Manganese Thiophene Tricarbonyl Complexes: Nucleophilic Addition to Sulfur and Synthesis of Thiophenium Salts

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New thiophene manganese derivatives, $[(2\text{-}R^1\text{-}C_4H_3S)Mn(CO)_3]^+$ **1**(sil) (R^1 = $Si(OCH_2CH_2)_3N$) and **1**(Mn) (R^1 = $(C_6H_6)Mn(CO)_3$), have been synthesized and their reaction with nucleophiles studied. Except for the Grignard reagent, nucleophiles (Nu^- = H^-, ^-CN, $^-P(O)(OR)_2$ (R = Me, Ph)) usually attack the C5 position. Grignard reagents attack the sulfur atom to yield manganese *S*-R-thiophene carbonyls **3**. To compare the reactivities of **1**(sil) and **1**(Mn) with that of $(thiophene)Mn(CO)_3^+$ with respect to Grignard reagent addition, the known compounds $[(thiophene)Mn(CO)_3]^+$ (thiophene = thiophene, 2-methylthiophene, 2,5-dimethylthiophene) have been synthesized and their reaction with Grignard reagents studied. In all cases, *S*-R-thiophene manganese carbonyls **3** were obtained as a sole product. Refluxing **3** (R = Ph, *p*-tolyl, 2-thienyl) with Me_3NO in benzene yielded diaryl sulfide. Treatment of **3** with $NOBF_4$ in CH_2Cl_2 led to S-R-thiophenium−manganese dicarbonyl nitrosyl cations **4**. Photolysis of **4** in acetone gave rise to *S*-R-thiophenium **5** in high yields. The molecular structures of $[\{2\text{-}exo\text{-}P(O)(OMe)_2\text{-}\eta^4\text{-}C_4H_3S\}Mn(CO)_3]$ (**2**(sil,P(O)(OMe)$_2$)), $[S\text{-}Ph\text{-}\eta^4\text{-}2\text{-}\{(\eta^5\text{-}C_6H_6)Mn(CO)_3\}SC_4H_3]Mn(CO)_3$ (**3**(Mn,Ph)), and $[p\text{-}CH_3C_6H_5\text{-}S\text{-}2\text{-}CH_3C_4H_3]$ (**5**(Me,*p*-tolyl)) have been determined by X-ray studies.

Introduction

Synthetic applications of $(arene)Mn(CO)_3^+$ complexes has evolved rapidly over the last two decades.[2] By comparison, heterocyclic analogues have received little attention.[3] Because of the possible relevance to thiophene hydrodesulfurization (HDS), $(thiophene)Mn(CO)_3^+$ was prepared and shown to be activated toward the addition of nucleophiles H^-, CN^-, and PBu^n_3 to the 2-position of the thiophene ring.[4] With the cuprate R_2CuLi as the nucleophile, however, addition occurs at the sulfur.[5] While investigating reactions with Grignard reagents, we independently observed addition at the sulfur to afford $(\eta^4\text{-thiophene})Mn(CO)_3$ complexes. In order to more thoroughly investigate the regioselectivity of nucleophilic addition to manganese thiophene complexes, we report herein the electrophilic behavior of the manganese 2-substituted thiophene derivatives, $[(\eta^5\text{-}2\text{-}N(CH_2CH_2O)_3Si\text{-}SC_4H_3)Mn(CO)_3]ClO_4$ (**1**(sil)), and $[2\text{-}\eta^5\text{-}(C_6H_6)Mn(CO)_3\text{-}SC_4H_3\}Mn(CO)_3]BF_4$ (**1**(Mn)). According to our previous studies,[6] the silatranyl moiety generally directs nucleophiles to a certain position in the $(silatranylarene)Mn(CO)_3^+$ cation; while the directing effect of a cyclohexadienylmanganese tricarbonyl moiety is unknown.

Herein, we compare the reactivities of **1**(sil) and **1**(Mn) with that of $(thiophene)Mn(CO)_3^+$ with respect to Grignard reagent addition. The X-ray structures of $[\{2\text{-}exo\text{-}P(O)(OMe)_2\text{-}\eta^4\text{-}C_4H_3S\}Mn(CO)_3]$, $[S\text{-}Ph\text{-}\eta^4\text{-}2\text{-}\{(\eta^5\text{-}C_6H_6)\text{-}Mn(CO)_3\}\text{-}SC_4H_3]Mn(CO)_3$, and $[p\text{-}CH_3C_6H_5\text{-}S\text{-}2\text{-}CH_3C_4H_3]$ are presented and discussed.

Experimental Section

General Information. All solvents were purified by standard methods, and all synthetic procedures were done

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(1) (a) X-ray analysis for **2**(sil,P(O)(OMe)$_2$). (b) X-ray analysis for **3**(Mn,Ph).

(2) (a) Sweigart, D. A.; Honig, E.; Kane-Maguire, L. A. P. *Chem. Rev.* **1984**, *84*, 525. (b) Pike, R. D.; Sweigart, D. A. *Synlett* **1990**, 565. (c) Sun, S.; Dullaghan, C. A.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1996**, 4493.

(3) (a) Ryan, WW. J.; Peterson, P. E.; Cao, Y.; Williard, P. G.; Sweigart, D. A.; Baer, C. D.; Thompson, C. F.; Chung, Y. K. Chung, T.-M. *Inorg. Chim. Acta* **1993**, *211*, 1. (b) Lee, S. S.; Chung, Y. K.; Lee, S. W. *Inorg. Chim. Acta* **1996**, *253*, 39.

(4) (a) Lesch, D. A.; Richardson, J. W., Jr.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901. (b) Huckett, S. C.; Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591.

(5) Chen, J.; Young, V. G., Jr.; Angelici, R. J. *Organometallics* **1996**, *15*, 325.

(6) (a) Lee, Y.-A; Chung, Y. K.; Jeong, J. H. *Organometallics* **1990**, *9*, 2851. (b) Lee, Y.-A; Chung, Y. K.; Kim, Y.; Lee, D.; Chung, G.; Jeong, J. H. *Organometallics* **1991**, *10*, 3707. (c) Oh, A.-S.; Chung, Y. K.; Kim, S. S. *Organometallics* **1992**, *11*, 1394. (d) Lee, J. S.; Lee, S. S.; Chung, Y. K. *Organometallics* **1993**, *12*, 4640. (e) Lee, S. S.; Jeong, E.; Chung, Y. K. *J. Organomet. Chem.* **1994**, *483*, 115. (f) Lee, S. S.; Lee, I.; Chung, Y. K. *Organometallics* **1996**, *15*, 5428.

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under a nitrogen atmosphere. Reagent grade chemicals were used without further purification. Compounds $[(SC_4H_4)Mn(CO)_3]^+$, $[(2\text{-Me-}SC_4H_3)Mn(CO)_3]^+$, $[(2,5\text{-Me}_2\text{-}SC_4H_2)Mn(CO)_3]^+$, and 2-trimethylsilylthiophene were prepared according to the published procedure.[4b,7]

Elemental analyses were done at the Chemical Analytic Center, College of Engineering, Seoul National University or the Chemical Analytic Center, KIST. ^{1}H NMR spectra were obtained with a Varian XL-200 or a Bruker AMX-500 instrument. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer (spectra measured as films on NaCl by evaporation of solvent). Mass spectra were recorded on a VG ZAB-E double-focusing mass spectrometer.

Synthesis of 2-Silatranylthiophene. Thiophene (4.0 mL, 50 mmol) was dissolved in 30 mL of THF and cooled to 0 °C. *n*-BuLi (20 mL, 2.5 M solution in hexanes) was added to the thiophene in THF solution 0 °C. The 2-thienyllithium solution was added very slowly (8 h) to the $SiCl_4$ (50 mL) in 200 mL of Et_2O at −78 °C. The resulting solution was allowed to warm to room temperature and stirred for overnight. The unreacted $SiCl_4$ and solvent were removed by using high vacuum. The trapped $SiCl_4$ was quenched with MeOH. The obtained crude 2-(trichlorosilyl)thiophene was used for further reaction. Ethanol (20 mL) was added slowly to the crude 2-(trichlorosilyl)-thiophene at 0 °C. After adding 20 mL of EtOH, 80 mL of EtOH was added in one portion. The resulting solution was stirred for overnight and heated 2 h at 40 °C. After removal of solvent, crude 2-(triethoxysilyl)thiophene was obtained. The crude 2-(triethoxysilyl)thiophene, $N(CH_2CH_2OH)_3$ (35 mmol), and KOH (two tiny crystals) were put in 200 mL of benzene and refluxed for 4 h. After removal of solvent, the residue was washed two to three times with MeOH and recrystalized in CH_2Cl_2/hexane. White crystalline solids (4.63 g) were obtained as a product. The overall yield from thiophene was 36%: ^{1}H NMR (acetone-d_6) δ 7.32 (m, 1 H), 7.16 (m, 1 H), 6.95 (m, 1 H), 3.78 (t, 5.86 Hz, 6 H), 3.00 (t, 5.86 Hz, 6 H) ppm Anal. Calcd for $C_{10}H_{15}NO_3SSi$: C, 46.07; H, 5.87; N, 5.44. Found: C, 46.19; H, 5.74; N, 5.56.

