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Formation, Reactivities, and Molecular Structures of Phosphine Derivatives of Titanocene. Isolation and Characterization of a Titanium Monoolefin π Complex

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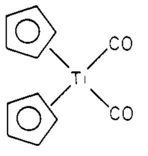
Abstract: Photolysis of a hexane solution of $Cp_2Ti(C^{18}O)_2$ in the presence of excess $C^{16}O$ results in the facile formation of $Cp_2Ti(C^{16}O)_2$, demonstrating that the carbonyl ligands of $Cp_2Ti(CO)_2$ (**1**) are photolabile. Photolysis of a hexane solution of **1** in the presence of excess PF_3 results in the formation of $Cp_2Ti(PF_3)_2$ (**3**) in 86% yield. The monophosphine complex $Cp_2Ti(CO)(PEt_3)$ (**2**) can be prepared from either photochemical or thermal reactions of **1** and PEt_3 in hydrocarbon solvents, whereas $Cp_2Ti(CO)(PPh_3)$ (**5**) can be obtained from a thermal reaction between **1** and PPh_3. The phosphine ligands in both **2** and **5** are very labile in solution. Complex **2** reacts readily with PF_3 and with $P(OPh)_3$ to produce $Cp_2Ti(CO)(PF_3)$ (**4**) and $Cp_2Ti(CO)[P(OPh)_3]$ (**6**), respectively. Reactions of **2** with $C_6H_5C{\equiv}CC_6H_5$ or $C_6F_5C{\equiv}CC_6F_5$ likewise lead to the respective π-acetylenic complexes $Cp_2Ti(CO)(\eta^2\text{-}C_6H_5C{\equiv}CC_6H_5)$ (**7**) and $Cp_2Ti(CO)(\eta^2\text{-}C_6F_5C{\equiv}CC_6F_5)$ (**8**) in high yields. Reactions between **2** and either dimethyl maleate or dimethyl fumarate in toluene solution at 0 °C lead to a single air- and heat-sensitive product, formulated as the monoolefin π complex $Cp_2Ti(CO)(\eta^2\text{-}trans\text{-}CH_3O_2CCH{=}CHCO_2CH_3)$ (**9**) on the basis of elemental analysis, molecular weight, and degradative and spectroscopic studies. Dimethyl maleate is also catalytically isomerized to dimethyl fumarate under these conditions. The ^1H NMR spectrum of **9** in toluene-d_8 solution is temperature dependent. The crystal and molecular structures of phosphine complexes **2** and **3** have been determined by X-ray diffraction techniques. Complex **2** crystallizes in the orthorhombic space group *Pbca* with unit cell parameters $a = 11.972$ (5) Å, $b = 16.977$ (7) Å, $c = 16.674$ (7) Å, and $D_c = 1.27$ g cm^{-3} for $Z = 8$. Least-squares refinement based on 2111 observed reflections led to a final R value of 0.044. Complex **3** belongs to the orthorhombic space group *C2cm* with $a = 7.811$ (4) Å, $b = 13.724$ (5) Å, $c = 37.649$ (11) Å, and $D_c = 1.75$ g cm^{-3} for $Z = 12$. The final R value based on 1037 independent observed reflections was 0.038. In **2**, the triethylphosphine ligand is coordinated to the titanium atom at a Ti–P separation of 2.585 (1) Å. The Ti–P lengths in the trifluorophosphine derivative **3**, however, average 2.34 (4) Å. These two extremes are probably due to steric crowding in the former (**2**) and appreciable back-bonding in the latter (**3**). The Ti–C(η^5) bond distances average 2.37 (2) Å in **2** and 2.34 (1) Å in **3**.

Recent joint studies in our laboratories have been concerned with the synthesis, spectra, molecular structures, and chemical reactivities of various group 4B metallocene derivatives, including those with carbonyl, metallacyclic, alkyl, and μ-oxo ligands.[2-8] In recent years, a variety of useful synthetic routes to the parent compound in this series, titanocene dicarbonyl (**1**), have been developed,[9-17] leading to extensive chemical studies of **1** as well as to our determinations of its molecular structure.[3] It is remarkable, however, that while replacement of carbon monoxide by a phosphine ligand represents one of the most fundamental substitution reactions in metal carbonyl chemistry, at the inception of our program only one phosphine derivative of **1** was known. This compound was $Cp_2Ti(CO)(PMe_3)$, and it was characterized only by its IR spectrum.[11,18,19]



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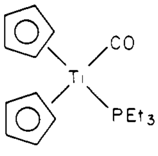

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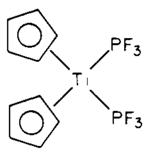

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In view of the possible importance of phosphine derivatives of the early transition metals to catalysis and other potentially useful applications and in order to learn more about the structural, bonding, and reactivity modes of such compounds, we have initiated a collaborative program of research concerning phosphine complexes of titanocene, zirconocene, and hafnocene. In the present paper, the syntheses of several new phosphine derivatives of titanocene under both thermally and photochemically induced conditions are described. The molecular structures of two of these complexes, $Cp_2Ti(CO)(PEt_3)$ (**2**) and $Cp_2Ti(PF_3)_2$ (**3**), have been elucidated by means of single-crystal X-ray diffraction methods, and the bonding modes of the respective phosphine ligands to titanium are compared. Finally, the utility of the triethylphosphine analogue **2** as a versatile intermediate for the generation of π-acetylenic and π-monoolefinic complexes of titanium is reported. A portion of this research has been previously described in communication form[7] and at a meeting.[20]

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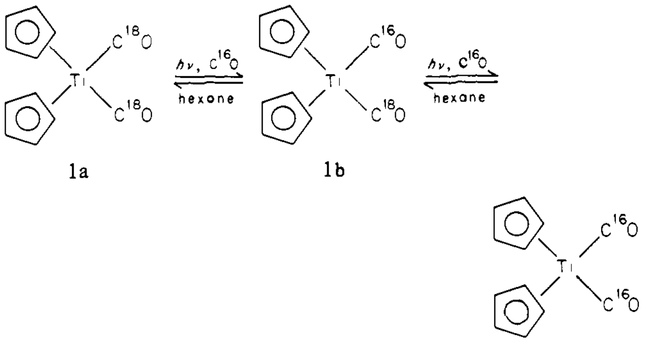
Results and Discussion

Previous studies in our laboratory have shown that both $Cp_2Zr(CO)_2$ and $Cp_2Hf(CO)_2$ are photolabile in hydrocarbon solvents. Irradiation of these group 4B metallocene dicarbonyls in hexane solution leads to the evolution of carbon monoxide and formation of insoluble, probably oligomeric, organometallic products, whereas irradiation in C_6D_6 leads to rapid decreases in the intensities of the cyclopentadienyl resonances, as measured by ^1H NMR spectrometry.[5,21] In contrast, solutions of **1** in hexane solution remain homogeneous when photolyzed. When this metal carbonyl is irradiated in C_6D_6, the relative intensity of the cyclopentadienyl resonance remains virtually constant relative to the resonance of cyclohexane as an internal standard.

Such a result could indicate that **1** is not photolabile in hydrocarbon solvents. It could also be explained by a process in which the photoinduced dissociation of a carbonyl ligand to generate a coordinatively unsaturated species, $[Cp_2Ti(CO)]$, does in fact occur; however, the rate of recombination of CO to re-form **1** is much greater than the rate of photodegradation of the intermediate.

In order to examine this latter possibility, $Cp_2Ti(C^{18}O)_2$ (**1a**) was prepared by the reductive carbonylation of Cp_2TiCl_2 in the presence of $C^{18}O$. This isotopically labeled titanocene dicarbonyl was then irradiated in hexane solution in a photolysis-type Schlenk tube at 15 °C while $C^{16}O$ was slowly sparged through the solution. The course of the reaction was conveniently monitored by IR spectroscopy. Bands due to the terminal carbonyl stretching frequencies of **1a** at 1934 and 1856 cm^{-1} were totally absent after a 15-min photolysis period, and four new bands appeared at 1959 and 1870 cm^{-1} and 1977 and 1899 cm^{-1}, which were assignable to $Cp_2Ti(C^{16})(C^{18}O)$ (**1b**) and $Cp_2Ti(C^{16}O)_2$ (**1c**), respectively. Upon continued irradiation and sparging with $C^{16}O$ for 30 min, only bands due to **1c** were observed.

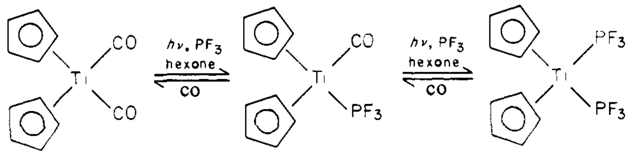


1a 1b 1c

In a related experiment, a solution of **1a** in heptane was sparged with $C^{16}O$ at 15 °C under nonphotochemical conditions. Metal carbonyl bands due to **1b** were barely detectable after 30 min. Even after 13 h of sparging, bands due to both **1a** and **1b** were clearly visible, although **1c** was the predominant species present. These results clearly demonstrate that the carbonyl ligands of **1** are indeed highly labile under photochemical conditions and point to a photoequilibrium between **1** and the coordinately unsaturated intermediate $[Cp_2Ti(CO)]$.[22]

In view of the photolability of the carbonyl ligands of **1**, it was of subsequent interest to examine its possible utility in the photochemical formation of trifluorophosphine derivatives of titanocene. Both PF_3 and CO are known to be weak σ donors and strong π acceptors toward transition metals, the stability of a PF_3–metal complex being attributed to strong d_π–d_π interaction between the ligand and the metal.[23-26] In spite of extensive research on trifluorophosphine complexes of the transition metals in recent years, PF_3 derivatives of titanium were unknown at the inception of our investigations in this area. Independent of our studies,[7] another stable PF_3–titanium complex, $Ti(CO)_2(PF_3)(dmpe)_2$, has also been recently described by Wreford and coworkers.[27]

When **1** was photolyzed in hexane at 15 °C and gaseous PF_3 was sparged through the solution, IR analysis of the reaction mixture indicated that a strong new metal carbonyl band had formed at 1932 cm^{-1} after 10 min of irradiation. Bands due to **1** were also present at this point, although they were greatly diminished in intensity. After 30 min of irradiation in the presence of PF_3, the band at 1932 cm^{-1}, assignable to the monocarbonyl complex $Cp_2Ti(CO)(PF_3)$ (**4**), was the only metal carbonyl absorption present. After a 1.5-h photolysis period, the solution had changed from red to golden yellow, and no metal carbonyl bands could be detected. Filtration and removal of the solvent produced the bis(trifluorophosphine) complex **3** as an air-sensitive yellow solid in 86% yield. The product could be further purified by crystallization from hexane at −20 °C or by slow vacuum sublimation. In a related experiment, PF_3 was sparged through a solution of **1** in hexane for 1.5 h. Analysis of the reaction mixture by IR spectroscopy indicated that strong bands due to **1** were still present, and only a very weak band at 1932 cm^{-1}, assignable to **4**, could be observed.



1 4 3

These results likewise demonstrate the photolability of **1** in solution. The PF_3 in this instance not only functions as a coordinative ligand but also tends to physically displace the photodissociated CO from the reaction mixture, leading ultimately to **3** in high yield.

