Formation of [(Diphenylphosphino)cyclopentadienyl]thallium and Its Utility in the Synthesis of Heterobimetallic Ti–Mn Complexes: The Molecular Structure of (η^5-Cyclopentadienyl)dicarbonyl{(η^5-cyclopentadienyl)[η^5-(diphenylphosphino)cyclopentadienyl]dichlorotitanium-*P*}manganese

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Abstract: A reaction between $(C_5H_5)P(C_6H_5)_2$ and TlOEt in ethyl ether produces $[C_5H_4P(C_6H_5)_2]Tl$ in quantitative yield. Treatment of $(\eta^5\text{-}C_5H_5)TiCl_3$ with $[C_5H_4P(C_6H_5)_2]Tl$ affords $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]TiCl_2$ in 95% yield. Reductive carbonylation of the latter complex yields $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]Ti(CO)_2$. Both of these phosphine-substituted titanocene derivatives react with $(\eta^5\text{-}C_5H_5)(CO)_2(THF)Mn$ to generate the respective bimetallic complexes $(\eta^5\text{-}C_5H_5)(CO)_2\{(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]TiCl_2\}Mn$ and $(\eta^5\text{-}C_5H_5)(CO)_2\{(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]Ti(CO)_2\}Mn$ in good yield. In the presence of air, the latter complex undergoes facile decomposition to yield $(\eta^5\text{-}C_5H_5)Mn(CO)_2[(C_5H_5)(C_6H_5)_2P]$. The crystal and molecular structure of the bimetallic complex $(\eta^5\text{-}C_5H_5)(CO)_2\{(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]TiCl_2\}Mn$ has been determined by X-ray diffraction methods.

Introduction

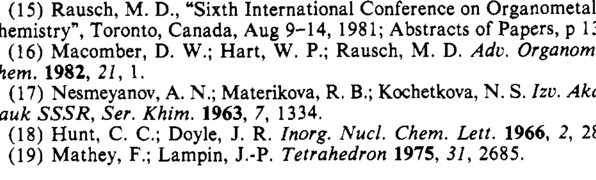
The cyclopentadienyl moiety and trisubstituted phosphines, together with carbon monoxide, constitute the most versatile ligands in organotransition-metal chemistry. Whereas the utility of chelating diphosphine ligands such as 1,2-bis(diphenylphosphino)ethane (diphos), 1,2-bis(dimethylphosphino)ethane (dmpe), and related systems are well-known in organometallic chemistry[2] and routes to bridged cyclopentadienyl anions (e.g., the fulvalene dianion) have also been developed,[3] intermediates which incorporate both a trisubstituted phosphine and a cyclopentadienyl substituent have received comparatively little attention.[4-6] Intermediates of this type could be utilized in the formation of bimetallic compounds, which in turn might prove useful in probing chemical reactions between two different metal centers which are not directly bonded to each other.[5] Chemical processes involving two or more organometallic units in combination with one another are becoming of increasing importance.[7-12]

In connection with our current research program concerning functionally substituted cyclopentadienylmetal compounds,[13-16] we have developed a high-yield route to the new heterodifunctional organometallic reagent [(diphenylphosphino)cyclopentadienyl]thallium (**2**). In this article, the utility of **2** in the formation of several new mixed titanium–manganese organometallic complexes is demonstrated. In addition, the molecular structure of one of these products, (η^5-cyclopentadienyl)dicarbonyl{(η^5-cyclopentadienyl)[η^5-(diphenylphosphino)cyclopetadienyl]dichlorotitanium-*P*}manganese (**6**), has been elucidated by means of single-crystal X-ray diffraction methods.

Results and Discussion

Cyclopentadienylthallium has played an important role in the development of cyclopentadienylmetal chemistry, since it is readily formed in quantitative yield, is relatively stable, is highly reactive with metal halides, and is therefore a convenient source of the cyclopentadienyl ligand.[14,17,18] We have recently shown that the (halocyclopentadienyl)thallium compounds $(C_5H_4X)Tl$ (X = Cl, Br, I) can readily be formed in high yield from reactions of the respective halocyclopentadienes and thallium ethoxide in ethyl ether solution.[14,15] It was therefore of interest to ascertain if this approach could likewise be applied to the metalation of 1-(diphenylphosphino)cyclopentadiene (**1**).[19]

Treatment of an ethyl ether solution of **1** with thallium ethoxide leads to the precipitation of [(diphenylphosphino)cyclopentadienyl]thallium (**2**) in quantitative yield. The product, a



1 **2**

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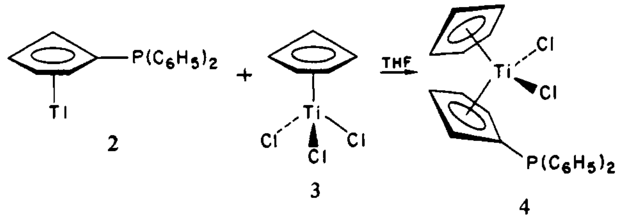
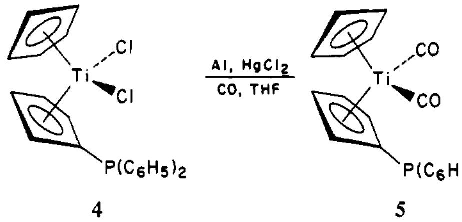
moderately air-stable white solid, was characterized by elemental analyses and by its ^{1}H NMR spectrum. Compound **2** can be purified by vacuum sublimation; however, considerable decomposition occurs during this process. As in the case of cyclopentadienylthallium, the original reaction product is sufficiently pure for further synthetic purposes.

