

Ligand Substitution Processes in Tetranuclear Carbonyl Clusters. 9. Reactions of $\text{Co}_4(\text{CO})_9(\text{tripod})$, $\text{tripod} = \text{HC}(\text{PPh}_2)_3$, and Its Derivatives[†]

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Reactions of $\text{Co}_4(\text{CO})_9(\text{tripod})$ with phosphorus donor ligands has resulted in a facile production of $\text{Co}_4(\text{CO})_8(\text{L})(\text{tripod})$ derivatives, where $\text{L} = \text{P}(\text{OMe})_3$, PMe_3 , and $\text{P}(n\text{-Bu})_3$. The reaction proceeds too rapidly to occur via a CO dissociative (D) mechanism and hence is ascribed to a ligand-dependent pathway (I_a) for CO substitution. Phosphorus ligand substitution occurs stereoselectively at the apical cobalt sites. Further substitution by nucleophilic PMe_3 ligands leads first to additional apical incorporation of PMe_3 , followed by a subsequent slower process that results in ligand rearrangement to relieve steric crowding where both apical and radial sites are occupied by PMe_3 . A similar bis(phosphine) species is formed upon reaction of bis(diphenylphosphino)methane with $\text{Co}_4(\text{CO})_9(\text{tripod})$. This derivative undergoes stereoselective carbonyl ligand exchange with ^{13}C O at a rate which is not greatly different from the analogous process involving the parent compound $\text{Co}_4(\text{CO})_9(\text{tripod})$. For example, the rate of dissociative CO loss in $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ is 5 times slower than the corresponding process in $\text{Co}_4(\text{CO})_9(\text{tripod})$, indicative of only a slight perturbation in the reactivity of carbon monoxide at a cobalt center upon phosphine ligand substitution. A discussion of ^{13}C and ^{31}P NMR spectra of all the derivatives reported upon herein is included.

Introduction

Synthesis and structural characterizations of molecular metal clusters have been actively pursued by organometallic chemists for well over a decade, with most recent efforts being directed at understanding the chemistry associated with these species.¹ Much of this attention has been motivated by Muetterties' well articulated presumption that transition-metal clusters may serve as simple homogeneous models of metal surfaces in both chemisorption and catalytic processes.² Because metal clusters may be useful models of catalytic surfaces, it is important to fully comprehend how incoming ligands (or substrate molecules) react at metal centers in clusters. To paraphrase Earl, insight gained from molecular coordination chemistry, if critically and carefully applied to metal surface chemistry, can be invaluable; for surface chemistry is coordination chemistry.³

Ligands are capable of interacting with the metal centers of a cluster in many ways. These include coordination modes not attainable by monomeric species, such as bridging two or more metal centers. Several factors determine how a ligand will bind to the metal centers of a cluster; it is not uncommon to find clusters with two or more identical ligands coordinated in different fashions. Indeed ligands capable of multiple-coordination modes often possess the ability to migrate about the cluster. This nonrigidity often makes it difficult to assign the initial site of ligand coordination or interaction. However, if the cluster is designed with sufficient constraints to restrict ligand migration, then it may be possible to isolate the site of ligand substitution.

Our investigations have been centered on displacement reactions involving dissociative loss of carbon monoxide and phosphorus donor ligands in tetranuclear metal cluster derivatives. Special emphasis has been placed on discernment of steric and electronic effects attributed to prior substitution by phosphorus donor ligands. In this paper we examine the ligand substitution reactions of Co_4

$(\text{CO})_9(\text{HC}(\text{PPh}_2)_3)$ ($\text{HC}(\text{PPh}_2)_3 = \text{tripod}$) with phosphorus ligands. We also report the kinetic parameters for the carbonyl exchange reaction of $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ ($\text{dppm} = \text{H}_2\text{C}(\text{PPh}_2)_2$). Kinetic investigations provide information pertinent to an understanding of the various steric and electron factors that govern ligand substitutional processes.⁴

Experimental Section

All manipulations were performed on a double-manifold Schlenk vacuum line under an atmosphere of dry nitrogen or in an argon-filled drybox. Solvents were dried and deoxygenated by distillation from the appropriate reagent (e.g., sodium benzophenone ketyl) under a nitrogen atmosphere. $\text{Co}_4(\text{CO})_{12}$, PMe_3 , $\text{P}(\text{OMe})_3$, $\text{P}(n\text{-Bu})_3$ and $\text{H}_2\text{C}(\text{PPh}_2)_2$ were purchased from Strem Chemicals, Inc., and used without further purification. $\text{HC}(\text{PPh}_2)_3$ was prepared from $(\text{Ph}_2\text{P})_2\text{CH-Li}(\text{TMEDA})^+$ and Ph_2PCl or purchased from Organometallics, Inc.^{5,6} Carbon monoxide (93 atm % ^{13}C , 12% ^{18}O) was obtained from Prochem, B.O.C. Ltd., London.

Infrared spectra were recorded in 0.10-mm matched NaCl sealed cells on a Perkin-Elmer 283B spectrophotometer or on an IBM FT-IR Model 85 spectrophotometer, using THF as the solvent. ^{31}P and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. Solutions were prepared by dissolving the sample in 3-5 mL of solvent and then filtering through silica gel into an NMR tube. ^{31}P spectra were run by using CD_2Cl_2 (99 atom % D_2) as the solvent or in CH_2Cl_2 spiked with benzene- d_6 . Chemical

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(2) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* 1975, 84, 959. (b) Muetterties, E. L. *Bull. Soc. Chim. Belg.* 1976, 85, 451. (c) Muetterties, E. L. *Science (Washington, D.C.)* 1977, 196, 839.

(3) Muetterties, E. L.; Wexler, R. M. *Surv. Prog. Chem.* 1983, 10, 61.

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(6) A brief report on these reactions has appeared previously. Bahren, A. A.; Osborn, J. A.; Voelken, C.; Bonnet, J. J.; Lavigne, G. *Organometallics* 1982, 1, 1114.