The bis(trifluorophosphine) complex **3** was characterized by elemental analysis, by spectroscopy, and by a single-crystal X-ray diffraction study (vide infra). The ^1H NMR spectrum of **3** exhibited a triplet at δ 4.56 (J_{H-P} = 3.5 Hz), assignable to the C_5H_5 protons coupled to the two equivalent ^{31}P nuclei. The IR spectrum of **3** contained a strong absorption at 850 cm^{-1} that is assignable to a P–F stretching vibration. The mass spectrum of **3** exhibited a molecular ion at *m/e* 354 as well as fragmentation peaks that are consistent with its structural formulation.

A number of attempts were made to generate the monocarbonyl complex **4** via thermal reactions of **1** and PF_3. Unfortunately, **4** prepared in this manner was invariably contaminated with **1**, and complete separation could not be achieved. Both **3** and **4** could readily be converted back to **1** under nonphotochemical conditions. For example, when CO was sparged through a hexane solution of **3** at 15 °C, a metal carbonyl band assignable to **4** appeared within 10 min. After 1.5 h, the solution had turned red, and the IR spectrum of the reaction mixture indicated that **1** was the only metal carbonyl species present.

Photolysis of a heptane solution of **1** containing an excess of triethylphosphine over a 2-h period at 15 °C led to the formation of the monocarbonyl complex **2**. This reaction could only be successfully carried out when an inert gas (Ar) was sparged through the solution during the photolysis period, a result that again demonstrates the importance of removal of photodissociated CO from the reaction system.

A more facile route to **2** involved a thermal reaction of **1** and triethylphosphine in refluxing hexane. Essentially pure **2** was produced in 60% yield in this manner, and analytically pure **2** could

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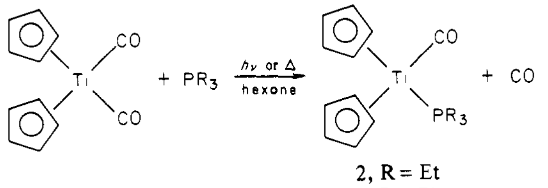


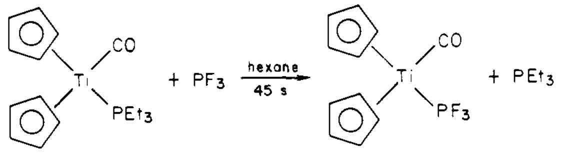
2, R = Et
5, R = Ph

be obtained by subsequent recrystallization of the product from hexane at −20 °C. The ^1H NMR spectrum of **2** exhibited a doublet at δ 4.75 (J_{H-P} = 1.5 Hz) and a multiplet centered at δ 0.86, assignable to the C_5H_5 and PEt_3 protons, respectively. The IR spectrum of **2** contained a strong terminal metal carbonyl band at 1864 cm^{-1}.

The related phosphine complex $Cp_2Ti(CO)(PPh_3)$ (**5**) could also be synthesized by thermolysis of **1** and triphenylphosphine in hexane solution, although longer reflux periods were required to successfully complete the reaction. The terminal carbonyl stretching frequencies for **2** (1864 cm^{-1}) and for **5** (1850 cm^{-1}) both occur at appreciably lower energies than does the corresponding frequency for **4** (1932 cm^{-1}). These results are consistent with the known enhanced π acceptor ability of PF_3 relative to trialkyl- or triarylphosphines in closely related phosphine–transition-metal complexes.[23-26] It is also noteworthy that bis(triethylphosphine) or bis(triphenylphosphine) complexes of titanocene analogous to **3** could not be detected in our studies, under either photochemical or thermal conditions.

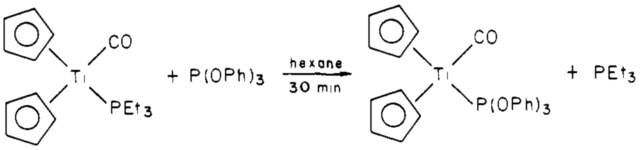
A subsequent investigation concerning the reactivities of **2** and **5** revealed, somewhat surprisingly, that the phosphine ligands in both these complexes were rather labile in the presence of various other reactive substrates. The triethylphosphine complex **2** was studied in greatest detail, since triethylphosphine was easier to remove in subsequent operations than was triphenylphosphine.

After sparging of a hexane solution of **2** with carbon monoxide for 1 min, **2** could no longer be detected by IR spectroscopy, and **1** could be isolated in 84% yield from the reaction mixture. A similar reaction of **2** with gaseous PF_3 led to **4** (ν_{CO} = 1932 cm^{-1}) in only 45 s, and **2** could not be detected after this brief reaction period. The ^1H NMR spectrum of **4** prepared in this manner exhibited a doublet (J_{H-P} = 3.5 Hz) at δ 4.59 assignable to the C_5H_5 protons, and the resonance at δ 4.75 due to **2** was completely absent. The conversion of **2** into **4** by this method represents the most facile current route to the latter complex, although attempts to obtain crystalline samples of analytical or X-ray diffraction quality have thus far not been successful.



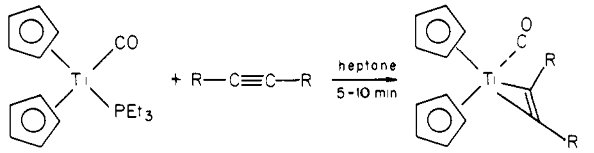
2 4

A reaction between **2** and triphenyl phosphite likewise resulted in facile replacement of the triethylphosphine ligand and formation of $Cp_2Ti(CO)P(OPh)_3$ (**6**) in 68% yield. The phosphite complex **6** was characterized by IR, ^1H NMR, and mass spectral methods.



2 6

Of perhaps even greater potential is the utility of **2** as an intermediate in the formation of new low-valent organotitanium compounds that contain π-hydrocarbon ligands. At the present time, the only known π-acetylenic complex of titanium is $Cp_2Ti(CO)(\eta^2\text{-}PhC{\equiv}CPh)$ (**7**), which is reportedly formed from a reaction between **1** and diphenylacetylene in heptane solution under reduced pressure over a 3-h period.[28] In contrast, a reaction between **2** and diphenylacetylene in heptane solution at room temperature appeared by spectroscopic studies to be complete in ca. 5 min, and the π-acetylenic complex **7** could be isolated in 91% yield. The spectral properties of **7** produced in this manner were identical with those reported earlier.[28]

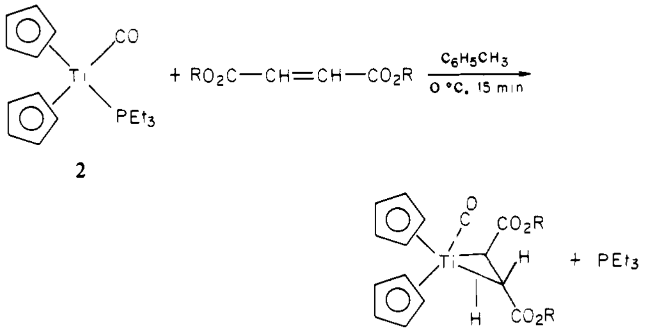


2 7, R = C_6H_5
8, R = C_6F_5

Bis(pentafluorophenyl)acetylene and **2** also reacted rapidly in heptane solution to afford the new π-acetylenic complex $Cp_2Ti(CO)(\eta^2\text{-}C_6F_5C{\equiv}CC_6F_5)$ (**8**). As anticipated for a complex containing this highly electronegative ligand, the coordinated acetylenic stretching frequency for **8** (1770 cm^{-1}) was slightly lower than the corresponding value for **7** (1785 cm^{-1}), whereas the terminal carbonyl stretching frequency for **8** occurred at slightly higher energy (2020 cm^{-1} for **8** vs. 2000 cm^{-1} for **7**). It is noteworthy, however, that the ^1H NMR shifts for the η^5-cyclopentadienyl protons in both **7** and **8** were identical at δ 4.95. The thermal and oxidative stabilities of **8** were appreciably enhanced relative to **7**, in accordance with the known stabilities of perfluorinated acetylenic metal complexes relative to their hydrocarbon counterparts.[29-31]

Monoolefin π complexes of titanium are frequently postulated as intermediates in numerous catalytic processes, including dimerization, oligomerization, hydrogenation, and in particular Ziegler–Natta polymerization of alkenes. While detailed reaction pathways by which these important catalytic processes occur are not fully understood at the present time, virtually all mechanisms propose the coordination of a monoolefin to a vacant coordination site on titanium as a key step.[32-37]

It is thus of special significance that **2** has also been found to serve as a precursor for the first fully characterized monoolefin complexes of titanocene, $Cp_2Ti(CO)(\eta^2\text{-}trans\text{-}RO_2CCH{=}CHCO_2R)$ (**9**, **10**).[38-40] Reactions between **2** and either dimethyl



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9, R = CH_3
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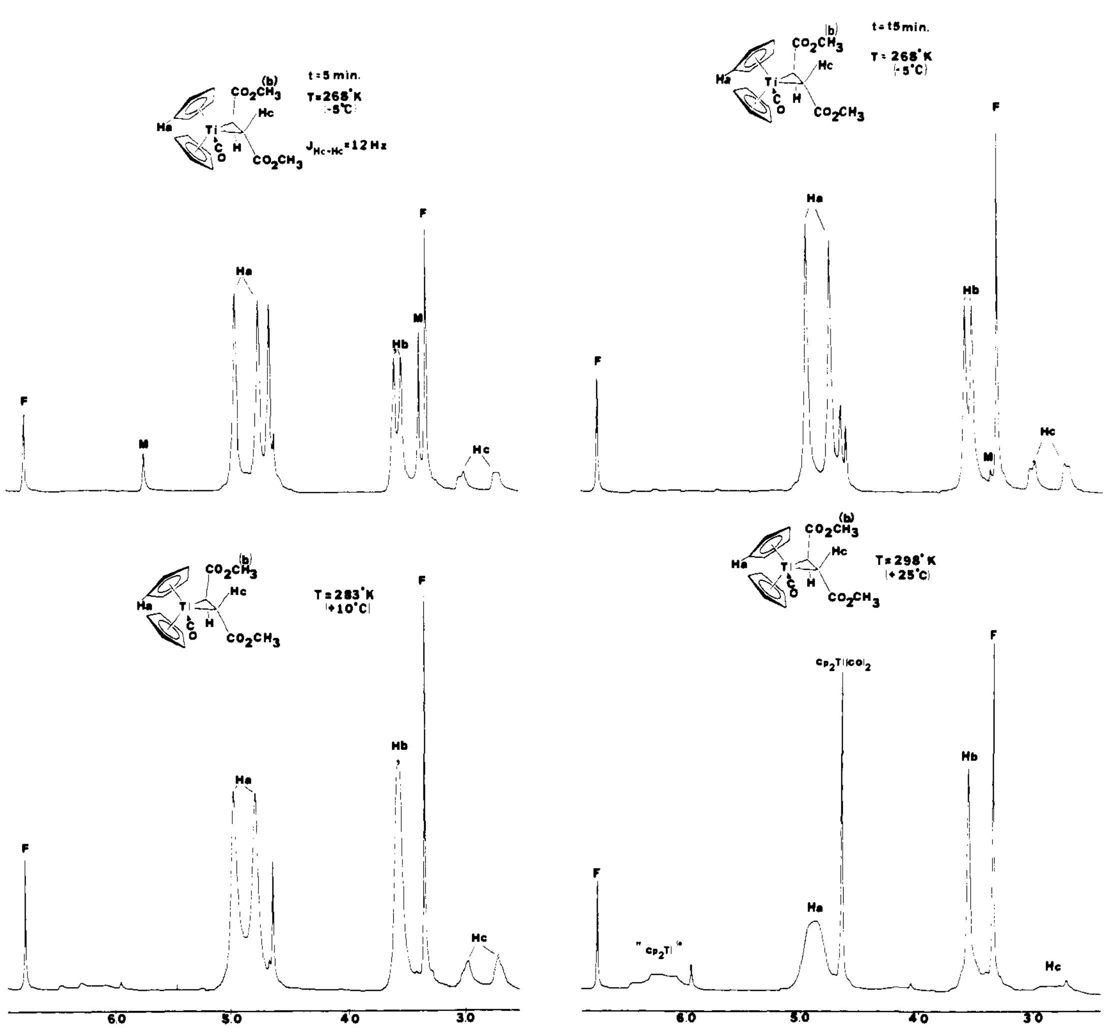

Figure 1. ^1H NMR spectra (270 MHz) of a reaction between $Cp_2Ti(CO)(PEt_3)$ (**2**) and dimethyl maleate in toluene-d_8 solution as a function of reaction time and temperature.

fumarate[41] or dimethyl maleate in benzene or toluene solution at 0 °C result in dark green solutions, from which a very air-sensitive green solid can be precipitated by the addition of cold pentane. The solid undergoes slow thermal decomposition, even under an argon atmosphere at 0 °C. Elemental analyses and a cryoscopic molecular weight determination of the product are in accord with a formulation corresponding to **9**. Degradation of the green solid by means of HCl-saturated toluene at 0 °C leads to the formation of Cp_2TiCl_2 in quantitative yield and dimethyl succinate in 60% yield. Oxidation of a freshly prepared toluene solution of the product, by bubbling in dry air at 0 °C, produces dimethyl fumarate quantitatively. On the basis of these results, we formulate the green solid as the monoolefin complex **9**, which can be isolated in 65% yield.

