stirred at room temperature for 3 hr during which time the color changed from purple to yellow. The CO was vented and the solution transferred to a schlenk flask. The volatiles were removed *in vacuo* to yield a yellow solid, which was washed twice with 2 mL of pentane and dried *in vacuo* to yield the product (590 mg, 1.25 mmol, 92%). The material can be recrystallized from diethyl ether at –50 °C (10 mg/mL). $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.80 (m, 2H), 7.37 (m, 3H), 6.33 (d, 1H, J = 3.7 Hz), 5.82 (d, 1H, J = 3.7 H z), 5.16 (s, 10H), 0.69 (d, 9H, J = 6.6 Hz), 0.33 (s, 9H); $^1$H NMR (90 MHz, THF-$d_8$) $\delta$ 7.33 (m, 2H), 7.04 (m, 2H), 6.81 (m, 1H), 6.04 (d, 1H, J = 3.9 Hz), 5.51 (d, 1H, J = 3.9 Hz), 5.42 (s, 10H), 1.38 (d, 9H, J = 7.1 Hz), 0.01 (s, 9H); $^{31}$P{$^1$H} NMR (36.3 MHz, THF-$d_8$, –20 °C) $\delta$ 5.25, $^{31}$P{$^1$H} NMR (36.3 MHz, $C_7D_8$, –20 °C) $\delta$ 3.06; $^{13}$C{$^1$H} NMR (22.5 MHz, THF-$d_8$, –20 °C) $\delta$ 190.3 (d, $J_{C-P}$ = 12.2 Hz), 155.7, 145.1, 128.0, 127.6, 12 2.4, 121.4, 104.8, 14.0 (d, $J_{C-P}$ = 14.6 Hz), 1.3; IR (nujol, cm$^{-1}$) KBr 1585 (w), 1520 (m), 1300 (m), 1280 (m), 1258 (m), 1235 (m), 1062 (w), 103 0 (w), 1015 (m), 975 (m), 960 (m), 910 (w), 870 (m), 855 (m), 838 (m), 825 (m), 805 (s). The absorption at 1520 cm$^{-1}$ shifts to 1492 cm$^{-1}$ upon the use of $^{13}$CO. Anal. Calcd. for $C_{26}H_{35}OPSiTi$: C, 66.37; H, 7.50. Found: C, 66.03; H, 7.29.

**$\eta^2$-(C,O)-2-Phenyl-3-Methyl Vinyl Ketene Titanocene Trimethylphosphine, 2c.**

A solution of 2-phenyl-3-methyl titanocenecyclobutene (200 mg, 0.649 mmol) and trimethylphosphine (70 $\mu$L, 0.69 mmol) in 2 mL of toluene was transferred into a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The transfer cannula and schlenk flask were rinsed twice with 0.5 mL portions of toluene. The pressure bottle was charged with 15 psi CO. The solution was stirred for 10 min during which time the color changed from dark-red to yellow. The CO was vented, the solution transferred to a schlenk flask, and the volatiles removed *in vacuo*. The yellow solid was washed twice with 2 mL portions of pentane and dried *in vacuo* to yield the product (215 mg, 0.521 mmol, 80%). Analysis by $^1$H NMR revealed two isomers in a 3:1 ratio. $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ major isomer 7.84 (m, 2H), 7.39 (m, 3H), 5.32 (m, 1H), 5.20 (m, 1H), 5.17 (s, 10H), 2.39 (m, 3H), 0.65 (br d, 9H); minor isomer 5.10 (s, 10H), 2.42 (br s, 3H), 0.65 (br d, 9H), vinyl resonances obscured. $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_7D_8$, -20°C) $\delta$ major isomer 188.6 (d, $J_{C-P}$ = 11.0 Hz), 146.8, 144.9, 138.3, 136.3, 129.3, 122.9, 106.2, 105.1 (d, $J_{C-P}$ = 3.7 Hz), 103.9, 24.9 (s), 13.3 (d, $J_{C-P}$ = 14.6 Hz); minor isomer 102.8; $^{31}P\{^1H\}$ NMR (36.3 MHz, $C_7D_8$-d8, -20 °C) $\delta$ major isomer 3.84, minor isomer 4.78; IR (nujol, cm$^{-1}$) KBr 1608 (w), 1575 (m), 1560 (m), 1525 (s), 1300 (w), 1278 (m), 1260 (w), 1062 (w), 1010 (s), 945 (s), 895 (m), 850 (m), 838 (m), 800 (s). The absorption at 1525 cm$^{-1}$ shifts to 1498 cm$^{-1}$ upon the use of $^{13}$CO. Anal. Calcd. for $C_{24}H_{29}OPTi$: C, 69.91; H, 7.09. Found: C, 69.58; H, 7.00.

**$\eta^2$-(C,O)-2,3-Dimethyl Vinyl Ketene Titanocene Trimethylphosphine, 1d.**

A solution of 2,3-dimethyl titanocenecyclobutene (200 mg, 0.812 mmol) and trimethylphosphine (100 $\mu$L, 0.986 mmol) in 2 mL of toluene were transferred into a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The schlenk flask and cannula were rinsed twice with 0.5 mL portions of toluene. The pressure bottle was charged with 15 psi of CO. The solution was stirred for 10 min during which time the color changed from red to yellow. The CO was vented and the solution transferred to a schlenk flask and the volatiles removed *in vacuo*. The yellow solid was washed twice with 2 mL of portions of pentane and dried *in vacuo* to yield the product (220 mg, 0.628 mmol, 77%). Analysis by $^1$H NMR revealed two isomers in approximately 2:1 ratio. $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ major isomer 5.15 (s, 10H), 4.95 (m, 2H), 2.61 (s, 3H), 2.45 (br s, 3H), 0.72 (d, 9H, J = 6.5 Hz); minor isomer 5.05 (s, 10H), 4.78 (m, 2H), 2.61 (s, 3H), 2.31 (s, 3H), 0.72 (d, 9H, J = 6.5 Hz); $^1$H NMR (500.13 MHz, $C_7D_8$) $\delta$ major isomer 5.126 (s, 10H), 4.885 (d, 1H, J = 2.1 Hz), 4.815 (br s, 1H), 2.411 (s, 3H), 2.355 (br s, 3H), 0.798 (br s, 9H) (irradiation of the signal at $\delta$ 2.355 results in the collapse of the signal at $\delta$ 4.815 to a doublet, J = 2.1 Hz); minor isomer 5.041 (s, 10H), 4.738 (d, 1H, J = 1.7 Hz), 4.575 (br s, 1 H), 2.455 (br s, 3H), 2.208 (s, 3H), 0.798 (br s, 9H) (irradiation of the signal at $\delta$ 2.455 results in the collapse of the signal at $\delta$ 4.575 to a doublet, J = 1.7 Hz); $^1$H NMR (500.13 MHz, $C_6D_6$) $\delta$ major isomer 5.154 (s, 10H), 5.074 (d, 1H, J = 2.5 Hz), 4.987 (br s, 1H), 2.603 (s, 3H), 2.450 (br s, 3H), 0.71 (br s, 9H); minor isomer 5.058 (s, 10H), 4.937 (d, 1H, J = 2.4 Hz), 4.772 (br s, 1H), 2.613 (br s, 3H), 2.31 3 (s, 3H), 0.71 (br s, 9H); $^1$H NMR (500.13 MHz, THF-$d_8$) $\delta$ major isomer 5.382 (s, 10H), 4.290 (d, 1H, J = 2.7 Hz), 4.245 (br s, 1H), 2.124 (s , 3H), 1.862 (s, 3H), 0.90 (v br, 9H) (irradiation of the signal at $\delta$ 2.124 results in the collapse

of the signal at $\delta$ 4.245 to a doublet, J = 2.7 Hz); minor isomer $\delta$ 5.316 (s, 10H, 4.116 (d, 1H, J = 2.7 Hz), 3.968 (br s, 1H), 2.012 (s, 3H), 1.912 (s, 3H), 0.90 (v br, 9H) (irradiation of the signal at $\delta$ 2.012 results in the collapse of the signal at $\delta$ 3.968 to a doublet, J = 2.7 Hz). $^{13}C$ labeled ketene complex: $^{1}H$ NMR (500.13 MHz, $C_7D_8$) $\delta$ major isomer 5.126 (s, 10H), 4.885 (d, 1H, J = 2.1 Hz), 4.815 (br s, 1H), 2.411 (d, 3H, $J_{C-H}$ = 4.4 Hz), 2.355 (s, 3H ), 0.798 (br s, 9H); minor isomer $\delta$ 5.041 (s, 10H), 4.738 (d, 1H, J = 1.7 Hz), 4.575 (br s, 1H), 2.455 (s, 3H), 2.208 (d, 3H, $J_{C-H}$ = 5.9 Hz ), 0.798 (br s, 9H); $^{1}H$ NMR (500.13 MHz, THF-$d_8$) $\delta$ major isomer 5.381 (s, 10H), 4.293 (d, 1H, J = 2.4 Hz), 4.247 (br s, 1H), 2.124 (s, 3H), 1.862 (d, 3H, $J_{C-H}$ = 4.3 Hz), 0.90 (v br, 9H); minor isomer 5.315 (s, 10H), 4.118 (d, 1H, J = 2.3 Hz), 3.968 (br s, 1H), 2.013 (s, 3H), 1.912 (d, 3H, $J_{C-H}$ = 5.89 Hz), 0.90 (v br, 9H); $^{31}P\{^{1}H\}$ NMR (36.3 MHz, $C_7D_8$, -20 °C) $\delta$ minor isomer 4.55, major isomer 3.53; $^{13}C\{^{1}H\}$ NMR (22.5 MHz, $C_7D_8$, -20 °C) $\delta$ major isomer 185.47 (d, $J_{C-P}$ = 11.0 Hz), 146.84, 103.83, 98.63, 98.36 (d, $J_{C-P}$ = 3.6 Hz), 22.95, 19.53, 13.14 (d, $J_{C-P}$ = 14.6 Hz); minor isomer 185.25 (d, $J_{C-P}$ = 9.8 Hz), 146.14, 102.91, 97.82 (d, $J_{C-P}$ = 9.8 Hz), 96.89, 24.84, 18.66, 13.14 (d, $J_{C-P}$ = 14.6 Hz); IR (nujol, $cm^{-1}$) KBr 1598 (m), 1558 (s), 1546 (s), 1421 (m), 1317 (m), 1300 (m), 1278 (m), 1205 (m), 1120 (w), 1020 (m), 1010 (m), 948 (s), 830 (m), 795 (s). The use of $^{13}CO$ results in a shift of the absorption at 1546 $cm^{-1}$ to 1523 $cm^{-1}$. Anal. Calcd. for $C_{19}H_{27}OPTi$: C, 65.15; H, 7.77. Found: C, 65.20; H, 7.55..Assignment of geometry by difference NOE experiments: Major isomer (Cp $\delta$ 5.382), irradiation of the signal at $\delta$ 1.862 results in enhancement of the signal at $\delta$ 4.290. Irradiation of the signal at $\delta$ 2.124 results in enhancement of the signals at $\delta$ 4.245 and 5.382. The $J_{C-H}$ of $\delta$ 1.862 with $^{13}CO$ is 4.3 Hz. Minor isomer (Cp $\delta$ 5.316), irradiation of the signal at $\delta$ 1.912 results in enhancement of the signal at 4.116. Irradiation of the signal at 2.012 results in enhancement of the signal at $\delta$ 3.968. The $J_{C-H}$ of $\delta$

1.912 with $^{13}CO$ is 5.8 Hz.

### $\eta^2$-(C,O)-Diethyl Vinyl Ketene Titanocene Trimethylphosphine, 1e.

A solution of 2,3-diethyl titanocenecyclobutene (150 mg, 0.547 mmol) and trimethylphosphine (60 $\mu$L, 0.590 mmol) in 1 mL of toluene was transferred into a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The cannula and schlenk flask were rinsed twice with 0.5 mL portions of toluene. The pressure bottle was charged with 20 psi of CO. The solution was stirred at room temperature for 10 min during which time the color changed from red to yellow. The excess CO was vented and the solution transferred to a schlenk flask and the volatiles removed *in vacuo*. The yellow solid was washed twice with 1 mL portions of pentane and dried *in vacuo* to yield the product (145 mg, 0.383 mmol, 70%). Analysis by $^1H$ NMR revealed two isomers in approximately a 3:1 ratio. $^1H$ NMR (500.13, MHz, $C_6D_6$) $\delta$ major isomer 5.175 (s, 10H), 5.158 (d, J = 1.93 Hz, 1H), 4.952 (br s, 1H), 2.988 (q, J = 7.29 Hz, 2H), 2.731 (q, J = 7.45 Hz, 2H), 1.516 (t, J = 7.45 Hz, 3H), 1.396 (t, J = 7.29 Hz, 3H), 0.711 (d, $J_{P-H}$ = 6.89 Hz, 9H); minor isomer 5.102 (s, 10H), 4.914 (d, J = 2.27 Hz, 1H), 4.876 (br s, 1H), 3.010 (q, J = 7.27 Hz, 2H), 2.787 (q, J = 7.29 Hz, 2H), 1.662 (t, J = 7.27 Hz, 3H), 1.2 84 (t, J = 7.29 Hz, 3H), 0.711 (d, $J_{P-H}$ = 6.89 Hz, 9H); $^1H$ NMR (90 MHz, THF-$d_8$) $\delta$ major isomer 5.39 (s, 10H), 4.49 (d, J = 2.2 Hz, 1H), 4.31 (br s, 1H), 2.44 (br q, J = 7.6 Hz, 2H), 2.35 (q, J = 7.3 Hz, 2H), 1.34 (d, $J_{P-H}$ = 6.8 Hz, 9H), 1.21 (t, J = 7.6 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H); $^{13}CO$ labeled product: $^1H$ NMR (90 MHz, $C_6D_6$) $\delta$ major isomer 5.17 (s, 10H), 5.13 (sh, 1H), 4.93 (br s, 1H), 2.97 (d of q, J = 7.3 H z, 4.4 Hz, 2H), 2.72 (q, J = 7.3 Hz, 2H), 1.51 (t, J = 7.3 Hz, 3H), 1.39 (t, J = 7.3 Hz, 3H), 0.71 (d, J = 6.6Hz, 9H); $^{13}C\{^1H\}$ NMR (22.5, MHz, THF-$d_8$, -20 °C) $\delta$ 185.9 (d, $J_{C-P}$ = 11.0 Hz), 152.2, 109.9, 104.6, 94.3, 27.2 (partially obscured by solvent), 15.8, 14.6, 13.7

(d, $J_{C-P}$ = 14.6 Hz). $^{31}P\{^1H\}$ NMR (36.3 MHz, THF-$d_8$, –20 °C) $\delta$ major isomer 5.55, minor isomer 6.06; IR (KBr, $cm^{-1}$) 3110 (w), 3085 (w), 3070 (w), 2965 (m), 29 20 (m), 2860 (m), 1590 (w), 1570 (m), 1538 (s), 1443 (m), 1420 (w), 1370 (w), 1355 (w), 1305 (w), 1286 (m), 1280 (m), 1264 (m), 1245 (w), 11 95 (m), 1130 (m), 1058 (w), 1015 (m), 948 (s), 845 (w), 808 (s). The use of $^{13}CO$ results in a shift of the absorption at 1538 $cm^{-1}$ to 1508 $cm^{-1}$. Anal. Calcd. for $C_{21}H_{31}OPTi$: C, 66.67; H, 8.26. Found: C, 66.92; H, 8.01.

**General Procedure for the Synthesis of Titanocene Vinyl Ketene Oligomer, 3a-d.**

A solution of the titanacyclobutene **1** in toluene was transferred into a pressure bottle fitted with a stirbar and pressure gauge. Carbon monoxide (~20 psi) was introduced with stirring. After approximately 15 minutes the solution was orange with a yellow precipitate. The CO was vented, the mixture transferred into a schlenk tube, and the volatiles removed *in vacuo*. The solid was sometimes purple due to an unidentified by-product, which may be removed by washing with pentane. The material was usually washed with pentane and dried *in vacuo* to yield the product, **3**, as a yellow powder.

