(a) *cis*-[$Pd(C_6X_5)_2(OC_4H_8)_2$] (X = F, Cl). X = F. $AgClO_4$ (0.256 g, 1.24 mmol) was added to a freshly distilled tetrahydrofuran solution (20 mL) of 0.944 g (0.62 mmol) of $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6F_5)_2]_2$[3] under nitrogen, and the mixture was stirred at room temperature for 20 min. The resulting suspension was evaporated to dryness, and the residue was extracted from the insoluble residue ($AgCl + NBu_4ClO_4$) with 50 mL of diethyl ether. The solution was evaporated to ca. 5 mL, and, by addition of 20 mL of *n*-hexane, a white solid was obtained (0.37 g, 90% yield).

X = Cl was obtained similarly: 0.45 g (0.257 mmol) of $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$[4] and 0.106 g (0.51 mmol) of $AgClO_4$ [0.3 g (80%) yield].

(b) [$(C_6X_5)_2M(\mu\text{-}X')_2M'(COD)]_n$ (1–12) (See Tables I–IV). Complexes 1–12 were obtained by reacting *cis*-[$M(C_6X_5)_2(THF)_2$] with [$M'X'_2(COD)$] (molar ratio 1:1) in CH_2Cl_2. A typical preparation is given below.

[$(C_6F_5)_2Pt(\mu\text{-}Br)_2Pd(COD)]_n$ (2). To a dichloromethane solution (20 mL) of *cis*-[$Pt(C_6F_5)_2(THF)_2$] (0.17 g, 0.25 mmol) was added 0.111 g (0.25 mmol) of [$PdBr_2(COD)$], and the solution was stirred for 10 min at room temperature. After evaporation to dryness the resulting residue was washed with *n*-hexane and stirred for 10 min with 10 mL of benzene. The yellow solid so obtained contains benzene of crystallization. This can be removed by heating (80 °C for 5 h), affording 0.15 g (61%) of pure complex 2. Crystals suitable for X-ray diffraction were obtained by solvent diffusion (CH_2Cl_2/*n*-hexane) at −30 °C.

Table IV collects pertinent information on the preparation of the other complexes.

Acknowledgment. We thank the CAICYT (Spain) for financial support and the Scientific Office of NATO for a travel grant.

Registry No. **1** (*n* = 1), 113778-23-7; **1** (*n* = 2), 113778-12-4; **2** (*n* = 1), 113778-24-8; **2** (*n* = 2), 113778-13-5; **3** (*n* = 1), 113778-33-9; **3** (*n* = 2), 113778-14-6; **4** (*n* = 1), 113778-25-9; **4** (*n* = 2), 113778-15-7; **5** (*n* = 1), 113778-26-0; **5** (*n* = 2), 113778-16-8; **6** (*n* = 1), 113778-27-1; **6** (*n* = 2), 113778-17-9; **7** (*n* = 1), 113778-28-2; **7** (*n* = 2), 113778-18-0; **8** (*n* = 1), 113778-29-3; **8** (*n* = 2), 113778-19-1; **9** (*n* = 1), 113778-30-6; **9** (*n* = 2), 113778-20-4; **10** (*n* = 1), 113778-31-7; **10** (*n* = 2), 113778-21-5; **11** (*n* = 1), 113778-32-8; **11** (*n* = 2), 113778-22-6; **12** (*n* = 1), 113792-86-2; **12** (*n* = 2), 113792-85-1; *cis*-[$Pd(C_6F_5)_2(OC_4H_8)_2$], 97877-50-4; *cis*-[$Pd(C_6Cl_5)_2(OC_4H_8)_2$], 97877-51-5; $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6F_5)_2]_2$, 74436-10-5; $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$, 86392-02-1; [$PdCl_2(COD)$], 12107-56-1; [$PdBr_2(COD)$], 12145-47-0; [$PtCl_2(COD)$], 12080-32-9; [$PtBr_2(COD)$], 12145-48-1; [$PtI_2(COD)$], 12266-72-7; *cis*-[*Pt*-$(C_6F_5)_2(OC_4H_8)_2$], 97877-52-6; *cis*-[$Pt(C_6Cl_5)_2(OC_4H_8)_2$], 97877-53-7.

Supplementary Material Available: Tables of H-atom coordinates and anisotropic thermal parameters (2 pages); a listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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X-ray Structural Studies of Tricarbonyl(cyclohexadienyl)manganese, Dicarbonylnitrosyl(cyclohexadienyl)manganese, and Dicarbonylnitrosyl(cyclohexadiene)manganese Complexes

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Received July 27, 1987

X-ray structures are reported for three complexes relevant to the chemistry of arene functionalization as mediated by the $Mn(CO)_3$ and $Mn(CO)_2NO$ fragments. $(C_6H_6Ph)Mn(CO)_3$ (4) crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.159$ (3) Å, $b = 9.711$ (3) Å, $c = 12.990$ (3) Å, $\beta = 94.73$ (2)°, $Z = 4$, $R = 0.029$, and $R_w = 0.030$. The phenyl group is positioned exo to the metal, and the dihedal angle between the planar dienyl carbons (C5–C6–C7–C8–C9) and the nonbonded plane (C5–C4–C9) is 36.5°. $[(C_6H_6Me)Mn(CO)_2NO]PF_6$ (5) crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.241$ (2) Å, $b = 9.292$ (2) Å, $c = 11.088$ (2) Å, $\beta = 104.87$ (1)°, $Z = 4$, $R = 0.032$, and $R_w = 0.041$. The methyl group is exo, and the dihedral angle between the bonded plane (C3–C4–C5–C6–C7) and the nonbonded plane (C3–C2–C7) of the cyclohexadienyl ring is 39.6°. $[(C_6H_6Ph\ PBu_3)Mn(CO)_2NO]PF_6$ (6) crystallizes in the monoclinc space group $P2_1/c$ with $a = 9.911$ (2) Å, $b = 14.624$ (3) Å, $c = 21.771$ (4) Å, $\beta = 100.41$ (2)°, $Z = 4$, $R = 0.049$, and $R_w = 0.047$. The PBu_3 group is exo, and the dihedral angle between the diene plane (C5–C6–C7–C8) and the nonbonded plane (C5–C4–C3–C8) is 40.8°. The NO ligand in 5 and 6 is positioned under the unsaturated part of the coordinated ring.