Further evidence for the structure of **9** is based on IR and ^1H NMR spectral studies. The IR spectrum of **9** in benzene exhibits strong bands at 2010 and 1675 cm^{-1}, assignable to terminal and ligand carbonyl stretching frequencies, respectively. The latter absorption is shifted to only 45 cm^{-1} lower energy than that of free dimethyl fumarate (1720 cm^{-1}), indicating that the ligand carbonyl groups most likely are not directly involved in coordination with the metal.[42]

The 270-MHz ^1H NMR spectra of **9** as a function of reaction time and temperature are illustrated in Figure 1. Figure 1 (top) represents a spectrum recorded at -5 °C within 5 min after mixing toluene-d_8 solutions of **2** and dimethyl maleate (in molar excess) at 0 °C. Resonances occur at δ 4.95 (s, 5 H) and 4.75 (s, 5 H), assignable to protons of the nonequivalent cyclopentadienyl rings (H_a), at δ 3.58 (s, 3 H) and 3.52 (s, 3 H), assignable to protons of the nonequivalent methoxy groups (H_b), and at δ 2.99 (d, J_{H-H} = 11 Hz, 1 H) and 2.71 (d, J_{H-H} = 11 Hz), assignable to the nonequivalent vinyl protons (H_c) of **9**. Also observable under these conditions is a moderately intense singlet at δ 4.66, representing the η^5-cyclopentadienyl protons of phosphine complex **2**, and a very weak resonance at δ 4.61 due to a small amount of **1** present.

It is noteworthy that the two resonances due to uncomplexed dimethyl maleate (M) decay in a matter of minutes and are replaced by resonances assignable to uncomplexed fumarate (F). Isomerization of excess dimethyl maleate to dimethyl fumarate is virtually complete after 15 min at -5 °C (Figure 1b). This process appears to be catalytic, since when the reaction was

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[38] A monoolefin complex of Ti(IV), $[Cp_2Ti(\pi\text{-TCNE})OCH_3]PPh_4$, has been briefly mentioned at a meeting, although detailed information has not been further reported [M. Pankowski, "Abstracts of Papers", Seventh International Conference on Organometallic Chemistry, Venice, Italy, Sept 1–5, 1975; p 98].

[39] Several η^4-butadiene complexes of titanium have been described previously: (a) Zwignengburg, A.; Van Oven, H. O.; Gronenboom, C. J.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1975**, *94*, 23. (b) Dutta, S.; Fischer, M. B.; Wreford, S. S. *Ibid.* **1980**, *188*, 353.

[40] Since completion of this research, we have learned of an independent study involving the synthesis and structural elucidation of an ethylene complex of decamethyltitanocene [Cohen, S. A.; Marsh, R. E.; Bercaw, J. E., "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, Aug 23–28, 1981; American Chemical Society: Washington, D.C., 1981; INOR 295].

[41] A reaction between **2** and diethyl fumarate under analogous conditions leads to monoolefin complex **10**, which exhibits physical and spectral properties similar to those of **9**.

[42] Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1046.

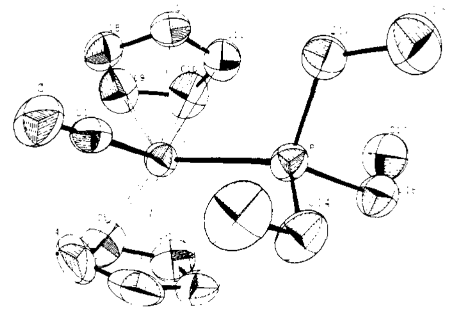

Figure 2. Molecular structure of $Cp_2Ti(CO)(PEt_3)$ (3), with the atoms represented by their 50% probability ellipsoids for thermal motion.

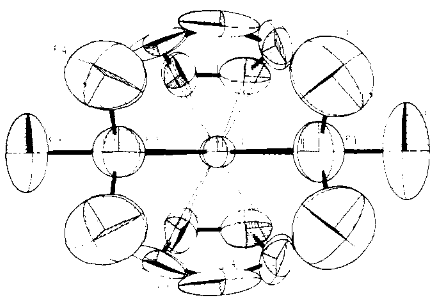

Figure 3. One of the two independent molecules in the asymmetric unit of $Cp_2Ti(PF_3)_2$ (3). This molecule resides on a crystallographic mirror plane.

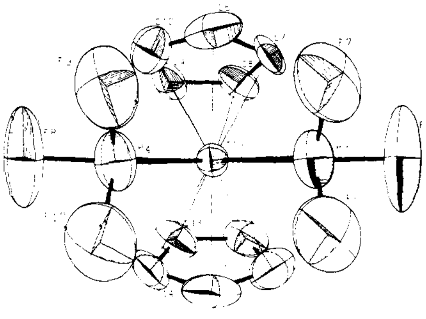

Figure 4. Second molecule of $Cp_2Ti(PF_3)_2$ (3), which possesses no crystallographically imposed symmetry.

Table I. Bond Distances (Å) and Angles (deg) for $Cp_2Ti(CO)(PEt_3)$ (2)

atoms	distance	atoms	distance
Ti-P	2.585 (1)	Ti-C(1)	2.009 (4)
Ti-C(2)	2.400 (4)	Ti-C(3)	2.348 (5)
Ti-C(4)	2.325 (5)	Ti-C(5)	2.367 (5)
Ti-C(6)	2.397 (4)	Ti-C(7)	2.370 (4)
Ti-C(8)	2.363 (4)	Ti-C(9)	2.385 (5)
Ti-C(10)	2.382 (5)	Ti-C(11)	2.388 (4)
P-C(12)	1.858 (4)	P-C(14)	1.845 (4)
P-C(16)	1.866 (4)	O-C(1)	1.152 (5)
C(2)-C(3)	1.409 (7)	C(2)-C(6)	1.372 (7)
C(3)-C(4)	1.382 (9)	C(4)-C(5)	1.379 (9)
C(5)-C(6)	1.424 (8)	C(7)-C(8)	1.420 (6)
C(7)-C(11)	1.417 (6)	C(8)-C(9)	1.395 (7)
C(9)-C(10)	1.415 (7)	C(10)-C(11)	1.378 (7)
C(12)-C(13)	1.491 (7)	C(14)-C(15)	1.508 (6)
C(16)-C(17)	1.490 (6)	Cent1-Ti	2.048
Cent2-Ti	2.055		

atoms	angle	atoms	angle
P-Ti-C(1)	90.3 (1)	Ti-P-C(12)	114.2 (1)
Ti-P-C(14)	117.1 (2)	C(12)-P-C(14)	102.0 (2)
Ti-P-C(16)	121.1 (2)	C(12)-P-C(16)	102.1 (2)
C(14)-P-C(16)	97.3 (2)	Ti-C(1)-O	174.7 (4)
C(3)-C(2)-C(6)	108.5 (5)	C(2)-C(3)-C(4)	107.3 (5)
C(3)-C(4)-C(5)	109.2 (5)	C(4)-C(5)-C(6)	107.3 (5)
C(2)-C(6)-C(5)	107.6 (5)	C(8)-C(7)-C(11)	107.5 (4)
C(7)-C(8)-C(9)	108.1 (4)	C(8)-C(9)-C(10)	107.3 (5)
C(9)-C(10)-C(11)	109.4 (5)	C(7)-C(11)-C(10)	107.7 (4)
P-C(12)-C(13)	118.8 (4)	P-C(14)-C(15)	115.7 (3)
P-C(16)-C(17)	115.4 (3)	Cent1-Ti-Cent2	138.73
Cent1-Ti-P	105.00	Cent1-Ti-C(1)	102.43
Cent2-Ti-P	107.18	Cent2-Ti-C(1)	102.52

conducted with a 7-fold excess of dimethyl maleate relative to **2**, complete isomerization to dimethyl fumarate occurred within 20 min, as evidenced by ^1H NMR analysis of the reaction mixture.

Earlier studies have shown that diethyl maleate isomerizes to diethyl fumarate upon coordiation to vanadocene, to produce the diethyl fumarate complex $Cp_2V[\eta^2\text{-}trans(C_2H_5O_2CCH{=}CHCO_2C_2H_5)]$.[42] The structure of the latter monoolefin complex has been confirmed by an X-ray diffraction study.[43] Except for these two examples in the early transition-metal series, maleate esters do not tend to isomerize to fumarate esters upon coordination to a metal. However, molybdenum derivatives can be isomerized at elevated temperatures,[44] and iron derivatives can be isomerized under photochemical conditions.[45]

Upon warming of a toluene-d_8 solution of **9** from −5 to 10 °C, coalescence of the two methoxy proton resonances occurs (Figure 1c), and on further warming to 25 °C, coalescence of both the two cyclopentadienyl proton resonances and the two vinyl proton resonances have also taken place (Figure 1d). These changes are reversible upon lowering the temperature. Concomitant decomposition of **9** in solution likewise occurs during the warming process, producing **1**, dimethyl fumarate, and what appears to be a form of titanocene (broad resonance from ca. δ 5.9 to 6.5).[9,15,16]

Whereas coalescence of the methoxy and vinyl proton resonances can be explained by simple rotation of the olefin about the titanium-olefin coordination axis, coalescence of the cyclopentadienyl resonances cannot. The free enthalpy of activation $\Delta G^\ddagger$ for the coalescence of *each* of these resonances is estimated[46] to be ca. 14 kcal/mol, suggesting that these phenomena may be the result of a single process.

While the observed catalytic isomerization of dimethyl maleate to dimethyl fumarate indicates that substitution of a coordinated olefin by free olefin occurs, the lack of convergence between resonances due to complexed and uncomplexed olefin negates such an exchange as being responsible for the observed coalescences. A bimolecular mechanism involving interchange of coordinated olefins could account for the temperature-dependent ^1H NMR results and may also be related to the thermal decomposition process, involving an apparent disproportionation of **9** to produce **1**, dimethyl fumarate, and titanocene. Floriani et al. have noted earlier that a disproportionation process occurs for the related acetylenic complex **7** in aromatic solvents upon warming.[28] An alternative pathway might involve a unimolecular isomerization process, in which the ligands of the complex undergo inversion about the pseudotetrahedral metal center. A similar mechanism has been postulated for the observed interconversion of $Cp_2Mo(H)[\eta^1\text{-}C(CF_3){=}C(CF_3)H]$ isomers.[44] Studies are in progress to further elucidate the mechanisms of this process.