[†]Dedicated to the memory of Professor Earl L. Muetterties, a friend and gentleman who is greatly missed for both his scientific and human qualities.

shift values are reported with positive values being downfield from H_3PO_4 . The samples were referenced by using 85% H_3PO_4 or $\text{P}(\text{OCH}_3)_3$ sealed in a capillary tube. ^{13}C samples were run in CD_2Cl_2 (99 atom % D_2) as the solvent and referenced by using the CD_2Cl_2 signal.

Preparations. $\text{Co}_4(\text{CO})_9(\text{HC}(\text{PPh}_2)_3)$ (**1**). A methylcyclohexene solution of $\text{HC}(\text{PPh}_2)_3$ was slowly added to a refluxing hexane solution of $\text{Co}_4(\text{CO})_{12}$ as previously reported.^{5,6} IR (cm^{-1}) 2044 (s), 1998 (vs), 1971 (sh), 1783 (s); ^{13}C NMR (CD_2Cl_2 , δ) 254.6, 203.2, 202.0.

$\text{Co}_4(\text{CO})_8(\text{L})(\text{HC}(\text{PPh}_2)_3)$ (**L** = PMe_3 , $\text{P}(\text{OMe})_3$, or $\text{P}(n\text{-Bu})_3$). In a typical synthesis 0.10 mL of the liquid phosphine or phosphite (>0.60 mmol) was added by syringe to 0.10 g (0.095 mmol) of $\text{Co}_4(\text{CO})_9(\text{HC}(\text{PPh}_2)_3)$ in 10 mL of THF in a septum-capped Schlenk flask under nitrogen. The reaction solution was stirred at ambient temperature, and after 5 min product formation was complete as demonstrated by infrared spectroscopy in the ν_{CO} region where only bands assignable to $\text{Co}_4(\text{CO})_8(\text{L})(\text{HC}(\text{PPh}_2)_3)$ were noted. Volatiles were removed under vacuum, and the product was purified by recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$.

$\text{Co}_4(\text{CO})_8(\text{PMe}_3)(\text{HC}(\text{PPh}_2)_3)$ (**2a**):⁶ brown-green; IR (cm^{-1}) 2011 (m), 1969 (s), 1927 (w), 1804 (w), 1772 (m), 1746 (m); ^{31}P NMR ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$, δ) 42.9 (d), 5.4 (m); ^{13}C NMR (CD_2Cl_2 , δ) 258.1, 206.8, 203.2.

$\text{Co}_4(\text{CO})_8(\text{P}(\text{OMe})_3)(\text{HC}(\text{PPh}_2)_3)$ (**2b**): green; IR (cm^{-1}) 2013 (m), 1976 (s), 1959 (m, sh), 1801 (w, sh), 1775 (m), 1764 (m); ^{31}P NMR (CD_2Cl_2 , δ) 42.4 (d), 166 (br); ^{13}C NMR (CD_2Cl_2 , δ) 255.3, 209.5, 204.4.

$\text{Co}_4(\text{CO})_8(\text{P}(n\text{-Bu})_3)(\text{HC}(\text{PPh}_2)_3)$ (**2c**): green; IR (cm^{-1}) 2007 (m), 1969 (s), 1958 (sh), 1803 (w), 1772 (m), 1746 (m).

$\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2(\text{HC}(\text{PPh}_2)_3)$ (**3a**). To prevent the volatile PMe_3 from escaping, a 50-mL Schlenk flask was fitted with a Dewar condenser cooled by a dry ice/acetone slush. To this flask was added 0.1023 g of $\text{Co}_4(\text{CO})_9(\text{HC}(\text{PPh}_2)_3)$ (0.0969 mmol), 10 mL of THF, and 0.1 mL of PMe_3 . The reaction mixture was then heated to reflux for 2 h. During this time the color of the solution changed from green to brown. At this time the infrared spectra consists of one major isomer $\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2(\text{HC}(\text{PPh}_2)_3)$: IR (cm^{-1}) 1973 (m), 1944 (vs), 1910 (w), 1791 (w), 1753 (m), 1737 (m). This product is believed to be the kinetic isomer **3a**, where the two trimethylphosphine ligands occupy the apical position. This cluster disproportionates with decomposition to **2a** and **3b** when a vacuum is applied: ^{31}P NMR ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$, δ) 26.5 (t), 2.9 (br); ^{13}C NMR (CD_2Cl_2 , δ) 263.7, 205.5.

$\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2(\text{HC}(\text{PPh}_2)_3)$ (**3b**). This was prepared analogous to **3a**, except the reaction time was increased to 5 h. After this time the solvent was removed by vacuum. The product was then washed with hexane to remove any trisubstituted cluster that formed (70% yield): IR (cm^{-1}) 1983 (s), 1950 (vs), 1897 (w), 1780 (w), 1740 (m), 1734 (m); ^{31}P NMR ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$, δ) 48.2 (dt), 45.8 (dd), -1.2 (s), -4.2 (br d); ^{13}C NMR (CD_2Cl_2 , δ) 266.8, 266.1, 212.5, 204.3.

$\text{Co}_4(\text{CO})_7(\text{H}_2\text{C}(\text{PPh}_2)_2)(\text{HC}(\text{PPh}_2)_3)$ (**4**). A 0.2330-g sample of $\text{Co}_4(\text{CO})_9(\text{HC}(\text{PPh}_2)_3)$ (0.221 mmol) and 0.1430 g of $\text{H}_2\text{C}(\text{PPh}_2)_2$ (0.372 mmol) were refluxed in 30 mL of THF for 2 h. The resulting green solution was then filtered through silica gel and evaporated to dryness. The green solid was then washed with diethyl ether to remove any unreacted $\text{H}_2\text{C}(\text{PPh}_2)_2$. A 0.3003-g sample of $\text{Co}_4(\text{CO})_7(\text{H}_2\text{C}(\text{PPh}_2)_2)(\text{HC}(\text{PPh}_2)_3)$ was recovered (0.217 mmol, 98%): IR (cm^{-1}) 1997 (s), 1964 (vs), 1945 (w), 1792 (vw), 1768 (m), 1717 (m); ^{31}P NMR ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$, δ) 45.6 (t), 44.2 (dd), 24.7 (d), 18.2 (br); ^{13}C NMR (CD_2Cl_2 , δ) 264.1, 257.8, 208.3, 203.8.