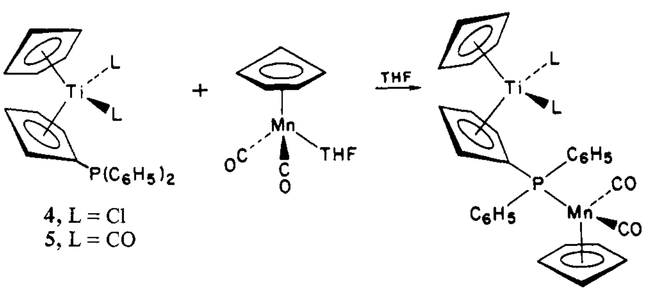
A reaction between thallium reagent **2** and (η^5-cyclopentadienyl)trichlorotitanium (**3**) produces (η^5-cyclopentadienyl)[η^5-(diphenylphosphino)cyclopentadienyl]dichlorotitanium (**4**) in 95% yield. Orange crystalline **4** is air-stable, soluble in tetrahydrofuran, chloroform, and methylene chloride, and insoluble in non-polar solvents. Elemental analyses and the ^{1}H NMR spectrum of **4** are in accordance with the proposed structure.



Using a method analogous to that employed for the reductive carbonylation of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$,[20] **4** was converted to (η^5-cyclopentadienyl)[η^5-(diphenylphosphino)cyclopentadienyl]dicarbonyltitanium (**5**) in 25% yield. Compound **5** is air and moisture sensitive and thermally decomposes at ca. 106 °C. The IR spectrum of **5** in THF displays metal carbonyl frequencies at 1960 and 1880 cm^{-1}. These absorptions are very similar to those observed for $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, which occur at 1965 and 1883 cm^{-1} in the same solvent.[21] These results indicate that the presence of the phosphine substituent does not significantly perturb the electronic environment about the titanium atom in **5**.



Both **4** and **5** can be coordinated through the unshared electron pairs on phosphorus to a second metal, demonstrating the utility of the (diphenylphosphino)cyclopentadienyl moiety as a heterodifunctional ligand capable of incorporating two different transition metals into a single molecule. Thus, reactions of either **4** or **5** with $(\eta^5\text{-}C_5H_5)(CO)_2(THF)Mn$ yielded the respective (dichlorotitanium)manganese complex (**6**) (77%) or the (dicarbonyltitanium)manganese complex (**7**) (39%).



4, L = Cl
5, L = CO

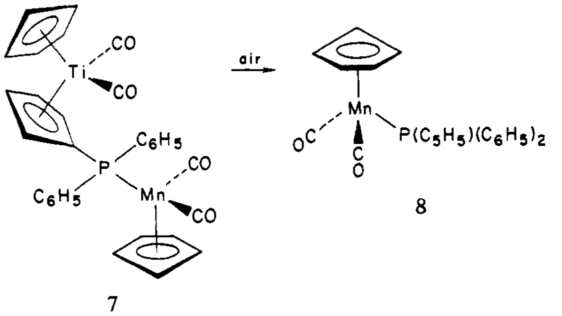
6, L = Cl
7, L = CO

The structural features of **6** and **7** have been confirmed by their ^{1}H NMR and IR spectra. The ^{1}H NMR spectrum of **6** in CD_2Cl_2 displays resonances at δ 7.32–7.72, assignable to the phenyl protons, at δ 6.92–7.10 and 6.49–6.74, assignable to the phosphine-substituted cyclopentadienyl ring protons, at δ 6.21, assignable to the titanium-complexed unsubstituted cyclopentadienyl ring protons, and at δ 4.36, assignable to the protons of the manganese-complexed cyclopentadienyl ring. A similar spectrum of **7** in C_6D_6 shows resonances at δ 7.20–7.68 and 6.83–7.11, assignable to protons of the phenyl groups, at δ 4.67–5.08, assignable to the phosphine-substituted cyclopentadienyl ring protons, at δ 4.46, assignable to the protons of the titanium-complexed unsubstituted cyclopentadienyl ring, and at δ 3.97, assignable to the manganese-complexed cyclopentadienyl ring protons. The splitting of the manganese-complexed cyclopentadienyl ring resonances of **6** and **7** into doublets ($J_{P\text{-}H}$ = 2.5 and 1.7 Hz, respectively) is consistent with the coordination of a phosphine ligand to the $(\eta^5\text{-}C_5H_5)(CO)_2Mn$ moiety.