The molecular structure and atom numbering scheme for **2** are presented in Figure 2 and those for the two independent molecules of **3** in Figures 3 and 4. In **3**, one molecule resides on a crystallographic mirror plane containing F(1), P(1), Ti, P(2), and F(3), while the second molecule possesses no crystallographically imposed symmetry. There is, however, no discernible difference between the two.

In keeping with the chemical reactivity of the Ti-P bond, the observed length in **2** of 2.585 (1) Å (Table I) is long by any account. Two independent methods of estimating a normal Ti-P bond length give values of 2.48 and 2.53 Å.[7] In **3**, the Ti-P distance, 2.34 (4) Å (Table II), is contracted because the PF_3

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(43) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1979**, *18*, 2282.

(44) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1972**, *94*, 1886.

(45) Schenck, G. O.; Koerner von Gustorf, E.; Jun, M.-J. *Tetrahedron Lett.* **1962**, 1059.

(46) Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

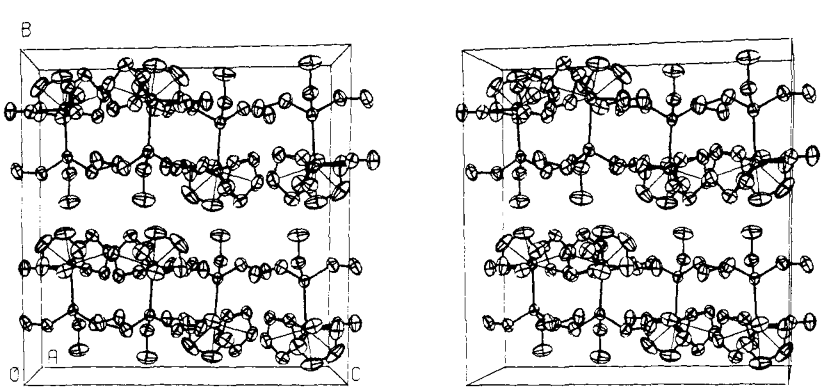

Figure 5. Stereoscopic view of the unit cell contents of $Cp_2Ti(CO)(PEt_3)$ (**2**).

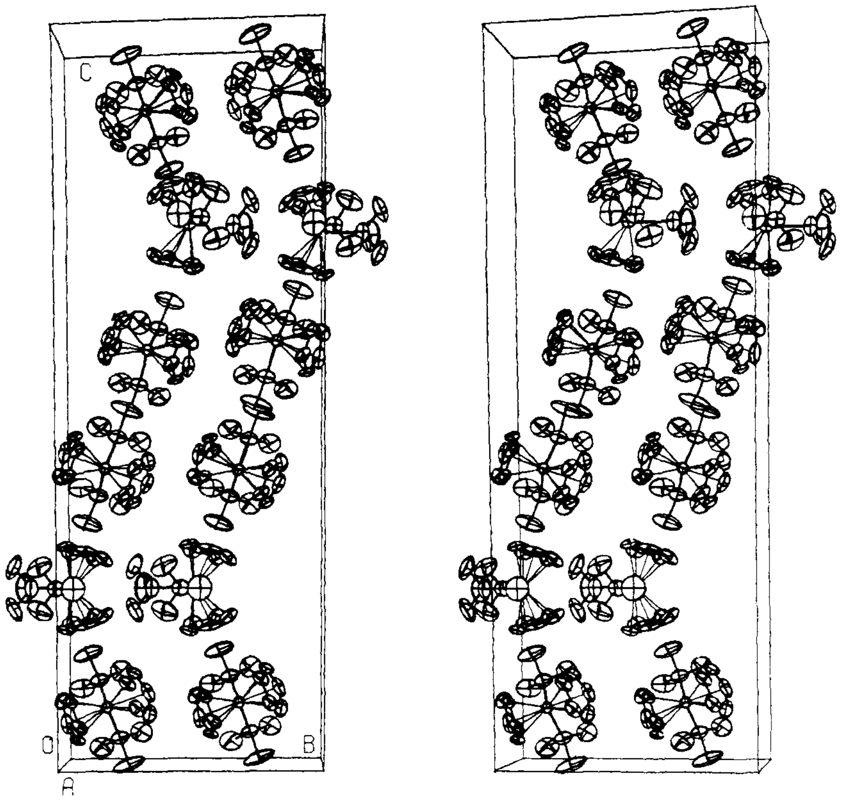

Figure 6. Stereoscopic view of the unit cell contents of $Cp_2Ti(PF_3)_2$ (**3**).

ligand has a substantial ability to back-bond.[23-26] The Ti–C-(carbonyl) distance, 2.009 (4) Å, is in close agreement with the 2.01 (1) and 2.03 (1) Å values found in $(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$[8] and **1**,[3] respectively.

The long Ti–P bond in **2** may well be attributable to steric crowding. In keeping with this, the average Ti–C(η^5)bond length, 2.37 (1) Å, in **2** is longer than the 2.34 (1) and 2.35 (1) Å distances in **3** and **1**, respectively. It is in fact near the 2.38 (1) Å value found for $(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$, a compound in which considerable ligand–ligand nonbonded repulsion was noted.[8]

Stereoscopic views of the unit cell contents of **2** and **3** are presented in Figures 5 and 6. No short intermolecular contacts were noted.

Experimental Section

All reactions were conducted under argon by using standard Schlenk and cannula techniques. The argon was dried with P_2O_5 and H_2SO_4, and trace oxygen was removed with BTS catalyst (BASF). Pentane, hexane, heptane, benzene, and toluene were dried over CaH_2 and freshly distilled from CaH_2 under argon before use. Ethyl ether and THF were predried over sodium and subsequently distilled under argon from sodium benzophenone. Deuterated solvents were put through three freeze–pump–thaw cycles, after which no gas evolved on melting. Photolyses were conducted with a 275-W General Electric sunlamp. The light source was placed 1–2 cm from the water-cooled vessel containing the solution to be photolyzed. ^1H NMR spectra were recorded on a Varian A-60 spectrometer at 60 MHz or a Brucker spectrometer at 270 MHz. IR spectra were obtained on a Perkin-Elmer 237-B spectrometer and were calibrated vs. polystyrene. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. $Cp_2Ti(CO)_2$ was best prepared by the method of Demerseman et al.[12] Diphenylacetylene[47] and bis(pentafluorophenyl)acetylene[29] were synthesized according to literature procedures. Cp_2TiCl_2 (Arapahoe), PF_3 (Research Organic/Inorganic), PEt_3 (Strem), PPh_3 (Eastman), diethyl maleate (Aldrich), dimethyl maleate (Eastman), and dimethyl fumarate (Eastman) were obtained from commercial sources. Carbon monoxide-^{18}O (99%) was obtained from Stohler Isotope Chemicals, Inc.

Preparation of $Cp_2Ti(C^{18}O)_2$. Cp_2TiCl_2 (1.39 g, 5.58 mmol), aluminum filings (0.50 g, 18.6 mmol), and mercuric chloride (1.00 g, 3.68 mmol) were placed in a Schlenk tube containing ca. 25 mL of THF. The stirred mixture was stoppered and the stopcock of the vessel was attached to a 10-cm piece of vacuum tubing, which was in turn connected to a T-shaped glass tube containing another stopcock on one leg of the T. The latter stopcock was connected to a vacuum line. The leg opposite to the Schlenk tube connection was attached to a 250-mL flask containing $C^{18}O$ via a 10-cm piece of vacuum hose. In the neck of the flask was a metal weight. The entire system, including the headspace of the Schlenk tube, was evacuated. The stopcock to the vacuum line was then closed, and

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[47] Cope, A. C.; Smith, D. S.; Cotter, R. J. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 377.

Table II. Bond Distances (Å) and Angles (deg) for $Cp_2Ti(PF_3)_2$ (3)

atoms	distance	atoms	distance
Ti(1)–P(1)	2.340 (6)	Ti(1)–P(2)	2.349 (6)
Ti(1)–C(1)	2.34 (1)	Ti(1)–C(2)	2.34 (1)
Ti(1)–C(3)	2.34 (1)	Ti(1)–C(4)	2.31 (1)
Ti(1)–C(5)	2.35 (1)	Ti(2)–P(3)	2.343 (4)
Ti(2)–P(4)	2.345 (4)	Ti(2)–C(6)	2.33 (1)
Ti(2)–C(7)	2.32 (1)	Ti(2)–C(8)	2.32 (1)
Ti(2)–C(9)	2.35 (1)	Ti(2)–C(10)	2.35 (1)
Ti(2)–C(11)	2.33 (1)	Ti(2)–C(12)	2.36 (1)
Ti(2)–C(13)	2.35 (1)	Ti(2)–C(14)	2.33 (1)
Ti(2)–C(15)	2.32 (1)	P(1)–F(1)	1.52 (2)
P(1)–F(2)	1.538 (9)	P(2)–F(3)	1.56 (1)
P(2)–F(4)	1.544 (8)	P(3)–F(5)	1.546 (9)
P(3)–F(6)	1.56 (1)	P(3)–F(7)	1.547 (9)
P(4)–F(8)	1.570 (7)	P(4)–F(9)	1.555 (8)
P(4)–F(10)	1.539 (9)	C(1)–C(2)	1.32 (2)
C(1)–C(5)	1.37 (2)	C(2)–C(3)	1.38 (2)
C(3)–C(4)	1.42 (2)	C(4)–C(5)	1.40 (2)
C(6)–C(7)	1.42 (2)	C(6)–C(10)	1.39 (2)
C(7)–C(8)	1.37 (2)	C(8)–C(9)	1.39 (2)
C(9)–C(10)	1.37 (2)	C(11)–C(12)	1.38 (2)
C(11)–C(15)	1.39 (2)	C(12)–C(13)	1.40 (2)
C(13)–C(14)	1.36 (2)	C(15)–C(14)	1.39 (2)
Cent1–Ti(1)	2.018	Cent2–Ti(2)	2.012
Cent3–Ti(2)	2.020		

