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

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The η^5 -thiophene complexes, $[(CO)_3Mn(\eta^5-T)]^+$ (1) and $[(CO)_3Mn(\eta^5-2,5-Me_2T)]^+$ (2), react with LiCuR₂ (R = Me or Ph) by adding R^- to the sulfur atom of the thiophene, which gives the η^4 -thiophene complexes, (CO)₃Mn(η^4 -T·R) and (CO)₃Mn(η^4 -2,5-Me₂T·R). An X-ray study of $(CO)_3Mn(\eta^4-T\cdot C_6H_5)$ (6) shows the $\eta^4-T\cdot C_6H_5$ 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⁻, CH₃O⁻, or $-CH(CO_2CH_3)_2$ nucleophiles result in the displacement of thiophene with the formation of $[(CO)_4Mn(\mu-SR)]_2$ or $Mn_2(CO)_{10}$. The structure of $[(CO)_4Mn(\mu-SC_6H_4CH_3-p)]_2$ (9), established by X-ray studies, is also reported.

Introduction

Reactions of $[(\eta^6\text{-}arene)Mn(CO)_3]^+$ complexes with nucleophiles lead¹ to cyclohexadienyl products (eq 1).



Oxidations² 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 $[(\eta^{5}-$ 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



reacted similarly. For the analogous 2-methylthiophene complex $[(\eta^5-2-MeT)Mn(CO)_3]^+$, hydride nucleophiles added at the 5-position. When using a 2,5-disubstituted thiophene such as $[(\eta^5-2,5-Me_2T)Mn(CO)_3]^+$, the only product isolated from the reaction with BH₄⁻ was Mn₂-

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 $(CO)_{10}$. 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 $[(\eta^5 -$ Thi)Mn(CO)₃]⁺, where Thi = thiophene (T) or 2,5dimethylthiophene (2,5-Me₂T).

Experimental Section

General Procedures. All reactions were carried out under a dry, oxygen-free N2 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 N₂ atmosphere until used. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl, while hexanes and CH₂Cl₂ were distilled from CaH₂. CH₃NO₂ was deoxygenated in vacuo and dried over 4-Å molecular sieves. The neutral Al₂O₃ (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) nitrogensaturated water, and stored under nitrogen, while the neutral SiO₂ (5 \times 0143U-1, 60–200 mesh) was deoxygenated under high vacuum at room temperature for 12 h. AgBF₄, thiophene, 2,5-dimethylthiophene, CuI, CH₃Li, C₆H₅Li, NaSCH₃, NaOCH₃, CH₂(COOCH₃)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 CDCl₃ solution with CHCl₃ as the internal reference, or in CD₃NO₂ solution with CH₃NO₂ 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 $[(CO)_3Mn(\eta^5-T)]BF_4$ (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 AgBF₄ (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 CH₃NO₂, and the solution was filtered to remove the insoluble graywhite solid. The filtrate was reduced in vacuo to ca. 2 mL, to which was added 90 mL of CH₂Cl₂ to precipitate the product. The yellow product was filtered and washed with CH₂Cl₂ and then dried under vacuum for 1 h to give 0.75 g (67%, based on Mn(CO)₅Br) of yellow powder 1. IR (CH₃NO₂) v(CO): 2077 vs, 2060 m, 2012 m cm⁻¹. ¹H NMR (CD₃NO₂): δ 6.87 (d, 2 H), 6.78 (d, 2 H). MS: m/e 307 (M⁺ - 2 H). Anal. Calcd for C₇H₄O₃BF₄SMn: 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 CH₂Cl₂ (40 mL) was added 1.50 g (7.70 mmol) of AgBF₄. 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-Me₂T. 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 (CH₃NO₂) ν (CO): 2097 m, 2072 vs, 2009 vs cm⁻¹. ¹H NMR (CDCl₃): δ 6.41 (s, 2 H), 2.53 (s, 6 H). MS: m/e 251 (M⁺ – BF₄), 250 (M⁺ – BF₄ – H). Anal. Calcd for C₉H₈O₃BF₄SMn: C, 31.99; H, 2.39. Found: C, 31.82; H, 1.98.