**3,4-Dimethyl Titanacyclopent-3-ene-1-one, 5.**

A solution of the dimethyltitanacyclobutene (112 mg, 0.455 mmol) and trimethylphosphine (50 $\mu$L, 0.493 mmol) in 1 mL of toluene was transferred in a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The schlenk flask and cannula were rinsed twice with 1 mL portions of toluene. The pressure bottle was briefly evacuated, cooled to –50°C, and 10 psi of CO added. The solution was warmed slowly from –50 °C with stirring. When the temperature had reached approximately –20°C to –10°C a color change from red → brown → green

was observed. The solution was immediately cooled to –78°C, excess CO vented, and placed under argon atmosphere. The solution was rapidly transferred by cannula into a precooled schlenk flask with no apparent change of color. The solution was layered with 4 mL of pentane and allowed to stand at –78°C for several hours. A green precipitate was deposited on the walls of the flask. The mother liquor was removed via cannula; the green solid was washed twice with 2 mL portions of –78°C pentane and dried *in vacuo* to yield 72 mg of green powder. The product was stored at –40 °C in the drybox. NMR data are reported from sealed tube reactions and formation of the intermediate *in situ*. $^1$H NMR (90 MHz, THF-$d_8$, –25°C) $\delta$ 6.20 (s, 10H), 2.42 (br s, 2H), 1.32 (s, 3H), 0.80 (br s, 3H). When $^{13}$CO is used, the signal at $\delta$ 2.42 becomes a broad doublet $J_{C-H}$ = 4.6 Hz; $^1$H NMR (90 MHz, $C_7D_8$, –30°C) $\delta$ 5.81 (s, 10H), 2.67 (br s, 2H), 1.46 (s, 3H), 0.70 (s, 3H); $^{13}$C{$^1$H} NMR (22.5 MHz, THF-$d_8$, –25°C) $\delta$ 294.0, 186.4, 121.6, 115.5, 61.3, 17.5, 16.5; $^{13}$C{$^1$H} NMR (22.5 MHz, $C_7D_8$, –30°C) $\delta$ 293.6, 185.6, 121.6, 114.8, 61.3, 17.7 , 16.7; labeled with $^{13}$CO: $^{13}$C{$^1$H} NMR (22.5 MHz, THF-$d_8$, –25°C) $\delta$ 294.0 (s), 185.2 (s), 121.6 (d, $J_{C-C}$ = 7± 1.8 Hz), 115.3 (s), 61.3 (d, $J_{C-C}$ = 13 ± 1.8 Hz), 17.5 (d, $J_{C-C}$ = 6 ± 1.8 Hz), 16.5 (s); $^{13}$C{$^1$H} NMR (22.5 MHz, $C_7D_8$, –30°C) $\delta$ 293.4 (s), 185.3 (s), 121. 2 (d, jcc = 5.5 ± 0.9 Hz), 114.5 (s), 61.0 (d, $J_{C-C}$ = 11.9 ± 0.9 Hz), 17.5 (d, $J_{C-C}$ = 5.5 ± 0.9 Hz), 16.3 (s). The resonance at $\delta$ 185 may be obscured by the ketene complex; the use of pyridine instead of trimethyl phosphine shifts the resonance of the ketene product to lower field. IR (KBr, cm$^{-1}$) 3090 (m), 2960 (m), 2890 (m), 2845 (s), 2820 (s), 2745 (m), 1615 (s), 1435 (m), 1365 (m), 1280 (w), 1168 (w), 1148 (w), 1128 (w), 1070 (m), 1050 (m), 1013 (s), 972 (w), 950 (m), 820 (s), 805 (s).

**3-Methyl-trans-3-pentenoyl Titanocene Chloride, 6.**

A solution of dimethyl titanocenecyclobutene **1d** (210 mg, 0.853 mmol) in 10 mL of diethyl ether was transferred into a 100 mL Lab-Glass pressure bottle fitted with a pressure gauge and stirbar. The solution was cooled to –78°C and 100 psi of CO added. The solution was warmed with stirring until the color began to change to a brown-green, then immediately cooled to –78°C to obtain a green solution with some green precipitate. To this mixture was added 25 psi of anhydrous HCl gas (Matheson) to bring the total pressure to 125 psi. Over 15 min at –78°C with stirring, all of the green color disappeared and a yellow-orange precipitate was formed. The pressure was vented and the reaction vessel evacuated at –78°C for several hours. To speed the removal of solvent, the diethylether mixture was splashed onto the warmer sides of the vessel where the solvent immediately evaporated. After the solvent had been removed, the solid was dried overnight *in vacuo* to yield 175 mg of a red-orange powder. NMR analysis ($CDCL_3$) indicated the material was approximately 66% $Cp_2TiCl_2$ and 34% acyl chloride, **5** (0.192 mmol, 22%). $^1H$ NMR (400 MHz, $CDCL_3$) $\delta$ 5.77 (s, 10H), 5.57 (d of q, J = 6.8, 1.2 Hz, 1H), 3.95 (br s, 2H), 1.81 (d, J = 1.2, 3H), 1.69 (d of t, J = 6.8, 1.2 Hz, 3H); IR (KBr, $cm^{-1}$) 1610. The acyl chloride may be cleaved to the aldehyde and $Cp_2TiCl_2$ by treatment with HCl at >–20°C. The aldehyde was characterized by $^1H$ NMR (90 MHz, $C_6D_6$) $\delta$ 9.48 (t, J = 2.3 Hz, 1H), 5.03 (br q, 1H), 2.17 (br t, J = 2.3 Hz, 2H), $CH_3$groups obscured by residual diethyl ether. The aldehyde was immediately converted to the 2,4-DNP derivative, mp. 135°.

**Trapping Experiments of 3 by t-Butyl Isocyanide.**

Compound **3** (16 mg, 0.058 mmol) was weighed into an NMR tube in the drybox; the tube was capped with a septum, removed from the box and cooled

to –78°C . Toluene-$d_8$ (400 $\mu$L) was added by syringe through the septum at a rate such that the solvent cooled as it flowed down the side of the tube. The t-butyl isocyanide (22 $\mu$L, 0.23 mmol) was then added by syringe to the sample. The tube was shaken to dissolve the solid and the sample warmed quickly to room temperature. An immediate color change from green to red was observed and the $^1$H NMR recorded at room temperature. The major products had resonances at $\delta$ 6.05 and 5.47. The $^1$H NMR $\eta^5$-cyclopentadienyl resonance of the imino acyl insertion product **5**, was well separated at $\delta$ 5.20. The resonances at $\delta$ 6.05 and 5.47 were confirmed to be derived from reaction of the ketene complex oligomer **2d** with t-butyl isocyanide by independent reactions. Integration of the $\eta^5$-cyclopentadienyl resonances yielded a ratio of ketene products to metallacyclobutene products of 15 to 1.

**Kinetics Study of the Isomerization of 2d.**

Two NMR tubes were charged with 14 mg (0.051 mmol) of the phosphine-free ketene oligomer of **3d**. To each tube was added 400 $\mu$L of benzene-$d_6$, and then each was capped with a septum. The tubes were removed from the drybox and frozen in an ice bath. To one tube was added 6 $\mu$L (0.059 mmol) trimethylphosphine via syringe. To the second tube 18 $\mu$L (0.177 mmol) of trimethylphosphine was added. Both samples were thawed simultaneously at room temperature, and the progress of the isomerization followed by $^1$H NMR integration of the $CH_3$ resonances. The initial NMR spectrum showed a >30:1 ratio of isomers. Over 18 hrs the reaction was monitored periodically until an equilibrium ratio of 0.60 $\pm$ 0.1 ($\delta$ 5.15 isomer to $\delta$ 5.05 isomer) was reached. The forward and reverse rate constants were calculated in the usual manner.

**Reaction to Determine $^{13}CO/^{12}CO$ Exchange.**

A solution of the dimethyl titanacyclobutene (100 mg, 0.406 mmol) in 4 mL diethyl ether was transferred into a Lab- Glass pressure bottle fitted with a stirbar and pressure gauge. The cannula was rinsed twice with 0.5 mL portions of toluene. The pressure bottle was partially evacuated, cooled to –78°C, and 15 psi of $^{13}CO$ (90% $^{13}C$) were introduced. The reaction mixture was allowed to warm slowly to about –10°C to 0°C at which time a clear green solution had formed. The reaction was immediately cooled to –78°C and CO vented. The pressure bottle was refilled with 100 psi of $^{12}CO$ (natural abundance) and allowed to warm to –30°C with stirring. The rearrangement as noted by the loss of green color was complete in approximately 15 min. The ketene complex was isolated as previously described to yield 70 mg (0.255 mmol, 63%) of product. Analysis by $^1H$ NMR ($C_6D_6$) showed the signal at $\delta$ 2.61 to be a singlet, indicative of no incorporation of $^{13}CO$ in the product.

**2-t-Butylimino-4,5-Diphenyltitanocenecyclopentene, 4a.**

A stirred solution of 2,3 diphenyltitanocenecyclobutene, **2a**, (310 mg, 0.837 mmol) in 2 ml of toluene was treated with t-butylisocyanide (160 $\mu$L, 1.64 mmol) at room temperature. The color of the solution immediately changed from purple to orange and the volatiles removed *in vacuo*. The solid was dissolved in the minimum amount of toluene at 50°C ($\sim$ 3 ml) and slowly cooled to –50°C. The crystals were collected, washed with 3 $\times$ 0.5 ml of cold pentane and dried *in vacuo* to yield 216 mg (0.496 mmol, 59%) of **4a**: $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 7.28-6.94 (m, 10H), 5.276 (s, 10H), 4.127 (s, 2H), 0.927 (s, 9H). The crystals had occluded 1 molecule of toluene per 2 molecules of **4a**. $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) $\delta$ 220.08, 194.68, 156.11, 142.04, 141.42, 129.86, 129.26, 128.49, 128.11, 127.25,

125.64, 125.14, 122.84, 106.28, 60.19, 52.80, 29.81. IR (KBr, $cm^{-1}$) 1772 (s). Anal. Calcd for $C_{30}H_{31}NTi \cdot 0.5$ toluene: C, 80.55; H, 7.06; N, 2.80. Found: C, 80.61; H, 7.03, N, 2.79.

**2-t-Butylimino-4-Trimethylsilyl-5-Phenyl-Titanacyclopentene, 4b.**

A stirred solution of 2-phenyl-3-trimethylsilyl titanacyclobutene, **1b** (260 mg, 0.709 mmol) in 2 ml of toluene was treated with t-butylisocyanide (110 $\mu$L, 1.09 mmol) at room temperature. The color immediately changed from red to orange. The solution was stirred for approximately 5 minutes and the volatiles removed *in vacuo*. The orange solid was dissolved in 1 ml of toluene at 50°C and slowly cooled to –50°C. The crystals were collected at –50°C, washed with cold pentane (3 × 0.5ml), and dried *in vacuo* to yield 165 mg (0.367, 52%) of **4b**: $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.13 (m, 4H), 6.91 (m, 1H), 5.09 (s, 10H), 3.89 (s, 2H), 0.801 (s, 9H), 0.00 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) $\delta$ 227.02, 213.75, 157.47, 144.81, 125.86, 123.37, 112.63, 106.08, 60.22, 54.37, 29.83, 2.18. IR (KBr, $cm^{-1}$) 1758 (s). Anal. Calcd for $C_{27}H_{35}NSiTi$: C, 72.14; H, 7.85; N, 3.12. Found: C, 71.81; H, 7.71, N, 3.14.

**2-t-Butylimino-4-Methyl-5-Phenyltitanacyclopentene, 4c.**

A stirred solution of 3-methyl-2phenyl titanacyclobutene, **2c** (250 mg, 0.811 mmol) in 2 ml of toluene was treated with t-butylisocyanide (160 $\mu$L, 1.62 mmol) at room temperature. The color immediately changed from red to orange. The mixture was stirred at room temperature for 5 minutes; then the volatiles were removed *in vacuo*. The orange solid was dissolved in the minimum amount of toluene (3.5 ml) at 50°C, then slowly cooled to –50°C. The crystals were collected at –50°C, washed 3 × 0.5 ml with cold pentane and dried *in vacuo* to yield 179 mg (0.457 mmol, 56%) of **4c**: $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.36 (m, 2H), 7.27 (m, 2H),

7.08 (m, 1H), 5.25 (s, 10H), 3.55 (s, 2H), 1.87 (s, 3H), 0.925 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) $\delta$ 222.89, 187.25, 156.73, 136.19, 126.52, 122.83, 112.73, 106.13, 59.98, 52.71, 29.83, 18.65. IR (KBr, $cm^{-1}$) 1775 (s). Anal. Calcd for $C_{25}H_{29}NTi$: C, 76.72; H, 7.47; N, 3.58. Found: C, 76.42; H, 7.36, N, 3.62.

**2-t-Butylimino-4,5-Dimethyltitanocenecyclobutene, 4d.**

A stirred solution of 2,3- dimethyltitanocenecyclobutene (166 mg, 0.67 mmol) in 1 mL of THF was treated with t-butylisocyanide (68 $\mu$L, 0.74 mmol) at room temperature. An immediate color change from red to orange was observed. The mixture was stirred at room temperature for 15 minutes, then the volatiles removed *in vacuo*. The solid was extracted with 4 mL of hexane, the solution filtered and cooled to –50°C. The orange crystals were isolated, washed twice with 0.5 mL portions of cold pentane, and dried *in vacuo* to yield the 112 mg of the product (0.34, 51%). $^1H$ NMR (90 MHz, $C_6D_6$) $\delta$ 5.24 (s, 10H), 3.55 (br s, 2H), 2.14 (br s, 3H), 1.98 (br, s, 3H), 0.93 (s, 9H); $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 224.81, 181.75, 134.70, 105.36, 59.68, 52.93, 29.88, 26.55, 16.02; IR (Nujol, KBr, $cm^{-1}$) 1770. Anal. Calcd for $C_{20}H_{27}NTi$: C, 72.94; H, 8.26; N, 4.25. Found: C, 72.88; H, 8.06, N, 4.23.

**Reaction of 3a with Acetylene.**

A Fischer-Porter bottle fitted with a stirbar was charged with diphenyltitanocene vinyl ketene oligomer, **3a** (330 mg, 0.837 mmol) dissolved in 3 ml of toluene. Approximately 10 psi of acetylene gas were introduced from a cylinder with stirring. Immediately the color began to change from yellow to green. After 3 minutes, the ketene complex had dissolved and green crystals began to precipitate. After an additional 5 minutes the excess acetylene was vented, and the volatiles were removed *in vacuo* to yield 310 mg of a light-green powder (0.730 mmol, 87%):

$^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.88 (d of d, J=8.4, 1.2 Hz, 2H), 7.75 (d of d, J=7.7, 1.2 Hz, 2H), 7.21 (d, J=8.3 Hz, 2H), 7.13 (d, J+7.7 Hz, 2H), 7.01 (m, 1H), 6.96 (m, 1H), 6.96 (d, J=9.0 Hz, 1H), 6.46 (d, J=9.0 Hz, 1H), 5.90 (d, J=9.0 Hz, 1H), 5.52 (d, J=2.0 Hz, 1H), 5.79 (s, 10H). Difference NOE experiments: irradiation of $\delta$ 6.96 enhances $\delta$ 7.21, 6.46, 5.79; irradiation of $\delta$ 6.46 enhances $\delta$ 6.96; irradiation of $\delta$ 5.79 enhances $\delta$ 7.88, 7.75, 6.96. $^{13}$C{$^1$H} NMR (22.5 MHz, $C_6D_6$) $\delta$ 202.33 (CH), 162.67, 148.59, 142.52, 140.73, 139.48 (CH), 128.76, 128.54, 127.24, 127.51, 124.48, 117.33 ($CH_2$), 116.08 (Cp), 111.85. IR (KBr, cm$^{-1}$) 3090 (w), 3030 (w), 1605 (m), 1580 (m), 1540 (s), 1510 (s), 1495 (s). Anal. Calcd. for $C_{28}H_{24}OTi$: C, 79.24; H, 5.70. Found: C, 76.94; H, 5.59.

**Reaction of 3a with Ethylene.**

A Fischer-Porter bottle fitted with a pressure gauge and stirbar was charged with diphenyltitanocene vinyl ketene oligomer, **3a** (304 mg, 0.821 mmol), 6 ml of toluene and 20 psi of ethylene. The reaction mixture was placed in a 70°C oil bath for 12 hours during which the color changed from yellow to purple and much of the oligomer dissolved. The mixture was cooled to room temperature, the excess ethylene vented, and the mixture transferred to a schlenk flask. The volatiles were removed *in vacuo* and the residue extracted with diethylether. The extract was filtered and the solvent removed *in vacuo* to yield 250 mg (0.628 mmol, 76%) of the product: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.74 (m, 4H), 7.30-6.90 (m, 6H), 5.87 (d, J=2.0 Hz, 1H), 5.78 (s, 10H), 5.37 (d, J=2.0 Hz, 1H), 3.71 (t, J=7.3 Hz, 2H), 1.85 (t, J=7.3 Hz, 2H). $^{13}$C{$^1$H} NMR (22.5 MHz, $C_6D_6$) $\delta$ 163.65, 149.13, 142.03, 141.27, 130.33, 128.60, 128.43, 127.54, 125.67, 123.94, 116.52 ($CH_2$), 115.27 (Cp), 113.96, 108.17, 54.54 ($CH_2$), 54.06 ($CH_2$). IR (KBr, cm$^{-1}$) 3090 (w), 3040 (w), 2920 (s), 1560 (s), 1495 (m). Anal. Calcd. for $C_{28}H_{26}OTi$: C, 78.87; H, 6.15.

Found: C, 78.05; H, 6.20.

**Reaction of 3a with Propyne.**

An NMR tube was charged with **3a** (36 mg, 0.091 mmol) in the drybox, attached to a teflon valve and degassed on the vacuum line. The solvent, $C_6D_6$, was condensed into the tube followed by propyne (0.128 mmol) and the tube sealed. The solvent was thawed at room temperature and over 30 minutes the starting material dissolved to yield a green solution: $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.87 (d, J=7.8 Hz, 2H), 7.76 (d, J=7.6 Hz, 2H), 7.21 (t, J=7.8 Hz, 2H), 7.13 (t, J=7.6 Hz, 2H), 7.00 (m, 2H), 6.95 (m, 2H), 6.30 (q, J=1.5 Hz, 1H), 5.935 (d, J=2.2 Hz, 1H), 5.831 (s, 10H), 5.543 (d, J=1.95 Hz, 1H), 1.613 (d, J=1.7 Hz, 3H). Difference NOE experiments: irradiation of $\delta$ 1.61 enhances $\delta$ 6.30; irradiation of $\delta$ 6.30 enhances $\delta$ 1.61; irradiation of $\delta$ 5.83 enhances $\delta$ 7.87, 7.76, 6.30, 1.61. $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_6$) $\delta$ 212.04, 160.60, 148.48, 142.36, 140.71, 136.36 (CH), 128.62, 128.52, 128.41, 128.12, 127.88, 127.84, 127.50, 127.22, 124.24, 117.41 ($CH_2$), 116.15 (Cp), 114.07, 106.48, 29.05.