The IR spectrum for **6** in CH_2Cl_2 exhibits two carbonyl stretching bands at 1920 and 1855 cm^{-1}, as anticipated for such a manganese dicarbonyl derivative. On the basis of these absorptions and those of **5**, the following assignments can be made for the four carbonyl stretching bands observed for a benzene solution of **7**. The absorptions at 1960 and 1880 cm^{-1} correspond to the two carbonyl ligands of titanium, and the bands at 1930 and 1860 cm^{-1} correspond to the two carbonyl ligands of manganese. It should also be noted that the carbonyl stretching bands for the manganese portions of compounds **6** and **7** are very similar to those observed for a chloroform solution of $(\eta^5\text{-}C_5H_5)(CO)_2[P(C_6H_5)_3]Mn$, which occur at 1934 and 1862 cm^{-1}.[22]

Compound **6** is an air-stable, deep-purple crystalline solid which is soluble in tetrahydrofuran, methylene chloride, and chloroform, moderately soluble in acetone, and insoluble in ethyl ether and nonpolar solvents like hexane. Solutions of **6** slowly decompose when exposed to air. Compound **7** is an air-sensitive, brown crystalline solid, which is soluble in aromatic solvents, methylene chloride, and chloroform and sparingly soluble in hexane and pentane.

Solutions of **7** are rapidly decomposed on exposure to air, leading to the formation of $(\eta^5\text{-}C_5H_5)(CO)_2[(C_5H_5)(C_6H_5)_2P]Mn$ (**8**). Compound **8** was identified by a comparison of its melting point and ^{1}H NMR and IR spectra with those of an authentic sample prepared independently from $(\eta^5\text{-}C_5H_5)(CO)_2(THF)Mn$ and **1**. Compound **8** is an air-stable, yellow crystalline solid which is soluble in aromatic solvents, ethyl ether, and tetrahydrofuran and insoluble in nonpolar solvents such as hexane. Solutions of **8** are slowly decomposed upon exposure to air.



The IR spectrum of **8** in CH_2Cl_2 exhibits two carbonyl stretching frequencies at 1920 and 1850 cm^{-1}. The ^{1}H NMR spectrum of **8** in CD_2Cl_2 solution exhibits resonances at δ 7.25–7.32, assignable to the phenyl protons, at δ 6.41–7.00, assignable to the vinyl protons of the cyclopentadienyl group, at δ 4.37, assignable to the protons of the η^5-cyclopentadienyl ligand, and at δ 3.21 and 3.02, assignable to the methylene protons of the cyclopentadienyl group. The η^5-cyclopentadienyl resonance appears as a multiplet rather than a doublet as might be anticipated from hydrogen–phosphorus spin–spin coupling. The reason for this result is not completely clear at the present time. Although such a splitting pattern could possibly be explained by the existence

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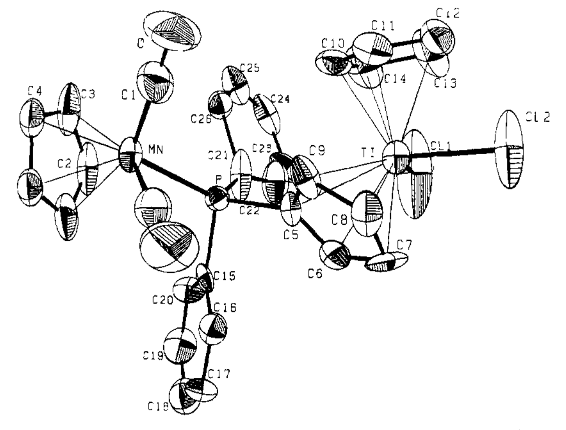

Figure 1. Molecular structure and atom numbering scheme for **6** with the atoms represented by their 50% probability ellipsoids for thermal motion.

of different cyclopentadienyl–phosphine isomers, the free phosphine **1** is believed to exist as the 1-isomer, inferring that the complexed phosphine ligand in **8** also exists as the 1-isomer. Further studies to elucidate the nature of the NMR spectra of **8** are in progress.

In order to obtain further structural information on these bimetallic complexes, a single-crystal X-ray diffraction study of **6** was undertaken. The result, shown in Figure 1, fully verifies the structure expected on the basis of the spectroscopic investigations. Unfortunately, the crystallographic disorder has precluded a detailed discussion of the bonding parameters in the molecule.

Experimental Section

All reactions, manipulations, and crystallizations were conducted under an atmosphere of dry argon, using standard Schlenk tube and cannula techniques. Hexane, benzene, and methylene chloride were dried over CaH_2 and freshly distilled from CaH_2 under argon before use. Ethyl ether and tetrahydrofuran (THF) were predried over sodium and subsequently distilled under argon from sodium–benzophenone. CAMAG neutral-grade alumina was deactivated with 5% by weight argon-saturated water before use. ^1H NMR spectra were recorded on a Varian A-60 spectrometer. IR spectra were obtained on a Perkin-Elmer 237-B spectrometer and were calibrated vs. polystyrene. Mass spectra were obtained on a Perkin-Elmer-Hitachi RMU-6L instrument at 70 eV. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Cyclopentadienylthallium[18] and η^5-cyclopentadienyltrichlorotitanium[23,24] were prepared according to literature methods. (η^5-Cyclopentadienyl)tricarbonylmanganese was generously donated by the Ethyl Corp. Thallium ethoxide and chlorodiphenylphosphine were obtained from Ventron-Alfa, and the latter was distilled prior to use.

