Reactions of $[(CO)_3Mn(\eta^5\text{-Thi})]^+$ (Thi = Thiophene or 2,5-Dimethylthiophene) with Nucleophiles

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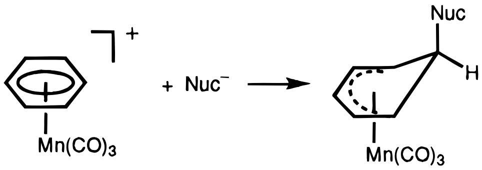
The η^5-thiophene complexes, $[(CO)_3Mn(\eta^5\text{-T})]^+$ (**1**) and $[(CO)_3Mn(\eta^5\text{-2,5-Me}_2T)]^+$ (**2**), react with $LiCuR_2$ (R = Me or Ph) by adding R^- to the sulfur atom of the thiophene, which gives the η^4-thiophene complexes, $(CO)_3Mn(\eta^4\text{-T}\cdot R)$ and $(CO)_3Mn(\eta^4\text{-2,5-Me}_2T\cdot R)$. An X-ray study of $(CO)_3Mn(\eta^4\text{-T}\cdot C_6H_5)$ (**6**) shows the $\eta^4\text{-T}\cdot C_6H_5$ ligand to be coordinated to the manganese through the four thiophene carbon atoms, while the sulfur bearing the phenyl group is bent away from the metal. The structure of **6** supports previous suggestions that the sulfur in η^5-thiophene complexes is an electrophilic center. Reactions of **1** or **2** with RS^-, CH_3O^-, or $^-CH(CO_2CH_3)_2$ nucleophiles result in the displacement of thiophene with the formation of $[(CO)_4Mn(\mu\text{-SR})]_2$ or $Mn_2(CO)_{10}$. The structure of $[(CO)_4Mn(\mu\text{-SC}_6H_4CH_3\text{-}p)]_2$ (**9**), established by X-ray studies, is also reported.

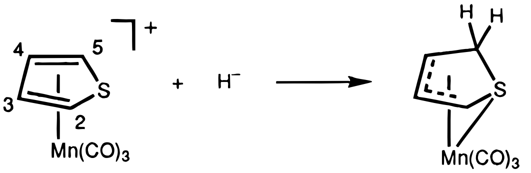
Introduction

Reactions of $[(\eta^6\text{-arene})Mn(CO)_3]^+$ complexes with nucleophiles lead[1] to cyclohexadienyl products (eq 1).



(1)

Oxidations[2] of these products give the free substituted arenes Ar-Nuc. Such reactions were particularly successful for carbon nucleophiles such as LiPh, LiMe, Grignard reagents, and stabilized enolates. Earlier, we showed[3,4] that the analogous thiophene complexes $[(\eta^5\text{-T})Mn(CO)_3]^+$ undergo attack at the 2-position by hydride nucleophiles such as BH_4^-, $HFe(CO)_4^-$ and $HW(CO)_5^-$ (eq 2). The nucleophiles CN^- and PR_3



(2)

reacted similarly. For the analogous 2-methylthiophene complex $[(\eta^5\text{-2-MeT})Mn(CO)_3]^+$, hydride nucleophiles added at the 5-position. When using a 2,5-disubstituted thiophene such as $[(\eta^5\text{-2,5-Me}_2T)Mn(CO)_3]^+$, the only product isolated from the reaction with BH_4^- was $Mn_2(CO)_{10}$. Thus, the methyl groups prevented H^- addition at the 2- and 5-positions.

In the present report, we extend our studies of the $[(\eta^5\text{-thiophene})Mn(CO)_3]^+$ complexes to reactions with carbon, sulfur, and oxygen nucleophiles. They lead to quite different products, depending on the nucleophile. We also report improved syntheses of the complexes $[(\eta^5\text{-Thi})Mn(CO)_3]^+$, where Thi = thiophene (T) or 2,5-dimethylthiophene (2,5-Me_2T).

Experimental Section

General Procedures. All reactions were carried out under a dry, oxygen-free N_2 atmosphere using standard Schlenk techniques. All solvents employed were reagent grade and were dried by refluxing over appropriate drying agents and stored over 4-Å molecular sieves under an N_2 atmosphere until used. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl, while hexanes and CH_2Cl_2 were distilled from CaH_2. CH_3NO_2 was deoxygenated in vacuo and dried over 4-Å molecular sieves. The neutral Al_2O_3 (Brockmann, activity I, 80−100 mesh) used for chromatography was deoxygenated under high vacuum at room temperature for 16 h, deactivated with 5% (w/w) nitrogen-saturated water, and stored under nitrogen, while the neutral SiO_2 (5 × 0143U-1, 60−200 mesh) was deoxygenated under high vacuum at room temperature for 12 h. $AgBF_4$, thiophene, 2,5-dimethylthiophene, CuI, CH_3Li, C_6H_5Li, $NaSCH_3$, $NaOCH_3$, $CH_2(COOCH_3)_2$, and NaH were purchased from Aldrich Chemical Co. $Mn(CO)_5Br$[5] and $NaSC_6H_4CH_3$[6] were prepared by literature methods.

Elemental analyses were performed by Galbraith Laboratory, Inc., or National Chemical Consulting, Inc. The IR spectra were recorded on a Nicolet 710 FT-IR spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature on samples in $CDCl_3$ solution with $CHCl_3$ as the internal reference, or in CD_3NO_2 solution with CH_3NO_2 as the internal reference, using a Nicolet NT-300 spectrometer. Electron ionization mass spectra (EIMS) and chemical ionization mass spectra (CIMS) were run on a Finnigan 4000 spectrometer at 70 eV. Melting points were recorded in sealed nitrogen-filled capillaries and are uncorrected.

Preparation of $[(CO)_3Mn(\eta^5\text{-T})]BF_4$ (T = Thiophene) (1). To a solution of $Mn(CO)_5Br$ (1.0 g, 3.6 mmol) in CH_2Cl_2

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(15 mL) was added an equimolar amount of $AgBF_4$ (0.71 g, 3.6 mmol). The mixture was refluxed in the dark for 0.5 h to give a red solution containing a gray-white solid, which was cooled to room temperature. To this was added thiophene (1.0 mL, 1.05 g, 12.4 mmol), and then the mixture was refluxed for 1 h (in the dark). After vacuum removal of the solvent, the resulting yellow solid residue was dissolved in CH_3NO_2, and the solution was filtered to remove the insoluble gray-white solid. The filtrate was reduced in vacuo to ca. 2 mL, to which was added 90 mL of CH_2Cl_2 to precipitate the product. The yellow product was filtered and washed with CH_2Cl_2 and then dried under vacuum for 1 h to give 0.75 g (67%, based on $Mn(CO)_5Br$) of yellow powder **1**. IR (CH_3NO_2) ν(CO): 2077 vs, 2060 m, 2012 m cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 6.87 (d, 2 H), 6.78 (d, 2 H). MS: *m/e* 307 ($M^+ - 2$ H). Anal. Calcd for $C_7H_4O_3BF_4SMn$: C, 27.13; H, 3.30. Found: C, 26.78; H, 3.35.