Synthesis of [(2-Silatranylthiophene)Mn(CO)$_3$][BF$_4$] 1(sil). 2-Silatranylthiophene (0.83 g, 3.2 mmol) was added to the solution of $Mn(CO)_5ClO_4$ (1.00 g, 3.6 mmol) in 150 mL of CH_2Cl_2. The reaction mixture was heated at reflux for 20 h under N_2. After filtration, the filtrate was concentrated and precipitated with excess diethyl ether. The yield was 1.22 g (76%): mp 164 °C; IR (NaCl) ν (CO) 2000, 1915 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.04 (d, 3.0 Hz, 1H, H^5), 6.75 (t, 3.0 Hz, 1 H, H^4), 6.48 (d, 2.8 Hz, 1 H, H^3), 3.91 (t, 5.9 Hz, 6 H, OCH_2), 3.22 (t, 5.9 Hz, 6 H, NCH_2) ppm. Anal. Calcd for $C_{13}H_{15}ClMnNO_{10}SSi$: C, 31.49; H, 3.05; N, 2.83. Found: C, 31.6; H, 3.12; N, 3.12.

Synthesis of [{2-((η^5-C$_6$H$_6$)Mn(CO)$_3$)-thiophene}Mn(CO)$_3$][BF$_4$] (1(Mn)). To $[(C_6H_6)Mn(CO)_3]PF_6$ (0.30 g, 0.83 mmol) suspended in 30 mL of THF, 2-thienylmagnesium bromide (1.5 equiv, generated in situ by the reaction of 2-bromothiophene with magnesium turnings at 0 °C in Et_2O) was added dropwise at 0 °C. After stirring for 30 min, 30 mL of diethyl ether was added and the reaction mixture was quenched with 50 mL of aqueous NH_4Cl. The organic layer was collected and chromatographed on a silica gel column with hexane eluant. The product, (2-thienylcyclohexadienyl)Mn(CO)$_3$, was obtained in 94% yield as needle-shaped yellow crystals: IR (NaCl) ν (CO) 2004, 1906 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.05 (d, 5.2 Hz, 1 H), 6.83 (dd, 3.6, 5.0 Hz, 1 H), 6.57 (d, 3.4 Hz, 1 H), 5.82 (t, 5.4 Hz, 1 H), 4.95 (t, 6.2 Hz, 2 H), 3.99 (t, 6.0 Hz, 1 H), 3.48 (t, 6.2 Hz, 2 H) ppm. Anal. Calcd for $C_{13}H_9MnO_3S$: C, 52.03; H, 3.02; S, 1.07. Found: C, 52.25; H, 2.99; S, 1.00.

Coordination of $Mn(CO)_3^+$ to the thiophene substituent was effected by adding $Mn(CO)_5BF_4$ (2.0 mmol) to the cyclohexadienyl precursor (2-thienylcyclohexadienyl)Mn(CO)$_3$ (0.50 g, 1.67 mmol) in 20 mL of CH_2Cl_2. The reaction flask was wrapped with aluminum foil, and the reaction mixture refluxed for 20 h. After filtration through the Celite pad, the filtrate was concentrated and the product was precipitated by adding excess diethyl ether. The product **1**(Mn) was purified by recrystallization from acetone/diethyl ether: yield 87%; IR (acetone) ν (CO) 2070, 2016, 1998, 1935 cm^{-1}; ^{1}H NMR (acetone-d_6) major isomer, δ 7.04 (d, 3.4 Hz, 1 H, H^5), 6.86 (d, 2.9 Hz, 1 H, H^3), 6.64 (br t, 1 H, H^4), 6.24 (t, 5.4 Hz, 1 H, H$^{3'}$), 5.44 (t, 6.3 Hz, 2 H, H$^{2'}$ and H$^{4'}$), 4.24 (t, 6.1 Hz, 1 H, H$^{6'}$), 3.63 (br t, 2 H, H$^{1'}$ and H$^{5'}$), 2.68 (s, 3 H, CH_3) ppm; minor isomer, δ 7.19 (d, 4.9 Hz, 1 H, H^5), 6.83 (d, 2.9 Hz, 1 H, H^3), 6.64 (br, 1 H, H^4), 6.06 (t, 5.8 Hz, 1 H, H$^{3'}$), 5.19 (t, 6.3 Hz, 2 H, H$^{2'}$ and H$^{4'}$), 4.05 (t, 6.1 Hz, 1 H, H$^{6'}$), 3.63 (br t, 2 H, H$^{1'}$ and H$^{5'}$), 2.68 (s, 3 H, CH_3) ppm. Anal. Calcd for $C_{16}H_9BF_4Mn_2O_6S$: C, 36.54; H, 1.72. Found: C, 36.18; H, 1.61.

Reaction of 1(sil) with NaCN. To a stirred suspension of **1**(sil) (0.99 g, 0.2 mmol) and NaCN (0.05 g, 1 mmol) in 10 mL of THF at 0 °C was added 0.5 mL of water. After stirring for 30 min, the solution was concentrated and the neutral product extracted with diethyl ether (50 mL × 2). The ether extracts were dried over $MgSO_4$ and evaporated to give a yellow solid (59%). Mp 198 °C dec; IR (NaCl) ν (CO) 2000, 1930, 1885 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.77 (d, 3.7 Hz, 1 H, H^3), 4.16 (d, 2.2 Hz, 1 H, H^5), 3.91 (t, 5.8 Hz, 6 H, OCH_2), 3.22 (dd, 2.2, 3.7 Hz, 1 H, H^4), 2.99 (t, 5.8 Hz, 6 H, NCH_2) ppm. Anal. Calcd for $C_{14}H_{15}MnN_2O_6SSi$: C, 39.81; H, 3.58; N, 6.64. Found: C, 39.80; H, 3.66; N, 6.33.

Reaction of 1(sil) with NaBH$_4$. To a stirred suspension of **1**(sil) (0.99 g, 0.2 mmol) in 10 mL of THF at 0 °C was added a slight excess $NaBH_4$. After stirring for 30 min, the reaction mixture was poured into water and the product was extracted with diethyl ether (50 mL × 2). The ether extracts were dried over $MgSO_4$ and evaporated to give a yellow solid (62%): mp 210 °C; IR (NaCl) ν (CO) 1990, 1870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.68 (d, 3.7 Hz, 1 H, H^3), 3.92 (t, 5.9 Hz, 6 H, OCH_2), 3.51 (dd, 2.0, 9.3 Hz, 1 H, H^{5-endo}), 3.15 (m, 1 H, H^4), 3.11 (d, 9.3 Hz, 1 H, H^{5-exo}), 2.98 (t, 5.9 Hz, 6 H, NCH_2) ppm. Anal. Calcd for $C_{13}H_{16}MnNO_6SSi$: C, 39.30; H, 4.06; N, 3.53. Found: C, 39.21; H, 4.00; N, 3.32.

Reaction of 1(sil) with NaP(O)(OMe)$_2$. Complex **1**(sil) (0.99 g, 0.2 mmol) was stirred in 15 mL of THF at 0 °C under N_2 while $NaP(O)(OMe)_2$ (1 mmol in 5 mL of THF) was added dropwise. After stirring for 30 min, the reaction mixture was poured into water and the product extracted with diethyl ether. The ether extracts were dried over $MgSO_4$ and evaporated to give a yellow solid (48%): mp 154 °C; IR (NaCl) ν (CO) 2000, 1915, 1895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.70 (1 H, H^3), 3.98(1 H, H^5), 3.90 (t, 5.9 Hz, 6 H, OCH_2), 3.77 (d, 10.5 Hz, 6 H, P(OMe)$_2$), 3.25 (1 H, H^4), 2.98 (t, 5.9 Hz, 6 H, NCH_2) ppm. Anal. Calcd for $C_{15}H_{21}MnNO_9PSSi$: C, 35.65; H, 4.19; N, 2.77. Found: C, 35.07; H, 4.51; N, 2.67.