Preparation of [(Diphenylphosphino)cyclopentadienyl]thallium. With use of the method of Mathey and Lampin,[19] 1-(diphenylphosphino)cyclopentadiene was prepared in situ by adding 11.9 g (9.67 mL, 53.9 mmol) of chlorodiphenylphosphine to a stirred suspension of 14.5 g (53.8 mmol) of cyclopentadienylthallium in 100 mL of ethyl ether. The mixture was stirred for 1 h, and the precipitated thallium chloride was filtered by means of a frit. The filtrate was then treated dropwise with 13.4 g (3.81 mL, 53.7 mmol) of thallium ethoxide, immediately producing a white precipitate. In order to ensure complete reaction, the mixture was stirred for 1 h. The white precipitate was allowed to settle out and the mother liquor decanted. The product was washed several times with ethyl ether and then dried under high vacuum, producing 23.9 g (98%) of white $[C_5H_4P(C_6H_5)_2]Tl$. This material is of sufficient purity for further synthetic purposes. Analytically pure material was obtained by sublimation at 120 °C (10^{-3} mmHg) for 30–40 h: ^1H NMR $[(CD_3)_2SO]$ δ 7.24–7.36 (m, 10 H, C_6H_5), 5.91–6.01 (m, 4 H, C_5H_4). Anal. Calcd for $C_{17}H_{14}PTl$: C, 45.01; H, 3.11; P, 6.83. Found: C, 44.87; H, 2.95; P, 6.71.

Preparation of (η^5-Cyclopentadienyl)[η^5-(diphenylphosphino)cyclopentadienyl]dichlorotitanium. A 500-mL Schlenk flask was charged with 7.19 g (32.8 mmol) of $(\eta^5\text{-}C_5H_5)TiCl_3$, 15.85 g (34.9 mmol) of $[C_5H_4P(C_6H_5)_2]Tl$, and 250 mL of tetrahydrofuran. The resulting mixture was stirred overnight, during which time it turned dark red with the formation of a fine white precipitate. The reaction mixture was filtered through a plug of Celite contained on a frit, and the solvent was removed from the filtrate under reduced pressure. The residue was dried under high vacuum for several hours, then dissolved in a minimum amount of methylene chloride, and filtered as above. The solvent was evaporated via a water aspirator and the resulting dark greenish red solid further dried under high vacuum. The solid was then washed with hexane until a homogeneous orange powder was obtained. The product was dried under high vacuum for several hours, yielding 13.46 g (95%) of relatively pure, air-stable $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]TiCl_2$. Analytically pure material was obtained by dissolving a sample of the product in methylene chloride and adding hexane until either the solution became cloudy or until an equal volume of hexane had been introduced. In the latter case, the more volatile methylene chloride was evaporated with a water aspirator until the mixture became cloudy. The solution was then placed in a freezer (−20 °C) overnight, producing dark greenish red crystals. The mother liquor was decanted and the product washed as above with hexane and dried for several hours under high vacuum, producing orange crystals: mp 130–132 °C; ^1H NMR ($CDCl_3$) δ 7.42 (m, 10 H, C_6H_5), 6.68 (m, 4 H, C_5H_4), 6.51 (s, 5 H, C_5H_5). Anal. Calcd for $C_{22}H_{19}Cl_2PTi$: C, 61.00; H, 4.42. Found: C, 60.81; H, 4.70.

Preparation of (η^5-Cyclopentadienyl)[η^5-(diphenylphosphino)cyclopentadienyl]dicarbonyltitanium. Into a 200-mL Schlenk flask was added 3.50 g (8.08 mmol) of $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]TiCl_2$, 0.732 g (27.1 mmol) of aluminum turnings, and 1.46 g (5.38 mmol) of mercuric chloride. The flask was then flushed with carbon monoxide for several minutes followed by the addition of 100 mL of tetrahydrofuran. The reaction vessel was fitted with a gas outlet valve connected to a mercury overpressure valve and the mixture stirred overnight while a gentle stream of carbon monoxide was passed over the solution. The reaction mixture changed from red-brown to purple. The solution was filtered through a plug (3 × 7 cm) of alumina on a jacketed frit which had been cooled to 0 °C. The solvent was then removed from the red-brown filtrate under vacuum and the resulting residue dissolved in a minimum amount of 4/1 hexane/ether and filtered as above. Evaporation of the solvent from the filtrate under vacuum yielded 0.841 g (35%) of $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]Ti(CO)_2$. An analytically pure sample was obtained by recrystallization from hexane/ether at −20 °C: mp 106 °C dec; ^1H NMR (CD_2Cl_2) δ 7.39 (m, 10 H, C_6H_5), 5.12–5.30 and 4.77–4.91 (m, 4 H, C_5H_4), 4.72 (s, 5 H, C_5H_5); IR (THF) ν_{CO} 1960, 1880 cm^{-1}. Anal. Calcd for $C_{24}H_{19}O_2PTi$: C, 68.92; H, 4.58. Found: C, 69.25; H, 4.74.

