Organometallics 1989, *8*, 583-589 583

and polarization corrections were applied to all data collected. Since it was not possible to confidently assign crystal faces, no absorption correction was attempted. In view of the fairly regular shape and relatively small value of μ this is not considered to be a major source of error and the low merging R factor for averaging 1134 symmetry-equivalent data is consistent with this observation. The structure was solved as indicated. In the final cycles of least squares hydrogen atoms on the phenyl rings were placed in calculated positions. A subsequent ΔF Fourier map contained a peak at (0.277, 0.066, 0.125) of reasonable height which was in a chemically sensible position to be the H-atom bridging Pt and Mn. Least squares refinement of this atom produced no drastic shifts in its position. Full-matrix least squares refinements minimizing $\sum w\Delta F^2$ then converged to the indicated residuals. No extinction corrections were considered necessary. In the refinements programs of the Enraf-Nonius SDP system on a PDP 11/23 computer were used throughout. The final atomic positional parameters are given in Table III, and selected bond lengths and bond angles are given in Table IV.

Acknowledgment. We are grateful to the Natural Science and Engineering Research Council of Canada for financial support of this work.

Registry No. **1a**, 118398-33-7; **1b**, 118398-34-8; **1c**, 118398-35-9; **6**, 118417-94-0; **7**, 118398-36-0; **8**, 118398-37-1; $Mn(CO)_5SiMe_2H$, 118398-31-5; $Mn(CO)_5SiPh_2H$, 118398-32-6; $Mn(CO)_5SiCl_2H$, 20347-38-0; $Pt(C_2H_4)(PPh_3)_2$, 12120-15-9; $Pt(PPh_3)_4$, 14221-02-4.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen atom positional parameters, and bond lengths and angles for **8** (5 pages); a listing of final structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

Synthesis, Reactivity and Kinetic Studies of Bis(η^5-cyclopentadienyl)titanium Methylidene Phosphine Complexes

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Received March 3, 1988

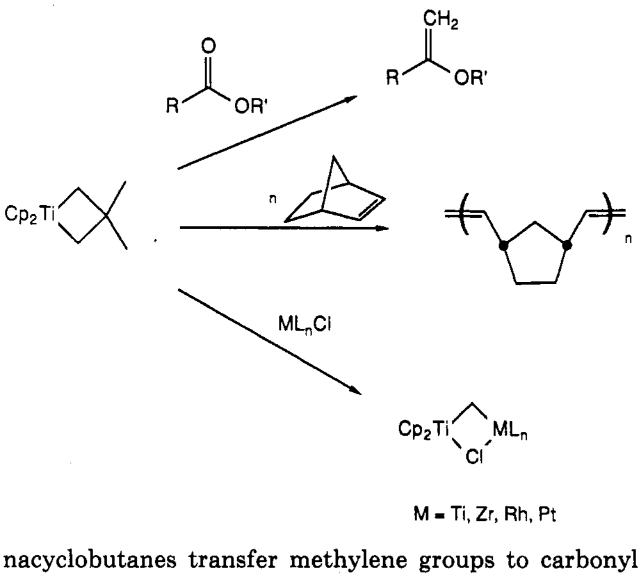
Syntheses of several bis(η^5-cyclopentadienyl)titanium methylidene phosphine complexes are reported. The titanocene methylidene phosphine complexes are generated from thermolysis of titanocene metallacyclobutanes in the presence of excess phosphine. Spectral data and reactivity are consistent with a methylidene phosphine complex rather than an ylide complex. The titanocene methylidene phosphine complexes react with olefins to form metallacyclobutanes, alkynes to form metallacyclobutenes, and CO to form a ketene complex. The phosphine ligand is labile, and an equilibrium mixture is rapidly established if a second phosphine is added. The kinetics of this equilibration and the kinetics of the reaction of titanocene methylidene phosphine complexes with alkynes and olefins are reported. The reactions proceed by rate-determining loss of phosphine followed by rapid trapping of titanocene methylidene.

Introduction

Metal alkylidene complexes have been implicated as intermediates in many important reactions, including alkene metathesis,[1] alkene[2] and alkyne polymerization,[3] cyclopropanation of olefins,[4] and methylenation of carbonyl compounds.[5] Surface-bound alkylidenes have been postulated to be intermediates in Fischer–Tropsch chemistry.[6] As models for these and other reactions, several bimetallic bridging methylidene compounds have been synthesized and studied.[7] Many carbene complexes containing heteroatom substituents have also been synthesized; their chemistry is quite different from methylidene complexes of the early transition metals[8] and other terminal methylene complexes.[9-12]

Titanocene dichloride and trimethylaluminum[13] react to yield a stable, soluble dimethylaluminum chloride–titanocene methylidene complex (Tebbe's reagent, **1**).[14] The Tebbe reagent is an olefin metathesis catalyst, readily methylenates carbonyl compounds, and serves as a precursor to other methylidene derivatives.[15] A titanocene methylidene species has been implicated as the active species in many of these reactions.

Scheme I. Reactivity of Titanocene Metallacyclobutanes



Titanacyclobutanes can be isolated from the reaction of **1** with olefins in the presence of Lewis bases.[16] Titanacyclobutanes transfer methylene groups to carbonyl functionalities,[5] ring-open polymerize strained cyclic ole-

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[†] Contribution No. 7738.

