3664 *Organometallics* **1996,** *15,* 3664−3669

# Preparation of Chromium−Manganese Diarene Heterobimetallic Complexes Using a $Mn(CO)_3^+$ Transfer Reaction

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*Received March 12, 1996*[⊗]

The reaction of mono-$Cr(CO)_3$ complexes of a number of aromatic compounds containing two arene groups with the $Mn(CO)_3^+$ transfer agent $[(naphthaleneMn(CO)_3]^+$ gave new Cr/Mn diarene heterobimetallic compounds, e.g., $(OC)_3Cr(\eta^6\text{-}C_6H_5CH{=}CHC_6H_5\text{-}\eta^6)Mn(CO)_3^+$. This and two others of these compounds were characterized by X-ray diffraction. The two metal carbonyl groups were found to be on the same face of the aromatic hydrocarbon molecules in a *syn* arrangement.

Heterobimetallic compounds have received considerable attention due to the opportunity for observing cooperative chemical behavior.[2] Although a wide variety of heterobimetallic compounds have been prepared,[3] it is difficult to systematically devise a strategy for the synthesis of particularly desired products, e.g., $\pi$-hydrocarbon-bridged chromium−manganese heterobimetallic compounds.

Recently we found the easy and general method to make (arene)$Mn(CO)_3^+$ via transfer of $Mn(CO)_3^+$ from the (polyarene)$Mn(CO)_3^+$.[4] It seems likely that the $Mn(CO)_3^+$ transfer might serve as a valuable and important reaction to Cr−Mn diarene heterobimetallic complexes generated by substitution of the labile polyarene ligand of (polyarene)$Mn(CO)_3^+$ by an incoming (diarene)chromium ligand. In hopes of discovering a rational route to the synthesis of new Cr−Mn diarene heterobimetallic compounds, (naphthalene)$Mn(CO)_3^+$ was reacted with (diarene)chromium complexes. In this paper, we report the synthesis of new Cr−Mn diarene heterobimetallic compounds **2**, **4**, **6**, **8**, **10**, **12**, **14**, and **16** (Scheme 1).

## Experimental Section

All reactions were conducted under nitrogen using standard Schlenk type flasks. Workup procedures were done in air.

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

Compounds **1**, **3**, **5**, **7**, **9**, and **11** in Scheme 1, $[(C_{10}H_8)Mn(CO)_3]BF_4$, *trans*-styrylthiophene and *trans*,*trans*-1-phenyl-4-thienyl-1,3-butadiene were synthesized according to the published procedures.[4−6]

**Synthesis.** Typical procedure: To 20 mL of $CH_2Cl_2$ in a Schlenk flask were added (arene)$Cr(CO)_3$ (0.56 mmol) and [(naphthalene)$Mn(CO)_3]BF_4$ (0.56 mmol). The resulting solution was refluxed for 7 h. During refluxing, some of the product was deposited as solids. After evaporation of the solvent, the residue was dissolved in acetone or nitromethane (5 mL) and then precipitated by adding excess diethyl ether (50 mL). The precipitates were filtered out and washed with $CH_2Cl_2$ (10 mL × 2) or diethyl ether (10 mL × 2).

**[($\mu$-$\eta^6$:$\eta^6$-biphenyl)CrMn(CO)$_6$]BF$_4$ (2).** Yield: 31%. IR: $\nu$(CO) 2072, 2012, 1970, 1892 cm$^{-1}$. $^1H$ NMR ($d_6$-acetone): $\delta$ (7.25 (d, 6.8 Hz, 2 H, H$^{6,10}$), 7.16 (t, 6.7 Hz, 2 H, H$^{7,9}$), 6.89 (t, 6.2 Hz, 1 H, H$^8$), 6.52 (d, 6.3 Hz, 2 H, H$^{1,5}$), 6.04 (t, 6.1 Hz, 1 H, H$^3$), 5.91 (t, 6.4 Hz, 2 H, H$^{2,4}$) ppm. Anal. Calcd for $C_{18}H_{10}BCrF_4MnO_6$: C, 41.88; H, 1.94. Found: C, 41.35; H, 1.95.

**[($\mu$-$\eta^6$:$\eta^6$-9,10-dihydroanthracene)CrMn(CO)$_6$]BF$_4$ (4).** Yield: 73%. IR: $\nu$(CO) 2096, 2032, 1962, 1872 cm$^{-1}$. $^1H$ NMR ($d_6$-acetone): $\delta$ 7.09 (dd, 4.9, 2.9 Hz, 2 H, H$^{1,4}$), 6.88 (dd, 4.9, 2.9 Hz, 2 H, H$^{2,3}$), 5.99 (dd, 4.8, 2.8 Hz, 2 H, H$^{6,9}$), 5.74 (dd, 4.8, 2.8 Hz, 2 H, H$^{7,8}$), 4.36 (d, 18.0 Hz, 2 H, H$^{5,10}$), 4.18 (d, 18.0 Hz, 2 H, H$^{5,10}$) ppm. Anal. Calcd for $C_{20}H_{12}BCrF_4MnO_6$: C, 44.32; H, 2.23. Found: C, 44.37; H, 2.34.