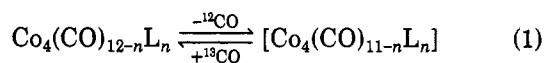
$\text{Co}_4(^{13}\text{C})_6(\pi\text{-C}_7\text{H}_8)(\text{HC}(\text{PPh}_2)_3)$ (**5**).⁶ A 0.1073-g (0.1016 mmol) of $\text{Co}_4(\text{CO})_9(\text{tripod})$ was put into an evacuated 50-mL Schlenk flask. The flask was then filled with an atmosphere of ^{13}CO and 30 mL of THF added. The flask was then placed into a constant temperature bath and heated to 50 °C. After 6 h the flask was degassed and backfilled with fresh ^{13}CO and then left overnight at 50 °C. The THF was then removed in vacuo. The flask was fitted with a condenser and 30 mL of toluene added. The mixture was heated to reflux for 6 h. During this time the solution changed from green to brown. The reaction mixture was then pumped to dryness, and 0.0947 g (0.0883 mmol, 87%) of product was recovered: IR (cm^{-1}) 1961 (w), 1907 (vs), 1868 (w), 1761 (w), 1707 (m), 1672 (w); ^{13}C NMR (toluene/ C_6D_6 , δ) 258.3 (q, $J = 9.8$ Hz), 206.3 (d, $J = 3.2$ Hz).

$\text{Co}_4(\text{CO})_6(\text{PMe}_3)_3(\text{HC}(\text{PPh}_2)_3)$ (**6**). This cluster was prepared analogous to **3a** and **3b** by increasing the reaction time to 10 h. Alternatively, it can be prepared by refluxing PMe_3 and $\text{Co}_4(\text{CO})_9(\text{tripod})$ in dimethoxyethane for 3 h. After this time the solution consists of a mixture of **3b** and **6**. $\text{Co}_4(\text{CO})_6(\text{PMe}_3)_3$ [tripod] can be separated from disubstituted derivative by dissolving it in hexane, filtering, and then removing the solvent in vacuo. The product was isolated in 10% yield: IR (cm^{-1}) 1977 (w), 1910 (vs), 1870 (sh), 1731 (w), 1712 (m).

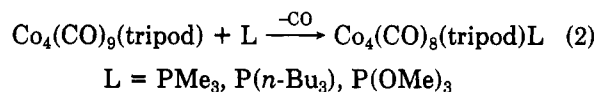
Kinetic Measurements. The reaction of $\text{Co}_4(\text{CO})_7(\text{dppm})$ (tripod) with ^{13}CO was carried out in a 50-mL Schlenk flask. In a typical experiment 0.15 g of $\text{Co}_4(\text{CO})_9(\text{dppm})(\text{tripod})$ (0.11 mmol) was dissolved in 10 mL of THF. The solution was evacuated and then backfilled with an atmosphere of ^{13}CO (2.0 mmol or 10 times excess of ^{13}CO). The reaction flask was covered with aluminum foil to protect the solution from room light and then placed in a constant temperature bath equilibrated to a predetermined temperature. The reaction was monitored by intermittently withdrawing samples with a hypodermic syringe and examining the infrared spectra in the $\nu(\text{CO})$ region. At temperatures below 60 °C, ^{13}CO was exchanged only in an apical position. When the temperature was higher than 60 °C, ^{13}CO was incorporated into the basal positions, presumably by ligand migration. The rate of this migration is much slower than carbonyl exchange.

Results and Discussion

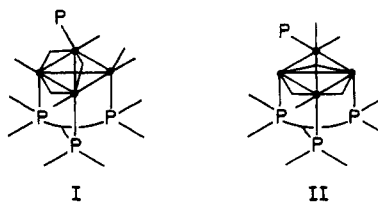
We have previously reported on carbon monoxide exchange reactions of $\text{Co}_4(\text{CO})_9(\text{tripod})$ employing ^{13}CO as incoming ligand.⁵ Results of cumulative investigations involving $\text{Co}_4(\text{CO})_{12}$, $\text{Co}_4(\text{CO})_9(\text{tripod})$, and a variety of phosphorus donor ligand substituted derivatives have led us to conclude that intermolecular carbon monoxide exchange in all these species occurs via a common mechanistic pathway, namely, a simple CO dissociative (D) process (eq 1).^{5,7} On the contrary, reactions involving the more nucleophilic phosphorus donor groups as entering ligands ensue at rates faster than would be consistent with CO substitution by a dissociation mechanism.



$\text{Co}_4(\text{CO})_9(\text{tripod})$ reacts rapidly with a variety of phosphorus donor ligands at room temperature to afford monosubstituted cluster derivatives (eq 2).⁶ In principal



several isomers are possible for these species. These include either apical or basal substitution, and in the case of apical substitution, alternative arrangements for bridging CO ligands with attendant alterations in terminal CO ligands as for example in species I are conceivable. On



the basis of steric considerations phosphine substitution at the apical position would be favored over the basal sites. Further support for apical substitution is provided by the related tetrakisphosphine clusters $\text{M}_4(\text{CO})_8\text{P}_4$ ($\text{M} = \text{Co}, \text{Rh}$,

(7) (a) Darendbourg, D. J.; Incorvia, M. J. *J. Organomet. Chem.* **1979**, *171*, 89. (b) Darendbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1980**, *19*, 2585. (c) Darendbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1981**, *20*, 1911. (d) Darendbourg, D. J.; Peterson, B. S.; Schmidt, R. E., Jr. *Organometallics* **1982**, *1*, 306.

