Novel Reactions of Cationic Carbyne Complexes of Manganese and Rhenium with Polymetal Carbonyl Anions. An Approach to Trimetal Bridging Carbyne Complexes[†]

Nu Xiao,[‡] Qiang Xu,*,[§] Susumu Tsubota,[§] Jie Sun,[‡] and Jiabi Chen*,[‡]

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China, and National Institute of Advanced Industrial Science and Technology, AIST, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Received February 19, 2002

The reaction of a cationic carbyne complex of manganese, $[(\eta\text{-}C_5H_5)(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**), with $[(Ph_3P)_2N]_2[Ru_3(CO)_{11}]$ (**3**) in THF at low temperature gave the heteronuclear trimetal bridging carbyne complex $[MnRu_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (**7**). A cationic carbyne complex of rhenium, $[(\eta\text{-}C_5H_5)(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**), reacts similarly with **3**, affording the corresponding bridging carbyne complex $[ReRu_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)\text{-}(CO)_6(\eta\text{-}C_5H_5)]$ (**8**) and neutral Re−carbyne dimer $[Re(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}CC_6H_5)]_2$ (**9**). The compound $[(Ph_3P)_2N]_2[Os_3(CO)_{11}]$ (**4**) only reacts with **1** to give the trimetal bridging carbyne complex $[MnOs_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (**10**) and neutral Mn−carbyne dimer $[Mn(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}CC_6H_5)]_2$ (**11**). $[(Ph_3P)_2N]_2[Fe_4(CO)_{13}]$ (**5**) also reacts with cationic carbyne complexes **1** and **2** to give the trimetal bridging carbyne complexes $[MnFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (**12**) and $[ReFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (**13**), respectively. Product **13**, when treated with an excess of PPh_3, gave the PPh_3-substituted bridging carbyne complex $[ReFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_5(PPh_3)(\eta\text{-}C_5H_5)]$ (**14**). In contrast to carbonylmetal anions **3**−**5**, $[Mo(\eta\text{-}C_5H_5)_2(H)CO][Mn_3(CO)_9(\mu\text{-}SC_6H_5)_4]$ (**6**) reacts with **1** to produce not the analogous bridging carbyne complexes but rather the mercapto−carbene complex $[(\eta\text{-}C_5H_5)(CO)_2Mn{=}C(SC_6H_5)C_6H_5]$ (**15**) and the thiolato-bridged Mo−Mn carbonyl complex $[Mo\text{-}(\eta\text{-}C_5H_5)(CO)_2(\mu\text{-}SC_6H_5)_2Mn(CO)_3]$ (**16**), while the analogous reaction of **2** with **6** yields the mercaptocarbene complex $[(\eta\text{-}C_5H_5)(CO)_2Re{=}C(SC_6H_5)C_6H_5]$ (**17**) and phenylcarbene complex $[(\eta\text{-}C_5H_5)(CO)_2Re{=}C(H)C_6H_5]$ (**18**). The structures of **7**, **9**, **13**, **14**, and **16** have been established by X-ray diffraction studies.

Introduction

Our interest in the synthesis, structure, and chemistry of di- and polymetal bridging carbene and bridging carbyne complexes stems from the fact that metal−metal-bonded cluster complexes are well known to play an important role in many catalytic reactions[1−3] and that many di- and polynuclear metal bridging carbene and bridging carbyne complexes are themselves metal clusters or the precursors of metal cluster complexes. A considerable number of dimetal bridging carbene and bridging carbyne complexes have been synthesized by

Stone and co-workers[4,5] by reactions of carbene or carbyne complexes with low-valent metal species or by reactions of neutral or anionic carbyne complexes with metal hydrides or cationic metal compounds, and several trimetal bridging carbyne complexes have also been synthesized[4,5] by Stone et al. by reactions of alkylidyne complexes, such as $[W({\equiv}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, with low-valent metal species. Recently, we have shown a convenient method for the preparation of the bridging carbene and carbyne complexes: the reactions[6,7] of highly electrophilic cationic carbyne complexes of manganese and rhenium, $[(\eta\text{-}C_5H_5)(CO)_2M{\equiv}CC_6H_5]BBr_4$ (M

[†] Dedicated to Professor Robert J. Angelici on the occasion of his 65th birthday and in recognition of his brilliant contributions to organometallic chemistry.

[‡] Shanghai Institute of Organic Chemistry.

[§] National Institute of Advanced Industrial Science and Technology.

(1) Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41.

(2) (a) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: Weinheim, Germany, 1990; p 392. (b) Maire, G. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knoezinger, H., Eds.; Elsevier: Amsterdam, The Netherlands, 1986; p 509. (c) Dickson, R. S.; Greaves, B. C. *Organometallics* **1993**, *12*, 3249.

(3) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, S. G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, p 50.

(4) Stone, F. G. A. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1989; p 11.

(5) Stone, F. G. A. *Pure Appl. Chem.* **1986**, *58*, 529.

(6) (a) Chen, J.-B.; Yu, Y.; Liu, K.; Wu, G.; Zheng, P.-J. *Organometallics* **1993**, *12*, 1213. (b) Yu, Y.; Chen, J.-B.; Chen, J.; Zheng, P.-J. *J. Chem. Soc., Dalton Trans.* **1996**, 1443.

(7) (a) Tang, Y.-J.; Sun, J.; Chen, J.-B. *Organometallics* **1999**, *18*, 4337. (b) Tang, Y.-J.; Sun, J.; Chen, J.-B. *J. Chem. Soc., Dalton Trans.* **1998**, 931. (c) Tang, Y.-J.; Sun, J.; Chen, J.-B. *J. Chem. Soc., Dalton Trans.* **1998**, 4003. (d) Tang, Y.-J.; Sun, J.; Chen, J.-B. *Organometallics* **1998**, *17*, 2945. (e) Tang, Y.-J.; Sun, J.; Chen, J.-B. *Organometallics* **2000**, *19*, 72. (f) Tang, Y.-J.; Sun, J.; Chen, J.-B. *Organometallics* **1999**, *18*, 2459.

= Mn, Re), with mono- or dimetal carbonyl anions or mixed-dimetal carbonyl anions.

In a continuation of our interest in developing the methodologies of the synthesis of transition-metal bridging carbene and carbyne complexes, we are now interested in developing a more convenient method for the preparation of trimetal bridging carbyne complexes. Thus, we carried out the study of the reactivity of tri- and polymetalcarbonyl anions with highly electrophilic cationic carbyne complexes of manganese and rhenium, $[(\eta\text{-}C_5H_5)(CO)_2M{\equiv}CC_6H_5]BBr_4$ (**1**, M = Mn; **2**, M = Re). These reactions have produced a series of new heteronuclear trimetal bridging carbyne complexes. Herein we describe these unusual reactions and the structures of the resulting products.