Preparation of [(CO)$_3$Mn(η^5-2,5-Me$_2$T)]BF$_4$ (2). To a solution of $Mn(CO)_5Br$ (2.0 g, 7.28 mmol) in CH_2Cl_2 (40 mL) was added 1.50 g (7.70 mmol) of $AgBF_4$. The mixture was refluxed in the dark for 30−45 min and then allowed to cool to room temperature. To this mixture was added 1.5 mL (1.48 g, 13.2 mmol) of 2,5-Me$_2$T. The mixture was refluxed for 1 h (in the dark). Further treatment of the resulting mixture as described earlier for the preparation of **1** gave 1.74 g (71%, based on $Mn(CO)_5Br$) of yellow powder **2**. IR (CH_3NO_2) ν(CO): 2097 m, 2072 vs, 2009 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.41 (s, 2 H), 2.53 (s, 6 H). MS: *m/e* 251 ($M^+ - BF_4$), 250 ($M^+ - BF_4 - H$). Anal. Calcd for $C_9H_8O_3BF_4SMn$: C, 31.99; H, 2.39. Found: C, 31.82; H, 1.98.

Reaction of 1 with LiCuMe$_2$ To Give (CO)$_3$Mn(η^4-T·CH$_3$) (3) and [(CO)$_4$MnI]$_2$ (4). To a suspension of CuI (0.123 g, 0.65 mmol) in THF (20 mL) at 0 °C was added 0.90 mL (1.37 mmol, 1.5 M solution) of $LiCH_3$ with stirring. The reaction solution was stirred at 0 °C for 10 min. The resulting LiCuMe$_2$[7] solution was added to a solution of [(CO)$_3$Mn(η^5-T)]BF$_4$ (**1**) (0.200 g, 0.645 mmol) in 30 mL of THF at −60 °C. The solution turned red immediately. The reaction solution was stirred while warming from −60 to 15 °C over a 12-h period; the resulting dark-red solution was evaporated under vacuum to dryness, and the dark residue was chromatographed on SiO_2 (neutral) with hexanes/CH_2Cl_2 (15:1) as the eluant. The light yellow band that eluted first was collected, and then the red band was eluted with CH_2Cl_2/Et_2O (2:1). After vacuum removal of the solvents from the preceding two eluates, the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction, 0.085 g (55%, based on **1**) of light yellow crystals of **3** was obtained (mp 86−88 °C (dec)). IR (CH_2Cl_2) ν(CO): 1995 vs, 1904 vs br cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.28 (s, 2 H), 2.40 (s, 2 H), 1.85 (s, 3 H). MS: *m/e* 238 (M^+), 223 ($M^+ - CH_3$), 167 ($M^+ - CH_3 - 2CO$), 139 ($M^+ - CH_3 - 3CO$). Anal. Calcd for $C_8H_7O_3SMn$: C, 40.35; H, 2.96. Found: C, 39.09; H, 2.88. From the second fraction, 0.045 g (24%, based on **1**) of orange-red crystals of **4**[8] was obtained (mp 165 °C (dec)). IR (CH_2Cl_2) ν(CO): 2088 s, 2034 vs, 2006 s, 1973 s cm^{-1}. MS: *m/e* 558 (M^+). Anal. Calcd for $C_8O_8I_2Mn_2$: C, 16.35. Found: C, 16.61.

Reaction of 2 with LiCuMe$_2$ To Give (CO)$_3$Mn(η^4-2,5-Me$_2$T·CH$_3$) (5) and 4. As described for the reaction of **1** with LiCuMe$_2$, 0.300 g (0.888 mmol) of **2** in THF (40 mL) at −60 °C was treated with fresh LiCuMe$_2$ [prepared by the reaction of CuI (0.169 g, 0.887 mmol) with $LiCH_3$ (1.28 mL of 1.5 M solution, 1.78 mmol)].[7] The mixture was allowed to warm to −5 °C over a 10-h period, during which time the light-yellow solution turned to dark red. Further treatment of the resulting solution in a manner similar to that described earlier for the reaction of **1** with LiCuMe$_2$ yielded 0.115 g (49%, based on **2**) of light-yellow crystals of **5** and 0.080 g (31%, based on **2**) of orange-red crystalline **4**. **5**: mp 98−100 °C (dec). IR (CH_2Cl_2) ν(CO): 1987 vs, 1896 vs br cm^{-1}. ^{1}H NMR ($CDCl_3$): 4.84 (s, 2 H), 1.90 (s, 3 H), 1.65 (s, 6 H). MS (CI): *m/e* 267 ($M^+ +$ H). Anal. Calcd for $C_{10}H_{11}O_3SMn$: C, 45.12; H, 4.17. Found: C, 45.16; H, 3.66. **4** was identified by its melting point and IR spectrum.

Reaction of 1 with LiCuPh$_2$ To Give (CO)$_3$Mn(η^4-T·C$_6$H$_5$) (6) and 4. To a suspension of CuI (0.246 g, 1.29 mmol) in THF (20 mL) was added 1.60 mL of 1.8 M (2.75 mmol) LiC_6H_5 at −10 °C. The solution turned dark yellow and the solid CuI dissolved. After 10 min of stirring at −5 to 0 °C, the resulting solution of LiCuPh$_2$[7] was added to a solution of **1** (0.400 g, 1.29 mmol) dissolved in THF (30 mL) at −60 °C. The reaction solution rapidly turned dark yellow and was stirred initially at −60 °C and then allowed to warm to 15 °C over 12 h. After the solution was evaporated to dryness under vacuum, the dark green-yellow residue was chromatographed on SiO_2 (neutral) with hexanes/CH_2Cl_2 (3:1) as the eluant. The yellow band that eluted first was collected, and then the red band was eluted with CH_2Cl_2/Et_2O (4:1). After vacuum removal of the solvents from the preceding two eluates, the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction, 0.145 g (37%, based on **1**) of **6** was obtained as yellow crystals (mp 106−107 °C (dec)). IR (CH_2Cl_2) ν(CO): 1996 vs, 1907 vs br cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.54−7.01 (m, 5 H), 5.28 (s, 2 H), 2.72 (s, 2 H). MS: *m/e* 300 (M^+). Anal. Calcd for $C_{13}H_9O_3SMn$: C, 52.01; H, 3.02. Found: C, 52.31; H, 2.98. From the second fraction, 0.105 g (28%, based on **1**) of orange-red crystalline **4** was obtained; it was identified by its melting point and IR spectrum.