**[($\mu$-$\eta^6$:$\eta^6$-xanthene)CrMn(CO)$_6$]BF$_4$ (6).** Yield: 37%. IR: $\nu$(CO) 2072, 2020, 1966, 1879 cm$^{-1}$. $^1H$ NMR ($d_6$-acetone): $\delta$ 7.28 (td, 1.0, 6.5 Hz, 1 H, H$^7$), 7.09 (dd, 1.2, 6.1 Hz, 1 H, H$^6$), 6.85 (dd, 1.0, 7.1 Hz, 1 H, H$^9$), 6.58 (td, 1.2, 6.3

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

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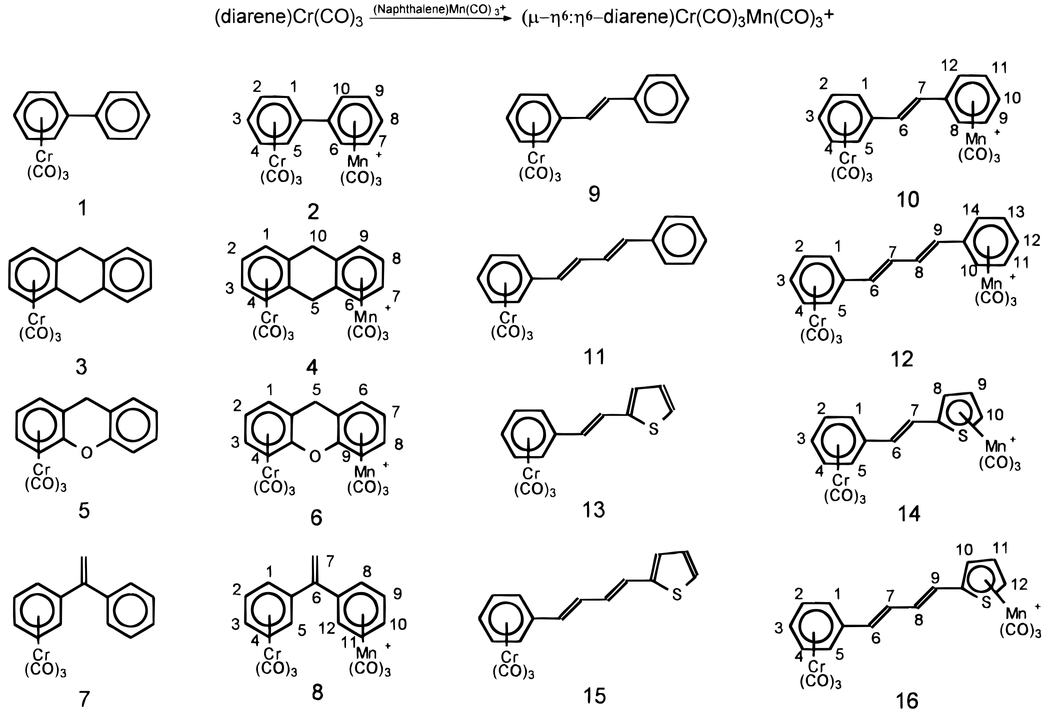
S0276-7333(96)00189-6 CCC: $12.00

**Scheme 1**



Hz, 1 H, $H^8$), 6.07 (d, 6.1 Hz, 1 H, $H^4$), 5.88 (m, 2 H, $H^{1,3}$), 5.50 (m, 1 H, $H^2$), 4.67 (d, 20.6 Hz, 1 H, $H^5$), 4.35 (d, 20.6 Hz, 1 H, $H^5$) ppm. Anal. Calcd for $C_{19}H_{10}BCrF_4MnO_7$: C, 41.93; H, 1.84. Found: C, 41.53; H, 1.86.

**[(μ-η⁶:η⁶-1,1-diphenylethylene)CrMn(CO)₆]BF₄ (8).** Yield: 39%. IR: ν(CO) 2080, 2024, 1962, 1880 $cm^{-1}$. $^1H$ NMR ($d_6$-acetone): δ 7.15 (dd, 2.0, 6.8 Hz, 2 H, $H^{8,12}$), 7.00 (m, 3 H, $H^{9,10,11}$), 6.38 (d, 1.0 Hz, 1 H, $H^{7a}$), 6.34 (d, 1.0 Hz, 1 H, $H^{7b}$), 5.96 (dd, 1.0, 6.6 Hz, 2 H, $H^{1,5}$), 5.86 (t, 6.1 Hz, 1 H, $H^3$), 5.73 (t, 6.8 Hz, 2 H, $H^{2,4}$) ppm. Anal. Calcd for $C_{20}H_{12}BCrF_4MnO_6$: C, 44.30; H, 2.22. Found: C, 43.81; H, 2.27.

