nificant maxima. The scattering factors coefficients and anomalous dispersion coefficients come respectively from ref 27 and 28.

Acknowledgment. We wish to thank Dr. F. Mathey for stimulating discussions and Dr. R. Schimpf of SADIS Bruker Spectrospin S.A., Wissembourg, France, for the measurements of the deuterium spectra.

Registry No. $1^+ \cdot PF_6^-$, 100945-90-2; **2**, 100993-21-3; **2**-*3,5*-d_2, 100945-92-4; **3**, 100945-87-7; **4**, 100993-22-4; **4**-*3(endo),5*-d_2, 100945-93-5; **5**, 100945-88-8; **5**-*3,5*-d_2, 101052-75-9; **6**, 101052-74-8; **6**-*3,5*-d_2, 100945-94-6; 2,4,6-triphenylphosphabenzene, 13497-36-4; 2,4,6-triphenylphosphabenzene-*1,3*-d_2, 100945-91-3; ferrocene, 102-54-5; trityl hexaflourophosphate, 437-17-2; 2,4,6-triphenylpyrylium-*1,3*-d_2 tetrafluroborate, 100945-95-7; acetophenone-ω-d_3, 17537-31-4.

Supplementary Material Available: Table III, thermal factors (U_{ij}) for anisotropic atoms, Table IV, hydrogen atoms parameters, and Table V, observed and computed structure factor amplitudes (×10) for all observed reflections (16 pages). Ordering information is given on any current masthead page.

---

(27) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2b.

(28) Cromer, D. T. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England; 1974; Vol. IV, Table 2.3.1.

Derivatives of the (Arene)M(CO)$_2$ (M = Mn or Re) Fragment. The Molecular Structure of (η^6-C$_6$Me$_6$)Mn(CO)$_2$Cl

Randal J. Bernhardt, Marie A. Wilmoth, Jerry J. Weers, Daniel M. LaBrush, and Darrell P. Eyman*

Department of Chemistry, The University of Iowa, Iowa City, Iowa 52242

John C. Huffman

Department of Chemistry, The University of Indiana, Bloomington, Indiana 47405

Received August 9, 1985

The compounds $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2X$ (X = I (**3a**), Br (**3b**), and Cl (**3c**)) have been prepared by the photolysis of the cation $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_3^+$ in water saturated with NaX. These compounds as well as $(\eta^6\text{-}C_6H_n(CH_3)_{6-n})Mn(CO)_2I$ (n = 1 (**3d**), 3 (**3e**), and 6 (**3f**)), $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2(PR_3)PF_6$ (R = C_6H_5, OCH_3), $(\eta^6\text{-}C_6H(CH_3)_5)Mn(CO)_2(P(C_6H_5)_3)PF_6$, and $(\eta^6\text{-}C_6(CH_3)_6)Re(CO)_2I$ have been synthesized in CH_2Cl_2, from the corresponding $(\eta^6\text{-arene})M(CO)_3PF_6$ (M = Mn, Re), by the $(CH_3)_3NO$-induced displacement of CO, in the presence of $(n\text{-}C_4H_9)_4NX$ or the phosphine. Compounds **3b** and **3f** undergo rapid halide displacement with CH_3Li to form $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2CH_3$ (**6a**) and $(\eta^6\text{-}C_6H_6)Mn(CO)CH_3$. Reaction of NaCN with **3b** or **3f** gives $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2CN$ or $(\eta^6\text{-}C_6H_6)Mn(CO)_2CN$. Treatment of **3a** with $NaBH_4$ in THF gives the hydride $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2H$ (**8**). Deprotonation of **8**, with CH_3Li, gives the anion $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2^-$, which is also produced by the reaction of **3a** with $NaC_{10}H_8$ in THF. This anion is methylated by CH_3I to form **6a**. These compounds have been characterized by analytical and spectroscopic techniques, and the structure of **3c** has been determined by single-crystal X-ray diffraction studies. This compound crystallizes in the space group $P2_1/c$ with unit-cell dimensions a = 8.701 (3) Å, b = 13.618 (5) Å, c = 13.266 (4) Å, β = 120.82 (1)°, Z = 4, V = 1349.8 Å^3, R = 0.0332, and R_w = 0.0391. The "piano stool" structure involves an η^6-arene with the carbonyls and chloride staggered relative to the arene carbons.

Introduction

(Arene)manganese tricarbonyl cations, $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_3^+$ (**1**), have been and continue to be the topic of extensive investigation.[1,2] This is due in part to the rich chemistry associated with nucleophilic attack at the aromatic ring leading to the formation of cyclohexadienylmanganese tricarbonyl compounds.[3] In contrast, little is known about the compounds $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2N$, where N is not carbonyl and the compound is neutral. All compounds in this class, reported to date, have been formed from **1**.

Coffield and Clossen[3a] observed that increasing methylation of **1** increases steric inhibition of nucleophilic attack at the arene ring in deference to formation of products arising from attack at the carbonyl. Addition of the nucleophiles Me$^-$, $C_6H_5^-$, MeO$^-$, and RNH$^-$ to $(\eta^6\text{-}C_6Me_6)Mn(CO)_3^+$ gave products arising from attack at the carbonyl carbon.[2d] When H$^-$ is used as the nucleophile,[3b] reduction occurs at the ring to yield the cyclohexadienyl derivative *endo*-$(\eta^5\text{-}C_6H_{7-n}Me_n)Mn(CO)_3$ and at the carbonyl to give $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2Me$ (**6**). The latter compound has also been synthesized[4] from **1** and Me_2CuLi as well as by photolysis of $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2C(O)Me$.[3b] The latter technique has also led to the formation of the phenyl analogue from the benzoyl derivative. Hy-

---

(1) Bernhardt, R. J.; Eyman, D. P. *Organometallics* **1984**, *3*, 1445.

