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π-Arene Complexes. 6.[1] Synthesis and Characterization of η^6-Arene Complexes of Manganese with Sulfur-Containing Ligands

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The neutral complexes $(\eta^6\text{-}C_6R_6)Mn(CO)_2(SPh)$ (R = H (**1a**), 3 H, 3 Me (**1b**), Me (**1c**)) have been prepared in high yields from the reaction of $[(\eta^6\text{-}C_6R_6)Mn(CO)_3]PF_6$ with Me_3NO and subsequent treatment of the reaction mixture with PhSH. Exchanging PhSH for PhSR′ (R′ = Ph, Me) in this reaction led to the formation of the cationic compounds $[(\eta^6\text{-}C_6H_3Me_3)Mn(CO)_2(S(R')Ph)]PF_6$ (R′ = Me (**5**), Ph (**6**)). Methylation of **1b** with $MeOSO_2F$ again yielded **5**. Protonation of **1a–c** with HBF_4 afforded the benzenethiol complexes $[(\eta^6\text{-}C_6R_6)Mn(CO)_2(S(H)Ph)]BF_4$ (R = H (**4a**), 3 H, 3 Me (**4b**), Me (**4c**)), which were characterized spectroscopically. Treatment of $[(\eta^6\text{-}C_6R_6)Mn(CO)_2(THF)]PF_6$ with thiophenol gave the cationic dimeric compounds $[((\eta^6\text{-}C_6R_6)Mn(CO)_2)_2SPh]PF_6$ (R = H (**2a**), 3 H, 3 Me (**2b**), Me (**2c**)) in quantitative yields. The structures of **1a** and **2b** have been determined crystallographically. The neutral complex $(\eta^6\text{-}C_6H_6)Mn(CO)_2SPh$ crystallizes in the monoclinic space group $P2_1/n$ with a = 8.046 (3) Å, b = 14.735 (6) Å, c = 10.595 (5) Å, β = 98.11 (3)°, Z = 4, V = 1243 (1) Å^3, R = 0.058, and R_w = 0.051. The structure adopted a staggered conformation of the two carbonyls and the sulfur ligand relative to the π-arene carbon atoms. The cationic compound $[((\eta^6\text{-}C_6H_3Me_3)Mn(CO)_2)_2SPh]PF_6$ crystallizes in the monoclinic space group $P2_1/n$ with a = 8.340 (1) Å, b = 28.273 (3) Å, c = 13.350 (2) Å, β = 104.87 (1)°, Z = 4, V = 3043 (1) Å^3, R = 0.059, and R_w = 0.047. The eclipsed conformations of the carbonyls and the sulfur ligands relative to the respective π-arene ring carbon atoms are slightly distorted.

Introduction

The activation of benzene derivatives by coordination in transition-metal complexes has attracted considerable interest in recent years, due mainly to potential application in organic synthesis. Especially exploited is the electrophilic character of the π-coordinated arene ring in chromium tricarbonyl complexes.[2] The arene ring in $[(\eta^6\text{-arene})Mn(CO)_3]^+$ is known to be far more electrophilic than in $(\eta^6\text{-arene})Cr(CO)_3$, and nucleophilic attack of the former is a topic of current interest.[3-5] We are presently studying and comparing chemical reactivities of compounds of different transition metals that have similar spectroscopic properties. As potential target compounds we decided to prepare $(\eta^6\text{-arene})Mn(CO)_2(SPh)$, first because we were interested in the synthetic challenge posed in the formation of neutral π-arene complexes of manganese, results of which are reported in this paper, and second because we envisaged that these compounds could be used to imitate the $(\pi\text{-arene})Cr(CO)_3$ system. The probability of introducing anionic or neutral nucleophilic ligands directly onto the metal center could be enhanced if a vacant coordination site is generated beforehand. Effective labilization of a carbonyl ligand can be accomplished with trimethylamine *N*-oxide and is well documented in the literature.[6] Sweigart[7] and co-workers used this technique to isolate $[(\eta^6\text{-arene})Mn(CO)_2(THF)]^+$, which they used as precursors to effect metal coordination by olefinic ligands.

Notable is the scarcity of well-characterized metal complexes with thiol ligands.[8] Owing to their acidic nature,

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these compounds are easily deprotonated to afford metal thiolates. The acidity of thiophenol[9] is increased by orders of magnitude through its coordination in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(S(H)Ph)]BF_4$ and was found to be more comparable in acidity to $PhSH_2^+$. Another aspect relevant to our study deals with the basicity of a coordinated sulfur in monodentate transition-metal thiolate complexes.[10,11] Substitution of other labile ligands generally occurs, yielding dimers or trimers with bridging thiolate ligands. A typical example is the formation of $[(Mn(CO)_4(SPh))_2]$.[12]

In this paper we shall report on the synthesis and characterization of three classes of π-arene complexes of manganese with sulfur-donor ligands. The preparation of neutral mononuclear and cationic dimeric η^6-arene complexes of manganese with benzenethiolate, as well as cationic benzenethiol and thioether complexes, is described. The crystal structure of $(\eta^6\text{-}C_6H_6)Mn(CO)_2(SPh)$ is of special interest, as it represents the first structure of a neutral mononuclear complex of manganese with an unsubstituted π-bonded benzene ligand and a nonbridging thiolate. In addition, and for comparison, the related structure of a bridging thiolate in a bimetallic compound without a metal–metal bond was also determined.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl prior to use, and other solvents were purified, degassed, and dried according to standard methods. Reagent grade chemicals were used without further purification. Bromopentacarbonylmanganese(I) was prepared from manganese carbonyl according to the procedure by Angelici.[13] (Hexamethylbenzene)-, (mesitylene)-, and (benzene)tricarbonylmanganese hexafluorophosphate salts were prepared according to published procedures.[14] (η^6-Arene)dicarbonyl(tetrahydrofuran)manganese cations were prepared according to the method of Sweigart.[7] Photolyses were run in Pyrex flasks with water-cooled jackets and a Philips medium-pressure mercury arc. Column chromatography on SiO_2 (0.063–0.200 mm) was performed on columns cooled by recycling cold (−20 °C) methanol through column jackets. Microanalyses were obtained from F. Pascher and E. Pascher, Microanalytical Laboratories, Remagen, West Germany, and from the P C M T Division of the Council for Scientific and Industrial Research, Pretoria, South Africa. Melting points were recorded on a Gallenkamp hot-stage apparatus and are uncorrected. NMR solvents were degassed by several freeze–pump–thaw cycles, and NMR tubes were sealed under a nitrogen atmosphere. ^1H NMR spectra were recorded at 300 MHz with a Bruker 300 AC NMR spectrometer. Infrared spectra were recorded with a Bomem Michelson-100 FT spectrometer and calibrated against polystyrene. Mass spectra were recorded on a Perkin-Elmer RMU-6H instrument operating at 70 eV.