(1) (a) Grubbs, R. H. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 9, Chapter 54, pp 499–552. (b) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1–50.

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Table I. Phosphine-Exchange Equilibrium Constants

complex	equil ratio	equil const (K_{eq})
3a ⇌ **3b**	3.5 ± 0.2:1	0.13 ± 0.02
3b ⇌ **3c**	5.6 ± 0.3:1	0.03 ± 0.01

fins,[2] and form binuclear bridging methylene complexes[17] (Scheme I). The existence of titanocene methylidene or a titanocene methylidene olefin complex is implicated by the reactivity and reaction kinetics of titanacyclobutanes.[18] However, the nature of the methylidene complex is still under investigation.[17,19,20]

This paper addresses the formation, isolation, characterization, and reactivity of titanocene methylidene phosphine complexes. These compounds provide another entry into titanocene methylidene intermediates and information about transition-metal–carbon multiple bonding. In addition, these compounds provide the opportunity for kinetic investigations which distinguish among displacement, dissociative, or associative reaction mechanisms for titanocene methylidene ligand complexes ($Cp_2Ti(L)CH_2$).

Results

Preparation of Titanocene Methylidene Phosphine Complexes. Treatment of a solution[16d,20] of β,β-dimethyltitanacyclobutane, **2a**, or β-methyl-β-propyltitanacyclobutane, **2b**, with excess trialkylphosphine (trimethyl-, dimethylphenyl-, or triethylphosphine) at room temperature yields the corresponding titanocene methylidene phosphine complex, **3a–c**, in equilibrium with the metallacycle (eq 1).

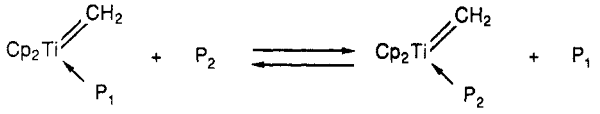
(1)

2. a: $R_1=R_2=CH_3$
b: $R_1=CH_3, R_2=C_3H_7$

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

If the volatile olefin is removed from the reaction mixture, the equilibrium is shifted entirely to product. The phosphine methylidene complexes are isolated as extremely air- and moisture-sensitive, thermally unstable, yellow-brown powders, soluble in aromatic solvents, moderately soluble in diethyl ether, and insoluble in pentane.

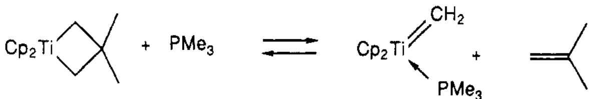
The relative stability of the different phosphine complexes reflects the size of the phosphine.[21] The stability order if $PMe_3 > PMe_2Ph \gg PEt_3$. The measured ($^{31}P$ NMR) equilibria (eq 2) for the different complexes are shown in Table I. The trimethylphosphine complex **3a** is stable as a solid in a N_2 drybox at −40 °C for months and in solution at room temperature for hours. The other phosphine complexes **3b** and **3c** are less stable in solution.



(2)

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

The equilibrium constant at 25 °C for the initial reaction of phosphine with metallacyclobutane has also been determined by NMR integration (eq 3).



(3)

$K_{eq} = 45 \pm 10$

2a **3a**

The phosphine complexes **3a–c** exhibit a characteristic low-field ^1H NMR resonance for the CH_2 group at δ 12.1. The CH_2 and the η^5-cyclopentadienyl ligands exhibit ^{31}P coupling of 6.8 and 2.0 Hz, respectively. The methylidene carbon in **3a** atom has a ^{13}C shift of δ 286 and a J_{C-H} coupling constant of 127 ± 1 Hz.

The small J_{C-H} coupling constant of **3a** prompted the synthesis of the H–D labeled methylidene phosphine complex **3d** (eq 4a). The secondary ^2H isotope effect on the metallacycle **2c** cleavage resulted in a 2:1 mixture of **3a** and **3d**.[17] Isotopic substitution results in an upfield shift of (0.01 ppm) 5.02 Hz for the methylidene proton in **3d** relative to **3a**. No J_{H-D} coupling was observed in **3d** even with resolution enhancement. Infrared spectral analysis of **3d** revealed a single new peak at 2190 cm^{-1}. Synthesis of **3e** was accomplished from the reaction of β,β-dimethyltitanocene metallacyclobutane-d_{10} **2d** with PMe_3 (eq

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(2) (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733–42. (b) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mehtal, R. *J. Am. Chem. Soc. Chem. Commun.* 1978, 604–606.

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(14) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613. (b) Klaubunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37–51.

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(19) The results found in ref 18 indicate the possibility of a titanocene methylidene olefin complex as the reactive intermediate, whereas the following reference concluded that uncoordinated titanocene vinylidenes are the reactive intermediates generated from α-*exo*-alkylidene titanocene metallacyclobutanes. Hawkins, J. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2821–2823.