Reaction of 1 with LiCuMe₂ To Give (CO)₃Mn(η^4 -T·CH₃) (3) and [(CO)₄MnI]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 LiCH₃ with stirring. The reaction solution was stirred at 0 °C for 10 min. The resulting LiCuMe₂⁷ solution was added to a solution of $[(CO)_3Mn(\eta^5-T)]$ -BF₄ (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 SiO₂ (neutral) with hexanes/CH₂Cl₂ (15:1) as the eluant. The light yellow band that eluted first was collected, and then the red band was eluted with CH₂Cl₂/Et₂O (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 (CH₂Cl₂) ν (CO): 1995 vs, 1904 vs br cm⁻¹. ¹H NMR (CDCl₃): 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⁺ - CH₃ - 2CO), 139 (M⁺ - CH₃ - 3CO). Anal. Calcd for C₈H₇O₃SMn: 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 48 was obtained (mp 165 °C (dec)). IR (CH₂Cl₂) v(CO): 2088 s, 2034 vs, 2006 s, 1973 s cm⁻¹. MS: *m*/*e* 558 (M⁺). Anal. Calcd for C₈O₈I₂Mn₂: C, 16.35. Found: C. 16.61.

Reaction of 2 with LiCuMe₂ To Give (CO)₃Mn(\eta^{4}-2,5-Me₂T·CH₃) (5) and 4. As described for the reaction of 1 with LiCuMe₂, 0.300 g (0.888 mmol) of 2 in THF (40 mL) at -60 °C was treated with fresh LiCuMe₂ [prepared by the reaction of CuI (0.169 g, 0.887 mmol) with LiCH₃ (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 LiCuMe₂ 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 (CH₂-Cl₂) ν (CO): 1987 vs, 1896 vs br cm⁻¹. ¹H NMR (CDCl₃): 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 C₁₀H₁₁O₃SMn: 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 LiCuPh₂ To Give (CO)₃Mn(η^4 -T·C₆H₅) (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) LiC₆H₅ 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 LiCuPh₂⁷ 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 SiO₂ (neutral) with hexanes/CH₂Cl₂ (3:1) as the eluant. The yellow band that eluted first was collected, and then the red band was eluted with CH₂Cl₂/Et₂O (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 (CH₂-Cl₂) ν (CO): 1996 vs, 1907 vs br cm⁻¹. ¹H NMR (CDCl₃): 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 C₁₃H₉O₃SMn: 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 LiCuPh₂ To Give (CO)₃Mn(η^4 -2,5-Me₂T·C₆H₅) (7) and 4. This reaction was conducted as described earlier for the reaction of **1** with LiCuPh₂. A solution of LiCuPh₂ prepared by the reaction of CuI (0.169 g, 0.887 mmol) with LiC₆H₅ (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 $^{\circ}\text{C},$ the solution was evaporated to dryness under vacuum. Further treatment of the residue as described for the reaction of 1 with LiCuPh₂ 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 (CH₂Cl₂) ν(CO): 1989 vs, 1899 vs br cm⁻¹. ¹H NMR (CDCl₃): 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 NaSCH₃ To Give [(CO)₄Mn(SCH₃)]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 NaSCH₃. 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 Al₂O₃ (neutral) with hexanes/CH₂Cl₂ (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/CH₂Cl₂ 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 (CH₂Cl₂) ν (CO): 2072 s, 2019 vs, 2000 w, 1960 s cm⁻¹. ¹H NMR (CDCl₃): δ 1.99 (s, 6 H). MS: m/e 428 (M⁺). Anal. Calcd for C₁₀H₆O₈S₂Mn₂: C, 28.05; H, 1.41. Found: C, 28.19; H, 1.67.

Reaction of 2 with NaSCH₃ To Give 8. Following the procedure described for the reaction of **1** with NaSCH₃, the reaction of **2** (0.300 g, 0.888 mmol) with NaSCH₃ (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 ¹H NMR spectra.

Reaction of 1 with NaSC₆H₄CH₃-*p* **To Give [(CO)₄Mn-(SC₆H₄CH₃-***p***]₂ (9). To a solution of 1 (0.300 g, 0.968 mmol)**

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⁽⁹⁾ Treichel, P. M.; Morris, J. H.; Stone, F. G. A. J. Chem. Soc. 1963, 720.

dissolved in THF (30 mL) at 0 °C was added 0.146 g (0.999 mmol) of NaSC₆H₄CH₃-*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 Al₂O₃ (neutral) with hexanes/CH₂Cl₂ (10: 1) as the eluant. The yellow band was collected. After vacuum removal of the solvent, the residue was recrystallized from hexanes/CH₂Cl₂ 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 (CDCl₃): δ 7.81–7.11 (m, 8 H), 2.31 (s, 6 H). MS: *m/e* 580 (M⁺). Anal. Calcd for C₂₂H₁₄O₈S₂Mn₂: C, 45.53; H, 2.43. Found: C, 45.57; H, 2.46.