Synthesis. Synthesis of $(\eta^6\text{-}C_6R_6)Mn(CO)_2(SPh)$ (1a–c). Method A. Preparation of (η^6-Benzene)(benzenethiolato)dicarbonylmanganese(I) (1a). A stirred solution of (benzene)tricarbonylmanganese hexafluorophosphate (1.09 g, 3 mmol) in dichloromethane (50 mL) was treated with trimethylamine *N*-oxide (0.45 g, 6 mmol) at −30 °C. The mixture was removed from the cold and stirred for 5 min at room temperature, after which the solution changed from pale yellow to pink. The reaction mixture was again cooled to −30 °C, 0.31 mL of thiophenol (3 mmol) was added, and stirring was continued. The color changed from pink to dark red, and the mixture was stirred for another 15 min at room temperature. After removal of the solvent the residue was chromatographed with an acetone/hexane mixture (1/1) as eluent.

Several bands separated, of which only the four main zones were collected. The first yellow band gave ((phenylthio)cyclohexadienyl)tricarbonylmanganese and was only characterized spectroscopically (infrared and ^1H NMR spectroscopy, vide infra). The second dark red band was collected and the solvent removed under reduced pressure to give a red solid. Recrystallization of this material from a dichloromethane/ether mixture yielded dark red crystals of **1a** (0.35 g, 39% based on $[(\eta^6\text{-}C_6H_6)Mn(CO)_3]PF_6$). A pink zone followed, which was identified as (η^6-benzene)((phenylthio)carbonyl)dicarbonylmanganese (**3a**). During spectroscopic studies this compound decomposed to the yellow complex collected as the first zone. The fourth red band afforded the dimeric compound $[((\eta^6\text{-}C_6H_6)Mn(CO)_2)_2SPh]PF_6$ (**2a**) in low yield (0.12 g, 5%).

An improved synthesis of compound **2a** and analytical data are given below.

1a: mp 85 °C. Anal. Calcd for $C_{14}H_{11}MnO_2S$: C, 56.4; H, 3.7. Found: C, 56.9; H, 4.0. FAB-MS (*m/z*): 298 (2%) [M^+], 242 (7%) [$MnC_6H_6SPh^+$], 164 (14%) [$MnSPh^+$), 133 (2%) [$MnC_6H_6^+$], 55 (15%) [Mn^+].

Preparation of (η^6-Mesitylene)(benzenethiolato)dicarbonylmanganese(I) (1b). This compound was prepared in an identical fashion as described above for **1a**. The first dark red band eluted from the column, **1b**, was followed by a pink zone, **3b**, which interconverts to the yellow cyclohexadienyl complex. In addition to the third red zone, **2b**, a fourth orange compound was collected and characterized spectroscopically. This last product, which was also fairly unstable in polar solvents, was identified as the cationic benzenethiol complex and was characterized as the BF_4 salt (**4b**).

1b: dark red crystals; yield 0.66 g, 49%; mp 95–97 °C. Anal. Calcd for $C_{17}H_{17}MnO_2S$: C, 60.0; H, 5.0. Found: C, 60.8; H, 5.5.

Preparation of (η^6-Hexamethylbenzene)(benzenethiolato)dicarbonylmanganese(I) (1c). The same procedure as described above for **1a** was followed to isolate the first red band as **1c**. The pink zone, which eluted after the cyclohexadienyl complex, was collected and characterized after being recrystallized from a dichloromethane/hexane mixture. The pink crystals of **3c** were much more stable than its analogues **3a** and **3b**.

1c: red crystals; yield 0.52 g, 45%; mp 111 °C dec. Anal. Calcd for $C_{20}H_{23}MnO_2S$: C, 62.8; H, 6.0. Found: C, 63.2; H, 6.3. FAB-MS (*m/z*): 382 (2%) [M^+], 326 (80%) [$MnC_6Me_6SPh^+$], 217 (6%), [$MnC_6Me_6^+$], 164 (12%) [$MnSPh^+$], 55 (16%) [Mn^+].

3c: pink solid; yield 0.27 g, 22%. FAB-MS (*m/z*): 410 (1%) [M^+], 382 (10%) [$MnC_6Me_6SPh(CO)_2^+$], 326 (80%) [$Mn(SPh)C_6Me_6^+$], 217 (6%) [$MnC_6Me_6^+$], 164 (62%) [$MnSPh^+$], 55 (40%) [Mn^+].

Method B. Preparation of (η^6-Arene)(benzenethiolato)dicarbonylmanganese(I) (1a–c). A stirred solution of 3 mmol of (η^6-arene)tricarbonylmanganese hexafluorophosphate in 50 mL of THF was irradiated for 1 h. After 6 mmol (0.62 mL) of thiophenol was added and the mixture was stirred for 10 min, no reaction was apparent. The solution was cooled to −30 °C, and 6 mmol (0.45 g) of Me_3NO was added, after which the color immediately changed from pale yellow to pink. The reaction flask was removed from the cold, and the contents were stirred for 5 min at room temperature. The resultant dark red solution was stripped of solvent, the residue was purified by chromatography, and the main products **1a–c** recrystallized as described above. Higher yields of the desired complexes **1a–c**, and less of the cyclohexadienyl derivatives, were obtained by this method. Yields: **1a**, 78%; **1b**, 73%; **1c**, 68%.

Reaction of (η^6-Benzene)tricarbonylmanganese Hexafluorophosphate with Lithiated Thiophenol. (i) Without Irradiation. A stirred solution of thiophenol (3 mmol, 0.31 mL) in THF was treated with *n*-butyllithium (3.98 mL of a 1.3 mol dm^{-3} solution in hexane, 3 mmol) at −40 °C. The clear solution was stirred for another 1 h at room temperature and added dropwise to a solution of (η^6-benzene)tricarbonylmanganese cation in THF (40 mL) at −40 °C. The reaction mixture was stirred for a further 15 min at room temperature. The solvent was evaporated from the reaction mixture, the residue was chromatographed, and

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two products were isolated. ((Phenylthio)cyclohexadienyl)tricarbonylmanganese was obtained in high yields (76%), but very little of **3c** (5%).

(ii) With Irradiation. A solution of (η^6-hexamethylbenzene)tricarbonylmanganese hexafluorophosphate in THF was irradiated for 1.5 h with a medium-pressure Hg lamp at room temperature. An equimolar solution of lithium phenyl mercaptide (prepared as above under (i)) was added dropwise to a cooled solution (−40 °C) of the photochemically treated manganese compound. The reaction mixture was stirred at room temperature for 15 min and the solvent removed in vacuo. After column chromatography it was again found that the main product was the cyclohexadienyl complex of manganese (51%). In addition to **3c** (11%), **1c** also formed in low yield (18%).

(iii) With Me_3NO. To a stirred solution of (η^6-hexamethylbenzene)tricarbonylmanganese cation (3 mmol) in THF (50 mL) at −40 °C was added Me_3NO (3 mmol). After the reaction flask was removed from the cold, the solution changed from pale yellow to pink. The reaction mixture was cooled again (−40 °C) and an equimolar solution of the lithiated thiophenol (see (i) above) added dropwise. The mixture was stirred for 5 min in the cold and a further 10 min at room temperature, after which the solvent was removed under reduced pressure. The only product that formed in a significant quantity was the cyclohexadienyl complex of manganese (42%).