(2) (a) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807. (b) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1677. (c) Winkhaus, G. *Z. Anorg. Allg. Chem.* **1963**, *405*, 319. (d) Walker, J. C.; Mawby, R. *J. Chem. Soc., Dalton Trans.* **1973**, 622. (e) Kane-Maguire, L. A. P.; Sweigart, D. A. *Inorg. Chem.* **1979**, *18*, 700.

(3) (a) Coffield, T. H.; Closson, R. D. (to Ethyl Corp.) U.S. Patent 693, 1962; *Chem. Abstr.* **1963**, 59, 11558. (b) Munroe, G. A.; Pauson, P. L. *Isr. J. Chem.* **1976/1977**, *2*, 258. (c) Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta.* **1973**, *7*, 621. (d) Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972**, *11*, 1754.

(4) Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* **1982**, *1*, 173.

0276-7333/86/2305-0883$01.50/0 © 1986 American Chemical Society

drazine reacts with $(\eta^6\text{-}C_6Me_6)Mn(CO)_3^+$ to form the isocyanate derivative.[3d]

To date, the examples previously mentioned, and some of their arene-methylated homologues, are the only known derivatives of this class of compounds. The yields of the reactions used to prepare these compounds are usually very low, and in some cases the products were not isolated but were characterized by spectroscopic techniques.

A synthon, which affords general access to these compounds, would greatly facilitate exploration of their chemistry. Pauson[3b] suggested that $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2X$ (X = I, Br, and Cl) or $((\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2)_2$ could act as precursors to this class of compounds, just as $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$, FpX, and Fp_2 do for the isolelectronic FpN species.[5] It would also be expected that the $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2N$ derivatives would display the same rich chemistry exhibited by the FpN derivatives.

Our preliminary studies[1] and the studies reported herein were initiated to develop a convenient technique for the synthesis of $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2X$ (X = I, Br, and Cl). In addition to the photochemical technique,[1] Me_3NO-promoted carbonyl substitution has been utilized to make the desired compounds. The latter approach was pursued because of the numerous reports of its use in the displacement of carbon monoxide in higher yields than afforded by thermal or photochemical substitution.[6]

An additional objective of these studies is to explore the utility of (arene)manganese dicarbonyl halides as precursors to a range of derivatives formed by nucleophilic displacement of the halide. The synthesis and characterization of $(\eta^6\text{-}C_6Me_6)Mn(CO)_2H$ (**9**) are of special interest because this compound represents the first reported (arene)metal carbonyl hydride.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. The ^1H NMR spectra were recorded on a Perkin-Elmer R12 spectrometer operating at 60 MHz and 35 °C. The ^{13}C NMR spectra were recorded at 360 MHz on a Bruker WM-360 operating at 25 °C. Infrared data were collected on a Perkin-Elmer 421 grating spectrophotometer or on a IBM/Bruker IR98 interferometer. Mass spectra were recorded on a Hewlett-Packard 5985B GC–MS system using the direct inlet probe at 30 eV. Photoreactions were performed in a Rayonet Photoreactor with 350-nm source. Analyses were performed by The University of Iowa Analytical labs or by Mic-Anal, Tuscon, AZ. All reactions were performed under nitrogen unless otherwise specified. Solvents were purified by techniques described in Perrin and Perrin[7] and out gassed before use. All (arene)manganese tricarbonyl cations were prepared by the methods of Wilkinson and Winkhouse.[2a,b,8] $Mn(CO)_5Br$ was synthesized by standard literature techniques.[9] Triphenylphosphine, trimethyl phosphite, ammonium hexafluorophosphate, and tetra-*n*-butylammonium halides were purchased from the Aldrich Chemical Co. and used as received. Trimethylamine *N*-oxide hydrate was dehydrated by azeotroping the water from a toluene solution.

Synthesis of $(\eta^6\text{-}C_6Me_6)Mn(CO)_2X$ (3). General Procedure (Photolysis Method). To an aqueous solution (0.01 M) of $(\eta^6\text{-}C_6Me_6)Mn(CO)_3^+$ (**1a**), obtained as the hydrolysate of $(\eta^6\text{-}C_6Me_6)Mn(CO)_3AlCl_3Br$, was added enough of the appropriate sodium halide to saturate the mixture. The solution was subjected to photolysis for approximately 2 h. The red solid that formed was filtered, washed with water, and carefully recrystallized from an acetone/water mixture. The filtrate was again subjected to photolysis, and the filtration–recrystallization procedure was repeated every 2 h until no more of the crude product could be isolated. This process required approximately 8–10 h for completion. The crude product was purified by liquid chromatography on a silica column using hexane/acetone as the eluent. Recrystallization from hexane/acetone gave the final purified product. Yields were calculated on the basis of $Mn(CO)_5Br$.

Table I. ^1H NMR and IR Data

compd	^1H NMR δ	IR ν(CO), cm^{-1}
3a	2.36 (s, 18 H)[a]	1968, 1920[b]
3b	2.25 (s, 18 H)[a]	1971, 1921[b]
3c	2.25 (s, 18 H)[a]	1972, 1920[b]
3d	2.30 (s, 9 H), 2.23 (s, 6 H), 5.13 (m, 1 H)[a]	1961, 1911[e]
3e	2.43 (s, 9 H), 5.1 (s, 3 H)[a]	1981, 1937[b]
3f	5.90 (s, 6 H)[b]	1995, 1955[d]
4a	2.05 (s), 7.47 (m, 15 H)[a]	1982, 1941[e]
4b	2.05 (s), 2.45 (s, 6 H),[a] 2.55 (s, 3 H), 7.60 (m, 15 H)	1985, 1937[e]
4c	2.40 (s, 18 H), 3.35 (d, 9 H)[b]	1995, 1946[e]
5	2.19 (s, 18 H)[a]	1964, 1906[c]
8	2.35 (s, 18 H), –10.9 (s, 1 H)[c]	1945, 1890[c]
9		1840[d]

[a] $CDCl_3$. [b] $CD_3C(O)CD_3$. [c] CH_2Cl_2. [d] THF. [e] KBr.