Table I. Infrared in the ν_{CO} Region of Some Cobalt-tripod Cluster Derivatives^a

$\text{Co}_4(\text{CO})_9(\text{tripod})$ (1)	2044 (2)	1998 (vs)	1971 (m, sh)	1783 (s)		
$\text{Co}_4(\text{CO})_8(\text{P}(\text{OMe})_3)(\text{tripod})$ (2b)	2013 (m)	1976 (s)	1959 (m, sh)	1801 (w, sh)	1775 (m)	1764 (m)
$\text{Co}_4(\text{CO})_8(\text{PMe}_3)(\text{tripod})$ (2a)	2011 (m)	1969 (s)	1927 (w)	1804 (w)	1772 (m)	1746 (m)
$\text{Co}_4(\text{CO})_8(\text{P}(n\text{-Bu})_3)(\text{tripod})$ (2c)	2007 (m)	1969 (s)	1958 (sh)	1803 (w)	1772 (m)	1746 (m)
$\text{Co}_4(\text{CO})_8(\text{dppm})(\text{tripod})$ (4)	1997 (s)	1964 (vs)	1945 (w)	1772 (vw)	1768 (m)	1717 (m)
$\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2(\text{tripod})^b$ (3a)	1973 (m)	1944 (vs)	1910 (w)	1791 (w)	1753 (m)	1737 (m)
$\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2(\text{tripod})^b$ (3b)	1983 (s)	1950 (vs)	1897 (w)	1780 (w)	1740 (m)	1734 (m)
$\text{Co}_4(\text{CO})_6(\pi\text{-toluene})(\text{tripod})^c$ (5)	1974 (w)	1951 (vs)	1746 (m)			
$\text{Co}_4(\text{CO})_6(\text{PMe}_3)_3(\text{tripod})$ (6)	1977 (w)	1910 (vs)	1870 (sh)	1731 (w)	1712 (m)	

^a The spectra were recorded by using tetrahydrofuran as the solvent. ^b The kinetic (3a) and thermodynamic (3b) isomers of $\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2(\text{tripod})$. ^c Spectra were recorded in dimethoxyethane as the solvent.

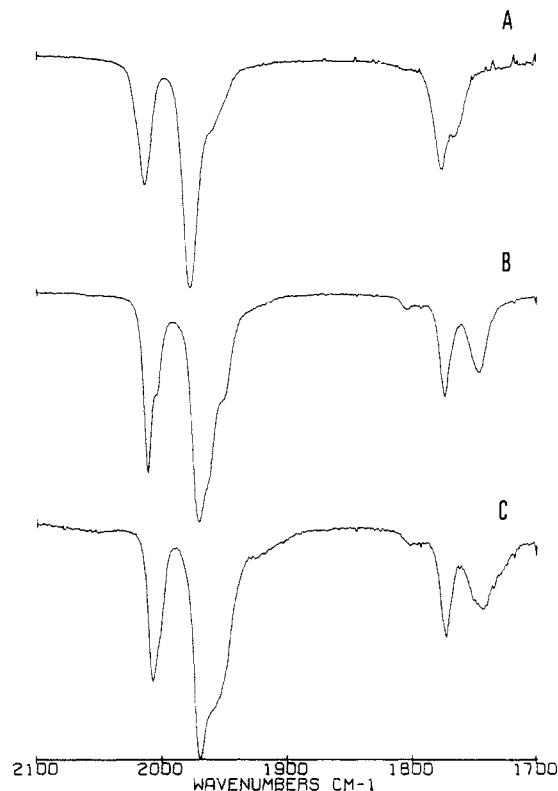


Figure 1. Infrared spectra in ν_{CO} region of $\text{Co}_4(\text{CO})_8(\text{L})(\text{tripod})$ derivatives in tetrahydrofuran: A, L = $\text{P}(\text{OMe})_3$; B, L = PMe_3 ; C, L = $\text{P}(n\text{-Bu})_3$.

Ir),⁸ where each metal center has only one phosphine ligand attached.

The infrared spectra of the three monophosphine-substituted tripod clusters (Table I) all display identical patterns, indicating that they are all isostructural (Figure 1). If the cluster has the molecular arrangement of species II, then ligands with a small cone angle will not disrupt the C_{3v} symmetry of the bridging carbonyls as much as ligands with a large cone angle. This is consistent with the infrared spectra of the monosubstituted cobalt tripod clusters (Figure 1). $\text{P}(\text{OMe})_3$ has a small cone angle of 107° and does not perturb the bridging groups as much as PMe_3 or $\text{P}(n\text{-Bu})_3$.⁹

The ^{31}P NMR spectra for $\text{Co}_4(\text{CO})_8(\text{PMe}_3)(\text{tripod})$ and $\text{Co}_4(\text{CO})_8(\text{P}(\text{OMe})_3)(\text{tripod})$ shows two signals with a relative intensity of 3:1, supporting the apical location of the phosphorus donor ligand. Basal substitution or apical substitution with alternative bridging CO arrangement such as in species I would make one of the phosphorus atoms of the tripod ligand different from the other two

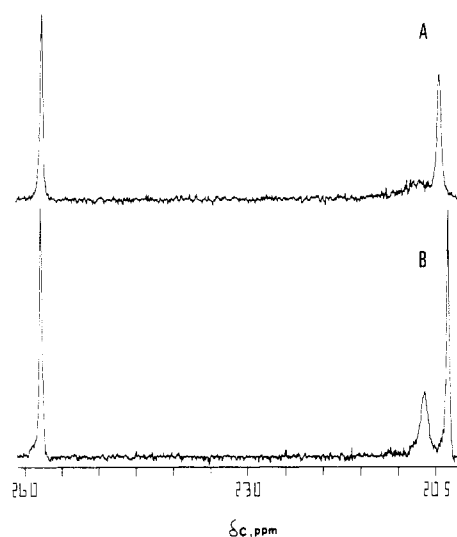


Figure 2. ^{13}C NMR spectra of $\text{Co}_4(\text{CO})_8(\text{PMe}_3)(\text{tripod})$: A, ambient temperature; B, -80°C .