atoms	angle	atoms	angle
P(1)–Ti(1)–P(2)	88.1 (2)	P(3)–Ti(2)–P(4)	87.3 (1)
Ti(1)–P(1)–F(1)	123.7 (7)	Ti(1)–P(1)–F(2)	121.2 (4)
F(1)–P(1)–F(2)	93.1 (7)	Ti(1)–P(2)–F(3)	124.0 (6)
Ti(1)–P(2)–F(4)	121.2 (4)	F(3)–P(2)–F(4)	93.0 (6)
Ti(2)–P(3)–F(5)	121.4 (4)	Ti(2)–P(3)–F(6)	124.8 (4)
F(5)–P(3)–F(6)	94.4 (6)	Ti(2)–P(3)–F(7)	120.9 (4)
F(5)–P(3)–F(7)	95.6 (6)	F(6)–P(3)–F(7)	92.3 (6)
Ti(2)–P(4)–F(8)	123.6 (4)	Ti(2)–P(4)–F(9)	121.1 (4)
F(8)–P(4)–F(9)	94.2 (5)	Ti(2)–P(4)–F(10)	121.0 (4)
F(8)–P(4)–F(10)	93.8 (5)	F(9)–P(4)–F(10)	95.9 (6)
F(2)–P(1)–F(2)	97.0 (8)	F(4)–P(2)–F(4)	97.0 (8)
C(2)–C(1)–C(5)	110 (1)	C(1)–C(2)–C(3)	110 (1)
C(2)–C(3)–C(4)	107 (2)	C(3)–C(4)–C(5)	106 (2)
C(1)–C(5)–C(4)	107 (2)	C(7)–C(6)–C(10)	106 (1)
C(6)–C(7)–C(8)	107 (1)	C(7)–C(8)–C(9)	109 (1)
C(8)–C(9)–C(10)	107 (1)	C(6)–C(10)–C(9)	110 (1)
C(12)–C(11)–C(15)	108 (1)	C(11)–C(12)–C(13)	107 (1)
C(12)–C(13)–C(14)	109 (1)	C(13)–C(14)–C(15)	108 (1)
C(11)–C(15)–C(14)	107 (1)	Cent1–Ti(1)–Cent1	137.09
Cent1–Ti(1)–P(1)	105.64	Cent1–Ti(1)–P(2)	104.85
Cent2–Ti(1)–Cent3	138.02	Cent2–Ti(1)–P(3)	105.25
Cent2–Ti(1)–P(4)	104.42	Cent3–Ti(1)–P(3)	105.43
Cent3–Ti(1)–P(4)	104.96		

the flask was tilted downward such that the metal weight ruptured the break-seal of the flask. The $C^{18}O$ flowed into the evacuated area, and the reaction mixture was subsequently allowed to stir under the $C^{18}O$ atmosphere for 1 week. After this time, the THF was removed under reduced pressure, leaving a dark red residue. The residue was extracted with hexane and poured onto a filter frit containing a plug (2 × 5 cm) of 5% deactivated, degassed alumina. The resulting red solution was evaporated to dryness, leaving 0.70 g (53%) of $Cp_2Ti(C^{18}O)_2$: IR (hexane) ν_{CO} 1934, 1856 cm^{-1}.

Photolysis of $Cp_2Ti(C^{18}O)_2$ with $C^{16}O$. A 30-mL heptane solution of $Cp_2Ti(C^{18}O)_2$ (0.06 g, 0.25 mmol) was irradiated in a photolysis Schlenk tube while $C^{16}O$ was sparged slowly through the solution by means of a syringe needle. The total photolysis time was 30 min. The progress of the reaction was monitored by means of IR spectroscopy. Before photolysis, metal carbonyl bands due to $Cp_2Ti(C^{18}O)_2$ were present at 1934 and 1856 cm^{-1}. After a 15-min photolysis period, these bands were absent, and four new metal carbonyl bands appeared at 1959 and 1870 cm^{-1} and at 1977 and 1899 cm^{-1}, assignable to $Cp_2Ti(C^{16}O)(C^{18}O)$ and $Cp_2Ti(C^{16}O)_2$, respectively. After a 30-min period of photolysis, only bands due to $Cp_2Ti(C^{16}O)_2$ were present.

In a related experiment, a 30-mL heptane solution of $Cp_2Ti(C^{18}O)_2$ (0.06 g, 0.25 mmol) was sparged with $C^{16}O$ in the dark (nonphotochemical conditions). After 30 min, $Cp_2Ti(C^{18}O)_2$ was the predominant species present as evidenced by IR spectroscopy, with bands due to $Cp_2Ti(C^{16}O)(C^{18}O)$ barely detectable. After 3 h, bands due to $Cp_2Ti(C^{16}O)_2$ were first observed. After 13 h, $Cp_2Ti(C^{16}O)_2$ appeared to be the predominant species present, although bands due to $Cp_2Ti(C^{16}O)(C^{18}O)$ and $Cp_2Ti(C^{18}O)_2$ were still clearly evident.

Preparation of $Cp_2Ti(PF_3)_2$. A solution of $Cp_2Ti(CO)_2$ (0.43 g, 1.84 mmol) in 86 mL of hexane was placed in a photolysis Schlenk tube that was capped with a rubber septum, and the Schlenk tube was connected to a mercury overpressure valve. Trifluorophosphine was then gently sparged through the stirred solution via a syringe needle, while the reaction mixture was irradiated. The total photolysis time was 90 min, and the progress of the reaction was monitored by IR spectroscopy. After 10 min of photolysis, a new, strong metal carbonyl band at 1932 cm^{-1} could be observed in addition to bands due to $Cp_2Ti(CO)_2$ at 1977 and 1899 cm^{-1}. After a 30-min photolysis period, the band at 1932 cm^{-1}, assignable to $Cp_2Ti(CO)(PF_3)$, was the only metal carbonyl absorption present. After 90 min of irradiation, the solution had turned to golden yellow and exhibited no metal carbonyl bands. The reaction mixture was then filtered and the filtrate evaporated to dryness, leaving 0.56 g (86%) of $Cp_2Ti(PF_3)_2$. NMR (C_6D_6) δ 4.56 (t, J_{H-P} = 3.5 Hz, C_5H_5); IR (Nujol) ν_{P-F} 850 cm^{-1}; MS *m/e* 354 (M^+), 266 ($Cp_2TiPF_3^+$), 247 ($Cp_2TiPF_2^+$), 197 (Cp_2TiF^+), 178 (Cp_2Ti^+).

An analytically pure sample of $Cp_2Ti(PF_3)_2$ was obtained by recrystallization of the product from hexane at −20 °C. Anal. Calcd for $C_{10}H_{10}F_6P_2Ti$: C, 33.93; H, 2.85. Found: C, 34.02; H, 2.74.

In a related experiment, the above reaction was run in the absence of light. After trifluorophosphine had been sparged through the solution for 90 min, a weak band at 1932 cm^{-1} assignable to $Cp_2Ti(CO)(PF_3)$ was observed in addition to strong bands due to $Cp_2Ti(CO)_2$. After 120 min, there was essentially no change in the IR spectrum of the reaction mixture.

Thermolysis of $Cp_2Ti(CO)_2$ and Trifluorophosphine. Attempts To Isolate $Cp_2Ti(CO)(PF_3)$. $Cp_2Ti(CO)_2$ (0.42 g, 1.80 mmol) and 15 mL of hexane were placed in a pressure-type Schlenk tube equipped with a Teflon-threaded cap. The tube was immersed in liquid nitrogen until the red solution had frozen. The space above the solid was then evacuated and an excess of trifluorophosphine was bled into the tube. After the vessel had been allowed to warm to room temperature, it was placed in an oil bath at 60 °C for 6 h. On cooling to room temperature, the red solution was filtered through a frit, and the filtrate cooled to −20 °C overnight, resulting in the precipitation of dark red crystals. An IR spectrum of this solid indicated it to be a mixture of $Cp_2Ti(CO)_2$ and $Cp_2Ti(CO)(PF_3)$. The solution was concentrated, ca. 0.50 g of 5% deactivated, degassed alumina was added, and the solution was taken to dryness. The coated alumina was then added to a dry-packed column (1 × 30 cm) of 5% deactivated, degassed alumina. Elution with hexane removed a red band, which was concentrated to dryness. IR and ^1H NMR spectra of the residue revealed it to be a mixture of $Cp_2Ti(CO)_2$ and $Cp_2Ti(CO)(PF_3)$; no separation had been achieved. Spectral data for $Cp_2Ti(CO)(PF_3)$: NMR (C_6D_6) δ 4.59 (d, J_{H-P} = 3.5 Hz, C_5H_5); IR (hexane) ν_{CO} 1932 cm^{-1}; MS, *m/e* 294 (M^+).

Preparation of $Cp_2Ti(CO)(PEt_3)$. A 100-mL, three-necked flask was fitted with a condenser and gas inlet valves. To the flask was added 1.03 g (4.40 mmol) of $Cp_2Ti(CO)_2$, 50 mL of hexane, and 1.2 mL (0.97 g, 8.21 mmol) of triethylphosphine. The stirred solution was then heated to reflux overnight. There was essentially no color change during this period. After cooling to room temperature, the solution was cooled to −20 °C overnight, resulting in brown-red crystals. The solution was decanted via a cannula. The crystals were washed several times with cold pentane and were dried under high vacuum to afford 0.86 g (60%) of $Cp_2Ti(CO)(PEt_3)$. IR and NMR spectra indicated that the crude product was contaminated with a small amount of $Cp_2Ti(CO)_2$. Three successive recrystallizations of the product from hexane at −20 °C afforded an analytically pure sample: NMR (C_6D_6) δ 4.75 (d, J_{H-P} = 1.5 Hz, 10 H, C_5H_5), 0.42–1.33 (m, 15 H, PEt_3); IR (hexane) ν_{CO} 1864 cm^{-1}. Anal. Calcd for $C_{17}H_{25}TiOP$: C, 62.97; H, 7.77. Found: C, 62.98; H, 7.75.

Photolysis of $Cp_2Ti(CO)_2$ and Triethylphosphine. A 28-mL heptane solution of $Cp_2Ti(CO)_2$ (0.14 g, 0.60 mmol) and triethylphosphine (0.81 g, 6.86 mmol) was photolyzed for a total of 160 min while argon was sparged through the solution via a syringe needle. The progress of the reaction was monitored via IR spectroscopy. At initiation, only bands due to $Cp_2Ti(CO)_2$ at 1977 and 1899 cm^{-1} were present; however, after photolysis for 10 min, a new, strong metal carbonyl band at 1864 cm^{-1} could be observed. After a 60-min photolysis period, this band, assignable to $Cp_2Ti(CO)(PEt_3)$, was the strongest absorption present. After 120 min, the IR spectrum showed little change, and bands due to $Cp_2Ti(CO)_2$ were still present. At this point, an additional 0.4 mL of triethylphosphine was added and the reaction mixture further irradiated. After 120 min, an IR spectrum of the solution showed essentially only $Cp_2Ti(CO)(PEt_3)$ to be present. When this same reaction was performed without the use of an argon sparge, no net reaction occurred.

Preparation of $Cp_2Ti(CO)(PPh_3)$. A 50-mL, 3-necked flask was fitted with a condenser and gas inlet valves. To the flask was added 0.83 g (3.55 mmol) of $Cp_2Ti(CO)_2$, 25 mL of hexane, and 1.40 g (5.34 mmol) of triphenylphosphine. The stirred solution was heated to reflux for 48 h, during which time the solution darkened and a red-brown precipitate formed. On cooling to room temperature, the solution was decanted, and the resulting solid was washed with hexane and subsequently dried under high vacuum. There remained 1.05 g (63%) of $Cp_2Ti(CO)(PPh_3)$, which by IR and ^1H NMR spectroscopy was shown to be contaminated with a small amount of $Cp_2Ti(CO)_2$. Attempts to remove $Cp_2Ti(CO)_2$ by additional washings with hexane failed to yield uncontaminated $Cp_2Ti(CO)(PPh_3)$: NMR (C_6D_6) δ 4.67 (br s, 10 H, C_5H_5); 7.0–8.0 (m, 15 H, PPh_3); IR (THF) ν_{CO} 1850 cm^{-1}.