**[(μ-η⁶:η⁶-*trans*-stilbene)CrMn(CO)₆]BF₄ (10).** Yield: 51%. IR: ν(CO) 2080, 2024, 1958, 1883 $cm^{-1}$. $^1H$ NMR ($d_6$-acetone): δ 7.58 (d, 16.3 Hz, 1 H, $H^7$), 7.29 (d, 16.3 Hz, 1 H, $H^6$), 7.12 (m, 2 H, $H^{8,12}$), 7.07 (m, 2 H, $H^{9,11}$), 6.79 (m, 1 H, $H^{10}$), 6.10 (dd, 1.2, 5.9 Hz, 2 H, $H^{1,5}$), 5.75 (m, 3 H, $H^{2,3,4}$) ppm. Anal. Calcd for $C_{20}H_{12}BCrF_4MnO_6$: C, 44.30; H, 2.22. Found: C, 43.97; H, 2.21.

**[(μ-η⁶:η⁶-1,4-diphenyl-1,3-butadiene)CrMn(CO)₆]BF₄ (12).** Yield: 68%. IR: ν(CO) 2076, 2020, 1958, 1885 $cm^{-1}$. $^1H$ NMR ($d_6$-acetone): δ 7.66 (dd, 15.4, 10.4 Hz, 1 H, $H^8$), 7.20 (dd, 15.4, 3.2 Hz, 1 H, $H^9$), 7.03 (m, 4 H, $H^{10,11,13,14}$), 6.73 (m, 3 H, $H^{6,7,12}$), 5.99 (d, 2.6 Hz, 2 H, $H^{1,5}$), 5.73 (t, 2.6 Hz, 3 H, $H^{2,3,4}$) ppm. Anal. Calcd for $C_{22}H_{14}BCrF_4MnO_6$: C, 46.52; H, 2.48. Found: C, 46.63; H, 2.68.

**[{η⁶-*trans*-1-phenyl-2-(2′-thienyl)ethene}Cr(CO)₃] (13).** 1-Phenyl-2-(2′-thienyl)ethene (0.145 g, 0.78 mmol), *n*-$Bu_2O$ (30 mL), and THF (10 mL) were charged into a Schlenk flask equipped with reflux condenser. After addition of $Cr(CO)_6$ (0.25 g, 1.27 mmol) to the flask, the reaction mixture was refluxed for 2 days. The reaction mixture was cooled to room temperature under $N_2$. The crude product was purified by column chromatography on silica gel eluting with *n*-hexane/$Et_2O$ (v/v, 4/1). The product was obtained as red solids (0.217 g, 87%). IR: ν(CO) 1949, 1859 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ 7.20 (d, 17.8 Hz, 1 H, $H^7$), 7.09 (d, 3.4 Hz, 1 H, $H^8$), 7.08 (d, 3.6 Hz, 1 H, $H^{10}$), 7.01 (dd, 3.6, 5.2 Hz, 1 H, $H^9$), 6.44 (d, 15.8 Hz, 1 H, $H^6$), 5.50 (d, 6.6 Hz, 2 H, $H^{1,5}$), 5.42 (t, 7.6 Hz, 2 H, $H^{2,4}$), 5.28 (dd, 6.0 Hz, 1 H, $H^3$) ppm. Anal. Calcd for $C_{15}H_{10}CrO_3S$: C, 55.68; H, 3.25. Found: C, 55.90; H, 3.31.

**[{μ-η⁶:η⁶-*trans*-1-phenyl-2-(2′-thienyl)-ethene}CrMn(CO)₆]BF₄(14).** [(naphthalene)Mn(CO)₃]BF₄ (0.263 g, 0.74 mmol) and **13** (0.20 g, 0.62 mmol) were dissolved in 30 mL of $CH_2Cl_2$. After being refluxed for 2 h, the reaction mixture was cooled to room temperature and concentrated. Deep red solids (0.256 g, 75%) were obtained by recrystallization with $CH_3NO_2$ and diethyl ether. IR: ν(CO) 2064, 2012, 1964, 1892 $cm^{-1}$. $^1H$ NMR ($CD_3NO_2$): (7.03 (d, 2.0 Hz, 2 H, $H^{8,9}$), 6.81 (t, 2.4 Hz, 1 H, $H^{10}$), 6.77 (d, 14.0 Hz, 1 H, $H^7$), 6.70 (d, 16.0 Hz, 1 H, $H^6$), 5.93 (t, 5.8 Hz, 2 H, $H^{2,4}$), 5.79 (t, 5.8 Hz, 1 H, $H^3$), 5.60 (d, 6.4 Hz, 2 H, $H^{1,5}$) ppm. Anal. Calcd for $C_{18}H_{10}BCrF_4MnO_6S$: C, 39.42; H, 1.84. Found: C, 39.05; H, 1.90.