Synthesis of $[((\eta^6\text{-}C_6R_6)Mn(CO)_2)_2SPh]PF_6$ (2a–c). Preparation of (Benzenethiolato)bis[(η^6-arene)dicarbonylmanganese] Hexafluorophosphate. All of these complexes were synthesized by the same procedure. An excess of thiophenol (0.51 mL, 5 mmol), was added to a stirred solution of the (η^6-arene)dicarbonyl(tetrahydrofuran)manganese cation (3 mmol) in dichloromethane (30 mL). After it was stirred for 15 min at room temperature, the mixture was concentrated. The solution was filtered and an equivalent volume of hexane carefully added to form two separated layers of solvent. After the mixture was cooled slowly, red-brown crystals formed, which were washed with hexane. The product obtained was purified by recrystallization from dichloromethane and hexane.

2a: yield 42%. Anal. Calcd for $C_{22}H_{17}Mn_2O_4SPF_6$: C, 41.8; H, 2.7. Found: C, 42.3;, H, 2.9. **2b**: yield 68%. Anal. Calcd for $C_{28}H_{29}Mn_2O_4SPF_6$: C, 46.9; H, 4.1. Found: C, 47.3; H, 4.3. **2c**: yield 36%. Anal. Calcd for $C_{34}H_{41}Mn_2O_4SPF_6$: C, 51.0; H, 5.1. Found: C, 51.3; H, 5.3.

Synthesis of $[(\eta^6\text{-}C_6R_6)Mn(CO)_2(S(R')Ph)]X$ (R = 3-H, 3-Me; R′ = Me (5), Ph (6), H (4a–c); X = BF_4, PF_6). Preparation of Cationic (η^6-Arene)manganese Complexes with Thioether Ligands. A. (i) Preparation of (η^6-Mesitylene)dicarbonyl(methyl phenyl thioether)manganese(I) Hexafluorophosphate (5). A stirred solution of (η^6-mesitylene)tricarbonylmanganese(I) hexafluorophosphate (1.21 g, 3 mmol) in tetrahydrofuran (50 mL) was treated with trimethylamine *N*-oxide (0.30 g, 4 mmol) at −30 °C. The reaction flask was removed from the cold, and the contents were stirred for a further 20 min at room temperature, after which the solution turned dark red. The mixture was cooled again to −30 °C, 0.8 mL (5 mmol) of methyl phenyl sulfide was added, and after the contents were stirred for 15 min, the flask was removed from the cold. The solution turned red-brown, and after 2 h the solution was concentrated and hexane added slowly. An orange precipitate formed, from which the solvent was decanted. The precipitate was washed with hexane, dissolved in a minimum amount of dichloromethane, and precipitated again with hexane to give the orange solid **5** in high yield.

(ii) Preparation of (η^6-Mesitylene)dicarbonyl(diphenyl thioether)manganese(I) Hexafluorophosphate (6). This compound was prepared in a fashion identical with that described above for **5**, with use of diphenyl sulfide with CH_2Cl_2 as solvent instead of THF.

B. Reaction of (η^6-Mesitylene)(benzenethiolato)dicarbonylmanganese(I) (1b) with $MeOSO_2F$. An equivalent amount of $MeOSO_2F$ was added to a solution of **1b** in THF. An orange precipitate formed when hexane was added, and the mixture was stirred for 15 min. The solution was decanted and the precipitate washed with hexane. The product contained the same cation as **5**.

Reaction of (η^6-Arene)(benzenethiolato)dicarbonylmanganese (1a–c) with HBF_4. A solution of the complexes **1a–c** in dichloromethane was treated with HBF_4 by slowly adding an ether solution of the latter. After the mixture was stirred for 20 min, hexane was added, resulting in an orange suspension, which was separated, washed with pentane, and dried in vacuo to give almost quantitative yields of **4a–c**.

Table I. Summary of Crystal Data

	1a	**2b**
empirical formula	$MnC_{14}H_{11}O_2S$	$Mn_2C_{28}H_{29}F_6O_4PS$
mol wt	298	716
cryst dimens, mm	0.10 × 0.25 × 0.32	0.13 × 0.19 × 0.20
space group	$P2_1/n$	$P2_1/n$
cell dimens		
a, Å	8.046 (3)	8.340 (1)
b, Å	14.735 (6)	28.273 (3)
c, Å	10.595 (5)	13.350 (2)
β, deg	98.11 (3)	104.87 (1)
Z	4	4
V, Å^3	1243 (1)	3043 (1)
D(calc), g cm^{-3}	1.74	1.56
μ(Mo Kα), cm^{-1}	11.45	9.49
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα (0.7107)
T, °C	25	25
F(000)	655	1456
scan type (ω:2θ)	1:1	1:1
scan range (θ), deg	$3 \le \theta \le 28$	$3 \le \theta \le 25$
max scan speed (variable), deg min^{-1}	5.49	3.30
scan angle ($\omega + 0.34 \tan \theta$), deg	0.85	0.49
aperture size, mm	1.3 × 4.0	1.9 × 4.0
no. of rflns collected	3281	5444
no. of unique reflns used (>2σI)	1354	2959
no. of params refined	164	400
R_w	0.051	0.047
R	0.058	0.059

X-ray Data Collection, Structure Solution, and Refinement. Diffraction-quality single crystals of **1a** and **2b** were obtained after recrystallization. Data collection and structure solution parameters are presented in Table I. Empirical absorption corrections based on ψ scans of nine reflections with $\psi \approx 90°$, from the EAC program[15] of the Enraf-Nonius software, were applied to both data sets. The structures were solved by using conventional Patterson and Fourier methods and refined by full-matrix least-squares methods with SHELX 76.[16] All the non-hydrogen atoms were refined anisotropically with use of $\sigma^{-2}(F)$ weights. Neutral atomic scattering factors and anomalous dispersion terms were taken from the literature.[17] The hydrogen atoms were placed in calculated positions and refined with common isotropic temperature factors that converged to 0.064 (9) and 0.102 (6) Å^2 for **1a** and **2b**, respectively. For both structures the final difference Fourier syntheses were featureless, the largest peaks being 0.59 and 0.46 e Å^{-3} (1 Å from Mn) for **1a** and **2b**, respectively. The fractional atomic coordinates for **1a** and **2b** are listed in Tables II and III, respectively.

Results and Discussion

Synthetic Studies. The synthesis of neutral η^6-arene complexes of manganese with a PhS ligand (**1a–c**) was studied via the different routes outlined in Scheme I. Reaction of the parent cationic tricarbonyl with phenyl mercaptide in THF leads almost exclusively to the formation of pale yellow (phenylthio)cyclohexadienyl complexes of manganese (**7**).[18]

In addition, very unstable compounds also formed in low yields. These complexes (**3a–c**) could be investigated by