$(\eta^6\text{-}C_6Me_6)Mn(CO)_2I$ (3a): purple crystals; decompose at 135 °C; ^1H NMR and IR in Table I; yield 70%; mass spectral data, *m/z* (ion) 400 $((C_6Me_6)Mn(CO)_2I^+)$, 344 $((C_6Me_6)MnI^+)$, 217 $(C_6Me_6Mn^+)$. Anal. Calcd for $C_{14}H_{18}IO_2Mn$: C, 42.03; H, 5.13. Found: C, 41.45, H, 4.54.

$(\eta^6\text{-}C_6Me_6)Mn(CO)_2Br$ (3b): purple crystals; decompose at 126 °C; ^1H NMR and IR in Table I; yield 64%; mass spectral data, *m/z* (ion) 298, 296 $(C_6Me_6MnBr^+)$, 217 $(C_6Me_6Mn^+)$, 162 (C_6Me_6). Anal. Calcd for $C_{14}H_{18}BrO_2Mn$: C, 47.62; H, 5.13. Found: C, 47.24; H, 5.06.

$(\eta^6\text{-}C_6Me_6)Mn(CO)_2Cl$ (3c): red crystals; decompose at 114 °C; ^1H NMR and IR in Table I; yield 19%; mass spectral data, *m/z* (ion) 273 $(C_6Me_6Mn(CO)_2^+$, 254, 252 $(C_6Me_6MnCl^+)$, 245 $(C_6Me_6MnCO^+)$, 217 (C_6Me_6Mn), 162 (C_6Me_6). Anal. Calcd for $C_{14}H_{18}ClO_2Mn$: C, 54.48; H, 5.87. Found: C, 54.05; H, 5.61.

$(\eta^6\text{-}C_6H_3Me_3)Mn(CO)_2I$ (3e): red solid; characterized by spectroscopic comparison with $(\eta^6\text{-}C_6Me_6)Mn(CO)_2I$; isolated yield <1%.

Synthesis of (Arene)$Mn(CO)_2X$ (3). General Procedure (Me_3NO Method). $(\eta^6$-Arene)$Mn(CO)_3[PF_6]$ (5.60 mmol), 6.10 mmol of Me_3NO, and 6.78 mmol of *n*-Bu_4NX were combined in a 500-mL round-bottom flask. The system was flushed with argon, and 250 mL of CH_2Cl_2 was added. The resulting deep red solution was stirred for 30 min, after which the solvent was removed by vacuum evaporation. The crude product was then purified by using the same procedure as described in the photolysis method.

$(\eta^6\text{-}C_6Me_6)Mn(CO)_2X$ (X = Cl (3c), Br (3b), and (3a)). The physical and spectroscopic properties found for these compounds were identical with those found for the same compounds isolated from the photolysis method; yield 23% (**3c**); 79% (**3b**); 80% (**3a**).

$(\eta^6\text{-}C_6HMe_5)Mn(CO)_2I$ (3d): purple crystals; mp 92 °C, ^1H NMR and IR in Table I; yield 40%.[10]

$(\eta^6\text{-}C_6H_3Me_3)Mn(CO)_2I$ (3e): purple crystals; mp 84 °C; ^1H NMR and IR in Table I; yield 40%. Anal. Calcd for $C_{11}H_{12}IO_2Mn$: C, 36.89; H, 3.35. Found: C, 36.75; H, 3.34.

$(\eta^6\text{-}C_6H_6)Mn(CO)_2I$ (3f): purple crystals; mp 113 °C; ^1H NMR and IR in Table I; yield 70%.[11]

Synthesis of (Arene)$Mn(CO)_2(PR_3)[PF_6]$ (4). General Procedure (Me_3NO Method). $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_3[PF_6]$ (2.20 mmol) and 4.40 mmol of PR_3 were dissolved in 40 mL of

---

(5) (a) Miyaka, A.; Kondo, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 631. (b) Wilford, J. B.; Forester, A.; Stone, F. G. A. *J. Chem. Soc.* **1965**, 6519.

(6) (a) Blumer, D. J.; Barnett, K. W.; Brown, T. L. *J. Organomet. Chem.* **1979**, *173*, 71. (b) Elzihga, J.; Hogevan, H. *J. Chem. Soc., Chem. Commun.* **1977**, 705. (c) Neumann, M. F.; Brion, F.; Martina, P. *Tetrahedron Lett.* **1978**, 5033. (d) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1975**, 829. (e) Koelle, U. *J. Organomet. Chem.* **1977**, *133*, 53.

(7) *Purification of Laboratory Chemicals*; Perrin, D. D.; Armatego, W. L. F.; Perrin, D. R. Pergamon press.

(8) Winkhaus, G.; Singer, H. *Z. Naturforsch., B: B, Anorg. Chem., Org. Chem.* **1963**, *18B*, 418.

(9) Quick, M. H.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 160.

(10) Anal. Calcd for $C_{13}H_{16}IO_2Mn$: C, 39.32; H, 4.15. Found: C, 40.43; H, 4.15.

(11) Anal. Calcd for $C_8H_6IO_2Mn$: C, 30.40; H, 1.91. Found: C, 29.90; H, 1.84.

CH_2Cl_2. As Me_3NO (2.20 mmol) was added in one portion under a stream of argon, there was vigorous evolution of gas and the reaction mixture turned red. After the mixture was stirred at room temperature for 6 h, the solvent was removed by vacuum evaporation. The yellow residue, when placed on a silica column and eluted with $CHCl_3$, gave a yellow eluent which had no hexamethylbenzene resonance in the ^1H NMR. Subsequent elution with acetone caused the desired cationic complex to move down the column as a yellow band. Water was added to the concentrated acetone solution until it became cloudy. Cooling the mixture overnight precipitated the product.

(η^6-C_6Me_6)Mn(CO)$_2$(P(C_6H_5)$_3$)[PF_6] (4a): yellow crystals; ^1H NMR and IR in Table I; yield 65%. Anal. Calcd for $C_{32}H_{33}F_6O_2P_2Mn$: C, 56.48; H, 4.85. Found: C, 56.64; H, 5.02.