**[{η⁶-(*1E,3E*)-1-phenyl-4-(2′-thienyl)butadiene}Cr(CO)₃] (15).** 1-Phenyl-4-(2′-thienyl)-butadiene (0.30 g, 1.41 mmol), *n*-$Bu_2O$ (30 mL), and THF (10 mL) were charged into a Schlenk flask equipped with reflux condenser. After addition of $Cr(CO)_6$ (0.467 g, 2.12 mmol) to the flask, the reaction mixture was refluxed for 2 days. The reaction mixture was cooled to room temperature under $N_2$. The crude product was purified by column chromatography on silica gel eluting with *n*-hexane/$Et_2O$ (v/v, 4/1). The product was obtained as red solids (0.438 g, 89%). IR: ν(CO) 1953, 1867 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ 7.22 (d, 4.6 Hz, 1 H, $H^{12}$), 7.02 (d, 3.0 Hz, 1 H, $H^{10}$), 6.99 (t, 3.6 Hz, 1 H, $H^{11}$), 6.95−6.59 (m, 3 H, $H^{7,8,9}$), 6.16 (d, 14.8 Hz, 1 H, $H^6$), 5.47 (d, 6.0 Hz, 2 H, $H^{1,5}$), 5.40 (t, 6.4 Hz, 2 H, $H^{2,4}$), 5.27 (m, 1 H, $H^3$) ppm. Anal. Calcd for $C_{17}H_{12}CrO_3S$: C, 58.62; H, 3.47. Found: C, 58.45; H, 3.73.

**[{μ-η⁶:η⁶-(*1E,3E*)-1-phenyl-4-(2′-thienyl)butadiene}CrMn(CO)₆]BF₄(16).** [(naphthalene)Mn(CO)₃]BF₄ (0.24 g, 0.68 mmol) and **15** (0.20 g, 0.57 mmol) were dissolved in 30 mL of $CH_2Cl_2$. After being refluxed for 2 h, the reaction mixture was cooled to room temperature and concentrated. Deep red solids (0.178 g, 54%) were obtained by recrystallization with $CH_3NO_2$ and diethyl ether. IR: ν(CO) 2058, 2014, 1955, 1875 $cm^{-1}$. $^1H$ NMR ($d_3$-nitromethane): (7.35 (d, 5.2 Hz, 1 H, $H^{12}$), 7.14 (d, 2.2 Hz, 1 H, $H^{10}$), 7.06 (t, 3.8 Hz, 1 H, $H^{11}$), 7.03−6.60 (m, 3 H, $H^{6,7,8}$), 6.33 (d, 15.4 Hz, 1 H, $H^9$), 5.84 (m, 2 H, $H^{1,5}$), 5.67 (m, 3 H, $H^{2,3,4}$) ppm. Anal. Calcd for $C_{20}H_{12}BCrF_4MnO_6S$: C, 41.84; H, 2.11. Found: C, 41.69; H, 2.19.

**[(μ-η⁶:η⁶-9,10-dihydroanthracene)CrMn(CO)₅PPh₃]BF₄ (17).** Yield: 84%. IR: ν(CO) 1997, 1958, 1870 $cm^{-1}$. $^1H$ NMR ($d_6$-acetone): δ 7.64 (m, 15 H, $PPh_3$), 6.67 (dd, 3.17, 4.64 Hz, 2 H, $H^{5,8}$), 5.97 (m, 4 H, $H^{1,4,6,7}$), 5.71 (dd, 2.80, 4.64 Hz, 2 H, $H^{2,3}$), 4.26 (d, 17.33 Hz, 2 H, $H^{9,10}$), 4.10 (d, 18.0 Hz, 2 H, $H^{9,10}$) ppm. Anal. Calcd for $C_{37}H_{27}BCrF_4MnO_5P$: C, 57.25; H, 3.51. Found: C, 57.18; H, 3.47.

**Table 1. Crystal Data and Structure Refinements for 10, 14, and 16**

| | **10** | **14** | **16** |
|---|---|---|---|
| formula | $C_{20}H_{12}BCrF_4MnO_6$ | $C_{18}H_{10}BCrF_4MnO_6S$ | $C_{20}H_{12}BCrF_4MnOS$ |
| fw | 542.05 | 548.07 | 574.11 |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/n$ | $P2_1/a$ |
| $a$, Å | 9.8778(8) | 7.323(2) | 12.408(4) |
| $b$, Å | 20.053(2) | 23.822(3) | 13.276(4) |
| $c$, Å | 11.633(1) | 11.990(2) | 14.028(6) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 108.397(7) | 99.81(2) | 101.41(3) |
| $\gamma$, deg | 90 | 90 | 90 |
| $V$, Å$^3$ | 2186.5(3) | 2060.9(6) | 2265.3(13) |
| $Z$ | 4 | 4 | 4 |
| $d$(calcd), Mg/m$^3$ | 1.647 | 1.766 | 1.683 |
| cryst size, mm$^3$ | 0.5 × 0.4 × 0.2 | 0.1 × 0.2 × 0.4 | 0.5 × 0.4 × 0.2 |
| tot. no. of observns | 2835 | 2956 | 2983 |
| no. of unique data ($I > 2((I)$) | 2663 | 2738 | 2810 |
| $2\theta$ range/deg | 4−45 | 3.4−50 | 4.2−50 |
| no. params refined | 298 | 308 | 326 |
| $R1 = (\Sigma\|F_o - F_c\|)/\Sigma\|F_o\|$ | 0.0598 | 0.0630 | 0.0801 |
| w$R2^a$ | 0.1509 | 0.1595 | 0.2370 |
| GOF on $F^2$ | 1.065 | 1.070 | 1.081 |

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c2)]\}/\Sigma[w(F_o^2)^2]\}^{1/2}$.