**Reaction of 3d with Acetylene.**

To a suspension of vinyl ketene oligomer **3d** (13 mg, 0.047 mmol) in 400 $\mu$L of $C_6D_6$ in an NMR tube was added 4 $\mu$L (1 equivalent) of THF. Some of the ketene complex dissolved. To this mixture was added acetylene (5 ml, 0.11 mmol) *via* syringe. During the following 10 minutes the solution turned green, and after 20 minutes the reaction was > 90% complete by NMR. The NMR indicated only one isomer. $^1$H NMR (200 MHz, $C_6D_6$) $\delta$ 6.97 (d, J=8.8 Hz, 1H), 6.68 (d, J=8.8 Hz, 1H), 5.84 (s, 10H), 5.11 (br d, J=2.9 Hz, 1H), 5.02 (d of q, J=2.9, 1.5 Hz, 1H), 1.95 (br s, 3H), 1.86 (s, 3H). During the next several hours the initial isomer isomerized to produce approximately a 1:1 ratio of products. New isomer $^1$H NMR (200 MHz,

$C_6D_6$) $\delta$ 7.08 (d, J=8.8 Hz, 1H), 6.52 (d, J=8.8 Hz, 1H), 5.77 (s, 10H), 5.07 (br d, J=2.2 Hz, 1H), 4.97 (br s, 1H), 2.13 (br s, 3H), 2.02 (s, 3H). The isomer at $\delta$ 5.78 will eventually become the major isomer at equilibrium (57:43). The reaction and isomerization do not require THF and can be accelerated by warming to 80°C, although copious amounts of polyacetylene are also produced. $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ mixture of isomers 201.30 (CH), 197.24 (CH), 161.80, 159.42, 146.37, 145.72, 137.81 (CH), 137.21 (CH), 115.59 (Cp are isochronous), 112.40, 109.91, 109.74, 105.57, 25.67 ($CH_3$), 23.39 ($CH_3$), 16.73 ($CH_3$), 14.18 ($CH_3$).

**Reaction of 3d with Propyne.**

An NMR tube was charged in the drybox with vinyl ketene complex **3d** (35 mg, 0.128 mmol), attached to a teflon adapter and 400 $\mu$L of $C_6D_6$ transferred into the tube. Propyne (0.13 mmol) was condensed into the tube and the tube sealed. The mixture was thawed at room temperature and the ketene complex reacted over several days to yield two isomeric titanaoxacyclopentenes in a 56:44 ratio: major isomer $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 6.28 (s, 1H), 5.79 (s, 10H), 5.06 (d, J=1.2 Hz, 1H), 4.95 (br s, 1H), 2.14 (br s, 3H), 2.04 (s, 3H), 1.74 (br s, 3H). Minor isomer $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 6.51 (s, 1H), 5.86 (s, 10H), 5.13 (d, J=2.4 Hz, 1H), 5.04 (br s, 1H), 1.98 (s, 3H), 1.88 (s, 3H), 1.76 (br s, 3H). $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ (mixture of isomers) 211.27, 206.93, 159.80, 157.20, 146.42, 145.77, 135.15, 134.23, 115.59 (Cp are isochronous), 112.18, 109.42, 108.55, 108.12, 107.68, 105.68, 104.00, 28.50, 28.43, 25.77, 23.50, 16.67, 14.13.

**Synthesis of Lactone 11a.**

To a stirred solution of diphenylketene complex, **3a** (150 mg, 0.376 mmol), in 1 ml of THF was added acetaldehyde (25 $\mu$L, 0.72 mmol) at room temperature. The reaction mixture immediately changed color from brown to purple. The reaction

was stirred at room temperature for 18 hours. The reaction was quenched with 1 ml of 15% aqueous NaOH and 2 ml of diethylether.The aqueous layer was extracted with 4 × 2 ml of diethylether, the organic extracts combined, dried over $MgSO_4$, and concentrated at reduced pressure to yield 94 mg of an amber oil. The product could be flash-chromatographed (diethylether : petroleum ether, 1:1) to yield 44 mg ( 0.167 mmol, 44%) of lactone **11a** as a crystalline solid. $^1H$ NMR (400 MHz, $CDCL_3$) $\delta$ 7.215-7.012 (m, 10H), 4.793 (d of d of q, J=11.72, 3.66, 6.35 Hz, 1H), 2.888 (d of d, J=17.57, 11.72 Hz, 1H), 2.771 (d of d, J=17.57, 3.66 Hz, 1H), 1.529 (d, J=6.35 Hz, 3H). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CDCL_3$) $\delta$ 165.63, 151.44, 138.49, 134.86, 130.74, 128.63, 128.36, 128.09, 127.76, 127.33, 73.10, 37.72, 20.60. IR (KBr, $CCl_4$, $cm^{-1}$) 1700 (s).

**Synthesis of Lactone 11b.**

To a stirred solution of dimethyl ketene complex, **3d** (150 mg, 0.547 mmol), in 2 ml of THF was added p-tolualdehyde (71 $\mu$L, 0.602 mmol) *via* syringe at room temperature. The color immediately changed from yellow-brown to purple and after several minutes a purple solid began to precipitate. Toluene, 2 ml, was added to redissolve to solid. The mixture was stirred for 1 hour at room temperature, then quenched with 15% aqueous NaOH. The pH was adjusted to near neutral with aqueous HCl and the mixture stirred for 12 hours. The mixture was extracted with 2 × 10 ml of diethylether, the organic extracts combined, dried over $MgSO_4$, and concentrated at reduced pressure. The material was flash-chromatographed on silica gel (petroleum ether : diethylether, 60:40) to yield 30 mg (0.139 mmol, 25%) of lactone **11b** an oil that crystallized on standing: $^1H$ NMR (400 MHz, $CDCL_3$) $\delta$ 7.280 (d, J=8.0 Hz, 2H), 7.170 (d, J=8.0 Hz, 2H), 5.290 (d of d, J=3.9, 12.45 Hz, 1H), 2.688 (bf t, J=16.6 Hz, 1H), 2.405 (d of d, J=3.9, 17.09 Hz, 1H), 2.350 (s,

10H), 1.970 (s, 3H), 1.939 (d, J=0.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CDCL_3$) $\delta$ 166.22, 148.40, 138.12, 136.00, 129.17, 125.92, 122.51, 77.60, 38.21, 21.04, 20.12, 12.48. IR (KBr, $CCl_4$, $cm^{-1}$) 1720 (s).

**Reaction of 3a with Acetaldehyde.**

Treatment of a suspension of diphenyl vinyl ketene complex **3a** (14 mg, 0.035 mmol) in 400 $\mu$L of $C_6D_6$ with acetaldehyde (4 $\mu$L, 0.06 mmol) immediately yields a new purple product: $^1H$ NMR (90 MHz, $C_6D_6$) $\delta$ 7.63 (m, 4H), 7.15-6.77 (m, 6H), 5.85 (s, 5H), 5.76 (s, 5H), 4.66 (m, 1H), 2.51 (m, 2H), 1.11 (d, J=6.6 Hz, 3H). The compound decomposed over several hours to species that had very broad NMR signals. Infrared analysis of the purple intermediate displayed an absorption at 1595 $cm^{-1}$, which shifted to 1560 $cm^{-1}$ when $^{13}C$ labeled ketene complex was used. $^{13}C$ NMR analysis of the purple intermediate from the $^{13}C$ labeled complex displayed an intense singlet at $\delta$ 276.16.

**Reaction of 3a with Pivaldehyde.**

Treatment of a suspension of **3a** (28 mg, 0.070 mmol) in 400 $\mu$L of $C_6D_6$ with pivaldehyde (8 $\mu$L, 0.118 mmol) immediately produced a new species: $^1H$ NMR (200 MHz, $C_6D_6$) $\delta$ 7.80 (m, 4H), 7.20-6.90 (m, 6H), 6.07 (s, 5H), 5.81 (s, 5H), 4.44 (d, J=7.3 Hz, 1H), 2.54 (d, J=14.2 Hz, 1H), 2.35 (d of d, J=13.6, 7.6 Hz, 1H), 0.92 (s, 9H). The material decomposed to brown paramagnetic species during the next 12 hours.

**Reaction of 3a with t-Butylacetylene.**

Treatment of a suspension of diphenyl ketene oligomer **3a** (32 mg, 0.080 mmol) in 400 $\mu$L of $C_6D_6$ with t-butylacetylene (11 $\mu$L, 0.20 mmol) reacted over several hours to yield a red solution. Warming the reaction mixture to 80 °C accelerated

the reaction. The product was identified as the titanaoxacyclopentene insertion product: $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.60 (d, J=7.6 Hz, 2H), 7.55 (d, J=7.6 Hz, 2H), 7.39 (s, 1H), 7.22 (t, J=7.8 Hz, 2H), 7.11 (t, J=7.6 Hz, 2H), 7.02 (m, 2H), 5.806 (s, 10H), 1.33 (s, 9H). Difference NOE experiments: irradiation of $\delta$ 5.81 enhanced $\delta$ 7.39.

**Reaction of 3a with Phenylacetylene.**

A suspension of ketene complex **3a** (36 mg, 0.09 mmol) in 400 $\mu$L of $C_6D_6$ was treated with phenylacetylene (11 $\mu$L, 0.116 mmol) at room temperature. After 1 hour the ketene complex had dissolved to yield a red solution: $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.61-7.51 (m, 6H), 7.21-6.90 (m, 9H), 5.815 (s, 10H), 5.33 (d, J=1.95 Hz, 1H), 5.31 (d, J=1.95, 1H). A minor product was also observed at $\delta$ 5.97 (s, Cp).

**Reaction of 3a with Dimethylaluminum Chloride.**

A suspension of complex, **3a**, (25 mg, 0.063 mmol) in $C_6D_6$ was treated with a solution of dimethylaluminum chloride (2M in $C_6D_6$, 32 $\mu$L, 0.064 mmol) at room temperature. An immediate reaction occurred to yield an orange solution: $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.42 (d, J=7.6 Hz, 4H), 7.23 (t, J=7.6 Hz, 2H), 7.14-6.98 (m, 4H), 5.49 (s, 10H), 5.34 (d, J=1.9 Hz, 1H), 5.14 (d, J=1.9 Hz, 1H), -0.451 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_6$) $\delta$ 184.8, 149.1, 143.0, 141.3, 137.1, 136.6, 128.7, 127.9, 127.8, 127.7, 127.5, 126.8, 125.6, 117.3, 115.1, 111.5 (Cp), -6.48 (br s). The complex was stable for hours at room temperature. The complex did not react with propene.

**Reaction of 3a with Trimethylaluminum.**

A suspension of complex **3a** (25 mg, 0.063 mmol) in $C_6D_6$ was treated with trimethylaluminum (2M in $C_6D_6$, 32 $\mu$L, 0.064 mmol) at room temperature. An im-

mediate reaction occurred to yield a red-brown solution: $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.67 (d, J=7.1 Hz, 2H), 7.41 (d, J=7.1 Hz, 2H), 7.28 (d, J=7.6 Hz, 2H), 7.10-6.96 (m, 4H), 5.49 (s, 10H), vinyl $CH_2$ not observed, -0.899 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) $\delta$ 188.6, 148.9, 142.5, 139.8, 128.7, 127.9, 127.6, 127.4, 127.2, 126.9, 125.3, 124.3, 114.7, 113.6, 112.5 (Cp), 111.5, -8.99 (br s). The trimethylaluminum complex was less stable than the dimethylaluminum complex and did not react with propene.

**Reaction of 3d with Dimethylaluminum Chloride.**

A suspension of complex **3d** (26 mg, 0.095 mmol) in 400 $\mu$L of $C_6D_6$ was treated with dimethylaluminum chloride (2M in $C_6D_6$, 47 $\mu$L, 0.094 mmmol) at room temperature. The ketene complex immediately dissolved to yield an orange solution: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 5.56 (s, 10H), 4.91 (br s, 2H), 2.03 (s, 3H), 1.63 (s, 3H), -0.25 (s, 6H).

**Reaction of 3d with Trimethylaluminum.**

A suspension of complex **3d** (26 mg, 0.095 mmol) in 400 $\mu$L of $C_6D_6$ was treated with dimethylaluminum chloride (2M in $C_6D_6$, 47 $\mu$L, 0.094 mmmol) at room temperature. The ketene complex immediately dissolved to yield an orange solution: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 5.75 (s, 10H), 4.87 (br s, 2H), 2.19 (s, 3H), 1.27 (s, 3H), -0.68 (s, 9H).

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# Chapter 4

## Insertion of Carbon-Heteroatom Multiple Bonds into Bis($\eta^5$-Cyclopentadienyl) Titanacyclobutenes

## Introduction

Insertion of unsaturated organic molecules into transition-metal carbon bonds has received much attention during the past thirty years. Insertion of carbon-carbon multiple bonds into transition-metal alkyl complexes has been the focus of many laboratories due to the economic importance of poly-olefins.[1] Carbon-heteroatom multiple bonds (*i.e.* ketone, ester, nitrile, and imine) also insert into transition-metal alkyl complexes.[2] Application of transition-metal alkyl complexes rather than main group complexes for nucleophilic addition to carbon-heteroatom bonds has the potential to alter the reactivity and selectivity by the appropriate combination of ancillary ligands.

Organic chemistry contains many examples of metal alkyl addition to carbon-heteroatom multiple bonds. The Grignard reaction is a classic example of this type of reaction. Alkyl and aryl compounds derived from Li, Na, Al, and Cd are commonly used in organic synthesis.[3] The reactivity of these complexes is generally 1,2 addition to carbonyl groups, with varying selectivity.

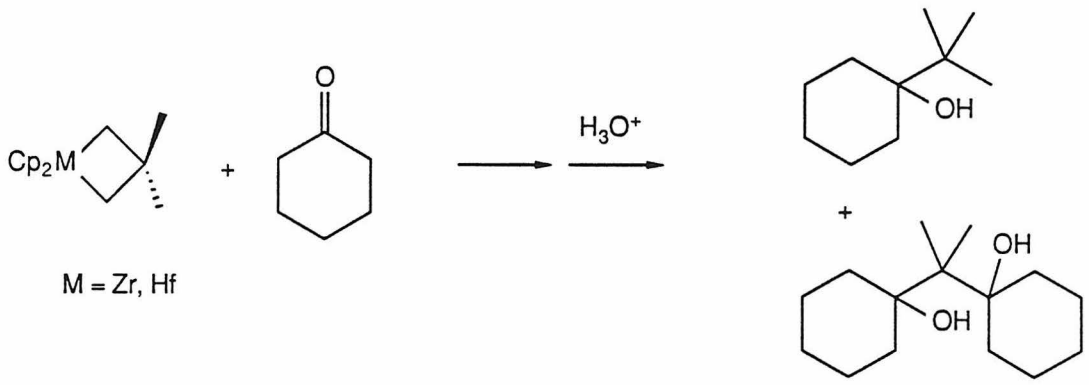
Few transition-metal organometallic reagents have been developed for addition to carbon-heteroatom functionality. Dialkyl cuprate complexes ($R_2CuLi$) add to $\alpha,\beta$–unsaturated ketones in a 1,4 sense to yield a $\gamma$-alkylated ketone.[4] In contrast, an alkyl lithium reagent adds in a 1,2 sense to the same ketone to yield an alcohol. This modified selectivity of a main group complex *via* a transition metal may provide new methods for regio- and stereo-controlled reactions.

Likewise, $(^{i}PrO)_3TiCl$, when treated with a Grignard reagent, forms an alkyl titanium derivative, which is selective for aldehydes in the presence of ketones and nitriles.[5] Thus, the need for protection-deprotection of sensitive functionality may be reduced. This same titanium reagent also reacts in a highly diastereoselective manner with ketones and aldehydes. Transition metal alkyl complexes from the left

half of the transition block are highly reactive toward carbonyl compounds due to the oxophilicity of the metal.

Several reactions are known where a transition metal complex serves as a catalyst, transferring or coupling alkyl groups from a donor complex to the unsaturated substrate.[6]

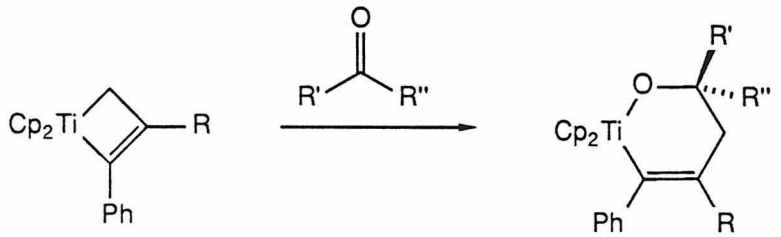
Recently, 1,2–addition of carbonyl compounds to metallacyclobutane complexes has been postulated by product analysis.[7]




Due to the lack of methylene transfer chemistry of titanacyclobutenes, the reactivity of titanacyclobutenes with carbon-heteroatom bonds was investigated. Titanacyclobutenes offer a unique template for the study of insertion into titanium-carbon bonds.

**Results**

Treatment of a solution of diphenyl titanocenecyclobutene, **1a**, with acetone at room temperature for 2 days yields titanoceneoxacyclohexene, **2a**, in quantitative yield (Equation 1). The reaction is greatly accelerated by warming the sample to 80°C for approximately 10-15 minutes. The methyl phenyl titanacyclobutene, **1b**, works equally as well. The titanaoxacyclohexenes, **2**, are isolated as yellow solids.




(1)

**1a** : R = Ph
**1b** : R = $CH_3$

**2**

The reaction is general for a variety of organic ketones (Table 1). Methylene transfer reaction to the ketone is not observed. Enolization of the ketone by the titanacyclobutene is not a significant side reaction.

However, titanacyclobutenes with $\beta$-hydrogens do not insert ketones to an appreciable extent. The metallacycle begins to react, and the insertion product decomposes rapidly at room temperature.[16]

The kinetics of the insertion reaction of acetone into **1a** was monitored by NMR (Equation 2). The rate expression was first order in metallacycle and ketone, second order overall. At 50°C a second-order rate constant was calculated, $k_{323} = 5.94(3) \times 10^{-4}\ M^{-1}sec^{-1}$. The activation parameters were determined by Eyring analysis of the rate constants over a 40°C temperature range (Table 2).