Reaction of $Cp_2Ti(PF_3)_2$ with Carbon Monoxide. Carbon monoxide was gently sparged through a 12-mL hexane solution of $Cp_2Ti(PF_3)_2$ (0.10 g, 0.28 mmol) in a Schlenk tube by means of a syringe needle. The progress of the reaction was monitored by IR spectroscopy. After 10 min of CO sparging, metal carbonyl bands appeared at 1977 and 1899 cm^{-1}, assignable to $Cp_2Ti(CO)_2$, and at 1932 cm^{-1}, assignable to $Cp_2Ti(CO)(PF_3)$. As the exchange reaction progressed, the bands due to $Cp_2Ti(CO)_2$ grew in intensity, while the band due to $Cp_2Ti(CO)(PF_3)$ gradually diminished in intensity. After 90 min of CO sparging, the solution had turned red, and the IR spectrum indicated that $Cp_2Ti(CO)_2$ was the only metal carbonyl species present.

Reaction of $Cp_2Ti(CO)(PF_3)$ with Bis(pentafluorophenyl)acetylene. Into an NMR tube was placed $Cp_2Ti(CO)(PEt_3)$ (0.063 g, 0.194 mmol) and 0.6 mL of C_6D_6. An NMR spectrum was recorded and exhibited a doublet at δ 4.75 (J_{H-P} = 1.5 Hz). Trifluorophosphine was then gently bubbled through the solution via a syringe needle for 45 s. An NMR spectrum was recorded and now exhibited a new doublet at δ 4.59 (J_{H-P} = 3.5 Hz) assignable to $Cp_2Ti(CO)(PF_3)$. Bis(pentafluorophenyl)acetylene (0.10 g, 0.28 mmol) was added and the tube was shaken for 1 min, during which time the color of the solution lightened slightly. An NMR spectrum was again recorded and still exhibited a doublet due to $Cp_2Ti(CO)(PF_3)$; however, a weak singlet also appeared in the spectrum at δ 4.95, assignable to $Cp_2Ti(CO)(C_6F_5C{\equiv}CC_6F_5)$. A small amount of the reaction mixture was withdrawn from the tube and placed in an IR cell. The IR spectrum exhibited a metal carbonyl band at 1932 cm^{-1}, due to $Cp_2Ti(CO)(PF_3)$, but also a weak band at 2020 cm^{-1}, assignable to $Cp_2Ti(CO)(C_6F_5C{\equiv}CC_6F_5)$.

An analogous reaction between $Cp_2Ti(CO)(PF_3)$ and diphenylacetylene was attempted in C_6D_6. No NMR resonances or IR bands assignable to $Cp_2Ti(CO)(C_6H_5C{\equiv}CC_6H_5)$ were observable after a 1-min reaction period.

Reaction of $Cp_2Ti(CO)(PEt_3)$ with Carbon Monoxide. Carbon monoxide was gently bubbled through a 15-mL hexane solution of $Cp_2Ti(CO)(PEt_3)$ (0.23 g, 0.71 mmol) via a syringe needle for 1 min. An IR spectrum of the solution after reaction with CO exhibited only bands due to $Cp_2Ti(CO)_2$ in the metal carbonyl region and no band at 1864 cm^{-1} due to the starting material, $Cp_2Ti(CO)(PEt_3)$. The reaction mixture was then poured through a filter frit which contained a layer (1.0 × 1.5 cm) of 5% deactivated, degassed alumina. The red filtrate was evaporated to dryness, leaving 0.14 g (84%) of crystalline $Cp_2Ti(CO)_2$.

Reaction of $Cp_2Ti(CO)(PEt_3)$ with Trifluorophosphine. Trifluorophosphine was gently bubbled through a 15-mL solution of $Cp_2Ti(CO)(PEt_3)$ (0.27 g, 0.83 mmol) via a syringe needle for 45 s. The color of the solution changed from dark red to orange-red, and a small amount of green solid precipitated. The reaction mixture was filtered and the filtrate concentrated to dryness, leaving an oily residue. An IR spectrum of this product in hexane solution exhibited an intense metal carbonyl stretching frequency at 1932 cm^{-1} assignable to $Cp_2Ti(CO)(PF_3)$, and no trace of the frequency at 1864 cm^{-1} due to the starting material, $Cp_2Ti(CO)(PEt_3)$. An NMR spectrum of the product in C_6D_6 solution exhibited a doublet (J_{H-P} = 3.5 Hz) at δ 4.59 in the cyclopentadienyl region, assignable to $Cp_2Ti(CO)(PF_3)$. The doublet (J_{H-P} = 1.5 Hz) at δ 4.75 due to $Cp_2Ti(CO)(PEt_3)$ was completely absent. On the basis of these spectral results, the phosphine exchange reaction was essentially quantitative. However, attempts to prepare a high purity crystalline sample of $Cp_2Ti(CO)(PF_3)$ by either crystallization or sublimation techniques were not successful.

Preparation of $Cp_2Ti(CO)[P(OPh)_3]$. A 15-mL hexane solution of $Cp_2Ti(CO)(PEt_3)$ (0.13 g, 0.40 mmol) was filtered through a fit and subsequently treated with 0.50 mL of triphenyl phosphite (0.59 g, 1.90 mmol). The reaction mixture was then stirred at room temperature for 30 min and subsequently cooled to −20 °C for 1 day, at which time dark red crystals of $Cp_2Ti(CO)[P(OPh)_3]$ resulted. They were washed with two 3-mL portions of hexane and dried under high vacuum, leaving 0.14 g (68%) of product: NMR (C_6D_6) δ 4.72 (d, J_{H-P} = 2.5 Hz, 10 H, C_5H_5), 6.7–7.5 [m, 15 H, $P(OPh)_3$]; IR (hexane) ν_{CO} 1900 cm^{-1}; MS, m/e 516 (M^+).

Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compound	$Cp_2Ti(CO)(PEt_3)$ (2)	$Cp_2Ti(PF_3)_2$ (3)
M_r	324.3	354.0
space group	*Pbca*	*C2cm*
cell constant, *a*, Å	11.972 (5)	7.811 (4)
b, Å	16.977 (7)	13.724 (5)
c, Å	16.674 (7)	37.649 (11)
cell vol, $Å^3$	3389.0	4035.9
molecules/unit cell	8	12
ρ(calcd), g cm^{-1}	1.27	1.75
μ(calcd), cm^{-1}	6.12	9.56
radiation	Mo Kα	Mo Kα
max crystal dimensions, mm	0.25 × 0.75 × 1.75	0.52 × 0.24 × 0.10
scan width	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ
standard reflections	(600), (080), (008)	(008), (111)
decay of standards	±2%	+7%
reflections measured	3586	2019
2θ range	2–50°	2–50°
reflections collected	2111	1037
no. of parameters varied	181	264
GOF	0.76	0.45
R	0.044	0.038
R_w	0.046	0.037

Table IV. Final Fractional Coordinates for $Cp_2Ti(CO)(PEt_3)$ (2)

atom	*x/a*	*y/b*	*z/c*
Ti	0.46865 (6)	0.34946 (4)	0.39452 (4)
P	0.44391 (8)	0.19843 (6)	0.38632 (6)
O	0.5908 (3)	0.3378 (2)	0.5620 (2)
C(1)	0.5475 (3)	0.3382 (3)	0.5003 (3)
C(2)	0.2703 (3)	0.3331 (3)	0.4073 (3)
C(3)	0.3166 (4)	0.3480 (4)	0.4835 (3)
C(4)	0.3598 (5)	0.4235 (4)	0.4821 (4)
C(5)	0.3422 (4)	0.4559 (3)	0.4073 (5)
C(6)	0.2870 (4)	0.3981 (4)	0.3599 (3)
C(7)	0.6537 (3)	0.3293 (3)	0.3483 (3)
C(8)	0.6446 (4)	0.4090 (3)	0.3733 (3)
C(9)	0.5702 (5)	0.4471 (3)	0.3220 (3)
C(10)	0.5323 (5)	0.3907 (3)	0.2658 (3)
C(11)	0.5827 (4)	0.3193 (3)	0.2811 (3)
C(12)	0.5766 (4)	0.1431 (3)	0.3735 (3)
C(13)	0.5732 (5)	0.0552 (3)	0.3741 (4)
C(14)	0.3813 (4)	0.1491 (3)	0.4741 (2)
C(15)	0.4470 (4)	0.1549 (3)	0.5510 (3)
C(16)	0.3528 (4)	0.1527 (3)	0.3084 (3)
C(17)	0.3783 (4)	0.1758 (3)	0.2241 (3)
H(1)[C(2)]	0.2251	0.2810	0.3928
H(2)[C(3)]	0.3093	0.3062	0.5390
H(3)[C(4)]	0.3868	0.4632	0.5273
H(4)[C(5)]	0.3590	0.5136	0.3841
H(5)[C(6)]	0.2650	0.4062	0.3043
H(6)[C(7)]	0.7153	0.2784	0.3785
H(7)[C(8)]	0.6952	0.4410	0.4200
H(8)[C(9)]	0.5320	0.5070	0.3299
H(9)[C(10)]	0.4819	0.4080	0.2243
H(10)[C(11)]	0.5738	0.2654	0.2422
H(11)[C(12)]	0.6302	0.1675	0.4211
H(12)[C(12)]	0.6162	0.1620	0.3132
H(13)[C(13)]	0.6601	0.0274	0.3647
H(14)[C(13)]	0.5036	0.0268	0.3412
H(15)[C(13)]	0.5567	0.0264	0.4233
H(16)[C(14)]	0.3683	0.0949	0.4552
H(17)[C(14)]	0.3037	0.1802	0.4795
H(18)[C(15)]	0.5187	0.1299	0.5476
H(19)[C(15)]	0.4659	0.2113	0.5666
H(20)[C(15)]	0.4203	0.1279	0.5922
H(21)[C(16)]	0.3585	0.0918	0.3179
H(22)[C(16)]	0.2822	0.1678	0.3216
H(23)[C(17)]	0.3303	0.1474	0.1844
H(24)[C(17)]	0.3633	0.2338	0.2112
H(25)[C(17)]	0.4513	0.1640	0.2082

Preparation of $Cp_2Ti(CO)(C_6H_5C{\equiv}CC_6H_5)$. A 25-mL heptane solution of $Cp_2Ti(CO)(PEt_3)$ (0.28 g, 0.86 mmol) was filtered through a frit and then treated with powdered diphenylacetylene (0.17 g, 0.95