Preparation of (η^5-Cyclopentadienyl)dicarbonyl{(η^5-cyclopentadienyl)[η^5-(diphenylphosphino)cyclopentadienyl)dichlorotitanium-*P*}manganese. A solution of $(\eta^5\text{-}C_5H_5)(CO)_2(THF)Mn$ was prepared by photolyzing 1.01 g (4.95 mmol) of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ in 250 mL of tetrahydrofuran in an immersion well as 15 °C for 4 h while stirring. The solution was transferred via a cannula to a Schlenk tube containing 1.82 g (4.21 mmol) of $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]TiCl_2$ and the resulting mixture stirred overnight. The solvent was removed under reduced pressure and the residue washed with hexane, dissolved in methylene chloride, and filtered through a plug of Celite. The filtrate was concentrated to ca. 20 mL, and an equal volume of hexane was carefully layered on top of the methylene chloride by cannula. The Schlenk tube was left undisturbed for 36–72 h, during which time dark red crystals had formed. The mother liquor was decanted and the product washed several times with hexane. The solid was recrystallized a second time as described above. The hexane-washed crystals were then rinsed 3–4 times with acetone and dried for several hours under high vacuum, yielding 1.97 g (77%) of deep purple, analytically pure $(\eta^5\text{-}C_5H_5)(CO)_2\{(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]TiCl_2\}Mn$: mp 165 °C dec; ^1H NMR (CD_2Cl_2) δ 7.32–7.72 (m, 10 H, C_6H_5), 6.92–7.10 and 6.49–6.74 (m, 4 H, C_5H_4), 6.21 (s, 5 H, C_5H_5), 4.36 (d, J_{P-H} = 2.5 Hz, 5 H, C_5H_5); IR (CH_2Cl_2) ν_{CO} 1920, 1855 cm^{-1}. Anal. Calcd for $C_{29}H_{24}Cl_2MnO_2PTi$: C, 57.17; H, 3.97. Found: C, 56.89; H, 4.04.

Preparation of (η^5-Cyclopentadienyl)dicarbonyl{(η^5-cyclopentadienyl)[η^5-(diphenylphosphino)cyclopentadienyl]dicarbonyltitanium-*P*}manganese. A solution of $(\eta^5\text{-}C_5H_5)(CO)_2(THF)Mn$ was prepared by photolyzing 0.500 g (2.46 mmol) of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ in 200 mL of tetrahydrofuran in an immersion well as 15 °C while stirring. The solution was transferred via a cannula to a Schlenk tube containing 0.722 g (1.72 mmol) of $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]Ti(CO)_2$ and the resulting mixture stirred overnight. Approximately 2 g of alumina was added and the solvent removed under reduced pressure. The resulting residue was placed on an alumina column (2 × 36 cm). Elution with hexane produced a rapidly moving yellow band which was collected, and the solvent was evaporated under vacuum to give 0.013 g of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$. Continued elution with 5/1 hexane/benzene developed a brown band which was collected and the solvent removed under reduced pressure, leaving 0.036 g of $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]Ti(CO)_2$. Further elution with 1/1 hexane/benzene produced a faint yellow band which was col-

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

compd	$(\eta^5\text{-}C_5H_5)(CO)_2\{(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]TiCl_2\}Mn$ (6)
mol wt	609.2
space group	*Pnma*
cell const	
a, Å	20.436 (9)
b, Å	12.336 (6)
c, Å	10.412 (6)
cell vol, Å^3	2624.8
molecules/unit cell	4
ρ(calcd), g cm^{-3}	1.54
μ(calcd), cm^{-1}	11.09
radiation	Mo Kα
max crystal dimens, mm	0.52 × 0.85 × 1.10
scan width	0.80 + 0.20 tan θ
std reflctns	(12, 0, 0), (0, 6, 0)
variatn of std	±2%
reflctns measd	1949
2θ range	2–44°
reflctns obsd ($I \geq 3\sigma(I)$)	1479
no. of parameters varied	268
GOF	3.07
R	0.073
R_w	0.072

