6718 *J. Am. Chem. Soc.* **1993,** *115,* 6718-6729

Hydride Ion Transfer from Carbon-Hydrogen Bonds to CS_2, COS, and CO_2. Synthesis, Reactivity, and Structure of (η^5-$C_6Me_nH_{7-n}$)Mn(CO)LL′ Derivatives

Daniel B. Snyder, Steven J. Schauer, Darrell P. Eyman,* Jeffrey L. Moler, and Jerry J. Weers

Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

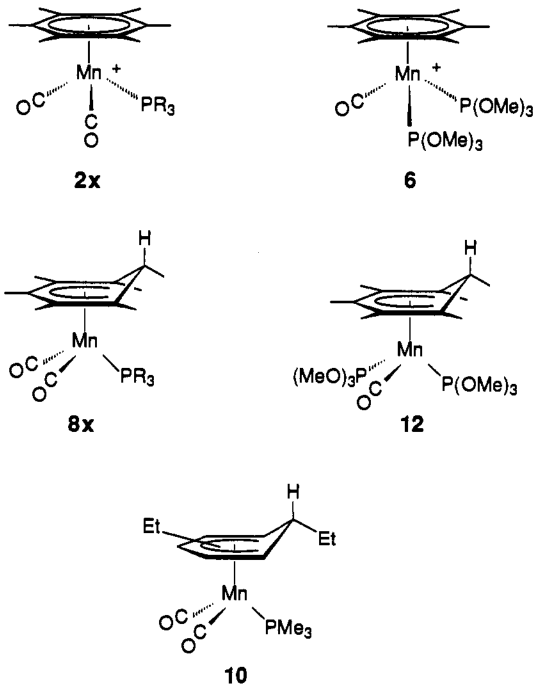
Received January 8, 1993

Abstract: A series of manganese complexes, *endo*-(η^5-$C_6Me_nH_{7-n}$)Mn(CO)LL′ (n = 0, 3, 6; L, L′ = CO, PR_3), transfer hydride ion to CS_2 and COS in THF to produce HCS_2^- and $HC(O)S^-$, respectively, and the cation [(η^6-$C_6Me_nH_{6-n}$)Mn(CO)LL′]$^+$. In THF, *endo*-(η^5-C_6Me_6H)Mn(CO)LL′ (where L = CO and L′ = $P(OMe)_3$ (**8c**); L and L′ = $P(OMe)_3$ (**12**)) transfers hydride ion to CO_2 to form HCO_2^-. The cationic precursors to these complexes, [(η^6-$C_6Me_nH_{6-n}$)Mn(CO)LL′]PF_6 (n = 0, 3, 6; L, L′ = CO, PR_3), are prepared by the reaction of [(η^6-$C_6Me_nH_{6-n}$)$Mn(CO)_3$]PF_6 with Me_3NO and PR_3. The addition of borohydride reagents to these cations results in formation of the cyclohexadienyl complexes *endo*-(η^5-$C_6Me_nH_{7-n}$)Mn(CO)LL′. Kinetic data for the reaction of *endo*-(η^5-$C_6Me_nH_{7-n}$)Mn(CO)LL′ with CS_2 under pseudo-first-order conditions are presented. The rate data correlate with the relative amounts of electron density on the metal, as reflected in the carbonyl stretching frequencies, ν_{CO}. The methylated cyclohexadienyl complexes increase in reactivity as the relative electron density in the complex increases. Non-methylated complexes (η^5-C_6H_7)$Mn(CO)_2L$ (L = CO, PR_3) show no reactivity with CS_2. Reactions of *endo*-(η^5-C_6Et_6H)$Mn(CO)_2PMe_3$ and two isomers of (η^5-$C_6Me_3H_4$)$Mn(CO)_2PMe_3$ with CS_2 are discussed. A stereoelectronic argument is presented to explain the 3 × 10^4 rate enhancement of hydride ion transfer accompanying phosphine substitutions for carbonyls. The structures of two complexes, determined by X-ray analysis, are reported: **8c**, orthorhombic, space group $P2_12_12_1$, a = 8.945 (6) Å, b = 12.911 (4) Å, c = 16.528 (6) Å, Z = 4, R_1 = 0.025 for 3861 averaged observed reflections; **12**, triclinic, space group $P\bar{1}$, a = 10.606 (4) Å, b = 14.056 (8) Å, c = 16.162 (7) Å, α = 92.45 (5)°, β = 97.27 (4)°, γ = 91.44 (6)°, Z = 4, R_1 = 0.055 for 4468 averaged observed reflections.

Introduction

There are a number of examples of carbon-hydrogen bonds acting as formal donors of hydride (e.g. the Cannizzaro reaction, Meerwein-Ponndorf-Verley-Oppenauer reactions, and enzymatic reductions involving the coenzyme NADH).[1] Murray[2] and co-workers have established a concerted one-step hydride ion transfer mechanism assisted by proton transfer in an NADH analog. We report a unique example of concerted one-step hydride ion transfer from a saturated carbon-hydrogen bond in a metal-coordinated π-carbocycle. Ordinarily, carbon-hydrogen bonds are relatively unreactive, but those activated by carbon-metal bonds or adjacent lone pairs can be good formal donors of hydride. Wuest[3] demonstrated that stannaadamantane reduces activated alkyl halides to hydrocarbons by a formal hydride transfer, but the mechanism was not proposed as hydride ion transfer. During NMR studies of *endo*-(η^5-C_6Me_6H)$Mn(CO)_3$ in CS_2, we discovered that the exo hydrogen transfers to CS_2 formally as H^-, to form HCS_2^- and (η^6-C_6Me_6)$Mn(CO)_3^+$. This is a report of studies directed at characterizing the scope and mechanism of this reaction. General structures of the η^6-arene and η^5-cyclohexadienyl manganese complexes used in these studies are illustrated in Chart I.

Chart I



2x **6** **8x** **12** **10**

The reaction of borohydride and aluminum hydride reagents with coordinated η^6-arene complexes to produce η^5-cyclohexadienyl complexes is a well-known method for arene activation and functionalization.[4,5] The addition of neutral or anionic nucleophiles to η^6-arene complexes of $[CoCp]^+$,[6] $[Cr(CO)_3]$,[7]

---

[1] (a) Bunting, J. W. *Bioorg. Chem.* **1991**, *19*, 456 and references therein. (b) Watt, C. I. F. *Adv. Phys. Org. Chem.* **1988**, *24*, 57 and references therein.

[2] Coleman, C. A.; Rose, J. G.; Murray, C. J. *J. Am. Chem. Soc.* **1992**, *114*, 9755.

[3] (a) Ducharme, Y.; Latour, S.; Wuest, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 1499. (b) Kobayashi, M.; Wuest, J. D. *Organometallics* **1989**, *8*, 2843. (c) Durcharme, Y.; Latour, S.; Wuest, J. D. *Organometallics* **1984**, *3*, 208. (d) Beauchamp, A. L.; Latour, S.; Olivier, M. J.; Wuest, J. D. *J. Organomet. Chem.* **1984**, *254*, 283. (e) Beauchamp, A. L.; Latour, S.; Olivier, M. J.; Wuest, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 7778.

[4] For reviews, see: (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047. (b) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, 525.

[5] Morken, A. M.; Eyman, D. P.; Wolff, M. A.; Schauer, S. J. *Organometallics* **1993**, *12*, 725.

[6] Tam, W.; Volhardt, K. P. C. *J. Organomet. Chem.* **1981**, *216*, 97.

0002-7863/93/1515-6718$04.00/0

$[Mn(CO)_3]^+$,[8] and $[FeCp]^+$ [9] results in the formation of η^5-cyclohexadienyl complexes with the nucleophile in the exo position. It is also known that the exo hydride in these cyclohexadienyl complexes is susceptible to removal by hydride abstracting agents such as Ph_3C^+ and $C_7H_7^+$, leading to formation of the η^6-arene cationic complexes.[10] Two mechanistic routes have been proposed for this reaction.[11] The first involves a one-step transfer of the hydride ion to the abstracting reagent. The second proceeds by a two-step process that initially involves a single-electron-transfer (SET) step followed by a hydrogen atom transfer. The corresponding endo hydride derivatives, exo isomers, are unreactive except under chemical oxidation conditions.[12] Spectroscopic data support the assertion that the exo carbon–hydrogen bond in η^5-cyclohexadienyl complexes is not typical for a hydrogen atom bound to carbon. For example, IR data for these complexes show that the carbon–hydrogen stretch for this bond is as much as 110 cm^{-1} lower than that for normal (2840–3000 cm^{-1}) hydrocarbon C–H bonds.[13,14]

Results and Discussion

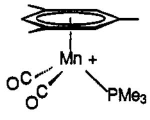
Preparation of $[(\eta^6\text{-arene})Mn(CO)LL']PF_6$ and *endo*-(η^5-cyclohexadienyl)Mn(CO)LL′ Derivatives. Preparation of the phosphine substituted complexes $[(\eta^6\text{-}C_6Me_nH_{6-n})Mn(CO)_2PR_3]PF_6$ was accomplished by a method similar to that used for the halide derivatives, $(\eta^6\text{-}C_6Me_6)Mn(CO)_2X$.[15] The addition of Me_3NO and PR_3 to $[(\eta^6\text{-}C_6Me_6)Mn(CO)_3]PF_6$ (**1**) in CH_2Cl_2 permitted isolation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2PR_3]PF_6$ (**2a–e**) after solution workup, eq 1. ^{1}H and ^{13}C NMR resonances for the arene portion of these complexes are similar to those of the starting material **1**. As anticipated, the carbonyl stretching frequencies observed in the IR spectra for these complexes (Table I) are much lower than those observed for **1**, because of increased electron density on manganese accompanying the phosphine substitution. $[(\eta^6\text{-}C_6H_6)Mn(CO)_2PR_3]PF_6$ (**3a,b**, eq 2) (R = Me, OMe), $[(\eta^6\text{-}C_6Me_3H_3)Mn(CO)_2PMe_3]PF_6$ (**4**), and $[(\eta^6\text{-}C_6Et_6)Mn(CO)_2PMe_3]PF_6$ (**5**) were prepared in a similar manner from the corresponding tricarbonyl derivatives, $[(\eta^6\text{-arene})Mn(CO)_3]PF_6$.

$$\underset{\mathbf{1}}{[(\eta^6\text{-}C_6Me_6)Mn(CO)_3]PF_6} \xrightarrow[PR_3]{Me_3NO} [(\eta^6\text{-}C_6Me_6)Mn(CO)_2PR_3]PF_6 \quad (1)$$

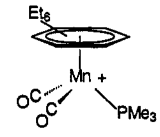
2a; R = Ph
2b: R = OPh
2c: R = OMe
2d: R = Me
2e: R = *n*-Bu

$$[(\eta^6\text{-}C_6H_6)Mn(CO)_3]PF_6 \xrightarrow[PR_3]{Me_3NO} [(\eta^6\text{-}C_6H_6)Mn(CO)_2PR_3]PF_6 \quad (2)$$

3a: R = Me
3b: R = OMe



4



5

The substitution of a single carbonyl in **1** is easily effected using the reagent Me_3NO. The decreasing electrophilicity of the carbonyl carbons upon phosphine substitution hinders removal of a second carbonyl from complex **2c**. Addition of excess Me_3NO and $P(OMe)_3$ to $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(OMe)_3]PF_6$ (**2c**) in CH_2Cl_2, followed by stirring at room temperature for 36 h, resulted in the formation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)(P(OMe)_3)_2]PF_6$ (**6**, eq 3) in low yields (10–30%). Higher yields (45–50%) of **6** were obtained when the reaction was permitted to proceed at 40 °C for 24 h with the addition of MeOH to solubilize Me_3NO. Complex **6** has two $P(OMe)_3$ ligands as evidenced by the appearance of a triplet at 3.71 ppm (J_{P-H} = 5.5 Hz) in the ^{1}H NMR spectrum, corresponding to the spin coupled splitting of the $P(OMe)_3$ methyls by two equivalent phosphorus nuclei. ^{1}H NMR spectra also indicate that the hexamethylbenzene ligand is η^6-coordinated. The solution infrared spectrum shows a single intense ν_{CO} at 1911 cm^{-1} which indicates the relatively high electron density in the complex. The same synthetic procedure was performed with **3b** to produce $[(\eta^6\text{-}C_6H_6)Mn(CO)(P(OMe)_3)_2]PF_6$ (**7**). A ν_{CO} at 1947 cm^{-1} is consistent with lower electron density on the metal due to lack of methylation of the aromatic ring.[16]

$$\mathbf{2c} \xrightarrow[P(OMe)_3]{Me_3NO} \underset{\mathbf{6}}{[(\eta^6\text{-}C_6Me_6)Mn(CO)(P(OMe)_3)_2]PF_6} \quad (3)$$

The addition of $(n\text{-}Bu)_4NBH_4$ to the cationic complexes **2a–e**, **3a,b**, and **5** in THF resulted in formation of the corresponding cyclohexadienyl complexes, *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2PR_3$ (**8a–e**, eq 4), $(\eta^5\text{-}C_6H_7)Mn(CO)_2PR_3$ (**9a,b**, eq 5), and *endo*-$(\eta^5\text{-}C_6Et_6H)Mn(CO)_2PMe_3$ (**10**, eq 6), respectively, as a result of hydride attack on an arene ring carbon from the exo side of the ring. The products, all yellow, were isolated in good yields (70–90%) after 10–15 min of stirring and workup of the reaction mixture. The ^{1}H NMR spectra confirmed that exo attack of the hydride on the arene had produced the endo isomers.[17] IR carbonyl stretching frequencies of the complexes are shifted to lower values as a result of the transformation from a cationic to a neutral species which elevates electron density on the manganese. The range of ν_{CO} for the cyclohexadienyl complexes **8a–e** (Table I) illustrates the effect of differences in phosphine ligand σ-donating abilities. IR spectroscopy has been a very effective tool in this work because the electron density on the metal dramatically influences the hydride ion transfer ability of these cyclohexadienyl complexes toward electrophiles. The reaction of $(n\text{-}Bu)_4NBH_4$ with $[(\eta^6\text{-}C_6Me_3H_3)Mn(CO)_2PMe_3]PF_6$ (**4**) resulted in formation of two isomers of $(\eta^5\text{-}C_6Me_3H_4)Mn(CO)_2PMe_3$ (**11a,b**, eq 7) by hydride attack on two inequivalent sites on the exo side of the coordinated η^6-mesitylene ligand. Pre-

---

(7) Semmelhack, M. F. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 36.

(8) (a) Chung, Y. K.; Sweigart, D. A.; Connelly, N. G.; Sheridan, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 2388. (b) Chung, Y. K.; Choi, H. S.; Sweigart, D. A.; Connelly, N. G. *J. Am. Chem. Soc.* **1982**, *104*, 4245. (c) Brookhardt, M.; Lukacs, A. *J. Am. Chem. Soc.* **1984**, *106*, 4161. (d) Brookhardt, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638. (e) Lamanna, W.; Brookhardt, M. *J. Am. Chem. Soc.* **1981**, *103*, 989.