phosphorus atoms. The peak assigned to the tripod ligand is split into a doublet by the apical phosphorus ligand, with a coupling constant of 50 and 48 Hz for the PMe_3 and $\text{P}(\text{OMe})_3$ derivatives, respectively. Low temperature is needed to observe the remaining peak assigned to the appended ligand, which appears as a broad multiplet. The temperature dependence of this peak appears to be indicative of substitution at an apical position and is believed to be caused by the cobalt quadrupole. The ^{13}C NMR spectra of the two clusters consists of three signals of relative intensity 3:2:3, consistent with the structure of species II. The low-field peak is assigned to the bridging carbonyls. The high-field signal is attributed to the terminal carbonyls in the basal plane. The remaining signal shows a significant dependence on temperature and is assigned to the apical carbonyls (Figure 2). This is in contrast to the work of Stuntz and Shapley,¹⁰ who found that in $\text{Ir}_4(\text{CO})_{12-n}(\text{PPh}_2\text{Me})_n$ ($n = 1-4$) clusters the basal resonances appear 7–15 ppm downfield from the remaining terminal sites. This reversal of the basal and apical positions appears to be unique for $\text{Co}_4(\text{CO})_9(\text{tripod})$ clusters. Osborn and co-workers have reported that in $\text{Rh}_4(\text{CO})_9(\text{tripod})$ the basal resonances are 2.9 ppm downfield from the apical resonances.⁶ As a check for our assignments we examined the ^{13}C NMR spectra of $\text{Co}_4(\text{CO})_8(\pi\text{-toluene})(\text{tripod})$. In this cluster the apical position is occupied by a toluene group, and hence the remaining carbonyls should not display the temperature dependence discussed above. Indeed this turned out to be the case. The spectra consists of two peaks in the carbonyl region, both of which are readily seen at ambient temperature. The low-field peak at 258.3 ppm is assigned to the bridging carbonyls and is

(8) (a) Carre, F. H.; Cotton, F. A.; Frenz, B. *Inorg. Chem.* 1976, 15, 380. (b) Huq, R.; Poe, A. *J. Organomet. Chem.* 1982, 226, 277. (c) Darensbourg, D. J.; Baldwin-Zuschke, B. *J. Inorg. Chem.* 1981, 20, 3846. (9) Tolman, C. A. *Chem. Rev.* 1977, 77, 313.

(10) Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* 1977, 99, 607.

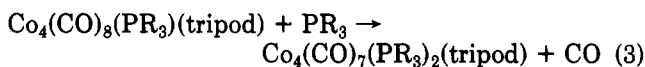
Table II. ^{31}P NMR Data of Some Cobalt-tripod Derivatives^a

complex	phosphorus ligand	shift, ppm	rel intens	multiplicity ^c (coupling const)
$\text{Co}_4(\text{CO})_9(\text{tripod})^{b,7}$ (1)	$\text{HC}(\text{PPh}_2)_3$	44.3		br s
$\text{Co}_4(\text{CO})_8(\text{P}(\text{OMe})_3)(\text{tripod})^b$ (2b)	$\text{P}(\text{OMe})_3$	166	1	br
$\text{Co}_4(\text{CO})_8(\text{PMe}_3)(\text{tripod})$ (2a)	$\text{HC}(\text{PPh}_2)_3$	42.4	3	d (48 Hz)
	$\text{HC}(\text{PPh}_2)_3$	42.9	3	d (50 Hz)
$\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2(\text{tripod})$ (3a)	PMe_3	5.4	1	br
	$\text{HC}(\text{PPh}_2)_3$	26.5	3	t (64 Hz)
$\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2(\text{tripod})$ (3b)	PMe_3	2.9	2	br
	$\text{HC}(\text{PPh}_2)_3$	48.2	1	dt (120, 31 Hz)
$\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ (4)		45.8	2	dd (31, 30 Hz)
	PMe_3 (basal)	-1.2	1	s
	PMe_3 (apical)	-4.2	1	br d (120 Hz)
	$\text{HC}(\text{PPh}_2)_3$	45.6	1	t (28 Hz)
		44.2	2	dd (54, 28 Hz)
		24.7	1	d (55 Hz)
$\text{Co}_4(\text{CO})_6(\pi\text{-toluene})(\text{tripod})^{b,7}$ (5)	dppm (basal)	18.2	1	br
	$\text{HC}(\text{PPh}_2)_3$	19.2	1	br s

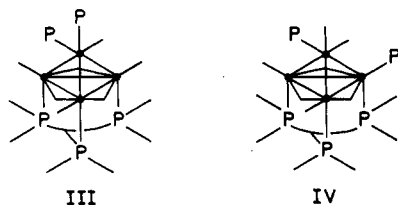
^a Spectra were recorded at -80°C , using $\text{CH}_2\text{Cl}_2/\text{benzene-}d_6$ as the solvent unless otherwise stated. ^b CD_2Cl_2 was used as the solvent. ^c s = singlet, d = doublet, t = triplet, br = broad, dd = doublet of doublets, dt = doublet of triplets.

split into a quartet by the three phosphorus atoms of the tripod ligand, $J = 9.8$ Hz. The terminal carbonyl resonance at 206.3 ppm is split into a doublet with $J = 3.2$ Hz.

Substitution of a carbon monoxide ligand by a second phosphorus donor group (eq 3) is much slower than the first substitution process and most likely occurs via a



CO-dissociative mechanism. For example, the ligand displacement reaction described in eq 3 is greatly retarded in the presence of carbon monoxide. These bis(phosphine) $\text{Co}_4(\text{CO})_8(\text{tripod})$ derivatives, of course, require that one of the cobalt centers bear two phosphine ligands. Reaction of $\text{Co}_4(\text{CO})_8(\text{PMe}_3)(\text{tripod})$ with PMe_3 initially affords an isomer containing two PMe_3 ligands in the apical position (III). Upon further refluxing in THF this isomer is con-



verted to an isomer that contains one PMe_3 in a basal site and one PMe_3 in the apical position (IV). Consistent with this structural assignment, the bis apically substituted species III, where steric hinderance between the two phosphine ligands is significant, readily reacts at ambient temperature with CO to afford the monosubstituted derivative II, whereas isomer IV reacts with CO only slowly at 50°C to again provide II.