Introduction

It recently has been demonstrated that manganese-mediated functionalization of arenes is a promising synthetic procedure.[1] Thus, the addition of phosphorus, hydride, and carbon donor nucleophiles to $(arene)Mn(CO)_3^+$ occurs with high regio- and stereoselectivity as shown in Scheme I. The functionalized arene can be

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[†] Contribution no. 4526.

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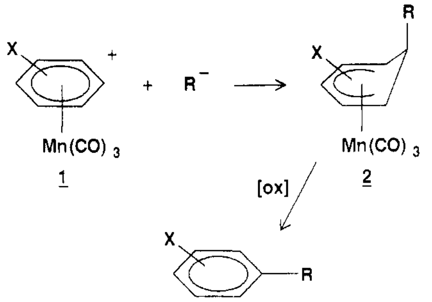
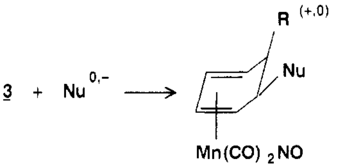
Table I. Summary of X-ray Diffraction Data

	4	5	6
complex	$(C_6H_6Ph)Mn(CO)_3$	$[(C_6H_6Me)Mn(CO)_2NO]PF_6$	$[(C_6H_6Ph{\cdot}PBu_3)Mn(CO)_2NO]PF_6$
formula	$C_{15}H_{11}O_3Mn$	$C_9H_9NO_3PF_6Mn$	$C_{26}H_{38}NO_3P_2F_6Mn$
fw	294.19	380.10	643.47
a, Å	10.159 (3)	13.241 (2)	9.911 (2)
b, Å	9.711 (3)	9.292 (2)	14.624 (3)
c, Å	12.990 (3)	11.088 (2)	21.771 (4)
β, deg	94.73 (2)	104.87 (1)	100.41 (2)
V, A^3	1277.2	1318.53	3103.35
Z	4	4	4
ρ(calcd), g cm^{-3}	1.530	1.914	1.377
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
temp, °C	-100	-100	20
radiatn	Mo Kα, 0.71069 Å	Mo Kα, 0.71069 Å	Mo Kα, 0.71069 Å
μ, cm^{-1}	10.83	11.6	5.71
2θ limits, deg	4-55	4-55	3.5-45
observns	3332	3405	3307
unique data	2288 [$I \geq 2\sigma(I)$]	2417 [$I \geq 2\sigma(I)$]	2927 [$I \geq 2\sigma(I)$]
final no. of variables	216	226	426
R	0.029	0.032	0.049
R_w	0.030	0.041	0.047

Scheme I



liberated from 2 by oxidative procedures. Replacement of a CO ligand in 1 by an alkene or alkyne is readily achieved,[2,3] and the resultant $(arene)Mn(CO)_2(olefin)^+$ cations are preferentially attacked by nucleophiles at the olefin to give σ-bonded complexes. Replacement of a CO ligand in 2 by NO^+ produces cationic (cyclohexadienyl)-$Mn(CO)_2NO^+$ (3) complexes that rapidly react with phosphorus, nitrogen, and hydride donors at the carbon adjacent to the saturated one according to eq 1.[4-10] While most nucleophiles attack 3 in an exo fashion, hydride is most unusual in that it is positioned stereospecifically endo in the diene product.



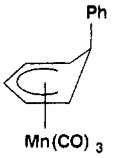
(1)

Carbon donors usually react with 3 to give electron-transfer products. However, this unwanted pathway can be eliminated by substituting PBu_3 or diphos for one or two of the coordinated CO ligands in 3.[11]

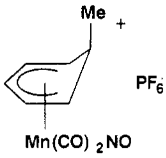
Table II. Fractional Coordinates ($\times 10^4$) for $(C_6H_6Ph)Mn(CO)_3$

atom	x	y	z
Mn	2969.7 (2)	3800.8 (3)	1561.0 (2)
O1	5011 (1)	5842 (2)	1149 (1)
O2	4803 (2)	1659 (2)	925 (1)
O3	1472 (2)	4193 (2)	-461 (1)
C1	4211 (2)	5066 (2)	1326 (2)
C2	4084 (2)	2490 (2)	1169 (2)
C3	2083 (2)	4024 (2)	314 (1)
C4	372 (2)	3771 (2)	2049 (1)
C5	1321 (2)	4978 (2)	2172 (1)
C6	2431 (2)	4928 (2)	2875 (1)
C7	2995 (2)	3650 (2)	3196 (1)
C8	2401 (2)	2450 (2)	2746 (1)
C9	1295 (2)	2545 (2)	2042 (1)
C10	-670 (2)	3704 (2)	2832 (1)
C11	-2001 (2)	3674 (2)	2487 (1)
C12	-2967 (2)	3599 (2)	3178 (2)
C13	-2620 (2)	3556 (2)	4230 (2)
C14	-1297 (2)	3582 (2)	4584 (2)
C15	-330 (2)	3658 (2)	3894 (1)
H4	-110 (20)	3840 (20)	1380 (10)
H5	1060 (20)	5850 (20)	1890 (10)
H6	2870 (20)	5730 (20)	3010 (20)
H7	3750 (20)	3620 (20)	3660 (10)
H8	2800 (20)	1620 (20)	2840 (20)
H9	990 (20)	1730 (20)	1690 (20)
H11	-2240 (20)	3670 (20)	1760 (10)
H12	-3860 (20)	3570 (20)	2930 (20)
H13	-3260 (20)	3530 (20)	4720 (20)
H14	-1040 (20)	3560 (20)	5360 (20)
H15	550 (20)	3670 (20)	1690 (20)