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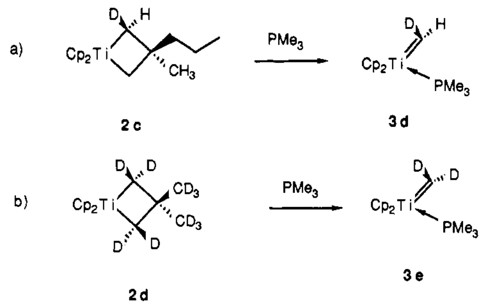
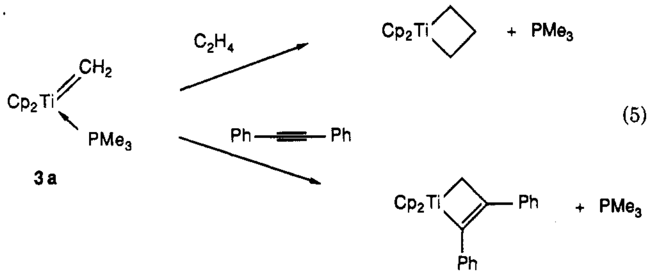


(4)

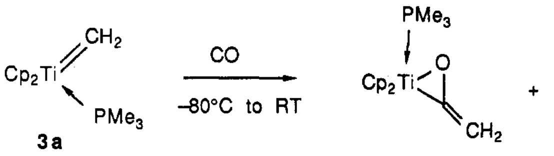
4b). Infrared spectral analysis of **3e** revealed two new peaks at 2165 and 2095 cm^{-1}. In addition, comparison to the infrared spectrum of **3a** revealed that two peaks at 2940 and 2885 cm^{-1} were missing. All attempts to form single crystals for X-ray diffraction and to prepare adducts of Cp_2TiCH_2 with other Lewis bases such as pyridine, trimethyl phosphite, and trifluorophosphine were unsuccessful.

Reactivity of Titanocene Methylidene Phosphine Complexes. The reaction of unsaturated substrates with the phosphine methylidene complexes was investigated. The phosphine methylidene complexes react cleanly with olefins to generate titanocene metallacyclobutanes[16] and with disubstituted alkynes to form titanocene metallacyclobutenes[15] (eq 5).



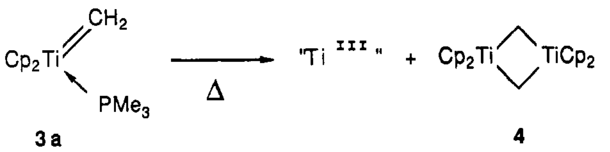
(5)

Treatment of a toluene-d_8 solution of **3a** (eq 6) with CO yields a mixture of products after warming from −80 °C to room temperature. Two of the products were identified by ^{1}H NMR as $Cp_2Ti(CO)_2$ (δ 4.58) and $Cp_2Ti(CO)(PMe_3)$ (δ 4.62 (d, J_{C-P} = 2 Hz)).[22] A product identified as $Cp_2Ti(CH_2CO)(PMe_3)$ is also observed and appears to be the major initial product when the reaction is carried out at −80 °C.[23] This ketene complex decomposes in solution at room temperature under the reaction conditions, and no NMR signals attributable to ketene or ketene dimer result from this decomposition. Carbonylation of complex **3b** gives similar results.



$$Cp_2Ti(CO)_2 + Cp_2Ti(CO)(PMe_3) \qquad (6)$$

Upon standing at room temperature, solutions of phosphine methylidene complexes yield paramagnetic materials and a trace of the methylidene dimer **4** (eq 7). Thermolysis of the phosphine methylidene complexes does not yield the same distribution of hydrocarbons as the thermolysis of titanacyclobutanes **2** or the dimer **4**. While the dimer **4** yields primarily methane (93%), the phosphine complex **3b** yields mostly ethane (>75%) and little methane on thermolysis.[19a]



Kinetic Studies. The rate of equilibrium of **3a** or **3b** with other phosphines was studied as a function of the concentration of added phosphine. Figure 1 displays the pseudo-first-order rate observed when **3a** or **3b** is allowed to react with PMe_2Ph or PMe_3, respectively. The rate was determined over the first 20% of reaction since the rate decreases as equilibrium is approached. The graph shows that a limiting rate of equilibration is attained at high concentrations of added phosphine.

The rate of reaction of **3a** to yield titanocene metallacyclobutanes and titanocene metallacyclobutenes was determined as a function of the concentration of added alkene or alkyne, respectively. Figure 2 displays the pseudo-first-order rate constants observed when **3a** is allowed to react with different concentrations of 3-hexyne, 4-octyne, diphenylacetylene, and neohexene. There is a linear relationship between diphenylacetylene or neohexene concentration and k, but there is considerable curvature similar plots for 3-hexyne and 4-octyne. For 3-hexyne or 4-octyne concentrations of 6.5 and 5.1, respectively, the plots appear to be curving down. Since these reactions solution are 75% alkyne, the ^{1}H NMR integrations of the product and reactant cyclopentadienyl resonances are less precise for these two points. All attempts at performing the reactions in neat alkyne failed due to the low solubility and consequently low signal to noise ratio of the ^{1}H NMR resonances of the cyclopentadienyl ligands. Despite these errors the graph shows that a limiting rate of reaction is approached at high concentrations of alkyne. A plot of $1/k_{obsd}$ (for the reaction of **3a** with 3-hexyne) versus the concentrations of added trimethylphosphine [O] to 3-hexyne [T] yields a straight line with a slope of 883.9 s^{-1} and an intercept of 131.9 s. The graph is displayed in Figure 3.