**[($\mu$-$\eta^6$:$\eta^6$-*trans*-stilbene)CrMn(CO)$_5$PPh$_3$]BF$_4$ (18).** Yield: 52%. IR: $\nu$(CO) 2008, 1965, 1893 cm$^{-1}$. $^1$H NMR ($d_6$-acetone): $\delta$ 7.61 (m, 15 H, PPh$_3$), 7.27 (d, 15.9 Hz, 1 H, H$^7$), 7.08 (d, 16.4 Hz, 1 H, H$^6$), 6.42 (m, 4 H, H$^{8,9,11,12}$), 6.23 (m, 1 H, H$^{10}$), 6.00 (m, 2 H, H$^{1,5}$), 5.74 (m, 3 H, H$^{2,3,4}$) ppm. Anal. Calcd for $C_{37}H_{27}BCrF_4MnO_5P$: C, 57.25; H, 3.51. Found: C, 56.79; H, 3.65.

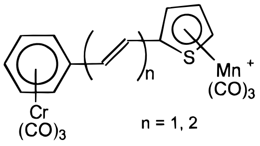
**[($\eta^6$-9,10-dihydroanthracene)Cr(CO)$_2$PPh$_3$] (19).** Yield: 29%. IR: $\nu$(CO) 1878, 1824 cm$^{-1}$. $^1$H NMR (CDCl$_3$): (7.31 (m, 19 H, Ph and H$^{5,6,7,8}$), 4.90 (m, 2 H, H$^{2,3}$), 4.30 (m, 2 H, H$^{1,4}$), 3.95 (d, 16.8 Hz, 2 H, H$^{9,10}$), 3.66 (d, 17.1 Hz, 2 H$^{9,10}$) ppm. HRMS ($m/z$): M$^+$ calc, 550.1154; obsd, 550.1026.

**[($\eta^6$-*trans*-stilbene)Cr(CO)$_2$PPh$_3$] (20).** Yield: 54%. IR: $\nu$(CO) 1872, 1827 cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 7.33 (m, 20 H, Ph and H$^{8,9,10}$), 6.76 (d, 16.1 Hz, 1 H, H$^6$), 6.57 (d, 17.1 Hz, 1 H, H$^7$), 4.88 (m, 2 H, H$^{2,4}$), 4.82 (m, 1 H, H$^3$), 4.68 (m, 2 H, H$^{1,5}$) ppm.

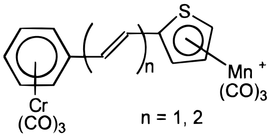
**X-ray Structure Determinations of 10, 14, and 16.** All X-ray data were collected with use of an Enraf-Nonius CAD4 automated diffractometer equipped with an Mo X-ray tube and a graphite crystal monochromator.

Red-colored crystals of **10** were grown from a nitromethane/diethyl ether solution of **10**. A red crystal of approximate dimensions 0.5 × 0.4 × 0.2 mm$^3$ was used for crystal and intensity data collection. Details on crystal and intensity data for **10** are given in Table 1. Red-colored crystals of **14** were grown from nitromethane/diethyl ether solution of **14**. A red crystal of approximate dimensions 0.4 × 0.2 × 0.1 mm$^3$ was used for crystal and intensity data collection. Details on crystal and intensity data for **14** are given in Table 1. Red-colored crystals of **16** were grown from nitromethane/diethyl ether solution of **16**. A red crystal of approximate dimensions 0.5 × 0.2 × 0.4 mm$^3$ was used for crystal and intensity data collection. Details on crystal and intensity data for **16** are given in Table 1.

The orientation matrix and unit cell parameters were determined from 25 machine-centered reflections. Axial photographs were used to verify the unit cell choice. Intensities of three check reflections were monitored after every 1 h during data collection. Data were corrected for Lorentz and polarization effects. The intensity data were empirically corrected with $\psi$-scan data. All calculations were carried out on a personal computer with the SHELXS-86 and SHELXL-93 programs;[7,8] the structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares with SHELXL-93. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically using a riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached. Final atomic positional parameters for non-hydrogen atoms for **10**, **14**, and **16** are in the Supporting Information. The anion tetrafluoroborate is disordered and the thermal ellipsoids at C10 of **14** and C12 of **16** indicated possible disorders. The thiophene rings in **14** and **16** can be disordered due to the presence of two diastereomers **A** and **B**. At first, an occupancy ratio of 1:1 was used to refine the crystal structures. Finally the occupancy ratios converged to 77:23 and 87:13 for **14** and **16**, respectively. The selected bond distances and bond angles for **10**, **14**, and **16** are shown in Table 2. The parameters listed in Tables 1 and 2 are for the structures refined with consideration of the disordering.