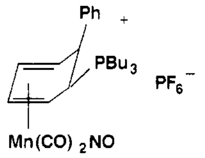
It is important that structural characterization accompany the development of these manganese-mediated reactions. In this paper we report X-ray diffraction studies of three relevant complexes, namely, 4, 5, and 6.



4



5



6

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Table III. Selected Bond Distances (Å) and Angles (deg) for $(C_6H_6Ph)Mn(CO)_3$

		Bond Distances			
Mn–C1	1.804 (2)	C13–C14	1.385 (2)	C5–C6	1.391 (2)
Mn–C2	1.804 (2)	C14–C15	1.385 (2)	C6–C7	1.415 (2)
Mn–C3	1.801 (2)	C15–C10	1.394 (2)	C7–C8	1.417 (2)
Mn–C5	2.227 (2)	C11–H11	0.952 (17)	C8–C9	1.392 (2)
Mn–C6	2.137 (2)	C12–H12	0.937 (18)	C9–C4	1.516 (2)
Mn–C7	2.127 (1)	C13–H13	0.940 (19)	C4–H4	0.964 (15)
Mn–C8	2.138 (2)	C14–H14	1.025 (19)	C5–H5	0.947 (16)
Mn–C9	2.224 (2)	C15–H15	0.929 (17)	C6–H6	0.909 (18)
C4–C10	1.528 (2)	C1–O1	1.146 (2)	C7–H7	0.936 (17)
C10–C11	1.390 (2)	C2–O2	1.151 (2)	C8–H8	0.905 (18)
C11–C12	1.385 (2)	C3–O3	1.149 (2)	C9–H9	0.950 (18)
C12–C13	1.383 (3)	C4–C5	1.518 (2)		
		Bond Angles			
C1–Mn–C2	88.23 (7)	Mn–C8–C9	74.79 (9)	C7–C8–C9	120.7 (2)
C2–Mn–C3	96.32 (7)	Mn–C9–C8	68.07 (9)	C8–C9–C4	120.9 (1)
C3–Mn–C1	94.06 (7)	C5–Mn–C9	64.31 (7)	C5–C4–C10	115.6 (1)
C3–Mn–C5	85.63 (6)	C5–Mn–C6	37.11 (8)	C9–C4–C10	115.7 (1)
C3–Mn–C9	88.90 (6)	C6–Mn–C7	38.77 (8)	C5–C4–H4	108.3 (9)
C1–Mn–C5	105.50 (7)	C7–Mn–C8	38.80 (9)	C9–C4–H4	108.6 (9)
C2–Mn–C9	101.80 (7)	C8–Mn–C9	37.14 (8)	C10–C4–H4	105.7 (9)
Mn–C5–C4	93.21 (9)	Mn–C1–O1	177.6 (2)	C4–C10–C11	119.7 (1)
Mn–C9–C4	93.39 (9)	Mn–C2–O2	179.4 (2)	C4–C10–C15	122.1 (1)
Mn–C5–C6	67.91 (9)	Mn–C3–O3	177.0 (1)	C10–C15–C14	120.7 (1)
Mn–C6–C5	74.98 (9)	C5–C4–C9	102.6 (1)	C15–C14–C13	120.5 (2)
Mn–C6–C7	70.26 (9)	C4–C5–C6	121.0 (1)	C14–C13–C12	119.2 (2)
Mn–C7–C6	70.97 (9)	C5–C6–C7	120.7 (2)	C13–C12–C11	120.3 (2)
Mn–C7–C8	71.01 (9)	C6–C7–C8	116.8 (1)	C10–C11–C12	121.0 (1)
Mn–C8–C7	70.19 (9)				

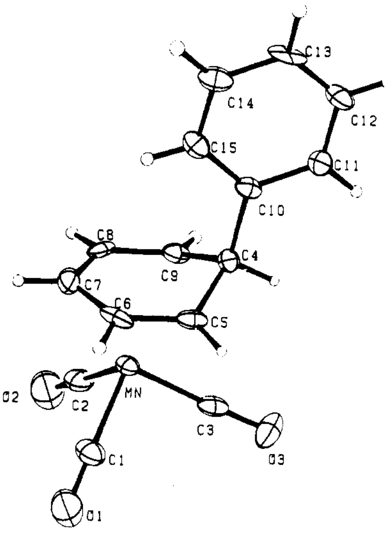

Figure 1. An ORTEP drawing of $(C_6H_6Ph)Mn(CO)_3$ with the thermal ellipsoids at the 50% probability level.