The NMR of the reaction solution at room temperature shows sharp signals

**Table 1. Ketone Insertion into Titanacyclobutenes.**

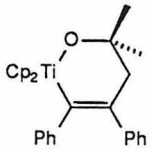
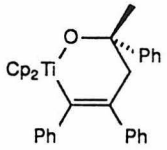
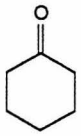
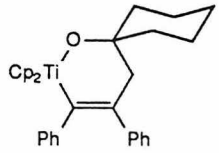
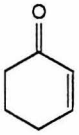
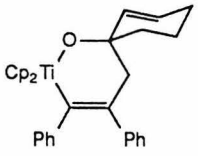
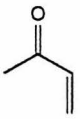
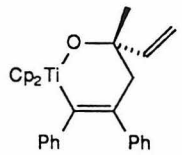
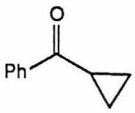
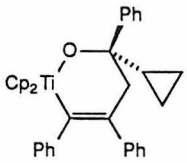
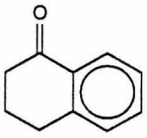
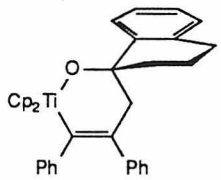
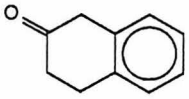
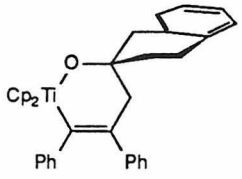
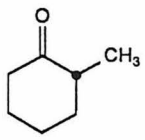
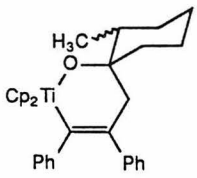
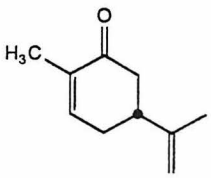
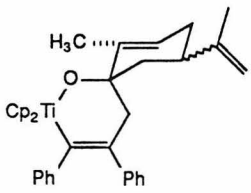
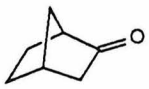
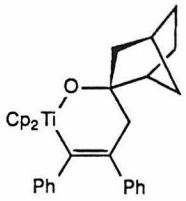
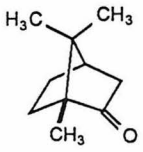
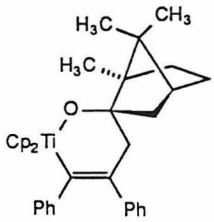
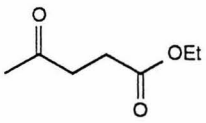
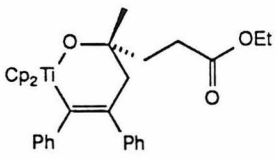
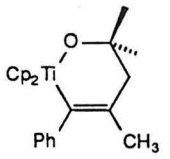
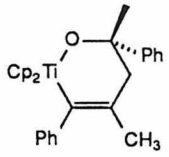
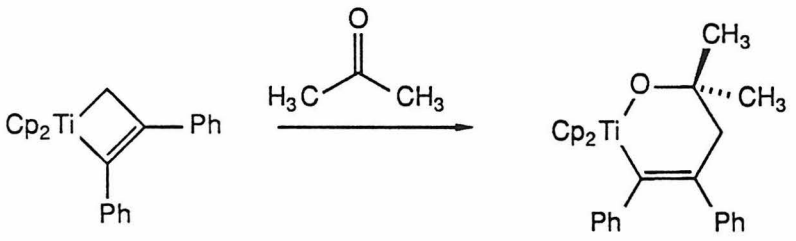
| Ketone | Titanacycle | Product | |
|---|---|---|---|
|  | **1a** |  | **2a** |
|  | **1a** |  | **2b** |
|  | **1a** |  | **2c** |
|  | **1a** |  | **2d** |
|  | **1a** |  | **2e** |
|  | **1a** |  | **2f** |
|  | **1a** |  | **2g** |
|  | **1a** |  | **2h** |

**Table 1. (cont.)**

| Ketone | Titanacycle | Product | |
|---|---|---|---|
|  | **1a** |  | **2i** |
|  | **1a** |  | **2j** |
|  | **1a** |  | **2k** |
|  | **1a** |  | **2l** |
|  | **1a** |  | **2m** |
|  | **1b** |  | **2n** |
|  | **1b** |  | **2o** |




1a 2a (2)

**Table 2.** Rate Constants and Activation Parameters for Acetone Insertion into **2a**.

| Temperature (K) | k ($M^{-1}sec^{-1} \times 10^4$) |
|---|---|
| 293 | 3.51(7) |
| 301 | 5.9(1) |
| 313 | 16.8(2) |
| 323 | 29.5(4) |

$\Delta G^{\ddagger}_{301} = 22.0(5)$ kcal $mol^{-1}$

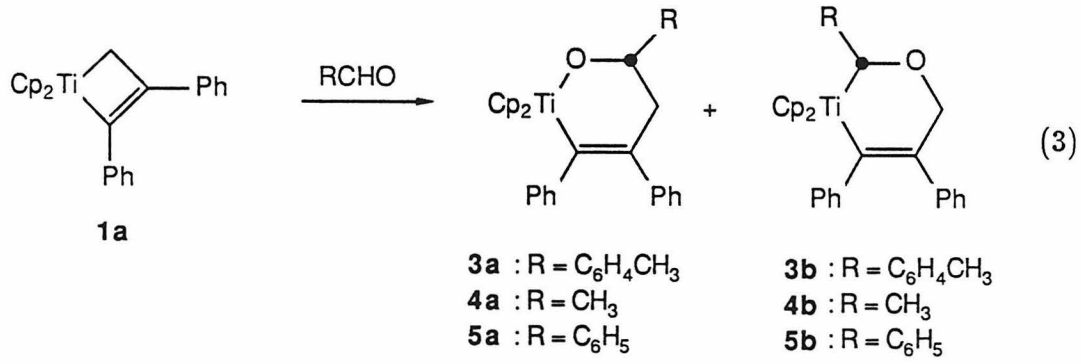
$\Delta H^{\ddagger} = 13.1(4)$ kcal $mol^{-1}$

$\Delta S^{\ddagger}_{301} = -29(1)$ eu

for the metallacycle but a broad signal for the acetone. Upon cooling, the acetone signal broadens and disappears at ca. –40°C at 90 MHz. Upon further cooling to –80°C, the acetone signal begins to sharpen but does not split into a resolved doublet.

Aldehydes also insert cleanly into titanacyclobutenes (Equation 3). Treatment of a solution of **1a** with p-tolualdehyde at room temperature cleanly results on disappearance of the starting material. Examination of the reaction mixture by

NMR reveals the formation of two products in a 2:1 ratio. The major product is the expected isomer **3a** containing a titanium-oxygen bond. However, the second product appears to be a regioisomer, **3b**, in which the aldehyde has inserted in the opposite sense, forming a titanium-carbon bond. The dialkyl titanocene species, **3b**, is much less stable than **3a**. The titanaoxacyclohexenes are moderately air-stable and may be chromatographed on silica. The dialkyl isomers, **3b**, are air-sensitive and decompose upon warming to 80°C. Insertion of acetaldehyde also yields two isomeric insertion products **4a** and **4b** in a nearly 1:1 ratio.




**1a**

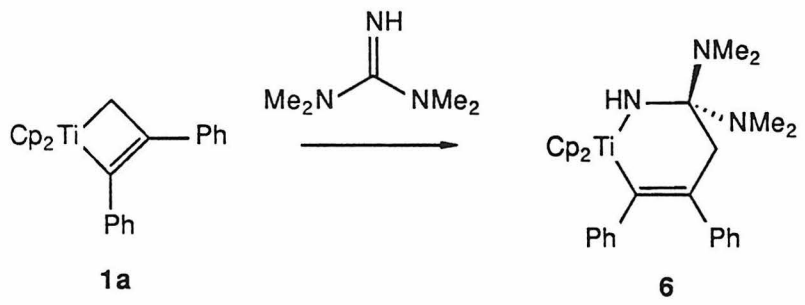
**3a** : R = $C_6H_4CH_3$
**4a** : R = $CH_3$
**5a** : R = $C_6H_5$

**3b** : R = $C_6H_4CH_3$
**4b** : R = $CH_3$
**5b** : R = $C_6H_5$

(3)

The insertion of benzaldehyde into **1a** has also been studied by K. Brown-Wensley.[8] Again, two products **5a** and **5b** were observed in a 2:1 ratio. The isomers were physically separated and hydrolyzed with HCl. The organic products were identified and are consistent with proposed regiochemistry.

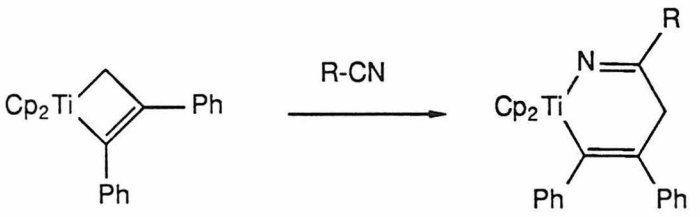
Several other carbon-heteroatom multiple bonds add to titanacycles **1a**. Tetramethylguanidine inserts to yield a titanocene amidocyclohexene **6** (Equation 4). The 90 MHz $^1H$ NMR exhibits a broad singlet for the $N(CH_3)_2$ groups at room temperature. The signal passes through coalescence at +15°C, and becomes two singlets ($\Delta\nu$ = 47.8 Hz) at –80°C. The $\eta^5$-cyclopentadienyl resonance also is a singlet until –47°C when it passes through coalescence and becomes two singlets



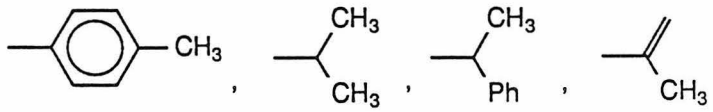

1a 6 (4)

($\Delta\nu$ = 73.5 Hz) at –80 °C.

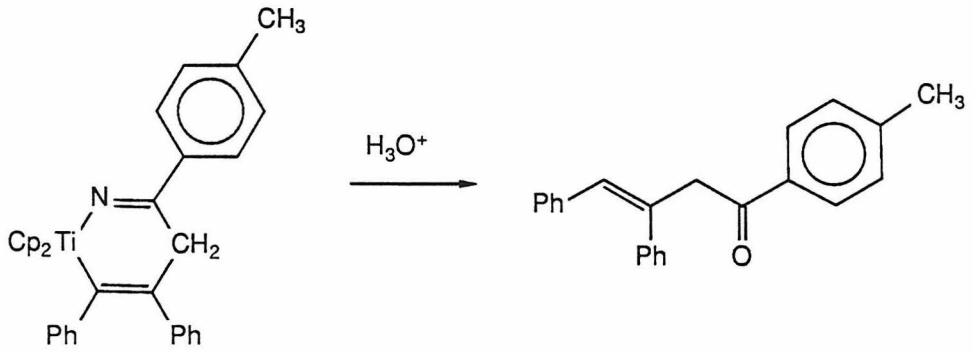
Nitriles also react with titanocyclobutenes (Equation 5); however, the reactions are not as clean as ketone insertions, and the products are not as stable. Treatment of a solution of **1a** in 400 $\mu$L of $C_6D_6$ with one equivalent of benzonitrile yielded, over 24 hours, a titanocene iminocyclohexene complex, **7**. The product was stable for days in solution but eventually decomposed. The insertion reaction works for a variety of nitriles: p-tolyl, $\alpha$-methyl propyl, $\alpha$-phenyl propyl, and methacrylonitrile. Acetonitrile yielded several products that decomposed rapidly at room temperature. Insertion of nitriles into titanacycle **1b** was also facile. Hydrolysis of the insertion products yields the corresponding ketones (Equation 6).




1a 7 (5)

R = 

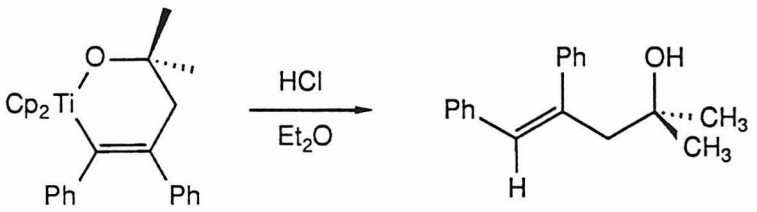

A variety of substrates do not react with the titanacyclobutenes: esters, car-




(6)

bonates, $CO_2$, $CS_2$, and imines.

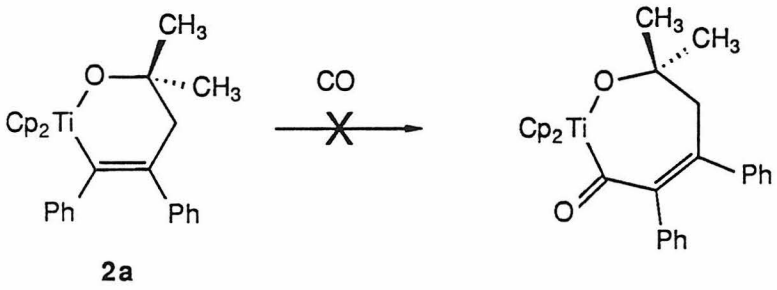
The titanaoxacyclohexenes **2a** can be removed from the metal fragment by hydrolysis with HCl to yield a homo-allylic alcohol in high yield (Equation 7).




(7)

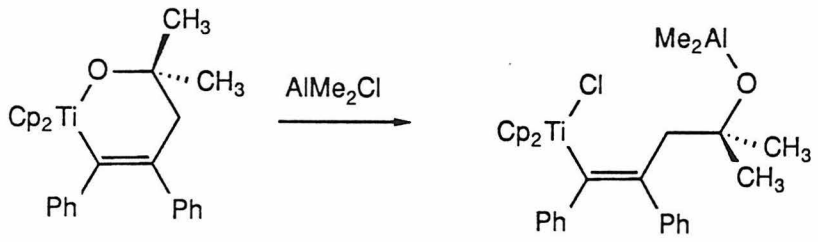
We had hoped to insert CO into the remaining titanium-carbon bond of **2a** to eventually yield a lactone (Equation 8). However, all attempts to react **2a** with CO either thermally or photochemically failed.

Lewis acids are known to accelerate migratory insertions of CO into metal-carbon bonds.[9] Treatment of **2a** with one equivalent of dimethylaluminum chloride results in immediate formation of a new complex. The new complex was dark-red and the NMR spectrum was very complex. Treatment of this complex with CO yielded starting material **2a**. The deep-red color of the reaction mixture and




**2a** (8)

analysis of the NMR spectrum suggest that the Ti–O bond transmetallates to the dimethylaluminum chloride, forming a titanocene alkenyl chloride and aluminum alkoxide (Equation 9). Trimethyl tin chloride did not react with **2a**.



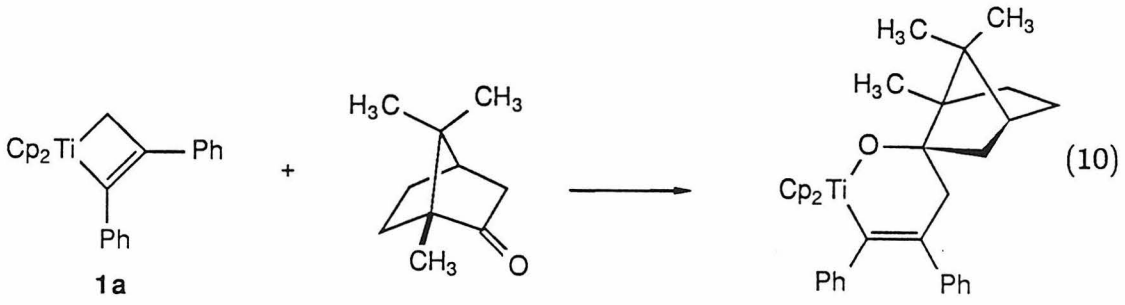

(9)

## Discussion

Titanocenecyclobutenes readily insert ketones to yield titanoceneoxacyclohexenes. The reaction is quite general for many ketones, and a few examples deserve mention.

The insertion shows very little facial selection for cyclohexenone derivatives. Insertion of 2-methylcyclohexanone yields two diastereomeric products in nearly equal ratios. Insertion of *l*-carvone gives two diastereomeric products in a 62:38 ratio. The lack of diasteroselection reflects both a lack of adverse steric interactions at the transition state and the relatively high reaction temperature. Attempting to increase the diastereoselection by reducing the temperature is impractical because of the slow reaction rate at room temperature.

Titanacyclobutenes will add very sterically crowded ketones, such as *d*-camphor, although the reaction is much slower. The NMR data and difference NOE experiments suggest that the metallacycle adds to the *endo*-face of the camphor molecule (Equation 10).[20]




(10)

Phenylcyclopropyl ketone inserts without any rearrangement to produce a single product in high yield. If the insertion mechanism involved a one-electron reduction or oxidation of the ketone, the cyclopropyl carbinyl radical could open.[11]

Although rearrangement is not observed, this experiment does not conclusively rule out a radical mechanism.

Ethyl leuvinate reacts exclusively at the methyl ketone to yield the expected oxacyclohexene, **2m**. Simple esters such as methyl benzoate do not react with the titanacyclobutenes. This selectivity for ketones over esters may arise from two factors. Esters are slightly weaker bases than ketones (1-2 $pK_a$ units).[10] The carbonyl carbon of an ester is less electrophilic compared to a ketone, due to resonance from the other oxygen atom.[18] Both factors, the less basic carbonyl oxygen and the less electrophilic carbon, contribute to the selectivity. Steric factors are not significant. Unlike ketones, which display an exchanged broadened NMR signal for the ketone during reaction, the NMR signals of the ester remain sharp.