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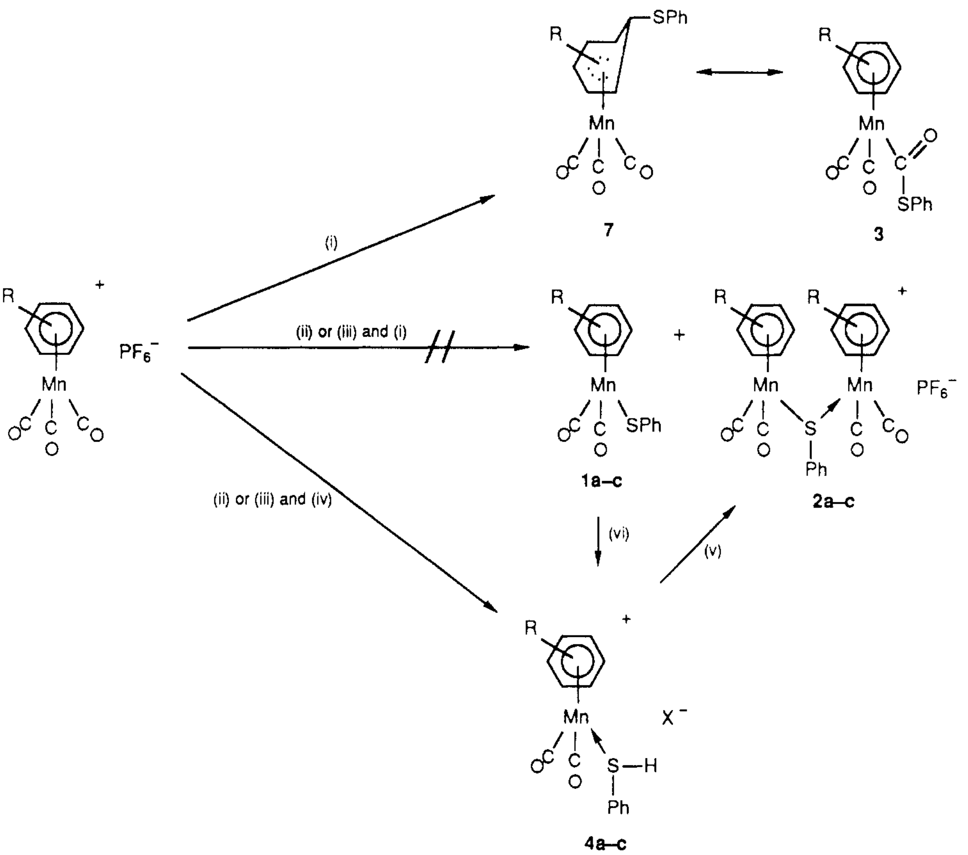
Scheme I[a]



[a] Legend for reactions: (i) PhS⁻; (ii) $h\nu$; (iii) Me_3NO; (iv) PhSH; (v) Me_3N; (vi) HBF_4. (a) R = H; (b) R = 3 H, 3 Me; (c) R = Me; X = PF_6^-, BF_4^-.

Table II. Fractional Coordinates (×10⁴) and Equivalent Thermal Factors (×10³ Å²) for Compound 1a

	x/a	y/b	z/c	U_{eq}[a]
Mn	2350 (2)	264 (1)	2271 (1)	30 (1)
C(1)	413 (11)	–159 (6)	2675 (7)	36 (2)
O(1)	–833 (8)	–421 (4)	2928 (6)	54 (2)
C(2)	3002 (10)	509 (7)	3888 (9)	45 (2)
O(2)	3431 (8)	668 (6)	4962 (6)	67 (2)
C(3)	4977 (10)	160 (8)	2021 (8)	45 (2)
C(4)	4340 (11)	–705 (7)	2222 (8)	42 (2)
C(5)	2931 (11)	–1034 (6)	1500 (9)	41 (2)
C(6)	2088 (10)	–498 (6)	475 (8)	40 (2)
C(7)	2674 (10)	369 (7)	255 (7)	39 (2)
C(8)	4133 (10)	694 (7)	1046 (8)	42 (2)
S	1196 (3)	1730 (2)	2025 (2)	44 (1)
C(9)	–623 (11)	1884 (6)	2745 (8)	36 (2)
C(10)	–692 (11)	1672 (6)	4012 (9)	44 (2)
C(11)	–2119 (12)	1852 (7)	4562 (9)	53 (3)
C(12)	–3514 (11)	2238 (7)	3821 (11)	56 (3)
C(13)	–3465 (12)	2461 (6)	2598 (10)	49 (3)
C(14)	–2019 (12)	2271 (6)	2065 (9)	42 (2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

means of ¹H NMR and IR spectroscopy. Whereas the complexes **3a** and **3b** changed color quickly in solution from pink to pale yellow during the recording of their spectra, **3c** was more stable and only decomposed over a longer period of time. The band at 1578 cm⁻¹ in the infrared spectrum of the neutral hexamethylbenzene complex of manganese was assigned to the acyl vibrations and corresponds to values reported for $(\eta^6\text{-}C_6Me_6)Mn(CO)_2(C(O)R')$ (R′ = Me, Ph[19] and R′ = NHC_6H_{11}[20]). The formation of the thioacyl complexes **3** was attributed to the attack by the mercaptide on a carbonyl ligand. A different pattern of decomposition for **3a** and **3b**, compared to that for **3c**, was observed. This is evident from the fact that the former, which have hydrogens on the arene ring, gave resonances in the ¹H NMR spectra typical of cyclohexadienyl complexes. In contrast, **1c** was also formed from **3c** and less of the cyclohexadienyl compound was observed.

Preliminary efforts to characterize the pale yellow (phenylthio)cyclohexadienyl complexes **7** by infrared spectroscopy were frustrated by a color change after a few minutes to pink. Bands observed in the spectra indicated a mixture. From the color differences, data obtained for **3c**, and documented data for similar $(\eta^5\text{-}C_6H_6R)Mn(CO)_3$[23] and $(\eta^6\text{-}C_6H_6)Mn(C(O)R)(CO)_2$[19] complexes we infer that the ν_{CO} bands (CH_2Cl_2, cm⁻¹) at 2078, 1993, 1907, and 2019, 1967, 1578 (acyl) result from $(\eta^5\text{-}PhSC_6H_6)Mn(CO)_3$ (**7a**) and $(\eta^6\text{-}C_6H_6)Mn(C(O)SPh)(CO)_2$ (**3a**), respectively. Similar results were obtained for the mesitylene analogues. Attempts to separate and fully characterize the (phenylthio)carbonyl and cyclohexadienyl complexes were complicated by the nature of the solvent and ease of decomposition to secondary products that could not be identified. More work is needed, which is presently being done to make conclusions as to the mechanism whereby these conversions take place. These results verified the highly electrophilic character of the unsubstituted arene rings, which inhibits attack of nucleophiles on the carbonyl carbons.

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Table III. Fractional Coordinates (×10^4) and Equivalent Thermal Factors (×10^3 Å^2) for Compound 2b