Experimental Section

All reactions were performed under a dry, oxygen-free N_2 atmosphere using standard Schlenk techniques. All solvents employed were of reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under N_2. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl, while petroleum ether (30–60 °C) and CH_2Cl_2 were distilled from CaH_2. Neutral alumina (Al_2O_3) was deoxygenated under high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water, and stored under N_2. The complexes $[(\eta\text{-}C_5H_5)(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**)[8] and $[(\eta\text{-}C_5H_5)(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**)[9] were prepared as previously described. The compounds $[(Ph_3P)_2N]_2[Ru_3(CO)_{11}]$ (**3**),[10] $[(Ph_3P)_2N]_2[Os_3(CO)_{11}]$ (**4**),[10] $[(Ph_3P)_2N]_2[Fe_4(CO)_{13}]$ (**5**),[11] and $[Mo(\eta\text{-}C_5H_5)_2(H)CO][Mn_3(CO)_9(\mu\text{-}SC_6H_5)_4]$ (**6**)[12] were all prepared by literature methods.

The IR spectra were measured on a Perkin-Elmer 983G spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature in acetone-d_6 with TMS as the internal reference using a Bruker AM-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Hewlett-Packard 5989A spectrometer. Melting points obtained on samples in sealed, nitrogen-filled capillaries are uncorrected.

Reaction of $[(\eta\text{-}C_5H_5)(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (1) with $[(Ph_3P)_2N]_2[Ru_3(CO)_{11}]$ (3) To Give $[MnRu_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (7). To 0.59 g (1.0 mmol) of freshly prepared (in situ) compound **1** dissolved in 60 mL of THF previously cooled to −100 °C was added 1.01 g (0.52 mmol) of $[(Ph_3P)_2N]_2[Ru_3(CO)_{11}]$ (**3**). The solution turned immediately from brown-red to dark brown. The reaction mixture was stirred at −100 to −50 °C for 4 h, during which time the dark brown solution turned dark brown-red. The resulting mixture was evaporated to dryness under vacuum at −50 to −45 °C, and the dark brown-red residue was chromatographed on an alumina (neutral, 100–200 mesh) column (1.6 × 15–25 cm) at −25 °C with petroleum ether/CH_2Cl_2 (5:2) as the eluant. The brown-red band was eluted and collected. The solvent was removed under vacuum at −20 °C, and the residue was recrystallized from petroleum ether/CH_2Cl_2 at −80 °C to give 0.161 g (51%, based on **1**) of brown-red crystals of **7**: mp 146–148 °C dec; IR (CH_2Cl_2) ν(CO) 2091 (s), 2071 (vs), 2030 (vs), 1999 (s), 1929 (m), 1835 (s, br) cm^{-1}; ^1H NMR (CD₃COCD₃) δ 7.86–7.21 (m, 5H, C_6H_5), 4.64 (s, 5H, C_5H_5), −18.08 (s, 1H,

μ-H); MS m/e 294 [M$^+$ − Ru₂(CO)₅] 204 [Mn(CO)₃(C₅H₅)]$^+$, 176 [Mn(CO)₂(C₅H₅)]$^+$, 148 [Mn(CO)(C₅H₅)]$^+$. Anal. Calcd for $C_{20}H_{11}O_8MnRu_2$: C, 37.75; H, 1.74. Found: C, 37.59; H, 2.00.

Reaction of $[(\eta\text{-}C_5H_5)(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (2) with 3 To Give $[ReRu_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (8) and $[Re(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}CC_6H_5)]_2$ (9). Similar to the procedures used in the reaction of **1** with **3**, freshly prepared compound **2** (0.80 g, 1.10 mmol) was treated with **3** at −100 to −50 °C for 4 h, during which time the brown solution turned dark brown-red. After removal of the solvent under vacuum at −50 to −45 °C, the dark brown-red residue was chromatographed on Al_2O_3 at −25 °C with petroleum ether/CH_2Cl_2 (5:2) as the eluant. The brown-red band which eluted first was collected, and then a deep red band was eluted with petroleum ether/CH_2Cl_2 (2:1). The solvents were removed from the above two eluates under vacuum, and the residues were recrystallized from petroleum ether/CH_2Cl_2 at −80 °C. From the first fraction, 0.201 g (48%, based on **2**) of **8** as brown-red crystals were obtained: mp 106–108 °C dec; IR (CH_2Cl_2) ν(CO) 2086 (m), 2062 (vs), 2022 (vs, br), 1999 (w), 1928 (m), 1868 (m) cm^{-1}; ^1H NMR (CD₃COCD₃) δ 7.62 (m, 2H, C_6H_5), 7.33 (m, 2H, C_6H_5), 7.08 (m, 1H, C_6H_5), 5.36 (s, 5H, C_5H_5), −17.52 (s, 1H, μ-H); MS m/e 686 (M$^+$ − 3CO), 500 [M$^+$ − Ru(CO)₃], 342 [M$^+$ − Ru₂(CO)₅], 252 [Re(CO)(C₅H₅)]$^+$. Anal. Calcd for $C_{20}H_{11}O_8ReRu_2$: C, 31.30; H, 1.45. Found: C, 31.24; H, 1.66. From the second fraction, 0.090 g (21%, based on **2**) of blackish red crystalline **9** was obtained: mp 100–102 °C dec; IR (CH_2Cl_2) ν(CO) 1975 (s), 1943 (s) cm^{-1}; ^1H NMR (CD₃COCD₃) δ 7.79–7.32 (m, 10H, C_6H_5), 5.09 (s, 10H, C_5H_5); MS m/e 794 (M$^+$), 766 [M$^+$ − CO], 682 [M$^+$ − 4CO], 486 [M$^+$ − 2CO − C₅H₅Re], 430 [M$^+$ − 4CO − C₅H₅Re], 336 [Re(CO)₃(C₅H₅)]$^+$, 252 [Re(CO)(C₅H₅)]$^+$. Anal. Calcd for $C_{28}H_{20}O_4Re_2$: C, 42.42; H, 2.54. Found: C, 42.08; H, 2.80.