The NMR spectra during the reaction suggest that the ketone is associated with the metallacycle prior to reaction. Titanacyclobutenes are formally 16–electron complexes and have a vacant orbital into which the carbonyl may coordinate. Variable temperature NMR experiments confirm a dynamic process with a very low activation barrier, possibly ketone coordination, occurs. Kinetic data and activiation parameters (Table 2) are consistent with a second-order reaction. A rapid pre-equilibrium does not change the observed rate analysis.[12]

The regiochemistry of aldehyde insertion also provides information about the mechanism. Formation of a titanium–carbon bond compared to a more thermodynamically stable titanium–oxygen bond is very unusual. The estimated energy difference of a Ti–C and a Ti–O bond is ~50 kcal $mol^{-1}$.[19] The formation of a Ti–C bond has been observed in the head-to-tail coupling of diphenyl ketene units in a titanium diphenyl ketene complex.[23]

A possible explanation for the product distribution is kinetic control of the insertion proceeding *via* a $\pi$-bound aldehyde complex. An organic carbonyl group can

coordinate either in a $\pi$-sense or $\sigma$-sense to the metallacycle. A $Cp_2V(acetone)^+$ complex in which the acetone molecule is $\eta^1$–coordinated through the $sp^2$ lone pair of the oxygen atom has been structually characterized.[21] The variable temperature NMR results may be explained, by a reversible coordination of the carbonyl group in either geometry. However, a $\pi$–complex is the necessary transition state for the insertion due to orbital overlap constraints.[13] If $\eta^1$-coordination of the oxygen atom lead directly to product, then only **3** should be formed because the carbon would never interact with the titanium. A $\pi$–complex could give two isomeric complexes, one with the oxygen atom toward the metallacycle and one with the oxygen away from the metallacycle. Due to steric interactions, ketones react only with the alkyl substituents directed away from the $\eta^5$-cyclopentadienyl rings, resulting in the observed regiospecificity. Since aldehydes have only one alkyl group, they can twist slightly to accommodate reaction in either direction (Figure 1). Larger substituents on the aldehyde favor the Ti–O product as predicted. The metal center is $d^0$, and a rotation barrier resulting from back-bonding to the $\pi^*$ orbital should not exist.

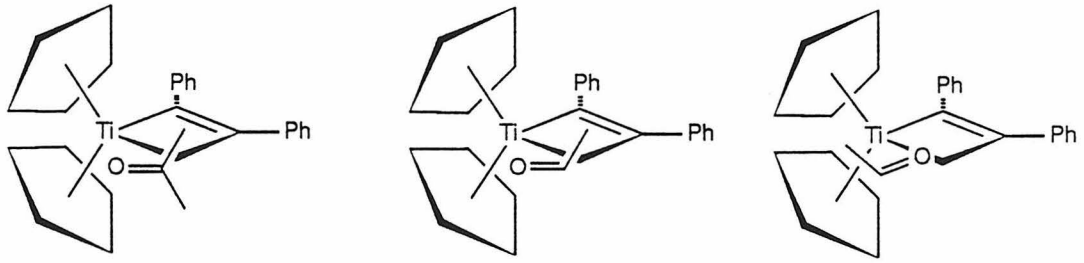



**Figure 1.** Proposed Carbonyl Complexes of **2a**

The products are also consistent with an early transition state. Based on the Hammond postulate, an early transition state should be "reactant-like" and not reflect the relative stability of the products.[24] A substituent-effect study of the kinetics may provide information about the polarization of the transition state. A proposed reaction coordinate is shown in Figure 2.

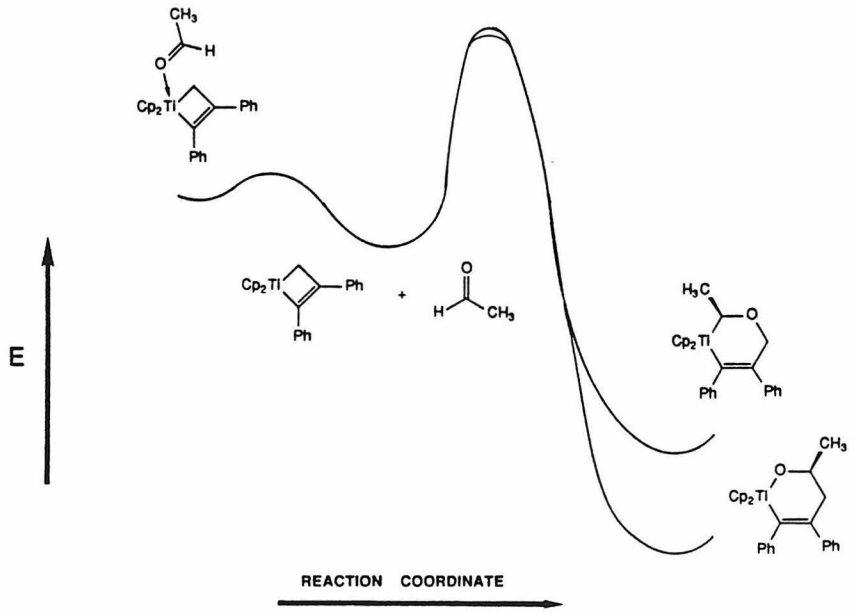
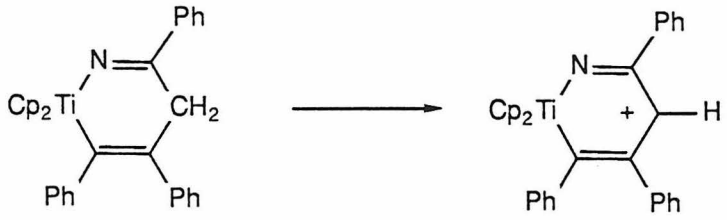



**Figure 2.** Proposed Energy Profile for Aldehyde and Ketone Insertion

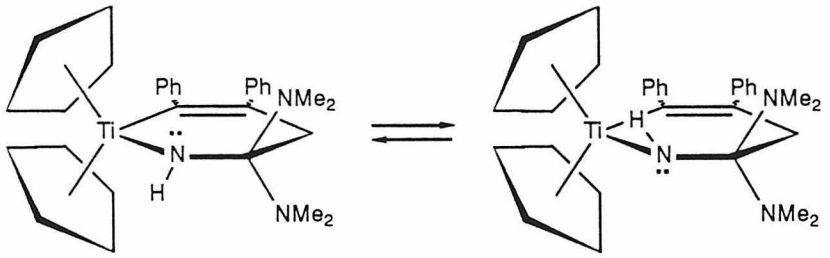
Insertion of nitriles is analogous to insertion of ketones. However, the products appear to be less stable. The remaining methylene group at the $\gamma$-position may be quite acidic due to resonance delocalization (Equation 11), and deprotonation could lead to decomposition. Nitrile insertions into zirconocene hydride and alkyl complexes yield stable complexes.[14] If the nitrile insertion product is immediately hydrolyzed, the expected ketone is isolated in low yield.

The most unusual substrate that inserts into titanacyclobutenes is tetramethylguanidine. The insertion product, **6**, has two fluxional processes by NMR.[15] The higher-energy process coalesces at +15°C at 90 MHz, yielding a $\Delta G^{\ddagger} = 14.2 \pm$




(11)

0.3 kcal $mol^{-1}$. This process is attributable to hindered rotation of the $N(CH_3)_2$ groups. The lower-energy process coalesces at –47°C, yielding a $\Delta G^{\ddagger} = 10.9 \pm$ 0.3 kcal $mol^{-1}$. This process is attributable to the inversion of the NH group bonded to the titanium. The nitrogen lone pair presumably interacts with the vacant LUMO on the metal (Equation 12).[22] This interaction would lead to inequivalent $\eta^5$-cyclopentadienyl rings, if the rate were slowed below the NMR time scale.




(12)

The lack of carbonylation of **2a** is consistent with other titanium and zirconium alkyl alkoxide complexes. The lack of carbonylation is usually explained by invoking donation of the oxygen lone-pair into the LUMO on the titanium. Dative interaction from the oxygen fills the orbital, which would be used for coordination

of the CO. This $\pi$–donation from the oxygen of titanium alkoxides has been structurally verified.[17] Attempts to complex the oxygen to another Lewis acid failed. Dimethylaluminum chloride appeared to transmetallate the Ti–O bond, although the resulting complex did not react with CO.

## Conclusions

Titanacyclobutenes readily insert ketones, aldehydes, and nitriles to form new organometallic complexes. These reactions proceed in good yield with titanacyclobutenes that have a phenyl group at the $\alpha$–position. Titanacyclobutenes that have alkyl substituents at the $\alpha$–position form unstable products.

The reaction is general for many ketones and highly selective for ketones and aldehydes over esters. Aldehydes yield two products, the predicted Ti–O bound isomer but also the Ti–C bound isomer. The product distribution is consistent with a $\pi$-bound carbonyl group at the rate-determining transition state. A detailed kinetics study of the insertion, including substituent effects, would be useful in understanding the mechanism.

Insertion of nitriles forms an analogous product; however, they are less stable than the ketone products.

The titanaoxacyclohexenes, **2**, may be hydrolyzed to the corresponding homoallylic alcohols in high yield. Unfortunately, the titanaoxacyclohexenes would not insert CO under any of the conditions used. Extensions of this work utilizing functionalized titanacyclobutenes and different Lewis acids may find use in organic synthesis.

## Experimental Section

See Chapter 1 for Gereral Considerations and Instrumentation.

**Materials.** Titanacyclobutenes were synthesized as previously described. Ketones, aldehydes, and nitriles were purchased from Aldrich Chemical Co. and used as received. Tetramethylguanidine was obtained from Kodak and dried over 4 Å molecular sieves.

### Insertion of Ketones into Titanacyclobutenes 1a and 1b.

All reactions were performed by the same general procedure. A stirred solution or suspension of the titanacyclobutene (typically 0.5 M in toluene) was treated with the ketone. The mixture was stirred for 24 - 48 hours at room temperature, at which time the solution was clear orange. As an alternate method, the reaction mixture was heated to 80°C for 10-15 minutes and cooled to room temperature. The orange solution was filtered and the volatiles removed, the solid washed with pentane or ether, and dried *in vacuo* to yield the product.

### 3,3-Dimethyl-5,6 Diphenyl-2-oxo-titanocenecyclohex-5-ene 2a.

Yield: 93%. $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.08-6.64 (m, 10H), 5.77 (s, 10H), 2.67 (s, 2H), 1.21 (s, 6H). $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 190.32, 154.32, 147.23, 134.30, 129.82, 127.55, 124.68, 122.87, 113.64 (Cp), 88.16, 58.79, 28.64. IR (KBr, $cm^{-1}$) 3010 (w), 2960 (m), 2920 (m), 1650 (w), 1155 (s), 995 (s), 800, (s). Anal. Calcd. for $C_{28}H_{28}OTi$: C, 78.50; H, 6.59. Found: C, 78.50; H, 6.72.

### 3-Methyl-3,5,6-Triphenyl-2-oxa-titanocenecylotex-5-ene, 2b.

Yield: 87%. $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.267-6.789 (m, 15H), 5.954 (s, 5H), 5.591 (s, 5H), 3.089 (d, J=15.4 Hz, 1H), 2.962 (d, J=15.4 Hz, 1H), 1.578 (s, 3H). Difference NOE experiments: irradiation of $\delta$ 5.954 enhances $\delta$ 7.220, 6.789, 5.591,

3.089; irradiation of $\delta$ 5.591 enhances $\delta$ 6.789, 5.954. $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 190.7 154.2, 150.6, 147.3, 133.9, 129.8, 128.3, 127.7, 126.4, 124.9, 123.1, 114.9 (Cp), 113.2 (Cp), 90.8, 58.3, 29.3. IR (KBr, $cm^{-1}$) 3025 (m), 2975 (m), 1600 (w), 1090 (s), 1068 (s), 1000 (s), 804 (s). Anal. Calcd. for $C_{33}H_{30}OTi$: C, 80.81; H, 6.16. Found: C, 79.70; H, 6.06.

**Reaction of Cyclohexanone with 1a, 2c.**

Yield: 90%. $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 7.029 (m, 6H), 6.883 (t of t, J=7.0, 2.0 Hz, 1H), 6.767 (m, 3H), 5.775 (s, 10H), 2.646 (s, 2H), 1.710 (m, 2H), 1.472 (m, 5H), 1.349 (m, 2H), 1.239 (m, 1H). Difference NOE experiments: irradiation of $\delta$ 5.775 enhances $\delta$ 6.767, 2.646, 1.710; irradiation of $\delta$ 2.646 enhances $\delta$ 5.775, 1.349. $^{13}C\{^1H\}$ NMR (50 MHz, $C_6D_6$) $\delta$ 189.4, 154.7, 147.6, 133.6, 129.9, 128.3, 124.6, 122.8, 113.5 (Cp), 89.9, 57.1, 37.8 ($\times$ 2), 26.6, 23.6 ($\times$ 2). IR (KBr, $cm^{-1}$) 3030 (m), 2925 (s), 1068 (s), 995 (s), 800 (s). Anal. Calcd. for $C_{31}H_{32}OTi$: C, 79.48; H, 6.88. Found: C, 78.62; H, 6.69.

**Reaction of Cyclohex-2-ene-1-one with 1a, 2d.**

Yield: 57%. $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 7.062-7.046 (m, 6H), 6.868 (m, 1H), 6.804 (m, 3H), 6.044 (d, J=10.0 Hz, 1H), 5.841 (s, 5H), 5.742 (s, 5H), 5.74 (d, overlapping Cp, 1H), 2.838 (d, J=15.4 Hz, 1H), 2.750 (d, J=15.4 Hz, 1H), 1.932-1.755 (m, 3H), 1.641-1.518 (m, 3H). Difference NOE experiments: irradiation of $\delta$ 5.841 enhances $\delta$ 6.84, 2.838; irradiation of $\delta$ 5.742 enhances $\delta$ 6.044, 2.750. $^{13}C\{^1H\}$ NMR (50 MHz, $C_6D_6$) $\delta$ 190.7 154.2, 147.2, 133.3, 133.6, 129.9, 128.7, 128.3, 127.8, 124.8, 122.9, 113.9 (Cp), 113.7 (Cp), 87.4, 57.8, 36.6, 25.9, 25.4, 20.3. IR (KBr, $cm^{-1}$) 3015 (w), 2920 (m), 1068 (s), 993 (s), 805 (s). Anal. Calcd. for $C_{29}H_{28}OTi$: C, 79.08; H, 6.41. Found: C, 77.09; H, 6.67.

**3-Cyclopropyl-3,5,6 Triphenyl-2-oxa-titanocenecyclohex-5-ene, 2e.**

Yield: 77%. $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.23-6.76 (m, 15H), 5.842 (s, 5H), 5.673 (s, 5H), 3.381 (d, J=15.4 Hz, 1H), 3.283 (d, J=15.4 Hz, 1H), 1.472 (m, 1H), 0.430 (m, 2H), 0.295 (m, 1H), 0.198 (m, 1H). Difference NOE experiments: irradiation of $\delta$ 5.842 enhances $\delta$ 7.06 6.77, 3.28; irradiation of 5.673 enhances $\delta$ 6.77, 1.47, 0.43, 0.198. $^{13}$C{$^1$H} NMR (22.5 MHz, $C_6D_6$) $\delta$ 189.3, 154.4, 147.6, 146.7, 133.7, 130.1, 127.5, 127.7, 126.4, 124.9, 123.0, 115.1 (Cp), 112.8 (Cp), 91.7, 57.1, 22.8, 2.19, 1.47. IR (KBr, $cm^{-1}$) 3010 (m), 2930 (w), 1030 (s), 810 (s) Anal. Calcd. for $C_{35}H_{32}OTi$: C, 81.39; H, 6.24. Found: C, 76.34; H, 6.13.

**Reaction of $\alpha$-tetralone with 1a, 2f.**

Yield: 96%. $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.940 (d, J=7.6 Hz, 1H), 7.237 (m, 1H), 7.108 (m, 1H), 7.044 (m, 8H), 6.860 (m, 2H), 6.796 (m, 1H), 5.998 (s, 5H), 5.673 (s, 5H), 3.150 (d, J=16.1 Hz, 1H), 2.920 (d, J=16.1 Hz, 1H), 2.643 (m, 1H), 2.588 (m, 1H), 2.320 (m, 1H), 1.923 (m, 1H), 1.815 (m, 2H). Difference NOE experiments: irradiation of $\delta$ 5.998 enhances $\delta$ 7.940, 6.860, 5.673, 3.150; irradiation of $\delta$ 5.673 enhances $\delta$ 6.860, 5.998, 2.920, 1.923.

**Reaction of $\beta$-tetralone with 1a, 2g.**

Yield: 77%. $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.236-6.911 (m, 14H), 5.961 (s, 1H), 5.561 (s, 5H), 3.270 (d, J=16.3 Hz, 1H), 2.942 (m, 1H), 2.920 (d, J=15.6 Hz, 1H), 2.880 (d, J=16.6 Hz, 1H), 2.722 (d, J=15.6 Hz, 1H), 1.825 (m, 1H), 1.780 (m, 1H). Difference NOE experiments: irradiation of $\delta$ 5.961 enhances $\delta$ 6.91, 5.561, 2.920; irradiation $\delta$ 5.561 enhances $\delta$ 6.91, 5.961, 3.270.