Reaction of 1(sil) with NaP(O)(OPh)$_2$. The same procedure as with $NaP(O)(OMe)_2$ was followed: yield 30%; mp 174 °C; IR (NaCl) ν (CO) 1997, 1895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.1−7.3 (m, 10 H, Ph), 5.79 (1 H, H^3), 4.24 (1 H, H^5), 3.87 (6 H, OCH_2), 3.35 (1 H, H^4), 2.96 (6 H, NCH_2) ppm. Anal. Calcd for $C_{25}H_{25}MnNO_9PSSi$: C, 47.70; H, 4.00; N, 2.22. Found: C, 47.62; H, 4.00; N, 2.16.

Reaction of 1(sil) with RMgBr (R = Me, Et, and **Ph) (Synthesis of 3(sil,R)).** To a solution containing **1**(sil) (0.20 g, 0.4 mmol) in 10 mL of CH_2Cl_2 was added 2 equiv of RMgBr in THF at 0 °C under N_2. After stirring for 30 min, the reaction mixture was allowed to warm to room temperature. To the resulting solution, diethyl ether (50 mL) and water (30 mL) were added. The organic layer was collected, dried over $MgSO_4$, and evaporated. The remnant was redissolved in diethyl ether and precipitated by adding excess hexane. The precipitate was washed with hexane (3 × 20 mL) and dried.

Reaction with MeMgBr 3(sil,Me): yield 48%; IR (NaCl) ν (CO) 1980, 1890 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 5.36 (dd, 1.1, 2.8

(7) (a) Desobry, V.; Kündig, E. P. *Helv. Chim. Acta* **1981**, 1288. (b) Loft, M. S.; Widdowson, D. A.; Mowlem, T. J. *Synlett* **1992**, 135.

Hz, 1 H, H^5), 5.26 (vt, 2.68 Hz, H^4), 3.77 (t, 5.86 Hz, 6 H, OCH_2), 2.84 (t, 5.86 Hz, 6 H, NCH_2), 2.29 (dd, 1.1, 2.56 Hz, H^3), 1.77 (s, CH_3) ppm. Anal. Calcd for $C_{14}H_{18}MnNO_6SSi$: C, 40.91; H, 4.41; N, 3.41. Found: C, 40.77; H, 4.45; N, 3.38.

Reaction with EtMgBr, 3(sil,Et): yield 62%; IR (NaCl) ν(CO) 1974, 1884, 1868 cm^{-1}; ^1H NMR (CD_2Cl_2): δ 5.36 (dd, 1.1, 2.8 Hz, 1 H, H^5), 5.22 (t, 2.68 Hz, 1 H, H^4), 3.76 (t, 5.86 Hz, 6 H, OCH_2), 2.83 (t, 5.86 Hz, 6 H, NCH_2), 2.30 (dd, 1.1, 2.56 Hz, 1 H, H^3), 2.01 (m, 2 H, CH_2), 0.90 (dd, 7.57, 7.81 Hz, 3 H, CH_2CH_3) ppm. Anal. Calcd for $C_{15}H_{20}MnNO_6SSi$: C, 42.35; H, 4.74; N, 3.29. Found: C, 42.5; H, 5.01; N, 3.52.

Reaction with PhMgBr, 3(sil,Ph): yield 68%; IR (NaCl) ν (CO) 1978, 1888, 1870 cm^{-1}; ^1H NMR (CD_2Cl_2): δ 7.35 (s, 5 H, Ph), 5.41 (dd, 1.1, 2.8 Hz, 1 H, H^5), 5.33 (t, 2.68 Hz, 1 H, H^4), 3.69 (t, 5.86 Hz, 6 H, OCH_2), 2.80 (t, 5.86 Hz, 6 H, NCH_2), 2.58 (dd, 0.98, 2.56 Hz, 1 H, H^3) ppm. Anal. Calcd for $C_{19}H_{20}MnNO_3SSi$: C, 48.17; H, 4.26; N, 2.96. Found: C, 48.2; H, 4.60; N, 2.93.

Reaction of 1(Mn) with RMgBr (R = Et, Ph). A procedure was used essentially identical to that described above except for the purification step. The crude product was purified by chromatography on silica gel eluting with hexane and diethyl ether.

Reaction with PhMgBr, 3(Mn,Ph): yield 74%; IR (NaCl) ν (CO) 2004, 1979, 1916, 1883 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.46 (m, 5 H, Ph), 5.52 (t, 5.0 Hz, 1 H, $H^{3'}$), 5.14 (br s, 1 H, H^3), 5.06 (br s, 1 H, H^4), 4.93 (t, 6.1 Hz, 1 H, $H^{2'}$ or $H^{4'}$), 4.24 (t, 6.1 Hz, 1 H, $H^{2'}$ or $H^{4'}$), 3.26 (t, 6.0 Hz, 1 H, $H^{1'}$ or $H^{5'}$), 3.04 (t, 6.0 Hz, 1 H, $H^{1'}$ or $H^{5'}$), 2.91 (t, 6.0 Hz, 1 H, $H^{6'}$), 2.62 (br s, 1 H, H^5) ppm; HRMS M^+ (*m*/*z*) calcd 515.9272, obsd 515.9337. Anal. Calcd for $C_{22}H_{14}Mn_2O_6S$: C, 51.18; H, 2.73. Found: C, 51.2; H, 2.75.

Reaction with EtMgBr, 3(Mn,Et): yield 59%; IR (NaCl) ν (CO) 1980, 1889 cm^{-1}; ^{1} H NMR ($CDCl_3$) δ 5.74 (t, 5.2 Hz, 1 H, $H^{3'}$), 5.06 (d, 2.9 Hz, 1 H, H^3), 5.04 (t, 5.4 Hz, 1 H, $H^{2'}$ or $H^{4'}$), 4.89 (dd, 1.2, 2.9 Hz, 1 H, H^4), 4.82 (t, 5.4 Hz, 1 H, $H^{2'}$ or $H^{4'}$), 3.39 (t, 5.6 Hz, 1 H, $H^{1'}$ or $H^{5'}$), 3.36 (t, 5.6 Hz, 1 H, $H^{1'}$ or $H^{5'}$), 2.78 (t, 5.6 Hz, 1 H, $H^{6'}$), 2.19 (br s, 1 H, H^5), 2.18 (dq, 7.6, 36 Hz, 2 H, CH_2), 1.00 (t, 7.6 Hz, 3 H, CH_3) ppm; HRMS M^+ (*m*/*z*) calcd 467.9272, obsd 467.9256.

Reaction of 1(Mn) with $NaBH_3CN$. The same procedure was used as with the reaction of **1**(sil) and $NaBH_4$: yield 95%; IR (NaCl) ν (CO) 1995, 1899 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.85 (td, 1.2, 5.4 Hz, 1 H, $H^{3'}$), 5.25 (d, 4.2 Hz, 1 H, H^3), 5.09 (t, 5.4 Hz, 1 H, $H^{2'}$ or $H^{4'}$), 4.97 (t, 5.4 Hz, 1 H, $H^{2'}$ or $H^{4'}$), 3.79 (t, 5.6 Hz, 1 H, $H^{6'}$), 3.66 (td, 1.1, 5.6 Hz, 2 H, $H^{1'}$ and $H^{5'}$), 3.53 (dd, 2.4, 9.8 Hz, 1 H, H^{5-endo}), 3.24 (d, 9.8 Hz, 1 H, H^{5-exo}), 2.98 (m, 1 H, H^4) ppm; HRMS M^+ (*m*/*z*) calcd 439.8959, obsd 439.8962. Anal. Calcd for $C_{16}H_{10}MnO_6S$: C, 43.66; H, 2.29. Found: C, 43.8; H, 2.24.

Reaction of 1(Mn) with $NaBD_4$. yield 95%; IR (NaCl) ν (CO) 2004, 1915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.85 (t, 5.4 Hz, 1 H, $H^{3'}$), 5.24 (d, 4.2 Hz, 1 H, H^3), 5.09 (t, 5.8 Hz, 1 H, $H^{2'}$ or $H^{4'}$), 4.97 (t, 5.8 Hz, 1 H, $H^{2'}$ or $H^{4'}$), 3.79 (t, 5.6 Hz, 1 H, $H^{6'}$), 3.66 (t, 6.1 Hz, 2 H, $H^{1'}$ and $H^{5'}$), 3.50 (d, 2.0 Hz, 1 H, H^{5-endo}), 2.97 (dd, 2.5, 4.0 Hz, 1 H, H^4) ppm; HRMS M^+ (*m*/*z*) calcd 440.9022, obsd 440.9056.

Reaction of (Thiophene)$Mn(CO)_3^+$ (1) with RMgBr. The procedure was the same as with the reaction between **1**(Mn) and RMgBr.