The structures of species III and IV were assigned on the basis of their ^{13}C and ^{31}P NMR spectra (see Tables II and III). The ^{13}C NMR spectrum of III contains one resonance in the bridging CO region at 263.7 ppm, whereas species IV has two carbon resonances at 266.1 and 266.8 ppm of intensity ratio 1:2. Similarly, the ^{31}P spectrum of III displays one signal due to the tripod ligand that is split by the two apical PMe_3 ligands into a triplet ($J_{\text{P-P}} = 64$ Hz). The resonance due to the apical PMe_3 ligands give rise to a broad multiplet (vide supra). On the other hand the ^{31}P of isomer IV is considerably more complex. ^{31}P resonances in the tripod ligand are seen as a doublet of triplets, which results from the unique phosphorus atom (bound to cobalt bearing PMe_3) being coupled to the apical PMe_3 group ($J_{\text{P-P}} = 120$ Hz) and the two remaining

Table III. ^{13}C NMR Frequency Assignments of Some Cobalt-tripod Derivatives^a

complex	bridging	Apical	Equatorial
$\text{Co}_4(\text{CO})_9(\text{tripod})$ (1)	254.6	203.2	202.0
$\text{Co}_4(\text{CO})_8(\text{P}(\text{OMe})_3)(\text{tripod})$ (2b)	256.4	209.4	204.6
$\text{Co}_4(\text{CO})_8(\text{PMe}_3)(\text{tripod})$ (2a)	258.1	206.8	203.2
$\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2(\text{tripod})$ (3a)	263.7	b	205.5
$\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2(\text{tripod})$ (3b)	266.8, 266.1	212.5	204.3
$\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ (4)	264.1, 257.8	208.3	203.8
$\text{Co}_4(\text{CO})_6(\pi\text{-toluene})(\text{tripod})^c$ (5)	258.3 ^d	206.3 ^e	

^a Spectra recorded by using CD_2Cl_2 as the solvent. The reported frequencies are in ppm downfield from Me_4Si . ^b Peak assignable to apical position was not observed. ^c Spectra run in toluene using benzene- d_6 for the deuterium lock. ^d Quartet, $J_{\text{P-C}} = 9.3$ Hz. ^e Doublet, $J_{\text{P-C}} = 3.2$ Hz.

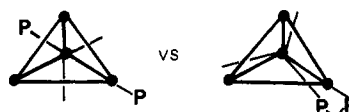


Figure 3. Disposition of two appended phosphine ligands in $\text{Co}_4(\text{CO})_7(\text{PMe}_3)_2[\text{tripod}]$ and $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$.

phosphorus atoms of the tripod ligand ($J_{\text{P-P}} = 31$ Hz), and a doublet of doublets, which arises from the two equivalent phosphorus atoms being split by the apical PMe_3 group ($J_{\text{P-P}} = 30$ Hz) and the unique phosphorus atom of the tripod ligand ($J_{\text{P-P}} = 31$ Hz). The apical PMe_3 shows up as a broad doublet ($J_{\text{P-P}} = 120$ Hz at -4.2 ppm), and the equatorial PMe_3 ligand is a singlet at -1.2 ppm.

The reaction of $\text{Co}_4(\text{CO})_9(\text{tripod})$ with dppm (bis(diphenylphosphino)methane) results in the formation of a bis(phosphine) derivative that is similar in structure to species IV. However, these derivatives differ from one another by way of the disposition of the two appended phosphorus ligands with respect to each other (see Figure 3).¹¹ The ^{31}P and ^{13}C NMR spectral data are consistent with this formulation when account is taken of the significantly greater magnitude of phosphorus-phosphorus

(11) Several of these $\text{Co}_4(\text{CO})_9[\text{tripod}]$ derivatives are currently the subject of X-ray crystallographic investigation. Indeed the structure of species 2a has been completed, indicating the structural assignment based on spectral data to be correct.

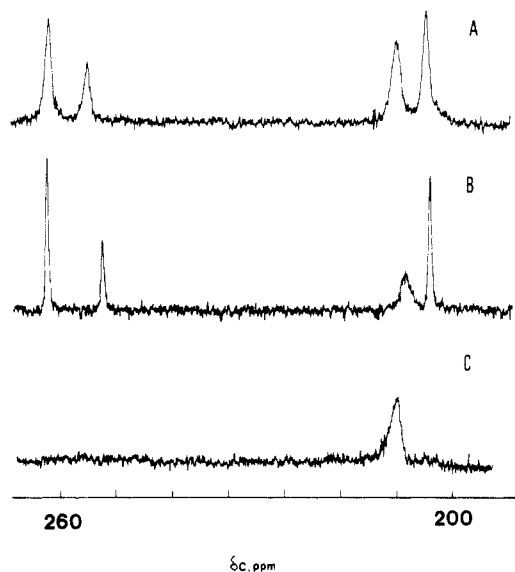
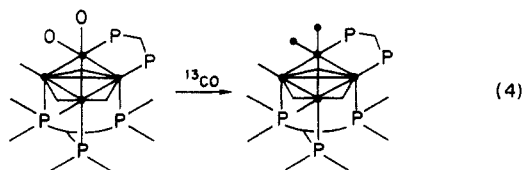


Figure 4. ^{13}C NMR spectra of $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$: A, -80°C ; B, ambient temperature; C, exchange product of ^{13}CO and $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ at -80°C .

coupling constants in the trans arrangement as compared with the cis.

The ^{13}C NMR spectra at $+25$ and -80°C of $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$, prepared from a randomly ^{13}C -enriched sample of $\text{Co}_4(\text{CO})_9(\text{tripod})$, is depicted in Figure 4. The resonance due to the two apical carbonyl groups is assigned to the peak at 208.3 ppm on the basis of its temperature characteristics. When $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ is reacted with ^{13}CO , a stereoselective CO exchange reaction occurs



involving the apical carbon monoxide ligands (eq 4). This molecule has provided us with the first case of a tetranuclear cluster carbonyl derivative where intermolecular CO exchange takes place at a rate faster than intramolecular CO rearrangement. Above 60°C the labeled ^{13}CO ligand was observed to appear in the other carbonyl sites in the cluster, presumably by a ligand migration pathway. Similar stereoselectivity was observed for ^{13}CO exchange reactions of the monoapically substituted $\text{Co}_4(\text{CO})_9(\text{tripod})$ derivative $\text{Co}_4(\text{CO})_8(\text{PMe}_3)(\text{tripod})$, where the rate for dissociative CO loss was approximately half the rate ($5.50 \times 10^{-5} \text{ s}^{-1}$ at 50°C) of the analogous process in $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$.