(9) (a) Abd El-Aziz, A. S.; Lee, C. C.; Piorko, A.; Sutherland, R. G. *J. Organomet. Chem.* **1988**, *348*, 95. (b) Astruc, D. Tetrahedron Report No. 157. *Tetrahedron* **1983**, *39*, 4027.

(10) (a) Pauson, P. L. *J. Organomet. Chem.* **1980**, *200*, 207. (b) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* (*C*) **1968**, 2267. (c) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458. (d) Winkhaus, G.; Singer, H. *Z. Naturforsch. B* **1963**, *18*, 418.

(11) Mandon, D.; Astruc, D. *Organometallics* **1990**, *9*, 341.

(12) Snyder, D. B.; Morken, A. M.; Schauer, S. J.; Wolff, M. A.; Eyman, D. P., manuscript in preparation.

(13) (a) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* (*C*) **1969**, 2024. (b) Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950.

(14) Snyder, D. B.; Eyman, D. P.; Mundt, D., manuscript in preparation.

(15) (a) Bernhardt, R. J.; Wilmoth, M. A.; Weers, J. J.; Labrush, D. M.; Eyman, D. P. *Organometallics* **1986**, *5*, 883. (b) Bernhardt, R. J.; Eyman, D. P. *Organometallics* **1984**, *3*, 1445.

(16) Brill, T. B.; Kotlar, A. J. *Inorg. Chem.* **1974**, *13*, 470.

(17) Endo and exo isomers can be differentiated by the ^{1}H NMR shift of the endo or exo methyl bound to the saturated carbon. (a) Munro, G. A. M.; Pauson, P. L. *Isr. J. Chem.* **1976**, *15*, 258. (b) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807. (c) Wilmoth, M. A.; Bernhardt, R. J.; Eyman, D. P. *Organometallics* **1986**, *5*, 2559.

sumably for steric reasons,[4,18] as well as enhanced electrophilicity, the preferred site of attack by hydride is on a non-methylated carbon, and its product constitutes 94% of the isomeric mixture.

$$\mathbf{2a–e} \xrightarrow{BH_4^-} (\eta^5\text{-}C_6Me_6H)Mn(CO)_2PR_3 \quad (4)$$

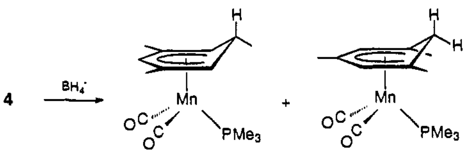
8a: R = Ph
8b: R = OPh
8c: R = OMe
8d: R = Me
8e: R = *n*-Bu

$$\mathbf{3a,b} \xrightarrow{BH_4^-} (\eta^5\text{-}C_6H_7)Mn(CO)_2PR_3 \quad (5)$$

9a: R = OMe
9b: R = Me

$$\mathbf{5} \xrightarrow{BH_4^-} endo\text{-}(\eta^5\text{-}C_6Et_6H)Mn(CO)_2PMe_3 \quad (6)$$

10



(7)

11a **11b**

Addition of excess borohydride reagent to the more electron rich complexes **6** and **7** resulted in the slow formation of the cyclohexadienyl complexes, *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)(P(OMe)_3)_2$ (**12**) and $(\eta^5\text{-}C_6H_7)Mn(CO)(P(OMe)_3)_2$ (**13**). The borohydride reductions were much slower compared to those involving the mono-phosphine derivatives, and the isolated yields ranged from 20 to 30% for **12**. The addition of a stronger hydride donor, $LiB(CH_2CH_3)_3H$, to **6** resulted in a higher rate of formation of **12**, but IR spectra indicated only 50% conversion of **6** to **12** even after addition of excess borohydride. The formation of a cyclohexadienyl species was confirmed by a decrease in ν_{CO} of the single carbonyl and by the appearance of ^1H and ^{13}C NMR resonances characteristic of η^5-cyclohexadienyls. Complex **13** is stable at room temperature in solution and in the solid state over several hours, while **12** decomposes at room temperature in THF solution after 2 h. Hexane solutions of **12** are stable enough to permit use for several hours at room temperature. Carbonyl stretching bands at 1850 and 1861 cm^{-1} for **12** and **13**, respectively, indicate very high electron density on the manganese atom in these complexes.

Low reaction yields for the synthesis of complexes **6** and **12** prompted the search for an alternate synthetic route. The reaction of *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2P(OMe)_3$ (**8c**) with 2.5 equiv of $P(OMe)_3$ under photolytic conditions (254 nm) for 8 h at room temperature in THF increased the isolated yield of **12** to 44%. This method is similar to the one used by Rieger[19] and Sweigart[20] in the preparation of *exo*-$(\eta^5\text{-}C_6H_6Ph)Mn(CO)(PR_3)_2$ derivatives.

Table I. CO Stretching Frequencies for Manganese Complexes Used in This Study

compound	ν_{CO}[a]	ref
$(\eta^6\text{-}C_6Me_6)Mn(CO)_3^+$ (**1**)	2059, 2001	17b
$(\eta^6\text{-}C_6H_6)Mn(CO)_3^+$	2079, 2016	17b, 31
$(\eta^6\text{-}C_6Me_6)Mn(CO)_2PPh_3^+$ (**2a**)	1976, 1925	
$(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(OPh)_3^+$ (**2b**)	1995, 1948	
$(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(OMe)_3^+$ (**2c**)	1990, 1941	
$(\eta^6\text{-}C_6Me_6)Mn(CO)_2PMe_3^+$ (**2d**)	1970, 1922	
$(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(n\text{-}Bu)_3^+$ (**2e**)	1969, 1918	
$(\eta^6\text{-}C_6H_6)Mn(CO)_2PMe_3^+$ (**3a**)	1993, 1947	
$(\eta^6\text{-}C_6H_6)Mn(CO)_2P(OMe)_3^+$ (**3b**)	2013, 1968	
$(\eta^6\text{-}C_6Me_3H_3)Mn(CO)_2PMe_3^+$ (**4**)	1984, 1935	
$(\eta^6\text{-}C_6Et_6)Mn(CO)_2PMe_3^+$ (**5**)	1977, 1927	
$(\eta^6\text{-}C_6Me_6)Mn(CO)(P(OMe)_3)_2^+$ (**6**)	1911	
$(\eta^6\text{-}C_6H_6)Mn(CO)(P(OMe)_3)_2^+$ (**7**)	1947	
$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2PPh_3$ (**8a**)	1913, 1865	
$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2P(OPh)_3$ (**8b**)	1941, 1881	
$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2P(OMe)_3$ (**8c**)	1924, 1865	
$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2PMe_3$ (**8d**)	1910, 1847	
$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2P(n\text{-}Bu)_3$ (**8e**)	1908, 1846	
$(\eta^5\text{-}C_6H_7)Mn(CO)_2PMe_3$ (**9a**)	1926, 1862	
$(\eta^5\text{-}C_6H_7)Mn(CO)_2P(OMe)_3$ (**9b**)	1944, 1881	
$(\eta^5\text{-}C_6Et_6H)Mn(CO)_2PMe_3$ (**10**)	1910, 1846	
$(\eta^5\text{-}C_6Me_3H_4)Mn(CO)_2PMe_3$ (**11**)	1915, 1852	
$(\eta^5\text{-}C_6Me_6H)Mn(CO)(P(OMe)_3)_2$ (**12**)	1850	
$(\eta^5\text{-}C_6H_7)Mn(CO)(P(OMe)_3)_2$ (**13**)	1861	
$(\eta^5\text{-}C_6Me_6H)Mn(CO)_3$ (**14**)	1995, 1915	17b
$(\eta^5\text{-}C_6H_7)Mn(CO)_3$ (**23**)	2013, 1934	17b, 31
$(\eta^6\text{-}C_6Me_6)Mn(CO)_2SC(S)H$ (**18**)	1969, 1921	23
$(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(O)(OMe)_2$ (**19**)	1964, 1914	
$(\eta^6\text{-}C_6Me_6)Mn(CO)(P(OMe)_3)$- $(P(O)(OMe)_2)$ (**22**)	1888	

[a] Spectra obtained in THF.

Reactions of *endo*-(η^5-cyclohexadienyl)Mn(CO)LL′ with CS_2. Reaction of *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_3$ (**14**) with liquid CS_2 at room temperature over a period of 7–10 days or at elevated temperatures over a period of 2 h resulted in a slow color change from yellow to red and the precipitation of a mixture of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_3]S_2CH$ (**15**) and *exo*-$(\eta^5\text{-}C_6Me_6SC(S)H)Mn(CO)_3$ (**16**) as red solids (eq 8). The pseudo-first-order rate constant for the disappearance of **14** at 28 °C was determined to be 4.0×10^{-6} s^{-1} (Table II). Complexes **15** and **16** were shown by IR and ^1H NMR spectra to exist as an equilibrium mixture in solution. This system displayed a Le

$$\underset{\mathbf{14}}{endo\text{-}(\eta^5\text{-}C_6Me_6H)Mn(CO)_3} \xrightarrow{CS_2} \underset{\mathbf{15}}{[(\eta^6\text{-}C_6Me_6)Mn(CO)_3]S_2CH} \rightleftarrows \underset{\mathbf{16}}{exo\text{-}(\eta^5\text{-}C_6Me_6SC(S)H)Mn(CO)_3} \quad (8)$$

Châtelier shift when either **1** or KS_2CH was added to a CH_2Cl_2 solution of the mixture. In an independent experiment, the same equilibrium mixture was observed upon the addition of KS_2CH to a CH_2Cl_2 solution of **1**. The value of the equilibrium constant for this process ($K_{eq} = [(\eta^6\text{-}C_6Me_6)Mn(CO)_3^+][S_2CH^-]/[(\eta^5\text{-}C_6Me_6SC(S)H)Mn(CO)_3]$), determined using IR spectroscopy in CH_2Cl_2, is 2.0×10^{-3}. The carbonyl region of the IR spectrum displays bands at 2058 and 2004 (sh) cm^{-1} assigned to **15** and at 1996 and 1916 cm^{-1} assigned to **16**. These are similar to the bands for **1** and **14**, respectively (Table I). The ^1H NMR spectrum displays broad peaks at δ 2.61 and 11.40 ppm. The former resonance is attributed to the methyl groups on the C_6 rings of **15** and **16**, which would be in fast exchange between η^6- and η^5-coordination. The latter resonance is assigned to the dithioformate proton. A low-temperature ^1H NMR (−95 °C) spectrum did not display the anticipated four separate signals arising from inequivalent methyl groups in cyclohexadienyl complexes, but rather it displayed only a slight broadening of the methyl group peaks observed at room temperature. This equilibrium is similar to that reported for $(\eta^6\text{-arene})Mn(CO)_3^+$ complexes when PR_3 or CN^- is added.[18b] In these cases, the phosphine or cyanide nucleophiles reversibly attack exo positions on the arene ring forming cyclohexadienyl complexes. The values for the equilibrium constants decrease with increasing methylation of the coordinated arenes.

---

[18] (a) Walker, P. J. C.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1973**, 622. (b) Kane-Maguire, L. A.; Sweigart, D. A. *Inorg. Chem.* **1979**, *18*, 700.

[19] Pike, R. D.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 3913.

[20] Connelly, N. G.; Freeman, M. J.; Orpen, A. G.; Sheehan, A. R.; Sheridan, J. B.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1019.

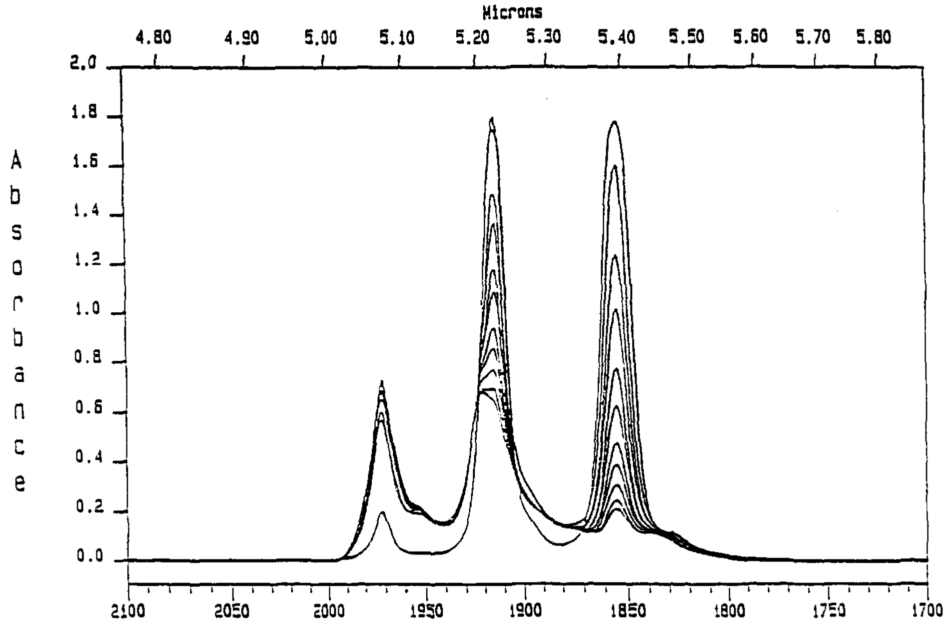


Figure 1. Infrared spectral changes for the reaction between *endo*-(η^5-C_6Me_6H)Mn(CO)$_2$PPh$_3$ and CS$_2$.

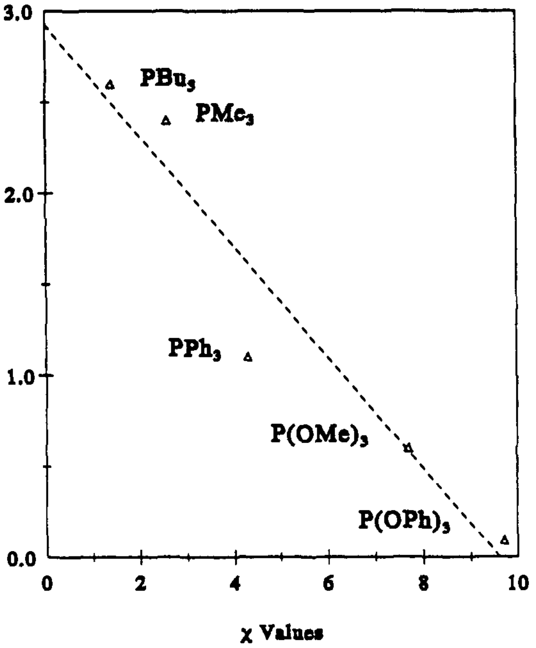


Figure 2. Rate constants vs substituent χ-values for the reaction of *endo*-(η^5-C_6Me_6H)Mn(CO)$_2$PR$_3$ complexes (**8a–e**) with CS$_2$.