Reaction of 1 with $[(Ph_3P)_2N]_2[Os_3(CO)_{11}]$ (4) To Give $[MnOs_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (10) and $[Mn(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}CC_6H_5)]_2$ (11). Compound **1** (0.60 g, 1.01 mmol) was treated, in a manner similar to that described above for the reaction of **1** with **3**, with $[(Ph_3P)_2N]_2[Os_3(CO)_{11}]$ (**4**; 1.02 g, 0.52 mmol) at −100 to −50 °C for 4 h, during which time the brown-red solution turned brown-green. Further treatment of the brown-green resulting solution similar to that described in the reaction of **2** with **3** afforded 0.190 g (47%, based on **1**) of brown-red crystals of **10** and 0.064 g (24%, based on **1**) of **11** as blackish red crystals. **10**: mp 138–140 °C dec; IR (CH_2Cl_2) ν(CO) 2088 (s), 2061 (vs), 2022 (vs), 1990 (s), 1921 (m), 1850 (m) cm^{-1}; ^1H NMR (CD₃COCD₃) δ 7.67–6.98 (m, 5H, C_6H_5), 4.54 (s, 5H, C_5H_5), −17.95 (s, 1H, μ-H); MS m/e 790 (M$^+$ − CO), 762 (M$^+$ − 2CO), 706 (M$^+$ − 4CO), 176 [Mn(CO)₂(C₅H₅)]$^+$. Anal. Calcd for $C_{20}H_{11}O_8MnOs_2$: C, 29.49; H, 1.36. Found: C, 29.65; H, 1.43. **11**: mp 121–123 °C dec; IR (CH_2Cl_2) ν(CO) 1978 (s), 1939 (s) cm^{-1}; ^1H NMR (CD₃COCD₃) δ 7.64–7.28 (m, 10H, C_6H_5), 4.96 (s, 10H, C_5H_5); MS m/e 530 (M$^+$), 502 [M$^+$ − CO], 418 [M$^+$ − 4CO], 298 [M$^+$ − 4CO − MnC₅H₅], 204 [Mn(CO)₃(C₅H₅)]$^+$. Anal. Calcd for $C_{28}H_{20}O_4Mn_2$: C, 63.41; H, 3.80. Found: C, 63.45; H, 4.02.

Reaction of 1 with $[(Ph_3P)_2N]_2[Fe_4(CO)_{13}]$ (5) To Give $[MnFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (12). The procedure used in the reaction of **1** (0.85 g, 1.42 mmol) with $[(Ph_3P)_2N]_2[Fe_4(CO)_{13}]$ (**5**; 1.11 g, 0.67 mmol) was the same as that for the reaction of **1** with **3** at −100 to −50 °C for 5–6 h, during which time the blackish solution gradually turned purple red. The resulting mixture was evaporated to dryness under vacuum at −50 to −45 °C, and the dark purple-red residue was chromatographed on Al_2O_3 at −25 °C with petroleum ether/CH_2Cl_2 (5:2) as the eluant. The purple-red band was eluted and collected. The solvent was removed under vacuum, and the residue was recrystallized from petroleum ether/CH_2Cl_2 (10:1) at −80 °C to give 0.33 g (85%, based on **1**)

(8) Fischer, E. O.; Meineke, E. W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 1140.

(9) Fischer, E. O.; Chen, J.-B.; Scherzer, K. *J. Organomet. Chem.* **1983**, *253*, 231.

(10) Karet, G. B.; Voss, E. J.; Sailor, M. J.; Shriver, D. F. *Inorg. Synth.* **1998**, *32*, 277.

(11) Whitmire, K. H.; Ross, J.; Cooper, C. B., III; Shriver, D. F. *Inorg. Synth.* **1982**, *21*, 66.

(12) Dias, A. R.; Galvao, A.; Garcia, M. H.; Villa de Brito, M. J. *J. Organomet. Chem.* **2001**, *620*, 276.

of **12**[13] as deep purple-red crystals: mp 106 °C dec; IR (CH$_2$-Cl$_2$) ν(CO) 2077 (s), 2048 (vs), 2014 (s), 1989 (s), 1868 (s, br), 1831 (w) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 8.01 (m, 2H, C$_6$H$_5$), 7.55 (m, 2H, C$_6$H$_5$), 7.33 (m, 1H, C$_6$H$_5$), 4.80 (s, 5H, C$_5$H$_5$), −23.80 (s, 1H, μ-H); MS m/e 546 (M$^+$), 518 [M$^+$ − CO], 490 [M$^+$ − 2CO], 462 [M$^+$ − 3CO], 434 [M$^+$ − 4CO], 406 [M$^+$ − 5CO], 378 [M$^+$ − 6CO], 350 [M$^+$ − 7CO], 322 [M$^+$ − 8CO]. 266 [M$^+$ − Fe$_2$(CO)$_6$]. Anal. Calcd for C$_{20}$H$_{11}$O$_8$MnFe$_2$: C, 44.00; H, 2.03. Found: C, 43.86; H, 2.08.

Reaction of 2 with 5 To Give [ReFe$_2$(μ-H)(μ-CO)$_2$(μ_3-CC$_6$H$_5$)(CO)$_6$(η-C$_5$H$_5$)] (13). Using the same procedures for the reaction of **1** with **5**, compound **2** (0.73 g, 1.00 mmol) was treated with **5** (0.828 g, 0.50 mmol) to give 0.300 g (88%, based on **2**) of deep purple-red crystals of **13**: mp 140 °C dec; IR (CH$_2$-Cl$_2$) ν(CO) 2072 (s), 2041 (vs), 2004 (s), 1982 (s), 1894 (s, br), 1851 (w) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.68 (m, 2H, C$_6$H$_5$), 7.36 (m, 2H, C$_6$H$_5$), 7.10 (m, 1H, C$_6$H$_5$), 5.40 (s, 5H, C$_5$H$_5$), −23.09 (s, 1H, μ-H); MS m/e 678 (M$^+$), 650 [M$^+$ − CO], 622 [M$^+$ − 2CO], 594 [M$^+$ − 3CO], 566 [M$^+$ − 4CO], 538 [M$^+$ − 5CO], 510 [M$^+$ − 6CO], 482 [M$^+$ − 7CO], 454 [M$^+$ − 8CO]. 398 [M$^+$ − Fe$_2$(CO)$_6$]. Anal. Calcd for C$_{20}$H$_{11}$O$_8$ReFe$_2$: C, 35.47; H, 1.64. Found: C, 35.27; H, 1.73.

Reaction of 13 with PPh$_3$ To Give [ReFe$_2$(μ-H)(μ-CO)$_2$-(μ_3-CC$_6$H$_5$)(CO)$_5$(PPh$_3$)(η-C$_5$H$_5$)] (14). To 0.010 g (0.015 mmol) of **13** dissolved in 30 mL of THF at −20 °C was added 0.015 g (0.057 mmol) of PPh$_3$. The mixture was stirred at −20 to 5 °C for 24 h, during which time the dark purple-red solution turned purple-red. After the solution was evaporated at 0 °C under vacuum to dryness, the residue was chromatographed on Al$_2$O$_3$ at 0 °C with petroleum ether/CH$_2$Cl$_2$ (5:1) as the eluant. The purple-red band was eluted and collected. The solvent was removed in vacuo, and the crude product was recrystallized from petroleum ether/CH$_2$Cl$_2$ at −80 °C to give 0.012 g (91%, based on **13**) of purple-red crystals of **14**: mp 166 °C dec; IR (CH$_2$Cl$_2$) ν(CO) 2048 (s), 1993 (vs), 1977 (sh), 1940 (s), 1867 (s, br), 1810 (m) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.39−7.36 (m, 20H, C$_6$H$_5$), 5.38 (m, 2H, CH$_2$Cl$_2$), 5.25 (s, 5H, C$_5$H$_5$), −22.06 (d, 1H, μ-H); MS m/e 568 (M$^+$ − PPh$_3$ − 3CO), 512 [M$^+$ − PPh$_3$ − 5CO], 398 [M$^+$ − PPh$_3$ − Fe$_2$(CO)$_5$], 84 (CH$_2$-Cl$_2$$^+$). Anal. Calcd for C$_{37}H_{26}O_7$PReFe$_2$·CH$_2Cl_2$: C, 45.81; H, 2.83. Found: C, 45.40; H, 3.22.