The stereoselectivity exhibited by reaction 4 is easily seen in the ^{13}C NMR spectrum of the initial product (Figure 4), where only the peak at 208.3 ppm is enhanced. Concomitantly, the ν_{CO} infrared spectrum indicates a portion of the terminal CO vibrations being shifted to lower frequency with no analogous shift occurring in the bridging CO region.¹² This observation supports our assumption that dissociation of the apical carbon monoxide ligands in $\text{Co}_4(\text{CO})_9(\text{tripod})$ stereoselectively occurs. Consistent with this assumption was that in the (tolu-

(12) The infrared spectrum of this species in tetrahydrofuran after ^{13}CO exchange exhibited peaks at 1977 (s), 1954 (vs), 1921 (w), 1909 (vw), 1773 (w), 1769 (m), and 1718 (m). On the other hand, the all ^{13}C -labeled derivative has ν_{CO} peaks at 1950 (s), 1919 (vs), 1902 (w), 1750 (w), 1730 (m), and 1678 (m) cm^{-1} .

Table IV. Temperature Dependence of the Rate of Reaction of $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod}) + ^{13}\text{CO}$

temp, $^\circ\text{C}$	$10^4 k, ^a \text{ s}^{-1}$	temp, $^\circ\text{C}$	$10^4 k, ^a \text{ s}^{-1}$
64.75	7.25 ± 0.75	49.50	1.20 ± 0.06
59.65	2.62 ± 0.43	44.82	0.63 ± 0.01
54.30	2.08 ± 0.14	39.50	0.34 ± 0.01

^a The rate of reaction is $1/2 k_{\text{obsd}}$, since there is selective dissociation of one of the two apical carbonyl groups. Error limits represent 90% confidence level.

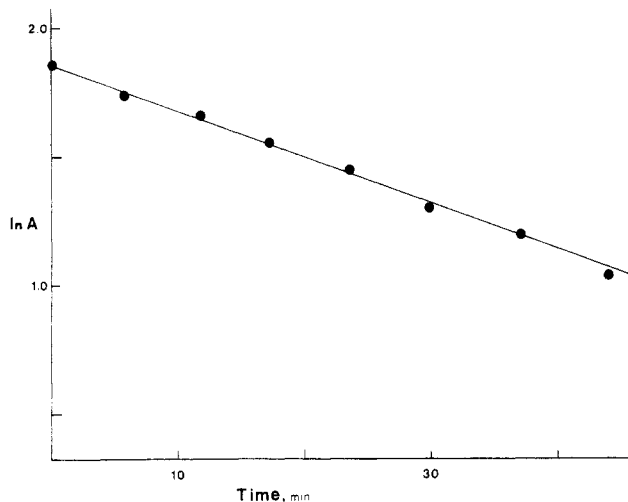


Figure 5. First-order rate plot for the disappearance of substrate for the reaction of $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ with ^{13}CO in THF at 49.5°C .

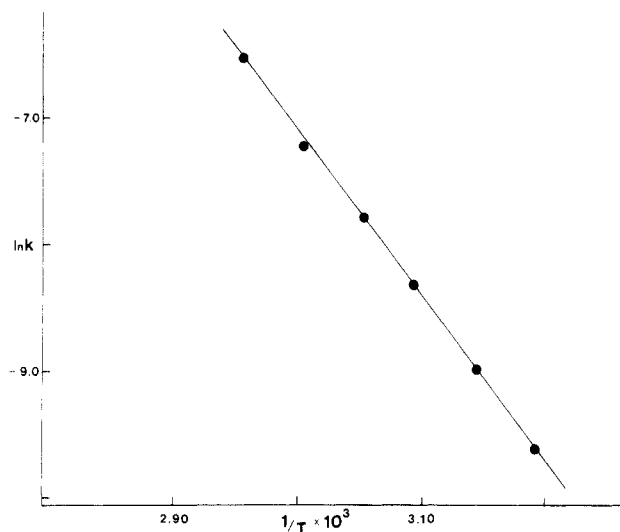


Figure 6. Arrhenius plot of $-\ln k$ vs. $1/T$ for the CO exchange reaction of $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ with ^{13}CO in THF.

ene) $\text{Co}_4(\text{CO})_8(\text{tripod})$ derivative, where there are no apical carbon monoxide ligands, no CO intermolecular exchange reactions were observed even at temperatures up to 160°C in decane. In addition, Osborn and co-workers⁶ have reported that the apical CO groups in $\text{Ir}_4(\text{CO})_9(\text{tripod})$ appear to undergo preferential intermolecular carbon monoxide exchange with ^{13}CO .

With the $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ molecule in hand we have the unique opportunity to unambiguously examine the effect of prior phosphine substitution at a cobalt center on the rate of CO dissociation from that particular metal center. Table IV contains temperature-dependent rate data for intermolecular carbon monoxide exchange reactions of the apical CO ligands in $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ with ^{13}CO . The exchange reaction is well-behaved as il-

Table V. Comparative Rates and Activation Parameters for Carbon Monoxide Displacement in $\text{Co}_4(\text{CO})_{12}$ Derivatives^a

complex	$10^4 k$, s^{-1}	ΔH^* , ^b kcal mol^{-1}	ΔS^* , ^b eu
$\text{Co}_4(\text{CO})_{12}$	3.27	24.9 ± 1.9	2.9 ± 5.9
$\text{Co}_4(\text{CO})_{11}\text{P}(\text{OMe})_3$	2.03	26.8 ± 1.0	8.2 ± 3.5
$\text{Co}_4(\text{CO})_{11}\text{P}(\text{OEt})_3$	3.37	27.5 ± 3.3	11.0 ± 10.2
$\text{Co}_4(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2$	4.77	27.1 ± 1.1	10.7 ± 3.7
$\text{Co}_4(\text{CO})_9(\text{tripod})$	1.71	24.2 ± 3.3	-0.52 ± 10.2
$\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$	0.355	24.7 ± 1.0	-0.83 ± 3.0

^a For the reaction $\text{Co}_4(\text{CO})_{12-n}\text{L}_n + (\text{excess})^{13}\text{CO} \rightarrow \text{Co}_4(^{13}\text{CO})_{12-n}\text{L}_n + ^{12}\text{CO}$ at 40 °C; values taken from ref 5 and 6. ^b Error limits represent 90% confidence limits.

illustrated by the representative plots of the data employed in computing rate constants and activation parameters for dissociative CO loss in this cobalt cluster species (Figures 5 and 6). Comparative rate constants and activation parameters for the system investigated herein, as well as those previously reported, are collected in Table V.