Discussion

Titanacyclobutanes are in equilibrium with either a methylidene olefin complex or free Cp_2TiCH_2, either of which may be trapped by a trialkylphosphine to yield titanocene methylidene phosphine complexes **3a–c**. Physical and chemical characterization of the phosphine methylidene complexes suggest the presence of a true methylidene phosphine complex rather than an ylide complex (eq 8).

(8)

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

The NMR chemical shifts for the methylidene ligand are noteworthy. The strong downfield shift in both the ^{1}H NMR and the ^{13}C NMR spectra are characteristic of an early-transition-metal methylidene complex. The

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[22] Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Wolf, B.; Thewalt, U. *J. Organomet. Chem.* **1985**, *297*, 159–169.

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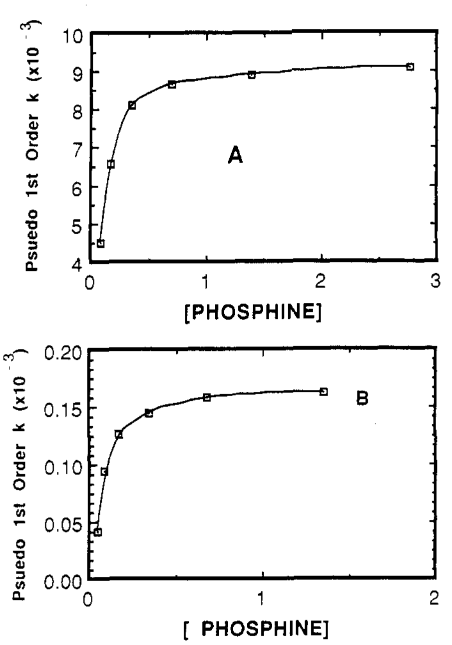


Figure 1. (a) Saturation kinetics on **3b** with PMe_3. (b) Saturation kinetics on **3a** with PMe_2Ph at 0 °C in C_7D_8.

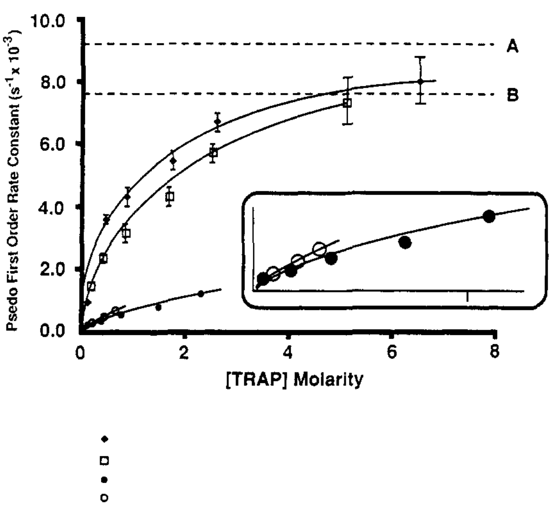


Figure 2. Pseudo-first-order kinetics on 0.1 M **8**: ◇, 4-octyne; ●, 3-hexyne; □, diphenylacetylene; ○, neohexene (at 25 °C in C_6D_6).

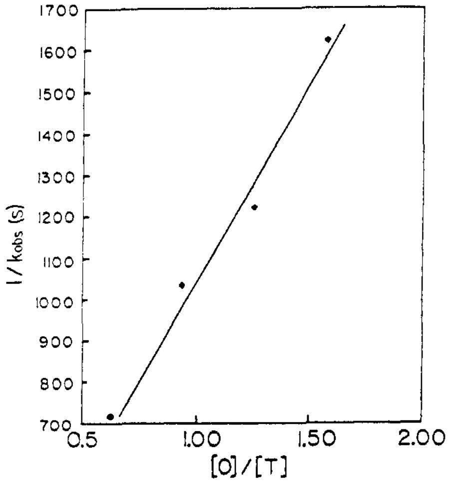
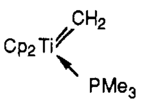
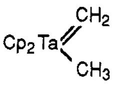
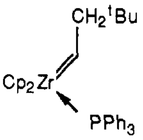
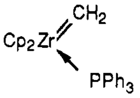
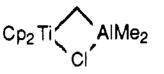
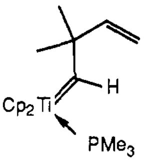
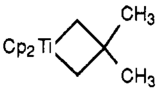


Figure 3. $1/k_{obsd}$ versus [O]/[T] for the reaction of **3a** with 3-hexyne: $\rho = 0.992$; [O] = [trimethylphosphine]; [T] = β-hexyne (at 25 °C in C_6D_6).

Table II. NMR Data of Selected Methylidene Complexes

	^1H δ	^{13}C δ	J_{C-H}, Hz	J_{P-H}, Hz	J_{C-P}, Hz	ref
	12.12	285.9	127	6.8	31.7	
$(CH_3)_3P{=}CH_2$	0.78	−1.5	149	6.5	90.5	25
	9.88	228	132			9
	−0.22	−4.0	122			9
	11.71	270		4.1		27
	11.0	248	121	4.8	14.6	26
	8.49	188	140			16
	8.72	235	126			19
	12.06	306.9	111	7.3	26.6	28
	2.50	83.5	137			16

carbon–hydrogen coupling constant of the methylidene group (127 Hz) is small for a formally sp^2 carbon atom. This may be attributed to an electronic effect caused by bonding to a very electropositive titanium.[24] Schrock has also observed a similarly small coupling constant for $CpTa(CH_3)CH_2$ (J_{C-H} = 132 Hz).[9] The carbon–phosphorus coupling constant for the methylidene group in **3a** (J_{C-P} = 31.7 Hz) is much less than that of the CH_2PMe_3 ylide (J_{C-P} = 90.5 Hz).[25] The magnitude of the coupling constants, together with the chemical reactivity, support the assignment of **3a–c** as phosphine methylidene complexes rather than ylide complexes.