Reaction of 2 with NaSC₆H₄CH₃-*p* **To Give 9.** The reaction of **2** (0.135 g, 0.399 mmol) with NaSC₆H₄CH₃-*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 NaSC₆H₄CH₃-*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 NaOCH₃ To Give Mn₂(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 NaOCH₃. 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 Al₂O₃ (neutral) with hexanes/CH₂Cl₂ (15:1) as the eluant. A yellow band eluted. The solvent was removed from it, and the yellow residue was recrystallized from hexanes/CH₂Cl₂ at -80 °C to give 0.085 g (45%, based on 1) of yellow crystalline 10, which was identified as Mn₂(CO)₁₀ by comparison of its melting point and IR spectrum with that of an authentic sample of Mn₂(CO)₁₀ [mp 150–152 °C (dec); IR (CH₂Cl₂) ν (CO) 2046 s, 2011vs br, 1979 s cm⁻¹].

Reaction of 2 with NaOCH₃ To Give 10. As described for the reaction of **1** with NaOCH₃, 0.300 g (0.888 mmol) of **2** was treated with NaOCH₃ (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(CO₂CH₃)₂ To Give 10. To a suspension of NaH (0.040 g, 1.67 mmol) [60% dispersion in mineral oil, washed with hexanes (5 \times 10 mL) before use] in THF (15 mL) at room temperature was added dropwise 0.20 g (1.5 mmol) of dimethyl malonate (CH₂(CO₂CH₃)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(CO₂CH₃)₂¹⁰ 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 Al₂O₃ (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/CH₂Cl₂ at -80 °C to give 0.115 g (46%, based on 1) of 10.

Reaction of 2 with NaCH(CO₂CH₃)₂ To Give 10. 2 (0.350 g, 1.04 mmol) was reacted with NaCH(CO₂CH₃)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(CO₂CH₃)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-(η^4 -T·C₆H₅) (6) and [(CO)₄Mn(SC₆H₄CH₃-*p*)]₂ (9). A lightyellow needle crystal of 6 was attached to the tip of a glass fiber and mounted on a Siemens P4RA diffractometer with monochromated CuK α radiation. High-angle cell constants

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

| | 6 | 9 |
|---|---|---------------------------------------|
| formula | C ₁₃ H ₉ MnO ₃ S | C33H21Mn3O12S3 |
| fw | 300.2 | 870.5 |
| cryst system | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/c$ |
| \dot{a} (Å) | 9.397(4) | 10.240(2) |
| $b(\dot{A})$ | 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) | $0.38 \times 0.18 \times 0.13$ | $0.45 \times 0.12 \times 0.08$ |
| μ , (mm ⁻¹) | 10.109 | 1.270 |
| diffractometer used | Siemens P4RA | Enraf-Nonius CAD4 |
| radiation | Cu K _α | Μο Κα |
| | $(\lambda = 1.541 \ 78\text{\AA})$ | $(\lambda = 0.710 \ 73 \ \text{\AA})$ |
| temp (K) | 213 | 298 |
| scan method | $2	heta{-}	heta$ | $\omega - 2\theta$ |
| data collection range, 2θ (deg) | 4.0-115.0 | 4.0-50.0° |
| no. of data collected | 3607 | 8975 |
| no. of unique data | 1683 ($R_{\rm int} = 0.0216$) | $6329 \ (R_{\rm int} = 0.0267)$ |
| no. of data with $E > 4.0 \sigma(E)$ | 1429 | 4115 |
| no. of parameters refined | 185 | 475 |
| transmission | 0.53/0.83 | 0.55/0.85 |
| factors: min/max | | |
| R^{a} | 0.0328 | 0.0404 |
| $R_{\rm w}{}^b$ | 0.0400 | 0.0493 |
| goodness-of-fit ^c | 1.45 | 1.02 |
| largest peak (e/Å ³) | 0.29 | 0.46 |
| largest shift/eds. | 0.0 | 0.0 |
| final cycle | | |