Reaction of 1 with [Mo(η-C$_5$H$_5$)$_2$(H)CO][Mn$_3$(CO)$_9$(μ-SC$_6$H$_5$)$_4$] (6) To Give [(η-C$_5$H$_5$)(CO)$_2$Mn=C(SC$_6$H$_5$)C$_6$H$_5$] (15) and [Mo(η-C$_5$H$_5$)(CO)$_2$(μ-SC$_6$H$_5$)$_2$Mn(CO)$_3$] (16). Compound **1** (0.57 g, 0.96 mmol) was treated, in a manner similar to that in the reaction of **1** with **3**, with [Mo(η-C$_5$H$_5$)$_2$(H)CO]-[Mn$_3$(CO)$_9$(μ-SC$_6$H$_5$)$_4$] (**6**) (1.06 g, 0.96 mmol) in THF at −100 to −50 °C for 5 h, during which time the brown-yellow solution turned brown-green. After the solution was evaporated at −50 to −45 °C under vacuum to dryness, the residue was chromatographed on Al$_2$O$_3$ at −25 °C with petroleum ether/CH$_2$-Cl$_2$ (5:1) as the eluant. The brown-yellow band was eluted with petroleum ether/CH$_2$Cl$_2$ (5:2) and collected, and then the brown-red band was eluted with petroleum ether/CH$_2$Cl$_2$ (2:1). The solvents were removed from the above two eluates under vacuum, and the two residues were recrystallized from petroleum ether/CH$_2$Cl$_2$ or petroleum ether/THF solution at −80 °C. From the first fraction, 0.180 g (50%, based on **1**) of **15**[14] as orange-red crystals was obtained: mp 116−118 °C dec; IR (CH$_2$Cl$_2$) ν(CO) 1965 (s), 1902 (s) cm^{-1}; ^{1}H NMR (CD$_3$-COCD$_3$) δ 7.13−6.62 (m, 10H, C$_6$H$_5$), 4.92 (s, 5H, C$_5$H$_5$); MS m/e 374 (M$^+$), 346 [M$^+$ − CO], 318 [M$^+$ − 2CO], 241 [M$^+$ − 2CO − C$_6$H$_5$], 209 [M$^+$ − 2CO − SC$_6$H$_5$]. Anal. Calcd for C$_{20}$H$_{15}$O$_2$SMn: C, 64.17; H, 4.04. Found: C, 64.02; H, 4.21. From the second fraction, 0.165 g (30%, based on **6**) of **16** as brown-red crystals was obtained: mp 150 °C dec; IR (CH$_2$Cl$_2$) ν(CO) 2023 (vs), 1982 (s), 1947 (s), 1913 (m) cm^{-1}; ^{1}H NMR

(CD$_3$COCD$_3$) δ 7.55−7.52 (m, 5H, C$_6$H$_5$), 7.28−7.22 (m, 5H, C$_6$H$_5$), 6.27 (s, 5H, C$_5$H$_5$); MS m/e 492 [M$^+$ − 3CO], 464 [M$^+$ − 4CO], 436 [M$^+$ − 5CO]. Anal. Calcd for C$_{22}$H$_{15}$O$_5$S$_2$MoMn: C, 46.01; H, 2.63. Found: C, 45.71; H, 2.90.

Reaction of 2 with 6 To Give [(η-C$_5$H$_5$)(CO)$_2$Re=C-(SC$_6$H$_5$)C$_6$H$_5$] (17) and [(η-C$_5$H$_5$)(CO)$_2$Re=C(H)C$_6$H$_5$] (18). Compound **2** (0.49 g, 0.67 mmol) was treated, as used in the reaction of **1** with **3**, with **6** (0.74 g, 0.67 mmol) at −100 to −45 °C for 5 h, during which time the orange-red solution gradually turned brown-red. Further treatment in a manner similar to that described in the reaction of **1** with **6** gave 0.160 g (47%, based on **2**) of gold-yellow crystals of **17**[14] and 0.070 g (26%, based on **2**) of red crystals of **18**.[6a,15] **17**: mp 118−120 °C dec; IR (CH$_2$Cl$_2$) ν(CO) 1961 (vs), 186 (s) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.14−6.74 (m, 10H, C$_6$H$_5$), 5.51 (s, 5H, C$_5$H$_5$); MS m/e 506 (M$^+$), 478 [M$^+$ − CO], 450 [M$^+$ − 2CO], 373 [M$^+$ − 2CO − C$_6$H$_5$], 341 [M$^+$ − 2CO − SC$_6$H$_5$]. Anal. Calcd for C$_{20}$H$_{15}$O$_2$SRe: C, 47.51; H, 2.99. Found: C, 47.45; H, 3.11. **18**: mp 70 °C dec; IR (CH$_2$Cl$_2$) ν(CO) 1965 (s), 1885 (s) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 16.53 (s, 1H, C$_{carbene}$−H), 7.91−7.39 (m, 5H, C$_6$H$_5$), 6.02 (s, 5H, C$_5$H$_5$); MS m/e 398 (M$^+$), 370 [M$^+$ − CO], 342 [M$^+$ − 2CO]. Anal. Calcd for C$_{14}$H$_{11}$O$_2$Re: C, 42.31; H, 2.79. Found: C, 42.19; H, 2.81.

X-ray Crystal Structure Determinations of Complexes 7, 9, 13, 14, and 16. Single crystals of complexes **7**, **9**, **13**, **14**, and **16** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH$_2$Cl$_2$ or petroleum ether/Et$_2$O at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 2525, 3996, 9476, and 1518 independent reflections, of which 1809, 3372, 5396, and 1080 with $I > 2.00\sigma$-(I) for **7**, **13**, **14**, and **16** and 3617 with $I > 3.00\sigma(I)$ for **9** were observable, were collected with a Rigaku AFC7R and Brock Smart diffractometer at 20 °C using Mo Kα radiation with an ω−2θ scan mode.