Reaction of 2 with LiCuPh$_2$ To Give (CO)$_3$Mn(η^4-2,5-Me$_2$T·C$_6$H$_5$) (7) and 4. This reaction was conducted as described earlier for the reaction of **1** with LiCuPh$_2$. A solution of LiCuPh$_2$ prepared by the reaction of CuI (0.169 g, 0.887 mmol) with LiC_6H_5 (0.99 mL of 1.8 M solution, 1.77 mmol) was added to a solution of **2** (0.300 g, 0.888 mmol) dissolved in THF (30 mL) at −60 °C. After being stirred for 10 h while being warmed to 0 °C, the solution was evaporated to dryness under vacuum. Further treatment of the residue as described for the reaction of **1** with LiCuPh$_2$ gave 0.095 g (33%, based on **2**) of yellow crystalline **7** and 0.070 g (27%, based on **2**) of **4**. **7**: mp 148−149 °C (dec). IR (CH_2Cl_2) ν(CO): 1989 vs, 1899 vs br cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.80 (m, 1 H), 7.48 (m, 2 H), 7.15 (m, 1 H), 4.95 (s, 2 H), 1.69 (s, 6 H). MS (CI): *m/e* 329 ($M^+ +$ H). Anal. Calcd for $C_{15}H_{13}O_3SMn$: C, 54.88; H, 3.99. Found: C, 54.55, H, 4.08. Compound **4** was identified by its melting point and IR spectrum.

Reaction of 1 with NaSCH$_3$ To Give [(CO)$_4$Mn(SCH$_3$)]$_2$ (8). To a solution of **1** (0.300 g, 0.968 mmol) dissolved in 40 mL of THF at 0 °C was added 0.073 g (1.04 mmol) of $NaSCH_3$. The mixture was stirred at room temperature for 48 h. The resulting light-yellow solution was evaporated under vacuum to dryness, and the residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1) as the eluant. A yellow band was eluted and collected. After removal of the solvent, the resulting yellow powder was recrystallized from hexanes/CH_2Cl_2 at −80 °C to give 0.112 g (54%, based on **1**) of golden-yellow crystals of **8**[9] (mp 112−114 °C (dec)). IR (CH_2Cl_2) ν(CO): 2072 s, 2019 vs, 2000 w, 1960 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 6 H). MS: *m/e* 428 (M^+). Anal. Calcd for $C_{10}H_6O_8S_2Mn_2$: C, 28.05; H, 1.41. Found: C, 28.19; H, 1.67.

Reaction of 2 with NaSCH$_3$ To Give 8. Following the procedure described for the reaction of **1** with $NaSCH_3$, the reaction of **2** (0.300 g, 0.888 mmol) with $NaSCH_3$ (0.065 g, 0.927 mmol) gave 0.095 g (50%, based on **2**) of golden-yellow crystals of **8**, which were identified by their melting point and IR and ^{1}H NMR spectra.

Reaction of 1 with NaSC$_6$H$_4$CH$_3$-*p* To Give [(CO)$_4$Mn(SC$_6$H$_4$CH$_3$-*p*)]$_2$ (9). To a solution of **1** (0.300 g, 0.968 mmol)

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dissolved in THF (30 mL) at 0 °C was added 0.146 g (0.999 mmol) of $NaSC_6H_4CH_3$-*p*. The mixture was stirred at room temperature for 24 h, during which time the solution gradually turned from light yellow to yellow green. After the solution was evaporated to dryness under vacuum, the residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1) as the eluant. The yellow band was collected. After vacuum removal of the solvent, the residue was recrystallized from hexanes/CH_2Cl_2 at −80 °C to give 0.160 g (57%, based on **1**) of **9** as orange-yellow crystals (mp 108−110 °C (dec)). IR (hexane) ν(CO): 2077 s, 2020 vs, 2004 w, 1968 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.81−7.11 (m, 8 H), 2.31 (s, 6 H). MS: *m/e* 580 (M^+). Anal. Calcd for $C_{22}H_{14}O_8S_2Mn_2$: C, 45.53; H, 2.43. Found: C, 45.57; H, 2.46.

Reaction of 2 with $NaSC_6H_4CH_3$-*p* To Give 9. The reaction of **2** (0.135 g, 0.399 mmol) with $NaSC_6H_4CH_3$-*p* (0.058 g, 0.397 mmol) and subsequent treatment of the product solution were performed in a manner similar to that described for the reaction of **1** with $NaSC_6H_4CH_3$-*p* to give 0.060 g (50%, based on **2**) of **9**, which was identified by its melting point and IR and ^1H NMR spectra.

Reaction of 1 with $NaOCH_3$ To Give $Mn_2(CO)_{10}$ (10). A 0.300-g (0.968 mmol) sample of **1** was dissolved in THF (40 mL). To this solution was added 0.055 g (1.02 mmol) of $NaOCH_3$. The mixture was stirred at room temperature for 24 h. The resulting light-yellow solution was evaporated to dryness, and the residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (15:1) as the eluant. A yellow band eluted. The solvent was removed from it, and the yellow residue was recrystallized from hexanes/CH_2Cl_2 at −80 °C to give 0.085 g (45%, based on **1**) of yellow crystalline **10**, which was identified as $Mn_2(CO)_{10}$ by comparison of its melting point and IR spectrum with that of an authentic sample of $Mn_2(CO)_{10}$ [mp 150−152 °C (dec); IR (CH_2Cl_2) ν(CO) 2046 s, 2011vs br, 1979 s cm^{-1}].

Reaction of 2 with $NaOCH_3$ To Give 10. As described for the reaction of **1** with $NaOCH_3$, 0.300 g (0.888 mmol) of **2** was treated with $NaOCH_3$ (0.052 g, 0.963 mmol) at room temperature for 36 h to give 0.090 g (52%, based on **2**) of **10**, which was identified by comparison of its melting point and IR spectrum with those of commercial $Mn_2(CO)_{10}$.

Reaction of 1 with $NaCH(CO_2CH_3)_2$ To Give 10. To a suspension of NaH (0.040 g, 1.67 mmol) [60% dispersion in mineral oil, washed with hexanes (5 × 10 mL) before use] in THF (15 mL) at room temperature was added dropwise 0.20 g (1.5 mmol) of dimethyl malonate ($CH_2(CO_2CH_3)_2$) (in 5 mL of THF) over a period of 5−8 min; H_2 gas evolution was observed. After being stirred for 10 min at room temperature, the solution of $NaCH(CO_2CH_3)_2$[10] was added to a solution of 0.400 g (1.29 mmol) of **1** dissolved in THF (50 mL) at −60 °C with stirring. The solution immediately turned from yellow to orange red. After being stirred while warming to 15 °C over a 10-h period, the solution was evaporated under vacuum to dryness, and the residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (15:1) as the eluant. The yellow band was collected, and the solvent was removed. The crude product was recrystallized from hexanes/CH_2Cl_2 at −80 °C to give 0.115 g (46%, based on **1**) of **10**.