Table IV. Fractional Coordinates (×10^4) for $[(C_6H_6Me)Mn(CO)_2NO]PF_6$

atom	*x*	*y*	*z*
Mn	2484.7 (3)	3910.1 (4)	351.3 (3)
P	4277.4 (5)	3255.2 (7)	-3332.9 (6)
F1	5130 (1)	3350 (2)	-2006 (2)
F2	3433 (1)	3164 (2)	-4656 (1)
F3	3458 (2)	4075 (3)	-2756 (2)
F4	5103 (1)	2442 (3)	-3901 (2)
F5	4675 (2)	4760 (2)	-3722 (2)
F6	3886 (2)	1758 (2)	-2931 (2)
O1	903 (1)	5600 (2)	1001 (2)
O2	1242 (2)	3142 (3)	-2234 (2)
O3	3517 (2)	6414 (2)	-564 (2)
N	1545 (2)	4911 (2)	747 (2)
C1	3787 (2)	-181 (3)	827 (3)
C2	3136 (2)	1089 (3)	139 (2)
C3	3765 (2)	2443 (3)	157 (2)
C4	4074 (2)	3263 (3)	1255 (2)
C5	3457 (2)	3225 (3)	2122 (2)
C6	2527 (2)	2377 (3)	1815 (2)
C7	2280 (2)	1550 (3)	737 (2)
C8	3111 (2)	5498 (3)	-204 (2)
C9	1735 (2)	3419 (3)	-1267 (2)
H1A	4189 (24)	93 (35)	1685 (29)
H1B	4291 (26)	-483 (37)	314 (28)
H1C	3323 (24)	-1027 (34)	844 (29)
H2	2832 (22)	797 (30)	-641 (26)
H3	4115 (24)	2595 (33)	-443 (29)
H4	4648 (21)	3950 (28)	1366 (23)
H5	3642 (21)	3784 (30)	2832 (26)
H6	2020 (23)	2551 (31)	2303 (27)
H7	1653 (23)	1126 (30)	520 (25)

Experimental Section

General Remarks. Complexes 4, 5, 6, $[(C_6H_6Ph)Mn(CO)_2NO]BF_4$ (**7a**), and $[(C_6H_6Ph)Mn(CO)_2NO]PF_6$ (**7b**) were synthesized and fully characterized as previously described.[1,7]

Collection and Refinement of X-ray Data. Crystals of 4 were obtained by slow cooling of a pentane solution at 20 °C. A crystal of dimensions 0.28 × 0.15 × 0.30 mm was mounted in a glass capillary under nitrogen. Data were collected on a Syntex P3 diffractometer at -100 °C. Intensity data were collected by the ω-scan technique (scan rate 4.0–10.0° min^{-1}); total background time equals scan time. Three standard reflections were monitored every 200 reflections. An absorption correction was made on the basis of ψ-scan data. After Lorentz and polarization corrections a total of 2288 unique reflections were used for the calculations. The structure was solved by direct methods using a program similar to MULTAN 78.[12] Non-hydrogen atoms were refined anisotropically to minimize $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)$ and $\sigma(F) = [\sigma(I)^2 + (0.02I)^2]^{1/2}$. All hydrogen atoms were found in a difference Fourier map and all refined to small isotropic temperature factors. The final difference Fourier map contained no significant residual electron density peaks.

Crystals of **7a** were grown by ether diffusion into a nitromethane solution at 0 °C. Data collection and treatment were similar to those above. The structure was solved by standard heavy-atom techniques, but refinement was plagued by disorder problems. All non-hydrogen atoms were located and the basic features of the structure were as anticipated, but metrical details were clearly unreasonable. After repeated attempts, the search for a suitable

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[12] Computer software written by J. C. Calabrese and is similar to MULTAN 78 (Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declerq, J. P.).

Table V. Selected Bond Distances (Å) and Angles (deg) for $[(C_6H_6Me)Mn(CO)_2NO]PF_6$