The structures of **7**, **9**, **13**, and **14** were solved by direct methods and expanded using Fourier techniques, while the structure of **16** was solved by heavy-atom Patterson methods and expanded using Fourier techniques. For complexes **7**, **13**, and **14**, the non-hydrogen atoms were refined anisotropically. For **9** and **16**, some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. For all five complexes, the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was respectively based on 1809, 3617, 3372, 5396, and 1080 observed reflections and 278, 314, 284, 445, and 248 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.049$ and $R_w = 0.051$ for **7**, $R = 0.043$ and $R_w = 0.049$ for **9**, $R = 0.0583$ and $R_w = 0.1628$ for **13**, $R = 0.0501$ and $R_w = 0.1115$ for **14**, and $R = 0.043$ and $R_w = 0.046$ for **16**, respectively.

The details of the crystallographic data and the procedures used for data collection and reduction information for **7**, **9**, **13**, **14**, and **16** are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively. The atomic coordinates and B_{iso}/B_{eq} values, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **7**, **9**, **13**, **14**, and **16** are given in the Supporting Information. The molecular structures of **7**, **9**, **13**, **14**, and **16** are given in Figures 1−5, respectively.

Results and Discussion

Two equivalents of a cationic carbyne complex of manganese, [(η-C$_5$H$_5$)(CO)$_2$Mn≡CC$_6$H$_5$]BBr$_4$ (**1**), reacts with 1 equiv of [(Ph$_3$P)$_2$N]$_2$[Ru$_3$(CO)$_{11}$] (**3**) in THF at low temperature (−100 to −50 °C) for 4−5 h. After workup as described in the Experimental Section, the Mn−Ru

(13) Wang, R.-T.; Xu, Q. Souma. Y.; Song, L.-C.; Sun, J.; Chen, J.-B. *Organometallics* **2001**, *20*, 2226.

(14) Qiu, Z.-L.; Sun, J. Chen, J.-B. *Organometallics* **1998**, *17*, 600.

(15) Fischer, E. O.; Frank, A. *Chem. Ber.* **1978**, *111*, 3740.

Table 1. Crystal Data and Experimental Details for Complexes 7, 9, 13, 14, and 16

	7	9	13	14·CH$_2$Cl$_2$	16·CH$_2$Cl$_2$
formula	C$_{20}$H$_{11}$O$_8$MnRu$_2$	C$_{32}$H$_{28}$O$_5$Re$_2$	C$_{20}$H$_{11}$O$_8$ReFe$_2$	C$_{38}$H$_{28}$O$_7$PRe Fe$_2$	C$_{23}$H$_{17}$O$_5$Cl$_2$S$_2$MoMn
fw	636.38	864.98	677.19	996.37	659.29
space group	Cc (No. 9)	P2$_1$/n (No. 14)	P2$_1$/c (No. 14)	P2$_1$/n (No. 14)	P2$_1$2$_1$2$_1$ (No. 19)
a (Å)	18.494(6)	10.925(3)	8.2317(9)	14.4098(13)	10.967(3)
b (Å)	8.541(2)	15.318(2)	9.0035(9)	12.5868(11)	23.803(4)
c (Å)	16.124(4)	17.434(2)	27.757(3)	22.727(2)	9.691(4)
α (deg)					90
β (deg)	125.25(1)	103.12(1)	90.517(2)	97.451(2)	90
γ (deg)					90
V (Å^3)	2079(1)	2841.4(9)	2057.1(4)	4087.3(6)	2529(1)
Z	4	4	4	4	4
D$_{calcd}$ (g/cm^3)	2.032	2.022	2.187	1.619	1.731
F(000)	1232.00	1640.00	1288	1952	1312.00
μ(Mo Kα) (cm^{-1})	20.77	85.56	73.07	38.68	14.08
radiation[a]	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71069 Å)
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Brock Smart	Brock Smart	Rigaku AFC7R
temp (°C)	20	20	20	20	20
orientation rflns: no.; range (2θ) (deg)	22; 14.0−21.4	23; 13.7−21.7	2.38−27.25	4.54−47.72	19; 14.1−16.4
scan method	ω−2θ	ω−2θ	ω−2θ	ω−2θ	ω−2θ
data collecn range, 2θ (deg)	5−55.0	5−51.0	2.94−52.0	3.18−56.66	5−51.0
unique data					
total no.	2525	5504	3996	9476	1518
no. with I > 2.00σ(I)	1809	3617 (I > 3.00σ(I))	3372	5396	1080
no. of params refined	278	314	284	445	248
correcn factors: max−min	0.9082−1.0000	0.4014−1.0000	0.5992−1.0000	0.7590−1.0000	0.7994−1.0000
R[b]	0.049	0.043	0.0583	0.0501	0.043
R$_w$[c]	0.051	0.049	0.1628	0.1115	0.046
quality of fit indicator[d]	1.30	1.57	1.110	0.909	1.34
max shift/esd, final cycle	0.01	0.02	0.006	0.00000(5)	0.01
largest peak (e/Å^3)	1.24	2.27	2.857	2.491	0.49
min peak (e/Å^3)	−1.14	−1.11	−1.706	−1.165	−0.69

[a] Monochromated in incident beam. [b] $R = \sum ||F_o| - |F_c||/\sum |F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [d] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.
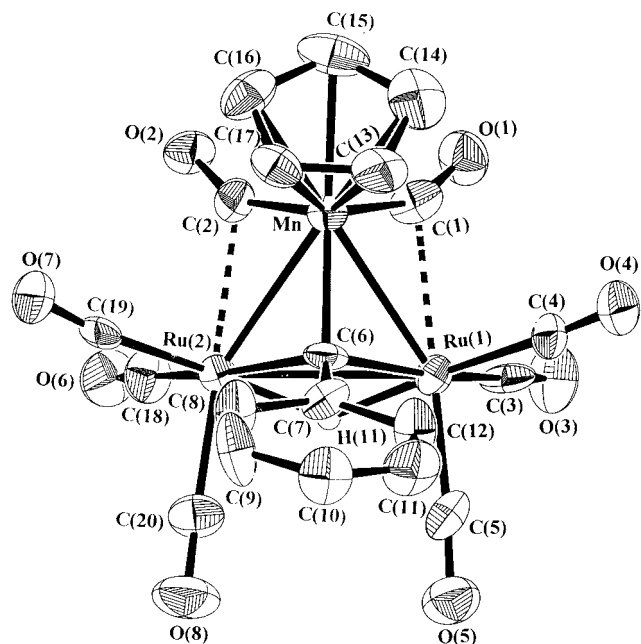

Figure 1. Molecular structure of **7**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability.