Reaction of the phosphine substituted cyclohexadienyl complexes **8a,b,d,e** with CS$_2$ at room temperature resulted in the quantitative formation of [(η^6-C_6Me_6)Mn(CO)$_2$PR$_3$]S$_2$CH (**17a–b,d–e**) derivatives (eq 9) as indicated by solution IR and ^{1}H NMR spectra. These cationic complexes display spectra similar to the original complexes [(η^6-C_6Me_6)Mn(CO)$_2$PR$_3$]PF$_6$ (**2a–b,d–e**) except for the presence of dithioformate (HCS$_2^-$) as the counterion. Pseudo-first-order rate constants for the reactions in CS$_2$, determined at 28 °C, are contained in Table II. Values of k_{obs} were obtained by monitoring the decrease of a carbonyl stretch in the IR spectrum of the starting material. A representative example of the spectra recorded during a reaction is shown in Figure 1. The observed rate constants were found to be dependent on the relative σ-donating ability of the coordinated phosphine, with P(n-Bu)$_3$ (**8e**) producing the fastest reaction and P(OPh)$_3$ (**8b**) the slowest. This indicates that the reaction rates are enhanced by increased electron density on the metal center resulting from σ-donation from the phosphine. The observed dependence is also consistent with the lower rate constant observed for **14**, which has lower electron density than the phosphine containing derivatives. Figure 2, a plot of the rate constants (k) versus electronic factors (Tolman χ-values)[21a] for the phosphines, shows a reasonable correlation between reaction rates and the relative electron density on the metal. This type of linear correlation between electronic and steric characteristics for phosphines versus reactivity data is also observed for many other metal complexes.[21] Reactivity and redox potentials can be affected by use of a variety of phosphines which change either the electron density or steric bulk on the metal by varying basicity or cone angles, respectively.[22] For the reactions shown in eq 9, the rate

$$\mathbf{8a\text{–}e} \xrightarrow{CS_2} [(\eta^6\text{-}C_6Me_6)Mn(CO)_2PR_3]^+\ S_2CH^- \qquad (9)$$

17a: R = Ph
17b: R = OPh
17c: R = OMe
17d: R = Me
17e: R = n-Bu

constants are thought to be influenced solely by electronic factors originating in the phosphine, because the phosphine is spatially isolated from the reaction site and no correlation is observed between phosphine cone angles and the rate constants. Negligible differences in pseudo-first-order rate constants for the reactions obtained in THF and hexane suggest there is no pre-equilibrium involving dissociation of hydride ion from the cyclohexadienyl.

Complexes **17a–b,d–e** were isolated from liquid CS$_2$. These species are unstable due to subsequent reactions that occur between the cationic manganese species and the HCS$_2^-$ counterion. The products formed are dependent on the type of phosphine present. Electronic factors as well as steric requirements of the phosphines play a role in determining the reaction pathway after initial formation of HCS$_2^-$ and **17**. Complexes **17a** and **17b** with phosphines PPh$_3$ and P(OPh)$_3$, respectively, both form the

---

(21) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Bartik, T.; Himmler, T.; Schulte, H. G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *27*, 29. (c) Clark, H. C. *Isr. J. Chem.* **1976/77**, *15*, 210.

(22) (a) Liu, H.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758. (b) Rahman, M. M.; Liu, H.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1. (c) Rahman, M. M.; Liu, H.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650. (d) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981.

previously characterized (η^6-C_6Me_6)Mn(CO)$_2$SC(S)H[23] (**18**) and free phosphine after an additional 2 h of stirring at room temperature (eq 10). The large cone angles of these two phosphines enhance their lability. Complex **17c** (R = OMe) could not be detected in the reaction of **8c** with CS_2 due to a subsequent fast reaction of the dithioformate ion with (η^6-C_6Me_6)-Mn(CO)$_2$P(OMe)$_3^+$ to produce (η^6-C_6Me_6)Mn(CO)$_2$P(O)(OMe)$_2$ (**19**). This is the result of nucleophilic attack by HCS_2^- on a trimethylphosphite carbon in a Michaelis–Arbuzov-like dealkylation reaction (eq 11).[24] The resulting methyl ester of dithioformate, $HC(S)SCH_3$, was detected by GC-MS with a *m*/*z* peak of 92. No further reactivity was observed between **19**, a dimethyl phosphonate complex, and CS_2. Complexes **8d** and **8e** (R = Me and *n*-Bu, respectively) react with CS_2 to produce **17d** and **17e**, which do not undergo further reactions that displace the phosphine. No evidence is seen in the IR or NMR spectra for the formation of cyclohexadienyl species by attack of the HCS_2^- on a ring carbon as was observed in the formation of **16**. This is probably due to reduced electrophilicity at the arene ring carbon atoms resulting from carbonyl replacement by phosphines. Solutions of **17d**, however, slowly reacted to form other products over a period of 1–2 days at room temperature probably by way of disproportionation and other decomposition reactions. Most of the products did not contain a coordinated hexamethylbenzene ligand, but they did contain carbonyls and a dithioformate ligand. The only product that was isolated (24% yield) and identified had the formula Mn(CO)$_2$(PMe$_3$)$_2$SC(S)H (**20**) as indicated by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies and HRMS (eq 12). Similarly, Mn(CO)$_2$(P(*n*-Bu)$_3$)$_2$SC(S)H (**21**) was isolated as a minor product in the reaction that formed **17e**.

$$\mathbf{17a,b} \rightarrow (\eta^6\text{-}C_6Me_6)Mn(CO)_2SC(S)H + PR_3 \quad (10)$$

$$\mathbf{17c} \rightarrow (\eta^6\text{-}C_6Me_6)Mn(CO)_2P(O)(OMe)_2 + HC(S)SCH_3 \quad (11)$$

$$\mathbf{17d} \rightarrow Mn(CO)_2(PMe_3)_2SC(S)H + \text{other products} \quad (12)$$

^{1}H NMR studies of **8d** indicated that hydride ion transfer to CS_2 is not reversible as shown by lack of formation of a cyclohexadienyl species upon addition of KS_2CH to **2d**.[25] The deuterium kinetic isotope effect, $k_{H/D}$, for the hydride ion transfer step for complex **8d** was determined to be 3.2 in CS_2 at 28 °C. Small primary kinetic isotope effects have been associated with both unsymmetrical hydrogen transfers and nonlinear atomic arrays.[26] The $k_{H/D}$ observed here and the observation of a monoatomic variation of the carbon–hydrogen bond stretch suggest C–H bond polarization is occurring.

IR data indicate significant[27] lowering of the saturated carbon–exo hydrogen stretching frequencies in the endo isomers which varies as a function of phosphine substitution.[14] There is no detectable reduction in the observed rate constants when 9,10-dihydroanthracene is added to the reaction mixtures. In addition, an ESR study at 77 K of the reaction of **8c** in CS_2 indicated no radical species are present in the reaction mixture. These results indicate that there is no intermediate radical species involved in the reaction, and they suggest that there is no involvement of an initial SET from the manganese species.[28]

Table II. Pseudo-First-Order Rate Constants and Relative Reactivity of (η^5-$C_6R_nH_{7-n}$)Mn(CO)LL′ with CS_2

complex	*n*	R	L	L′	k(s^{-1})	rel rate
14	6	Me	CO	CO	4.0×10^{-6}	1
8b	6	Me	CO	P(OPh)$_3$	9.4×10^{-5}	23
8c	6	Me	CO	P(OMe)$_3$	6.0×10^{-4}	149
8a	6	Me	CO	PPh$_3$	1.1×10^{-3}	280
8d	6	Me	CO	PMe$_3$	2.4×10^{-3}	593
8e	6	Me	CO	P(*n*-Bu)$_3$	2.6×10^{-3}	640
12	6	Me	P(OMe)$_3$	P(OMe)$_3$	N.A.[a]	>30000
10	6	Et	CO	PMe$_3$	2.4×10^{-5}	6.1
11a	3[b]	Me	CO	PMe$_3$	N.A.[c]	
11b	3[d]	Me	CO	PMe$_3$	N.R.[e]	
23	0		CO	CO	N.R.	
9a	0		CO	PMe$_3$	N.R.	
9b	0		CO	P(OMe)$_3$	N.R.	
13	0		P(OMe)$_3$	P(OMe)$_3$	3.0×10^{-5}	7.6

[a] Reaction was too fast to determine the pseudo-first-order rate constant, but the relative rate is estimated to be greater than 3×10^4. [b] Isomer with methyls in positions 1, 3, and 5. [c] The rate constant was not determined because of the low concentration of this isomer. [d] Isomer with methyls in positions 2, 4, and 6. [e] N.R. indicates no reaction occurred.

A mechanism involving SET followed by hydrogen atom transfer is further ruled out by consideration of the thermodynamics of electron transfer in this system determined by cyclic voltammetry studies.[14] Comparison of the $E_{1/2}$ values of **14** and **12** to those obtained for CS_2 and CO_2 indicates that hydride ion transfer is the most probable mechanism.[29] By contrast, Astruc[11] reported that intermediate radical species are produced in the reaction of (η^5-C_6Me_6H)(η^5-C_6Me_6R)Fe with Ph_3C^+, as a result of an initial SET step. In contrast, radical intermediates in the reactions of **14** and **8c** with halocarbons have been detected by ESR studies.[12] Transfer of hydride ion from the saturated carbon of the cyclohexadienyl moiety is also isomer specific. The corresponding exo isomers, *exo*-**14**, *exo*-**8c**, and *exo*-**12**, exhibit no reaction with CS_2.[14] The lack of reactivity of the exo isomers with CS_2 suggests there is no initial SET mechanism involved with the endo isomers because *exo*-**12** and *endo*-**12** possess nearly the same $E_{1/2}$ values.[30]

The observation of enhanced hydride ion transfer rates of the cyclohexadienyl complexes upon substitution of a phosphine ligand for a carbonyl led us to investigate the disubstituted phosphine species **12**. The observed low yields in conversion of **6** to **12** using borohydrides suggested that **12** would be a very strong hydride ion donor. As anticipated, **12** reacted completely with CS_2 within 10–20 s after addition. Quantitative formation of a single product possessing a ν_{CO} at 1888 cm^{-1} resulted. ^{1}H and ^{31}P NMR spectra indicated that the dimethyl phosphonate derivative, (η^6-C_6Me_6)Mn(CO)(P(OMe)$_3$)(P(O)(OMe)$_2$) (**22**), had formed. As in the formation of **19**, complex **22** apparently resulted from nucleophilic attack of the dithioformate ion on a phosphite methyl to give the Michaelis–Arbuzov-like reaction products (eq 13). The rate for this reaction was too great to determine the pseudo-first-order rate constant. However, the reaction went to completion in less than 20 s; which leads to an estimated lower rate limit with a magnitude greaterthan 3×10^4 relative to the rate for **14** under pseudo-first-order conditions.

---

[23] Schauer, S. J.; Eyman, D. P.; Bernhardt, R. J.; Wolff, M. A.; Mallis, L. M. *Inorg. Chem.* **1991**, *30*, 570.

[24] Brill, T. B.; Landon, S. J. *Chem. Rev.* **1984**, *84*, 577.

[25] Schauer, S. J. Ph.D. Thesis, University of Iowa, 1990.

[26] Stewart, R. *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1976; Vol. 2.

[27] ν_{C-H} = 2798 and 2729 cm^{-1} for **14** and **12**, respectively.

[28] The radical anion $CS_2^{\bullet-}$ has been characterized by ESR studies (Lea, J. S.; Symons, C. R. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84(4)*, 1181 and references therein).

[29] $E_{1/2}$ values for **14** and **12** are 1.09 and 0.04 V, respectively, with reference to the saturated calomel electrode (SCE), at a platinum working electrode, with 0.1 M [(*n*-Bu)$_4$N]BF$_4$ in CH_2Cl_2 as the supporting electrolyte. Under the same conditions the $E_{1/2}$ value for CS_2 was determined as −1.92 V vs SCE. The $E_{1/2}$ for CO_2 is −2.21 V vs SCE as determined in DMF (see: (a) Gressin, J. C.; Michelet, D.; Nadjo, L.; Savéant, J.-M. *Nouv. J. Chem.* **1979**, 545. (b) Amatore, C. A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 5021. (c) Lamy, E.; Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1977**, *78*, 403. (d) Hori, Y.; Murata, A.; Kikuchi, K.; Suzuki, S. *J. Chem. Soc., Chem. Commun.* **1987**, *13*, 728).

[30] $E_{1/2}$ values of *endo*-**12** and *exo*-**12** are virtually the same, 0.04 and 0.03 V, respectively, vs SCE.

$$\mathbf{12} \xrightarrow{CS_2} [(\eta^6\text{-}C_6Me_6)Mn(CO)(P(OMe)_3)_2]S_2CH \rightarrow (\eta^6\text{-}C_6Me_6)Mn(CO)(P(OMe)_3)(P(O)(OMe)_2) + HC(S)SCH_3 \quad (13)$$

The reaction of (η^5-C_6H_7)Mn(CO)$_3$[17b,31] (**23**) with CS_2 was studied to evaluate the hydride ion transfer reactivity of non-methylated cyclohexadienyl analogues. No reaction other than slow decomposition of the starting material to species lacking an arene and carbonyls was observed over a 1-week period at room temperature, or over a 24-h period at 100 °C. The same result was observed for two mono-phosphine derivatives, (η^5-C_6H_7)Mn(CO)$_2$PMe$_3$ (**9a**) and (η^5-C_6H_7)Mn(CO)$_2$P(OMe)$_3$ (**9b**) (eq 14). The only non-methylated cyclohexadienyl complex observed to react with CS_2 was (η^5-C_6H_7)Mn(CO)(P(OMe)$_3$)$_2$ (**13**). Surprisingly, the pseudo-first-order rate constant for the reaction of **13** with CS_2 was even lower than for the permethylated cyclohexadienyl mono-phosphine derivatives **8a–e**.

$$(\eta^5\text{-}C_6H_7)Mn(CO)_2L + CS_2 \xrightarrow{\Delta} N.R. \quad (14)$$

23: L = CO
9a: L = PMe$_3$
9b: L = P(OMe)$_3$

The non-methylated derivatives, **23** and **9a–b**, display ν_{CO} that are approximately 20–25 wavenumbers higher than their corresponding permethylated analogues. This trend is consistent with decreasing carbonyl stretching frequencies in the IR spectra of other π-carbocycles as a function of increasing alkylation about the coordinated arene.[18b] The rate constants for **8a–e** and **14** (Table II) clearly indicate that the ability of the cyclohexadienyl to transfer hydride ion to CS_2 is enhanced by phosphine substitution at the metal. However, this does not fully explain the lack of reactivity for **9a**, **9b**, and **23**, because the ν_{CO} for **9a** and **9b** appear at frequencies lower than those for **14**, which does display some reactivity with CS_2. This suggests that the presence of the methyl groups on the coordinated arene enhances the reactivity.