(η^6-C_6Me_6)Mn(CO)$_2$(P(OMe)$_3$)[PF_6] (4b): yellow crystals; ^1H NMR and IR in Table I; yield 60%. Anal. Calcd for $C_{17}H_{27}F_6O_5P_2Mn$: C, 37.64; H, 4.98. Found: C, 37.71; H, 5.12.

(η^6-C_6HMe_5)Mn(CO)$_2$(P(C_6H_5)$_3$)[PF_6] (4c): yellow crystals; ^1H NMR and IR in Table I; yield 70%. Anal. Calcd for $C_{31}H_{31}F_6O_2P_2Mn$: C, 55.85; H, 4.65. Found: C, 55.56; H, 4.47.

Synthesis of (η^6-C_6Me_6)Re(CO)$_2$I (5): A sample of (η^6-C_6Me_6)Re(CO)$_3$[PF_6] (**2**; 0.980 g, 1.70 mmol), prepared by the method of Sweigert,[6] Me_3NO (0.191 g, 2.55 mmol), and n-Bu_4NI (1.252 g, 3.39 mmol) were combined in a 250-mL round-bottom flask. The system was flushed with argon, and 75 mL of CH_2Cl_2 was added. The orange solution was stirred for 15 min, after which the solvent was removed by vacuum evaporation. The residue, after dissolution in $CHCl_3$ and separation from insolubles by filtration, was chromatographically purified on a silica column using $Et_2O/CHCl_3$ as the eluent. Evaporation of the solvent gave 0.090 g (10% yield) of yellow crystalline product: ^1H NMR and IR in Table I; mass spectral data, m/z (ion) 532, 530 ($C_6Me_6Re(CO)_2I^+$), 504, 502 ($C_6Me_6ReCOI^+$), 476, 474 ($C_6Me_6ReI^+$). Anal. Calcd for $C_{14}H_{18}IO_2Re$: C, 31.64; H, 3.14. Found: C, 31.62, H, 3.18.

Reactions of (Arene)Mn(CO)$_2$X. Synthesis of (η^6-C_6Me_6)-Mn(CO)$_2$Me (**6a**). Compound **3b** (0.353 g, 1.00 mmol) was placed in 35 mL of dry outgassed THF and cooled to −78 °C. When MeLi (0.645 mL, 1 mmol) was syringed into the stirred reaction mixture, the color changed from red to yellow. After the mixture was allowed to warm to room temperature, the solvent was removed by vacuum evaporation and the residue was extracted with hexane. The hexane extracts were combined, concentrated, and cooled to −78 °C. The resulting orange crystalline precipitate was spectroscopically identical (IR and ^1H NMR) with the compound Pauson[3b] assigned as (η^6-C_6Me_6)Mn(CO)$_2$Me. The conversion from **3b** to product was spectroscopically quantitative by IR and ^1H NMR.

Synthesis of (η^6-C_6Me_6)Mn(CO)$_2$CN (7a). Compound **3b** (0.353 g, 1.0 mmol) was refluxed with NaCN (0.0784 g, 1.6 mmol) in 50 mL of methanol. The reaction mixture, which changed color from red to yellow in 15 min, was allowed to cool to room temperature, and the solvent was removed by vacuum evaporation. The residue was extracted with $CHCl_3$, and the extract, after solvent removal, was recrystallized from CH_2Cl_2/Et_2O. The yellow solid product decomposed at 195 °C, (lit. 197 °C) and was spectroscopically identical with the compound reported by Mawby.[2d] The yield was quantitative by IR and ^1H NMR spectroscopy.

Synthesis of (η^6-C_6Me_6)Mn(CO)$_2$H (8). Compound **3a** (0.80 g, 2.0 mmol) was placed in 250 mL of dry outgassed THF. $NaBH_4$ (1.33 g, 35.1 mmol) was added against a counterstream of argon, and the reaction vessel was placed in a bath at 50 °C. The reaction was monitored by observation of the disappearance of the starting material carbonyl bands in the IR and the appearance of the product bands. The reaction proceeded quantitatively by IR and was complete in 2.5–5 h. The reaction mixture was allowed to cool to room temperature, and the remaining $NaBH_4$ was destroyed by addition of 10 mL of water. The aqueous THF was removed under vacuum, and the product was then sublimed from the residue at 50 °C and 0.001 torr: yellow crystalline solid; decompose at 124 °C; ^1H NMR and IR in Table I; yield 80% based on **3a**; mass spectral data, m/z (ion) 274, ($C_6Me_6Mn(CO)_2H^+$), 273 ($C_6Me_6Mn(CO)_2^+$), 245 ($C_6Me_6Mn(CO)^+$), 218 (C_6Me_6MnH), 217 ($C_6Me_6MnH^+$). Anal. Calcd for $C_{14}H_{19}O_2Mn$: C, 61.32; H, 6.98. Found: C, 61.23; H, 7.11.

Table II. Crystal Data Summary

empirical formula	$MnC_{14}H_{15}ClO_2$
color of crystal	red
crystal dimens, mm	0.15 × 0.18 × 0.17
space group	$P2_1/c$
cell dimens	
temp, °C	−158 °C
a, Å	8.701 (3)
b, Å	13.618 (5)
c, Å	13.266 (4)
β, deg	120.82 (1)
Z (molecules/cell)	4
vol, $Å^3$	1349.76
D(calcd), g/cm^3	1.519
wavelength, Å	0.710 69
mol wt	308.69
linear abs coeff, cm^{-1}	11.301
detector to sample dist, cm	22.5
sample to source dist, cm	23.5
av ω scan width at half-height	0.25
scan speed, deg/min	4.0
scan width (deg, + dispersion)	2.0
individual bkgd, s	8
aperture size, mm	3.0 × 4.0
2θ, range, deg	6–45
total no. of reflctns collected	4768
no. of unique intensities	2375
no. with $F > 3.00\ \sigma\ (F)$	2144
$R(F)$	0.033
$R_w(F)$	0.039
goodness of fit for the last cycle	1.154
max Δ/σ for last cycle	0.05

Synthesis of (η^6-C_6H_6)Mn(CO)$_2$Me (6b). This compound was prepared by the same method used in the preparation of **6a**, using **3f** as the starting material. The resulting yellow crystalline precipitate, isolated in 75.0% yield, was spectroscopically identical, by IR and ^1H NMR, with the compound Pauson[3b] assigned as (η^6-C_6H_6)Mn(CO)$_2$Me.