		Bond Distances			
Mn–N	1.699 (2)	P–F4	1.586 (2)	C5–C6	1.428 (4)
Mn–C3	2.229 (2)	P–F5	1.592 (2)	C6–C7	1.387 (4)
Mn–C4	2.170 (2)	P–F6	1.588 (2)	C1–H1A	0.998 (31)
Mn–C5	2.150 (2)	O1–N	1.156 (3)	C1–H1B	1.020 (33)
Mn–C6	2.149 (2)	O2–C9	1.133 (3)	C1–H1C	1.001 (32)
Mn–C7	2.263 (2)	O3–C8	1.133 (3)	C2–H2	0.898 (28)
Mn–C8	1.872 (3)	C1–C2	1.543 (4)	C3–H3	0.914 (30)
Mn–C9	1.870 (3)	C2–C3	1.506 (4)	C4–H4	0.975 (27)
P–F1	1.611 (2)	C2–C7	1.515 (4)	C5–H5	0.922 (28)
P–F2	1.602 (2)	C3–C4	1.406 (4)	C6–H6	0.977 (29)
P–F3	1.588 (2)	C4–C5	1.412 (3)	C7–H7	0.894 (28)
		Bond Angles			
N–Mn–C3	170.3 (1)	C6–Mn–C7	36.5 (1)	C2–C3–C4	120.1 (2)
N–Mn–C4	136.0 (1)	C6–Mn–C8	147.4 (1)	C3–C4–C5	119.0 (2)
N–Mn–C5	103.5 (1)	C6–Mn–C9	117.8 (1)	C4–C5–C6	117.8 (2)
N–Mn–C6	92.7 (1)	C7–Mn–C8	155.5 (1)	C5–C6–C7	120.6 (2)
N–Mn–C7	110.5 (1)	C7–Mn–C9	83.4 (1)	C2–C7–C6	119.7 (2)
N–Mn–C8	93.9 (1)	C8–Mn–C9	92.7 (1)	C2–C1–H1A	112 (2)
N–Mn–C9	97.9 (1)	Mn–N–O1	179.2 (4)	C2–C1–H1B	107 (2)
C3–Mn–C4	37.3 (1)	Mn–C8–O3	176.7 (2)	C2–C1–H1C	110 (2)
C3–Mn–C5	67.4 (1)	Mn–C9–O2	176.9 (3)	C1–C2–H2	107 (2)
C3–Mn–C6	78.2 (1)	Mn–C3–C2	94.6 (2)	C3–C2–H2	112 (2)
C3–Mn–C7	63.7 (1)	Mn–C3–C4	69.1 (1)	C7–C2–H2	108 (2)
C3–Mn–C8	92.2 (1)	Mn–C4–C3	73.6 (1)	C2–C3–H3	120 (2)
C3–Mn–C9	89.3 (1)	Mn–C4–C5	70.1 (1)	C4–C3–H3	117 (2)
C4–Mn–C5	38.2 (1)	Mn–C5–C4	71.7 (1)	C3–C4–H4	120 (2)
C4–Mn–C6	68.5 (1)	Mn–C5–C6	70.6 (1)	C5–C4–H4	120 (2)
C4–Mn–C7	78.1 (1)	Mn–C6–C5	70.6 (1)	C4–C5–H5	120 (2)
C4–Mn–C8	84.9 (1)	Mn–C6–C7	76.2 (1)	C6–C5–H5	123 (2)
C4–Mn–C9	126.0 (1)	Mn–C7–C2	93.0 (2)	C5–C6–H6	117 (2)
C5–Mn–C6	38.8 (1)	Mn–C7–C6	67.3 (1)	C7–C6–H6	122 (2)
C5–Mn–C7	67.3 (1)	C1–C2–C3	113.3 (2)	C2–C7–H7	120 (2)
C5–Mn–C8	108.0 (1)	C1–C2–C7	112.7 (2)	C6–C7–H7	118 (2)
C5–Mn–C9	148.2 (1)	C3–C2–C7	103.4 (2)		

model was abandoned in favor of using a different counterion.

Crystals of **7b** were grown as for **7a**. Data collection and treatment were similar to those above. The structure was once again solved by heavy-atom techniques. Refinement of the structure was only marginally better than the structure above. Metrical details were clearly inadequate for the structural comparison desired, so refinement was abandoned in favor of the methyl complex **5**.

Crystals of **5** were grown by slow diffusion of diethyl ether into a nitromethane solution at 0 °C. A crystal of dimensions 0.33 × 0.31 × 0.30 mm was mounted in a glass capillary and the X-ray data collected at −100 °C by the ω-scan technique as described above. An absorption correction was not made. A total of 2417 reflections were used in the refinement, which utilized the same program as for **4**. Anisotropic refinement of non-hydrogen atoms utilized the weighting scheme $w = 1/\sigma(F)$, where $\sigma(F) = [\sigma(I)^2 + 0.003(I^2)]^{1/2}$. The hydrogen atoms were readily located in a difference Fourier map and refined isotropically. The final difference Fourier map contained several peaks (0.2–0.3 e $Å^{-3}$) mainly in the region of bonds between non-hydrogen atoms.

Crystals of **6** were grown by diethyl ether diffusion into a dichloromethane solution at −5 °C. A suitable crystal was mounted on a glass fiber, and date were collected at 20 °C on a Nicolet R3m diffractometer using the θ–2θ scan technique. Three standard reflections were monitored every 100 reflections. An absorption correction was not made. The structure was solved by direct methods using the SHELXTL 4.0 program. Refinement involved least-squares minimization of $[\sum(w|F_c - F_o|^2/\sum wF_o^2]^{1/2}$ where $w = 1/[\sigma^2(F_o) + 0.0002(F_o^2)]$. The hydrogen atoms H3, H4, H5, H6, H7 and H8 were located in a difference Fourier map and refined isotropically with the bond length restriction $r = 0.96 \pm 0.04$ Å. The other hydrogen atoms were placed in calculated positions with $r = 0.96$ Å. The PF_6^- anion was disordered, which was successfully modeled by refining two orientations of the fluorine octahedra with respect to a common phoshorus atom center. The site occupancy factor was calculated to be 0.64 (unprimed F atoms in Table VI) and 0.36 (primed F atoms) for the two sets of fluorine atoms. The final difference Fourier map contained only peaks less than 0.2 e $Å^{-3}$.

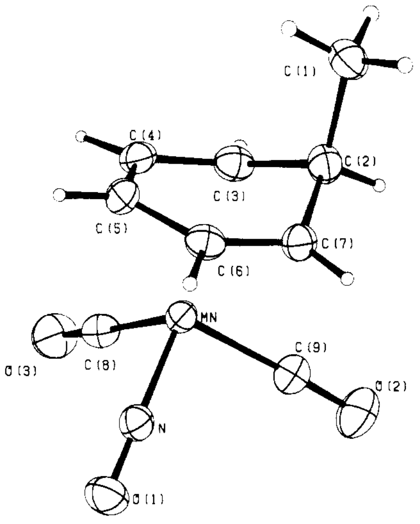

Figure 2. An ORTEP drawing of $[(C_6H_6Me)Mn(CO)_2NO]PF_6$ with the thermal ellipsoids at the 50% probability level.