 ${}^{a}R = \sum ||F_{0}| - |F_{c}||/\sum |F_{0}|. {}^{b}R_{w} = |\sum w(|F_{0}| - |F_{c}|)^{2}/\sum w|F_{0}|^{2}|^{1/2}; w = 1/\sigma^{2}(|F_{0}|). {}^{c}\text{Quality-of-fit} = [\sum w(|F_{0}| - |F_{c}|)^{2}/(N_{obs} - N_{parameters})]^{1/2}.$

were determined from a subset of intense reflections in the range of 35.0–50.0° for 2 θ . The data collection was conducted under a cryogenic stream of N₂ at 213 °C. An orange crystal of **9** was mounted on an Enraf-Nonius CAD4 diffractometer with monochromated Mo K α radiation at 298 °C. Pertinent data collection and reduction information are given in Table 1.

Lorentz and polarization corrections were applied for ${\bf 6}$ and ${\bf 9}$. 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 $[(CO)_3Mn(\eta^5-T)]^+$ (1) and $[(CO)_3Mn(\eta^5-2,5-Me_2T)]^+$ (2). The first reported synthesis¹² of $[(CO)_3Mn(\eta^5-T)]^+$ involved the reaction of $Mn(CO)_5Cl$

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Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for (CO)₃Mn(n^{4} -T·C₆H₅) (6)

| | - / - | (==)0 (1 | = 0 0/ (=/ | |
|-------|---------|----------|------------|----------------|
| atom | х | у | 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 Bon | d |
|----------|-------------------------------|---|---|
| Angle | es (deg) ^a for (C(| $O_{3}Mn(\eta^{4}-T\cdot C_{6}H_{5})$ (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.

with thiophene (T) in the presence of AlBr₃; 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 $[(CO)_3Mn(\eta^5-T)]^+$ and $[(CO)_3Mn(\eta^5-2,5-Me_2T)]^+$. It

$$Mn(CO)_{5}Br \xrightarrow{AgBF_{4}} \{Mn(CO)_{5}BF_{4}\} \xrightarrow{Thi} -2CO$$

$$(CO)_{3}Mn(\eta^{5}-Thi)^{+}BF_{4}^{-} \qquad (3)$$

$$1: Thi = T$$

$$2: Thi = 2,5-Me_{2}T$$

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-Me₂T) to give the

Table 4. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for [(CO)₄Mn(SC₆H₄CH₃-p)]₂ (9)

| atom | X | у | 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.

desired $[(CO)_3Mn(\eta^5-T)]^+$ products in good (67–71%) yield. This route is similar to that reported¹³ for the synthesis of $(CO)_3Mn(\eta^6\text{-arene})^+$ complexes.

Reactions of $[(CO)_3Mn(\eta^5-Thi)]^+$ (1 and 2) with **LiCuR₂**. Complexes 1 and 2 react (eq 4) with organocuprates to give the (CO)₃Mn(η^4 -T·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 known⁸ [Mn(CO)₄(μ -I)]₂, which presumably forms from reaction with I⁻ that is

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| Table 5. | Bond Leng | (ths (Å) ^a | and Sele | cted | Bond |
|----------|------------------------|-----------------------|-----------------------------------|--------------------------------|------|
| Angles | (deg) ^a for | (CO) ₄ Mn | (SC ₆ H ₄ C | H ₃)] ₂ | (9) |

| 0 0 | | | | | |
|----------------------|----------|----------------------|----------|--|--|
| 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) | 1724(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 LiCuR₂ + LiI.



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(sp²)-S single-bond distance



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

(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 longshort-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 $(1.714(1) \text{ Å})^{16,17}$ 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- $(\eta^{5}-2,5-\text{Me}_{2}\text{T})^{18}$ is staggered with respect to the CO ligands.