There are a few other examples of group 4 terminal alkylidene complexes. Schwartz has reported[26,27] a bis(η^5-cyclopentadienyl)zirconium methylidene phosphine complex, **5**, and a series of bis(η^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.[29] The physical characteristics and reactivity of these alkylidene complexes are similar to those of the phosphine methylidene complexes **3a–c**. Pertinent NMR data of various

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(24) The J_{C-H} of group IV metallocene methyl halide and dialkyl complexes have been correlated with electron density at the metal: (a) Grubbs, R. H.; Straus, D. A.; Meinhart, J. D., unpublished results. (b) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406–2413.

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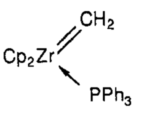

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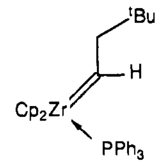

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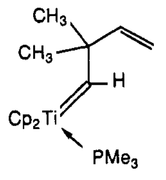

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methylidene complexes are tabulated in Table II.

The deuterium-labeled methylidene complex **3d** displays a C–D stretch at 2160 cm^{-1}. The C–H frequency calculated from this C–D stretch is 2944 cm^{-1}. The deuterium-labeled methylidene complex **3e** displays a C–D symmetric stretch at 2165 cm^{-1} and an asymmetric stretch at 2095 cm^{-1}. These stretches are shifted from 2940 and 2885 cm^{-1}, respectively, in **3a**. These frequencies are consistent with typical sp^2 C–H vibrations and suggest that there are no agostic interactions of the C–H bonds with the metal centers.[30] The 0.001 ppm isotope shift in the NMR is also indicative of no agositic interactions.[30]

The trimethylphosphine methylidene complex **3a** reacts with carbon monoxide to yield a titanocene ketene trimethylphosphine complex (eq 6). Titanocene ketene complexes are well-documented, and the dimethylphenyl phosphine complex is known.[23] The carbonylation most likely proceeds through an unobserved $Cp_2Ti(CH_2)(CO)$ complex and/or a C,C-bound ketene intermediate. The fate of the ketene and other organic fragments when the ketene complex thermally decomposes to $Cp_2Ti(CO)_2$ and $Cp_2Ti(CO)(PMe_3)$ is unknown. Similar CO insertions into terminal methylidene units to yield ketene complexes have also been observed for Mn,[31] Mo,[32] and W[33] systems.

The reactions of the titanocene methylidene phosphine complexes can be considered to proceed by two different pathways involving either phosphine displacement or dissociation. Two alternatives for titanocene methylidene phosphine equilibrations along with their kinetic expressions are given in Figure 4. Mechanism 1 in Figure 4 involves displacement of a coordinated phosphine by a phosphine in solution in a S_N2-type process. Mechanism 2 in Figure 4 involves phosphine dissociation to give a free titanocene methylidene intermediate which is trapped by phosphine. Mechanism 1 would yield first-order kinetics in both the titanocene methylidene phosphine complex and the uncoordinated phosphine whereas mechanism 2 would display saturation behavior at high concentrations of added phosphine with a rate-limiting k_1 value. In order to distinguish between these two mechanistic possibilities, the kinetics of the reaction of **3a** with PMe_2Ph and the kinetics of **3b** with PMe_3 were studied. The results are shown in Figure 1. The kinetics clearly exhibit saturation behavior at high phosphine concentrations. Thus, the kinetic results are best explained by mechanism 2 which involves a rate-determining dissociation of phosphine from the titanocene methylidene phosphine complex followed by rapid trapping of titanocene methylidene by phosphine.

The reaction of titanocene methylidene phosphine complexes with olefins and alkynes has been previously studied.[17] The reaction was concluded to proceed by preequilibrium between a titanocene methylidene phosphine complex and a titanocene methylidene alkyne complex followed by coupling to form a titanocene metallacyclobutene (mechanism 3, Figure 5). This conclusion was based on the assumption that at 70% of the saturated rate-limiting k_1 value, there should be curvature in the plot of k_{obsd} versus trap concentration. Figure 2 displays the graph previously published, but also includes two additional points at extremely high trap concentrations. These additional points demonstrate that the rate of reaction approaches a rate-limiting value but that the saturated value has not yet been achieved. Exact analysis is impossible due to the unknown solvent effect at these extremely high trap concentrations. Thus, mechanism 4 in Figure 5 best explains the observed kinetic results.[17]