3(H,Ph): yield 77%; IR (NaCl) ν (CO) 1994, 1885 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44 (m, 5 H), 5.36 (s, 2 H), 2.79 (s, 2 H) ppm. Anal. Calcd for $C_{13}H_9MnO_3S$: C, 52.01; H, 3.02; S, 10.66. Found: C, 52.13; H, 3.11; S, 10.65.

3(H,Et): IR (NaCl) ν (CO) 1987, 1885 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.30 (s, 2 H, $H^{3,4}$), 2.43 (s, 2 H, $H^{2,5}$), 2.07 (q, 7.6 Hz, 2 H, CH_2), 0.95 (t, 7.4 Hz, 3 H, CH_3) ppm; Anal. Calcd for $C_9H_9MnO_3S$: C, 42.86; H, 3.60. Found: C, 42.72; H, 3.50.

3(H, *p*-tolyl): IR ν (CO) 2002, 1918, 1912 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27−7.21 (m, 4 H, $H^{5,6,8,9}$), 5.34 (t, 2.0 Hz, 2 H, $H^{2,3}$), 2.78 (t, 2.0 Hz, 2 H, $H^{1,4}$), 2.35 (s, 3 H, CH_3) ppm; HRMS M^+ (*m*/*z*) calcd 313.9809, obsd 313.9941. Anal. Calcd for $C_{14}H_{11}MnO_3S$: C, 53.51; H, 3.53; S, 10.20. Found: C, 53.2; H, 3.31; S, 10.21.

3(H,2-thienyl): IR ν (CO) 2004, 1918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38 (dd, 1.2, 5.1Hz, 1 H, H^8), 7.12 (dd, 1.2, 3.7 Hz, 1 H, H^6), 6.95 (dd, 3.7, 5.1 Hz, 1 H, H^7), 5.36 (t, 2.0 Hz, 2 H, $H^{2,3}$), 2.94 (t, 2.0 Hz, 2 H, $H^{1,4}$) ppm; HRMS M^+ (*m*/*z*) calcd 305.9217, obsd 305.9132. Anal. Calcd for $C_{11}H_7MnO_3S_2$: C, 43.13; H, 2.30; S, 20.94. Found: C, 43.15; H, 2.14; S, 21.23.

3(Me,Ph): IR ν (CO) 1987, 1885 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5−7.2 (m, 5 H, Ph), 5.32 (t, 2.8 Hz, 1 H, H^4), 4.98 (dd, 1.2, 2.7 Hz, 1 H, H^3), 2.65 (dd, 1.0, 2.7 Hz, 1 H, H^5), 1.73 (s, 3 H, CH_3) ppm; HRMS M^+ (*m*/*z*) calcd 313.9809, obsd 313.9750. Anal. Calcd for $C_{14}H_{11}MnO_3S$: C, 53.51; H, 3.53. Found: C, 53.24; H, 3.36.

3(Me, *p*-tolyl): IR ν (CO) 1998, 1915, 1908 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29−7.19 (m, 4 H, $H^{5,6,8,9}$), 5.29 (t, 2.7 Hz, 1 H, H^3), 4.97 (v s, 1 H, H^2), 2.65 (v s, 1 H, H^4), 2.37 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3) ppm; HRMS M^+ (*m*/*z*) calcd 327.9966, obsd 327.9923. Anal. Calcd for $C_{15}H_{13}MnO_3S$: C, 54.88; H, 3.99. Found: C, 54.9; H, 3.95.

3(Me,2-thienyl): IR ν (CO) 2000, 1914 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42 (dd, 2.9, 5.1 z, 1 H, H^8), 7.13 (dd, 1.2, 3.7 Hz, 1 H, H^6), 6.70 (dd, 3.7, 5.1 Hz, 1 H, H^7), 5.25 (t, 2.9 Hz, 1 H, H^3), 5.02 (dd, 1.7, 2.9 Hz, 1 H, H^2), 2.85 (dd, 1.7, 2.9 Hz, 1 H, H^4), 1.73 (s, 3 H, CH_3) ppm; HRMS M^+ (*m*/*z*) calcd 319.9374, obsd 319.9348. Anal. Calcd for $C_{12}H_9MnO_3S_2$: C, 45.00; H, 2.83. Found: C, 45.2; H, 2.79.

3(2Me,Ph): IR (NaCl) ν (CO) 1975, 1869 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.5−7.6 (m, 5 H, Ph), 5.12 (s, 2 H, $H^{3,4}$), 1.79 (s, 6 H, CH_3) ppm. Anal. Calcd for $C_{15}H_{13}MnO_3S$: C, 54.89; H, 3.96; S, 9.76. Found: C, 54.79; H, 4.12; S, 9.32.

Synthesis of 4. A Typical Procedure. 3(H,Ph) (100 mg) was dissolved in 20 mL of CH_2Cl_2 under N_2. $NOBF_4$ (2 equiv) was added. After stirring for 1.5 h, the solvent was removed via a rotary evaporator, the residue was dissolved in CH_3NO_2, and the product was precipitated with diethyl ether.

4(H,Ph): yield 46%; IR ν (CO) 2076, 2036, ν (NO) 1784, ν (BF) 1050, 1027 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.67 (m, 5 H, Ph), 6.61 (s, 2 H), 4.29 (s, 2 H) ppm. Anal. Calcd for $C_{12}H_9BF_4MnNO_3S$: C, 37.02; H, 2.31; N, 3.59. Found: C, 37.00; H, 2.58; N, 3.10.

4(H, *p*-tolyl): IR ν (CO) 2082, 2044, ν (NO) 1804 cm^{-1}; ^1H NMR (acetone-d_6) δ 7.69 (d, 8.0 Hz, 2 H, $H^{6,10}$), 7.46 (d, 8.0 Hz, 2 H, $H^{7,9}$), 6.94 (t, 2.0 Hz, 2 H, $H^{2,3}$), 4.69 (t, 2.0 Hz, 2 H, $H^{1,4}$), 2.42 (s, 3 H, CH_3) ppm.

4(H,2-thienyl): IR ν (CO) 2088, 2052, ν (NO) 1807 cm^{-1}; ^1H NMR (acetone-d_6) δ 8.07 (dd, 1.2, 5.1 Hz, 1H, H^8), 7.75 (dd, 1.2, 3.8 Hz, 1 H, H^6), 7.26 (dd, 3.8, 5.1 Hz, 1 H, H^7), 6.95 (t, 2.2 Hz, 2 H, $H^{2,3}$), 4.82 (t, 2.2 Hz, 2 H, $H^{1,4}$) ppm.

4(Me,Ph): IR ν (CO) 2080, 2042, ν (NO) 1800 cm^{-1}; ^1H NMR (acetone-d_6) δ 7.94−7.84 (m, 5 H, H^{6-10}), 6.93 (t, 3.2 Hz, 1 H, H^3), 6.70 (m, 1 H, H^2), 4.57 (m, 1 H, H^4), 2.10 (3 H, CH_3) ppm.

4(Me,*p*-tolyl): IR ν (CO) 2078, 2040, ν (NO) 1798 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.48 (m, 4 H, $H^{6,7,9,10}$), 6.57 (t, 2.9 Hz, 1 H, H^3), 6.25 (m, 1 H, H^2), 4.11 (m, 1 H, H^4), 2.43 (s, 3 H, CH_3), 1.94 (s, 3 H, CH_3) ppm.

4(Me,2-thienyl): IR ν (CO) 2078, 2042, ν (NO) 1799 cm^{-1}; ^1H NMR (acetone-d_6) δ 8.14 (dd, 1.2, 5.1 Hz, 1 H, H^8), 7.85 (dd, 1.2, 3.9 Hz, 1 H, H^6), 7.32 (dd, 3.9, 5.1 Hz, 1 H, H^7), 6.87 (t, 3.2 Hz, 1 H, H^3), 6.86 (dd, 1.5, 3.2 Hz, 1 H, H^2), 4.73 (dd, 1.5, 3.2 Hz, 1 H, H^4), 2.10 (s, 3 H, CH_3) ppm. Compounds **4** except **4**(H,Ph) were obtained as a mixture of **4** and **5**. We were successful in separating **4** from a mixture. Thus, we could not obtain combustion data for **4**.

Synthesis of Thiophenium salts 5. Compound **4** (140 mg) was dissolved in 30 mL of acetone and irradiated by UV light. After stripping the solvent, the residue was washed with diethyl ether and then was precipitated from acetone with diethyl ether.