**3-Methyl-5,6-Diphenyl-3-Vinyl 2-oxa-titanocenecylohex-5-ene 2h.**

Yield: 62%. $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.03-6.76 (m, 10H), 5.97 (d of d,

J=10.5, 17.1 Hz, 1H), 5.938 (s, 5H), 5.612 (s, 5H), 5.100 (d of d, J=17.1, 2.2 Hz, 1H), 4.970 (d of d, J=10.5, 2.2 Hz, 1H), 2.910 (d, J=15.4 Hz, 1H), 2.58 (d, J=15.4 Hz, 1H), 1.34 s 3 . Difference NOE experiments: irradiation of $\delta$ 5.940 and 5.970 enhances $\delta$ 6.76, 5.61, 2.91; irradiation of $\delta$ 5.61 enhances $\delta$ 6.76, 5.94; irradiation of $\delta$ 1.34 enhances 7.02, 5.97, 5.61, 5.10, 2.58. $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 190.7, 154.3, 147.0, 146.1, 133.4, 129.9, 127.6, 124.8, 123.0, 114.5, 113.4, 110.3, 89.7, 57.0, 26.2. IR (KBr, $cm^{-1}$) 3005 (m), 2910 (s), 1015 (s), 987 (s), 800 (s). Anal. Calcd. for $C_{29}H_{28}OTi$: C, 79.08; H, 6.41. Found: C, 77.09; H, 6.67.

**Reaction of Ethyl Leuvinate with 1a. Synthesis of 2m.**

$^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 7.02-6.69 (m, 6H), 6.88 (t of t, J=7.0, 2.0 Hz, 1H), 6.75 (m, 3H), 5.901 (s, 5H), 5.596 (s, 5H), 4.010 (m, 2H), 2.720 (d, J=15.4 Hz, 1H), 2.460 (d, J=15.4 Hz, 1H), 2.315 (m, 2H), 2.138 (m, 1H), 2.01 (m, 1H), 1.77 (m, 1H), 1.134 (s, 3H), 1.020 (t, J=7.1 Hz, 3H). Difference NOE experiments: irradiation of $\delta$ 5.901 enhances $\delta$ 6.75 and 2.72; irradiation of $\delta$ 5.596 enhances $\delta$ 6.75. $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 190.52, 173.51, 154.27, 147.18, 133.85, 129.84 (CH), 127.62 (CH), 124.75 (CH), 122.96 (CH), 114.19 (Cp), 113.59 (Cp), 89.38 (quat), 60.07 ($CH_2$), 57.52 ($CH_2$), 37.53 ($CH_2$), 30.11 ($CH_2$), 24.64 ($CH_3$), 14.34 ($CH_3$).

**Reaction of *l*-Carvone with 1a. Synthesis of 2j.**

Major isomer: $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 7.31-6.75 (m, 10H), 6.076 (s, 5H), 5.441 (s, 5H), 5.32 (br s, 1H), 5.05 (t, J=1.0 Hz, 1H), 4.91 (t, J=1.0 Hz, 1H), 3.16 (d of d, J=15.8, 1.7 Hz, 1H), 2.70 (m, 1H), 2.69 (d, J=15.8 Hz, 1H), 2.50 (m, 2H), 1.95 (m, 1H), 1.83 (br s, 3H), 1.79 (s, 3H). Difference NOE experiments: irradiation of $\delta$ 6.074 enhances $\delta$ 6.880, 5.441, 3.16; irradiation of $\delta$ 5.441 enhances $\delta$ 6.076. $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 190.95, 154.22, 149.51, 147.45, 140.13, 134.34,

130.11, 129.95, 127.67, 125.94, 125.40, 124.08, 123.18, 123.07, 113.37 (Cp), 114.51 (Cp), 109.71, 93.33, 53.68, 40.89, 39.27, 31.89, 20.52, 19.22.

Minor isomer: $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.31-6.75 (m, 10H), 6.032 (s, 5H), 5.665 (s, 5H), 5.44 (br d, J=12 Hz, 1H), 5.01 (t, J=1.0 Hz, 1H), 4.89 (t, J=1.0 Hz, 1H), 3.35 (d, J=15.6 Hz, 1H), 2.41 (d, J=15.6 Hz, 1H), 2.70 (m, 1H), 2.50 (m, 2H), 1.95 (m, 1H), 1.88 (br s, 3H), 1.78 (s, 3H). Difference NOE experiments: irradiation of $\delta$ 6.032 enhances $\delta$ 6.75, 5.665, 3.35; irradiation of $\delta$ 5.665 enhances $\delta$ 6.75, 6.032. $^{13}$C{$^1$H} NMR (22.5 MHz, $C_6D_6$) $\delta$ 190.14, 154.44, 149.78, 147.12, 137.86, 134.23, 130.11, 129.95, 127.67, 125.94, 125.40, 124.08, 123.18, 123.07, 114.51 (Cp), 113.48 (Cp), 109.64, 91.00, 56.06, 41.81, 38.72, 32.33, 20.95, 19.54. (Some signals of the isomers overlap.)

**Reaction of Norcamphor with 1a. Synthesis of 2k.**

$^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.05-6.99 (m, 6H), 6.86 (t of t, J=7.1, 2.0 Hz, 1H), 6.78 (m, 3H), 5.825 (s, 5H), 5.692 (s, 5H), 2.84 (d, J=15.4 Hz, 1H), 2.73 (d, J=15.4 Hz, 1H), 2.18-2.15 (m, 2H), 1.81 (m, 1H), 1.73 (m, 1H), 1.53 (m, 1H), 1.35-1.15 (m, 4H), 0.93 (m, 1H). Difference NOE experiments: irradiation of $\delta$ 5.825 enhances $\delta$ 6.78, 5.692, 2.84; irradiation of $\delta$ 5.692 enhances $\delta$ 6.78, 5.825, 2.73, 1.35. $^{13}$C{$^1$H} NMR (22.5 MHz, $C_6D_6$) $\delta$ 190.30, 154.92, 147.34, 134.12, 129.90, 127.62, 127.51, 124.70, 122.85, 113.59 (Cp), 113.48 (Cp), 97.45, 57.52, 48.26, 45.44, 38.24, 37.42, 29.29, 22.85.

**Reaction of *d*-Camphor with 1a. Synthesis of 2l.**

$^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.14-6.99 (m, 6H), 6.86-6.78 (m, 4H), 5.961 (s, 10H), 5.641 (s, 10H), 2.940 (d, J=15.4 Hz, 1H), 2.360 (d, J=15.4 Hz, 1H), 2.195 (d of t, J=12.9, 1.5, 1H), 1.72 (t, J=4.6 Hz, 1H), 1.68 (d, J=13.2 Hz, 1H), 1.56 (m, 2H), 1.32 (m, 2H), 1.017 (s, 3H), 0.932 (s, 3H), 0.852 (s, 3H). Difference NOE

experiments: irradiation of $\delta$ 5.961 enhances $\delta$ 5.641, 2.96, 1.72, 0.932; irradiation of $\delta$ 5.641 enhances $\delta$ 5.961, 2.360, 2.195, 1.017. $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 190.57, 154.82, 147.77, 134.39, 129.95, 128.49, 127.67, 127.57, 124.75, 122.96, 113.64 (Cp), 113.37 (Cp), 100.80, 54.65, 54.43, 49.40, 45.88, 31.57, 27.51, 21.55, 21.39, 12.12.

**Reaction of 2-Methyl Cyclohexanone with 1a. Synthesis of 2i.**

First isomer: $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 7.06-6.75 (m, 10H), 6.000 (s, 5H), 5.644 (s, 5H), 2.80 (d, J=15.6 Hz, 1H), 2.56 (d, J=15.6 Hz, 1H), 2.01 (m, 1H), 1.56-1.10 (m, 8H), 0.995 (d, J=6.6 Hz, 3H). Second isomer: $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 7.06-6.75 (m, 10H), 5.943 (s, 5H), 5.601 (s, 5H), 2.96 (d, J=15.6 Hz, 1H), 2.53 (d, J=15.6 Hz, 1H), 2.01 (m, 1H), 1.56-1.04 (m, 8H), 0.950 (d, J=7.1 Hz, 3H). Difference NOE experiments: irradiation of $\delta$ 6.000 enhances $\delta$ 6.75, 2.80; irradiation of $\delta$ 5.943 enhances $\delta$ 6.75, 2.96; irradiation of $\delta$ 5.664 enhances $\delta$ 6.75, 2.56, 2.01, 1.53; irradiation of $\delta$ 5.601 enhances $\delta$ 6.75, 2.53, 2.01. $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 189.60, 189.27, 154.82, 154.55, 147.94, 147.61, 134.45, 134.28, 129.95, 127.62, 124.75, 122.91, 114.19, 114.02, 113.32, 113.05, 93.4, 92.52, 55.68, 50.15, 41.76, 41.43, 35.25, 31.79, 24.53, 24.42, 24.09, 23.94, 16.46.

**3,3-Bis(dimethylamino)-5,6-Diphenyl-2-aza-titanocene cyclohex-5-ene,6.**

Yield: 92%. $^1H$ NMR (90 MHz, $C_7D_8$) $\delta$ 7.30-6.24 (m, 10H), 5.72 (s, 10H), 2.56 (br s, 6H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_7D_8$) $\delta$ 178.70, 161.09, 158.76, 150.15, 129.29, 127.88, 127.34, 127.07, 124.09, 121.71, 110.28 (Cp), 39.20 (br), 30.96. IR (KBr, $cm^{-1}$) 3060 (w), 3020 (w), 2920 (m), 2870 (m), 1570 (s), 1485 (s), 1455 (s), 1425 (s), 1360 (s), 1122 (s), 1022 (s), 805 (s). Anal. Calcd for $C_{30}H_{35}N_3Ti$: C, 74.21; H, 7.27; N, 8.65. Found: C, 74.05; H, 7.18, N, 8.52.

**3,3,5-Trimethyl-6-Phenyl-2-oxa-titanocenecyclohex-5-ene, 2n.**

Yield: 74%. $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.38-6.87 (m, 5H), 5.74 (s, 10H), 2.26 (s, 2H), 1.64 (s, 3H), 1.13 (s, 6H). $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 186.8, 155.0, 123.0, 113.6, 88.0, 57.4, 28.5, 24.2. IR (KBr, $cm^{-1}$) 3020 (w), 2980 (m), 2910 (m), 1000 (s), 805 (s). Anal. Calcd. for $C_{23}H_{26}OTi$: C, 75.41; H, 7.15. Found: C, 75.16; H, 7.03.

**3,5-Dimethyl-3,6-Diphenyl-2-oxa-titanocenecyclohex-5-ene, 2o.**

Yield: 85%. $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.33-6.95 (m, 10H), 5.88 (s, 5H), 5.62 (s, 5H), 2.83 (d of d, J=15.3, 1.0 Hz, 1H), 2.42 (d, J=15.3 Hz, 1H), 1.70 (d, J=1.0 Hz, 3H), 1.42 (s, 3H). $^{13}C\{^1H\}$ NMR (22.5 MHz, $C_6D_6$) $\delta$ 187.05, 154.87, 150.81, 128.27, 126.54, 126.37, 124.91, 123.40, 114.67 (Cp), 113.10 (Cp), 90.78, 56.82, 28.64, 24.42. IR (KBr, $cm^{-1}$) 3060 (w), 2990 (m), 2890 (m), 1100 (s), 1070 (s), 808 (s), Anal. Calcd. for $C_{28}H_{28}OTi$: C, 78.50; H, 659. Found: C, 77.57; H, 6.61.

**Acidolysis of 2a.**

A stirred suspension of **2a** (115 mg, 0.268 mmol) in 2 ml of diethyl ether at 0 °C was treated with anhydrous HCl gas (15 ml, 0.67 mmol). The mixture immediately turned red and a red precipitate formed. The reaction was warmed to room temperature over 15 minutes, diluted with 10 ml more diethylether, filtered through a 1-inch plug of silica gel and the filtrate concentrated at reduced pressure to yield an orange residue. The residue was extracted with petroleum ether: ether (3:1), the extract filtered through glass wool, and concentrated at reduced pressure to yield the product 2-methyl-4,5 diphenyl-pent-4-ene-2-al (61 mg, 0.242 mmol, 90%) as yellowish crystals. $^1$H NMR (400 MHz, $CDCL_3$) $\delta$ 7.279-7.198 (m, 5H), 7.100-7.052 (m, 3H), 6.940-6.921 (m, 2H), 6.522 (s, 1H), 2.768 (s, 2H), 1.497 (br s, 1H), 1.155 (s, 6H). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CDCL_3$) $\delta$ 141.41, 139.35, 137.13,

130.68, 129.00, 128.63, 127.82, 127.11, 126.35, 71.53, 53.71 ($CH_2$), 29.76 ($CH_3$).

**Reaction of p-Tolualdehyde with 1a.**

To a stirred suspension of titanacyclobutene **1a** (365 mg, 0.986 mmol) in 2 ml toluene at room temperature was added p-tolualdehyde (140 ml, 1.18 mmol). The mixture was stirred at room temperature for 12 hours, then the volatiles removed *in vacuo* to yield a red-orange form. The foam was triturated with diethylether, the yellow precipitate filtered from the red solution, and both fractions taken to dryness. The yellow fraction (150 mg , 0.307 mmol) was the insertion product **10a**: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.37-6.67 (m, 14H), 6.06 (s, 5H), 5.59 (s, 5H), 5.48 (m, 1H), 3.05 (s, 1H), 2.97 (d, J=3.2 Hz, 1H), 2.18 (s, 3H). $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.29-6.95 (m, 10H), 6.89 (t of t, J=7.1, 0.8 Hz, 2H), 6.78 (t of t, J=7.1, 0.8 Hz, 2H), 6.119 (s, 5H), 5.610 (s, 5H), 5.53 (d of d, J=10.1, 2.8 Hz, 1H), 3.07 (d of d, J=16.6, 2.9 Hz, 1H), 2.985 (d of d, J=16.6, 10.2 Hz, 1H), 2.18 (s, 3H). $^{13}$C{$^1$H} NMR (22.5 MHz, $C_6D_6$) $\delta$ 191.44, 153.03, 146.71, 136.51, 136.29, 130.06, 129.08, 128.43, 127.62, 125.72, 124.97, 123.23, 114.35 (Cp), 113.86 (Cp), 88.67, 57.09, 21.11. The diethylether soluble fraction revealed a 2:1 ration of products. The major product was the same as the yellow precipitate; the minor product had $^1$H NMR $\eta^5$-cyclopentadienyl resonances at $\delta$ 5.91, 5.82.

**Reaction of Acetaldehyde with 1a.**

To a stirred suspension of titanacyclobutene **1a** (320 mg, 0.864 mmol) in 3 ml of toluene at room temperature was added acetaldehyde (60 ml, 1.07 mmol) *via* syringe. The reaction vessel was wrapped in Al foil and the mixture stirred for 12 hours. The reaction mixture was taken to dryness and the red-orange solid was extracted with 2 ml toluene at –78°C. Both fractions were dried *in vacuo*. The extract was red-orange and the residue was dark-red. The red-orange extract

material was a 2:1 ratio of the Ti-O product. Orange isomer: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.34-6.57 (m, 10H), 5.98 (s, 5H), 5.60 (s, 5H), 4.66-4.29 (m, 1H), 2.70 (s, ?H), 2.64 (d, J=2.9 Hz, 1H), 1.06 (d, J=5.8 Hz, 3H). $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.406-6.728 (m, 10H), 5.982 (s, 5H), 5.592 (s, 5H), 4.498 (m, 1H), 2.70 (d of d, J=16.4, 2.8 Hz, 1H), 2.60 (d of d, J=16.4, 9.5 Hz, 1H), 1.06 (d, J=5.9 Hz, 3H). $^{13}$C{$^1$H} NMR (22.5 MHz, $C_6D_6$) $\delta$ 191.11, 153.30, 136.18, 130.49, 130.06, 128.33, 127.57, 124.91, 123.12, 114.19 (Cp), 113.54 (Cp), 83.25, 55.95, 23.77. Red isomer: $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.336-6.944 (m, 10H), 5.890 (s, 5H), 5.883 (s, 5H), 5.641 (q, J=6.35 Hz, 1H), 4.470 (d of d, J=10.0, 4.2 Hz, 1H), 1.48 (d, J=9.8 Hz, 1H), 1.215 (d, J=6.35 Hz, 3.H)$^{13}$C{$^1$H} NMR (22.5 MHz, $C_6D_6$) $\delta$ 181.76, 148.32, 146.09, 144.63, 143.06, 130.44, 130.00, 128.27, 127.57, 126.05, 125.67, 113.54 (Cp), 111.29 (Cp), 87.97, 59.42, 22.41.

**Reaction of Benzonitrile with 1a.**

A solution of titanacycle **1a** (34 mg, 0.092 mmol) in 400$\mu$L of $C_6D_6$ in an NMR tube was treated with benzonitrile (10$\mu$L, 0.098 mmol). After 24 hours the solution was dark orange and NMR analysis revealed a new compound: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.50-6.80 (m, 15H), 5.64 (s, 10H), 4.03 (s, 2H).

**Reaction of p-Tolunitrile with 1a.**

A solution of titanacyclobutene **1a** (38 mg, 0.103 mmol) in 400 $\mu$L of $C_6D_6$ in an NMR tube was treated with p-tolunitrile. After 18 hours the color had changed to dark-orange, and the NMR spectrum revealed the reaction as 90% complete: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.50-6.80 (m, 14H), 5.66 (s, 10H), 4.01 (s, 2H), 2.13 (s, 3H).

**Reaction of $\alpha$-phenylpropionitrile with 1a.**

A solution of **1a** (38 mg, 0.103 mmol) in 400 $\mu$L of $C_6D_6$ in an NMR tube was treated with $\alpha$-phenyl propionitrile (14$\mu$L, 0.105 mmol) at room temperature. The color changed slowly over 24 hours from red to dark-orange. NMR analysis revealed a single product and some remaining starting materials: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.15-6.60 (m, 15H), 5.63 (s, 5H), 5.61 (s, 5H), 3.54 (br s, 2H), 3.08 (q, J=7.0 Hz, 1H), 1.32 (d, J=7.0 Hz, 3H).