	x/a	y/b	z/c	U_{eq}[a]
C(1)	4581 (9)	1568 (3)	3798 (6)	59 (2)
C(2)	3719 (9)	2023 (3)	3440 (5)	42 (2)
C(3)	4154 (8)	2303 (3)	2696 (6)	47 (2)
C(4)	3402 (9)	2747 (3)	2386 (5)	48 (2)
C(5)	3958 (10)	3050 (3)	1606 (6)	69 (3)
C(6)	2151 (9)	2904 (2)	2835 (5)	48 (2)
C(7)	1667 (9)	2632 (3)	3605 (5)	44 (2)
C(8)	369 (9)	2820 (3)	4109 (6)	61 (2)
C(9)	2442 (8)	2189 (3)	3878 (5)	44 (2)
Mn(1)	1442 (1)	2211 (1)	2180 (1)	38 (1)
C(10)	−715 (10)	2337 (3)	1870 (6)	57 (2)
O(1)	−2105 (7)	2435 (2)	1667 (5)	93 (2)
C(11)	1356 (9)	2254 (3)	838 (6)	55 (2)
O(2)	1342 (8)	2300 (2)	−27 (4)	90 (2)
S(1)	961 (2)	1389 (1)	2035 (1)	42 (1)
C(12)	693 (10)	1216 (2)	708 (5)	45 (2)
C(13)	−812 (10)	1150 (3)	15 (6)	62 (2)
C(14)	−893 (12)	1006 (3)	−1005 (6)	77 (3)
C(15)	520 (15)	955 (3)	−1316 (7)	88 (3)
C(16)	2004 (13)	1021 (3)	−625 (7)	90 (3)
C(17)	2120 (10)	1153 (3)	376 (7)	69 (3)
Mn(2)	−1046 (1)	998 (1)	2683 (1)	43 (1)
C(18)	−980 (9)	1452 (3)	3609 (6)	49 (2)
O(3)	−1044 (7)	1734 (2)	4214 (4)	85 (2)
C(19)	−2732 (9)	1298 (3)	1856 (6)	50 (2)
O(4)	−3890 (6)	1485 (2)	1336 (4)	77 (2)
C(20)	246 (10)	481 (2)	3867 (6)	50 (2)
C(21)	−1449 (11)	524 (3)	3879 (7)	57 (2)
C(22)	−1903 (11)	628 (3)	4877 (6)	81 (3)
C(23)	−2641 (10)	444 (3)	2972 (7)	57 (2)
C(24)	−2252 (11)	330 (3)	2031 (7)	61 (3)
C(25)	−3585 (11)	239 (3)	1060 (7)	92 (3)
C(26)	−592 (12)	309 (3)	2034 (6)	62 (3)
C(27)	715 (11)	367 (3)	2952 (7)	57 (2)
C(28)	2503 (9)	316 (3)	2944 (7)	69 (3)
P(1)	3941 (3)	915 (1)	6585 (2)	71 (1)
F(1)	4864 (8)	586 (3)	7444 (6)	179 (3)
F(2)	2270 (7)	701 (2)	6702 (4)	117 (2)
F(3)	4012 (7)	536 (3)	5777 (5)	160 (3)
F(4)	−7044 (9)	1228 (3)	−4285 (5)	178 (3)
F(5)	5610 (7)	1113 (2)	6477 (4)	150 (2)
F(6)	3864 (9)	1289 (2)	7393 (5)	165 (3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

In the synthesis of **1a–c**, a different approach was tried to overcome this restriction of preferential attack on the arene ring or a carbonyl ligand. It was decided to generate a vacant coordination site on the manganese and only add the phenyl mercaptide afterwards. Recognized methods of achieving this result are by photolysis[21] of an aqueous solution of the manganese tricarbonyl cation and by the addition of a carbonyl labilizing agent[6] such as Me_3NO. Both techniques were used very effectively to synthesize the neutral complexes [(η^6-arene)$Mn(CO)_2X$] (X = I, Br, Cl).[22] We utilized the second method, whereby the manganese tricarbonyl cation was dissolved in CH_2Cl_2 and cooled to −30 °C and 1–2 molar equiv of Me_3NO added. The reaction mixture changed to pink with the evolution of gas, which indicated that a coordination site on the manganese was vacated. Subsequent treatment with phenyl mercaptide led mainly to decomposition, the formation of cyclohexadienyl complexes, and very little of the target compounds **1a–c**. However, addition of thiophenol instead yielded **1a–c** as fairly air- and light-sensitive dark red solids in reasonable yields (ca. 45%). Higher yields (>65%) were obtained with THF as solvent, together with the photochemical treatment of the cation prior to the addition of Me_3NO and the thiophenol. We ascribe this increase in yield (20%) to the assistance of irradiation in the labilization of the carbonyl. In contrast to previous reports[20,23] indicating that the degree of methylation on the arene ring affects the position of nucleophilic attack in the molecule, the method described above bypasses this problem by only generating the anionic ligand after coordination to the metal center. We found no distinction in yields or reactivity when a benzene ring was exchanged for the hexamethylbenzene ligand.

The complexes **1a–c** are examples of monodentate transition-metal thiolate complexes, which are relatively rare.[8,10] This class of compounds is isoelectronic with (η^5-C_5H_5)$(CO)_2FeSR'$ (R′ = Me,[24] Ph[25]) and (η^5-C_5H_5)$(CO)_3MSR'$ (M = Mo, W; R′ = Me[11]). Complexes **1a–c** were fully characterized (Table IV, Experimental Section), and final confirmation of their composition was established in a single-crystal X-ray analysis of **1a** (vide infra). Whereas the crystals of **1** are fairly stable under an inert atmosphere, they slowly decompose in air or as solutions in polar solvents. Initially, we anticipated that the product would be [(η^6-arene)$Mn(CO)_2(S(H)Ph)$]PF_6, which we intended to deprotonate with *t*-BuOK or *sec*-BuLi, but instead **1a–c** were obtained directly. We concluded that Me_3NO plays an important dual role during the reaction. It not only induces the carbonyl displacement through oxidation of a carbonyl to carbon dioxide but the in situ generated base, Me_3N, also deprotonates the coordinated thiophenol ligand. Furthermore, after the carbonyl ligand was labilized photochemically and the manganese cation was reacted with thiophenol, no reaction was apparent until after Me_3NO was added. Both Me_3NO and Me_3N have the ability to react with PhSH, but we deduced from the experimental observations that the proton was only abstracted after coordination to the metal. In a recent communication Sweigart[7] also referred to similar base properties of Me_3N toward coordinated acetylene. The high acidity of coordinated benzenethiol is well-known and was the topic under investigation for the complexes [(η^5-C_5H_5)$Fe(CO)_2(S(H)Ph)$]BF_4[9] and [(η^5-C_5H_5)$(CO)_3W$-$(S(H)Ph)$]BF_4.[26]

In the case of mesitylene an additional orange band, which was not observed for benzene and hexamethylbenzene, was identified as the cationic benzenethiol complex **4b**. A broad signal at δ 3.93 ppm in the ^1H NMR spectrum, which was found to be solvent and concentration dependent, was assigned to the SH resonance.

The formation of cationic dimanganese complexes with bridging benzenethiolate ligands (**2a–c**) was also observed in the above-mentioned preparation, but in low yields (5–8%). We speculate that they form due to either a side reaction of **1** with a coordinatively unsaturated intermediate generated by Me_3NO or the substitution of a coordinated thiophenol from **4**, since substitution of a PhS ligand of **1** by another from a second complex is unfavorable.