Results and Discussion

Figure 1 shows the structure of **4**; Tables I–III give crystal data, the atomic coordinates, and bond distances and angles, respectively. The cyclohexadienyl ring is symmetrical across a mirror plane, which coincides with a pseudo-mirror plane of the entire molecule containing the phenyl ring plane and the atoms C4, C7, Mn, C3, O3, H4, and C10. The dienyl carbon atoms C5, C6, C8, and C9 define a nearly perfect plane, from which C7 deviates by 0.019 (1) Å. Hydrogen atoms H5, H6, H8 and H9 deviate significantly (ca. 0.15 (2) Å) from this plane toward the metal. The cyclohexadienyl ring is folded about C5–C9

Table VI. Fractional Coordinates ($\times 10^4$) and Temperature Factors ($\times 10^3$) for $[(C_6H_6Ph \bullet PBu_3)Mn(CO)_2NO]PF_6$

atom	*x*	*y*	*z*	*U*, Å^2	atom	*x*	*y*	*z*	*U*, Å^2
Mn(1)	3745 (1)	1774 (1)	3977 (1)	54 (1)[a]	F(4′)	1045 (11)	7624 (7)	1850 (7)	202 (7)[a]
C(1)	2882 (5)	2678 (4)	4340 (2)	77 (2)[a]	F(5′)	−596 (7)	8696 (6)	1722 (4)	123 (4)[a]
O(1)	2363 (4)	3229 (3)	4582 (2)	121 (2)[a]	F(6′)	1325 (8)	8966 (8)	1422 (3)	134 (5)[a]
C(2)	5460 (5)	2259 (3)	4128 (2)	68 (2)[a]	H(3)	4803 (35)	2894 (23)	2728 (18)	80 (2)
O(2)	3686 (4)	591 (2)	5014 (2)	109 (2)[a]	H(4)	5948 (32)	1669 (25)	3026 (17)	80 (2)
N(1)	3737 (4)	1051 (3)	4575 (2)	72 (2)[a]	H(5)	4885 (32)	372 (20)	3415 (15)	80 (2)
O(3)	6553 (4)	2538 (3)	4226 (2)	106 (2)[a]	H(6)	2465 (37)	365 (22)	3357 (18)	80 (2)
C(3)	4155 (4)	2392 (2)	2671 (2)	41 (1)[a]	H(7)	1302 (31)	1812 (27)	3189 (18)	80 (2)
C(4)	5002 (4)	1485 (2)	2816 (2)	45 (1)[a]	H(8)	2850 (39)	3108 (21)	3122 (18)	80 (2)
C(5)	4354 (4)	925 (3)	3274 (2)	54 (2)[a]	H(10)	3418	215	2124	80 (2)
C(6)	2930 (4)	903 (3)	3255 (2)	58 (2)[a]	H(11)	3791	−639	1263	80 (2)
C(7)	2255 (4)	1752 (4)	3181 (2)	57 (2)[a]	H(12)	5851	−460	892	80 (2)
C(8)	3149 (4)	2493 (3)	3115 (2)	48 (1)[a]	H(13)	7560	467	1422	80 (2)
C(9)	5223 (4)	905 (2)	2264 (2)	47 (1)[a]	H(14)	7187	1364	2255	80 (2)
C(10)	4262 (4)	290 (2)	1972 (2)	58 (2)[a]	H(15a)	3621	2702	880	80 (2)
C(11)	4481 (5)	−223 (3)	1465 (2)	78 (2)[a]	H(15b)	4455	1895	1241	80 (2)
C(12)	5701 (5)	−128 (3)	1254 (2)	92 (2)[a]	H(16a)	6050	2963	1744	80 (2)
C(13)	6692 (5)	436 (3)	1557 (2)	82 (2)[a]	H(16b)	5247	3733	1329	80 (2)
C(14)	6480 (4)	960 (3)	2053 (2)	61 (2)[a]	H(17a)	6612	2275	880	80 (2)
C(15)	4195 (4)	2525 (3)	1265 (2)	45 (1)[a]	H(17b)	5716	2980	441	80 (2)
C(16)	5494 (4)	3098 (3)	1345 (2)	51 (1)[a]	H(18a)	8032	3323	530	80 (2)
C(17)	6308 (4)	2899 (3)	837 (2)	58 (2)[a]	H(18b)	8135	3450	1252	80 (2)
C(18)	7544 (5)	3507 (3)	852 (2)	82 (2)[a]	H(18c)	7255	4131	787	80 (2)
C(19)	2671 (4)	3806 (2)	1915 (2)	51 (1)[a]	H(19a)	3487	4169	2025	80 (2)
C(20)	1836 (4)	4206 (3)	1320 (2)	63 (2)[a]	H(19b)	2131	3855	2238	80 (2)
C(21)	1419 (5)	5189 (3)	1395 (2)	78 (2)[a]	H(20a)	1024	3842	1201	80 (2)
C(22)	584 (5)	5591 (3)	830 (2)	104 (3)[a]	H(20b)	2378	4180	997	80 (2)
C(23)	1677 (4)	1925 (3)	1687 (2)	51 (1)[a]	H(21a)	2235	5551	1506	80 (2)
C(24)	1133 (4)	1776 (3)	993 (2)	59 (2)[a]	H(21b)	899	5212	1727	80 (2)
C(25)	−210 (4)	1268 (3)	881 (2)	72 (2)[a]	H(22a)	369	6213	915	80 (2)
C(26)	−832 (5)	1176 (4)	204 (2)	103 (2)[a]	H(22b)	−251	5248	717	80 (2)
P(1)	3193 (1)	2624 (1)	1879 (1)	42 (1)[a]	H(22c)	1086	5575	493	80 (2)
P(2)	991 (1)	8555 (1)	2026 (1)	67 (1)[a]	H(23a)	963	2209	1864	80 (2)
F(1)	1305 (4)	9239 (3)	1537 (2)	116 (2)[a]	H(23b)	1885	1336	1874	80 (2)
F(2)	2553 (4)	8179 (3)	2107 (3)	114 (2)[a]	H(24a)	1797	1432	819	80 (2)
F(3)	761 (10)	7831 (5)	2532 (5)	111 (4)[a]	H(24b)	999	2361	792	80 (2)
F(4)	−487 (5)	8845 (4)	1946 (3)	149 (3)[a]	H(25a)	−846	1585	1089	80 (2)
F(5)	539 (5)	7774 (3)	1519 (2)	116 (2)[a]	H(25b)	−54	664	1053	80 (2)
F(6)	1498 (5)	9251 (4)	2543 (3)	143 (3)[a]	H(26a)	−1662	824	161	80 (2)
F(1′)	2440 (7)	8584 (7)	2360 (4)	135 (4)[a]	H(26b)	−197	875	−14	80 (2)
F(2′)	398 (23)	8329 (14)	2641 (10)	169 (10)[a]	H(26c)	−1037	1774	29	80 (2)
F(3′)	928 (18)	9603 (11)	2249 (8)	140 (8)[a]					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