5(H,Ph): yield 90%. Analytical data for *S*-phenylthiophenium salt: ^1H NMR (acetone-d_6) δ 8.32 (d, 5.5 Hz), 8.13 (d, 5.5 Hz), 8.07 (t, 7 Hz), 8.02 (d, 8.5 Hz), 7.95 (t, 7.5 Hz) ppm.

Table 1. Crystal Data for 2(sil,P(O)(OMe)$_2$), 3(Mn,Ph), and 5(Me,*p*-tolyl)

	2(sil,P(O)(OMe)$_2$)	**3**(Mn,Ph)	**5**(Me,*p*-tolyl)
chem formula	$C_{15}H_{21}MnNO_9PSSi$	$C_{22}H_{14}Mn_2O_6S$	$C_{12}H_{13}BF_4S$
fw	505.39	516.27	276.09
cryst size, mm	0.40 × 0.20 × 0.15	0.3 × 0.3 × 0.2	
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	9.8710(5)	10.37100(8)	11.377(2)
b, Å	10.0970(9)	13.747(2)	9.350(2)
c, Å	10.8490(3)	15.6090(10)	12.551(2)
α (deg)	78.4300(5)	90.000(10)	90.000
β (deg)	81.4300(3)	105.550(7)	99.892(13)
γ (deg)	85.6800(6)	90.000(8)	90.000
V, Å^3	1046.34(11)	2143.9(3)	1315.3(4)
Z	2	4	4
ρ_{calcd}, g cm^{-3}	1.604	1.599	1.394
θ range for data collect	1.93−22.50	2.01−29.96	1.82−24.96
no. of data	2283	5100	1406
no. of parameters	262	280	163
R	0.0561	0.0790	0.064
wR^2	0.1453	0.1606	0.1648

Anal. Calcd for $C_{10}H_9BF_4S$: C, 48.41; H, 3.63. Found: C, 48.27; H, 3.41.

5(Me,Ph): ^{1}H NMR (acetone-d_6) *δ* 7.91−7.88 (m, 2 H), 7.81−7.76 (m, 5 H), 7.45 (br s, 1 H), 2.44 (s, 3 H) ppm. Anal. Calcd for $C_{11}H_{11}BF_4S$: C, 50.41; H, 4.23. Found: C, 50.36; H, 4.29.

5(Me,*p*-tolyl): ^{1}H NMR (acetone-d_6) *δ* 7.85 (d, 5.6 Hz, 1 H), 7.77 (dd, 3.3, 5.6 Hz, 1 H), 7.67 (d, 8.4 Hz, 2 H), 7.59 (d, 8.4 Hz, 2 H), 7.42 (m, 1 H), 2.48 (s, 3 H), 2.43 (s, 3 H) ppm. Anal. Calcd for $C_{12}H_{13}BF_4S$: C, 52.20; H, 4.75. Found: C, 51.94; H, 4.49.

5(H, *p*-tolyl): ^{1}H NMR (acetone-d_6) *δ* 8.05 (d, 5.9 Hz, 2 H), 7.88 (d, 5.9 Hz, 2 H), 7.64 (d, 8.3 Hz, 2 H), 7.54 (d, 8.3 Hz, 2 H), 2.46 (s, 3 H) ppm. Anal. Calcd for $C_{11}H_{11}BF_4S$: C, 50.41; H, 4.23; S, 12.23. Found: C, 49.84; H, 3.87; S, 12.51.

5(H,2-thienyl): ^{1}H NMR (acetone-d_6) *δ* 8.31 (dd, 5.1, 1.2 Hz, 1 H), 8.22 (dd, 3.9, 1.2 Hz, 1 H), 8.12 (m, 2 H), 7.89 (m, 2 H), 7.43 (dd, 5.4, 3.9 Hz, 1 H) ppm. Anal. Calcd for $C_8H_7BF_4S_2$: C, 37.82; H, 2.78; S, 25.23. Found: C, 38.00; H, 2.45; S, 25.53.

5(Me,2-thienyl): ^{1}H NMR (acetone-d_6) *δ* 8.37 (dd, 5.3, 1.2 Hz, 1 H), 8.29 (dd, 3.8, 1.2 Hz, 1 H), 7.92 (br m, 1 H), 7.77 (br m, 1 H), 7.46 (dd, 5.3, 3.8 Hz, 1 H), 7.43 (br m, 1 H), 2.49 (d, 1.2 Hz, 3 H) ppm. Anal. Calcd for $C_9H_9BF_4S_2$: C, 40.32; H, 3.38. Found: C, 40.27; H, 3.30.

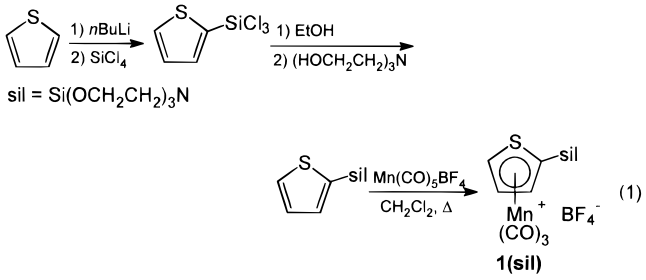
X-ray Structure Determinations of 2(sil,P(O)(OMe)$_2$), 3(Mn, Ph), and 5(Me,*p*-tolyl). Crystals of **2**(sil,P(O)(OMe)$_2$) were grown by slow evaporation of a solution of **2**(sil,P(O)(OMe)$_2$) in hexane. Crystals of **3**(Mn,Ph) were grown by slow evaporation of a solution of **3**(Mn,Ph) in hexane and diethyl ether. Crystals of **5**(Me,*p*-tolyl) were grown by slow diffusion hexane into a concentrated solution of **5**(Me,*p*-tolyl) in CH_2Cl_2. Diffraction was measured by an Enraf-Nonius CAD4 automated diffractometer with an $\theta-2\theta$ scan method. Unit cells were determined by centering 25 reflections in the appropriate 2θ range. Other relevant experimental details are listed in Table 1. The selected bond distances and bond angles are shown in Table 2. The structure was solved by direct method using SHELXS-86[8] and refined by full-matrix least squares with SHELXL-93.[9] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically using riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2(sil,P(O)(OMe)$_2$), 3(Mn,Ph), and 5(Me,*p*-tolyl)

	2(sil,P(O)(OMe)$_2$)		
C1−Si	1.893(5)	Mn−C11	1.820(7)
C2−C3	1.408(8)	C3−C4	1.500(7)
C1−S	1.792(5)	Mn−C1	2.109(6)
C4−P	1.824(6)	C1−C2	1.407(7)
C4−S	1.824(6)	Si−N	2.079(5)
S−C4−C3	97.1(3)	C1−Si−N	176.6(2)
C1−S−C4	94.6(2)	CO1−Mn−CO2	92.5(3)
	3(Mn,Ph)		
S1−C17	1.780(5)	C17−C18	1.427(8)
C19−C20	1.422(9)	Mn2−C20	2.116(6)
Mn2−C5	1.797(8)	C11−C17	1.508(8)
S1−C20	1.755(6)	C18−C19	1.404(8)
Mn2−C17	2.126(5)	Mn2−S1	2.776(2)
Mn2−C6	1.790(6)	C11−C12	1.522(7)
C17−S1−C20	86.2(3)	C12−C11−C16	102.6(4)
Mn2−C5−O5	178.9(5)	C18−C19−C20	110.1(5)
S1−C20−C19	111.3(5)	C13−C14−C15	117.4(6)
	5(Me,*p*-tolyl)		
S−C4	1.746(6)	C1−C2	1.332(8)
C3−C4	1.313(8)	S−C5	1.788(5)
S−C1	1.781(6)	C2−C3	1.430(9)
C2−C1−C11	133.1(6)	C4−S−C1	92.9(3)
C5−S−C4	105.1(3)	S−C1−C2	107.1(5)
C11−C1−S	119.7(5)	C1−C2−C3	115.3(6)

Results and Discussion

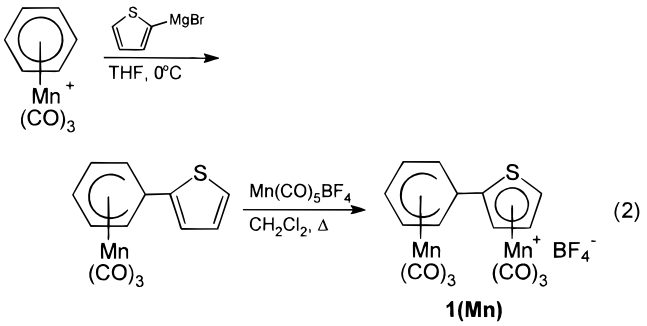
Syntheses of 1(sil) and 1(Mn). The manganese 2-silatranylthiophene complex [{2-N(CH$_2$CH$_2$O)$_3$Si-SC$_4$H$_3$}Mn(CO)$_3$][BF$_4$] **1**(sil)), was prepared according to eq 1. The overall yield from thiophene was 27%.