A



B

## Results and Discussion

In the thermal preparation of tricarbonylchromium complexes of polycyclic arenes by the reaction of polycyclic arene and Cr(CO)$_6$, if the reaction time was prolonged or if a large excess of Cr(CO)$_6$ was used, then the second product, bis(tricarbonylchromium) complexes, was obtained. Thus, under controlled reaction condition, mono(tricarbonylchromium) complexes of polycyclic arenes were obtained. The uncoordinated ring will be available for complexing with other organometallic moieties such as Mn(CO)$_3^+$. However, the second coordination usually requires severe reaction conditions such as quite basic or quite acidic conditions. Thus there have been relatively rare examples of diarene heterobimetallic compounds. Recently we have published the mild Mn(CO)$_3$ + transfer via (naphthalene)-Mn(CO)$_3^+$.[4]

(Diarene)chromium complexes **1**, **3**, **5**, **7**, **9**, and **11** are known compounds.[5] Compounds **13** and **15** are synthesized from *trans*-styrylthiophene and *trans*,*trans*-1-phenyl-4-thienyl-1,3-butadiene in the yields 87% and

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(7) Scheldrick, G. M. SHELXS-86, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1986.

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

**Table 2. Selected Bond Distances (Å) and Bond Angles (deg)**

| | | | | | |
|---|---|---|---|---|---|
| | | Compound **10** | | | |
| Cr1–C1 | 2.212(6) | Cr1–C11 | 1.836(7) | C1–C2 | 1.408(9) |
| Mn2–C21 | 2.207(6) | Mn2–C24 | 2.163(6) | C21–C22 | 1.391(9) |
| C11–O11 | 1.154(8) | C32–O32 | 1.144(9) | C21–C27 | 1.511(11) |
| C7–C27 | 1.204(11) | C1–C7 | 1.502(11) | C5–C6 | 1.396(10) |
| C12–Cr1–C11 | 89.4(3) | Cr1–C11–O11 | 178.9(7) | C6–C1–C2 | 118.1(6) |
| C1–C7–C27 | 125.4(10) | C31–Mn2–C32 | 89.9(3) | Mn2–C31–O31 | 178.6(6) |
| C22–C21–C26 | 122.0(6) | C22–C21–C27 | 114.0(7) | C23–C24–C25 | 119.9(6) |
| | | Compound **14** | | | |
| Mn–C03 | 1.809(7) | Mn–C9 | 2.197(8) | Mn–C12 | 2.13(3) |
| Mn–S | 2.329(4) | S–C9 | 1.751(9) | S–C12 | 1.71(2) |
| C9–C10 | 1.40(2) | C9–C8 | 1.494(11) | C7–C8 | 1.240(11) |
| C1–C7 | 1.496(11) | C1–C6 | 1.411(10) | Cr–C1 | 2.223(6) |
| C02–Mn–C01 | 91.4(3) | C9–Mn–S | 45.4(2) | C10–Mn–S | 70.7(4) |
| C10–C9–S | 110.6(8) | C9–C8–C7 | 124.1(8) | C1–C7–C8 | 123.2(9) |
| C2–C1–C6 | 117.2(6) | Cr–C04–O04 | 178.2(7) | C1–Cr–C4 | 79.0(2) |
| | | Compound **16** | | | |
| Cr–C02 | 1.843(9) | Cr–C1 | 2.222(9) | Cr–C4 | 2.190(9) |
| C1–C2 | 1.396(12) | C02–O02 | 1.144(10) | C1–C7 | 1.478(11) |
| C8–C9 | 1.435(11) | C9–C10 | 1.310(13) | Mn–S | 2.335(4) |
| Mn–C11 | 2.180(8) | Mn–C05 | 1.810(9) | C05–O05 | 1.146(11) |
| C01–Cr–C02 | 89.6(4) | Cr–C01–O01 | 178.7(8) | C2–C1–C6 | 118.1(8) |
| C1–C7–C8 | 128.6(9) | C8–C9–C10 | 128.1(9) | Mn–C05–O05 | 176.9(9) |
| C11–S–C14 | 90.2(5) | S–C11–C12 | 113.7(10) | C9–C10–C11 | 124.0(10) |

89%, respectively.[6] Interestingly, the $Cr(CO)_3$ moiety coordinated only the phenyl ring. The marked preference of the $Cr(CO)_3$ group for the phenyl rather than heterocyclic ring has been demonstarted in (benzothiophene)$Cr(CO)_3$,[9] (dibenzothiophene)$Cr(CO)_3$,[10] (benzofuran)$Cr(CO)_3$,[11] (indole)$Cr(CO)_3$,[12] and (2-phenylthiophene)$Cr(CO)_3$.[13] The coordination of the $Cr(CO)_3$ group to the phenyl ring was verified by the upfield shifts of the phenyl ring protons in $^1H$ NMR spectra and X-ray structural studies of **10**, **14**, and **16**. In contrast with the phenyl preference of $Cr(CO)_3$ moiety, the $Mn(CO)_3^+$ group prefers heterocyclic rings to phenyl rings.[14]