As is indicated in Table V, the rates of CO ligand dissociation from the apical cobalt sites of $\text{Co}_4(\text{CO})_9(\text{tripod})$ and $\text{Co}_4(\text{CO})_7(\text{dppm})(\text{tripod})$ are quite similar, with the

latter species being some 5 times slower. The activation parameters for the two processes are the same within experimental error. Hence, substitution of the CO ligands at a cobalt center in the tetranuclear cluster by a phosphine ligand only slightly retards the rate for dissociation of the remaining carbon monoxide groups from that cobalt center. This result serves to underscore our contention that the rate acceleration for CO dissociation displayed by some metal carbonyl clusters upon phosphorus donor ligand substitution¹³ is due, to a large part, to steric induction by virtue of the cluster's framework dictating spatial confrontations between ligands.¹⁴

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Halide, Hydride, Alkyl, and Dinitrogen Complexes of Bis(pentamethylcyclopentadienyl)hafnium^{†,‡}

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Bis(pentamethylcyclopentadienyl)hafnium dichloride ($\text{Cp}^*_2\text{HfCl}_2$, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) is obtained by treatment of HfCl_4 with lithium pentamethylcyclopentadienide in refluxing xylenes. The diiodide derivative is obtained from $\text{Cp}^*_2\text{HfCl}_2$ with BI_3 . The dihydrido derivative is obtained via treatment of $\text{Cp}^*_2\text{HfCl}_2$ with *n*-butyllithium under an atmosphere of H_2 . Treatment of $\text{Cp}^*_2\text{HfH}_2$ with alkyl halides (RX) affords either $\text{Cp}^*_2\text{HfX}_2$ or Cp^*_2HfHX and alkane depending on the nature of RX. The reaction of phenyllithium and $\text{Cp}^*_2\text{HfH}_2$ provides a novel route to the phenyl hydride derivative $\text{Cp}^*_2\text{HfH}(\text{Ph})$. The variance of the chemical shift of the hydride with X for complexes of the type $\text{Cp}^*_2\text{HfH}(\text{X})$ (X = hydride, alkyl, alkenyl, aryl, halide, alkoxide, amide) is discussed in terms of paramagnetic shielding. The dinitrogen complex $\{\text{Cp}^*_2\text{HfN}_2\}_2$ is obtained in modest yield by Na/K reduction of $\text{Cp}^*_2\text{HfI}_2$ and is isostructural with the zirconium analogue. $\text{Cp}^*_2\text{HfH}_2$ forms an adduct with CO. Under high pressures of CO, reductive elimination of H_2 and generation of $\text{Cp}^*_2\text{Hf}(\text{CO})_2$ is observed. Treatment of $\text{Cp}^*_2\text{Hf}(\text{CO})_2$ with H_2 (3 atm) at 125 °C cleanly affords $\text{Cp}^*_2\text{HfH}(\text{OCH}_3)$ and 1 equiv of CO; $\text{Cp}^*_2\text{Hf}(\text{CO})_2$ with Cp^*_2MH_2 (M = Zr, Hf) under H_2 yields *cis*-($\text{Cp}^*_2\text{HfH}(\text{Cp}^*_2\text{MH})(\mu\text{-OCH}=\text{CHO})$). Warming of $\text{Cp}^*_2\text{HfH}_2(\text{CO})$ under H_2 yields $\text{Cp}^*_2\text{HfH}(\text{OCH}_3)$, *cis*-($\text{Cp}^*_2\text{HfH}(\mu\text{-OCH}=\text{CHO})$), *trans*-($\text{Cp}^*_2\text{HfH}(\mu\text{-OCH}=\text{CHO})$), and ($\text{Cp}^*_2\text{HfH}(\mu\text{-OCH}_2\text{CH}_2\text{O})$). The relative yields of the individual products depend critically on reaction conditions, and the complexity of these reactions has thwarted all attempts to elucidate their mechanisms. Treatment of $\text{Cp}^*_2\text{HfH}_2$ with olefins of the formula $\text{CH}_2=\text{CRR}'$ or *tert*-butylacetylene gives alkyl hydrides $\text{Cp}^*_2\text{HfH}(\text{CH}_2\text{CHRR}')$ or the alkenyl hydride $\text{Cp}^*_2\text{HfH}(\text{CH}=\text{CHCMe}_3)$, which are very resistant to reductive elimination. Ethylene induces loss of alkane ($\text{CH}_3\text{CHRR}'$) or $\text{CH}_2=\text{CHCMe}_3$; however, with formation of the hafnacyclopentane derivative $\text{Cp}^*_2\text{Hf}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)$. Hydrogenation of the alkyl hydride complexes or $\text{Cp}^*_2\text{HfH}(\text{CH}_2=\text{CHCMe}_3)$ affords $\text{Cp}^*_2\text{HfH}_2$ and $\text{CH}_3\text{CHRR}'$ or $\text{CH}_3\text{CH}_2\text{CMe}_3$.

Introduction

The chemistry of organometallic derivatives of titanium and zirconium bearing two pentamethylcyclopentadienyl groups as ancillary ligands has proven to be rich and

varied. Permethyltitanocene and permethylzirconocene derivatives are often more stable than the ($\eta^5\text{-C}_5\text{H}_5$) analogues and offer the practical advantages of higher solubility and crystallinity. Moreover, the steric bulk of the pentamethylcyclopentadienyl group discourages oligomerization through single atom bridges (e.g., H, O, N), thus rendering permethylmetallocene derivatives monomeric. In view of the greater stability of the organometallic de-

[†] Dedicated to Earl L. Muetterties, respected scientist and friend.

[‡] Contribution No. 7048.