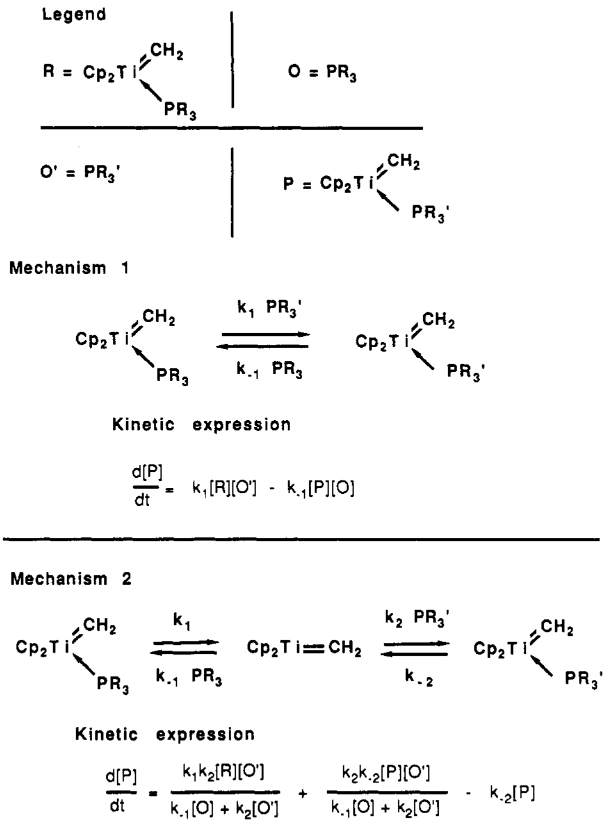
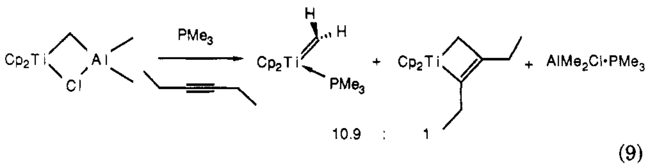


Figure 4. Proposed mechanisms for phosphine exchange.

In order to further probe the saturation behavior of the reaction of **3a** with alkynes, two experiments were performed to determine the expected rate-limiting k_1 value. The first test was to measure the relative trapping rates of trimethylphosphine and 3-hexyne (k_{-1}/k_2, eq 10). This was accomplished by adding trimethylphosphine and 3-hexyne to a solution of Tebbe's reagent **1** (eq 9) to yield a mixture of phosphine complex and metallacyclobutene. The reaction of the phosphine complex with 3-hexyne to yield metallacyclobutene was followed by ^1H NMR. The kinetics were then extrapolated back to time zero to determine the initial ratio of phosphine complex to metallacyclobutene. The ratio (k_{-1}/k_2) was found to be 10.9. The extent of saturation was calculated to be 70% when the trap is in a 25-fold excess ([T]/[O] = 25) (as with 3-hexyne, Figure 2), the trapping rate constant by phosphine is 10.9 times that of the alkyne, and eq 10 defines the relationship of k_1 to k_{obsd}. Since at a 25-fold excess of



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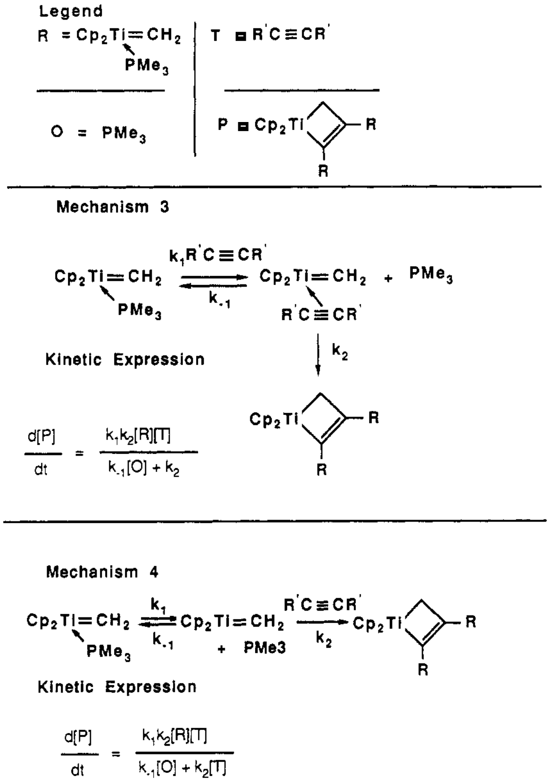

Figure 5. Proposed mechanism for the reaction of titanocene methylidene phosphine complexes with alkynes and olefins.

3-hexyne, the rate is predicted to be 70% of the saturated rate, one can calculate the rate limiting k_1 value from eq 10 to be 9.64×10^{-3} s^{-1}. This rate-limiting value is displayed in Figure 2 as line A.

A second independent experiment to determine the predicted rate-limiting k_1 value was performed. The reciprocal of the kinetic expression for mechanism 4 is given in eq 10.

$$\frac{1}{k_{\mathrm{obsd}}} = \left(\frac{k_{-1}[\mathrm{O}]}{k_1 k_2[\mathrm{T}]} + \frac{1}{k_1}\right) \qquad (10)$$

Examination of the kinetics of several reactions of **3a** with varying ratios of a large excess of both 3-hexyne and trimethylphosphine yields a plot of $1/k_{\mathrm{obsd}}$ versus [O]/[T] (O = phosphine, T = trap) with an intercept of $1/k_1$ and a slope of k_{-1}/k_1k_2. The results are displayed in Figure 3. The k_1 value was found to be 7.58×10^{-3} s^{-1}. This rate limiting value is displayed in Figure 4 as line B. The k_{-1}/k_2 ratio was found to be 6.7. Thus, Figure 2 shows that the reaction of **3a** with olefins and alkynes approaches the saturated rate-limiting value when the solution is 75% by volume alkyne.