heteronuclear trimetal bridging carbyne complex [MnRu$_2$-(μ-H)(μ-CO)$_2$(μ$_3$-CC$_6$H$_5$)(CO)$_6$(η-C$_5$H$_5$)] (**7**) (eq 1) was obtained in 51% isolated yield. A cationic carbyne complex of rhenium, [(η-C$_5$H$_5$)(CO)$_2$Re≡CC$_6$H$_5$]BBr$_4$ (**2**), reacts similarly with **3** to afford the corresponding trimetal bridging carbyne complex [ReRu$_2$(μ-H)(μ-CO)$_2$(μ$_3$-CC$_6$H$_5$)-(CO)$_6$(η-C$_5$H$_5$)] (**8**) and the neutral Re−carbyne dimer
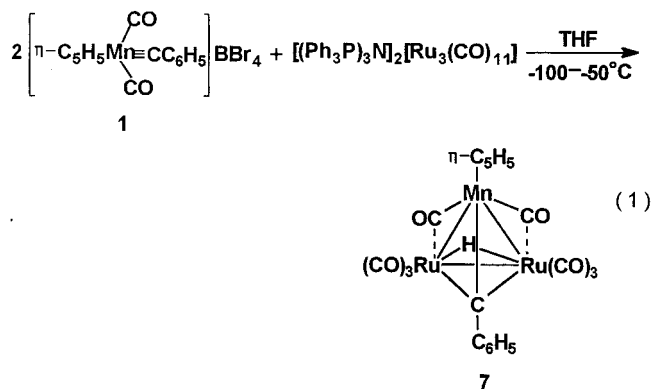
[Re(CO)$_2$(η-C$_5$H$_5$)(μ-CC$_6$H$_5$)]$_2$ (**9**) in 48% and 21% yields, respectively (eq 2).
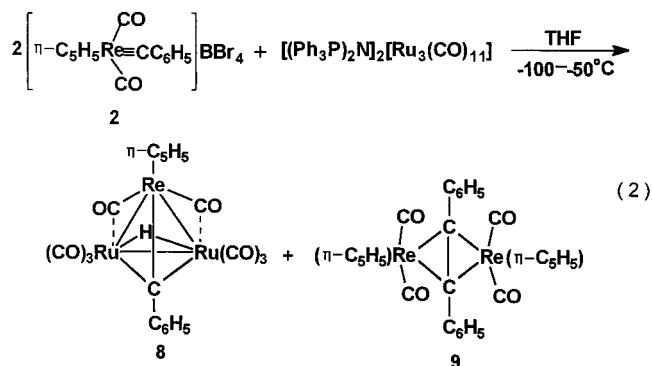
Unlike the ruthenium anionic compound **3**, the osmium anionic compound [(Ph$_3$P)$_2$N]$_2$[Os$_3$(CO)$_{11}$] (**4**) re-

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 7, 13, and 14

	7 (M = Mn, M′ = Ru)	13 (M = Re, M′ = Fe)	14 (M = Re, M′ = Fe)
M−M′(1)	2.703(3)	2.709(2)	2.7209(11)
M- M′(2)	2.708(2)	2.715(2)	2.7282(9)
M′(1)−M′(2)	2.860(2)	2.626(3)	2.6420(14)
M−C(1)	1.81(2)	1.923(18)	1.904(9)
M−C(2)	1.81(2)	1.926(16)	1.940(8)
M−C(6)	1.99(1)	2.062(12)	2.092(7)
M′(1)-C(6)	2.07(2)	1.966(12)	1.952(7)
M′(2)-C(6)	2.08(1)	1.973(11)	1.965(7)
M′(1)−C(CO) (av)	1.92	1.792	1.787
M′(2)−C(CO) (av)	1.93	1.794	1.755
M′(1)−C(1)	2.36(2)	2.526(15)	2.587(10)
M′(2)−C(2)	2.34(2)	2.476(19)	2.383(7)
M′(2)−P			2.290(2)
C(6)−C(7)	1.51(2)	1.478(19)	1.485(10)
M′(1)−H(11)	1.60	1.68(2)	1.80(2)
M′(2)−H(11)	1.70	1.68(2)	1.80(2)
M−C(Cp) (av)	2.136	2.242	2.274
M−M′(1)−M′(2)	58.17(6)	61.16(6)	61.14(3)
M−M′(2)−M′(1)	58.02(6)	60.92(6)	60.86(3)
M′(1)−M−M′(2)	63.82(6)	57.92(6)	58.00(3)
M−M′(1)−C(6)	46.9(4)	49.3(3)	49.9(2)
M−M′(2)−C(6)	46.8(4)	49.1(3)	49.7(2)
M′(1)−M−C(6)	49.5(4)	46.2(3)	45.58(19)
M′(2)−M−C(6)	49.6(4)	46.3(3)	45.79(18)
M−C(6)−M′(1)	83.6(5)	84.5(5)	84.5(3)
M−C(6)−M′(2)	83.6(5)	84.6(4)	84.5(3)
M′(1)−M′(2)-C(6)	46.2(4)	48.1(3)	47.4(2)
M′(2)−M′(1)−C(6)	46.4(4)	48.3(3)	47.78(19)
M′(1)−C(6)−M′(2)	87.3(6)	83.6(5)	84.8(3)
M−C(6)−C(7)	129(1)	131.6(9)	127.3(5)
M′(1)−C(6)−C(7)	128(1)	128.4(8)	131.2(5)
M′(2)−C(6)−C(7)	128(1)	127.7(9)	128.5(5)
M−M′(2)−P			124.83(6)
M−C(1)−O(1)	155(1)	162.8(16)	166.6(7)
M−C(2)−O(2)	152(1)	161.9(17)	157.6(6)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

acts only with cationic carbyne complex **1** under the same conditions to form the heterotrimetal bridging carbyne complex [MnOs$_2$(μ-H)(μ-CO)$_2$(μ_3-CC$_6$H$_5$)(CO)$_6$-(η-C$_5$H$_5$)] (**10**) and the neutral Mn−carbyne dimer [Mn-(CO)$_2$(η-C$_5$H$_5$)(μ-CC$_6$H$_5$)]$_2$ (**11**) in 47% and 24% isolated yields (eq 3), respectively.