**Reaction of $\alpha$-methyl propionitrile with 1a.**

A solution of **1a** (38 mg, 0.103 mmol) in 400 $\mu$Lof $C_6D_6$ in an NMR tube was treated with $\alpha$-methyl propionitrile (10$\mu$L, 0.11 mmol) at room temperature. The color changed slowly over 24 hours from red to dark-orange. NMR analysis revealed a single product and some remaining starting materials: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.15-6.60 (m, 10H), 5.60 (s, 10H), 3.51 (s, 2H), 1.94 (septet, J=7.1 Hz, 1H), 0.93 (d, J=7.1 Hz, 6H).

**Reaction of Methacrylonitrile with 1a.**

A solution of **1a** (26 mg, 0.071 mmol) in 400 $\mu$L of $C_6D_6$ was treated with methacrylonitrile (6 $\mu$L, 0.071 mmol) at room temperature. After 12 hours the reaction was ~60% complete by NMR analysis: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.16-6.50 (m, 10H), 5.60 (s, 5H), 5.58 (s, 5H), 5.03 (m, 2H), 3.87 (s, 2H), 1.82 (br s, 3H).

**Hydrolysis of the Insertion Product of 1a and p-Tolunitrile.**

To a stirred solution of metallacycle **1a** (200 mg, 0.54 mmol) in 3 ml of THF was added p-tolunitrile (75 $\mu$L, 0.627 mmol) at room temperature. The reaction was stirred at room temperature for 24 hours. The volatiles were removed *in vacuo*

and the solid suspended in diethylether and hydrolyzed with 5% aqueous HCl for 30 minutes. The aqueous phase was separated and extracted with diethylether 3 × 5 ml, the organic phases combined, dried over $MgSO_4$, and concentrated *in vacuo*. The product was flash-chromatographed ($CHCL_3$) to yield 41 mg of the product ketone: $^1$H NMR (90 MHz, $CDCL_3$) $\delta$ 7.80-7.00 (m, 14H), 6.55 (br s, 1H), 4.11 (d, J=1.2 Hz, 2H), 2.37 (s, 3H).

**Reaction of p-Tolunitrile with 1b.**

A solution of metallacycle **1b** (97 mg, 0.315 mmol) in 500 $\mu$L of $C_6D_6$ was treated with p-tolunitrile (36 $\mu$L, 0.32 mmol) at room temperature. The reaction was complete within 4 hours to yield a dark-orange solution: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 7.50-6.80 (m, 9H), 5.70 (s, 10H), 3.68 (s, 2H), 2.20 (s, 3H), 1.65 (s, 3H).

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# Appendix I.

## X-ray Structure Determination of $Cp_2TiC_4H_2O(C_6H_5)(Si(CH_3)_3)(P(CH_3)_3)$

A thin crystalline prism (0.023 × 0.033 × 0.198mm) of ($\eta^5$-$C_5H_5)_2$Ti(C,O-$\eta^2$-$CH_2$=C($Me_3Si$)C($C_6H_5$)=CO) ($PMe_3$), obtained after slow cooling of an ether solution to −50°Cfor 5 days, was mounted approximately along **c** in a glass capillary under $N_2$. A series of oscillation and Weissenberg photographs indicated monoclinic symmetry and the space group $P2_1/c$ ($0k0$ absent for $k$ odd, $h0l$ absent for $l$ odd); data were collected on a locally modified Syntex $P2_1$ diffractometer with graphite monochromator and Mo$K\alpha$ radiation ($\lambda$ = 0.7107 Å). The unit cell parameters (Table 1) were obtained by least-squares refinement of the average $2\theta$-values from four sets of seventeen reflections: '$\pm 2\theta$' $hkl$ and '$\pm 2\theta$' $\overline{hkl}$, $20 < 2\theta < 39°$. The three check reflections indicated no decomposition. No absorption correction was performed. The data were averaged over the Laue symmetry and reduced to $F_o^2$; the form factors were taken from Table 2.2B, *International Tables for X-Ray Crystallography* (1974); those for Ti, Si, and P were corrected for anomalous dispersion. The details of data collection are summarized in Table 1.

The position of the Ti atom was derived from the Patterson map, and the Fourier map phased on the Ti atom revealed the remainder of the structure. Hydrogen atoms H(1) and H(2) were located from the difference map and refined with isotropic $U$; the remaining H-atoms were introduced into the model with fixed coordinates and isotropic Gaussian amplitudes at idealized positions. Least-squares refinement of the non-hydrogen atoms with anisotropic $U_{ij}$'s, minimizing $\Sigma w[F_o^2 - (F_c/k)^2]^2$, using all the data (3038 reflections) led to $S = 1.66$, $R_F = 0.050$, and $R_F' = 0.084$;* final shift/errors < 0.10. A correction for secondary extinction (A.C. Larson, *Acta. Cryst.*, 23 , 664-665 (1967), Eqn. 3) was included, and the final

value of the extinction coefficient was $0.22(4)\times10^{-6}$. All calculations were carried out on a VAX 11/780 computer using the CRYRM system of programs.

*$R_F = \Sigma||F_o| - |F_c||/\Sigma F_o$, $S = \sqrt{\Sigma w\Delta^2/(n-v)}$, $R'_F = \sqrt{\Sigma w\Delta^2/\Sigma F_o^4}$, $w^{-1} = [s + r^2b + (0.02s)^2]k^4/(Lp)^2$, s = scan counts, r = scan-to-background time ratio, b = total background counts, k = 0.9813(19) (scale factor on $F_o$), $\Delta = F_o^2 - (F_c/k)^2$, n = 3038, v = 280.

**Table 1. Summary of Crystal Data and Intensity Collection Information.**

| | |
|---|---|
| Formula | $C_{26}H_{35}OPSiTi$ |
| Formula weight | 470.528 |
| Space group | $P2_1/c$ |
| a | 9.625(2)Å |
| b | 16.217(2)Å |
| c | 16.917(4)Å |
| $\beta$ | 101.28(10)° |
| V | 2589.5(9)Å$^3$ |
| Z | 4 |
| $D_{calc}$ | 1.207(4) g/ml |
| Crystal size | 0.023 × 0.033 × 0.198 mm |
| $\lambda$ | 0.710733 Å |
| $\mu$ | 0.403 mm$^{-1}$ |
| Scan range | 1.0° above K$\alpha_1$, 1.0° below K$\alpha_2$ |
| Reflections | $+h$, $\pm k$, $\pm l$ |
| Collected | 6717 reflections |
| Averaged | 3038 reflections |
| | (2735 I > 0, 1775 I > $3\sigma_I$) |

**Table 2. Atom Coordinates ($\times 10^5$) and $U_{eq}$'s (Å$^2$, $\times 10^4$).**

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Ti | 8771(11) | 18445(5) | 12208(5) | 428(2) |
| O | −8753(34) | 12452(18) | 5749(18) | 455(9) |
| C(1) | −8238(54) | 19629(28) | 2415(27) | 400(14) |
| C(2) | −17514(54) | 23268(29) | −3578(28) | 399(15) |
| C(3) | −15991(62) | 32106(31) | −5892(26) | 428(14) |
| C(4) | −3481(77) | 35419(41) | −5976(35) | 591(20) |
| C(5) | −30079(55) | 18565(31) | −8108(29) | 457(14) |
| C(6) | −33087(62) | 19017(33) | −16466(32) | 579(16) |
| C(7) | −43925(74) | 14425(38) | −20938(36) | 757(20) |
| C(8) | −52114(70) | 9553(39) | −17036(46) | 817(26) |
| C(9) | −49157(72) | 9048(37) | −8757(49) | 822(26) |
| C(10) | −38185(64) | 13463(34) | −4264(34) | 617(19) |
| P | 5140(17) | 4885(8) | 19660(9) | 526(4) |
| C(31) | −12764(65) | 4069(37) | 21720(38) | 861(21) |
| C(32) | 6118(75) | −4444(32) | 13873(34) | 898(22) |
| C(33) | 16238(67) | 2245(34) | 29331(32) | 782(19) |
| Si | −31867(20) | 38989(10) | −6651(11) | 681(5) |
| C(41) | −25827(79) | 49961(36) | −5992(48) | 1219(31) |
| C(42) | −44557(87) | 38229(47) | −16036(54) | 1686(37) |
| C(43) | −40140(82) | 36777(42) | 1964(56) | 1415(32) |
| C(11) | 12870(84) | 31759(34) | 18116(37) | 678(20) |
| C(12) | −918(87) | 31429(36) | 14584(31) | 656(19) |
| C(13) | −7633(67) | 25683(42) | 18789(42) | 721(20) |
| C(14) | 2791(94) | 22492(35) | 24968(35) | 728(20) |
| C(15) | 15625(76) | 26241(39) | 24530(36) | 705(20) |
| C(21) | 19603(63) | 17483(38) | 708(32) | 627(17) |
| C(22) | 21772(62) | 9852(34) | 4615(35) | 613(18) |
| C(23) | 30543(67) | 11054(40) | 12212(38) | 720(20) |
| C(24) | 34013(62) | 19455(42) | 12966(36) | 713(23) |
| C(25) | 27213(65) | 23425(36) | 5931(38) | 647(19) |

**Table 3. Bond Lengths(Å).**

| | |
|---|---|
| Ti–O | 2.064(3) |
| Ti–C(1) | 2.098(5) |
| Ti–P | 2.592(2) |
| Ti–C(11) | 2.380(7) |
| Ti–C(12) | 2.369(6) |
| Ti–C(13) | 2.408(7) |
| Ti–C(14) | 2.431(7) |
| Ti–C(15) | 2.417(7) |
| Ti–C(21) | 2.385(6) |
| Ti–C(22) | 2.405(6) |
| Ti–C(23) | 2.413(6) |
| Ti–C(24) | 2.412(6) |
| Ti–C(25) | 2.380(6) |
| O–C(1) | 1.298(6) |
| C(1)–C(2) | 1.349(7) |
| C(2)–C(3) | 1.500(7) |
| C(2)–C(5) | 1.506(7) |
| C(3)–C(4) | 1.321(8) |
| C(3)–Si | 1.876(5) |
| C(4)–H(1) | 0.92(5) |
| C(4)–H(2) | 1.09(3) |
| C(5)–C(6) | 1.389(7) |
| C(5)–C(10) | 1.384(8) |
| C(6)–C(7) | 1.380(8) |
| C(7)–C(8) | 1.373(9) |
| C(8)–C(9) | 1.376(10) |
| C(9)–C(10) | 1.375(9) |
| P–C(31) | 1.828(6) |
| P–C(32) | 1.814(6) |
| P–C(33) | 1.822(6) |
| Si–C(41) | 1.868(7) |
| Si–C(42) | 1.808(8) |
| Si–C(43) | 1.828(8) |
| C(11)–C(12) | 1.345(9) |
| C(11)–C(15) | 1.392(9) |

| | |
|---|---|
| C(12)–C(13) | 1.404(9) |
| C(13)–C(14) | 1.399(10) |
| C(14)–C(15) | 1.391(9) |
| C(21)–C(22) | 1.399(8) |
| C(21)–C(25) | 1.412(8) |
| C(22)–C(23) | 1.406(9) |
| C(23)–C(24) | 1.403(9) |
| C(24)–C(25) | 1.398(9) |
| CP(1)–Ti | 2.091 |
| CP(2)–Ti | 2.081 |

**Table 4. Bond Angles(°).**

| | |
|---|---|
| C(1)–Ti–O | 36.4(2) |
| C(1)–O–Ti | 73.2(2) |
| O–C(1)–Ti | 70.4(2) |
| C(2)–C(1)–Ti | 158.9(4) |
| C(2)–C(1)–O | 130.0(4) |
| C(3)–C(2)–C(1) | 122.0(4) |
| C(5)–C(2)–C(1) | 120.5(4) |
| C(5)–C(2)–C(3) | 117.4(4) |
| C(4)–C(3)–C(2) | 121.8(5) |
| Si–C(3)–C(2) | 117.8(4) |
| Si–C(3)–C(4) | 119.3(4) |
| H(1)–C(4)–C(3) | 125(3) |
| H(2)–C(4)–C(3) | 128(2) |
| H(2)–C(4)–H(1) | 106(4) |
| C(5)–C(6)–C(7) | 120.9(5) |
| C(6)–C(7)–C(8) | 119.4(6) |
| C(7)–C(8)–C(9) | 120.0(6) |
| C(8)–C(9)–C(10) | 121.0(6) |
| C(9)–C(10)–C(5) | 119.6(5) |
| C(10)–C(5)–C(6) | 119.1(5) |
| C(11)–C(12)–C(13) | 108.2(6) |
| C(12)–C(13)–C(14) | 106.9(6) |
| C(13)–C(14)–C(15) | 108.2(6) |
| C(14)–C(15)–C(11) | 106.7(6) |
| C(15)–C(11)–C(12) | 110.0(6) |
| C(21)–C(22)–C(23) | 108.4(5) |
| C(22)–C(23)–C(24) | 107.9(5) |
| C(23)–C(24)–C(25) | 107.8(5) |
| C(24)–C(25)–C(21) | 108.5(5) |
| C(25)–C(21)–C(22) | 107.3(5) |
| C(3)–Si–C(41) | 108.8(3) |
| C(3)–Si–C(42) | 114.9(3) |
| C(3)–Si–C(43) | 107.7(3) |
| C(41)–Si–C(42) | 105.4(4) |
| C(42)–Si–C(43) | 111.2(4) |

| | |
|---|---|
| C(43)–Si–C(41) | 108.6(3) |
| C(31)–P–C(32) | 101.1(3) |
| C(32)–P–C(33) | 101.9(3) |
| C(33)–P–C(31) | 102.7(3) |
| P–Ti–O | 71.6(1) |
| CP(1)–Ti–CP(2) | 131.2 |

**Table 5. Gaussian amplitudes ($\times 10^4$).**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Ti | 470(8) | 350(5) | 445(5) | 5(5) | 40(5) | −10(5) |
| O | 426(26) | 359(20) | 522(21) | −6(18) | −52(18) | 14(16) |
| C(1) | 349(40) | 409(33) | 436(30) | −36(26) | 58(27) | −44(25) |
| C(2) | 264(39) | 452(32) | 462(31) | 4(27) | 21(28) | −3(25) |
| C(3) | 419(43) | 434(31) | 404(29) | 4(32) | 8(27) | 27(26) |
| C(4) | 444(54) | 624(43) | 669(41) | −14(43) | 17(37) | 159(33) |
| C(5) | 391(41) | 384(29) | 570(34) | 121(30) | 23(30) | 44(29) |
| C(6) | 532(45) | 522(34) | 618(37) | −39(33) | −50(32) | −32(31) |
| C(7) | 719(56) | 614(40) | 835(47) | −23(39) | −106(42) | −34(35) |
| C(8) | 509(56) | 628(45) | 1147(63) | −30(37) | −251(48) | −76(43) |
| C(9) | 458(53) | 623(43) | 1338(67) | −89(37) | 59(49) | 198(43) |
| C(10) | 429(47) | 589(39) | 806(44) | −28(34) | 48(38) | 151(33) |
| P | 549(12) | 390(8) | 578(9) | −15(8) | −40(8) | 49(7) |
| C(31) | 625(51) | 773(45) | 194(54) | −77(39) | 199(42) | 342(40) |
| C(32) | 1443(67) | 397(34) | 786(44) | 4(41) | 46(43) | −82(31) |
| C(33) | 812(53) | 704(42) | 710(40) | −143(37) | −153(38) | 240(32) |
| Si | 567(14) | 460(10) | 980(14) | 87(9) | 57(11) | 46(9) |
| C(41) | 1109(67) | 453(41) | 2168(83) | 119(43) | 494(62) | −58(48) |
| C(42) | 1198(76) | 1141(65) | 2224(97) | 524(61) | −886(70) | −421(64) |
| C(43) | 1076(70) | 927(57) | 2544(101) | 428(53) | 1091(70) | 411(61) |
| C(11) | 1028(62) | 313(31) | 721(43) | −175(38) | 234(42) | −161(32) |
| C(12) | 1049(65) | 435(35) | 479(36) | 211(41) | 135(41) | −57(31) |
| C(13) | 658(55) | 783(47) | 756(47) | 46(40) | 217(43) | −380(38) |
| C(14) | 1214(72) | 550(39) | 441(36) | 10(45) | 211(43) | 41(30) |
| C(15) | 800(61) | 649(44) | 582(41) | 33(41) | −76(40) | −101(34) |
| C(21) | 603(48) | 675(41) | 631(37) | 66(37) | 183(34) | 41(34) |
| C(22) | 513(48) | 643(41) | 688(41) | 161(34) | 124(36) | −71(33) |
| C(23) | 525(51) | 781(45) | 853(47) | 217(39) | 127(40) | 86(38) |
| C(24) | 350(45) | 885(50) | 864(47) | −26(38) | 14(36) | −68(40) |
| C(25) | 441(47) | 688(43) | 825(46) | 17(35) | 152(38) | 128(36) |