The interpretation of these results do not significantly alter the conclusions previously published.[17] In the study of the mechanism of cleavage of titanocene metallacyclobutanes,[17] different product ratios were observed when the titanacyclobutane and titanocene methylidene phosphine adducts were competitively trapped with two different olefins or acetylenes. This result demonstrates that the titanacycles and methylidene phosphine adducts react via different intermediates. Since we have now shown that the phosphine adducts react via titanocene methylidene, the most reasonable intermediate in the titanacycles reactions is the titanocene methylidene olefin adduct. Although these well documented differences in reactivity between the metallacycles and phosphine carbene complexes are at first surprising, further considerations of olefin and phosphine complexes suggests that the bonding in these are sufficiently different to account for the change in mechanistic pathways. For example, earlier work on the isotope effects in the decomposition of metallacycles suggested that the carbons in the olefin of the intermediate olefin carbene complex showed considerable sp^3 character. A similar metallacyclopropane like structure is not possible in the phosphine complex.

Table III. Equilibrium of 3a and 3b

compd	phosphine	phosphine µL	phosphine equiv	T, °C	k_{obsd}, s^{-1}
3a	PMe$_2$Ph	2	0.45	0	4.11×10^{-5}
3a	PMe$_2$Ph	4	0.91	0	9.40×10^{-5}
3a	PMe$_2$Ph	8	1.80	0	1.26×10^{-4}
3a	PMe$_2$Ph	16	3.64	0	1.45×10^{-4}
3a	PMe$_2$Ph	32	7.27	0	1.58×10^{-4}
3a	PMe$_2$Ph	64	14.5	0	1.63×10^{-4}
3b	PMe$_3$	2	0.93	0	4.45×10^{-3}
3b	PMe$_3$	4	1.86	0	6.59×10^{-3}
3b	PMe$_3$	8	3.72	0	8.14×10^{-3}
3b	PMe$_3$	16	7.45	0	8.67×10^{-3}
3b	PMe$_3$	32	14.9	0	8.92×10^{-3}
3b	PMe$_3$	64	29.8	0	9.10×10^{-3}

Conclusions

A series of titanocene methylidene phosphine complexes has been isolated. The bonding is best described as a methylidene phosphine complex rather than an ylide complex. The complexes are quite reactive toward unsaturated substrates such as alkenes, alkynes, and CO. The only distinction between the reactivity of methylidene phosphine complexes and titanocene metallacyclobutanes is the thermal decomposition. Titanocene methylidene phosphine complexes react with other phosphines or unsaturated C–C bonds by a rate-determining loss of phosphine to yield titanocene methylidene, followed by rapid trapping.

Experimental Section

General Consideration. All manipulations of air- and/or water-sensitive compounds were performed by 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.,[34] using silica Woelm 32-63 (32–63 µm). Thin-layer chromatography was performed on EM Reagents 0.25-mm silica Gel 6-F plates and visualized with either iodine vapor or phosphomolybdic acid/ethanol spray. All reaction temperatures were measured externally.

Materials. Toluene, diethyl ether, and tetrahydrofuran were stirred over CaH$_2$ then transferred to purple sodium–benzophenone ketyl. Pentane and hexane were stirred over concentrated H$_2$SO$_4$, washed with H$_2$O), dried over CaH$_2$, and then transferred to purple sodium–benzophenone ketyl with tetraglyme. Dichloromethane was stirred over P$_2$O$_5$ or CaH$_2$ and degassed. 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's reagent and bis(η^5-cyclopentadienyl)titanacyclobutanes were prepared by the reported procedures.[35] Carbon monoxide

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Table IV. $1/k_{obsd}$ Kinetics

compd	alkyne	alkyne, μL	PMe_3, μL	T, °C	k_{obsd}, s^{-1}
3a	3-hexyne	40	20	25	1.39×10^{-3}
3a	3-hexyne	40	30	25	9.65×10^{-4}
3a	3-hexyne	40	40	25	8.17×10^{-4}
3a	3-hexyne	40	50	25	6.15×10^{-4}

(CP) and carbon dioxide (Bone-Dry) were obtained from Matheson Gas Co. Alkylphosphines were purchased from Strem Chemical Co. and degassed prior to use. Deuterated metallacycles were prepared from either the deuterated olefin or d_2 Tebbe's reagent.[17] The deuterated olefins were prepared by hydrozirconation of the corresponding alkyne.[36]