Table II. Final Fractional Coordinates[a] for **6**

atom	*x/a*	*y/b*	*z/c*	*U*(eqv)[b]
Ti	0.58574 (9)	0.2500	0.1210 (2)	0.036
Mn	0.75168 (8)	0.2500	−0.2945 (2)	0.038
Cl(1)	0.4803 (2)	0.2500	0.0529 (4)	0.173
Cl(2)	0.5635 (2)	0.2500	0.3378 (3)	0.110
P	0.6526 (2)	0.3091 (3)	−0.2264 (4)	0.028
O	0.7949 (5)	0.0828 (7)	−0.1164 (8)	0.135
C(1)	0.7765 (5)	0.1492 (9)	−0.1878 (9)	0.071
C(2)	0.7143 (6)	0.2500	−0.487 (1)	0.073
C(3)	0.7530 (5)	0.1555 (9)	−0.4685 (8)	0.073
C(4)	0.8190 (4)	0.1921 (7)	−0.4387 (7)	0.050
C(5)	0.6446 (6)	0.336 (1)	−0.052 (1)	0.032
C(6)	0.605 (1)	0.410 (1)	0.001 (2)	0.061
C(7)	0.6204 (9)	0.427 (1)	0.134 (2)	0.054
C(8)	0.6770 (8)	0.361 (2)	0.157 (2)	0.055
C(9)	0.6913 (7)	0.300 (1)	0.043 (1)	0.047
C(10)	0.6179	0.0877	0.0163	0.057
C(11)	0.6489	0.0921	0.1404	0.055
C(12)	0.5955	0.0653	0.2244	0.071
C(13)	0.5427	0.0634	0.1577	0.094
C(14)	0.5576	0.0737	0.0165	0.074
C(15)	0.6323 (6)	0.443 (1)	−0.289 (1)	0.027
C(16)	0.6574 (7)	0.535 (1)	−0.228 (2)	0.042
C(17)	0.6469 (8)	0.639 (1)	−0.273 (2)	0.045
C(18)	0.6069 (9)	0.655 (2)	−0.382 (2)	0.063
C(19)	0.5798 (9)	0.564 (2)	−0.443 (2)	0.065
C(20)	0.5920 (7)	0.459 (1)	−0.398 (2)	0.042
C(21)	0.5811 (6)	0.2500	−0.271 (1)	0.069
C(22)	0.5177 (6)	0.2500	−0.265 (1)	0.066
C(23)	0.4657 (8)	0.206 (1)	−0.306 (2)	0.054
C(24)	0.477 (1)	0.097 (2)	−0.347 (2)	0.072
C(25)	0.539 (1)	0.056 (2)	−0.350 (2)	0.060
C(26)	0.5929 (9)	0.116 (1)	−0.313 (2)	0.044

[a] Coordinates for the disordered atoms are listed only for those shown in Figure 1. The others can be obtained by operating a mirror plane on the *y* coordinate of those given here. [b] $U(\text{eqv}) = (U_{11} + U_{22} + U_{33})/3$; U's as defined in SHELX.

Table III. Bond Distances (Å) and Angles (deg) for **6**

	Bond Distances		
Ti–Cl(1)	2.268 (4)	Ti–Cl(2)	2.303 (4)
Ti–C(5)	2.41 (1)	Ti–C(6)	2.37 (2)
Ti–C(7)	2.30 (2)	Ti–C(8)	2.35 (2)
Ti–C(9)	2.39 (1)	Ti–C(10)	2.37 (2)
Ti–C(11)	2.35 (2)	Ti–C(12)	2.53 (2)
Ti–C(13)	2.49 (2)	Ti–C(14)	2.50 (2)
Mn-P	2.266 (4)	Mn–C(1)	1.74 (1)
Mn–C(2)	2.14 (1)	Mn–C(3)	2.154 (8)
Mn–C(4)	2.157 (7)	P–C(5)	1.85 (1)
P–C(15)	1.83 (1)	P–C(21)	1.70 (1)
O–C(1)	1.17 (1)	C(2)–C(3)	1.42 (1)
C(3)–C(4)	1.45 (1)	C(4)–C(4)	1.43 (2)
C(5)–C(6)	1.33 (2)	C(5)–C(9)	1.44 (2)
C(6)–C(7)	1.44 (2)	C(7)–C(8)	1.43 (2)
C(8)–C(9)	1.44 (2)	C(10)–C(11)	1.44 (2)
C(10)–C(14)	1.24 (2)	C(11)–C(12)	1.44 (3)
C(12)–C(13)	1.28 (3)	C(13)–C(14)	1.51 (3)
C(15)–C(16)	1.39 (2)	C(15)–C(20)	1.42 (2)
C(16)–C(17)	1.39 (2)	C(17)–C(18)	1.41 (2)
C(18)–C(19)	1.40 (3)	C(19)–C(20)	1.40 (2)
C(21)–C(22)	1.30 (2)	C(21)–C(26)	1.73 (2)
C(22)–C(23)	1.27 (2)	C(23)–C(24)	1.43 (3)
C(24)–C(25)	1.36 (3)	C(25)–C(26)	1.38 (2)
Cent1-Mn	1.772	Cent2-Ti	2.030
Cent3--Ti	2.139		
	Bond Angles		
Cl(1)-Ti–Cl(2)	96.8 (2)	P-Mn–C(1)	106.8 (3)
Mn-P-C(5)	116.3 (5)	Mn-P-C(15)	112.5 (4)
C(5)-P-C(15)	99.6 (7)	Mn-P–C(21)	123.1 (4)
C(5)-P-C(21)	105.6 (6)	C(15)-P-C(21)	95.5 (5)
Mn-C(1)-O	178 (1)	P-Mn–C(1)	80.2 (4)
C(1)-Mn–C(1)	91.0 (6)	C(2)–C(3)–C(4)	106.8 (9)
C(3)-C(2)-C(3)	110 (1)	C(3)–C(4)–C(4)	108.1 (6)
P–C(5)–C(6)	126 (1)	P–C(5)–C(9)	124 (1)
C(6)–C(5)–C(9)	109 (1)	C(5)–C(6)–C(7)	112 (2)
C(6)–C(7)–C(8)	104 (1)	C(7)–C(8)–C(9)	109 (1)
C(5)–C(9)–C(8)	106 (1)	C(11)–C(10)–C(14)	116 (2)
C(10)–C(11)–C(12)	102 (2)	C(11)–C(12)–C(13)	108 (2)
C(12)–C(13)–C(14)	111 (2)	C(10)–C(14)–C(13)	102 (2)
P–C(15)–C(16)	119 (1)	P-C(15)-C(20)	123 (1)
C(16)–C(15)–C(20)	118 (1)	C(15)–C(16)–C(17)	123 (1)
C(16)–C(17)–C(18)	119 (2)	C(17)–C(18)–C(19)	119 (2)
C(18)–C(19)–C(20)	122 (2)	C(15)–C(20)–C(19)	120 (2)
P–C(21)–C(22)	147.8 (7)	P–C(21)–C(26)	111.1 (9)
C(22)–C(21)–C(26)	98.8 (7)	C(21)–C(22)–C(23)	145 (1)
C(22)–C(23)–C(24)	112 (2)	C(23)–C(24)–C(25)	120 (2)
C(24)–C(25)–C(26)	123 (2)	C(21)–C(26)–C(25)	118 (2)
Cent1–Mn–P	120.7	Cent1–Mn–C(1)	123.6
Cent2–Ti–Cent3	130.6	Cent2–Ti–Cl(1)	119.2
Cent2–Ti–Cl(2)	116.4	Cent3–Ti–Cl(1)	92.6
Cent3–Ti–Cl(2)	93.4		