**Table 6. Hydrogen Atom Coordinates ($\times 10^4$) and B's ($Å^2$, $\times 10^4$).**

| | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| H(1) | −189(57) | 4086(32) | −712(30) | 84(21) |
| H(2) | 672(37) | 3230(18) | −543(16) | −3(8) |
| H(6) | −2706 | 2282 | −1951 | 89 |
| H(7) | −4612 | 1465 | −2731 | 89 |
| H(8) | −6045 | 643 | −2047 | 89 |
| H(9) | −5562 | 518 | −620 | 89 |
| H(10) | −3636 | 1304 | 200 | 89 |
| H(11) | 2057 | 3551 | 1649 | 89 |
| H(12) | −575 | 3484 | 978 | 89 |
| H(13) | −1851 | 2405 | 1752 | 89 |
| H(14) | 106 | 1820 | 2925 | 89 |
| H(15) | 2520 | 2480 | 2822 | 89 |
| H(21) | 1350 | 1863 | −491 | 89 |
| H(22) | 1739 | 427 | 220 | 89 |
| H(23) | 3404 | 649 | 1649 | 89 |
| H(24) | 4021 | 2222 | 1806 | 89 |
| H(25) | 2777 | 2970 | 461 | 89 |
| H(311) | −1300 | 634 | 2696 | 152 |
| H(312) | −1580 | −152 | 2153 | 152 |
| H(313) | −1929 | 745 | 1783 | 152 |
| H(321) | 394 | −926 | 1685 | 152 |
| H(322) | 1564 | −511 | 1270 | 152 |
| H(323) | −76 | −432 | 881 | 152 |
| H(331) | 1635 | 716 | 3312 | 152 |
| H(332) | 1295 | −229 | 3149 | 152 |
| H(333) | 2570 | 175 | 2890 | 152 |
| H(411) | −2128 | 5134 | −27 | 152 |
| H(412) | −3336 | 5365 | −728 | 152 |
| H(413) | −1913 | 5097 | −929 | 152 |
| H(421) | −5133 | 3342 | −1622 | 152 |
| H(422) | −5005 | 4324 | −1758 | 152 |
| H(423) | −3983 | 3695 | −2075 | 152 |
| H(431) | −3526 | 3965 | 667 | 152 |
| H(432) | −3958 | 3097 | 318 | 152 |
| H(433) | −4984 | 3838 | 95 | 152 |

**Table 7. Least-Squares Planes.**

Phenyl Ring

| Atom | Deviation(Å) |
|---|---|
| C(5) | 0.004 |
| C(6) | 0.006 |
| C(7) | −0.013 |
| C(8) | 0.009 |
| C(9) | 0.002 |
| C(10) | −0.008 |

Ketene Fragment

| Atom | Deviation(Å) |
|---|---|
| Ti | 0.011 |
| O | 0.008 |
| C(1) | −0.040 |
| C(2) | 0.021 |
| C(3) | 0.131 |
| C(5) | 0.009 |
| P | 0.425 |

Vinyl Fragment

| Atom | Deviation(Å) |
|---|---|
| C(2) | 0.024 |
| C(3) | −0.070 |
| C(4) | 0.028 |
| Si | 0.019 |

$\eta^5$-Cyclopentadienyl Ring - CP(1)

| Atom | Deviation(Å) |
|---|---|
| C(11) | 0.006 |
| C(12) | −0.005 |
| C(13) | 0.002 |
| C(14) | 0.002 |
| C(15) | −0.004 |
| Ti | −2.091 |

$\eta^5$-Cyclopentadienyl Ring - CP(2)

| Atom | Deviation(Å) |
|---|---|
| C(21) | −0.001 |
| C(22) | 0.004 |
| C(23) | −0.006 |
| C(24) | 0.005 |
| C(25) | −0.003 |
| Ti | −2.081 |

**Table 8. Torsion Angles (°).**

| Atom | Angle(°) |
|---|---|
| C(1)–C(2)–C(3)–C(4) | 38.5(8) |
| C(1)–C(2)–C(3)–Si | −129.3(4) |
| C(1)–C(2)–C(5)–C(10) | 42.7(7) |
| C(1)–C(2)–C(5)–C(6) | −133.5(5) |
| O–C(1)–C(2)–C(5) | −7.0(8) |
| O–C(1)–C(2)–C(3) | 171.7(5) |
| Ti–C(1)–C(2)–C(3) | 7.3(13) |
| Ti–C(1)–C(2)–C(5) | −171.4(8) |
| C(2)–C(3)–C(4)–H(1) | −177(4) |
| C(2)–C(3)–C(4)–H(2) | 10(2) |

# Appendix II.

## Crystal Structure Determination of $Cp_2TiC_8H_{11}N(C_6H_5)_2$

A single crystal of $(\eta^5 - C_5H_5)_2Ti(C = N(C_4H_9)CH_2C(C_6H_5) = C(C_6H_5))$, obtained from slow cooling of a toluene solution was sealed in a thin-walled glass capillary under $N_2$. Oscillation and Weissenberg photographs of the crystal showed only one axis of symmetery, which characterizes monoclinic cells. The crystal was then optically centered on an Enraf-Nonius CAD 4 diffractometer equipped with a graphite monochromator and Mo$K\alpha$ radiation. Space group $P2_1/n$, a special setting of # 14, was chosen based on systematic absences ($h0l$ absent for $h+l$ = 2n+1, and $0k0$ absent for $k$ = 2n+1). A total of 1325 reflections was collected with $10 \leq \theta \leq 15°$in the quadrant $(\pm h, +k, +l)$. The crystal data parameters are in Table 1.

Crystal decay was monitored by 3 check reflections, which were collected every 123 reflections. The check reflection intensities decreased at an average rate of 17.0% over the 10.46 hours of exposure. The reflection intensities were scaled accordingly.

The position of the titanium atom was determined from a Patterson map, and the Fourier map phased on the Ti atom revealed the remainder of the structure. All hydrogen atoms were placed at idealized positions with fixed coordinates and isotropic Gaussian amplitudes. The titanium atom was refined with an anisotropic $U_{ij}$, and all other non-hydrogen atoms were refined with isotropic parameters. Least-squares refinement, minimizing $\Sigma w[F_o^2 - (F_c/k)^2]^2$, converged to $R_F$=0.1415 for 1097 reflections (I > 0) and $R_F{}' = 0.111$ for $F_0 > 3\sigma F_0^2$. The goodness-of-fit was 4.50 for n=1097 reflections and p=137 parameters. A molecule of solvent, toluene, was found at the center of symmetry. Due to large distortion, the solvent was modeled as benzene, and no refinement was done on the coordinates.

Final parameters are listed in Tables 2, 3, and 4. All calculations were performed on a VAX 11/750 computer using the CRYRM system of programs.

**Table 1. Summary of Crystal Data and Intensity Collection Information.**

| | |
|---|---|
| Formula | $C_{30}H_{31}NTi$ |
| Formula weight | 453.9 g/mol |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$(# 14) |
| a | 18.430(9)Å |
| b | 14.335(4)Å |
| c | 10.776(5)Å |
| $\beta$ | 106.41(4)° |
| V | 2731(2)Å$^3$ |
| Z | 4 |
| $D_{calc}$ | 1.119 g/ml |
| $\lambda$ | 0.710733 Å |
| $\mu$ | 0.403 mm$^{-1}$ |
| Scan range | 1.0°above $K\alpha_1$, 1.0°below $K\alpha_2$ |
| Reflections | $\pm h, +k, +l$ |
| Collected | 1325 |
| | 1097 I > 0 |

**Table 2. Atom Coordinates ($\times 10^4$) and B's and U's ($Å^2 \times 10^4$).**

| Atom | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| Ti | 1709(3) | 842(3) | 2090(5) | 3.25(9)* |
| C1 | 2806(14) | 1238(18) | 2576(30) | 3.3(8) |
| C2 | 3246(14) | 1755(17) | 1731(28) | 3.6(8) |
| C3 | 2683(15) | 1816(17) | 432(27) | 2.5(7) |
| C4 | 1964(14) | 1504(16) | 271(25) | 1.5(7) |
| N | 2818(10) | 914(14) | 3600(23) | 2.1(5) |
| C5 | 3391(16) | 836(21) | 4831(30) | 4.6(8) |
| C6 | 3034(17) | 819(23) | 5901(32) | 8.8(10) |
| C7 | 3836(18) | −56(24) | 4810(34) | 9.2(11) |
| C8 | 3924(19) | 1694(25) | 4929(34) | 9.6(11) |
| C11 | 1261(15) | 1654(19) | 3719(26) | 3.3(8) |
| C12 | 1567(14) | 2330(17) | 3069(28) | 2.2(7) |
| C13 | 1111(15) | 2374(17) | 1852(27) | 2.8(7) |
| C14 | 556(14) | 1707(19) | 1641(27) | 3.2(7) |
| C15 | 672(15) | 1277(17) | 2827(30) | 3.3(8) |
| C21 | 1465(17) | −704(18) | 2616(27) | 4.5(8) |
| C22 | 911(16) | −517(18) | 1525(32) | 5.0(9) |
| C23 | 1257(17) | −357(19) | 496(29) | 5.1(9) |
| C24 | 2026(16) | −499(18) | 1031(29) | 4.0(8) |
| C25 | 2147(15) | −728(19) | 2296(30) | 4.5(8) |
| C31 | 2958(15) | 2319(18) | −529(27) | 2.5(7) |
| C32 | 2575(16) | 2938(21) | −1364(32) | 5.2(9) |
| C33 | 2832(18) | 3440(21) | −2296(31) | 6.6(10) |
| C34 | 3578(18) | 3250(20) | −2284(28) | 5.1(9) |
| C35 | 3997(15) | 2601(21) | −1512(30) | 4.3(8) |
| C36 | 3716(15) | 2111(18) | −633(26) | 3.4(7) |
| C41 | 1433(4) | 1477(17) | −1048(26) | 1.3(6) |
| C42 | 798(16) | 2027(17) | −1406(27) | 2.7(7) |
| C43 | 308(14) | 1981(19) | −2643(30) | 3.4(8) |
| C44 | 457(16) | 1330(21) | −3497(28) | 4.3(8) |
| C45 | 1069(17) | 788(19) | −3162(29) | 4.3(8) |
| C46 | 1582(13) | 855(19) | −1923(28) | 2.8(7) |
| C91 | 5230 | 514 | 1252 | 14.4(15) |
| C92 | 5532 | 855 | 49 | 15.9(16) |

| | | | | | |
|---|---|---|---|---|---|
| C93 | 5257 | 375 | −1188 | 15.1(16) | |

| * | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Ti | 347(35) | 446(38) | 547(45) | −36(38) | 302(33) | −17(46) |

**Table 3. Hydrogen Atom Coordinates ($\times 10^4$) and B's ($Å^2 \times 10^4$).**

| Atom | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| H1 | 3282 | 1472 | 2397 | 4.6 |
| H2A | 3502 | 2309 | 2210 | 4.6 |
| H2B | 3753 | 1348 | 1812 | 4.6 |
| H6A | 3485 | 775 | 6853 | 9.4 |
| H6B | 2876 | 1462 | 6081 | 9.4 |
| H6C | 2750 | 419 | 5865 | 9.4 |
| H7A | 4311 | −131 | 5355 | 10.1 |
| H7B | 3913 | −121 | 3820 | 10.1 |
| H7C | 3536 | −606 | 4809 | 10.1 |
| H8A | 4286 | 1682 | 5893 | 11.4 |
| H8B | 4212 | 1586 | 4452 | 11.4 |
| H8C | 3651 | 2202 | 4835 | 11.4 |
| H11 | 1505 | 1412 | 4598 | 3.9 |
| H12 | 2018 | 2757 | 3478 | 3.9 |
| H13 | 1163 | 2881 | 1225 | 3.9 |
| H14 | 182 | 1566 | 776 | 3.9 |
| H15 | 322 | 822 | 2993 | 3.9 |
| H21 | 1378 | −740 | 3478 | 5.2 |
| H22 | 381 | −497 | 1328 | 5.2 |
| H23 | 1014 | −151 | −462 | 5.2 |
| H24 | 2424 | −470 | 621 | 5.2 |
| H25 | 2669 | −942 | 2938 | 5.2 |
| H32 | 2041 | 3144 | −1351 | 5.7 |
| H33 | 2525 | 3933 | −2888 | 5.7 |
| H34 | 3794 | 3597 | −2957 | 5.7 |
| H35 | 4493 | 2512 | −1552 | 5.7 |
| H36 | 4024 | 1622 | −78 | 5.7 |
| H42 | 695 | 2461 | −740 | 4.1 |
| H43 | −121 | 2424 | −3019 | 4.1 |
| H44 | 120 | 1213 | −4353 | 4.1 |
| H45 | 1237 | 345 | −3761 | 4.1 |
| H46 | 2045 | 378 | −1636 | 4.1 |
| H91 | 5357 | 873 | 2024 | 10.0 |
| H92 | 5881 | 1357 | 149 | 10.0 |

| | | | | |
|---|---|---|---|---|
| H93 | 5374 | 602 | −1937 | 10.0 |

**Table 4. Bond Lengths (Å).**

| Atom | Atom | Distance(Å) |
|---|---|---|
| Ti | C1 | 2.02(3) |
| Ti | C4 | 2.34(3) |
| Ti | N | 2.23(2) |
| Ti | C11 | 2.44(3) |
| Ti | C12 | 2.43(3) |
| Ti | C13 | 2.44(3) |
| Ti | C14 | 2.39(3) |
| Ti | C15 | 2.35(3) |
| Ti | C21 | 2.36(3) |
| Ti | C22 | 2.41(3) |
| Ti | C23 | 2.41(3) |
| Ti | C24 | 2.39(3) |
| Ti | C25 | 2.38(3) |
| Ti | CP1* | 2.11 |
| Ti | CP2* | 2.08 |
| C1 | C2 | 1.57(4) |
| C1 | N | 1.19(4) |
| C2 | C3 | 1.49(4) |
| C3 | C4 | 1.36(4) |
| C3 | C31 | 1.47(4) |
| C4 | C41 | 1.48(4) |
| N | C5 | 1.45(4) |
| C5 | C6 | 1.48(4) |
| C5 | C7 | 1.52(5) |
| C5 | C8 | 1.56(5) |
| C11 | C12 | 1.40(4) |
| C12 | C13 | 1.34(4) |
| C13 | C14 | 1.37(4) |
| C14 | C15 | 1.38(4) |
| C15 | C11 | 1.34(4) |
| C21 | C22 | 1.35(4) |
| C22 | C23 | 1.45(4) |
| C23 | C24 | 1.39(4) |
| C24 | C25 | 1.36(4) |

| | | |
|---|---|---|
| C25 | C21 | 1.39(4) |
| C31 | C32 | 1.32(4) |
| C32 | C33 | 1.42(4) |
| C33 | C34 | 1.40(4) |
| C34 | C35 | 1.34(4) |
| C35 | C36 | 1.39(4) |
| C36 | C31 | 1.46(4) |
| C41 | C42 | 1.37(4) |
| C42 | C43 | 1.38(4) |
| C43 | C44 | 1.39(4) |
| C44 | C45 | 1.33(4) |
| C45 | C46 | 1.40(4) |
| C46 | C41 | 1.38(4) |

*Centroid of $\eta^5$-cyclopentadienyl Rings

Table 5. Bond Angles (°).

| Atoms | Angle(°) |
|---|---|
| C1 – Ti – C4 | 71(1) |
| Ti – C1 – C2 | 128(2) |
| Ti – C4 – C3 | 116(2) |
| N – C1 – Ti | 83(2) |
| R1 – Ti – R2 | 134(3) |
| N – C1 – C2 | 147(3) |
| C3 – C2 – C1 | 103(2) |
| C4 – C3 – C2 | 119(2) |
| C31 – C3 – C2 | 113(2) |
| C31 – C3 – C4 | 126(2) |
| C41 – C4 – C3 | 119(2) |
| C5 – N – C1 | 134(2) |
| C6 – C5 – N | 110(2) |
| C7 – C5 – N | 107(2) |
| C8 – C5 – N | 106(2) |
| C7 – C5 – C6 | 110(3) |
| C8 – C5 – C6 | 111(3) |
| C8 – C5 – C7 | 109(3) |
| C15 – C11 – C12 | 106(2) |
| C13 – C12 – C11 | 106(2) |
| C14 – C13 – C12 | 111(2) |
| C15 – C14 – C13 | 104(2) |
| C14 – C15 – C11 | 111(3) |
| C25 – C21 – C22 | 107(3) |
| C23 – C22 – C21 | 108(3) |
| C24 – C23 – C22 | 106(3) |
| C25 – C24 – C23 | 108(3) |
| C24 – C25 – C21 | 109(3) |
| C32 – C31 – C3 | 126(3) |
| C36 – C31 – C3 | 118(2) |
| C36 – C31 – C32 | 115(3) |
| C33 – C32 – C31 | 126(3) |
| C34 – C33 – C32 | 114(3) |
| C35 – C34 – C33 | 122(3) |

| | |
|---|---|
| C36 – C35 – C34 | 120(3) |
| C35 – C36 – C31 | 119(2) |
| C42 – C41 – C4 | 122(2) |
| C46 – C41 – C4 | 117(2) |
| C46 – C41 – C42 | 119(2) |
| C43 – C42 – C41 | 121(3) |
| C44 – C43 – C42 | 118(3) |
| C45 – C44 – C43 | 121(3) |
| C46 – C45 – C44 | 120(3) |
| C45 – C46 – C41 | 118(3) |

**Table 6. Torsion Angles (°).**

| Atoms | Angle(°) |
|---|---|
| Ti – C1 – N – C5 | −177(2) |
| Ti – C1 – C2 – C3 | −4(3) |
| C1 – C2 – C3 – C4 | 3(3) |
| C2 – C3 – C4 – TI | −2(3) |
| Ti – C4 – C41 – C42 | 74(3) |
| C4 – C3 – C31 – C32 | 36(5) |

**Table 7. Least-Squares Planes.**

$\eta^5$-cyclopentadienyl– R1

| Atoms | Deviation(Å) |
|---|---|
| C11 | 0.0215 |
| C12 | −0.0274 |
| C13 | 0.0232 |
| C14 | −0.0089 |
| C15 | −0.0084 |
| Ti | −2.1074 |

$\eta^5$-cyclopentadienyl– R2

| Atoms | Deviation(Å) |
|---|---|
| C21 | −0.0219 |
| C22 | 0.0181 |
| C23 | −0.0075 |
| C24 | −0.0057 |
| C25 | 0.0170 |
| Ti | −2.0789 |

Metallacycle Plane

| Atoms | Deviation(Å) |
|---|---|
| Ti | 0.0112 |
| C1 | −0.0240 |
| C2 | 0.0259 |
| C3 | −0.0145 |
| C4 | 0.0014 |
| N | −0.0604 |
| C5 | −0.0743 |
| C31 | 0.0837 |
| C41 | −0.1807 |