As a further test of the effect of arene methylation on the reactivity of the cyclohexadienyl moiety, (η^5-$C_6Me_3H_4$)Mn(CO)$_2$PMe$_3$ (**11**) was synthesized using the mesitylene derivative [(η^6-$C_6Me_3H_3$)Mn(CO)$_2$PMe$_3$]PF$_6$ (**4**). Two isomers were produced in the reaction, one with the exo hydride on a tertiary carbon (**11a**) (6%) and one with the hydride on a secondary carbon (**11b**) (94%). Addition of CS_2 to this isomeric mixture at room temperature resulted in relatively fast and complete reaction of **11a** to produce [(η^6-$C_6Me_3H_3$)Mn(CO)$_2$PMe$_3$]S$_2$CH (**24a**). No reaction was observed after 24 h, however, with **11b** and CS_2. This result indicates that the hydride ion transfer ability of these compounds is influenced more by the alkylation of the ring carbon bearing the exo hydride than by the extent of arene alkylation.

The reaction of **10** with CS_2 to form [(η^6-C_6Et_6)Mn(CO)$_2$PMe$_3$]S$_2$CH (**25**) has a much lower rate constant than the analogous hexamethyl derivative **8d** (eq 15). This may be

$$endo\text{-}(\eta^5\text{-}C_6Et_6H)Mn(CO)_2PMe_3 + CS_2 \rightarrow [(\eta^6\text{-}C_6Et_6)Mn(CO)_2PMe_3]S_2CH \quad (15)$$

attributable to steric requirements of the ethyl groups hindering the approach of the electrophile. This observation suggests a bimolecular or concerted nature for this reaction. Decreased reactivity of other complexes possessing hexaethylbenzene has been attributed to the steric requirements of the ethyl groups.[32] Additional results to be presented in a subsequent paper support the proposal that hydride ion transfer proceeds in a bimolecular fashion.[14]

Reactions of (η^5-cyclohexadienyl)Mn(CO)LL′ with COS and CO_2. The reaction of **14** with COS (40 psi) at 70 °C over a period of 7 days resulted in a slow color change from yellow to orange-red, and a minor amount of **15** and **16** was isolated. Unreacted **14** and hexamethylbenzene were the major species recovered in this reaction. The formation of **15** and **16**, instead of [(η^6-C_6Me_6)Mn(CO)$_3$]S(O)CH, suggests that COS disproportionates to CS_2 and CO_2, and/or HC(O)S$^-$ disproportionates to HCS_2^- and HCO_2^- under thermolysis conditions. The fact that dithioformate is more stable than monothioformate or formate is consistent with the observed results.[33] Complexes **8a–b,d–e** transferred their exo hydride ion to COS (40 psi) at 70 °C more slowly than to CS_2 as expected with a less reactive electrophile.[33] The reaction of **8a,d–e** with COS resulted in formation of the cationic complexes [(η^6-C_6Me_6)Mn(CO)$_2$PR$_3$]S(O)CH (**27a,d–e**) as the major product indicated by solution IR and by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. These cationic complexes are spectroscopically similar to **17a,d–e**. Complexes **17a–b** were also isolated as minor products in the reactions of **8a–b** with COS, indicating that disproportionation of COS and arene loss had occurred. The ^{1}H NMR spectrum indicated the presence of the monothioformate counterion, HC(O)S$^-$, at 10.52 ppm for **27d**. The ^{13}C NMR resonance of HC(O)S$^-$ for **27d** is at 199.3 ppm. A heteronuclear multiple quantum coherence 2-D experiment correlated this carbon resonance with the proton resonance of HC(O)S$^-$ in **27d**. Darensbourg[34] observed ^{1}H and ^{13}C NMR (CD_3CN) resonances of 10.52 and 198.3 ppm, respectively, for the pentacarbonylchromium monothioformate anion, Cr(CO)$_5$SC(O)H$^-$. The reaction of **8d–e** with COS gave **20** and **21**, respectively, as minor products. As in the reaction with CS_2, the initial product of the reaction of **8c** underwent a Michaelis–Arbuzov-like dealkylation reaction to quantitatively form **19** after 3 days at ambient temperature. The methylated product, HC(O)SCH$_3$, which resulted from nucleophilic attack of HC(O)S$^-$ on the trimethyl phosphite carbon was detected by GC-MS (m/z = 76). The reaction of COS with **12** at ambient temperature resulted in complete formation of **22** and HC(O)SCH$_3$ after 2.5 h. Complex **8c** quantitatively transferred hydride ion to CO_2 (800 psi) to form HCO_2^- as confirmed by identification of **19** and HC(O)OCH$_3$ (m/z = 60) after 6 days at 100 °C. The significant enhancement of the hydride ion transfer ability of **12** relative to the mono-phosphine complex **8c** is illustrated by the reaction of **12** with CO_2. Under the same conditions, **12** reacted completely to transfer hydride ion to CO_2 in 10.5 h as evidenced by quantitative formation of the Michaelis–Arbuzov-like dealkylation reaction products, **22** and HC(O)OCH$_3$.

Stereoelectronic Requirements in Hydride Ion Transfer Reactions of *endo*- and *exo*-(η^5-$C_6Me_{n-7}H_n$)Mn(CO)LL′ Derivatives. A large body of experimental evidence has been accumulated which shows that the reactivity of most types of organic molecules depends upon the relative orientation of particular electron pairs, bonded and nonbonded.[35] Consideration of the concept of stereoelectronic effects[35] in hydride ion transfer from the saturated carbon–hydrogen bond of *endo*-(η^5-$C_6Me_{n-7}H_n$)Mn(CO)LL′ derivatives enhances our understanding of this unique reaction.

---

(31) (a) Winkhaus, G.; Wilkinson, G. *Proc. Chem. Soc.* **1960**, 311.

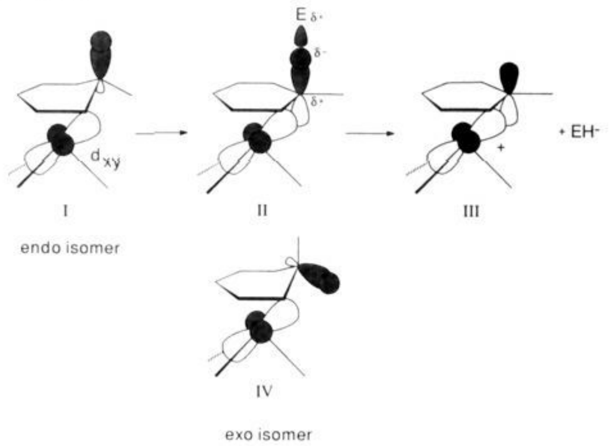
(32) (a) Meng, Q.; Huang, Y.; Ryan, W. J.; Sweigart, D. A. *Inorg. Chem.* **1992**, *31*, 4051. (b) Blount, J. F.; Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1984**, 170. (c) Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1984**, 172. (d) McGlinchey, M. J.; Fletcher, J. L.; Sayer, B. G.; Bougeard, P.; Faggiani, R.; Lock, C. J. L.; Bain, A. D.; Rodger, C.; Kündig, E. P.; Astruc, D.; Hammon, R. J.; Le Maux, P.; Top, S.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1983**, 634. (e) Hunter, G.; Iverson, D. J.; Mislow, K.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5942.

(33) The electron affinities of CS_2, COS, and CO_2 (1.0, 0.46, and –0.6 eV, respectively, as determined by Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1975**, *63*, 3821) correlate well with the observed reactivities of CS_2, COS, and CO_2 ligands toward basic metal complexes (see: Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57).

(34) (a) Darensbourg, D. J.; Rokicki, A. *J. Am. Chem. Soc.* **1982**, *104*, 349. (b) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685.

(35) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Elmsford, NY, 1983; Organic Chemistry Series, Vol. 1.

Scheme I



Hoffmann[36] concluded that the dihedral angle between the planes within the cyclohexadienyl ligand in a number of transition metal π-carbocycles arises from repulsive interactions between the filled metal d_{xy} orbital and the endo substituent of the cyclohexadienyl ligand. Connelly and Sweigart[37] investigated the nature of the highest occupied molecular orbital (HOMO) of *exo*-(η^5-C_6H_6(Ph))Mn(CO)DPPE by extended Hückel molecular orbital (EHMO) theory. The results of this analysis will be used as a model for *endo*- and *exo*-(η^5-$C_6Me_{n-7}H_n$)Mn(CO)LL′ derivatives because these complexes are structurally similar to *exo*-(η^5-C_6H_6(Ph))Mn(CO)DPPE.

In this model the HOMO of the ML_3 fragment has d_{xy} orbital character. A lobe of the metal d_{xy} orbital is oriented below the saturated carbon of the cyclohexadienyl moiety **I** (Scheme I). Increasing the electron density at the metal center by phosphine substitution increases the repulsive interaction of the d_{xy} orbital with the saturated carbon and the exo substituent. Hydride ion elimination from *endo*-(η^5-$C_6Me_{n-7}H_n$)Mn(CO)LL′ derivatives can be envisioned as a concerted intramolecular displacement of hydride ion, as in an S_N2 reaction, in which the effective nucleophile is the filled metal d_{xy} orbital. This filled orbital must approach the saturated carbon of the π-carbocycle from a direction opposite the leaving group, the exo hydride. The stereochemistry of the resulting transition state is shown in **II**. As this transition state develops, the carbon at the reaction center approaches sp^2 hybridization. The resulting unhybridized carbon p-orbital has one lobe overlapping with the filled d_{xy} orbital and the other with the leaving group as shown in **II**. The mechanism of hydride ion transfer is therefore controlled by electronic effects dependent upon the energy and orientation of the metal d_{xy} orbital. As the electron density in the metal d_{xy} orbital is increased by phosphine substitution, the activation energy for formation of the transition state is decreased. The enhanced reaction rate for species having alkyl substitution at the saturated ring carbon is consistent with anticipated lower activation energies when the metal d_{xy} orbital repulsion of the endo substituent is largest. This repulsion is anticipated to be larger for alkyl groups than for hydrogen.

This mechanism is consistent with the observation that the estimated pseudo-first-order rate constant for the reaction of **12** with CS_2 is more than the square of that for **8c**. This enhanced reactivity is too large for the electronic effect to be transmitted through the carbon–carbon σ-bonds (i.e. C_1–C_2 and C_6–C_1, Figures 3 and 4) of the cyclohexadienyl ligand. Electronic effects transmitted through σ-bonding systems are anticipated to be truncated relative to those transmitted through π-bonding systems. Such a large enhancement would be explained by direct interaction of the metal centered HOMO and an orbital of the saturated ring carbon.

The lack of hydride ion transfer reactivity of the corresponding exo isomers **IV** can be rationalized by using a similar stereoelectronic argument, illustrated in Scheme I. Because the leaving group, endo hydride, is oriented such that the metal d_{xy} orbital cannot approach it from an opposite direction, the transition state cannot be reached.

Conclusions

In conclusion, hydride ion transfer has been observed in the reaction of manganese cyclohexadienyl complexes with CS_2, COS, and CO_2. These carbon-centered hydride ion sources are surprisingly reactive and fascinating when compared to metal hydride complexes.[38] The proposed hydride ion transfer mechanism for *endo*-(η^5-$C_6Me_nH_{7-n}$)Mn(CO)LL′ derivatives is supported by the following observations: (1) The deuterium-labeled derivative, *endo*-(η^5-C_6Me_6D)Mn$(CO)_2PMe_3$, transfers deuteride ion to CS_2 to produce DCS_2^- and the cation $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2PMe_3]^+$. (2) Substitution of phosphine ligands for CO results in significant rate enhancement in CS_2 reactions. Relative to **14** a rate enhancement greater than 3×10^4 is observed with the bis phosphine complex **12**. (3) The stereoelectronic requirements for hydride ion transfer from the endo isomers allow us to interpret the variation in rates as arising from factors which influence the metal d_{xy} orbital electron density which in turn influences transition state formation. Consideration of stereoelectronic effects in this system also explains the lack of reactivity in the corresponding exo isomers. (4) Concerted one-step hydride ion transfer as opposed to a SET mechanism followed by hydrogen atom transfer is supported by cyclic voltammetry studies and the lack of evidence for the involvement of radical intermediates. Additional studies are in progress to determine the scope of the relationship between the metal d_{xy} orbital electron density and hydride ion transfer rates. These involve supporting evidence from cyclic voltammetry and additional kinetic studies. Syntheses of cyclohexadienyl complexes made more hydridic by incorporation of phosphine substituents, including chelating alkylphosphine ligands, are allowing us to explore the reactivity of *endo*-(η^5-C_6Me_6H)Mn(CO)LL′ with other electrophiles.

Crystallographic Study of 8c and 12. An X-ray crystallographic study of **8c** and **12** was performed to establish the molecular orientations of the phosphite and carbonyl ligands relative to the saturated ring carbon atom, C1, of the cyclohexadienyl ligand. The solid state structures of **8c** and **12** are illustrated by ORTEP plots in Figures 3 and 4, respectively. Selected bond lengths and angles for **8c** and **12** are given in Tables IV and V, respectively. Complex **12** crystallized as an enantiomorphic pair, but only one enantiomorph of **8c** was found in the crystal studied. The manganese atoms of both **8c** and **12** are in pseudooctahedral environments with the cyclohexadienyl ligands occupying three facial coordination sites. In **8c**, the two CO and the $P(OMe)_3$ ligands, the "legs" of a three legged "piano stool", have bond angles of 87.67 (8)° (P–Mn–C13), 95.88 (8)° (P–Mn–C14), and 92.4 (1)° (C13–Mn–C14). In **12**, the CO and the two phosphite ligands have averaged bond angles of 94.4 (2)° (C19–Mn–P1), 86.8 (5)° (C19–Mn–P2), and 94.0 (5)° (P1–Mn–P2). These ligand positions affirm that the manganese atoms in both **8c** and **12** have pseudooctahedral ligand environments. In **8c**, the cyclohexadienyl ring is positioned with the saturated ring

---

[36] Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.

[37] Connelly, N. G.; Freeman, M. J.; Orpen, A. G.; Sheehan, A. R.; Sheridan, J. B.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1019.

[38] For reviews see: (a) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (b) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1. (c) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231 and references therein. (d) Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83. (e) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33.

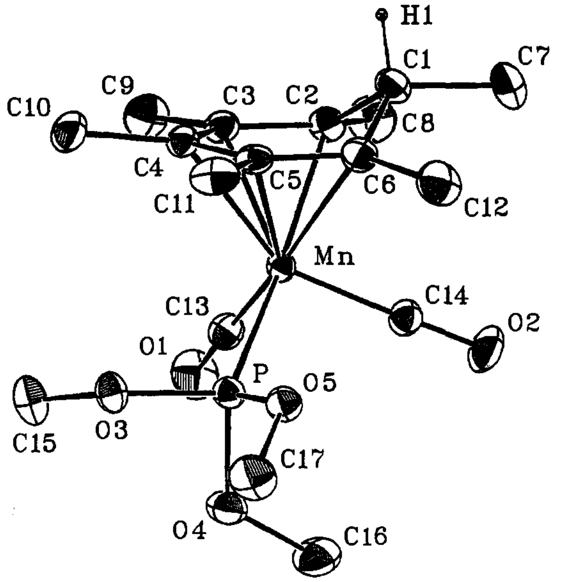


Figure 3. ORTEP drawing of *endo*-(η^5-C_6Me_6H)$Mn(CO)_2P(OMe)_3$ (**8c**) with 25% probability ellipsoids.