Reaction of 2 with $NaCH(CO_2CH_3)_2$ To Give 10. **2** (0.350 g, 1.04 mmol) was reacted with $NaCH(CO_2CH_3)_2$, prepared by the reaction of NaH (0.029 g, 1.21 mmol) with $CH_2(CO_2CH_3)_2$ (0.145 g, 1.10 mmol), in a manner similar to that described for the reaction of **1** with $NaCH(CO_2CH_3)_2$. Yellow crystals of **10** (0.098 g, 48% based on **2**) were isolated and identified by their melting point and IR spectrum.

X-ray Crystal Structure Determinations of $(CO)_3Mn(\eta^4\text{-T}\cdot C_6H_5)$ (6) and $[(CO)_4Mn(SC_6H_4CH_3\text{-}p)]_2$ (9). A light-yellow needle crystal of **6** was attached to the tip of a glass fiber and mounted on a Siemens P4RA diffractometer with monochromated CuKα radiation. High-angle cell constants were determined from a subset of intense reflections in the range of 35.0−50.0° for 2θ. The data collection was conducted under a cryogenic stream of N_2 at 213 °C. An orange crystal of **9** was mounted on an Enraf-Nonius CAD4 diffractometer with monochromated Mo Kα radiation at 298 °C. Pertinent data collection and reduction information are given in Table 1.

Table 1. Crystal and Data Collection Parameters for $(CO)_3Mn(\eta^4\text{-T}\cdot C_6H_5)$ (6) and $[(CO)_4Mn(SC_6H_4CH_3\text{-}p)]_2$ (9)

	6	9
formula	$C_{13}H_9MnO_3S$	$C_{33}H_{21}Mn_3O_{12}S_3$
fw	300.2	870.5
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	9.397(4)	10.240(2)
b (Å)	14.341(3)	9.281(2)
c (Å)	9.649(2)	37.924(4)
β (deg)	105.57(2)	90.38(2)
V (Å^3)	1252.6(2)	3604.0(4)
Z	4	4
d_{calc} (Mg/m^3)	1.592	1.604
crystal size (mm)	0.38 × 0.18 × 0.13	0.45 × 0.12 × 0.08
μ, (mm^{-1})	10.109	1.270
diffractometer used	Siemens P4RA	Enraf-Nonius CAD4
radiation	Cu K$_\alpha$ (λ = 1.541 78Å)	Mo K$_\alpha$ (λ = 0.710 73 Å)
temp (K)	213	298
scan method	$2\theta-\theta$	$\omega-2\theta$
data collection range, 2θ (deg)	4.0−115.0	4.0−50.0°
no. of data collected	3607	8975
no. of unique data	1683 (R_{int} = 0.0216)	6329 (R_{int} = 0.0267)
no. of data with $F_o > 4.0\ \sigma(F)$	1429	4115
no. of parameters refined	185	475
transmission factors: min/max	0.53/0.83	0.55/0.85
R^a	0.0328	0.0404
$R_w{}^b$	0.0400	0.0493
goodness-of-fit^c	1.45	1.02
largest peak (e/Å^3)	0.29	0.46
largest shift/eds. final cycle	0.0	0.0

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = |\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

Lorentz and polarization corrections were applied for **6** and **9**. Both were also corrected for decay and for absorption by using the semiempirical method based on several azimuthal scans.

The space group for **6** was determined to be $P2_1/n$ on the basis of systematic absences and intensity statistics. All non-hydrogen atoms were placed directly from the E-map using direct methods. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined as riding atoms. The final positional and isotropic displacement parameters are given in Table 2. Bond distances and selected angles are presented in Table 3.

The solution and refinement of **9** in space group $P2_1/c$ was performed in the same manner as for **6**. The final positional and isotropic displacement parameters are given in Table 4. Selected bond lengths and angles are presented in Table 5. Both **6** and **9** were solved and refined using SHELXTL-Plus.[11]

Results and Discussion

Synthesis of $[(CO)_3Mn(\eta^5\text{-T})]^+$ (1) and $[(CO)_3Mn(\eta^5\text{-2,5-Me}_2\text{T})]^+$ (2). The first reported synthesis[12] of $[(CO)_3Mn(\eta^5\text{-T})]^+$ involved the reaction of $Mn(CO)_5Cl$

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times 10^3$) for $(CO)_3Mn(\eta^4\text{-}T{\cdot}C_6H_5)$ (6)

atom	x	y	z	U_{eq}[a]
Mn	2179(1)	8390(1)	7197(1)	29(1)
S	2130(1)	8867(1)	9956(1)	35(1)
C(1)	1187(4)	9346(3)	8305(4)	37(1)
C(2)	2166(4)	9805(3)	7659(4)	35(1)
C(3)	3581(5)	9470(3)	8178(4)	32(1)
C(4)	3621(4)	8745(3)	9215(4)	29(1)
C(5)	2462(4)	9771(2)	11303(3)	31(1)
C(6)	2752(4)	9491(3)	12726(4)	41(1)
C(7)	3018(5)	10160(3)	13797(4)	50(2)
C(8)	2976(5)	11089(3)	13463(4)	45(2)
C(9)	2697(5)	11361(2)	12040(4)	43(2)
C(10)	2431(4)	10712(2)	10955(4)	36(1)
C(11)	1367(4)	7340(3)	7616(3)	36(1)
O(11)	809(4)	6673(2)	7886(3)	58(1)
C(12)	3493(5)	7819(3)	6466(4)	42(1)
O(12)	4338(3)	7430(2)	5989(3)	68(1)
C(13)	945(4)	8515(3)	5457(4)	44(1)
O(13)	125(4)	8608(2)	4323(3)	70(1)

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

Table 3. Bond Lengths (Å)[a] and Selected Bond Angles (deg)[a] for $(CO)_3Mn(\eta^4\text{-}T{\cdot}C_6H_5)$ (6)

	Bond Lengths		
Mn−S	2.761(2)	Mn−C(1)	2.104(4)
Mn−C(2)	2.079(4)	Mn−C(3)	2.088(4)
Mn−C(4)	2.114(3)	Mn−C(11)	1.781(4)
Mn−C(12)	1.777(5)	Mn−C(13)	1.775(4)
S−C(1)	1.743(4)	S−C(4)	1.744(4)
S−C(5)	1.803(3)	C(1)−C(2)	1.407(6)
C(2)−C(3)	1.376(5)	C(3)−C(4)	1.437(5)
C(5)−C(6)	1.386(5)	C(5)−C(10)	1.390(5)
C(6)−C(7)	1.383(5)	C(7)−C(8)	1.367(6)
C(8)−C(9)	1.384(6)	C(9)−C(10)	1.372(5)
C(11)−O(11)	1.155(5)	C(12)−O(12)	1.163(6)
C(13)−O(13)	1.164(4)		
	Bond Angles		
C(1)−S−C(4)	86.1(2)	S−C(4)−C(3)	109.8(3)
C(1)−S−C(5)	108.8(2)	S−C(5)−C(10)	122.4(3)
S−C(1)−C(2)	110.9(3)	Mn−C(11)−O(11)	178.4(4)
Mn−S−C(5)	146.0(1)	Mn−C(12)−O(12)	178.8(4)
C(4)−S−C(5)	111.4(2)	Mn−C(13)−O(13)	179.0(4)
C(1)−C(2)−C(3)	111.0(3)	C(11)−Mn−C(12)	95.0(2)
C(2)−C(3)−C(4)	110.4(4)	C(11)−Mn−C(13)	95.1(2)
S−C(5)−C(6)	117.2(3)	C(12)−Mn−C(13)	91.1(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times 10^3$) for $[(CO)_4Mn(SC_6H_4CH_3\text{-}p)]_2$ (9)