(1)

Complex **1**(sil) is stable in air but unstable in polar organic solvents such as acetone and acetonitrile due to ready displacement of the thiophene to form Mn(CO)$_3$(solvent)$_3^+$. The dimanganese thiophene complex [{2-(η^5-C$_6$H$_6$)Mn(CO)$_3$)-SC$_4$H$_3$}Mn(CO)$_3$][BF$_4$] **1**(Mn)), was prepared as shown in eq 2. Treatment of (benzene)-Mn(CO)$_3^+$ with 2-thienylmagnesium bromide resulted in the formation of (thienylcyclohexadienyl)Mn(CO)$_3$ (94%), which was treated with Mn(CO)$_5$BF$_4$ in CH_2Cl_2

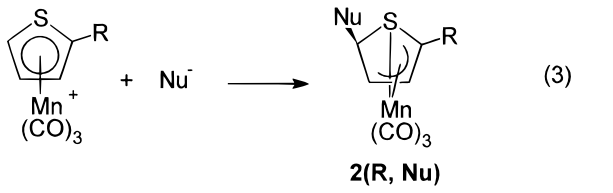
(8) Scheldrick, G. M. SHELXS-86, Program for Crystal Structure Determination; University of Göttingen, Germany, 1986.
(9) Scheldrick, G. M. SHELXL-93, Program for Crystal Structure Determination; University of Göttingen, Germany, 1993.



(2)

to afford **1**(Mn) in 87% yield. According to the ^{1}H NMR spectrum in acetone-d_6, there were two isomers present in a ratio of 4:1; these may reflect the relative direction of two $Mn(CO)_3$ groups.

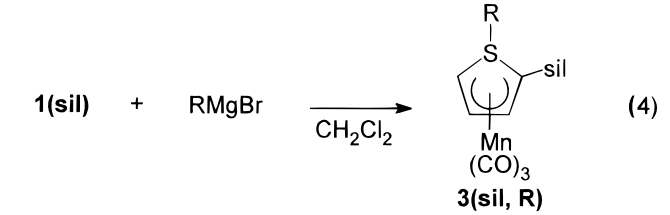
Reactions of Thiophene Manganese Cations with Nucleophiles. The cationic thiophene complexes are highly susceptible to nucleophilic addition, which most often occurs at a position adjacent to the sulfur (eq 3).[4] With **1**(sil), H^-, ^-CN, and $^-P(O)(OR)_2$ (R = Me,



(3)

Ph) were, judged from ^{1}H NMR spectra, to add to C5. Single crystals of [{5-exo-$(MeO)_2P(O)$-η^4-2-$N(CH_2CH_2O)_3$-Si-SC_4H_3}$Mn(CO)_3$] **2**(sil,P(O)$(OMe)_2$)) suitable for X-ray study (Figure 1) were grown from hexane and an X-ray structural study confirmed that the nucleophile is attached to C5 in an *exo* fashion (vide infra).

When **1**(sil) was treated with RMgBr (R = Me, Et, Ph) in CH_2Cl_2 at room temperature, compounds [{*S*-R-η^4-2-$N(CH_2CH_2O)_3Si$-SC_4H_3}$Mn(CO)_3$] **3**(sil,R); R = Me, 65%; R = Et, 62%; R = Ph, 68%) were obtained (eq 4).



(4)

The ^{1}H NMR spectra of these products are quite different from those obtained with the other nucleophiles, as mentioned above. The methyl peak of **3**(sil,Me) appears at δ 1.77 ppm as a singlet, and the methyl group (CH_2CH_3) of **3**(sil,Et) appears as a doublet of doublets due to the coupling to diastereotopic methylene protons (CH_2CH_3). If the methyl group in **3**(sil, Me) were situated at one of the C3−C5 atoms, the methyl peak should appear as a doublet. The three ring protons of [{5-exo-Nu-η^4-2-$N(CH_2CH_2O)_3Si$-SC_4H_3}$Mn(CO)_3$] **2**(sil,Nu); (Nu = H, CN, $P(O)(OR)_2$), appear at δ 5.7 ± 0.1, 4.0 ± 0.5, and 3.2 ± 0.1 ppm. However, the three ring protons of **3**(sil,Me), **3**(sil,Et), and **3**(sil,Ph) appear at δ 5.37 ± 0.04, 5.27 ± 0.06, and 2.4 ± 0.2 ppm. From this

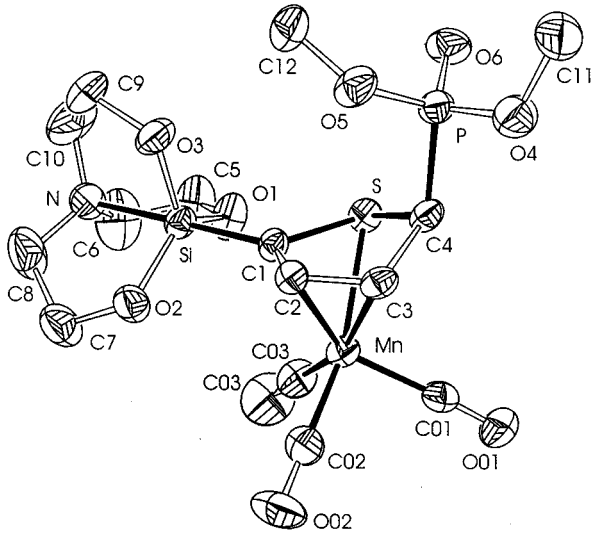


Figure 1. ORTEP drawing of **2**(sil,$P(O)(OMe)_2$).

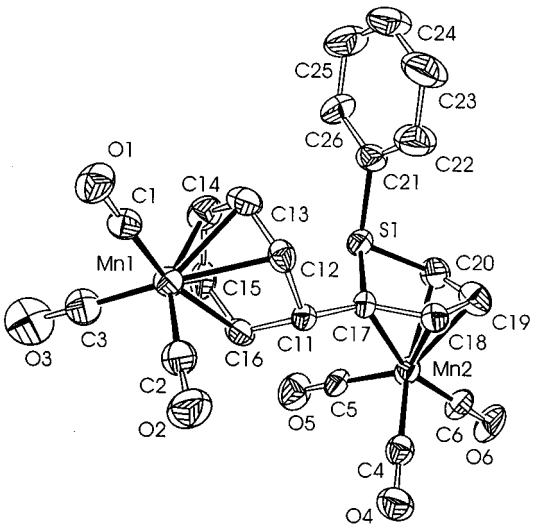
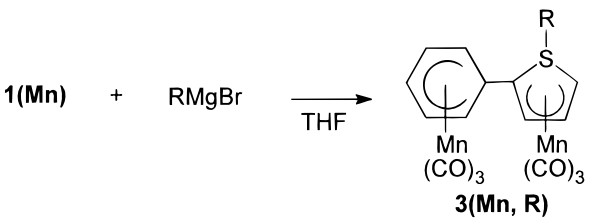


Figure 2. ORTEP drawing of **3**(Mn,Ph).

information, we concluded that the Grignard reagents added to the sulfur atom. Attempts to grow single crystals of **3**(sil,Me), **3**(sil,Et), and **3**(sil,Ph) were not successful. However, the Grignard addition to the sulfur atom was indirectly verified by the X-ray crystal structure of [S-Ph-η^4-2-{(η^5-C_6H_6)$Mn(CO)_3$}-SC_4H_3]$Mn(CO)_3$, (**3**(Mn,Ph)) (vide infra).

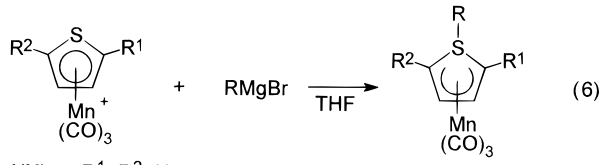
Addition of $NaBH_4$ and NaCN to **1**(Mn) resulted in the formation of [5-*exo*-Nu-η^4-2-{(η^5-C_6H_6)$Mn(CO)_3$}-SC_4H_3]$Mn(CO)_3$ (**2**(Mn,Nu); (Nu = H, CN). The ^{1}H NMR spectra of **2**(Mn,H) and **2**(Mn,CN) are similar to those of **2**(sil,H) and **2**(sil,CN). Likewise, the Grignard addition products [*S*-R-η^4-2-{(η^5-C_6H_6)$Mn(CO)_3$}-SC_4H_3]-$Mn(CO)_3$, **3**(Mn,R) (R = Et, Ph), have ^{1}H NMR spectra similar to those of **3**(sil,Et) and **3**(sil,Ph) (eq 5). The



(5)

X-ray structure of **3**(Mn, Ph) showed that nucleophile addition had occurred at the sulfur atom (Figure 2).