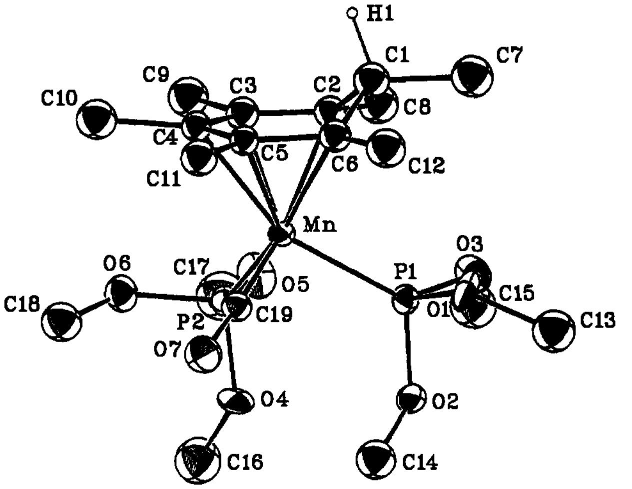


Figure 4. ORTEP drawing of *endo*-(η^5-C_6Me_6H)Mn(CO)$(P(OMe)_3)_2$ (**12**) with 25% probability ellipsoids.

carbon atom, C1, eclipsed with one of the carbonyls. The remaining carbonyl and phosphite ligands of **8c** eclipse atoms C5 and C3, respectively. In **8c**, a small amount of localization of π-bond electron density is observed in the cyclohexadienyl ligand; the C2–C3 and C5–C6 bond lengths are 1.394 (3) Å, while the C3–C4 and C4–C5 bond lengths are 1.431 (3) Å. In **8c**, the cyclohexadienyl ring centroid is shifted off-center relative to the $Mn(CO)_2P(OMe)_3$ "piano stool" tripod, and away from the phosphite ligand. The Mn–C6 bond, 2.231 (2) Å, is longer than the Mn–C2, Mn–C5, and Mn–C4 bonds, 2.197 (2), 2.178 (2), and 2.165 (2) Å, respectively. The Mn–C3 bond, eclipsed by the phosphite ligand, is the shortest with a distance of 2.148 (2) Å. In **12**, one of the phosphite ligands is eclipsed with the saturated carbon atom, C1(C1′),[39] of the cyclohexadienyl ligand. All the unsaturated C–C bond lengths for C2(C2′) through C6(C6′) in the cyclohexadienyl ligands of the enantiomorphs of **12** are equivalent within experimental error. In **12**, the cyclohexadienyl ring centroid is shifted away from the phosphite ligand under C5(C3′). The Mn–C2(C6′) and Mn–C6(C2′) bonds, 2.244 (7) and 2.255 (7) Å, respectively, are longer than the Mn–C3(C5′) bond, 2.194 (7) Å. The Mn–C4(C4′) and Mn–C5(C3′) bonds are the shortest, 2.143 (7) and 2.140 (10) Å, respectively. For **8c**, the PLANES program[40] calculated a dihedral angle of 47.5° between the plane of the five unsaturated carbon atoms, C2/C3/C4/C5/C6, and the plane formed from atoms C1/C2/C6. The saturated ring carbon atom, C1, is 0.705 Å above the plane of unsaturated carbon atoms of the cyclohexadienyl ring. The methyl carbon atoms C9 and C11 are distorted below the plane by 0.087 and 0.017 Å, respectively. Methyl carbon atom C10 is 0.172 Å above the plane while C8 and C12 are below the ring plane at distances of 0.162 and 0.177 Å, respectively. The averaged calculated dihedral angle between the plane of the five unsaturated carbon atoms, C2/C3/C4/C5/C6, and the plane of C1/C2/C6 is 47.4° in **12**. The averaged distance of C1(C1′) above the unsaturated ring carbon atoms is 0.690 Å. The methyl carbon atoms C9(C11′) and C10(C10′) deviate above the plane of the unsaturated ring carbon atoms by 0.063 and 0.172 Å,

Table III. Crystallographic Data and Refinement Parameters for Complexes *endo*-(η^5-C_6Me_6H)$Mn(CO)_2P(OMe)_3$ (**8c**) and *endo*-(η^5-C_6Me_6H)Mn(CO)$(P(OMe)_3)_2$ (**12**)

	8c	**12**
formula	$C_{17}H_{28}MnO_5P$	$C_{19}H_{37}MnO_7P_2$
color	yellow	yellow
crystal size, mm	0.58 × 0.19 × 0.51	0.68 × 0.27 × 0.25
fw, amu	398.32	494.38
a, Å	8.945(6)	10.606(4)
b, Å	12.911(4)	14.056(8)
c, Å	16.528(6)	16.162(7)
α, deg		92.45(5)
β, deg		97.27(4)
γ, deg		91.44(6)
V, Å^3	1909(5)	2387(5)
space group	$P2_12_12_1$	$P\bar{1}$
Z	4	4
d(calcd), g cm^{-3}	1.386	1.372
μ, cm^{-1} (Mo Kα)	7.7	6.9
λ(Mo Kα), Å	0.71073	0.71073
data collectn temp, °C	23	22
systematic absences	h00, h $\neq$ 2n 0k0, k $\neq$ 2n 00l, l $\neq$ 2n	none
θ range	1–25	1–25
no. of reflns measd	7547 (half sphere)	8900 (full sphere)
no. of reflns after averaging	3861	4468
no. of reflns > 3σ used in least squares refinement	3380	3271
no. of parameters refined	217	403
$R_1(F_o)$[a]	0.025	0.0549
$R_2(F_o)$[b]	0.033	0.0940
residual electron density in final DF map, e$^-$/Å^3	0.372	0.61
largest shift/esd	0.00	0.07

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/s^2(F)$, where $s^2(F) = s^2(F)' + (PWT \times F)^2$, PWT = 0.07 (**8c**) and 0.06 (**12**).

Table IV. Selected Bond Distances (Å) and Angles (deg) for *endo*-(η^5-C_6Me_6H)$Mn(CO)_2P(OMe)_3$ (**8c**)

Mn–C2	2.197(2)	C14–O2	1.152(3)
Mn–C3	2.148(2)	Mn–P	2.1790(7)
Mn–C4	2.165(2)	C1–C2	1.516(4)
Mn–C5	2.178(2)	C1–C6	1.520(4)
Mn–C6	2.231(2)	C2–C3	1.394(3)
Mn–C13	1.772(3)	C3–C4	1.431(3)
C13–O1	1.167(3)	C4–C5	1.431(3)
Mn–C14	1.772(3)	C5–C6	1.394(3)
P–Mn–C13	87.67(8)	C2–C3–C4	119.0(2)
P–Mn–C14	95.88(8)	C3–C4–C5	118.6(2)
C13–Mn–C14	92.4(1)	C4–C5–C6	118.5(2)
Mn–C13–O1	176.5(2)	C5–C6–C1	117.4(2)
Mn–C14–O2	177.5(2)	C6–C1–C7	114.2(2)
C2–C1–C6	102.6(2)	C2–C1–C7	115.4(2)
C1–C2–C3	116.7(2)		

---

[39] Atoms in parentheses refer to the corresponding atoms in the other enantiomorph.

[40] Frenz, B. A. *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: College Station, TX, 1981.

Table V. Selected Bond Distances (Å) and Angles (deg) for *endo*-(η^5-C_6Me_6H)Mn(CO)(P(OMe)$_3$)$_2$ (**12**)

Mn–C2	2.256(7)	Mn′–C2′	2.250(7)
Mn–C3	2.190(7)	Mn′–C3′	2.150(7)
Mn–C4	2.138(7)	Mn′–C4′	2.148(7)
Mn–C5	2.130(7)	Mn′–C5′	2.198(7)
Mn–C6	2.238(7)	Mn′–C6′	2.253(7)
Mn–C19	1.741(9)	Mn′–C19′	1.746(8)
C19–O7	1.181(9)	C19′–O7′	1.180(8)
Mn–P1	2.173(2)	Mn′–P1′	2.174(2)
Mn–P2	2.164(2)	Mn′–P2′	2.157(2)
C1–C2	1.51(1)	C1′–C2′	1.50(1)
C2–C3	1.39(1)	C2′–C3′	1.418(9)
C3–C4	1.39(1)	C3′–C4′	1.41(1)
C4–C5	1.42(1)	C4′–C5′	1.41(1)
C5–C6	1.41(1)	C5′–C6′	1.40(1)
C6–C1	1.51(1)	C6′–C1′	1.50(1)
C19–Mn–P1	94.4(2)	C19′–Mn′–P1′	94.5(2)
C19–Mn–P2	86.3(3)	C19′–Mn′–P2′	87.3(3)
P1–Mn–P2	94.6(2)	P1′–Mn′–P2′	93.5(8)
Mn–C19–O7	175.3(9)	Mn′–C19′–O7′	171.9(5)
C1–C2–C3	116.3(6)	C1′–C2′–C3′	116.3(6)
C2–C3–C4	119.8(6)	C2′–C3′–C4′	118.4(6)
C3–C4–C5	118.9(7)	C3′–C4′–C5′	119.5(6)
C4–C5–C6	118.7(6)	C4′–C5′–C6′	119.1(7)
C5–C6–C1	116.7(6)	C5′–C6′–C1′	115.3(7)
C6–C1–C2	102.7(6)	C6′–C1′–C2′	104.2(6)
C6–C1–C7	115.4(7)	C6′–C1′–C7′	115.9(7)
C2–C1–C7	114.9(6)	C2′–C1′–C7′	113.4(7)

respectively, while C11(C9′) is 0.054 Å below this plane. The methyl carbon atoms C8(C12′) and C12(C8′) are located slightly below the ring plane by 0.096 and 0.012 Å, respectively.

Experimental Section

General Data. All reactions and manipulations were performed under nitrogen or argon using standard Schlenk or glovebox techniques. All solvents were dried and deoxygenated prior to use. Microanalyses were performed by Desert Analytics, Tucson, AZ. All IR solution spectra as well as the data for the kinetic determinations were recorded on a Mattson Cygnus 25 FTIR spectrometer using 0.1 mm or 0.5 mm potassium bromide cells. ^1H and ^{31}P nuclear magnetic resonance spectra were obtained on a JEOL FX-90Q and/or a Bruker WM-360 spectrometer. ^{13}C NMR were recorded on a Bruker WM-360 spectrometer. Two-dimensional heteronuclear multiple quantum coherence NMR spectra were obtained on a Bruker AMX-600 spectrometer. Positive chemical shifts are given in ppm downfield from tetramethylsilane for proton and carbon spectra and from external H_3PO_4 for phosphorus spectra. Chromatographic separations were performed using untreated silica gel (60–200 mesh) or neutral alumina. ESR experiments were performed on a Varian E-104 X-band spectrometer at 77 K. Mass spectra were recorded on a VG TRIO 1 or a VG ZAB-HF mass spectrometer. EI MS spectra were recorded on the VG TRIO 1 instrument using the VG LAB BASE data system operating with a 70 eV electron beam and a 150 mA trap current. High resolution accurate mass measurements were obtained on a VG ZAB-HF mass spectrometer in the fast atom bombardment (FAB) ionization mode using xenon as the fast atom source. Mass spectrometry data were obtained at the University of Iowa Mass Spectrometry Center and the Midwest Center for Mass Spectrometry.

Complexes **1**,[17b] **14**,[17b] **23**,[17b,31] $[(\eta^6\text{-}C_6Me_3H_3)Mn(CO)_3]PF_6$,[17b] $[(\eta^6\text{-}C_6H_6)Mn(CO)_3]PF_6$,[17b,31] $[(\eta^6\text{-}C_6Et_6)Mn(CO)_3]PF_6$,[41] and KSC(S)H[42] were prepared using published procedures. Me_3NO was purchased from Eastman Kodak Co. as the dihydrate and dried by removing the water as an azeotrope with benzene. Phosphine, phosphite, and borohydride reagents were purchased from Aldrich Chemical Co. and used as received. COS and CO_2 were obtained from Matheson and used without further purification.

Preparation of $[(\eta^6\text{-arene})Mn(CO)_2L]PF_6$ Derivatives. To a stirred CH_2Cl_2 (300 mL) solution of $[(\eta^6\text{-arene})Mn(CO)_3]PF_6$ (1.0 g, 3.3 mmol) and a phosphine or phosphite (4.4 mmol) was added Me_3NO (0.38 g, 5.0 mmol) in one portion. The yellow solution immediately began to turn red upon addition of the solids. The solution was stirred for an additional 2 h, during which time the solution gradually lightened to an orange color. The solution was filtered and the solvent was removed under vacuum. Elution of the product from a column of silica with chloroform caused a single yellow band to be isolated. Spectral analysis of this product indicated that the arene ring had been displaced from the manganese, so this fraction was discarded. A 10% acetone/chloroform mixture eluted a second yellow band which proved to be the desired product. The solvent was removed and the product was recrystallized from acetone/water.

$[(\eta^6\text{-}C_6Me_6)Mn(CO)_2PPh_3]PF_6$ (2a): yellow crystals; 52% yield; ^1H NMR ($CDCl_3$) δ 7.6–7.4 (m, 15 H, Ph), 2.05 (s, 18 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 233.8 (CO), 134.2, 132.6, 130.1, 129.9 (PPh_3), 109.4 (C_6Me_6), 17.8 (C_6Me_6); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 79.7; IR (THF) ν_{CO} 1976, 1925 cm^{-1}. Anal. Calcd for $C_{32}H_{33}F_6O_2P_2Mn$: C, 56.47; H, 4.85. Found: C, 56.64; H, 5.02.

$[(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(OPh)_3]PF_6$ (2b): yellow crystals; 55% yield; ^1H NMR (CD_3COCD_3) δ 7.3–7.0 (m, 15 H, Ph), 2.31 (s, 18 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 228.1 (CO), 148.8, 129.5, 124.1, 120.4 ($P(OPh)_3$), 109.7 (C_6Me_6), 17.1 (C_6Me_6); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 170.3; IR (THF) ν_{CO} 1995, 1948 cm^{-1}. Anal. Calcd for $C_{32}H_{33}F_6O_5P_2Mn$: C, 52.76; H, 4.57. Found: C, 52.78; H, 4.54.

$[(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(OMe)_3]PF_6$ (2c): yellow crystals; 78% yield; ^1H NMR (CD_3COCD_3) δ 3.85 (d, $P(OMe)_3$, $J_{P\text{–}H}$ = 11.3 Hz), 2.44 (s, C_6Me_6); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 227.6 (d, CO, $J_{C\text{–}P}$ = 47.6 Hz), 109.5 (C_6Me_6), 55.1 (d, $P(OMe)_3$), 16.8 (C_6Me_6); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 185.7; IR (THF) ν_{CO} 1990, 1941 cm^{-1}. Anal. Calcd for $C_{17}H_{27}F_6O_5P_2Mn$: C, 37.64; H, 4.98. Found: C, 37.71; H, 5.12.