atom	x	y	z	U_{eq}[a]
Mn(1)	3867(1)	1963(1)	1828(1)	39(1)
Mn(2)	3706(1)	−1596(1)	1449(1)	41(1)
S(1)	2403(1)	−46(1)	1802(1)	40(1)
S(2)	5124(1)	484(1)	1438(1)	40(1)
C(1)	2881(5)	2659(5)	1451(1)	51(2)
O(1)	2250(4)	3045(4)	1227(1)	79(2)
C(2)	4738(5)	1036(5)	2196(1)	46(2)
O(2)	5226(4)	434(4)	2420(1)	66(1)
C(3)	2909(5)	2999(5)	2139(1)	49(2)
O(3)	2328(4)	3692(4)	2330(1)	75(2)
C(4)	5047(5)	3420(5)	1807(1)	49(2)
O(4)	5777(4)	4343(4)	1796(1)	78(2)
C(5)	2709(5)	−853(5)	1075(1)	52(2)
O(5)	2114(4)	−424(5)	851(1)	84(2)
C(6)	4828(6)	−2165(5)	1815(1)	50(2)
O(6)	5553(4)	−2496(4)	2021(1)	70(1)
C(7)	4617(6)	−2716(5)	1150(1)	54(2)
O(7)	5164(4)	−3472(4)	961(1)	82(2)
C(8)	2558(6)	−3063(5)	1517(1)	55(2)
O(8)	1851(5)	−3976(4)	1556(1)	87(2)
C(11)	1986(4)	−708(5)	2229(1)	40(1)
C(12)	1205(5)	143(5)	2440(1)	53(2)
C(13)	804(5)	−314(6)	2767(1)	61(2)
C(14)	1150(5)	−1664(6)	2892(1)	54(2)
C(15)	1897(5)	−2524(6)	2679(1)	59(2)
C(16)	2323(5)	−2055(5)	2352(1)	51(2)
C(17)	706(6)	−2175(6)	3253(1)	78(2)
C(21)	5327(5)	1215(5)	1003(1)	41(1)
C(22)	5647(5)	315(5)	731(1)	56(2)
C(23)	5833(6)	845(6)	395(1)	61(2)
C(24)	5697(5)	2284(5)	321(1)	48(2)
C(25)	5437(6)	3191(5)	595(1)	62(2)
C(26)	5254(6)	2669(5)	936(1)	59(2)
C(27)	5769(6)	2842(6)	−53(1)	67(2)
Mn(1′)	501(1)	3504(1)	269(1)	40(1)
S(1′)	1247(1)	4778(1)	−242(1)	43(1)
C(1′)	1467(5)	4846(5)	526(1)	49(2)
O(1′)	2055(4)	5646(4)	687(1)	76(2)
C(2′)	−579(5)	2234(5)	29(1)	54(2)
O(2′)	−1245(4)	1414(5)	−96(1)	92(2)
C(3′)	1880(5)	2264(5)	240(1)	51(2)
O(3′)	2732(4)	1505(5)	220(1)	79(2)
C(4′)	−58(5)	2641(5)	667(1)	52(2)
O(4′)	−403(4)	2037(4)	911(1)	79(2)
C(11′)	1319(5)	3770(5)	−643(1)	44(2)
C(12′)	1181(7)	2304(6)	−662(1)	77(2)
C(13′)	1231(7)	1601(7)	−985(2)	87(3)
C(14′)	1437(5)	2311(6)	−1293(1)	58(2)
C(15′)	1682(6)	3760(6)	−1269(1)	70(2)
C(16′)	1623(6)	4480(6)	−949(1)	65(2)
C(17′)	1431(6)	1540(8)	−1647(1)	88(3)

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

with thiophene (T) in the presence of $AlBr_3$; however, the yield was poor (3.5%). A higher yield route (74%) involved the reaction of $Mn(CO)_5(O_3SCF_3)$ with T;[3] however, this method required the prior synthesis of $Mn(CO)_5(O_3SCF_3)$ and a large excess of thiophene. In this paper, we describe a more efficient preparation (eq 3) of $[(CO)_3Mn(\eta^5\text{-}T)]^+$ and $[(CO)_3Mn(\eta^5\text{-}2,5\text{-}Me_2T)]^+$. It

$$Mn(CO)_5Br \xrightarrow[-AgBr]{AgBF_4} \{Mn(CO)_5BF_4\} \xrightarrow[-2CO]{Thi} (CO)_3Mn(\eta^5\text{-}Thi)^+BF_4^- \qquad (3)$$

1: Thi = T
2: Thi = 2,5-Me_2T

begins with the in situ formation of $Mn(CO)_5BF_4$ from the reaction of $Mn(CO)_5Br$ with $AgBF_4$ in CH_2Cl_2 solvent; this intermediate is then reacted with thiophene (T) or 2,5-dimethylthiophene (2,5-Me_2T) to give the desired $[(CO)_3Mn(\eta^5\text{-}T)]^+$ products in good (67−71%) yield. This route is similar to that reported[13] for the synthesis of $(CO)_3Mn(\eta^6\text{-arene})^+$ complexes.

Reactions of $[(CO)_3Mn(\eta^5\text{-}Thi)]^+$ (1 and 2) with $LiCuR_2$. Complexes **1** and **2** react (eq 4) with organocuprates to give the $(CO)_3Mn(\eta^4\text{-}T{\cdot}R)$ complexes (**3**, **5**−**7**) in 33−55% yield. These products are stable for a few hours in air in the solid state. A byproduct (24−31%) in all of these reactions is the known[8] $[Mn(CO)_4(\mu\text{-}I)]_2$, which presumably forms from reaction with I^- that is

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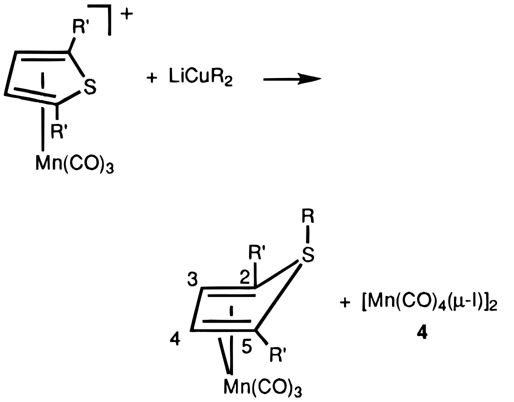
Table 5. Bond Lengths (Å)[a] and Selected Bond Angles (deg)[a] for $(CO)_4Mn(SC_6H_4CH_3)]_2$ (9)