lected and the solvent evaporated via a water aspirator, yielding 0.061 g of $(\eta^5\text{-}C_5H_5)[(C_5H_5)(C_6H_5)_2P](CO)_2Mn$. This product was identified by a comparison of its melting point IR and ^{1}H NMR spectra with those of an authentic sample (see following experiment). Subsequent elution with 4/1 benzene/hexane developed a broad brown band which was collected and the solvent removed under reduced pressure to give 0.401 g (39%) of $(\eta^5\text{-}C_5H_5)(CO)_2\{(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4P(C_6H_5)_2]Ti(CO)_2\}Mn$. An analytically pure sample was prepared by recrystallization from methylene chloride/hexane at −20 °C: mp, slow dec above 100 °C; ^{1}H NMR (C_6D_6) δ 7.20–7.68 and 6.83–7.11 (m, 10 H, C_6H_5), 4.67–5.08 (m, 4 H, C_5H_4), 4.46 (s, 5 H, C_5H_5), 3.97 (d, J_{P-H} = 1.7 Hz, 5 H, C_5H_5); IR (C_6H_6): ν_{CO} 1960, 1930, 1880, 1860 cm^{-1}. MS, *m/e* 594 (M$^+$). Anal. Calcd for $C_{31}H_{24}MnO_4PTi$: C, 62.65; H, 4.07. Found: C, 62.68; H, 4.22.

Preparation of (η^5-Cyclopentadienyl)dicarbonyl[(diphenylphosphino)cyclopentadiene-*P*]manganese. A solution of $(\eta^5\text{-}C_5H_5)(CO)_2(THF)Mn$ was prepared by photolyzing 0.964 g (4.73 mmol) of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ in 250 mL of tetrahydrofuran in an immersion well at 15 °C for 4 h while stirring. The reaction mixture was transferred via a cannula to a Schlenk tube containing a 30-mL solution of $(C_5H_5)P(C_6H_5)_2$, prepared from 0.991 g (3.68 mL, 4.49 mmol) of chlorodiphenylphosphine and 1.210 g (4.49 mmol) of cyclopentadienylthallium as described above. The resulting solution was allowed to stir overnight. Approximately 2 g of alumina was added to the reaction mixture and the solvent removed under reduced pressure. The residue was placed on an alumina column (2 × 36 cm). Elution with hexane produced a yellow band, which was collected and the solvent removed via a water aspirator, producing 0.023 g of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$. Continued elution with 4/1 hexane/ether developed a second yellow band which was collected, and the solvent evaporated under vacuum. The residue was washed several times with hexane and dried under high vacuum, yielding 1.42 g (74%) of yellow, crystalline $(\eta^5\text{-}C_5H_5)[(C_5H_5)(C_6H_5)_2P](CO)_2Mn$. An analytical sample was obtained by recrystallization from ether/hexane at −20 °C: mp 149 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.25–7.32 (m, 10 H, C_6H_5), 6.41–7.00 (m, 3 H, CH), 4.37 (m, 5 H, C_5H_5), 3.09 and 3.21 (m, 2 H, CH_2); IR

(CH_2Cl_2) ν_{CO} 1920, 1850 cm^{-1}. Anal. Calcd for $C_{24}H_{19}MnPO_2$: C, 67.61; H, 4.73. Found: C, 67.65; H, 4.92.