To confirm the generality of Grignard reagent addition to the sulfur atom, [(thiophene)$Mn(CO)_3$][BF_4] (**1**(H)), [(2-methylthiophene)$Mn(CO)_3$][BF_4] (**1**(Me)), and [(2,5-dimethylthiophene)$Mn(CO)_3$][BF_4] (**1**(**2**Me)) were prepared by known methods.[4] Reaction with RMgBr (R = Ph or Et) at 0 °C in THF gave (*S*-Ph-η^4-SC_4H_4)$Mn(CO)_3$ (**3**(H,Ph)), (*S*-Ph-η^4-2-Me-SC_4H_3)$Mn(CO)_3$ (**3**(Me,Ph)), (*S*-Ph-η^4-2-Me-5-Me-SC_4H_2)$Mn(CO)_3$ (**3**(2Me,Ph)), and (*S*-Et-η^4-SC_4H_4)$Mn(CO)_3$ (**3**(H,Et)) in 77, 45, 19, and 55% yields, respectively (eq 6). Interestingly, when the



(6)

1(H) $R^1=R^2=H$
1(Me) R^1=Me, R^2=H
1(2Me) $R^1=R^2$=Me

3(H, Ph)
3(Me, Ph)
3(2Me, Ph)
3(H, Et)

reactions were carried out in CH_2Cl_2, no addition products could be isolated, showing that the choice of reaction medium is important. Reactions of **1**(Me) and **1**(**2**Me) with EtMgBr did not give stable compounds. As the substitution increased, the yields of the products decreased. Compound **3**(H,Ph) prepared from **1**(H) and PhMgBr is spectroscopically identical to **3**(H,Ph) reported by Angelici et al.,[5] who prepared **3**(H,Ph) from the reaction of **1**(H) with Ph_2CuLi. Two decades ago, Sim et al.[10] reported the formation and X-ray structure of $(CO)_3Mn\{\mu$-$C_4(CF_3)_4S$-$C_6F_5\}$, having essentially the same structure of **3**(H, Ph), from the reaction of [$Mn(CO)_4(\mu$-$SC_6F_5)]_2$ with $CF_3C{\equiv}CCF_3$. Interestingly, Angelici et al. failed to obtain **3**(H,Ph) from the reaction of **1**(H) with PhMgCl. The reaction of PhMgCl with **1**(H) in THF at −60 to −10 °C did not give the S-addition product; only decomposition was observed. Their result for the reaction of [(thiophene)$Mn(CO)_3$]$^+$ with PhMgCl was quite different from ours.

Our results indicate that the addition of Grignard reagents to the sulfur atom occurs regardless of the presence of substituent at C2 of the thiophene ring. It is possible that Grignard reagents differ from the other nucleophiles studied with respect to the site of attack due to a propensity for an electron transfer pathway. There is considerable evidence for the intermediacy of radicals in the addition reactions of Grignard reagents.[11]

It is possible that the most electrophilic atom in the thiophene ligand is the sulfur atom. Several years ago, Rauchfuss et al.[12] reported that the reaction of OH^- and [$(C_5Me_5)Ru(C_4Me_4S)]^{2+}$ results in products indicative of attack of both C2 and S. It has been suggested that both products result from initial attack at the sulfur and that the sulfur may, in general, be the most electrophilic atom in η^5-thiophene ligands. To firmly establish this point, a more detailed investigation would be needed.

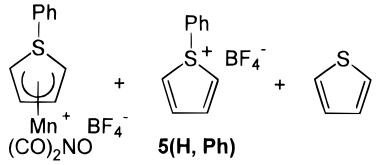
When **3**(H,Ph) was refluxed with Me_3NO in C_6H_6, to our surprise, diphenyl disulfide was obtained quantitatively (eq 7). The generation of diphenyl disulfide was

3(H, Ph) $\xrightarrow[C_6H_6,\ \Delta]{Me_3NO}$ PhS-SPh (7)

confirmed by IR, ^{1}H NMR, and MS. The liberation of diphenyl disulfide upon treatment with Me_3NO is quite general for all manganese *S*-Ph-thiophene derivatives. The mechanism for the formation of diphenyl disulfide is under investigation.

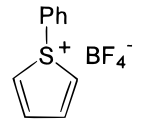
When **3**(H,Ph) was reacted with $NOBF_4$ in CH_2Cl_2, the nitrosyl complex [(1-Ph-η^4-SC_4H_4)$Mn(CO)_2(NO)$]-[BF_4] (**4**(H,Ph)) was obtained in 46% yield (eq 8). The

3(H, Ph) + $NOBF_4$ $\xrightarrow{CH_2Cl_2}$



4(H, Ph) **5(H, Ph)** (8)

yield of **4** was limited due to decomplexation of the reactant that occurred during the reaction. When **3**(H,Et) was reacted with $NOBF_4$ in CH_2Cl_2, dealkylation occurred and **1**(H) was obtained. The IR spectrum of **4**(H,Ph) shows two carbonyl stretching frequencies at 2076 and 2036 cm^{-1} and one nitrosyl frequency at 1784 cm^{-1}. Compared with other (cyclohexadienyl)$Mn(CO)_2$-NO^+ complexes,[13] these frequencies are low, from which we conclude that the positive charge is substantially localized at the sulfur atom. Complex **4**(H,Ph) was found to be highly light-sensitive. Thus, we expected that the $Mn(CO)_2(NO)$ moiety might be easily removed to liberate the thiophenium salt. Indeed, the thiophenium salt was easily liberated in high yield by irradiation of **4**(H,Ph), in acetone solution (eq 9). Other

4(H, Ph) $\xrightarrow[\text{acetone}]{h\nu}$ 

5(H, Ph) (9)

thiophenium salts were similarly obtained in high yields (Table 3). Compounds **4** were also found to convert to **5** in solid state. Compounds **5** are white crystalline solids and slowly decomposed in the air. The molecular structure of [S-*p*-$CH_3C_6H_5$-2-Me-SC_4H_3][BF_4] (**5**(Me,*p*-tolyl)) (Figure 3) was verified by an X-ray study, which, to our knowledge, represents the first crystal structure of a *S*-phenylthiophenium salt. When **3**(sil,Ph) was treated with $NOBF_4$, a mixture of the thiophenium salt [S-C_6H_5-2-$N(CH_2CH_2O)_3Si$-SC_4H_3][BF_4] (**5**(sil,Ph)), and

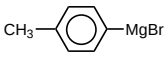
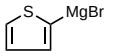
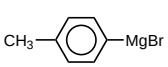
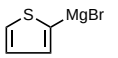
(10) (a) Barrow, M. J.; Davidson, J. L.; Harrison, W.; Sharp, D. W. A.; Sim, G. A.; Wilson, F. B. *J. Chem. Soc., Chem. Commun.* **1973**, 583. (b) Barrow, M. J.; Freer, A. A.; Harrison, W.; Sim, G. A.; Taylor, D. W.; Wilson, F. B. *J. Chem. Soc., Dalton Trans.* **1975**, 197.

(11) (a) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 291. (b) Taylor, S. K.; Bennett, S. G.; Heinz, K. J.; Lashley, L. K. *J. Org. Chem.* **1981**, *46*, 2194. (c) Uchida, A.; Nakazawa, T.; Kondo, I.; Iwata, N.; Matsuda, S. *J. Org. Chem.* **1972**, *37*, 3749. (d) Whitesides, G. M.; Gutowski, F. D. *J. Org. Chem.* **1976**, *41*, 2882.

(12) (a) Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8521. (b) Krautscheid, H.; Feng, Q.; Rauchfuss, T. B. *Organometallics* **1993**, *12*, 3273.

(13) (a) Chung, Y. K.; Choi, H. S.; Sweigart, D. A.; Connelly, N. G. *J. Am. Chem. Soc.* **1982**, *104*, 4245. (b) Chung, Y. K.; Sweigart, D. A.; Connelly, N. G.; Sheridan, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 2388.

Table 3. Yields of 3−5

			entry (%)		
entry	R	R′MgBr	3[a]	4[a]	5[b]
1	H	PhMgBr	77	46	90
2	H		64	40	90
3	H		47	90	90
4	CH_3	PhMgBr	45	58	90
5	CH_3		58	54	90
6	CH_3		43	47	90

[a] Isolated yields. [b] Calculated yields.