The reactions of (naphthalene)$Mn(CO)_3^+$ with (diarene)chromium complexes **1**, **3**, **5**, **7**, **9**, **11**, **13**, and **15** give the Cr–Mn diarene complexes **2**, **4**, **6**, **8**, **10**, **12**, **14**, and **16** in moderate yields (31–75%). Compounds **2**, **4**, **6**, **8**, **10**, **12**, **14**, and **16** have been characterized by IR, $^1H$ NMR, and elemental analysis, and all data are consistent with their formulations as compounds **2**, **4**, **6**, **8**, **10**, **12**, **14**, and **16**. Since the bridged ligands except 9,10-dihydroanthracene are $\pi$-delocalized systems, the Cr–Mn metal systems might be electronically linked. The stretching frequencies of metal carbonyls are sensitive to the change of electron density at the metal site or other ligands. A $Mn(CO)_3^+$ moiety has a stronger electron-attracting ability than a $Cr(CO)_3$ moiety. Thus, we expected that the carbonyl stretching frequencies of the $Cr(CO)_3$ moieties in **2**, **4**, **6**, **8**, **10**, **12**, **14**, and **16** would be shifted to the higher values. As expected, the carbonyl stretching frequencies (1970–1872 $cm^{-1}$) of the $Cr(CO)_3$ moieties in **2**, **4**, **6**, **8**, **10**, **12**, **14**, and **16** are somewhat higher than those (1958–1859 $cm^{-1}$) in **1**, **3**, **5**, **7**, **9**, **11**, **13**, and **15**. However, the carbonyl stretching frequencies (2096–2012 $cm^{-1}$) of the $Mn(CO)_3^+$ moieties in **2**, **4**, **6**, **8**, **10**, **12**, **14**, and **16** do not show any remarkable differences compared with those of monometallic manganese complexes. In the $^1H$ NMR, the protons of phenyl ring attached to the $Cr(CO)_3$ showed large upfield shifts. However, the protons of phenyl or thiophene rings coordinated to $Mn(CO)_3^+$ had very similar chemical shifts of the protons of free phenyl or thiophene rings.

Under the well-known Fischer–Hafner ($Mn(CO)_5Br$, $AlCl_3$),[15] silver salt (AgX (X = $ClO_4$, $BF_4$), $Mn(CO)_5Br$),[16] or trifluoroacetic anhydride (TFAA) reaction conditions ($Mn_2(CO)_{10}$, TFAA),[17] monometallic manganese complexes were obtained. During the metalation of manganese carbonyls, the chromium carbonyls are not tolerable and easily removed. Most of Cr–Mn heterobimetallic compounds except **8** are quite stable. The yields of Cr–Mn heterobimetallic compounds are quite dependent upon the bridging $\pi$-hydrocarbon rings. It is inferred that the poor yields and instabilities of Cr–Mn heterobimetallic compounds containing short bridging $\pi$-hydrocarbon rings might be due to the *syn* arrangement of the two metal moieties as can be seen in the crystal structures of **10**, **14**, and **16**. Thus, as the distance between Cr and Mn moieties decreases, the steric repulsion between the two metal moieties increases and the yield and stability decrease. When we compared the yield of **6** with that of **4**, we expected some electronic effects on the yields.

We have succeeded in solving the molecular structures of **10**, **14**, and **16**. The ORTEP drawings of the molecular structures of **10**, **14**, and **16** are shown in Figures 1–3 with the numbering scheme employed. Selected bond distances and angles for **10**, **14**, and **16** are given in Table 2. For the crystal structure of **10**,

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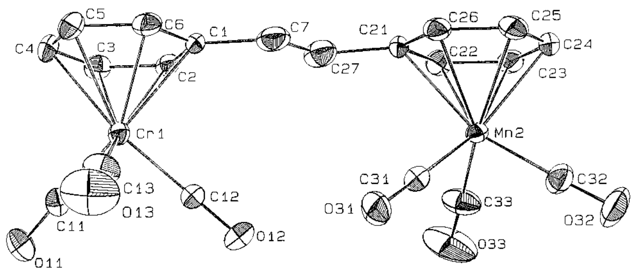