Synthesis of (η^6-C_6H_6)Mn(CO)$_2$CN (7b). This compound was prepared by the same method used to prepare **7a**, using **3f** as the starting material. The resulting yellow crystalline precipitate, which was isolated in 65% yield, was spectroscopically identical, by IR and ^1H NMR, with the compound reported by Mawby.[2d]

Synthesis of (η^6-C_6Me_6)Mn(CO)$_2^-$ (9). Method A. MeLi (1.0 mmol in ether) was syringed into a solution of **8** (0.274 g, 1.00 mmol) in 25 mL of THF. The addition was accompanied by gas evolution and a pronounced color change from yellow to deep red orange. The gas evolved was analyzed as methane by GC. The carbonyl bands of **8** disappeared completely, and a new broad intense band appeared at 1840 cm^{-1}. Upon addition of MeI (0.28 g, 2.0 mmol) **6a** was formed as established by spectroscopic (IR, ^1H NMR) comparison with an authentic sample. The yield of the anion alkylation was not determined by product isolation but appeared to be very low as spectroscopically determined. No other carbonyl-containing products were isolated or detected, suggesting that extensive decomposition had occurred.

Method B. 3a (0.40 g, 1.0 mmol) dissolved in 50 mL THF was syringed into a solution containing 1.5 mmol of sodium naphthalide. The deep green color of the sodium naphthalide solution immediately turned much darker, and the IR of this solution displayed an intense broad band at 1860 cm^{-1}. Upon addition of MeI the IR bands for **6a** grew in. Some decomposition had occurred during the reduction as evidenced by the formation of a precipitate that gave no carbonyl stretching bands.

X-ray Data Collection for 3c. A well-formed crystal was mounted on a glass fiber by using silicone grease and transferred to the goniostat where it was cooled to −158 °C with a gas flow cooling system. The diffractometer, general operating techniques, and data reduction formula have been described in detail previously.[12] Crystal and diffractometer data unique to this study are given in Table II.

---

[12] (a) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kerkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

Table III. Fractional Coordinates and Isotropic Thermal Parameters[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mn(1)	1461.3 (5)	8011.8 (3)	7883.3 (3)	10
Cl(2)	3102 (1)	6767 (1)	9248 (1)	22
C(3)	1051 (4)	7012 (2)	6436 (2)	14
C(4)	−549 (3)	7525 (2)	6080 (2)	13
C(5)	−526 (3)	8578 (2)	6172 (2)	13
C(6)	1104 (3)	9096 (2)	6590 (2)	13
C(7)	2710 (3)	8571 (2)	6890 (2)	14
C(8)	2690 (3)	7541 (2)	6841 (2)	13
C(9)	1073 (4)	5907 (2)	6389 (3)	19
C(10)	−2305 (4)	6984 (2)	5612 (3)	19
C(11)	−2259 (4)	9108 (2)	5789 (3)	20
C(12)	1153 (4)	10205 (2)	6669 (3)	18
C(13)	4411 (4)	9142 (2)	7274 (3)	17
C(14)	4387 (4)	6977 (2)	7207 (3)	19
C(15)	2670 (4)	8948 (2)	9053 (3)	16
O(16)	3295 (3)	9472 (2)	9697 (2)	26
C(17)	−271 (4)	7943 (2)	8288 (2)	19
O(18)	−1273 (3)	7923 (2)	8488 (2)	29

[a] The isotropic equivalent of the anisotropic thermal parameter is based on the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Structure Solution Refinement. The structure was solved by direct methods[13] and phasing and Fourier techniques. All atoms, including hydrogens, were located and refined by using isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all others. Neutral atom scattering factors were used[14] as well as anomalous dispersion terms for Mn and C. A final difference Fourier synthesis was featureless, the largest peak being 0.19 e/Å^3. Fractional coordinates are listed in Table III.

Results and Discussion

Synthesis and Characterization of (Arene)metal Dicarbonyl Halides. The photochemical approach to the synthesis of **3a–c** and **3e**, patterned after the method used by Sweigart,[2e] in the synthesis of (η^6-arene)Mn(CO)$_2$(PR$_3$)$^+$, is shown in eq 1.

$$(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_3^+ + X^- \rightarrow (\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2X + CO \quad (1)$$

The compounds **3a–f** are all deep red or purple crystalline solids that are stable in air. Solutions of **3a–f** decompose at different rates, usually within an hour. The thermal decompositions of **3a–c** display an interesting transition at temperatures of 136, 125, and 114 °C, respectively. At these temperatures they undergo a sharp elimination of a white solid which sublimes to the walls of the capillary and melts at 163 °C, the melting point of hexamethylbenzene. These observations suggest that the consistently low values obtained in the carbon hydrogen elemental analyses of compounds **3a–c** might be attributable to decomposition that occurs during sublimation and recrystallization.

The characterization of compounds **3a–c** presented a challenge since their IR carbonyl bands and ^{1}H NMR were very similar and relatively featureless (Table I). Compounds **3a–c** display a single sharp resonance in the ^{1}H NMR with a chemical shift between 2.25 and 2.36 ppm downfield from Me$_4$Si. This is not significantly different from hexamethylbenzene in the same solvent (δ 2.25). The singlet resonance in the ^{1}H NMR indicates that the η^6-arene structure is intact and that no cyclohexadienyl species is formed. The ^{13}C NMR of **3a** is very simple with three singlet resonances at 228.6 (M–*C*–O), 104.0 (M–*C*–C), and 16.75 ppm (M–C–*C*) downfield from Me$_4$Si. The resonances located at 228.6 ppm, assigned to the carbonyl carbon, is consistent with the chemical shifts of most transition-metal carbonyls. The upfield shift of the arene ring carbons, from the normal 119–136 ppm range expected for aromatic carbons, to 104.0 ppm is consistent with the effect of η^6-coordination of an arene to a transition metal.