with a dihedral angle of 36.5 (5)°. The phenyl substituent is positioned exo as expected from the manner in which 4 was synthesized,[1] namely, nucleophilic addition of PhMgBr to $(C_6H_6)Mn(CO)_3^+$.

An attempt was made to determine the X-ray structure of $[(C_6H_6Ph)Mn(CO)_2NO]BF_4$ (**7a**), which is readily synthesized from 4 by treatment with $NOBF_4$. Unfortunately, the structure could not be refined below a *R* value of 0.12 due to poorly resolved disorder in the cyclohexadienyl, $Mn(CO)_2NO$, and BF_4^- parts of the molecule. The final difference Fourier map showed many peaks between 0.5 and 2.5 e Å^{-3}, but no clear, refinable disorder model could be formulated. The PF_6^- salt (**7b**) likewise could not be well-characterized by X-ray diffraction. For this reason we chose to examine the methyl analogue of 7, namely, complex 5. An ORTEP drawing of 5 is given in Figure 2; atomic coordinates and bond distances and angles are in Tables IV and V, respectively. The five unsaturated carbon atoms of the cyclohexadienyl ring are essentially planar (maximum deviation 0.022 (1) Å). The C3–C7 plane makes a dihedral angle of 39.6 (5)° with the C2–C3–C7 plane. As occurs with complex 4, the hydrogen atoms H3, H4, H6 and H7 are displaced significantly (ca. 0.15 (2) Å) from the dienyl plane toward the Mn atom. As expected, the NO and CO ligands are bonded to the metal in a linear fashion and the methyl group is exo to the metal. Ignoring the difference between NO and CO, the molecule possesses an approximate mirror plane normal to the cyclohexadienyl ring. Carbonyl C9–O2 eclipses the saturated carbon C2. With respect to the plane through Mn–C5–C2, C1 deviates by only 0.010 (5) Å. C9 deviates from this plane by 0.19 Å while C8 and N are 1.5 and 1.0 Å away, respectively. The effect of replacing CO and Ph groups in 4 by NO$^+$ and Me to give 5 causes the Mn–C(O) bonds to lengthen by ca. 0.07 Å. This increase can be attributed to the positive charge and the NO ligand, which have the

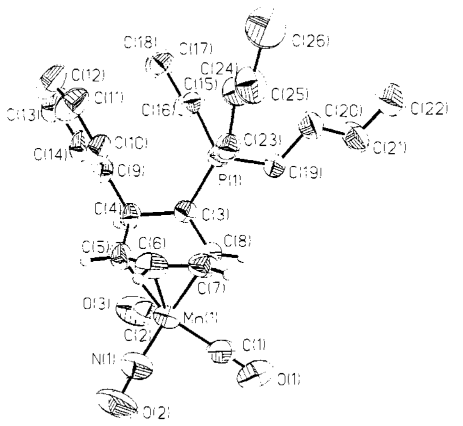

Figure 3. An ORTEP drawing of $[(C_6H_6Ph{\cdot}PBu_3)Mn(CO)_2NO]PF_6$ with the thermal ellipsoids at the 50% probability level.

Table VII. Selected Bond Distances (Å) and Angles (deg) for $[(C_6H_6Ph \cdot PBu_3)Mn(CO)_2NO]PF_6$