(3)
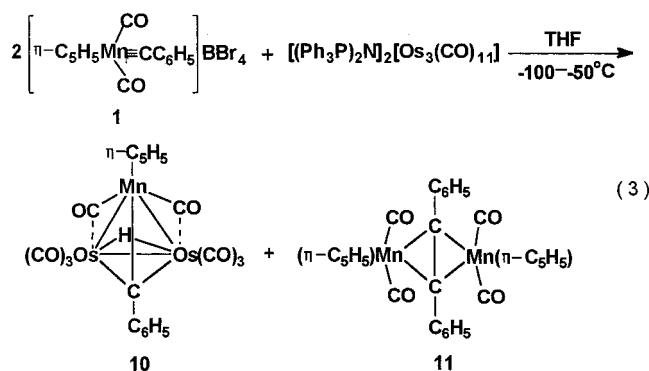
Complexes **7**−**11** are readily soluble in polar organic solvents but slightly soluble in nonpolar solvents. They are air-sensitive in solution but relatively stable as the solid. Products **7**, **8**, and **10** are formulated as heteronuclear trimetal bridging carbyne complexes possessing a μ-H bridged to the two Ru or Os atoms, while products **9** and **11** are formulated as neutral carbyne dimer complexes. The structures of complexes **7**, **8**, and **10** and complexes **9** and **11** have been established by their IR, ^{1}H NMR, and mass spectra. The existence of the bridging hydrogen in complexes **7**, **8**, and **10** was

Table 3. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 9 and 16

	Complex 9		
Re(1)−C(15)	2.23(1)	Re(1)−C(1)	1.90(1)
Re(1)−C(16)	2.30(1)	Re(1)−C(2)	1.91(1)
Re(2)−C(15)	2.29(1)	Re(2)−C(3)	1.91(1)
Re(2)−C(16)	2.25(1)	Re(2)−C(4)	1.86(1)
C(15)−C(16)	1.36(2)	Re(1)−C(Cp) (av)	2.288
C(15)−C(17)	1.46(2)	Re(2)−C(Cp) (av)	2.278
C(16)−C(23)	1.47(2)		
Re(1)−C(15)−Re(2)	113.3(5)	Re(1)−C(15)−C(17)	125.0(9)
Re(1)−C(16)−Re(2)	112.2(5)	Re(1)−C(16)−C(23)	120.0(8)
C(15)−Re(1)−C(16)	35.0(4)	Re(2)−C(15)−C(17)	118.9(8)
C(15)−Re(2)−C(16)	34.9(4)	Re(2)−C(16)−C(23)	124.4(8)
Re(1)−C(15)−C(16)	75.2(7)	C(17)−C(15)−C(16)	137(1)
Re(1)−C(16)−C(15)	69.8(6)	C(15)−C(16)−C(23)	140(1)
Re(2)−C(15)−C(16)	71.0(7)	Re(1)−C−O(CO) (av)	174.5
Re(2)−C(16)−C(15)	74.1(7)	Re(2)−C−O(CO) (av)	174.5
	Complex 16		
Mo−Mn	2.786(3)	Mn−C(3)	1.76(2)
Mo−S(1)	2.491(4)	Mn−C(4)	1.79(2)
Mo−S(2)	2.507(5)	Mn−C(5)	1.77(2)
Mn−S(1)	2.349(5)	S(1)−C(11)	1.76(2)
Mn−S(2)	2.344(5)	S(2)−C(17)	1.81(2)
Mo−C(1)	1.98(2)	Mo−C(Cp) (av)	2.32
Mo−C(2)	1.98(2)		
Mo−Mn−S(1)	57.3(1)	S(1)−Mn−S(2)	74.0(2)
Mo−Mn−S(2)	57.7(1)	Mo−S(1)−C(11)	117.9(5)
Mn−Mo−S(1)	52.5(1)	Mo−S(2)−C(17)	113.6(5)
Mn−Mo−S(2)	77.6(5)	Mn−S(1)−C(11)	112.9(5)
Mo−S(1)−Mn	70.2(1)	Mn−S(2)−C(17)	115.1(6)
Mo−S(2)−Mn	70.0(1)	Mo−C−O(CO) (av)	175.5
S(1)−Mo−S(2)	68.8(2)	Mn−C−O(CO) (av)	176.3

[a] Estimated standard deviations in the least significant figure are given in parentheses.

initially revealed by their ^{1}H NMR spectra, which showed high-field resonances at −18.08, −17.52, and −17.95 ppm, respectively, characteristic for a M−H−M species.

The structures of complexes **7** and **9** have been further confirmed by X-ray crystallography. The results of the X-ray diffraction work are summarized in Table 1, and their molecular structures are shown in Figures 1 and 2, respectively. In **7**, the triangular MnRuRu arrangement with a capping μ_3-CC$_6$H$_5$ ligand is confirmed. The three MnRuRu metal atoms construct an approximate isosceles triangle (Mn−Ru(1) = 2.703(3) Å, Mn−Ru(2) = 2.708(2) Å, and Ru(1)−Ru(2) = 2.860(2) Å). Although an analogous bridging carbyne complex with a trimetallatetrahedrane CMnFe$_2$ core, [MnFe$_2$(μ_3-CCH$_3$)(μ-CO)-(CO)$_3$(η-C$_5$H$_5$)$_2$], has been prepared by reaction[16] of [Mn$_3$(μ_3-H)$_3$(CO)$_{12}$] with *trans*-[Fe$_2$(μ-C=CH$_2$)(μ-CO)-(CO)$_2$(η-C$_5$H$_5$)$_2$], no analogous CMn−Ru$_2$ bridging carbyne complex has been reported. Only the triruthenium bridging carbyne complex [Ru$_3$(μ_3-COMe)(μ-H)$_3$(CO)$_9$] is known.[17] Complex **7** appears to be the first example of a species with Mn−Ru$_2$ and Ru−Ru bonds studied by X-ray crystallography, and hence, comparison of the Mn−Ru and Ru−Ru bond distances with others involving these elements is not possible. The two Mn−Ru bond lengths, 2.703(3) and 2.708(2) Å, respectively, are nearly the same. The Ru−Ru bond length of 2.860(2) Å in **7** is somewhat longer than that found in the triruthenium

(16) Brun, P.; Dawkins, G. M.; Green, M.; Mills, R. M.; Salaun, J. Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 1357.

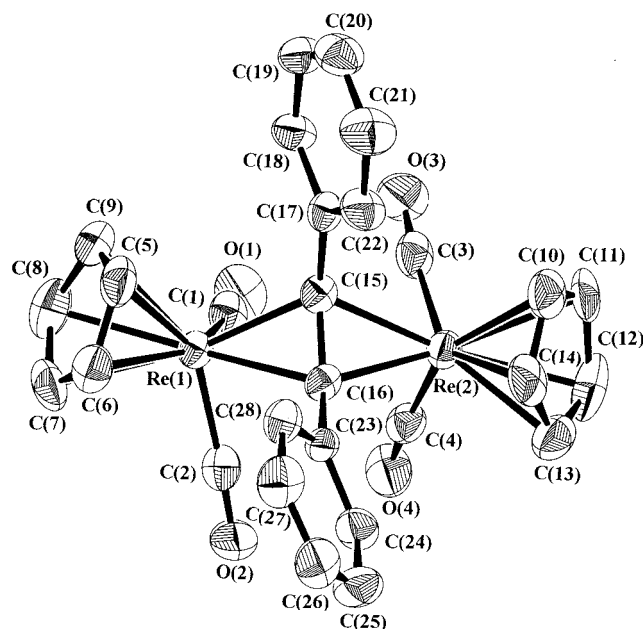(17) Keister, J. B.; Payne, M. W.; Muscatella, M. J. *Organometallics* **1983**, *2*, 219.