$[(\eta^6\text{-}C_6Me_6)Mn(CO)_2PMe_3]PF_6$ (2d): yellow crystals; 48% yield; ^1H NMR (CD_3COCD_3) δ 2.35 (s, 18 H, CH_3), 1.51 (d, 9 H, PMe_3, $J_{P\text{–}H}$ = 9.8 Hz); $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 210 K) δ 225.7 (d, CO, $J_{C\text{–}P}$ = 29.1 Hz), 110.2 (s, C_6Me_6), 18.5 (d, PMe_3, $J_{C\text{–}P}$ = 30.3 Hz), 17.2 (C_6Me_6); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 36.3; IR (THF) ν_{CO} 1970, 1922 cm^{-1}. Instability of this compound precluded elemental analysis. However, the corresponding cyclohexadienyl species **8d** gave an acceptable elemental analysis.

$[(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(n\text{-}Bu)_3]PF_6$ (2e): yellow crystals; 65% yield; ^1H NMR (CD_3COCD_3) δ 2.32 (s, 18 H, CH_3), 1.41 (m, 18 H, $P(n\text{-}Bu)_3$), 0.95 (t, 9 H, $P(n\text{-}Bu)_3$, $J_{H\text{–}H}$ = 6.3 Hz); $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 210 K) δ 226.8 (d, CO, $J_{C\text{–}P}$ = 29.5 Hz), 110.2 (C_6Me_6), 26.3–24.5 (m, $P(n\text{-}Bu)_3$), 17.3 (C_6Me_6); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 55.5; IR (THF) ν_{CO} 1969, 1918 cm^{-1}. Anal. Calcd for $C_{26}H_{45}F_6O_2P_2Mn$: C, 50.33; H, 7.31. Found: C, 50.41; H, 7.38.

$[(\eta^6\text{-}C_6H_6)Mn(CO)_2PMe_3]PF_6$ (3a): yellow crystals; 74% yield; ^1H NMR ($CDCl_3$) δ 6.15 (s, 6 H, C_6H_6), 1.59 (d, 9 H, PMe_3, $J_{P\text{–}H}$ = 9.7 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 223.3 (CO), 94.2 (C_6H_6), 19.6 (d, PMe_3, $J_{C\text{–}P}$ = 30.2 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 37.1; IR (THF) ν_{CO} 1993, 1947 cm^{-1}. Instability of this compound precluded elemental analysis. However, the corresponding cyclohexadienyl species **9a** gave an acceptable elemental analysis.

$[(\eta^6\text{-}C_6H_6)Mn(CO)_2P(OMe)_3]PF_6$ (3b): yellow crystals; 78% yield; ^1H NMR ($CDCl_3$) δ 6.05 (s, C_6H_6), 3.75 (d, $P(OMe)_3$, $J_{P\text{–}H}$ = 10.8 Hz); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 220.9 (d, CO, $J_{C\text{–}P}$ = 44.6 Hz), 99.5 (C_6H_6), 54.2 ($P(OMe)_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 184.3; IR (THF) ν_{CO} 2013, 1968 cm^{-1}. Instability of this compound precluded elemental analysis. However, the corresponding cyclohexadienyl species **9b** gave an acceptable elemental analysis.

$[(\eta^6\text{-}C_6Me_3H_3)Mn(CO)_2PMe_3]PF_6$ (4): yellow crystals; 58% yield; ^1H NMR ($CDCl_3$) δ 5.67 (s, 3 H, $C_6Me_3H_3$), 2.39 (s, 9 H, $C_6Me_3H_3$), 1.60 (d, 9 H, PMe_3, $J_{P\text{–}H}$ = 9.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 224.8 (CO), 114.8, 94.7 ($C_6Me_3H_3$), 20.1 ($C_6Me_3H_3$), 20.0 (d, PMe_3, $J_{P\text{–}H}$ = 31.4 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 37.5; IR (THF) ν_{CO} 1984, 1935 cm^{-1}. Instability of this compound precluded elemental analysis. However, the corresponding cyclohexadienyl species **11a,b** gave acceptable elemental analysis.

$[(\eta^6\text{-}C_6Et_6)Mn(CO)_2PMe_3]PF_6$ (5): ($[(\eta^6\text{-}C_6Et_6)Mn(CO)_2PMe_3]PF_6$ was prepared in a similar manner using $[(\eta^6\text{-}C_6Et_6)Mn(CO)_3]PF_6$ as the starting material) yellow crystals; 65% yield; ^1H NMR ($CDCl_3$) δ 2.67 (br s, 12 H, CH_2CH_3), 1.57 (d, PMe_3, $J_{P\text{–}H}$ = 9.8 Hz), 1.36 (br s, 18 H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 223.6 (d, CO, $J_{C\text{–}P}$ = 30.1 Hz), 113.7 (C_6Et_6), 24.9, 22.1 (CH_2), 19.9 (d, PMe_3, $J_{C\text{–}P}$ = 31.4 Hz), 16.8, 16.4, 15.6 (CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 37.2; IR (THF) ν_{CO} 1977, 1927 cm^{-1}. Instability of this compound precluded elemental analysis. However, the corresponding cyclohexadienyl species **10** gave an acceptable elemental analysis.

---

(41) This compound was prepared in a manner similar to the hexamethylbenzene analogue **1**.

(42) (a) Binder, H.; Diamantikos, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 203. (b) Engler, R.; Gattow, G.; Dräger, M. *Z. Anorg. Allg. Chem.* **1972**, *338*, 229.

Preparation of [(η^6-arene)Mn(CO)LL′]PF$_6$ Derivatives. In a typical experiment, [(η^6-arene)Mn(CO)$_2$PR$_3$]PF$_6$ (1 mmol) and Me$_3$NO (2 mmol) were taken up in CH$_2$Cl$_2$ (100 mL). To the yellow solution was added PR$_3$ (1.5 mmol). The mixture was stirred at room temperature for 48 h, during which time the color gradually turned a darker orange-brown. The solvent was removed under vacuum and the yellow solids were placed on a column of silica. Using chloroform, a small yellow band was eluted from the column and discarded. The addition of 10% acetone/CHCl$_3$ resulted in the elution of two additional yellow bands that were collected. The desired product was contained in the second band and the third band was identified by solution IR as unreacted starting material. The products were recrystallized using acetone/H$_2$O.

[(η^6-C$_6$Me$_6$)Mn(CO)(P(OMe)$_3$)$_2$]PF$_6$ (6): yellow crystals; 46% yield; ^{1}H NMR (CDCl$_3$) δ 3.71 (t, P(OMe)$_3$, $J_{\mathrm{P-H}}$ = 5.5 Hz), 2.20 (s, C$_6$Me$_6$); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$) δ 232.7 (d, CO, $J_{\mathrm{C-P}}$ = 34.5 Hz), 108.5 (C$_6$Me$_6$), 54.9 (P(OMe)$_3$), 17.8 (C$_6$Me$_6$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 187.1; IR (THF) ν_{CO} 1911 cm^{-1}. MW$_{\mathrm{calc}}$ for C$_{19}$H$_{36}$O$_7$P$_2$Mn (M$^+$) 493.132; MW$_{\mathrm{exp}}$ m/z 493.129 (Δm = −3.0 mmu).

[(η^6-C$_6$H$_6$)Mn(CO)(P(OMe)$_3$)$_2$]PF$_6$ (7): yellow crystals; 42% yield; ^{1}H NMR (CD$_3$COCD$_3$) δ 5.98 (t, C$_6$H$_6$, $J_{\mathrm{P-H}}$ = 2.2 Hz), 3.80 (t, P(OMe)$_3$, $J_{\mathrm{P-H}}$ = 5.5 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 224.2 (CO), 93.5 (C$_6$H$_6$), 53.7 (P(OMe)$_3$); ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$) δ 188.4; IR (THF) ν_{CO} 1947 cm^{-1}. MW$_{\mathrm{calc}}$ for C$_{13}$H$_{24}$F$_6$O$_7$P$_3$Mn (M$^+$) 554.174; MW$_{\mathrm{exp}}$ m/z 554.176 (Δm = +2.0 mmu).

Preparation of (η^5-cyclohexadienyl)Mn(CO)$_2$L Derivatives. To a mixture of [(η^6-arene)Mn(CO)$_2$L]PF$_6$ (1 mmol) and (n-Bu)$_4$NBH$_4$ (1 mmol) was added THF (40 mL). The solution was stirred for 30 min at room temperature, followed by solvent removal giving yellow solids. The products were purified on a column of silica using hexane as the eluant. The hexane was concentrated and cooled to −60 °C causing bright yellow crystals to form. Yields ranged from 70 to 90%.

***endo*-(η^5-C$_6$Me$_6$H)Mn(CO)$_2$PPh$_3$ (8a)**: yellow crystals; 83% yield; ^{1}H NMR (C$_6$D$_6$) δ 7.4–7.0 (m, 15 H, PPh$_3$), 2.37 (p, 1 H, *exo*-H), 2.12 (s, 3 H, CH$_3$), 1.59 (s, 6 H, CH$_3$), 1.36 (d, 3 H, *endo*-CH$_3$, $J_{\mathrm{H-H}}$ = 7.3 Hz), 1.27 (s, 6 H, CH$_3$); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$, 210 K) δ 235.4 (CO), 134.1, 130.1, 128.8, 128.7 (PPh$_3$), 104.6, 91.5, 59.2, 39.2 (C$_6$Me$_6$H), 16.8–15.4 (m, C$_6$Me$_6$H); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 79.9; IR (THF) ν_{CO} 1913, 1865 cm^{-1}. Anal. Calcd for C$_{32}$H$_{34}$O$_2$PMn: C, 71.63; H, 6.39. Found: C, 71.51; H, 6.23.

***endo*-(η^5-C$_6$Me$_6$H)Mn(CO)$_2$P(OPh)$_3$ (8b)**: yellow crystals; 74% yield; ^{1}H NMR (C$_6$D$_6$) δ 7.41–7.03 (m, 15 H, P(OPh)$_3$), 2.21 (s, 3 H, CH$_3$), 2.18 (p, 1 H, *exo*-H), 1.77 (s, 6 H, CH$_3$), 1.49 (s, 6 H, CH$_3$), 1.40 (d, 3 H, *endo*-CH$_3$, $J_{\mathrm{H-H}}$ = 7.2 Hz); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$) δ 143.7, 130.8, 128.2, 128.0 (OPh), 105.9, 91.7, 58.9, 39.5 (C$_6$Me$_6$H), 16.9–15.5 (CH$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 177.2; IR (THF) ν_{CO} 1941, 1882 cm^{-1}. Anal. Calcd for C$_{32}$H$_{34}$O$_5$PMn: C, 65.75; H, 5.86. Found: C, 65.59; H, 5.58.

***endo*-(η^5-C$_6$Me$_6$H)Mn(CO)$_2$P(OMe)$_3$ (8c)**: yellow crystals; 78% yield; ^{1}H NMR (C$_6$D$_6$) δ 3.33 (d, 9 H, P(OMe)$_3$, $J_{\mathrm{P-H}}$ = 11.7 Hz), 2.28 (p, 1 H, *exo*-H), 2.26 (s, 3 H, CH$_3$), 1.88 (s, 6 H, CH$_3$), 1.56 (s, 6 H, CH$_3$), 1.39 (d, 3 H, *endo*-CH$_3$, $J_{\mathrm{H-H}}$ = 7.2 Hz); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$, 210 K) δ 232.5 (CO), 105.7, 92.0, 57.7, 37.8 (C$_6$Me$_6$H), 51.2 (P(OMe)$_3$), 16.7–15.8 (m, C$_6$Me$_6$H); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 196.5; IR (THF) ν_{CO} 1924, 1865 cm^{-1}. Anal. Calcd for C$_{17}$H$_{28}$O$_5$PMn: C, 51.26; H, 7.04. Found: C, 51.55; H, 7.29.

***endo*-(η^5-C$_6$Me$_6$H)Mn(CO)$_2$PMe$_3$ (8d)**: yellow crystals; 90% yield; ^{1}H NMR (C$_6$D$_6$) δ 2.36 (p, 1 H, *exo*-H), 2.22 (s, 3 H, CH$_3$), 1.75 (s, 6 H, CH$_3$), 1.45 (s, 6 H, CH$_3$), 1.42 (d, 3 H, *endo*-CH$_3$, $J_{\mathrm{H-H}}$ = 7.2 Hz), 0.90 (d, 9 H, PMe$_3$, $J_{\mathrm{P-H}}$ = 7.7 Hz); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$, 210 K) δ 222.4 (CO), 108.4, 95.2, 62.1, 36.6 (C$_6$Me$_6$H), 20.1 (d, PMe$_3$, $J_{\mathrm{C-P}}$ = 22.8 Hz), 18.3–16.1 (m, CH$_3$); ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$) δ 36.3; IR (THF) ν_{CO} 1910, 1847 cm^{-1}. Anal. Calcd for C$_{17}$H$_{28}$O$_2$PMn: C, 58.28; H, 8.06. Found: C, 58.42; H, 7.95. *endo*-(η^5-C$_6$Me$_6$D)Mn(CO)$_2$PMe$_3$ was prepared in a similar manner using NaBD$_4$ as the reducing agent.

***endo*-(η^5-C$_6$Me$_6$H)Mn(CO)$_2$P(n-Bu)$_3$ (8e)**: yellow crystals; 85% yield; ^{1}H NMR (C$_6$D$_6$) δ 2.42 (s, 3 H, CH$_3$), 2.39 (p, 1 H, *exo*-H), 1.89 (s, 6 H, CH$_3$), 1.54 (s, 6 H, CH$_3$), 1.32 (m, 21 H, P(n-Bu)$_3$ and *endo*-CH$_3$), 0.98 (t, 9 H, P(n-Bu)$_3$, $J_{\mathrm{H-H}}$ = 6.1 Hz); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$, 210 K) δ 234.9 (CO), 105.1, 90.1, 56.8, 39.0 (C$_6$Me$_6$H), 28.6–25.1, 14.1 (m, P(n-Bu)$_3$), 17.1–16.4 (m, C$_6$Me$_6$H); ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$) δ 54.2; IR (THF) ν_{CO} 1908, 1846 cm^{-1}. Anal. Calcd for C$_{26}$H$_{46}$O$_2$PMn: C, 65.53; H, 9.73. Found: C, 65.76; H, 9.89.

(η^5-C$_6$H$_7$)Mn(CO)$_2$PMe$_3$ (9a): yellow crystals; 92% yield; ^{1}H NMR (CD$_3$COCD$_3$) δ 5.69 (t, 1 H, C$_6$H$_7$), 4.55 (q, 2 H, C$_6$H$_7$), 2.55 (m, 2 H, C$_6$H$_7$), 2.49 (q, 2 H, C$_6$H$_7$), 1.26 (d, 9 H, PMe$_3$, $J_{\mathrm{P-H}}$ = 7.6 Hz); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$, 210 K) δ 233.6 (CO), 97.2, 79.2, 45.1, 25.6 (C$_6$H$_7$), 19.3 (d, PMe$_3$, $J_{\mathrm{C-P}}$ = 26.3 Hz); ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$) δ 38.6; IR (THF) ν_{CO} 1926, 1862 cm^{-1}. Anal. Calcd for C$_{11}$H$_{16}$O$_2$PMn: C, 49.64; H, 6.06. Found: C, 49.74; H, 6.17.