Table V. Anisotropic Thermal Parameters for Non-Hydrogen Atoms of $Cp_2Ti(CO)(PEt_3)$ (2)

atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti	0.00539 (5)	0.00293 (3)	0.00269 (2)	0.00018 (3)	−0.00029 (3)	−0.00020 (2)
P	0.00517 (7)	0.00311 (4)	0.00270 (4)	−0.00035 (4)	−0.00036 (5)	−0.00001 (3)
O	0.0078 (3)	0.0064 (2)	0.0033 (1)	−0.0007 (2)	−0.0014 (2)	−0.0001 (1)
C(1)	0.0051 (3)	0.0039 (2)	0.0033 (2)	−0.0002 (2)	0.0006 (2)	−0.0002 (1)
C(2)	0.0043 (3)	0.0046 (2)	0.0067 (3)	0.0005 (2)	0.0002 (2)	−0.0007 (2)
C(3)	0.0064 (4)	0.0081 (3)	0.0045 (2)	0.0022 (3)	0.0014 (2)	−0.0006 (2)
C(4)	0.0086 (5)	0.0074 (4)	0.0072 (3)	0.0038 (4)	−0.0017 (3)	−0.0043 (3)
C(5)	0.0081 (4)	0.0035 (2)	0.0110 (4)	0.0019 (3)	−0.0016 (4)	−0.0006 (3)
C(6)	0.0065 (4)	0.0056 (3)	0.0062 (3)	0.0020 (3)	−0.0023 (3)	−0.0000 (2)
C(7)	0.0059 (3)	0.0042 (2)	0.0042 (2)	−0.0010 (2)	0.0016 (2)	−0.0003 (2)
C(8)	0.0074 (4)	0.0038 (2)	0.0044 (2)	−0.0019 (2)	0.0010 (2)	0.0001 (2)
C(9)	0.0125 (5)	0.0035 (2)	0.0046 (2)	−0.0008 (3)	0.0009 (3)	0.0005 (2)
C(10)	0.0124 (5)	0.0053 (2)	0.0033 (2)	−0.0019 (3)	−0.0002 (3)	0.0012 (2)
C(11)	0.0102 (5)	0.0044 (2)	0.0033 (2)	−0.0019 (3)	0.0022 (2)	−0.0003 (2)
C(12)	0.0068 (3)	0.0034 (2)	0.0050 (2)	0.0006 (2)	−0.0007 (2)	−0.0003 (2)
C(13)	0.0108 (5)	0.0037 (2)	0.0104 (4)	0.0013 (3)	−0.0015 (4)	−0.0007 (3)
C(14)	0.0080 (4)	0.0043 (2)	0.0034 (2)	−0.0014 (2)	−0.0005 (2)	0.0007 (2)
C(15)	0.0120 (5)	0.0057 (2)	0.0035 (2)	−0.0013 (3)	−0.0010 (3)	0.0017 (2)
C(16)	0.0067 (4)	0.0044 (2)	0.0039 (2)	−0.0005 (2)	−0.0009 (2)	−0.0005 (2)
C(17)	0.0098 (5)	0.0062 (3)	0.0034 (2)	−0.0002 (3)	−0.0019 (2)	−0.0005 (2)

[a] β as defined in ref 2.

mmol). The reaction mixture was then swirled for ca. 5 min, during which time the diphenylacetylene dissolved and the solution changed from dark red to yellow-orange. On cooling the reaction mixture to −20 °C for 2 days, a yellow-brown powder precipitated from the solution. The solution was carefully decanted from the solid, and the latter was subsequently washed with two 2-mL portions of cold hexane and dried under high vacuum, leaving 0.31 g (91%) of $Cp_2Ti(CO)(C_6H_5C{\equiv}CC_6H_5)$: NMR ($C_6D_6$) δ 4.95 (s, 10 H, C_5H_5), 7.1 (m, 10 H, C_6H_5); IR (Nujol) ν_{CO} 1995 (s), $\nu_{C{\equiv}C}$ 1780 (s) cm^{-1}; IR (C_6D_6) ν_{CO} 2000 (s), $\nu_{C{\equiv}C}$ 1785 cm^{-1}.

Preparation of $Cp_2Ti(CO)(C_6F_5C{\equiv}CC_6F_5)$. A 20-mL heptane solution of $Cp_2Ti(CO)(PEt_3)$ (0.25 g, 0.77 mmol) was filtered through a frit and treated with powdered bis(pentafluorophenyl)acetylene (0.25 g, 0.70 mmol). The reaction mixture was then gently swirled, and a yellow-green solid began to precipitate from solution within 20 s. The mixture was further swirled for ca. 10 min to ensure complete dissolution of the acetylene. The solution was then carefully decanted from the precipitate and the latter washed with two 10-mL portions of hexane. After drying under high vacuum, 0.25 g (64%) of analytically pure product, $Cp_2Ti(CO)(C_6F_5C{\equiv}CC_6F_5)$, was obtained: NMR ($C_6D_6$) δ 4.95 (s, C_5H_5); IR (Nujol) ν_{CO} 2025 (s), $\nu_{C{\equiv}C}$ 1770 (s) cm^{-1}; IR (C_6D_6) ν_{CO} 2020 (s), $\nu_{C{\equiv}C}$ 1770 (s) cm^{-1}; MS, *m/e* 536 ($M{-}CO^+$). Anal. Calcd for $C_{25}H_{10}F_{10}OTi$: C, 53.22; H, 1.79. Found: C, 53.20; H, 1.80.

Preparation of $Cp_2Ti(CO)(CH_3O_2CCH{=}CHCO_2CH_3)$. $Cp_2Ti(CO)(PEt_3)$ (0.804 g, 2.48 mmol) was dissolved in 30 mL of toluene and the solution cooled to 0 °C. Dimethyl maleate (0.308 mL, 0.356 g, 2.48 mmol) was then added dropwise and the resulting solution stirred for 15 min, after which time the original dark red mixture had turned deep green. The product was precipitated by the addition of pentane that had been previously cooled to −78 °C. The mother liquor was removed via a cannula. The remaining green solid was washed 3 times with cold (−78 °C) pentane and dried under high vacuum at −10 °C to yield 0.565 g (65%) of $Cp_2Ti(CO)(CH_3O_2CCH{=}CHCO_2CH_3)$.

This product is very air sensitive as well as being thermally unstable. It slowly decomposes in the solid state under argon at 0 °C or above. An analytically pure sample was prepared in a small jacketed filter frit as described above, except that the reaction mixture was filtered through the frit before the green precipitate was washed and dried. Elemental analyses were carried out *immediately* after drying. The molecular weight of the olefin–titanium complex was determined cryoscopically in benzene according to a standard procedure.[48] by using a sample that had been freshly prepared in a tared freezing point tube equipped with an argon inlet. NMR, see below and Figure 1; IR (C_6D_6) ν_{CO} 2010, 1675 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_5Ti$: C, 58.30; H, 5.18; Ti, 13.58; M_r 350. Found: C, 58.55; H, 5.51; Ti, 13.71; M_r 348.

Hydrogen Chloride Degradation of $Cp_2Ti(CO)(CH_3O_2CCH{=}CHCO_2CH_3)$. To 0.508 g (1.45 mmol) of freshly prepared $Cp_2Ti(CO)(CH_3O_2CCH{=}CHCO_2CH_3)$ at 0 °C was added 20 mL of HCl-saturated toluene that had also been cooled to 0 °C. The reaction mixture immediately turned red, with formation of a red precipitate. Hydrogen chloride was then bubbled through the reaction mixture for 15 min. The solvent was removed under vacuum, and the resulting residue was suspended in ethyl ether, filtered, washed with ether, and dried under high vacuum to afford 0.350 g (97%) of Cp_2TiCl_2. The combined filtrate and washings were concentrated to ca. 10 mL, placed on a 1.5 × 8 cm

Table VI. Final Fractional Coordinates for $Cp_2Ti(PF_3)_2$ (3)

atom	*x/a*	*y/b*	*z/c*
Ti(1)	0.0000	0.9919 (2)	0.7500
Ti(2)	0.2151 (5)	0.3254 (1)	0.91486 (4)
P(1)	−0.0724 (9)	1.1574 (4)	0.7500
P(2)	0.2891 (8)	1.0389 (4)	0.7500
P(3)	0.0224 (6)	0.2830 (3)	0.95998 (8)
P(4)	−0.0237 (6)	0.3616 (3)	0.87951 (8)
F(1)	−0.256 (3)	1.195 (1)	0.7500
F(2)	−0.018 (2)	1.2249 (6)	0.7806 (2)
F(3)	0.442 (2)	0.966 (1)	0.7500
F(4)	0.365 (1)	1.0995 (8)	0.7807 (2)
F(5)	−0.114 (1)	0.2031 (7)	0.9543 (2)
F(6)	0.075 (1)	0.246 (1)	0.9976 (3)
F(7)	−0.102 (1)	0.3592 (7)	0.9756 (2)
F(8)	−0.011 (1)	0.4059 (7)	0.8411 (2)
F(9)	−0.162 (1)	0.4353 (7)	0.8921 (2)
F(10)	−0.150 (1)	0.2813 (7)	0.8683 (2)
C(1)	−0.029 (3)	0.865 (1)	0.7091 (4)
C(2)	−0.176 (2)	0.913 (1)	0.7088 (3)
C(3)	−0.149 (2)	1.007 (1)	0.6964 (4)
C(4)	0.029 (3)	1.015 (1)	0.6894 (3)
C(5)	0.100 (2)	0.924 (2)	0.6968 (4)
C(6)	0.168 (2)	0.4804 (9)	0.9380 (4)
C(7)	0.294 (2)	0.4333 (9)	0.9593 (3)
C(8)	0.435 (2)	0.4191 (9)	0.9384 (3)
C(9)	0.404 (2)	0.4561 (8)	0.9046 (3)
C(10)	0.241 (2)	0.4936 (9)	0.9047 (4)
C(11)	0.274 (2)	0.1603 (9)	0.9231 (4)
C(12)	0.428 (2)	0.203 (1)	0.9142 (4)
C(13)	0.411 (2)	0.238 (1)	0.8795 (4)
C(14)	0.251 (2)	0.2176 (9)	0.8676 (3)
C(15)	0.163 (2)	0.1691 (9)	0.8944 (4)
H(1)[C(1)]	0.0036	0.7929	0.7176
H(2)[C(2)]	−0.2890	0.8770	0.7179
H(3)[C(3)]	−0.2540	1.0516	0.6948
H(4)[C(4)]	0.0700	1.0792	0.6811
H(5)[C(5)]	0.2323	0.9115	0.6945
H(6)[C(6)]	0.0486	0.5026	0.9451
H(7)[C(7)]	0.2673	0.4120	0.9856
H(8)[C(8)]	0.5459	0.3910	0.9484
H(9)[C(9)]	0.4855	0.4555	0.8831
H(10)[C(10)]	0.1740	0.5294	0.8834
H(11)[C(11)]	0.2357	0.1265	0.9444
H(12)[C(12)]	0.5322	0.2044	0.9321
H(13)[C(13)]	0.5140	0.2765	0.8668
H(14)[C(14)]	0.2089	0.2350	0.8414
H(15)[C(15)]	0.0316	0.1437	0.8945

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(48) Shoemaker, B. P.; Garland, C. W.; Steinfeld, J. I. "Experiments in Physical Organic Chemistry", 3rd ed.; McGraw-Hill: New York, 1974; p 174.