Bond Lengths			
Mn(1)−S(1)	2.394(1)	Mn(1)−S(2)	2.398(1)
Mn(1)−C(1)	1.860(5)	Mn(1)−C(2)	1.864(5)
Mn(1)−C(3)	1.816(5)	Mn(1)−C(4)	1.816(5)
Mn(2)−S(1)	2.381(1)	Mn(2)−S(2)	2.416(1)
Mn(2)−C(5)	1.875(5)	Mn(2)−C(6)	1.873(5)
Mn(2)−C(7)	1.803(5)	Mn(2)−C(8)	1.819(5)
S(1)−C(11)	1.788(4)	S(2)−C(21)	1.795(4)
C(1)−O(1)	1.120(6)	C(2)−O(2)	1.130(6)
C(3)−O(3)	1.137(6)	C(4)−O(4)	1.138(6)
C(5)−O(5)	1.114(6)	C(6)−O(6)	1.116(6)
C(7)−O(7)	1.149(6)	C(8)−O(8)	1.124(7)
Bond Angles			
S(1)−Mn(1)−S(2)	82.4(1)	S(1)−Mn(1)−C(1)	84.4(2)
S(2)−Mn(1)−C(1)	91.0(2)	S(1)−Mn(1)−C(2)	88.1(2)
S(2)−Mn(1)−C(2)	86.6(1)	C(1)−Mn(1)−C(2)	172.4(2)
S(1)−Mn(1)−C(3)	95.6(2)	S(2)−Mn(1)−C(3)	176.8(2)
C(1)−Mn(1)−C(3)	91.3(2)	C(2)−Mn(1)−C(3)	90.8(2)
S(1)−Mn(1)−C(4)	174.3(1)	S(2)−Mn(1)−C(4)	92.3(2)
C(1)−Mn(1)−C(4)	93.8(2)	C(2)−Mn(1)−C(4)	93.5(2)
C(3)−Mn(1)−C(4)	89.8(2)	S(1)−Mn(2)−S(2)	82.3(1)
S(1)−Mn(2)−C(5)	84.2(2)	S(2)−Mn(2)−C(5)	91.0(2)
S(1)−Mn(2)−C(6)	95.6(2)	S(2)−Mn(2)−C(6)	82.7(2)
C(5)−Mn(2)−C(6)	173.6(2)	S(1)−Mn(2)−C(7)	175.2(2)
S(2)−Mn(2)−C(7)	97.8(2)	C(5)−Mn(2)−C(7)	91.0(2)
C(6)−Mn(2)−C(7)	89.3(2)	S(1)−Mn(2)−C(8)	90.4(2)
S(2)−Mn(2)−C(8)	171.8(2)	C(5)−Mn(2)−C(8)	91.9(2)
C(6)−Mn(2)−C(8)	94.5(2)	C(7)−Mn(2)−C(8)	89.7(2)
Mn(1)−S(1)−Mn(2)	98.1(1)	Mn(1)−S(1)−C(11)	112.6(1)
Mn(2)−S(1)−C(11)	116.1(2)	Mn(1)−S(2)−Mn(2)	97.0(1)
Mn(1)−S(2)−C(21)	114.5(1)	Mn(2)−S(2)−C(21)	113.0(1)
Mn(1)−C(1)−O(1)	177.4(5)	Mn(1)−C(2)−O(2)	177.2(4)
Mn(1)−C(3)−O(3)	177.6(4)	Mn(1)−C(4)−O(4)	179.2(5)
Mn(2)−C(5)−O(5)	179.4(5)	Mn(2)−C(6)−O(6)	176.1(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

liberated in the formation of $LiCuR_2$ from CuI and LiR: $CuI + 2LiR \rightarrow LiCuR_2 + LiI$.



(4)

3: R = CH_3, R' = H
5: R = CH_3, R' = CH_3
6: R = C_6H_5, R' = H
7: R = C_6H_5, R' = CH_3

The molecular structure (Figure 1 with atom labels used in the following discussion of the structure) of **6** determined by X-ray diffraction studies shows that the phenyl group is bonded to the sulfur and the T·Ph ligand is η^4-coordinated to Mn through the four carbons of the thiophene. The sulfur is bent away from the Mn at a distance of 2.761(2) Å; the sulfur is out of the C(1)−C(2)−C(3)−C(4) plane by 0.645 Å and the dihedral angle between the C(1)−C(2)−C(3)−C(4) and C(1)−S−C(4) planes is 30.4°. The C(5)−S bond (1.803(3) Å) is slightly longer than a typical $C(sp^2)$−S single-bond distance (1.77 Å).[14,15] The dihedral angle between the planes of the phenyl group [C(5)−C(10)] and the four thiophene carbons [C(1)−C(4)] is 89.4°. The carbon−carbon distances in the thiophene ring appear to exhibit a long−short−long pattern, as observed in the following bond lengths: C(1)−C(2) = 1.407(6) Å, C(2)−C(3) = 1.376(5), C(3)−C(4) = 1.437(5). The Mn−C distances are slightly shorter to C(2) (2.079(4) Å) and C(3) (2.088(4) Å) than to C(1) (2.104(4) Å) and C(4) (2.114(3) Å). The C−S bond distances [C(1)−S = 1.743(4) Å, C(4)−S = 1.744(4)] are slightly longer than those (1.714(1) Å)[16,17] in thiophene itself. The C(11)−O(11) ligand is essentially eclipsed with the sulfur atom, as indicated by a C(5)−S−Mn−C(11) torsion angle of 174.3(2)°. In contrast, it might be noted that the sulfur in $(CO)_3Cr(\eta^5\text{-}2,5\text{-}Me_2T)$[18] is staggered with respect to the CO ligands.

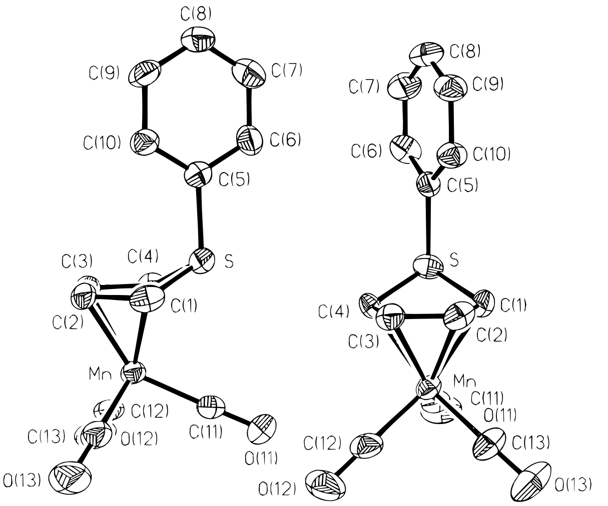
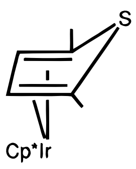
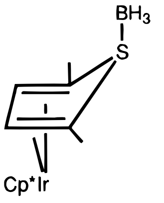


Figure 1. Two views of the molecular structure of $(CO)_3Mn(\eta^4\text{-T}\cdot C_6H_5)$ (**6**).