The carbonyl stretching regions of the IR spectra of compounds **3a–c** are all very similar, each displaying two intense bands as expected for a dicarbonyl species. As the data in Table I indicate, for (η^6-arene)Mn(CO)$_2$I, the carbonyl frequencies increase 4–5 cm^{-1} for each decrease in methyl substitution. This is consistent with observations in other η^5-cyclopentadienyl and η^6-arene transition-metal carbonyls.[15]

The photochemical synthetic technique cannot be successfully extended to the synthesis of partially or nonmethylated (arene)manganese carbonyl halides. The mesytilene derivative **3d** is formed in only 1% yield while no benzene derivative is produced. Instead of leading to carbonyl substitution, photolysis of partially methylated or non-methylated species resulted in gross decomposition. The photolytic synthetic technique apparently decomposes the halide substitution products of the mesitylene and benzene derivatives, while products **3a–c** are left intact, or less decomposed. Photolytic cleavage of the arene ligand from manganese is a probable mode of decomposition although displacement of the arene by solvent, as observed by Mawby[3c] in acetone, is also a possibility. Although compound **5** was detected by IR after the photolysis of **2** in saturated aqueous NaI, the isolated yield was not high enough to give sufficient quantities of product for further study.

A desire to develop a synthetic method permitting access to a broader range of arene derivatives led to exploration of the Me$_3$NO technique. Since all of the compounds **1** used in this study exhibit carbonyl stretching frequencies in excess of 2000 cm^{-1}, it was anticipated that the reactions shown in eq 2 should proceed in the solvent CH$_2$Cl$_2$.

$$(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_3^+ + Me_3NO \rightarrow (\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2NMe_3^+ + CO_2 \quad (2)$$

$$(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2NMe_3^+ + X^- \rightarrow (\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2X + Me_3N$$

When (η^6-C$_6$H$_n$Me$_{6-n}$)Mn(CO)$_3$[PF$_6$] is treated with Me$_3$NO in the presence of n-Bu$_4$NX (X = Cl, Br, or I), the reaction forming **3** is complete in 30 min. It is our observation that this preparative technique gives greater yields of **3** than the photochemical technique in all cases. This is explained by the observation that the less methylated homologues of **3** are all photosensitive solids. In addition, the air and thermal stability of the solid (η^6-arene)Mn(CO)$_2$I and that of its solutions decreases as the extent of methylation of the arene ring is decreased. Compounds **3d–f**, prepared by this method, were all purple solids. The NMR and IR spectra of these compounds are found in Table I.

Compounds **4a**, **4b**, and **4c** have also been prepared in good yields by the Me$_3$NO method. These compounds are not formed by thermal or photoinduced addition of PR$_3$ to the corresponding tricarbonyl cations, although the photochemical method does lead to product with the

---

(13) Main, P., et al. MULTAN78; University of York: York, England, 1978.

(14) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

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

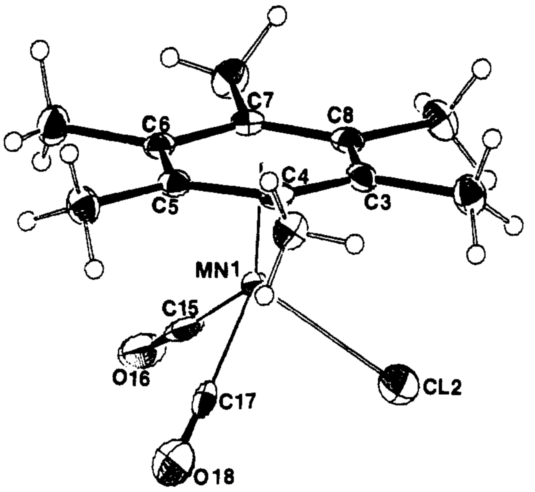

Figure 1. An ORTEP drawing of (η^6-$C_6(CH_3)_6$)Mn(CO)$_2$Cl.

benzene, toluene, xylene, and mesitylene analogues.[2e]

The rhenium compound **5** is formed in high yield, as determined spectroscopically, by both the photochemical and Me_3NO methods. The workup and purification, however, led to relatively low yields of isolated material. Comparison of the properties of this compound with those of **3a** are interesting and suggest significantly different bonding and electronic distributions. In contrast to the manganese analogue **3a**, which melts at 120 °C with loss of the arene, **5** melts with decomposition at 170 °C without loss of the arene. This suggests that the arene is more tightly bound in the rhenium compound. Evidence for stronger bonding between rhenium and the arene is also found in the mass spectrum of **5** which has $C_6Me_6ReI^+$ as the base peak. In comparison with the mass spectrum of **3a**, this spectrum shows a much higher portion of the ion current involving metal–arene species and even includes species involving rhenium bound to fragments of the arene. In contrast, the mass spectrum of **3a** shows no fragments having manganese bound to fragments of the arene and displays a base peak of m/z 147, the same as found in the mass spectrum of free hexamethylbenzene, corresponding to $M^+ - CH_3$.

Attempts to convert **5** to the hydride derivative (η^6-C_6Me_6)Re(CO)$_2$H using either $NaBH_4$ or (i-C_4H_9)$_2$AlH in THF have been unsuccessful. Additional studies of the chemical properties of **5**, the first member of a new class of compounds, are in progress.

Crystallographic Study of (η^6-C_6Me_6)Mn(CO)$_2$Cl. The spectroscopic similarities of **3a–c**, difficulties in obtaining good elemental analyses, and difficulties in obtaining parent ions in the mass spectra of **3b** and **3c** encouraged an X-ray crystallographic study of **3c** in order to establish the identity and structures of these compounds.