		Bond Distances			
Mn–C1	1.830 (5)	C3–P1	1.844 (3)	C15–C16	1.520 (5)
Mn–N	1.678 (4)	C4–C5	1.520 (6)	C15–P1	1.809 (4)
Mn–C2	1.816 (5)	C4–C9	1.517 (5)	C16–C17	1.510 (6)
Mn–C5	2.141 (4)	C5–C6	1.405 (6)	C17–C18	1.509 (6)
Mn–C6	2.071 (4)	C6–C7	1.406 (7)	C19–C20	1.522 (5)
Mn–C7	2.064 (4)	C7–C8	1.423 (6)	C19–P1	1.810 (4)
Mn–C8	2.138 (4)	C9–C10	1.379 (5)	C20–C21	1.513 (6)
C1–O1	1.135 (7)	C9–C14	1.406 (6)	C21–C22	1.475 (6)
C2–O3	1.141 (6)	C10–C11	1.383 (6)	C23–C24	1.524 (5)
N–O2	1.177 (5)	C11–C12	1.376 (8)	C23–P1	1.803 (4)
C3–C4	1.571 (5)	C12–C13	1.359 (6)	C24–C25	1.505 (6)
C3–C8	1.517 (6)	C13–C14	1.371 (6)	C25–C26	1.499 (6)
		Bond Angles			
C1–Mn–C2	97.7 (2)	Mn–C8–C7	67.4 (2)	Mn–C1–O1	177.9 (4)
C2–Mn–N	104.0 (2)	C4–C9–C10	123.0 (4)	Mn–N–O2	175.3 (4)
C2–Mn–C5	88.9 (2)	C10–C9–C14	117.7 (4)	C4–C3–P1	120.7 (2)
C1–Mn–C6	128.6 (2)	C10–C11–C12	119.1 (4)	C3–C4–C5	108.2 (3)
N–Mn–C6	98.4 (2)	C12–C13–C14	121.5 (5)	C5–C4–C9	110.8 (3)
C1–Mn–C7	93.1 (2)	C16–C15–P1	116.0 (3)	Mn–C5–C6	67.8 (2)
N–Mn–C7	122.6 (2)	C24–C23–P1	116.2 (3)	Mn–C6–C5	73.2 (2)
C6–Mn–C7	39.7 (2)	C3–P1–C19	103.8 (2)	C5–C6–C7	115.9 (4)
C2–Mn–C8	93.9 (2)	C3–P1–C23	112.4 (2)	Mn–C7–C8	73.1 (2)
C5–Mn–C8	74.1 (1)	C19–P1–C23	108.6 (2)	Mn–C8–C3	113.8 (2)
C7–Mn–C8	39.5 (2)	C1–Mn–N	93.0 (2)	C3–C8–C7	118.9 (4)
Mn–C2–O3	177.9 (4)	C1–Mn–C5	160.4 (2)	C4–C9–C14	119.3 (3)
C4–C3–C8	110.1 (3)	N–Mn–C5	103.4 (2)	C9–C10–C11	121.9 (4)
C8–C3–P1	106.9 (2)	C2–Mn–C6	127.0 (2)	C11–C12–C13	120.0 (5)
C3–C4–C9	117.5 (3)	C5–Mn–C6	38.9 (2)	C9–C14–C13	119.7 (4)
Mn–C5–C4	111.3 (2)	C2–Mn–C7	69.0 (2)	C3–P1–C15	114.5 (2)
Mn–C6–C7	69.8 (2)	C1–Mn–C8	87.0 (2)	C15–P1–C19	108.0 (2)
Mn–C7–C6	70.4 (2)	N–Mn–C8	162.0 (2)	C15–P1–C23	109.2 (2)
C6–C7–C8	113.1 (4)	C6–Mn–C8	68.2 (2)		

effect of reducing the electron density available on the Mn for π-back-bonding to the CO's. That the substitution of Me for Ph is not responsible for the increase can be inferred from the structures of other $(C_6H_6R)Mn(CO)_3$ complexes (R = H,[13] *exo*-P(O)(OEt)$_2$,[14] *endo*-P(O)(OMe)$_2$[14]), all of which have Mn-C(O) bond distances no greater than 1.81 Å. The Mn–C(ring) distances are slightly longer in **5** compared to **4**. The similarities between **4** and **5** are more noteworthy than the differences. Thus, the dienyl part of the ring is planar and the angle this plane makes with the saturated part of the ring is similar. The rotational disposition of the $(CO)_3$ and $(CO)_2NO$ ligand sets with respect to the ring in **4** and **5** are the same.

The addition of nucleophiles to $(C_6H_6Ph)Mn(CO)_2NO^+$ occurs at the ring to give cyclohexadiene complexes. The structure of the PBu_3 adduct (**6**) is shown in Figure 3. Atomic coordinates and bond distances and angles are given in Tables VI and VII, respectively. The structure shows that the PBu_3 group is positioned exo to the metal. The Mn–C–O and Mn–N–O linkages are linear. The diene fragment C5–C6–C7–C8 is planar (dihedral angle 1.9 (5)°) and forms a dihedral angle of 40.8 (5)° with the remainder of the cyclohexadiene ring (C5–C4–C3–C8). The increased electron density on the metal in **6** compared to **5** is evidenced by the shorter Mn–C(O) and Mn–N(O) distances in **6**. The carbonyl C3–O3 is positioned under the saturated portion of the cyclohexadiene ring. The nitrosyl ligand is located under the π-portion of the ring in **6** and **5** and in three other analogous manganese complexes we have structurally characterized.[5,11] This reluctance of the nitrosyl ligand to locate under the saturated carbons of the ring is particularly well-illustrated by $(C_6H_6Ph)Mn(diphos)L^+$ (L = CO, NO). The L = CO complex is symmetrical with the CO under the saturated carbon[15] while the L = NO analogue has a diphos P atom in this position.[11] DNMR studies underway[16] show that the two equivalent (enantiomeric) positions available for the NO ligand in $(cyclohexadienyl)Mn(NO)L_n^+$ complexes (like **5**) are separated by a rotational barrier ΔG^* of ca. 10–12 kcal.

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Supplementary Material Available: Tables of atomic coordinates for **4** and **5** and anisotropic thermal parameters for **4**, **5**, and **6** (7 pages); listings of observed and calculated structure factors for **4**, **5**, and **6** (46 pages). Ordering information is given on any current masthead page.

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