X-ray Data Collection, Structure Determination and Refinement for (η^5-C_5H_5)(CO)$_2${(η^5-C_5H_5)[η^5-$C_5H_4P(C_6H_5)_2$]$TiCl_2$}Mn (6). A crystal of **6** suitable for X-ray analysis was grown by carefully layering hexane onto a solution of **6** in methylene chloride. The resulting mixture was allowed to stand undisturbed for ca. 48 h, whereby diffusional mixing of the two layers had taken place, effecting the formation of purple crystals. Single crystals of the air-sensitive compound 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 ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. Systematic absences allowed the space group to be either *Pnma* or $Pn2_1a$. Subsequent structure solution and refinement in the centrosymmetric *Pnma* showed this to be the correct choice.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. The method has been previously described.[25] A summary of the data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[26] Neutral atom scattering factors for Ti, Mn, Cl, P, O, and C were taken from Cromer and Waber,[27] and the scattering for titanium and manganese were corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[28] Scattering factors for H were from ref 29.

The positions of the titanium, manganese, and chlorine atoms were revealed by the direct methods program MULTAN.[30] A difference Fourier map phased on these atoms revealed some disorder about the mirror plane in the centrosymmetric *Pnma*. Refinement in the noncentrosymmetric $Pn2_1a$ produced high correlations between atoms that were properly related by the mirror (O(1), C(1), C(2), and C(3)). The *R* factor for anisotropic refinement of all nonhydrogen atoms in $Pn2_1a$ was 0.135 and a difference Fourier map revealed peaks corresponding to the $CpPPh_2$ and the other Cp ligand on titanium as related by a mirror plane. The correct choice was then taken to be *Pnma* with Ti, Mn, Cl(1), Cl(2), and C(2) in the plane, O(1), C(1), C(3) and C(4) correctly related by the mirror, and all the other atoms disordered about the mirror plane with occupancy factors of 0.5. The two exceptions are atoms C(21) and C(22). These atoms would not refine off the mirror plane, and thus distortion is noted in the bond distances and angles involving these two atoms. Some disorder about the plane was noted for Cl(1) and Cl(2), but it could not be resolved. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.178$. The hydrogen atoms could not be located due to the nature of the disorder, and their contributions were therefore not included in the first refinement. Refinement with anisotropic temperature factors led to final values of $R = 0.073$ and $R_w = 0.072$. A final difference Fourier showed no feature greater than 0.4 e$^-$/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the fractional coordinates are given in Table II. The final values of the thermal parameters are available as supplementary materials.[31] Bond distances and angles for **6** are given in Table III.

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Registry No. 1, 58109-48-1; **2**, 85320-10-1; **3**, 1270-98-0; **4**, 85320-11-2; **5**, 85320-12-3; **6**, 85320-13-4; **7**, 85320-14-5; **8**, 85320-15-6; chlorodiphenylphosphine, 1079-66-9; (cyclopentadienyl)thallium, 34822-90-7.

Supplementary Material Available: A listing of thermal parameters, and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Carbon Dioxide Activation by Lithium Metal. 1. Infrared Spectra of $Li^+CO_2^-$, $Li^+C_2O_4^-$ and $Li_2^{2+}CO_2^{2-}$ in Inert-Gas Matrices

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Abstract: Lithium atoms react spontaneously with carbon dioxide to form $Li^+CO_2^-$ and $Li_2^{2+}CO_2^{2-}$ in inert gas matrices. Reaction of Li and CO_2 in an argon matrix leads also to the formation of $Li^+C_2O_4^-$. Two geometrical isomers of $Li^+CO_2^-$ have been isolated in solid argon. One has a ring structure in which the metal interacts symmetrically with the two oxygen atoms, while in the second isomer the lithium atom is bonded to only one of the two oxygens. It is found that $Li^+CO_2^-(C_s)$ rearranges upon photolysis with a Nernst glower IR source to the symmetric $Li^+CO_2^-(C_{2v})$. Similarly, $Li^+C_2O_4^-$ photolytically converts to an $LiCO_2$:CO_2 adduct. $Li_2^{2+}CO_2^{2-}$ is produced under high concentration of the alkali metal as a result of the reaction of dilithium or two lithium atoms with carbon dioxide. Lithium oxalate ($Li_2C_2O_4$) is formed in concentrated matrices. For the first time, all three expected intraionic infrared-active modes of CO_2^- as well as a Li^+–CO_2^- interionic mode have been identified for both $Li^+CO_2^-$ geometrical isomers. Isotopic shifts have been measured for lithium-6-, carbon-13-, and oxygen-18-enriched products. A CO_2^- valence bond angle equal to 125.7° has been calculated. Normal coordinate analyses have been carried out on $LiCO_2(C_{2v})$ and $LiCO_2(C_s)$ by using 22 and 30 measured frequencies, respectively, for all the isotopomers of the two geometrical isomers.

Introduction

In the search for new catalytic processes that may lead to the conversion of cheap available CO_2 into organic compounds, there have been many investigations of ways of activating the CO_2 molecule whether by coordination with transition metals[1,2] or transition-metal complexes,[3] by insertion into M–H, M–C, M–N, and M–O bonds,[3-16] or by electron transfer with an electron source

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