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) spectrometer. Chemical shifts are reported in δ, referenced to residual solvent signals (^{1}H: C_6H_6, δ 7.15; THF-d_8, δ 3.58 or 1.73; CD_2Cl_2, δ 5.32; $CDCl_3$, δ 7.24. ^{13}C: C_6D_6, δ 128.0; C_7D_8, δ 20.9; THF-d_8, δ 67.4; $CDCl_3$, δ 77.0). ^{31}P NMR data are referenced externally to 85% H_3PO_4 (positive 8, 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.[37] Gas chromatography analyses were performed on a Shimatzu GC-Mini-2 equipped with an SE-30 capillary column, flame-ionization detector, and a Hewlet-Packard 3390A integrator. Infrared spectra were recorded on a Beckman 4210, Shimadzu 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 μL, 1.27 mmol) was added to a stirred suspension of β,β-dimethyltitanacyclobutane (210 mg, 0.846 mmol) in 5 mL of diethyl ether at −20 °C. The mixture was allowed to warm to room temperature under a partial vacuum. Within 10 min, the color changed from red to yellow-orange, and a yellow solid precipitated. After an additional 15 min, the volatiles were removed under vacuum to yield a yellow-brown powder, which was dried at −20 °C. The solid (180 mg, 64%) was stored in a drybox at −40 °C. The material was suitable for most uses without further purification. However, the complex may be recrystallized in poor yield from either diethyl ether or toluene/pentane at −50 °C: ^{1}H NMR (90 MHz, C_7D_8, −20 °C) δ 12.12 (d, J_{P-H} = 6.8 Hz, 2 H), 5.30 (d, J_{P-H} = 2.0 Hz, 10 H), 0.72 (d, J_{C-P} = 6.3 Hz, 9 H); ^{13}C{^{1}H} NMR (22.5 MHz, C_7D_8, −20 °C) δ 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 δ 285.9 was determined to be 127.2 ± 1.9 Hz by polarization transfer techniques.[38] ^{31}P{^{1}H} NMR (36.3 MHz, C_7D_8, −20 °C): δ 11.9 (s). IR (Nujol, cm^{-1}): 1420 (m), 1300 (w), 1280 (m), 1125 (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, 62.59; H, 7.70. Analysis must be performed on freshly prepared samples that are warmed to room temperature for less than 1 h before sealing in a drybox.

Preparation of $Cp_2TiCH_2{\cdot}PMe_2Ph$ (3b). Dimethylphenylphosphine (64 μL, 0.46 mmol) was added via syringe to a well-stirred solution of β,β-dimethyltitanacyclobutane, **2** (104 mg, 0.42 mmol), in diethyl ether at −10 °C. The solution was warmed to room temperature over 15 min with periodic exposure 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 × 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) δ 12.36 (d, J_{P-H} = 6.59, 2 H), 7.07 (m, 5 H), 5.39 (d, J_{P-H} = 2.2 Hz, 10 H), 1.10 (d, J_{P-H} = 6.23 Hz, 6 H); ^{13}C{^{1}H} NMR (22.5 MHz, C_7D_8, −20 °C) δ 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) δ 25.77; IR (Nujol, 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), 695 (m). Too unstable for elemental analysis.

Preparation of $Cp_2TiCH_2{\cdot}PEt_3$ (3c). Triethylphosphine (260 μL, 1.78 mmol) was added via syringe to a well-stirred suspension of β,β-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 exposure to a vacuum to remove the isobutylene. The color changed from red to orange, and after 15 min, the solvent was removed in vacuo. The resulting yellow-brown powder was washed with −50 °C pentane (2 × 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) δ 12.13 (d, J_{P-H} = 5.13 Hz, 2 H), 5.33 (s, 10 H), 1.2–0.4 (m, 15 H); ^{13}C{^{1}H} NMR (22.5 MHz, C_7D_8, −20 °C) δ 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{^{1}H} NMR (36.3 MHz, C_7D_8, −20 °C) δ 38.97; IR (Nujol, cm^{-1}) 1305 (w), 1150 (w), 1035 (w), 1020 (m), 983 (w), 890 (w), 805 (m, sh), 790 (s), 755 (m). Too unstable for elemental analysis.

Phosphine-Exchange Equilibrium Measurements. The samples were prepared in septum-capped NMR tubes in a drybox. The reactant was dissolved in 400 μL 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 min in the NMR probe before measurement. The ^{31}P{^{1}H} 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 a drybox, attached to a Teflon needle valve adapter, and evacuated on a vacuum line. Approximately 400 μL of C_7D_8 was 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 by NMR at −80 °C. As the probe temperature was raised to room temperature, several new signals appeared. These signals corresponded to $Cp_2Ti(CO)_2$ (δ 4.56), $Cp_2Ti(CO)(PMe_2Ph)$ (δ 4.65 (d, J_{P-H} = 2 Hz)), and $Cp_2Ti(CH_2CO){\cdot}PMe_2Ph$ (δ 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%.

Kinetic Measurements. All sample weighing and preparation was done in a drybox by using either a Sartorius plan loader with a precision of 1 mg or an Sartorious Analytical balance with a precision of 0.1 mg. The 5-mm NMR samples were capped with a septum wrapped with parafilm. Saturation kinetics was tested for by preparing a solution such that 0.4 mL of the solution contained 10 mg of phosphine complex. The time required for equilibration of the sample in the NMR probe was determined to be 3 min, and therefore the NMR probe was always stabilized at the reaction temperature for at least 5 min before an experiment was started. The reactions were monitored by integration of the cyclopentadienyl ligand resonances of the reactant and product. Tables III and IV summarize the kinetics results and conditions for Figure 1–3. The reactions summarized in Tables III and IV were performed in toluene and benzene, respectively. All rate constants reported were obtained by a first-order kinetic analysis.

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Registry No. **3a**, 95044-99-8; **3b**, 108969-89-7; **3c**, 84254-01-3; **2**, 80122-07-2; $Cp_2Ti(PMe_3)(CH_2{=}C{=}O)$, 118458-17-6.

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