(η^5-C$_6$H$_7$)Mn(CO)$_2$P(OMe)$_3$ (9b): yellow crystals; 88% yield; ^{1}H NMR (C$_6$D$_6$) δ 5.53 (t, 1 H), 4.51 (q, 2 H), 3.47 (d, 9 H, P(OMe)$_3$, $J_{\mathrm{P-H}}$ = 10.8 Hz), 2.47 (q, 2 H), 2.03 (m, 2 H); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$) δ 230.3 (CO), 97.5, 79.7 (C$_6$H$_7$), 51.7 (P(OMe)$_3$), 25.6 (C$_6$H$_7$) ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 186.4; IR (THF) ν_{CO} 1944, 1881 cm^{-1}. Anal. Calcd for C$_{11}$H$_{16}$O$_5$PMn: C, 42.06; H, 5.13. Found: C, 42.17; H, 5.23.

Mixture of (η^5-C$_6$Me$_3$H$_4$)Mn(CO)$_2$PMe$_3$ (11a,b): yellow crystals; 86% yield; ^{1}H NMR (C$_6$D$_6$) δ 4.04 (d, 2 H), 2.21 (s, 3 H), 1.55 (s, 2 H), 1.48 (s, 6 H), 0.84 (d, 9 H, PMe$_3$, $J_{\mathrm{P-H}}$ = 8.0 Hz); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$) δ 232.9 (CO), 95.7, 86.3, 59.7, 23.8 (C$_6$Me$_3$H$_4$), 20.6 (d, PMe$_3$, $J_{\mathrm{P-C}}$ = 24.3 Hz), 20.5, 20.2 (CH$_3$); ^{31}P{^{1}H} NMR δ (CD$_3$COCD$_3$) 37.1; IR (THF) ν_{CO} 1915, 1852 cm^{-1}. Spectroscopic data are for isomer **11b** only. Isomer **11a** was present in too small of an amount to obtain ^{1}H and ^{13}C NMR data. Anal. Calcd for C$_{14}$H$_{22}$O$_2$PMn: C, 54.53; H, 7.20. Found: C, 54.91; H, 7.33.

***endo*-(η^5-C$_6$Et$_6$H)Mn(CO)$_2$PMe$_3$ (10)**: *endo*-(η^5-C$_6$Et$_6$H)Mn(CO)$_2$PMe$_3$ was prepared in a similar manner using [(η^6-C$_6$Et$_6$)Mn(CO)$_2$PMe$_3$]PF$_6$: yellow crystals; yield 84%; ^{1}H NMR (C$_6$D$_5$CD$_3$) δ 2.59, 2.33, 2.24, 1.82 (m, 12 H, CH$_2$), 1.36, 1.07, 0.99 (m, 18 H, CH$_3$), 0.89 (d, PMe$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_5$CD$_3$) δ 225.6 (CO), 114.2, 108.8, 99.3, 95.1, 63.9, 60.0, 42.5, 40.2 (C$_6$Et$_6$H), 35.0, 28.3, 27.6, 24.8, 24.5, 23.9, 18.5, 17.5, 16.5, 13.0, 12.3 (Et$_6$), 20.18 (d, PMe$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_5$CD$_3$) δ 36.5; IR (THF) ν_{CO} 1910, 1846 cm^{-1}. Anal. Calcd for C$_{23}$H$_{46}$O$_2$PMn: C, 63.58; H, 9.28. Found: C, 63.73; H, 9.21.

Preparation of (η^5-cyclohexadienyl)Mn(CO)LL′ Derivatives. *endo*-(η^5-C$_6$Me$_6$H)Mn(CO)(P(OMe)$_3$)$_2$ (12). Method A. A Schlenk flask containing [(η^6-C$_6$Me$_6$)Mn(CO)(P(OMe)$_3$)$_2$]PF$_6$ (**6**) (0.522 g, 0.818 mmol) was purged with nitrogen. THF (50 mL) was added to the flask and the solution was heated until all the starting material was dissolved. After cooling to room temperature, a 50 mL THF solution containing an excess of K(i-PrO)$_3$BH (11.5 mL, 2.65 mmol, 3.2 equiv) was added to the first solution via cannula. The resultant solution immediately turned from dull yellow to a brighter yellow-orange color. A solution IR spectrum of the reaction mixture indicated the formation of products after several minutes. After the removal of solvent under vacuum, the oily yellow-orange solids were extracted (3 × 25 mL) with dry deoxygenated hexane and transferred to a second flask. The volume of the extracts was reduced to half and the solution was transferred to a flask containing 15–20 mL of dry silica gel (60–200 mesh). The product **12** was eluted from the silica gel with hexane and recrystallized from hexane at lower temperature (−20 °C) after the solution was concentrated. Dark yellow crystals (0.136 g) were obtained with an isolated yield of 34.0%. ^{1}H NMR (C$_6$D$_6$) δ 3.42 (t, P(OMe)$_3$, $J_{\mathrm{P-H}}$ = 5.0 Hz), 2.47 (s, 3 H, CH$_3$), 2.45 (obscured by CH$_3$, 1 H, *exo*-H), 2.03 (s, 6 H, CH$_3$), 1.60 (s, 6 H, CH$_3$), 1.52 (s, 3 H, *endo*-CH$_3$, $J_{\mathrm{H-H}}$ = 7.3 Hz); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$) δ 236.5 (CO), 104.7, 88.5, 55.1, 39.7 (C$_6$Me$_6$H), 51.5 (P(OMe)$_3$), 16.8, 16.7, 16.4, 16.1 (CH$_3$); ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$) δ 196.0; IR (THF) ν_{CO} 1850 cm^{-1}. Anal. Calcd for C$_{19}$H$_{37}$O$_7$P$_2$Mn: C, 46.16; H, 7.54. Found: C, 46.52; H, 7.35.

Method B. A solution of (η^5-C$_6$Me$_6$H)Mn(CO)$_2$P(OMe)$_3$ (**8c**) (0.151 g, 0.379 mmol) in THF (20 mL) was added to a quartz reactor tube. P(OMe)$_3$ (0.30 mL, 2.5 mmol) was transferred via syringe into the solution. The resultant solution was irradiated with 10 UV bulbs (λ = 254 nm) in a Rayonet Photoreactor for 8.1 h. The temperature of the solution was maintained at ambient conditions using a cold finger inserted into the solution. Monitoring of the reaction by solution FTIR indicated when the reaction was complete. The product was purified via flash chromatography from neutral alumina using a 3:1 hexane/diethyl ether solvent mixture. The product **12** was isolated in 44% yield (0.082 g, 0.166 mmol) after recrystallization from hexane.

(η^5-C$_6$H$_7$)Mn(CO)(P(OMe)$_3$)$_2$ (13). To a Schlenk flask containing [(η^6-C$_6$H$_6$)Mn(CO)(P(OMe)$_3$)$_2$]PF$_6$ (**7**) (0.55 g, 1.0 mmol) and (n-Bu)$_4$NBH$_4$ (excess) was added THF (40 mL). The solution was stirred for 30 min at room temperature, followed by solvent removal giving yellow solids. The yellow solids were purified on a column of silica using hexane as the eluant. The hexane was concentrated and cooled to −60 °C. Bright yellow crystals of **13** (0.299 g) were obtained with an isolated yield of 73%. ^{1}H NMR (CD$_3$COCD$_3$) δ 5.47 (t, 1 H), 4.48 (q, 2 H), 3.59 (t, 9 H, P(OMe)$_3$, $J_{\mathrm{P-H}}$ = 5.1 Hz), 2.55 (m, 2 H), 2.19 (q, 2 H); ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$) δ 226.6 (CO), 95.4, 76.7, 43.5, 25.1 (C$_6$H$_7$), 51.5 (P(OMe)$_3$); ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$) δ 196.0; IR (THF) ν_{CO} 1861 cm^{-1}. Anal. Calcd for $C_{13}H_{25}O_7P_2Mn$: C, 38.06; H, 6.14. Found: C, 37.97; H, 6.02.

Kinetic Experiments. Solutions were prepared by dissolving 0.075 mmol of the cyclohexadienyl complex in 5.0 mL of CS_2, producing a 0.015 M solution. This was immediately followed by an injection of a sample of the solution into a 0.5 mm KBr solution IR cell. Reaction rate data were obtained by monitoring the disappearance of the cyclohexadienyl complex at 28 °C to produce $[(\eta^6\text{-arene})Mn(CO)_2PR_3]S_2CH$ **17a–b, d–e**. Concentration determinations were made by integrating the infrared peak of the low-frequency CO stretching band of the starting materials.

Reaction of 14 with CS_2. *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_3$ (**14**: 0.510 g, 1.69 mmol) was dissolved in CS_2 (25 mL), purged, and placed in the dark at room temperature for 7 days without stirring. Over the course of the reaction, the solution gradually turned from yellow to red and a red precipitate formed on the walls of the flask. The solids were separated from the solution by filtration and were washed with hexane to remove any starting material. Further purification was performed by eluting the product from silica with a 30% acetone/hexane mixture, followed by solvent removal and drying in vacuo to give **15** and **16** (0.572 g, 90% yield). ^1H NMR (CD_3COCD_3) δ 11.40 (s, 1 H, HCS_2), 2.61 (s, 18 H, CH_3); IR (THF) ν_{CO} 2058, 2004 (sh), 1996, 1916 cm^{-1}.

Reactions of (η^5-cyclohexadienyl)Mn(CO)LL′ Complexes with CS_2. To solutions of complexes **8a–e** (1 mmol) in THF (50 mL) was added CS_2 (5 mL, excess). The mixtures were kept at room temperature and monitored by solution IR. Spectroscopic identification of **17a–b,d–e** was obtained by adding liquid CS_2 to complexes **8a,b,d,e** (1 mmol). The mixtures were kept at room temperature and monitored by solution IR until reaction completion. Subsequent column chromatography on neutral alumina and elution with 50/50 chloroform/acetone yielded **17a–b,d–e**.

(a) *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2PPh_3$ (8a). The solution was stirred for 1.5 h during which there was a gradual color change to red, and the solution IR spectrum indicated the formation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2PPh_3]S_2CH$ (**17a**). The mixture was stirred for an additional 3 h, during which the solution turned dark red. After solvent removal and drying under vacuum, the product was eluted from a column of silica with acetone/hexane. Recrystallization from acetone/hexane produced 0.294 g (84% yield) of **18** as rust-red crystals. **17a** (0.424 g, 76% yield), yellow solids: ^1H NMR (CD_3COCD_3) δ 10.21 (s, 1 H, HCS_2), 7.75–7.54 (m, 15 H, PPh_3), 2.22 (s, 18 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 132.9, 132.8, 132.4, 129.4, 129.3 (m, PPh_3), 107.0 (C_6Me_6), 16.6 (C_6Me_6); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 76.8; IR (THF) ν_{CO} 1973, 1923 cm^{-1}.

(b) *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2P(OPh)_3$ (8b). The solution was kept at room temperature and stirred for 20 h, during which it turned dark red and the solution IR spectrum indicated the formation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(OPh)_3]S_2CH$ (**17b**), which eventually produced **18**. The solvent was removed under vacuum. Elution with an acetone/hexane mixture from a column of silica followed by recrystallization from acetone/hexane produced 0.273 g (78% yield) of **18** as rust-red crystals. **17b** (0.436 g, 72% yield), red-brown solids: ^1H NMR (CD_3COCD_3) δ 10.33 (s, 1 H, HCS_2), 7.48–7.16 (m, 15 H, $P(OPh)_3$), 2.46 (s, 18 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 223.4 (CO), 152.0, 131.2, 130.0, 121.3 ($P(OPh)_3$), 112.8 (C_6Me_6), 16.9 (C_6Me_6); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 172.8; IR (THF) ν_{CO} = 1995, 1949 cm^{-1}.

(c) *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2P(OMe)_3$ (8c). The solution was kept at room temperature and stirred for 3 h, during which the color changed from yellow to orange-red, but eventually changed back to yellow. The solution IR spectrum indicated quantitative formation of $(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(O)(OMe)_2$ (**19**). Under vacuum, the solvent was removed and the yellow product was dried. Elution on a column of silica with acetone/hexane followed by recrystallization with acetone/hexane at −20 °C produced 0.355 g (93% yield) of **19**. ^1H NMR ($CDCl_3$) δ 3.49 (d, 6 H, OMe, J_{P-H} = 10.3 Hz), 2.22 (s, 18 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 210 K) δ 226.8 (d, CO, J_{C-P} = 46.7 Hz), 108.9 (C_6Me_6), 49.8 (d, $P(OMe)_2$, J_{C-P} = 45.5 Hz), 16.9 (s, C_6Me_6); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 165.8; IR (THF) ν_{CO} 1964, 1914 cm^{-1}; (KBr) $\nu_{P=O}$ 1165 cm^{-1}. MW_{calc} for $C_{16}H_{25}O_5PMn$ (M + H) 383.082; MW_{exp} *m/z* 383.083 (Δm = +1.0 mmu).

(d) *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2PMe_3$ (8d). The solution was stirred at room temperature for 1 h, during which the color gradually turned red. A solution IR spectrum indicated quantitative formation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2PMe_3]S_2CH$ (**17d**). The solution was stirred for an additional 48 h at room temperature, followed by removal of the solvent. The red solid residue was placed on a silica column and eluted with a 10% acetone/hexane mixture. A small red band was eluted and collected. Red solids of **20** (0.082 g, 24% yield) were obtained upon solvent removal under vacuum. ^1H NMR (CD_3COCD_3) δ 11.02 (t, 1 H, HCS_2, J_{P-H} = 8.5 Hz), 1.52 (d, 18 H, PMe_3, J_{P-H} = 7.3 Hz); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 218.5 (CO), 17.8 (t, PMe_3, J_{C-P} = 13.1 Hz); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 22.2; IR (THF) ν_{CO} 1924, 1853 cm^{-1}. LREI MS: [M] 340, [M − 2CO]$^+$ 284, [M − 2CO − PMe_3]$^+$ 208, [M − 2CO − 2PMe_3]$^+$ 132. MW_{calc} for $C_9H_{19}O_2P_2S_2Mn$ (M$^+$) 339.9682; MW_{exp} *m/z* 339.9677 (Δm = −0.5 mmu). **17d** (0.334 g, 78% yield), orange solids: ^1H NMR (CD_3COCD_3) δ 10.27 (s, 1 H, HCS_2), 2.48 (s, 18 H, CH_3), 1.64 (d, 9 H, PMe_3, J_{P-H} = 10.0 Hz); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 110.6 (C_6Me_6), 19.2 (d, PMe_3, J_{C-P} = 30.4 Hz), 17.6 (C_6Me_6); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 37.0; IR (THF) ν_{CO} 1969, 1920 cm^{-1}. LREI MS: [M]$^+$ 349, [M − 2CO]$^+$ 293, [M − 2CO − PMe_3]$^+$ 217.