An improved synthesis of **2**, patterned after the method used by Sweigart[7] and co-workers, is shown in Scheme II. The isolation of the cation with weakly bonded THF in the coordination sphere has distinct advantages. Thiophenol reacts cleanly with the THF complex, and very little decomposition was observed. Bridge formation by the thiolate or thiophenol ligand is favored under these reaction conditions, and deprotonation of a cationic monomeric or dimeric intermediate can occur readily. Instead of the expected compounds [(η^6-arene)$Mn(CO)_2(S(H)Ph)$]$^+$ (cations of **4a–c**), the complexes **2** formed quantitatively and could be crystallized directly from the concentrated dichloromethane solutions when hexane was added. The

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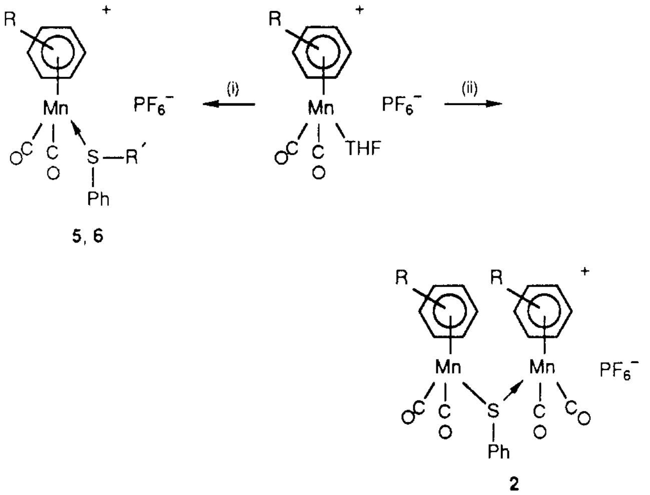
Table IV. ^{1}H NMR and IR Data

		^{1}H NMR chem shifts, δ, ppm				IR,[a] ν_{CO}, cm^{-1}			
		π-arene							
complex	solvent	H	Me	aryl	H/alkyl				
1a	$CDCl_3$	5.54 (6 H, s)		7.03 (3 H, m)			1985	1943	
				7.47 (2 H, m)					
1b	$CDCl_3$	4.96 (3 H, s)	2.24 (9 H, s)	7.00 (3 H, m)			1971	1925	
				7.45 (2 H, m)					
1c	$CDCl_3$		2.10 (18 H, s)	7.04 (3 H, m)					
				7.35 (2 H, m)			1973	1923	
2a	$(CD_3)_2CO$	6.04 (12 H, s)		7.19 (3 H, m)		2022	1990	1963	1907
				7.42 (2 H, m)		2022	1990	1946	1909[b]
2b	$CDCl_3$	5.08 (6 H, s)	2.24 (18 H, s)	7.22 (3 H, m)		1996	1975	1939	
				7.42 (2 H, m)		1992	1971	1934[b]	
2c	$(CD_3)_2CO$		2.17 (36 H, s)	7.28 (3 H, m)					
				7.53 (2 H, m)		1998	1974	1062	1912
3c	C_6D_6		2.11 (18 H, s)	6.89 (3 H, m)			1957	1907	1578
				7.40 (2 H, m)					
4a[d]	$CDCl_3$	5.76 (6 H, s)		7.40 (5 H, m)	3.28 (1 H, m)				
4b[d]	$CDCl_3$	5.28 (3 H, s)	2.14 (9 H, s)	7.23 (3 H, m)	3.47 (1 H, m)				
				7.47 (2 H, m)			1987	1941	
4c[d]	$CDCl_3$		2.19 (18 H, s)	7.04 (3 H, m)					
				7.35 (2 H, m)	3.93 (H, m)		1985	1941[c]	
5[e]	$CDCl_3$	5.59 (3 H, s)	2.36 (9 H, s)	7.41 (5 H, m)	2.67 (3 H, s)		2002	1957	
6[e]	$CDCl_3$	5.02 (3 H, s)	2.31 (9 H, s)	7.32 (10 H, m)			1993	1941	

[a] In CH_2Cl_2. [b] In Me_2CO. [c] In Nujol. [d] BF_4 salts. [e] PF_6 salts.

Scheme II[a]



[a] Legend for reactions: (i) PhSR′; (ii) PhSH. R′ = Me (**5**), Ph (**6**).

red-brown crystals were stable under an inert atmosphere but slowly decomposed in solutions with polar solvents. The complexes **2** exhibit three or four bands in the terminal C–O stretching region of their IR spectra. These complexes have a bridging benzenethiolate ligand with both metals formally in an oxidation state of +1 and without a manganese–manganese bond. A similar situation exists for the complexes $[((\eta^5\text{-}C_5H_5)(CO)FeSMe)_2]$ and $[((\eta^5\text{-}C_5H_5)Fe(CO)_2)_2SMe]Cl$,[11] where the metals are formally in oxidation state +2, bridging methanethiolates exist, and no metal–metal bonds are found. Higher oxidation states and metal–metal bonds were reported by Haines[27] in $[(Mn(\eta^5\text{-}C_5H_4Me)(CO)_2)_2SEt]ClO_4$ and Huttner[28] in $[(Mn(\eta^5\text{-}C_5H_5)(CO)_2)_2TePh]PF_6$.

Protonation of **1** with HBF_4 afforded the cationic thiophenol complexes **4a–c**. Owing to the high acidity of the proton on the coordinated sulfur, it is difficult to maintain these compounds and they are easily deprotonated in solution. The rapid conversion of **4a–c** into **2a–c** in acetone or ether also points to the cationic **4a–c** as possible intermediates for the formation of **1a–c**. We have no explanation for the fact that it was possible to isolate **4b** from the reaction mixture during our synthesis of **1b**. Addition of PhSR′ (R′ = Ph, Me) in the method used by Sweigart[7] gave **5** (R = Me) and **6** (R = Ph) as orange powders. In an alternative method, **1b** was methylated with $MeOSO_2F$ to give **5**.

The cationic complexes of manganese with thiol and thioether ligands extend the range of compounds known for (η^6-arene)manganese with different neutral heteroatom ligands. Complexes of this type with various phosphine[29] and phosphite[22] ligands have been known for some time. The retention of the nucleophilic character present in the corresponding free phenyl mercaptide ion is manifested by the ability of the terminal PhS ligand to undergo S-alkylation/*S*-protonation as well as the formation of S bridges. Whereas the isolation and characterization of **1a–c** are ascribed to mechanistic aspects of the reaction, enforced by the availability of specific intermediates at given times in the reaction mixture and the careful manipulation of solvents to avoid decomposition, the formation of **2** can be promoted by reversing some of these factors. In the reactions of $(\eta^5\text{-}C_5H_5)(CO)_2FeCl$ or $(\eta^5\text{-}C_5H_5)(CO)_3MCl$ (M = Mo, W) with Me_3SnSMe[11] the monomeric methanethiolates $(\eta^5\text{-}C_5H_5)(CO)_2FeSR'$ and $(\eta^5\text{-}C_5H_5)(CO)_3MSR'$ (M = Mo, W) formed in reasonable yields but spontaneously converted to the dimeric $[((\eta^5\text{-}C_5H_5)Fe(CO)_2)_2SMe]Cl$ or $[((\eta^5\text{-}C_5H_5)M(CO)_3)_2SMe]Cl$ (M = Mo, W) complexes.

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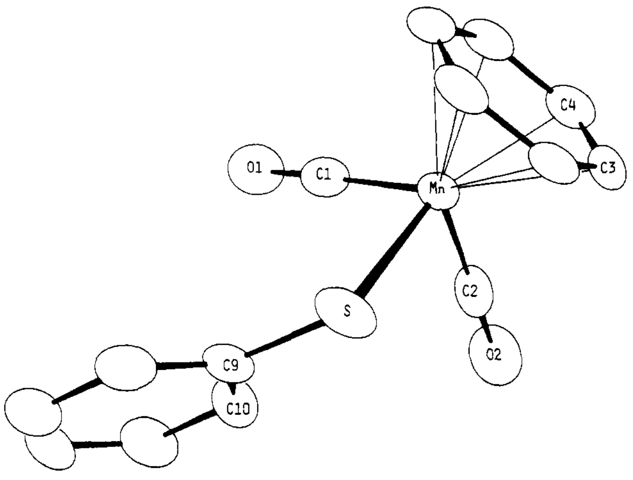

Figure 1. Molecular geometry of **1a** showing the atom-numbering scheme used.