The η^4-structure of the $T\cdot C_6H_5$ ligand in **6** is very similar to that of η^4 thiophene ligands[16,17] in $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**11**)[19] and $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T\cdot BH_3)$ (**12**).[20]



11



12

Several η^4-thiophene complexes, in which a second metal fragment coordinates to the sulfur,[17] also have the folded envelope structure of **6**, **11**, and **12**. The magnitude of the fold angle between the four-carbon plane and the C−S−C plane in **6** (30.4°) is significantly less than that in **11** (42°) and **12** (39.8°). This also affects the C−S−C angle, which is larger in **6** (86.1(2)°)

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than in **11** (80.8(6)°) and **12** (82.6(5)°). Also, the metal–sulfur distance is shorter in **6** (Mn–S = 2.761(2) Å) than in **11** (2.969(4) Å) and **12** (2.937(3) Å). The shorter Mn–S distance may be due, at least in part, to the smaller metallic radius[21] of Mn (1.27 Å) compared to that of Ir (1.36 Å). Molecular orbital calculations[22] on **11** indicate that there is an antibonding interaction between a sulfur 3p orbital and the iridium, which makes the sulfur an unusually strong Lewis base.[17] The shorter Mn–S distance (2.761(2) Å) in **6** suggests that there is less antibonding character to this interaction than there is in **11** or **12**. However, the Mn–S distance is not as short as a typical Mn–S single bond, as occurs in (η^6-C_6H_6)(CO)$_2$Mn(S-C_6H_5) (2.350(3) Å) and {[(η^6-mesitylene)(CO)$_2$Mn]$_2$(μ-SC_6H_5)}$^+$ (2.358(2), 2.347(2) Å).[23]

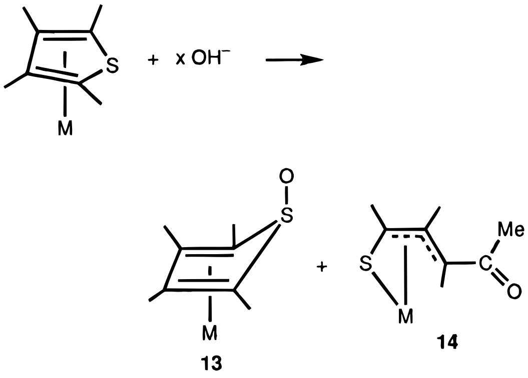
A complex (CO)$_3$Mn(η^4-$C_4(CF_3)_4S$-C_6F_5) having essentially the same structure as **6** was prepared previously by reaction[24,25] of [Mn(CO)$_4$(μ-SC_6F_5)]$_2$ with $CF_3C{\equiv}CCF_3$. All of the following structural parameters are very similar to those in **6**. The Mn–C distances are shorter to C(3) (2.062 Å) and C(4) (2.068 Å) than to C(2) (2.109 Å) and C(5) (2.103 Å). The dihedral angle between the plane of the four-coordinated carbon atoms and the C(2)–S–C(5) plane is 30.8°, while the Mn–S distance is 2.793 Å.

In **6**, three carbons are bonded to the sulfur, which suggests that there is a positive charge on the sulfur as in sulfonium ions (R_3S^+) and that the T-$C_6H_5^+$ ligand behaves as a four-electron donor to the Mn(CO)$_3$ group. This method of counting electrons gives the Mn(CO)$_3$ group a negative charge and the Mn atom an 18-electron count. Although we expected the negatively charged manganese to act as a donor toward Lewis acids, **3** did not react with W(CO)$_5$(THF) in THF at room temperature, nor did it react with Mo(CO)$_3$(NCMe)$_3$ or PhC≡CPh under the same conditions.

The similarity of their IR and ^{1}H NMR spectra suggest that complexes **3**, **5**, and **7** have the same basic structure as **6**. All have two ν(CO) bands at approximately 1990 (vs) and 1900 (vs br) cm^{-1}. In ^{1}H NMR spectra of **5** and **7**, the H(3) and H(4) (see eq 4 for the labeling scheme) protons of the η^4-2,5-Me$_2$T·R ligand occur at δ 4.84 and 4.95, which is considerably upfield of the same protons (δ 7.10) in thiophene. Such upfield shifts are characteristic of protons on thiophene carbons that are coordinated to metals.[17] The chemical shift for H(3) and H(4) in **6** is very similar to that in **11** (δ 4.53)[19] and **12** (δ 4.46).[20] The assignment of the H(3) and H(4) protons in **5** and **7** allows one to assign the δ 5.28 resonance of the η^4-T·R complexes (**3** and **6**) to H(3) and H(4). This leaves the upfield signals at δ 2.40 for **3** and δ 2.72 for **6** to be assigned to the H(2) and H(5) protons. The H(2) and H(5) protons (δ 3.08) are also upfield of H(3) and H(4) (δ 4.89) in Cp*Ir(η^4-T).[20]

The mechanism of R$^-$ group transfer (eq 4) from LiCuR$_2$ to [(CO)$_3$Mn(η^5-Thi)]$^+$ is not known. However, analogous reactions of organolithium (RLi) and Grignard reagents (RMgX) with π-hydrocarbon complexes, e.g., (CO)$_3$Mn(η^6-arene)$^+$, are often described[2] as involving nucleophilic attack by R$^-$ groups. The reactions of LiCuR$_2$ (eq 4) can be described in the same general manner. However, it should be noted that reactions of PhLi and PhMgCl with [(CO)$_3$Mn(η^5-T)]$^+$ in THF at −60 to −10 °C did not give the (CO)$_3$Mn(η^4-T·R) complexes; only decomposition was observed.

As discussed in the Introduction (eq 2), hydride nucleophiles add to the C(2)-position of thiophene in [(CO)$_3$Mn(η^5-T)]$^+$. Nucleophiles [H$^-$ sources, OR$^-$, SR$^-$, and $^-$CH(CO$_2$Me)$_2$] also attack C(2) of thiophene in CpRu(η^5-T)$^+$ to give products in which the C(2)–S bond is cleaved.[6,26] Reactions (eq 5) of Cp*Rh(η^5-Me$_4$T)$^{2+}$



(5)

(where Me$_4$T = tetramethylthiophene) and (η^6-arene)Ru(η^5-Me$_4$T)$^{2+}$ with OH$^-$ yield products resulting from OH$^-$ addition to either C(2) (**14**) or S (**13**). Rauchfuss[27,28] provides convincing evidence that initial attack leading to both types of products occurs at the sulfur. He suggests that sulfur may, in general, be the most electrophilic atom in the η^5-thiophene ligand.