(e) *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2P(n\text{-}Bu)_3$ (8e). The solution was stirred for 1 h, during which the color gradually changed from yellow to red and the solution IR spectrum indicated quantitative formation of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2P(n\text{-}Bu)_3]S_2CH$ (**17e**). The solution was stirred for an additional 48 h, followed by solvent removal under vacuum. The resulting red solids were placed on a column of silica and eluted with a 10% acetone/hexane mixture. A second red band was collected and the solvent was removed, producing 0.106 g (18% yield) of **21** as oily red solids. ^1H NMR (CD_3COCD_3) δ 10.72 (t, 1 H, HCS_2, J_{P-H} = 7.4 Hz), 1.48 (m, 36 H, $P(n\text{-}Bu)_3$), 0.91 (dt, 18 H, $P(n\text{-}Bu)_3$, J_{P-P} = 26.0 Hz, J_{P-H} = 7.0 Hz); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 49.9, 44.1; IR (THF) ν_{CO} 1919, 1847 cm^{-1}. **17e** (0.453 g, 82% yield), orange solids: ^1H NMR (CD_3COCD_3) δ 10.24 (s, 1 H, HCS_2), 2.49 (s, 18 H, CH_3), 1.46 (m, 18 H, $P(n\text{-}Bu)_3$), 0.96 (s, 9 H, $P(n\text{-}Bu)_3$); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 228.5 (CO), 110.4 (C_6Me_6), 25.7–24.5 (m, $P(n\text{-}Bu)_3$), 13.4 (C_6Me_6); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 58.8; IR (THF) ν_{CO} 1969, 1920 cm^{-1}.

Reaction of 14 with COS. To *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_3$ (**14**: 0.458 g, 1.52 mmol) in a Fischer-Porter/Lab-Crest Scientific 3 oz. aerosol pressure vessel[43] was added 40 mL of THF via cannula. This solution was pressurized to 40 psi with COS. The mixture was kept at 70 °C with stirring for 7 days. Over the course of the reaction, the solution gradually turned from yellow to orange-brown. After depressurization and solvent removal, the red-brown solids were chromatographed on a neutral alumina column. Hexane eluted a yellow band, which upon solvent removal in vacuo yielded yellow crystals identified by solution IR and ^1H NMR spectra as unreacted starting material and hexamethylbenzene. Acetone/hexane (50/50) eluted a small red-brown band, which upon solvent removal yielded the red-brown solids **15** and **16** (56 mg, 2% yield) as confirmed by solution IR and ^1H NMR spectra.

Reactions of (η^5-cyclohexadienyl)Mn(CO)LL′ Complexes with COS. Solutions of complexes **8a–e** and **12** in THF (40 mL) were pressurized to 40 psi with COS in a Fischer-Porter/Lab-Crest Scientific 3 oz. aerosol pressure vessel.[43]

(a) *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2PPh_3$ (8a). The yellow solution of **8a** (0.650 g, 1.21 mmol) gradually turned orange within 1 h at 70 °C. After 9 h at 70 °C, the solution turned darker orange in color. After depressurization and solvent removal in vacuo, the red solids were chromatographed on a neutral alumina column. Hexane eluted a yellow band, which upon solvent removal in vacuo yielded yellow crystals identified by solution IR and ^1H NMR spectra as starting material and hexamethylbenzene. Hexane/acetone (75/25) eluted an orange band, which upon solvent removal in vacuo yielded orange solids of **17a** (17 mg, 2% yield). Acetone/hexane (50/50) eluted a yellow orange band, which upon solvent removal in vacuo yielded yellow solids of $[(\eta^6\text{-}C_6Me_6)Mn(CO)_2PPh_3]S(O)CH$ (**27a**) (0.150 g, 21% yield): ^1H NMR (CD_3COCD_3) δ 10.32 (s, 1 H, S(O)CH), 7.62–7.53 (m, 15 H, PPh_3), 2.20 (s, 18 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 196.3 (S(O)CH), 134.0, 133.9, 132.3, 130.1, 130.0 (m, PPh_3), 111.4 (C_6Me_6), 16.9 (C_6Me_6); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 76.8; IR (THF) ν_{CO} 1978, 1928 cm^{-1}.

(b) *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2P(OPh)_3$ (8b). The yellow solution of **8b** (0.875 g, 1.50 mmol) gradually turned orange within 3 days at 70 °C. The mixture was kept at 70 °C with stirring for a total of 5 days. After depressurization and solvent removal in vacuo, the red-brown solids were chromatographed on a neutral alumina column. Hexane eluted a yellow band, which upon solvent removal in vacuo yielded yellow crystals identified by solution IR and ^1H NMR spectra as starting material and hexamethylbenzene. Hexane/acetone (50/50) eluted an orange-brown band, which upon solvent removal in vacuo yielded red-brown solid **17b** (45 mg, 5% yield).

(c) *endo*-$(\eta^5\text{-}C_6Me_6H)Mn(CO)_2P(OMe)_3$ (8c). The yellow solution of **8c** (0.059 g, 0.15 mmol) gradually turned darker yellow in color within

---

(43) Messerle, L. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington D.C., 1987, ACS Symp. Ser. 357, Chapter 7: Application 4.

3 days at room temperature. Solution IR and ^{1}H NMR spectra indicated quantitative formation of **19**, and GC-MS analysis of a headspace sample of the reactor contents indicated HC(O)SCH_3 ($m/z = 76$) had formed.

(d) *endo*-(η^5-C_6Me_6H)Mn$(CO)_2PMe_3$ (8d). The yellow solution of **8d** (0.525 g, 1.50 mmol) gradually turned orange within 0.5 h at 70 °C. After 4 h at 70 °C, the solution turned dark red in color. After depressurization and solvent removal in vacuo, the red solids were chromatographed on a neutral alumina column. Hexane eluted a yellow band and a red band. Solvent removal in vacuo of the initial yellow band yielded yellow crystals identified by solution IR and ^{1}H NMR spectra as starting material and hexamethylbenzene. Solvent removal in vacuo of the red band yielded red crystals identified by solution IR and ^{1}H NMR spectra as **20** (9 mg, 2% yield). Acetone/hexane (50/50) eluted a yellow orange band, which upon solvent removal in vacuo yielded yellow solid [(η^6-C_6Me_6)Mn$(CO)_2PMe_3$]S(O)CH (**27d**) (0.177 g, 28% yield): ^{1}H NMR (CD_3COCD_3) δ 10.52 (s, 1 H, S(O)CH), 2.48 (s, 18 H, CH_3), 1.63 (d, 9 H, PMe_3, $J_{P-H} = 9.9$ Hz); $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 210 K) δ 225.4 (d, CO, $J_{C-P} = 31.8$ Hz), 199.3 (S(O)CH), 110.0 (C_6Me_6), 18.4 (d, PMe_3, $J_{C-P} = 30.8$ Hz), 17.1 (C_6Me_6); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 36.8; IR (THF) ν_{CO} 1975, 1922 cm^{-1}. LREI MS: $[M]^+$ 349, $[M - 2CO]^+$ 293, $[M - 2CO - PMe_3]^+$ 217.

(e) *endo*-(η^5-C_6Me_6H)Mn$(CO)_2P(n\text{-}Bu)_3$ (8e). The yellow solution of **8d** (0.728 g, 1.53 mmol) gradually turned orange with 0.5 h at 70 °C. After 4 h at 70 °C, the solution turned dark red in color. After depressurization and solvent removal in vacuo, the red solids were chromatographed on a neutral alumina column. Hexane eluted a yellow band and a red band. Solvent removal in vacuo of the initial yellow band yielded yellow crystals identified by solution IR and ^{1}H NMR spectra as starting material and hexamethylbenzene. Solvent removal in vacuo of the red band yielded red crystals identified by solution IR and ^{1}H NMR spectra as **21** (8 mg, 1% yield). Acetone/hexane (50/50) eluted a yellow orange band, which upon solvent removal in vacuo yielded yellow solid [(η^6-C_6Me_6)Mn$(CO)_2P(n\text{-}Bu)_3$]S(O)CH (**27e**) (0.120 g, 15% yield): ^{1}H NMR (CD_3COCD_3) δ 10.54 (s, 1 H, S(O)CH), 2.46 (s, 18 H, CH_3), 1.47 (m, 18 H, $P(n\text{-}Bu)_3$), 0.94 (t, 9 H, $P(n\text{-}Bu)_3$, $J_{P-H} = 8.2$ Hz); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 226.9 (d, CO, $J_{C-P} = 27.5$ Hz), 200.4 (S(O)CH), 110.4, (C_6Me_6), 27.1–24.2 (m, $P(n\text{-}Bu)_3$), 17.5 (C_6Me_6); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 57.3; IR (THF) ν_{CO} 1967, 1918 cm^{-1}.

(f) *endo*-(η^5-C_6Me_6H)Mn(CO)$(P(OMe)_3)_2$ (12). The yellow solution of **12** (0.103 g, 0.210 mmol) gradually turned darker yellow in color within 2.5 h at room temperature. Solution IR and ^{1}H NMR spectra indicated quantitative formation of **22**, and GC-MS analysis of a headspace sample of the reactor contents indicated HC(O)SCH_3 ($m/z = 76$) had formed. ^{1}H NMR (CD_3COCD_3) δ 3.62 (d, 9 H, OMe, $J_{P-H} = 10.3$ Hz), 3.40 (d, 6 H, OMe, $J_{P-H} = 8.4$ Hz), 2.18 (s, 18 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 231.8 (CO), 104.8 (C_6Me_6), 52.2 ($P(OMe)_3$), 49.3 (d, $P(O)(OMe)_2$, $J_{C-P} = 38.1$ Hz), 16.9 (s, C_6Me_6); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 149.7 ($P(O)(OMe)_2$), 200.2 ($P(OMe)_3$); IR (THF) ν_{CO} 1888 cm^{-1}; (KBr) $\nu_{P=O}$ 1125 cm^{-1}. MW_{calc} for $C_{18}H_{33}O_7P_2Mn$ (M + H) 479.1160; MW_{exp} m/z 479.1154 ($\Delta m = -0.6$ mmu).

Reactions of 8c with CO_2. To *endo*-(η^5-C_6Me_6H)Mn$(CO)_2P(OMe)_3$ (**8c**: 0.122 g, 0.306 mmol) in a 100 mL stainless steel high pressure gas/solution reactor equipped with a glass sleeve, safety pressure release, sample withdrawal port, and quick connect hookup, was added 45 mL of dry, deoxygenated THF via cannula. This solution was purged with CO_2 and subsequently evacuated two times prior to pressurizing the reactor to 800 psi (54.4 atm) with CO_2. Over the course of 45 min, the temperature of the reactor was ramped to 100 °C using an oil bath. The resulting pressure at this temperature was 1000 psi (68.0 atm). After 6 days, the solution was cooled to ambient temperature and depressurized. The product **19**, identified using its solution IR spectrum, formed in quantitative yield. GC-MS analysis of a headspace sample of the reactor contents indicated HC(O)OCH_3 ($m/z = 60$) had formed.

Reactions of 12 with CO_2. To *endo*-(η^5-C_6Me_6H)Mn(CO)$(P(OMe)_3)_2$ (**12**: 0.104 g, 0.211 mmol) in a 100 mL stainless steel high pressure gas/solution reactor equipped with a glass sleeve, safety pressure release, sample withdrawal port, and quick connect hookup, was added 45 mL of dry, deoxygenated THF via cannula. This solution was purged with CO_2 and subsequently evacuated two times prior to pressurizing the reactor to 800 psi (54.4 atm) with CO_2. Over the course of 45 min, the temperature of the reactor was ramped to 100 °C using an oil bath. The resulting pressure at this temperature was 1000 psi (68.0 atm). After 7.5 h (10.5 h total reaction time), the solution was cooled to ambient temperature and depressurized. The product **22**, identified by its solution IR spectrum, formed in quantitative yield. GC-MS analysis of a headspace sample of the reactor contents indicated HC(O)OCH_3 ($m/z = 60$) had formed.

Crystal Structure Determinations. Suitable crystals of **8c** and **12** were grown by recrystallization from hexane solutions at −20 °C. Crystals on glass fibers were sealed in glass capillary tubes, mounted on a goniometer head, and optically centered on an Enraf-Nonius CAD4 diffractometer. The cell constants and an orientation matrix for data collection for each compound were obtained from refinement of 22 (**8c**) and 25 (**12**) randomly selected reflections in the range $2° < \theta < 25°$. Further details of the data collection for the two compounds can be found in Table III. The choice of each of the respective space groups was confirmed by determining the systematic absences in the observed reflections and subsequent least-squares refinement of the structures.

Data for each compound were collected using the ω–θ scan technique using a peak counting time to background time of 2:1. Variable scan rates of θ and ω varied from 1 to 7 deg/min and variable scan ranges calculated by θ scan width $= 0.80 + 0.35 \tan\theta$. Several standard reflections were monitored periodically during data collection and were used to correct for the small loss in intensity. Lorentz and polarization corrections were made for each data set. Only reflections with $F_o > 3\sigma(F_o)$ were used in the final least-squares refinements.

The positions of the manganese and phosphorus atoms were located by Patterson methods. Subsequent cycles of least-squares refinement and difference Fourier calculations, and reference to the DIRDIF program output, were used to locate all other non-hydrogen atoms and the exo hydrogen atom in **8c** and **12**. During the final stages of refinement for **8c**, the remaining hydrogen atom positions were calculated and idealized and the refinement continued with hydrogen atom positions fixed at C–H distances of 0.95 Å. No solvent molecules were found. For **8c**, the space group $P2_12_12_1$ provides a single position for an enantiomorph. Refinement on the other enantiomorph for **8c** resulted in an increase in R_1 from 2.5 to 3.6%. For **12**, anisotropic refinement was performed on all non-hydrogen atoms except for the carbon atoms of the methyl groups which were refined isotropically. During the final stages of refinement for **12**, the remaining hydrogen atom positions were calculated and idealized and the refinement continued with hydrogen atom positions fixed at C–H distances of 0.95 Å. Final values for atomic coordinates, anisotropic temperature factors, and F_{obs} and F_{calc} are provided in supplemental Tables SI–SXV.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This research was also funded by the Office of Research and Educational Development at the University of Iowa. The Bruker WM-360 NMR and the Enraf-Nonius CAD-4 diffractometer were purchased in part with funds from the National Science Foundation (CHE82-01836 and CHE85-07623, respectively). The Bruker AMX-600 NMR was purchased in part with funds from the National Institute of Health (Grant No. RR04087). Accurate mass results were obtained from the Midwest Center for Mass Spectrometry which is partially supported by the National Science Foundation, Biology Division (Grant No. DIR9017262). We also thank Professor Norman Baenziger for his assistance in X-ray diffraction analysis instruction and Professors Didier Astruc and Dwight Sweigart for fruitful discussions.

Supplementary Material Available: Tables containing the final values for the structural determinations (atomic coordinates, anisotropic temperature factors, and F_{obs} and F_{calc}) and additional ORTEP drawings (27 pages). Ordering information is given on any current masthead page.