The results of the X-ray crystallographic study are illustrated in the ORTEP plot in Figure 1. Selected distances and angles are listed in Table IV. As Figure 1 indicates, the molecule has a "piano stool" structure with an η^6-coordinated arene. The "legs" of this structure are oriented in a staggered configuration relative to the arene carbons.

It is interesting to note that the arene displays alternating long and short C–C bond lengths. The C–C distances for bonds trans to a carbonyl are 1.405 Å, the C–C distance *trans* to the Cl is 1.419 Å, and those between average 1.437 Å. The differences are significant, since the calculated esd's are 0.004 Å. The C–C(methyl) bond distances range from 1.506 to 1.513 Å. A least-squares plane analysis indicates the arene ring is folded along the C(4)···C(7) backbone at an angle of 2.916 ± 0.750°. One can see the effect of this folding in the Mn–C(arene) distances. Mn–C(5) and Mn–C(6) are 2.171 (3) and 2.162 (3) Å, respectively, while the remaining four Mn–C(arene) distances range from 2.221 (3) to 2.232 (3) Å. The distance Mn–plane[C(3)–C(4)–C(7)–C(8)] is 1.709 (3) Å while the distance Mn–plane[C(4)–C(5)–C(6)–C(7)] is 1.706 (3) Å. The shorter Mn–C(5) and Mn–C(6) distances and the longer C(5)–C(6) distance trans to Cl are indicative of a stronger manganese–ring interaction at the C(5)–C(6) site than at the C(3)–C(4) and C(7)–C(8) sites. This apparently induces a folding in the arene ring in addition to a small displacement of the manganese relative to the center of the ring. The manganese is displaced only 0.026 (3) Å, toward the C(3)–C(8) side of the ring, from a vector projecting from the C(4)–C(7) foldline and perpendicular to the plane defined by the atoms C(3)–C(4)–C(7)–C(8).

Table IV. Bond Distances and Angles for (η^6-C_6Me_6)Mn(CO)$_2$Cl

Bond Distances (Å)			
Mn–Cl	2.3543 (10)	Mn–C(17)	1.843 (4)
Mn–C(3)	2.2282 (26)	O(16)-C(15)	1.029 (3)
Mn-C(4)	i.2208 (25)	O(18)–C(17)	1.034 (4)
Mn–C(5)	2.1714 (26)	C(3)–C(4)	1.405 (4)
Mn–C(6)	2.1622 (25)	C(3)–C(8)	1.434 (4)
Mn–C(7)	2.2276 (25)	C(4)–C(5)	1.438 (4)
Mn–C(8)	2.2316 (25)	C(5)–C(6)	1.419 (4)
Mn–C(15)	1.862 (3)	C(7)–C(8)	1.405 (4)

Bond Angles (deg)			
C(4)–C(5)–C(11)	130.24 (19)	Cl–Mn–C(15)	89.51 (8)
C(5)–C(6)–C(7)	119.86 (24)	Cl–Mn–C(17)	90.19 (9)
C(6)–C(7)–C(8)	119.91 (23)	C(15)–Mn–C(17)	89.37 (11)
C(3)–C(8)–C(7)	120.36 (24)	C(4)–C(3)–C(8)	120.01 (24)
Mn–C(15)–O(16)	177.94 (25)	C(3)–C(4)–C(5)	119.11 (24)
Mn–C(17)–O(18)	177.74 (26)		

Reactions of 3a and 3f. Both **3a** and **3f** are converted in 15 min, in refluxing methanol with excess NaCN, to the previously reported corresponding cyanide derivatives **7a** and **7b**. These conditions are less severe than those used for the same conversion in the FpX[16] system which implies greater ease of nucleophilic displacement of the halide in the manganese analogues. The halide can also be displaced by Me^- to yield the previously reported **6a** and **6b** derivatives. Attempts to displace a CO from **3a**, using P(n-C_4H_9)$_3$ in THF, gave complete displacement of the arene in 1 h.

The compound (η^6-C_6Me_6)Mn(CO)$_2$H (**8**), which was synthesized by reaction of $NaBH_4$ with the halide **3a**,[1] is to our knowledge the first reported (η^6-arene)metal carbonyl hydride. This hydride behaves like (η^5-C_5Me_5)Fe(CO)$_2$H,[17] Fp′H, in that it does not display bimolecular elimination of H_2 up to 120 °C. The stabilities of **8** and Fp′H to bimolecular elimination, in contrast to the instability of FpH, which eliminates H_2 at 20 °C to form (Fp)$_2$, may be attributable to the increased steric hindrance to bimolecular interaction. Between 120 and 130 °C, **8** loses a white crystalline solid (mp 163 °C) which is probably C_6Me_6. This behavior is similar to that displayed by the halide derivatives **3a–c** and suggests that, in each of these compounds, the manganese–arene bonds are the weakest metal–ligand bonds in the molecule. Unlike many organometallic hydrides, solid **8** displays some stability to air oxidation and can be handled conveniently on the benchtop for periods of under 5 min without significant decomposition. Compound **8** is soluble in most polar and nonpolar organic solvents, but in solution it decomposes

---

[16] Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165.

[17] Lapinte, C.; Astruc, D. *J. Organomet. Chem.* **1984**, *260*, C13.

rapidly upon exposure to air.

Compound **8** has been observed to display some chemical properties which are characteristic of other transition-metal carbonyl hydrides.[18] It is deprotonated by strong bases to give **9**. It reacts rapidly at 25 °C with CCl_4 or $HCCl_3$ to produce **3c** but does not react with CH_2Cl_2. At 25 °C in THF, the arene is rapidly displaced by $P(C_6H_5)_3$ or $P(C_4H_9)_3$. In THF, hexane, or acetone solution, carbon monoxide reacts with **8** in a rather unusual reaction to produce *endo*-$(\eta^5\text{-}C_6HMe_6)Mn(CO)_3$. This reaction will be the topic of a subsequent publication.