**Figure 1.** ORTEP drawing of **10**.

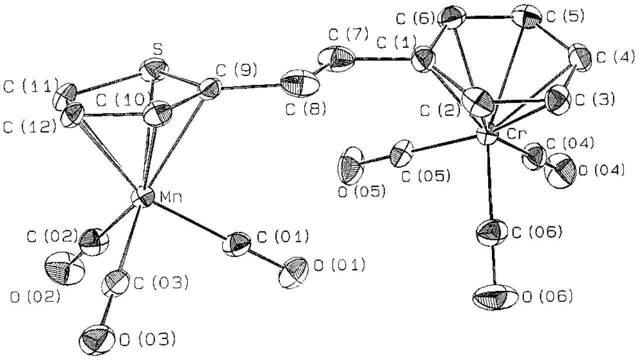

**Figure 2.** ORTEP drawing of **14**.

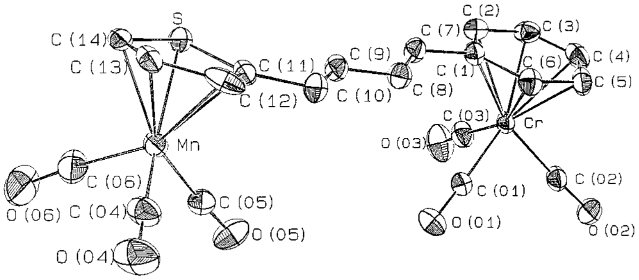

**Figure 3.** ORTEP drawing of **16**.

the anion tetrafluoroborate is disordered. For the crystal structures of **14** and **16**, there are disorders in thiophene rings as well as disorders in the counteranions. The thiophene rings in **14** and **16** can be disordered due to the presence of two diastereomers. The occupancy ratios converged to 77:23 and 87:13 for **14** and **16**, respectively. Thus the bond lengths and angles involving the disordered atoms are not very precise. A detailed discussion of the structural parameters is therefore inappropriate, but it is clear that the molecular structures consist of dinuclear systems with the Cr and Mn atoms bridged by the $\pi$-hydrocarbon ligands. Surprisingly, the two metals in **10**, **14**, and **16** are on the same face of bridging $\pi$-hydrocarbons in *syn* arrangements. At first we expected *anti* isomers due to the steric repulsion. Most bimetallic compounds linked by carbocyclic ligands have an *anti* arrangement.[18] However, there have been some reports on the *syn* arrangement.[19] Bell *et al.*[19b] reported the preparation and molecular structures of *cis*- and *trans*-($\mu$-2,7-dimethyl-*as*-indacene)bis(manganese tricarbonyl). According to their report, the *cis* isomer was a minor product. Recently, Amor *et al.* reported[20] the stereoselective synthesis of *cis* and *trans* isomers of $[\{Mo(CO)_3Cl\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H(SiMe_2))_2\}]$. They observed the stereoselective formation of the *cis* isomer even when a solution containing a mixture of both *cis* and *trans* isomers of the ligand was used. Thus they explained that the reaction was kinetically controlled, as the *trans* isomer would probably be thermodynamically preferred from steric considerations. However, in the cases of **10**, **14**, and **16** there should be more than one conformer in the solutions. Thus it seems likely that the isomeric mixture is separated during crystallization, toward the crystallization of the *syn* isomer. We anticipated that the *syn* arrangement would be achieved more good packing than the *anti* arrangement in the crystal lattice. For **10**, the manganese atom is located 1.670 Å below the plane of phenyl ring and the chromium atom is located 1.707 Å below the plane of the phenyl ring. The two phenyl rings are planar with maximum deviation of 0.007 Å. The torsion angle between the two phenyl rings is 3.4°. The carbon atoms on the *trans*-stilbene moiety are roughly in the same plane. For **14**, the manganese atom is located 1.771 Å below the plane of thiophene ring and the chromium atom is located 1.714 Å below the plane of the phenyl ring. The torsion angle between the phenyl and thiophene rings is 24°. For **16**, the manganese atom is located 1.770 Å below the plane of the thiophene ring and the chromium atom is located 1.706 Å below the plane of the phenyl ring. The torsion angle between the phenyl and thiophene rings is 12.63°. We expected that the *trans*-stilbene, *trans*-1-phenyl-2-(2′-thienyl)ethene, and *trans*,*trans*-1-phenyl-4-(2′-thienyl)butadiene would be rather rigid systems and the two complexed rings would be coplanar. However, the torsion angles between the phenyl and thiophene rings in **14** and **16** are larger than that in **10**. It is likely that steric interaction between the proton on the α carbon to the thiophene and the 3-H on the thiophene ring causes this lack of planarity.

Treatment of **4** and **10** with $PPh_3$ gave **17** and **18**, respectively (Scheme 2). Due to the high electrophilicities of $(arene)Mn(CO)_3{}^+$,[21] $PPh_3$ selectively attacks the manganese carbonyls. When the $PPh_3$-substituted chromium compounds $[(\eta^6\text{-9,10-dihydroanthracene})Cr(CO)_2PPh_3]$ (**19**) and $[(\eta^6\text{-}trans\text{-stilbene})Cr(CO)_2PPh_3]$ (**20**) were reacted with $(naphthalene)Mn(CO)_3{}^+$, we only recovered the reactants.

In conclusion, we have demonstrated that the synthesis of chromium−manganese heterobimetallic complexes using a $Mn(CO)_3{}^+$ transfer reaction constitutes an exceptionally mild procedure and can be utilized to

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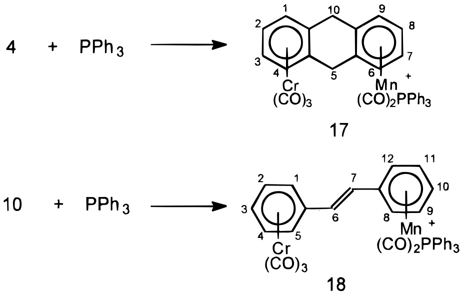
**Scheme 2**



coordinate arenes that fail to react satisfactorily by the other available methods. Current efforts are directed at exploring the potential cooperative chemical effects introduced by the near proximity of chromium and manganese centers.

**Acknowledgment.** This work was supported by grants through the Basic Research Institute Program from the Ministry of Education of Korea, the Ilju Foundation, the Center for Molecular Catalysis, and the Korea Science and Engineering Foundation.

**Supporting Information Available:** Tables of atomic coordinates and equivalent isotropic parameters, complete bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **10**, **14**, and **16** (17 pages). Ordering information is given on any current masthead page.

OM960189G