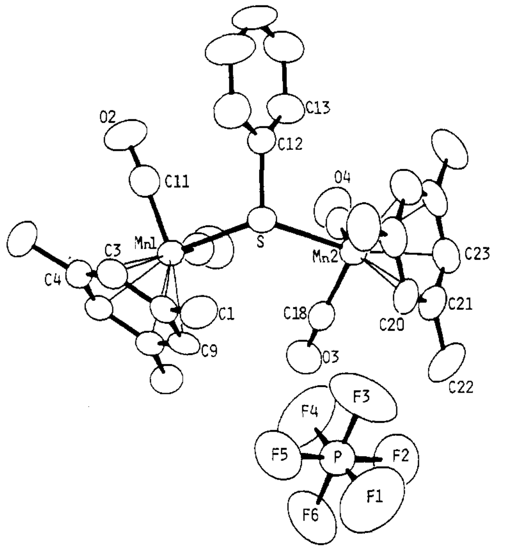

Figure 2. Molecular geometry of **2b** showing the atom-numbering scheme used.

Table V. Selected Bond Lengths (Å) and Valence Angles (deg) of 1a and 2b

	Compound **1a**		
Mn–C(1)	1.786 (9)	Mn–C(2)	1.757 (9)
Mn–C(3)	2.172 (8)	Mn–C(4)	2.151 (8)
Mn–C(5)	2.156 (8)	Mn–C(6)	2.194 (8)
Mn–C(7)	2.194 (7)	Mn–C(8)	2.161 (8)
Mn–S	2.350 (3)	C(1)–O(1)	1.141 (9)
C(2)–O(2)	1.165 (9)	C(3)–C(4)	1.401 (13)
C(3)—C(8)	1.396 (12)	C(4)–C(5)	1.364 (12)
C(5)–C(6)	1.434 (12)	C(6)–C(7)	1.394 (12)
C(7)–C(8)	1.425 (11)	S–C(9)	1.759 (8)
C(9)–C(10)	1.386 (11)	C(9)–C(14)	1.370 (11)
C(10)–C(11)	1.385 (11)	C(11)–C(12)	1.397 (13)
C(12)–C(13)	1.343 (13)	C(13)–C(14)	1.392 (12)
C(1)–Mn–C(2)	89.4 (4)	C(1)–Mn–S	90.2 (3)
C(3)–Mn–S	115.3 (3)	C(2)–Mn–S	88.8 (3)
C(5)–Mn–S	151.2 (3)	C(4)–Mn–S	153.0 (3)
C(7)–Mn–S	85.8 (3)	C(6)–Mn–S	112.7 (2)
Mn–S–C(9)	114.2 (3)	C(8)–Mn–S	87.1 (3)
	Compound **2b**		
C(1)–C2)	1.491 (8)	C(2)–C(3)	1.389 (8)
C(2)–C(9)	1.419 (8)	C(2)–Mn(1)	2.254 (7)
C(3)–C(4)	1.416 (9)	C(3)–Mn(1)	2.204 (6)
C(4)–C(5)	1.511 (8)	C(4)–C(6)	1.403 (8)
C(4)–Mn(1)	2.194 (7)	C(6)–C(7)	1.423 (8)
C(6)–Mn(1)	2.166 (7)	C(7)–C(8)	1.510 (8)
C(7)–C(9)	1.413 (8)	C(7)–Mn(1)	2.211 (7)
C(9)–Mn(1)	2.206 (6)	Mn(1)–C(10)	1.776 (8)
Mn(1)–C(11)	1.778 (7)	Mn(1)–S(1)	2.358 (2)
C(10)–O(1)	1.154 (7)	C(11)–O(2)	1.159 (7)
S(1)–C(12)	1.796 (7)	S(1)–Mn(2)	2.347 (2)
Mn(2)–C(18)	1.772 (7)	Mn(2)–C(19)	1.765 (8)
Mn(2)–C(20)	2.220 (7)	Mn(2)–C(21)	2.176 (7)
Mn(2)–C(23)	2.155 (7)	Mn(2)–C(24)	2.212 (8)
Mn(2)–C(26)	2.206 (7)	Mn(2)–C(27)	2.280 (7)
C(18)–O(3)	1.145 (7)	C(19)–O(4)	1.162 (7)
C(20)–C(21)	1.423 (9)	C(20)–C(27)	1.411 (9)
C(21)–C(22)	1.504 (9)	C(21)–C(23)	1.373 (10)
C(23)–C(24)	1.413 (10)	C(24)–C(25)	1.498 (9)
C(24)–C(26)	1.385 (10)	C(26)–C(27)	1.426 (10)
C(1)–C(2)–Mn(1)	133.4 (5)	C(5)–C(4)–Mn(1)	131.0 (5)
C(8)–C(7)–Mn(1)	131.3 (5)	C(2)–Mn(1)–S(1)	85.5 (2)
C(10)–Mn(1)–C(11)	88.6 (3)	C(4)–Mn(1)–S(1)	142.8 (2)
C(3)–Mn(1)–S(1)	106.3 (2)	C(7)–Mn(1)–S(1)	125.2 (2)
C(6)–Mn(1)–S(1)	161.5 (2)	C(10)–Mn(1)–S(1)	92.2 (2)
C(9)–Mn(1)–S(1)	93.9 (2)	Mn(1)–S(1)–C(12)	108.9 (2)
C(11)–Mn(1)–S(1)	91.4 (2)	C(12)–S(1)–Mn(2)	108.4 (2)
Mn(1)–(1)–Mn(2)	123.7 (1)	S(1)–Mn(2)–C(19)	94.2 (2)
S(1)–Mn(2)–C(18)	91.1 (2)	S(1)–Mn(2)–C(20)	108.1 (2)
C(18)–Mn(2)–C(19)	88.1 (3)	S(1)–Mn(2)–C(23)	160.0 (2)
S(1)–Mn(2)–C(21)	145.0 (2)	S(1)–Mn(2)–C(26)	93.5 (2)
S(1)–Mn(2)–C(24)	123.5 (3)	Mn(2)–C(21)–C(22)	130.6 (5)
S(1)–Mn(2)–C(27)	86.3 (2)	Mn(2)–C(27)–C(26)	68.7 (4)
Mn(2)–C(24)–C(25)	130.4 (6)		