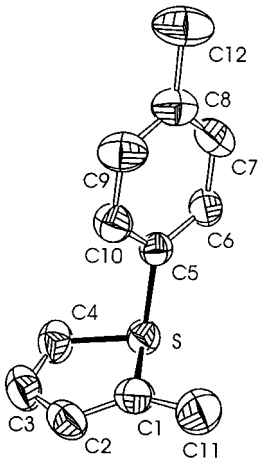


Figure 3. ORTEP drawing of **5**(Me,*p*-tolyl).

1(sil) was obtained depending upon the reaction temperature (eq 10). At 25 °C, **5**(sil,Ph) and **1**(sil) were

$$\mathbf{3}(\text{sil,Ph}) + \text{NOBF}_4 \rightarrow \mathbf{5}(\text{sil,Ph}) + 1(\text{sil}) \quad (10)$$

obtained in the ratio of 2:1 and at 0 °C, 10:1. At −78 °C, **5**(sil,Ph) was obtained as a sole product.

Molecular Structures of 2(sil,P(O)(OMe)$_2$), 3(Mn,Ph), and 5(Me,*p*-tolyl). An X-ray structure determination of **2**(sil,P(O)(OMe)$_2$) revealed that P(O)(OMe)$_2$ is situated in the *exo* position. The ORTEP drawing is shown in Figure 1, and selected bond angles and distances are given in Table 2. The stereochemistry of the Si atom is a distorted trigonal bipyramid. The N−Si bond distance is 2.079(5) Å and the Si−C1 bond distance is 1.893(5) Å. The N−Si−C1 angle is 176.6(2)°. In general, bond lengths and angles in the silatranyl portion of the structure are in agreement with the structures of other silatranyl transition metal complexes.[6,14] The bond distances of P═O and P−O (1.462(4) Å and average 1.572 Å, respectively) are similar to those (1.449 and 1.558 Å, respectively) in organic compounds[15] but are shorter than those (average 1.486 and 1.608 Å, respectively) of CpFe(CO)$_2${P(O)(OEt)$_2$}.[16]

The molecular structure of **2**(sil,P(O)(OMe)$_2$) is very similar to the structure of (CN-thiophene)Mn(CO)$_3$.[4a] The sulfur and three carbon atoms of the organic ring are planar within 0.049 Å while the remaining carbon atom (C4) is 0.577(6) Å out of this plane. The plane forms a dihedral angle of 33.5° with a plane passing through C3, S, and C4. The manganese atom is located 1.776(1) Å below the plane defined by S−C1−C2−C3. The carbonyl groups in this structure are positioned so that one carbonyl is eclipsed with the out-of-plane ring carbon atom. The Mn−C02 distance for the carbonyl which is approximately *trans* (161.7(2)°) to the sulfur atom, appears to be slightly shorter (0.02−0.04 Å) than the remaining two Mn−CO distances. The C−C bond distances for C1−C2 and C2−C3 are 1.407(7) and 1.409(7) Å, respectively. These distances are much shorter than a C−C single bond distance (1.526 Å). The two S−C bonds in this structure measure 1.792(5) and 1.824(6) Å for S−C1 and S−C4, respectively. Both are slightly longer than those typically observed in free thiophene (C−S = 1.718(4) Å).[17] The same trend can be seen in [(η^6-C_6Me_6)Ru(η^4-2,5-$Me_2C_4H_2$S-2-H)]PF_6 (1.91 Å).[18] Thus, a three carbon unit C1−C2−C3 can be described as an allyl system [4a,18] with a delocalized π-electron network.

An X-ray structure determination of **3**(Mn,Ph) revealed that the Ph is bonded to the sulfur atom. The ORTEP drawing is shown in Figure 2. Selected bond angles and distances are given in Table 2. The geometric parameters of (cyclohexadienyl)Mn(CO) portion of **3**(Mn,Ph) are in agreement with those found in other compounds.[19] The cyclohexadienyl ring is nearly planar (with a maximum deviation of 0.007 Å) and is folded about C12−C11−C16 with an angle of 38.0°. The manganese atom (Mn1) is located 1.683 Å from the cyclohexadienyl ring. The manganese atom (Mn2) is coordinated to the thiophene in an η^4-fashion. The C17−C18−C19−C20 segment is planar (with a maximum deviation of 0.006 Å), and the sulfur atom is displaced 0.644 Å from this plane. The dihedral angle between planes C17−C18−C19−C20 and C17−S−C20 is 29.9°. The bond distances S−C17 and S−C20 (1.780(5) and 1.755(6) Å, respectively) are longer than those typically observed in free thiophene (C−S = 1.718(4) Å).[15]

An X-ray structure determination of **5**(Me,*p*-tolyl) is shown in Figure 3. Selected bond angles and distances are given in Table 2. The ring defined by S, C1, C2, C3, and C4 is roughly planar. The dihedral angle between the planes C1−S−C4 and C1−C2−C3−C4 is 6.0°. Thus, the geometry around the sulfur atom is pyramidal, with C1, C4, and C5 basal apexes. The bond distances of S−C5 and S−C1 (1.788(5) and 1.781(6) Å, respectively) are similar to the bond distance 1.778 Å of S−C(sp^2) in thioether[15] and the Car−S bond distance

(14) (a) Chung, T.-M.; Lee, Y.-A; Chung, Y. K.; Jung, I. N. *Organometallics* **1990**, *9*, 1976. (b) Lee, J. S.; Chung, Y. K.; Hwang, D.-M.; Kim, K. *J. Organomet. Chem.* **1993**, *445*, 49.

(15) (a) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, S1. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1987**, S1.

(16) Nakazawa, H.; Morimasa, K.; Kushi, Y.; Yoneda, H. *Organometallics* **1988**, *7*, 458.

(17) Bak, B.; Christensen, D.; Rastrup-Anderson, J.; Tannenbaum, E. *J. Chem. Phys.* **1956**, *25*, 892.

(18) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8515.

(19) (a) Mawby, A.; Walker, P. J. C.; Mawby, R. J. *J. Organomet. Chem.* **1973**, *55*, C39. (b) Niemer, B.; Steimann, M.; Beck, W. *Chem. Ber.* **1988**, *121*, 1767. (c) Ittel, S. D. Whitney, J. F.; Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1988**, *7*, 1323. (d) Lee, T.-Y.; Yu, H.-K.; Chung, Y. K.; Hallows, W. A.; Sweigart, D. A. *Inorg. Chim. Acta* **1994**, *224*, 147. (e) Lee, S.-G.; Kim, J.- A; Chung, Y. K.; Shin, W.; Yoon, T.-S.; Kim, K. *Organometallics* **1995**, *14*, 1023.

in Car−S^+−X_2 (the Car represents the aryl carbon in six-membered rings)[15] and longer than those typically observed in free thiophene (C−S = 1.718(4) Å).[17] The S−C4 bond distance, 1.746(6) Å, is quite short compared to the value of 1.778 Å for S−C(sp^2) in thioether but is still longer than those typically observed in free thiophene. The bond distance of C1−C2 (1.332(8) Å) is the normal for C(sp^2)−C(sp^2). However, C1−C11 (1.463(9) Å) is rather shorter than those observed for other compounds.[15] The bond angles for C1−S−C4, C1−S−C5, and C4−S−C5 are 92.9(3)°, 104.7(3)°, and 105.1(3)°, respectively. The dihedral angle between the planes S−C1−C2−C3−C4 and C5−C6−C7−C8−C9−C10 is 89.2°, so that these planes are almost perpendicular.

In conclusion, we have synthesized two new manganese thiophene derivatives, **1**(sil) and **1**(Mn), and studied their reaction with nucleophiles. Except with Grignard reagents, nucleophiles usually attack the C5 position. Grignard reagents attack the sulfur atom to yield manganese *S*-R-thiophene carbonyls. Diaryl disulfides were obtained by refluxing manganese S-phenylthiophene carbonyls **3** with Me_3NO in benzene. *S*-Phenylthiophenium salts were liberated in reasonable yields from the reaction of manganese *S*-phenylthiophene carbonyls **3** with $NOBF_4$. The mechanism of the formation of compounds **3** is currently being explored.

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Supporting Information Available: Tables of atomic coordinates and equivalence isotropic displacement coordinates, anisotropic thermal parameters, full bond distances and bond angles, and hydrogen atom coordinates of **2**(sil,P(O)(OMe)$_2$), **3**(Mn,Ph), and **5**(Me,*p*-tolyl) (15 pages). Ordering information is given on any current masthead page.

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