Table VII. Anisotropic Thermal Parameters for Non-Hydrogen Atoms of $Cp_2Ti(PF_3)_2$ (3)

atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti(1)	0.0115 (5)	0.0051 (2)	0.00052 (2)	−0.0001 (3)	0.0000	0.0000
Ti(2)	0.0115 (3)	0.00372 (9)	0.00054 (1)	−0.0003 (2)	−0.00005 (8)	−0.00000 (4)
P(1)	0.029 (2)	0.0051 (4)	0.00138 (6)	0.0014 (6)	0.0000	0.0000
P(2)	0.015 (1)	0.0095 (4)	0.00104 (5)	−0.0024 (6)	0.0000	0.0000
P(3)	0.0195 (8)	0.0090 (3)	0.00075 (3)	−0.0004 (4)	0.0006 (1)	0.00046 (7)
P(4)	0.0132 (6)	0.0100 (3)	0.00077 (2)	−0.0002 (4)	−0.0004 (1)	0.00036 (7)
F(1)	0.046 (5)	0.010 (1)	0.0036 (2)	0.010 (2)	0.0000	0.0000
F(2)	0.074 (4)	0.0072 (5)	0.0024 (1)	−0.000 (2)	−0.0018 (8)	−0.0023 (2)
F(3)	0.018 (3)	0.017 (2)	0.0022 (2)	0.002 (2)	0.0000	0.0000
F(4)	0.026 (2)	0.021 (1)	0.0017 (1)	−0.012 (1)	−0.0007 (4)	−0.0021 (3)
F(5)	0.038 (2)	0.0159 (9)	0.00150 (9)	−0.012 (1)	0.0035 (4)	−0.0001 (2)
F(6)	0.034 (2)	0.030 (1)	0.00115 (7)	0.001 (2)	0.0017 (5)	0.0034 (3)
F(7)	0.039 (3)	0.017 (1)	0.00155 (9)	0.003 (1)	0.0042 (4)	−0.0000 (2)
F(8)	0.024 (2)	0.027 (1)	0.00107 (7)	−0.003 (1)	−0.0020 (4)	0.0029 (2)
F(9)	0.025 (2)	0.019 (1)	0.00141 (9)	0.011 (1)	−0.0010 (4)	0.0002 (2)
F(10)	0.026 (2)	0.0170 (9)	0.0019 (1)	−0.008 (1)	−0.0037 (4)	0.0004 (3)
C(1)	0.028 (4)	0.008 (1)	0.0011 (1)	0.002 (2)	−0.0012 (7)	−0.0014 (3)
C(2)	0.020 (3)	0.011 (1)	0.0006 (1)	−0.005 (2)	−0.0006 (5)	−0.0005 (3)
C(3)	0.029 (4)	0.010 (1)	0.0009 (1)	0.004 (2)	−0.0027 (6)	−0.0001 (4)
C(4)	0.059 (7)	0.012 (2)	0.00040 (9)	−0.012 (3)	−0.0010 (8)	0.0005 (3)
C(5)	0.024 (4)	0.016 (2)	0.0007 (1)	−0.001 (2)	0.0004 (6)	−0.0013 (4)
C(6)	0.025 (4)	0.0050 (9)	0.0014 (2)	0.001 (1)	0.0004 (7)	−0.0007 (3)
C(7)	0.034 (4)	0.0059 (9)	0.0007 (1)	−0.001 (2)	−0.0001 (6)	−0.0003 (3)
C(8)	0.019 (3)	0.0064 (9)	0.0010 (1)	−0.003 (1)	−0.0008 (6)	−0.0005 (3)
C(9)	0.025 (3)	0.0052 (8)	0.0007 (1)	−0.005 (1)	0.0005 (5)	−0.0000 (2)
C(10)	0.018 (3)	0.0056 (8)	0.0012 (1)	0.000 (1)	−0.0001 (6)	0.0003 (3)
C(11)	0.030 (4)	0.005 (1)	0.0015 (2)	0.001 (2)	0.0010 (7)	0.0004 (3)
C(12)	0.025 (3)	0.007 (1)	0.0011 (1)	0.007 (2)	−0.0016 (6)	−0.0005 (3)
C(13)	0.022 (3)	0.007 (1)	0.0011 (1)	0.001 (1)	0.0005 (6)	−0.0011 (3)
C(14)	0.024 (3)	0.0069 (9)	0.0006 (1)	−0.000 (2)	0.0004 (5)	−0.0005 (2)
C(15)	0.025 (4)	0.0043 (9)	0.0017 (2)	−0.002 (2)	0.0003 (8)	−0.0015 (4)

[a] β as defined in ref 2.

column of alumina, and eluted with ethyl ether. Removal of the solvent produced 0.127 g (60%) of dimethyl succinate, which was identified by a comparison of its IR and ^1H NMR spectra with those of an authentic sample (Eastman).

Oxidative Degradation of $Cp_2Ti(CO)(CH_3O_2CCH{=}CHCO_2CH_3)$. Cold, dry air was prepared by passing air through concentrated H_2SO_4, then through molecular sieves, and finally through a stainless steel coil immersed in a dry ice–acetone bath at −78 °C. The air was then bubbled through a solution of 0.550 g (1.60 mmol) of $Cp_2Ti(CO)(CH_3O_2CCH{=}CHCO_2CH_3)$ in 25 mL of toluene, prepared as above and cooled to 0 °C. After 60 min, the reaction mixture was yellow-brown with the formation of a yellow precipitate. The solvent was removed under vacuum, and the residue was extracted with ethyl ether and filtered through a pad of Celite. Removal of the solvent produced 0.225 g (98%) of dimethyl fumarate. The product was identified by comparison of its IR and ^1H NMR spectra with those of an authentic sample (Eastman).

Variable-Temperature ^1H NMR Experiments: Reaction of $Cp_2Ti(CO)(PEt_3)$ with Excess Dimethyl Maleate. In a typical experiment, 74.2 mg (0.229 mmol) of $Cp_2Ti(CO)(PEt_3)$ was added to an NMR tube, dissolved in ca. 0.25 mL of toluene-d_8, and cooled to 0 °C. Dimethyl maleate (39 μL, 46 mg, 0.32 mmol) was dissolved in ca. 0.25 mL of toluene-d_8 in a small Schlenk tube and similarly cooled to 0 °C. The dimethyl maleate solution was then added via a syringe to the phosphine complex and thoroughly mixed. The originally dark maroon solution turned dark green. The ^1H NMR spectra were recorded immediately at various temperatures. ^1H NMR at −5 °C (peaks assignable to the olefin–titanium complex) δ 4.95 (s, 5 H, C_5H_5), 4.75 (s, 5 H, C_5H_5), 3.58 (s, 3 H, OCH_3), 3.52 (s, 3 H, OCH_3), 2.99 (d, J = 1 H, CH), 2.71 (d, J = 11 Hz, 1 H, CH). For ^1H NMR spectra recorded at other temperatures and times, see Figure 1.

Reaction of $Cp_2Ti(CO)(PEt_3)$ with Dimethyl Fumarate. Equimolar amounts of the phosphine complex and dimethyl fumarate were used to prepare $Cp_2Ti(CO)(CH_3O_2CCH{=}CHCO_2CH_3)$ as described above. The ^1H NMR spectrum of the resulting reaction mixture was identical with that obtained by using dimethyl maleate in place of dimethyl fumarate.

Reaction of $Cp_2Ti(CO)(PEt_3)$ with Diethyl Fumarate. An NMR sample was prepared as described above by using equimolar amounts of diethyl fumarate and the phosphine complex. ^1H NMR at 0 °C (peaks assignable to the olefin–titanium complex) δ 4.95 (s, 5 H, C_5H_5), 4.76 (s, 5 H, C_5H_5), 4.14 (br s, 2 H, OCH_2), 4.04 (br s, 2 H, OCH_2), 3.00 (d, J = 11 Hz, 1 H, CH), 2.72 (d, J = 11 Hz, 1 H, CH). Peaks due to the methyl substituents could not be clearly assigned, since they were masked by the resonance due to triethylphosphine protons.

X-ray Data Collection, Structure Determination, and Refinement for $Cp_2Ti(CO)(PEt_3)$ (2). Single crystals of the air-sensitive compound, grown by crystallization from pentane, were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($2\theta > 40°$) accurately centered on the diffractometer are given in Table III. The space group was uniquely determined as *Pbca* from systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. The method has been previously described.[49] A summary of the data collection parameters is given in Table III. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[50] Neutral atom scattering factors for Ti, P, O, and C were taken from Cromer and Waber,[51] and the scattering for titanium was corrected for real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[52] Scattering factors for H were from reference 53.

The position of the titanium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the titanium atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.079$. The hydrogen atoms of the cyclopentadienyl rings were placed at calculated positions 1.08 Å from the bonded carbon atom and were not refined. The ethyl hydrogen atoms were located with the aid of a difference Fourier map and were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.044$ and $R_w = 0.046$. A final difference Fourier showed no feature greater than 0.3 e⁻/Å³. The weighting scheme was based on unit weights; no systematic variation of $|F_o| - |F_c|$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Tables IV and V.[54]

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X-ray Data Collection, Structure Determination, and Refinement for $Cp_2Ti(PF_3)_2$ (3). Single crystals of the compound, grown by slow vacuum sublimation, were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta >$ 40°) accurately centered on the diffractometer are given in Table III. Systematic absences allowed a space group choice of *C2cm*, *Cmc*2, and *Cmcm*. Successful solution and refinement of the structure indicated the correct choice to be the noncentrosymmetric *C2cm*.

Data were collected as described for the previous compound. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Neutral-atom scattering factors were obtained as noted above, and that of titanium was corrected for the real and imaginary components of anomalous dispersion.

The positions of the two independent titanium atoms were revealed by the inspection of a Patterson map, and the subsequent calculation of a difference Fourier map allowed the location of the remaining non-hydrogen atoms. Refinement with isotropic thermal parameters led to a reliability index of $R = 0.081$. The hydrogen atoms of the cyclopentadienyl rings were placed at calculated positions 1.08 Å from the bonded carbon atom and were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.038$ and $R_w = 0.037$. A final difference Fourier showed no feature greater than $0.3\ e^-/\text{Å}^3$. The weighting scheme was based on unit weights; no systematic variation of $|F_o| - |F_c|$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Tables VI and VII.[54]

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Supplementary Material Available: Tables of best planes results, and observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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[54] See paragraph at the end of paper regarding supplementary material.

Ab Initio Electronic Structures and Reactivities of Metal Carbene Complexes; Fischer-Type Compounds $(CO)_5Cr{=}CH(OH)$ and $(CO)_4Fe{=}CH(OH)$

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Abstract: Electronic structures and reactivities of the chromium and iron carbene complexes $(CO)_5Cr{=}CH(OH)$ and $(CO)_4Fe{=}CH(OH)$ are studied by the ab initio SCF MO method, and the nature of the double bond between the metal and carbene carbon atom, $M{=}C_{carb}$, is investigated. The equilibrium $M{=}C_{carb}$ length is calculated to be 2.00 Å for both Cr and Fe carbene complexes, in reasonable agreement with the experimental value 2.04 Å. The $M{=}C_{carb}$ bond energy is calculated to be 44.4 kcal/mol and 36.8 kcal/mol for the Cr and Fe carbenes, respectively. For the Fe carbene, the axial isomer is calculated to be more stable than the equatorial isomer by 8.1 kcal/mol. The barrier to rotation around the $M{=}C_{carb}$ bond is calculated to be very small (0.41 kcal/mol for $Cr{=}C_{carb}$ and 2.9 kcal/mol for $Fe{=}C_{carb}$), showing that the rotation is essentially free. This is in contrast to a large barrier of the C=C double bond in ethylene. The origins of the $M{=}C_{carb}$ double bond and of the smallness of the rotational barriers are clarified from the diagram of orbital correlation with the fragment orbitals. The differences in the natures of the $M{-}C_{carb}$ and M–CO bonds are clarified. The polarization of charge of the $M{=}C_{carb}$ bond is calculated to be $M^{\delta+}{-}C_{carb}{}^{\delta-}$ for both the Cr and Fe carbenes: the carbene carbon is calculated to be negatively charged in contradiction with the commonly accepted idea, though the electron is deficient in the π region of the carbene carbon atom. The electrophilic reactivity of the carbene carbon is not charge controlled, but is controlled by the frontier orbital, LUMO.

Metal carbene complexes, first synthesized by Fischer and co-workers,[2] are of remarkable importance as intermediates of many organometallic reactions[2-4] such as olefin metathesis[5] catalytic reduction of CO by H_2,[6] Ziegler–Natta polymerization reaction,[5,7] etc. The nature of the metal–carbon double bond involved is also of special interest as one of the typical bonding modes in organometallic chemistry. The varieties of geometries and spectroscopic properties are also of interest. In this series of papers, we study electronic structures and reactivities of metal carbene complexes. We are interested in the nature of the $M{=}C_{carb}$ bond, the origin of the reactivity of the carbene complexes, and their differences due to the difference in metal species. We report here the results of ab initio SCF MO calculations on the chromium and iron carbene complexes, $(CO)_5Cr{=}CH(OH)$ and

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