X-ray Crystallographic Studies. ORTEP views of **1a** and **2b** are presented in Figures 1 and 2. Selected bond distances and valence angles are listed in Table V. As indicated in Figure 3, the $Mn(CO)_2SPh$ tripod of **1a** is orientated in a staggered configuration relative to the π-coordinated arene carbons. This is the expected conformation for benzene or hexamethylbenzene ligands in (π-arene)ML_3 complexes.[30] The three ring C–C bonds, eclipsed by two carbonyls and a SPh ligand, appear to be slightly longer than the three noneclipsed C–C bonds, 1.42 (1) vs 1.39 (1) Å. This phenomenon of bond alternations follows from extended Hückel calculations[31] on [(η^6-benzene)$Cr(CO)_3$] and determinations by low-temperature X-ray and neutron diffraction techniques.[32] In contrast, the orientations of the $Mn(CO)_2SPh$ tripod in **2b**, for both arene rings, do not conform with the ideally expected eclipsed orientations relative to the methyl substituents on the benzene rings but are distorted. This may be a result of the steric and electronic effects of the bridging sulfur ligand. The mesitylene arene rings deviate slightly from planarity (maximum 0.034 (3) and 0.045 (2) Å for the two rings) and compare with the average deviation of the methyl carbon atoms of 0.035 (5) Å in (1,3,5-trimethylbenzene)tricarbonylmolybdenum.[33] The Mn–C(arene) distances (average 2.17 (1) Å) for **1a** are shorter than the corresponding averaged distance of 2.206 (2) Å for the complex [$Mn(\eta^6\text{-}C_6Me_6)(CO)_2Cl$][22] and identical with that obtained in [$Mn(\eta^6\text{-}C_6Me_6)(CO)_3$]$^+$.[1]

The structure of **2b** exhibits a conformation with both arene rings approximately on the same side of the manganese atoms, directed toward the PF_6 anion. A different conformation[27] was found for the complex [$(Mn(\eta^5\text{-}C_5H_4Me)(CO)_2)_2SEt$]$^+$, where the rings are on opposite sides of the manganese–manganese bond. The interatomic distance of 4.149 Å between the two manganese atoms and a valence angle for Mn(1)–S–Mn(2) or 123.8 (1)° indicate

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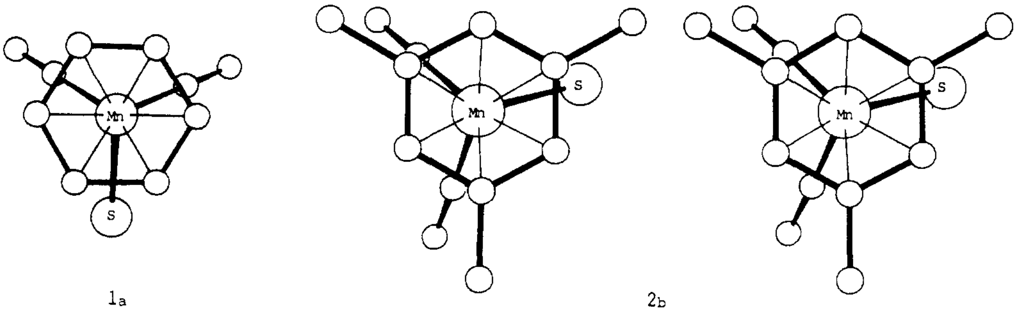
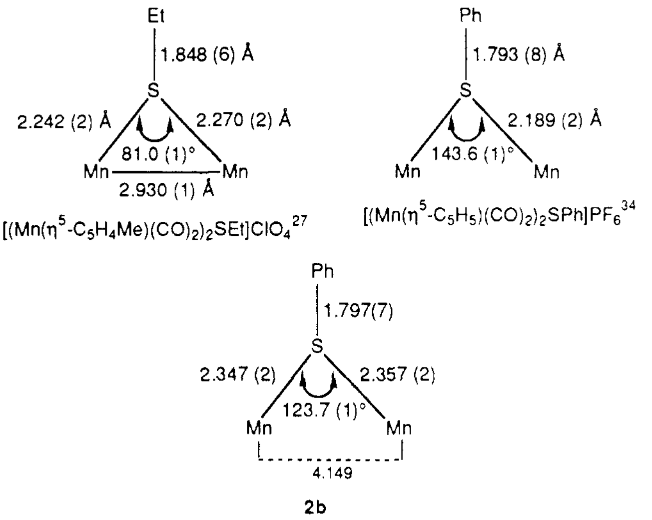


1a 2b

Figure 3. **1a** and **2b** viewed along the Mn–arene bond perpendicular to the arene rings.

Chart I



the absence of a metal–metal bond for **2b**.

The complex **2b** displays trigonal-pyramidal coordination around the sulfur atoms, and very little π-interaction with the metals is evident from the very long Mn–S bond lengths (2.357 (2) and 2.347 (2) Å). In contrast, the complex $[(Mn(\eta^5\text{-}C_5H_5)(CO)_2)_2SPh]^+$, which is also without a metal–metal bond, is coordinated in a trigonal-planar fashion[34] and has much shorter Mn–S bond lengths. Structural features relating to the sulfurs of **2b**, $[(Mn(\eta\text{-}C_5H_5)(CO)_2)_2SPh]$, and $[(Mn(\eta^5\text{-}C_5H_4Me)(CO)_2)_2SEt]^+$, are compared in Chart I. The possible introduction of a metal–metal bond by oxidation of **2b** is under investigation.

The Mn–C(carbonyl) and Mn–S bond distances do not differ significantly for **1a** and **2b**. This may be the result of two opposing effects. Whereas the electron density on the metal increases when benzene (**1a**) is replaced by mesitylene (**2b**), it decreases for the cation (**2b**) compared to that for the neutral compound (**1a**). The Mn–C(carbonyl) distance of 1.772 (8) Å (average) is significantly shorter than the value of 1.853 (9) Å (average) for $[Mn(\eta^6\text{-}C_6Me_6)(CO)_2Cl]$ and the distance of 1.822 (9) Å for $[Mn(\eta^6\text{-}C_6Me_6)(CO)_3]^+$.

In summary, the synthesis of **1a–c**, **2a–c**, and **4a–c** introduces new classes of manganese complexes with sulfur-containing ligands. A synthetic method was developed whereby heteroatom ligands could be introduced onto the manganese in the presence of activated arene ligands. The synthesis of neutral η^6-arene complexes of manganese with heteroatoms other than sulfur is presently being investigated. The activation of amines via coordination to manganese was insufficient to achieve deprotonation by Me_3N, and the use of stronger bases is being explored.

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Registry No. **1a**, 124200-50-6; **1b**, 124200-54-0; **1c**, 124200-60-8; **2a**, 124200-53-9; **2b**, 124200-57-3; **2c**, 124200-64-2; **3a**, 124200-51-7; **3b**, 124200-55-1; **3c**, 124200-61-9; **4a**, 124200-70-0; **4b**, 124200-59-5; **4c**, 124200-72-2; **5**, 124200-66-4; **6**, 124200-68-6; **7**, 124200-62-0; (η^6-benzene)tricarbonylmanganese hexafluorophosphate, 38834-51-4; tricarbonyl[(1,2,3,4,5,6-η)-hexamethylbenzene]manganese hexafluorophosphate, 38958-98-4; tricarbonyl[(1,2,3,4,5,6-η)-1,3,5-trimethylbenzene]manganese hexafluorophosphate, 35399-67-8; thiophenol, 108-98-5; methyl phenyl sulfide, 100-68-5; diphenyl sulfide, 139-66-2; lithium phenyl mercaptide, 2973-86-6.

Supplementary Material Available: Tables of anisotropic temperature factors, bond lengths, and bond angles (12 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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