The reactions (eq 4) of LiCuR$_2$ with [(CO)$_3$Mn(η^5-T)]$^+$ are examples of "nucleophilic" R$^-$ addition to the thiophene sulfur. In reactions (eq 2) of H$^-$ sources with [(CO)$_3$Mn(η^5-Thi)]$^+$, H$^-$ adds to C(2) or C(5) only when they do not bear methyl substituents. Thus, one might expect LiCuR$_2$ attack to occur at C(2) or C(5) when they are not methyl-substituted. However, both the η^5-T and η^5-2,5-Me$_2$T complexes (**1** and **2**) give the S-addition products. The lack of C(2)-addition products may be a result of the kinetically inert S–R bond, which prevents migration from S to C(2).

Reactions of [(CO)$_3$Mn(η^5-Thi)]$^+$ (1 and 2) with Other Nucleophiles. Thiolate (RS$^-$) nucleophiles react[6,26] with CpRu(η^5-T)$^+$ to give products resulting from RS$^-$ addition to C(2) and cleavage of the C(2)–S bond. Phenylthiolate adds to an arene carbon of [(CO)$_3$Mn(η^6-arene)]$^+$ to give the (phenylthio)cyclohexadienyl complexes (CO)$_3$Mn(η^5-C_6R_6·SPh).[1,2] Thus, it was expected that RS$^-$ would add to the η^5-Thi ring in [(CO)$_3$Mn(η^5-Thi)]$^+$. Instead, these reactions (eq 6) lead to loss of the thiophene and formation of [Mn(CO)$_4$(μ-SR)]$_2$ in 50–57% yield, based on the amount of starting Mn complex. Despite the reasonably high yields, the reactions must be complicated since each Mn in **1** and **2**

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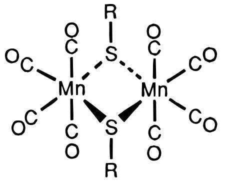
$$(CO)_3Mn(\eta^5\text{-Thi})^+ + {}^-SR \longrightarrow$$

Thi = T (**1**) or 2,5-Me$_2$ (**2**)



(6)

8: R = CH_3
9: R = $C_6H_4CH_3$-*p*

begins with three CO ligands but finishes with four in **8** and **9**. The dimeric products are known and have been prepared by more direct routes.[29] To our knowledge, no X-ray structural studies of $[(CO)_4Mn(\mu\text{-SR})]_2$ complexes have been reported. However, the structure of $[(CO)_4Mn(\mu\text{-SeCF}_3)]_2$ has been published[30] and is similar to that described for **9** herein.

The thermal ellipsoid drawing (Figure 2) of $[(CO)_4Mn(\mu\text{-SC}_6H_4CH_3\text{-}p)]_2$ (**9**) shows that the molecule has a planar Mn_2S_2 core with nearly equal Mn–S bond distances (from 2.381(1) to 2.416(1) Å, Table 5). These distances are slightly longer than those in the terminal thiolate complex $(\eta^6\text{-C}_6H_6)Mn(CO)_2(SPh)$ (2.350(3) Å) and the bridging thiolate $\{[(\eta^6\text{-1,3,5-C}_6Me_3H_3)(CO)_2Mn]_2(\mu\text{-SPh})\}^+$ (2.347(2), 2.358(2) Å).[23] The Mn–S–Mn angles (98.1(1), 97.0(1)°) in the Mn_2S_2 unit are relatively open compared with the S–Mn–S angles (82.4(1), 82.3(1)°). The Mn–CO bond distances (average = 1.868 Å) are distinctly longer for the CO ligands trans to each other than those (average = 1.813 Å) trans to the bridging sulfur ligands. This is consistent with stronger π-backbonding to the CO groups trans to the sulfur. The C–O distances are marginally shorter for the CO groups trans to each other (average = 1.120 Å) than those (1.137 Å) that are trans to the sulfur, which is also in agreement with π-backbonding to the CO ligands. The tolyl groups on the bridging sulfur atoms are anti to each other. Their size increases the S–Mn–CO$_{ax}$ angles to the axial COs that are on the same side of the Mn_2S_2 plane as the tolyl groups. Thus, the S(1)–Mn(1)–C(2) angle (88.1(2)°) is larger than the S(1)–Mn(1)–C(1) angle (84.4(2)°). Each manganese has an octahedral coordination geometry.

Reactions (eq 7) of the $[(CO)_3Mn(\eta^5\text{-Thi})]^+$ complexes with OCH_3^- or $^-CH(CO_2CH_3)_2$ lead to $Mn_2(CO)_{10}$ in 45–52% yield, based on the amounts of reactants **1** and **2**. This is clearly a complicated reaction involving reduction of the manganese and transfer of CO groups among manganese atoms.

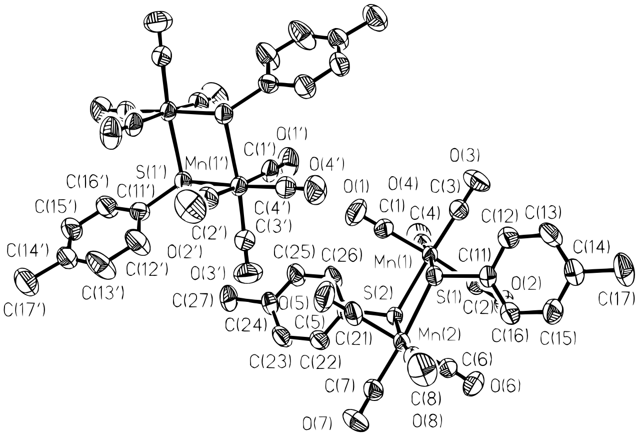


Figure 2. Thermal ellipsoid drawing of $[(CO)_4Mn(\mu\text{-SC}_6H_4CH_3\text{-}p)]_2$ (**9**).

$$\underset{\mathbf{1}\text{ or }\mathbf{2}}{(CO)_3Mn(\eta^5\text{-Thi})^+} + \begin{matrix} OCH_3^- \\ \text{or} \\ {}^-CH(CO_2Me)_2 \end{matrix} \longrightarrow Mn_2(CO)_{10} \qquad (7)$$

In conclusion, reactions of the $[(CO)_3Mn(\eta^5\text{-Thi})]^+$ complexes with nucleophiles give a variety of products. The most notable are those obtained from the organocuprates $LiCuR_2$, which give (eq 4) the $(CO)_3Mn(\eta^4\text{-Thi}{\cdot}R)$ complexes. These studies show that, depending on the nucleophile, $[(CO)_3Mn(\eta^5\text{-Thi})]^+$ may be attacked at the sulfur or C(2) or the thiophene can be displaced to form a range of other products.

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Supporting Information Available: Tables of bond distances and angles, torsion angles, and least-squares planes for **6** and **9** (10 pages). Ordering information is given on any current masthead page.

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