The η^4 -structure of the T·C₆H₅ ligand in **6** is very similar to that of η^4 thiophene ligands^{16,17} in Cp*Ir(η^4 -2,5-Me₂T) (**11**)¹⁹ and Cp*Ir(η^4 -2,5-Me₂T·BH₃) (**12**).²⁰



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 radius²¹ of Mn (1.27 Å) compared to that of Ir (1.36 Å). Molecular orbital calculations²² 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 -C₆H₆)(CO)₂Mn(S-C₆H₅) (2.350(3) Å) and {[(η^6 mesitylene)(CO)₂Mn]₂(μ -SC₆H₅)}⁺ (2.358(2), 2.347(2) Å).²³

A complex $(CO)_3Mn(\eta^4-C_4(CF_3)_4S-C_6F_5)$ having essentially the same structure as **6** was prepared previously by reaction^{24,25} of $[Mn(CO)_4(\mu-SC_6F_5)]_2$ 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 ¹H NMR spectra suggest that complexes 3, 5, and 7 have the same basic structure as 6. All have two $\nu(CO)$ bands at approximately 1990 (vs) and 1900 (vs br) cm⁻¹. In ¹H 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-Me₂T·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 LiCuR₂ to [(CO)₃Mn(η^5 -Thi)]⁺ is not known. However,

analogous reactions of organolithium (RLi) and Grignard reagents (RMgX) with π -hydrocarbon complexes, e.g., (CO)₃Mn(η^6 -arene)⁺, are often described² as involving nucleophilic attack by R⁻ groups. The reactions of LiCuR₂ (eq 4) can be described in the same general manner. However, it should be noted that reactions of PhLi and PhMgCl with [(CO)₃Mn(η^5 -T)]⁺ in THF at -60 to -10 °C did not give the (CO)₃Mn(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 $[(CO)_3Mn(\eta^5-T)]^+$. Nucleophiles $[H^-$ sources, OR^- , SR^- , and $^-CH(CO_2Me)_2]$ also attack C(2) of thiophene in $CpRu(\eta^5-T)^+$ to give products in which the C(2)–S bond is cleaved.^{6,26} Reactions (eq 5) of $Cp^*Rh(\eta^5-Me_4T)^{2+}$



(where Me_4T = tetramethylthiophene) and (η^6 -arene)-Ru(η^5 -Me₄T)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 LiCuR₂ with $[(CO)_3Mn(\eta^5-T)]^+$ are examples of "nucleophilic" R⁻ addition to the thiophene sulfur. In reactions (eq 2) of H⁻ sources with $[(CO)_3Mn(\eta^5-Thi)]^+$, H⁻ adds to C(2) or C(5) only when they do not bear methyl substituents. Thus, one might expect LiCuR₂ 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-Me₂T 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)₃Mn(\eta^{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)₃Mn(η^{6} -arene)]⁺ to give the (phenylthio)cyclohexadienyl complexes (CO)₃Mn(η^{5} -C₆R₆·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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Thi = T (1) or $2,5-Me_2(2)$



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 $[(CO)_4Mn(\mu-SR)]_2$ complexes have been reported. However, the structure of $[(CO)_4Mn(\mu-SeCF_3)]_2$ has been published³⁰ and is similar to that described for **9** herein.

The thermal ellipsoid drawing (Figure 2) of [(CO)₄Mn- $(\mu$ -SC₆H₄CH₃-p)]₂ (9) shows that the molecule has a planar Mn₂S₂ 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 (η^6 -C₆H₆)Mn(CO)₂(SPh) (2.350(3) Å) and the bridging thiolate $\{[(\eta^6-1,3,5-C_6Me_3H_3)(CO)_2 Mn_{2}(\mu-SPh)^{+}(2.347(2), 2.358(2) \text{ Å})^{23}$ The Mn-S-Mn angles (98.1(1), 97.0(1)°) in the Mn₂S₂ 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 $(88.1(2)^\circ)$ is larger than the S(1)-Mn(1)-C(1)angle $(84.4(2)^{\circ})$. Each manganese has an octahedral coordination geometry.

Reactions (eq 7) of the $[(CO)_3Mn(\eta^5-Thi)]^+$ complexes with OCH₃⁻ or $^-$ CH(CO₂CH₃)₂ lead to Mn₂(CO)₁₀ in 45–



Figure 2. Thermal ellipsoid drawing of $[(CO)_4Mn(\mu$ -SC₆H₄- CH₃-*p*)]₂ (9).

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.



In conclusion, reactions of the $[(CO)_3Mn(\eta^5-Thi)]^+$ complexes with nucleophiles give a variety of products. The most notable are those obtained from the organocuprates LiCuR₂, which give (eq 4) the $(CO)_3Mn(\eta^4-$ Thi·R) complexes. These studies show that, depending on the nucleophile, $[(CO)_3Mn(\eta^5-Thi)]^+$ 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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