The conjugate base of **8**, $(\eta^6\text{-}C_6Me_6)Mn(CO)_2^-$ (**9**), was synthesized by deprotonation of **8** with MeLi and by the reduction of **3a** with sodium naphthalide in THF. The IR spectrum, in THF solution in each case, displays one broad intense band, at 1840 cm^{-1} for the lithium salt and 1860 cm^{-1} for the sodium salt. The anion, formed by either method, was further characterized by its reaction with MeI to form **6a**. The nucleophilicity of **9**, demonstrated in this reaction, suggests that this anion would be an effective intermediate in the synthesis of a large number of derivatives of the $(\eta^6$-arene)manganese dicarbonyl fragment. Studies of the nucleophilicity of **9** toward organic and metal-containing substrates are in progress.

In summary, the syntheses of compounds **3a–f** and **5** introduce a new class of compounds which is isoelectronic with the extensively studied species $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$. It has been shown that the Me_3NO method of preparing compounds **3** and **4** is superior to the photolysis method, giving larger yields and requiring much shorter reaction times. It has also been shown that (arene)manganese carbonyl halides and the anion **8** can be synthesized and used in the preparation of derivatives that contain the $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2$ unit. The synthetic utility of compounds **3b** and **3f** is demonstrated in this study by their use in the synthesis of the species **6a**,**b**, **7a**,**b**, **8**, and **9**.

Acknowledgment. We wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank the Marshall H. Wrubel Computing Center for a generous gift of computing time.

Registry No. **1a**, 46930-53-4; **2**, 100858-08-0; **3a**, 91230-49-8; **3b**, 91230-50-1; **3c**, 91230-51-2; **3d**, 100858-01-3; **3e**, 91230-52-3; **3f**, 100858-02-4; **4a**, 100858-04-6; **4b**, 100898-52-0; **4c**, 100858-06-8; **5**, 100858-07-9; **6a**, 65643-58-5; **6b**, 65643-62-1; **7a**, 41638-97-5; **7b**, 34852-71-6; **8**, 91230-53-4; $(\eta^6\text{-}C_6Me_6)Mn(CO)_3[PF_6]$, 38958-98-4; $(\eta^6\text{-}C_6HMe_5)Mn(CO)_3[PF_6]$, 65643-64-3; $(\eta^6\text{-}C_6H_3Me_3)Mn(CO)_3[PF_6]$, 35399-67-8; $(\eta^6\text{-}C_6H_6)Mn(CO)_3[PF_6]$, 38834-51-4.

Supplementary Material Available: ORTEP drawings and stereoviews of compound **3c** and tables of fractional coordinates and isotropic thermal parameters, observed and calculated structure factors, anisotropic thermal parameters, bond lengths and bond angles, bond distances and angles involving the centroid of C_3–C_8, and least-squares plane analysis of the arene ring atoms for compound **3c** (27 pages). Ordering information is given on any current masthead page. Crystallographic data are also available, in microfiche form only, from the Chemistry Library, Indiana University, Bloomington, IN 47405. Request IUMSC Report 84902 when ordering.

---

[18] Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

Functionalized Group 4 Metallocene Complexes as Binucleating Ligands: Synthesis and Structural Characterization of Tetracarbonyl[[*P*,*P'*-bis((diphenylphosphino)cyclopentadienyl)]dichlorozirconium(IV)]molybdenum(0)

Wayne Tikkanen,*[†] Yoshiko Fujita,[†] and Jeffrey L. Petersen[‡]

Thompson Chemistry Laboratory, Williams College, Williamstown, Massachussetts 01267, Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

Received September 17, 1985

The metathesis of lithium (diphenylphosphino)cyclopentadienide with bis(tetrahydrofuran)tetrachlorozirconium in benzene leads to the formation of $[(C_6H_5)_2P(C_5H_4)]_2ZrCl_2$ (**1**) in 70% yield. This functionalized canted zirconocene species readily displaces the norbornadiene from (norbornadiene)tetracarbonylmolybdenum to give $[(C_6H_5)_2P(C_5H_4)]_2ZrCl_2Mo(CO)_4$ (**2**) in 88% yield. The CO stretches observed in the infrared spectrum of **2** are consistent with cis-disubstituted molybdenum tetracarbonyl complexes $L_2Mo(CO)_4$, where $L_2 = 2PPh_3$ or $(CH_2PPh_2)_2$. This heterobinuclear complex forms triclinic crystals of $P\bar{1}$ symmetry from chloroform/hexanes. The refined lattice parameters are $a = 9.866$ (2) Å, $b = 11.218$ (3) Å, $c = 17.900$ (4) Å, $\alpha = 85.32$ (2)°, $\beta = 83.88$ (2)°, $\gamma = 66.81$ (2)°, $V = 1808.8$ (7) Å^3, and $\rho_{calcd} = 1.597$ g cm^{-3}. Full-matrix least-squares refinement (based on F_o^2) converged with final discrepancy indices of $R(F_o) = 0.0288$ and $R(F_o^2) = 0.0399$. The zirconium–molybdenum separation in **2** of 4.8524 (3) Å rules out any direct metal–metal interaction. The structure of **2** is remarkable in that, despite the chelation of the molybdenum atom by **1**, the coordination spheres of both metals show very little difference from the individual mononuclear components, zirconocene dichloride and (bis(diphenylphosphino)methane)tetracarbonylmolybdenum. The chloride atoms in **2** can be substituted by methyl groups via reaction with methylmagnesium bromide to give $[(C_6H_5)_2P(C_5H_4)]_2Zr(CH_3)_2Mo(CO)_4$ (**3**) in 75% yield.

Bimetallic complexes in which two different metals with widely differing reactivity are in close proximity have received considerable attention.[1] This molecular arrangement provides the opportunity of introducing new patterns of reactivity arising from the interactions of the metals either with each other or with ligands on the adjacent metal. These interactions are important in understanding

---

[†] Williams College.

[‡] West Virginia University.

0276-7333/86/2305-0888$01.50/0