Figure 2. Molecular structure of **9**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability.
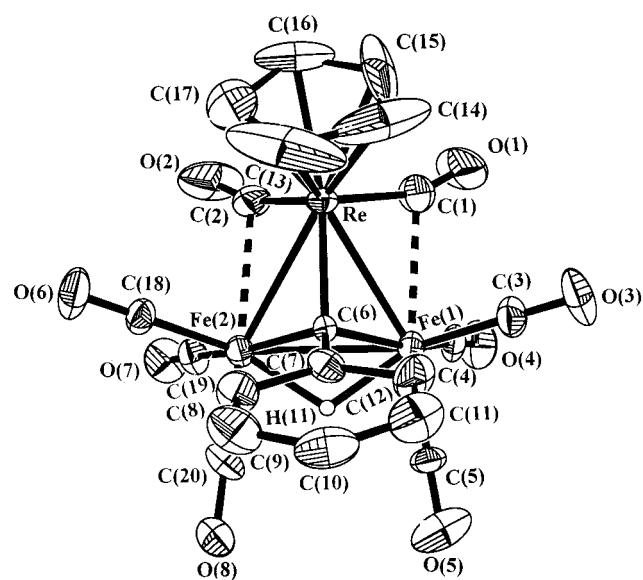

Figure 3. Molecular structure of **13**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 40% probability.
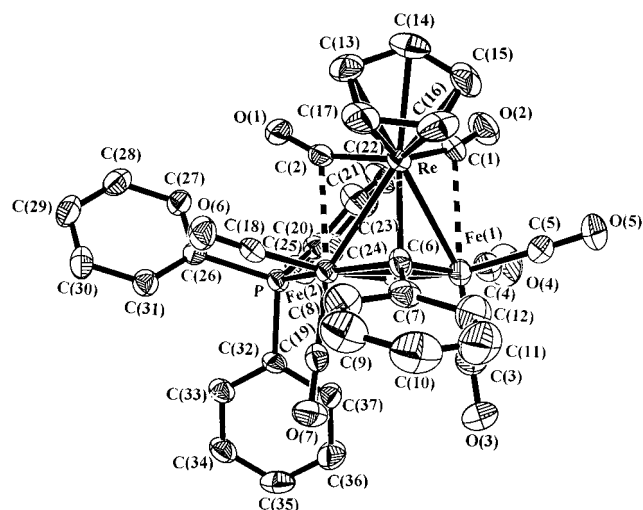

Figure 4. Molecular structure of **14**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability. CH_2Cl_2 has been omitted for clarity.
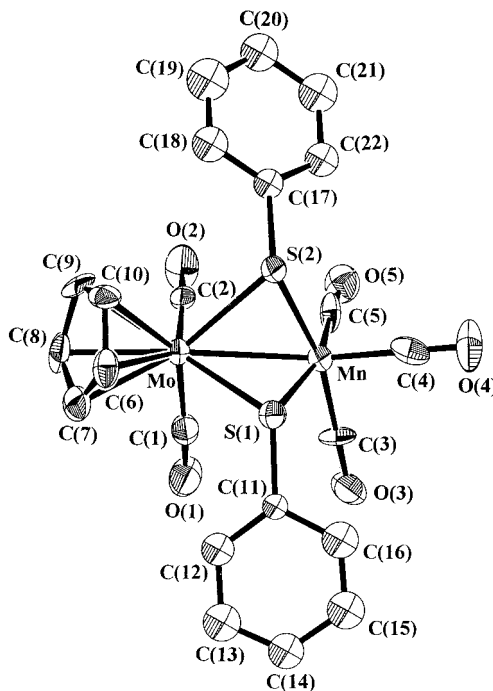

Figure 5. Molecular structure of **16**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability. CH_2Cl_2 has been omitted for clarity.

bridging carbyne complex $[Ru_3(\mu\text{-}CNMe_2)(\mu\text{-}H)(CO)_{10}]$ (average 2.818 Å).[18] The μ-C(6)−Mn, μ-C(6)−Ru(1), and μ-C(6)−Ru(2) distances are 1.99(1), 2.07(2), and 2.08-(1) Å, respectively, of which the μ-C(6)−Mn bond distance is closely related to that found in the complexes $[MnFeCo(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)]$ (1.94(1) Å)[7d] and $[MnFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (2.00-(1) Å),[13] and the two μ-C(6)−Ru bond lengths are essentially the same.

In complex **7** the Ru(1) and Ru(2) atoms are asymmetrically bridged by a hydrogen, the Ru(1)−H and Ru-(2)−H distances being 1.60 and 1.70 Å, respectively. The two Ru atoms each carry three terminal CO groups, and

the Mn atom carries two CO groups, being semibridging to the two Ru atoms, respectively (Mn−C(1)−O(1) = 155(1)°, Mn−C(1) = 1.81(2) Å; Mn−C(2)−O(2) = 152-(1)°, Mn−C(2) = 1.81(2) Å). The semibridging CO ligands reveal themselves in the IR spectrum with a strong and broad band at 1835 cm^{-1}. Compound **7** is a 48-CVE (cluster valence electron) complex, where the Mn and Ru atoms formally have 19 and 17 electrons, respectively, which probably accounts for the presence of the semibridging carbonyl and bridging hydrogen. Several di- and polynuclear ruthenium complexes with semibridging carbonyl and bridging hydrogen ligands have been reported.[19−22] The analogous 48-valence-

(18) Churchill, M. R.; Deboer, B. G.; Rotella, F. J.; Abel, E. W.; Rowly, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 7158.

(19) (a) Yawney, D. B. W.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 502. (b) Gilmore, C. J.; Woodward, P. *J. Chem. Soc. A* **1971**, 3453.

electron structure was found in the complexes $[MW_2-(\mu_3\text{-}C_2R_2)(CO)_7(\eta\text{-}C_5H_5)]$ (M = Ru, Os),[23] $[ReFeCo(\mu_3\text{-}CC_6H_5)(CO)_8(\eta\text{-}C_5H_5)]$,[7d] and $[MnFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$.[13]

The complex **9** was shown by X-ray crystallography to have a $\mu\text{-}C_2Re_2$ core arranged as a "butterfly" (interplanar angle 121.58°), with the two Re atoms each occupying one of the "wingtips" and carrying a cyclopentadienyl ligand. The molecular structure of **9** (Figure 2) shows that the two Re atoms bridged by the two PhC groups are not directly bonded to each other. The two Re atoms each carry two terminal CO groups, in addition, to bond a cyclopentadienyl group and the two μ-carbons of the PhC groups, thus giving each Re atom 18 valence electrons. In **9**, the two phenyl groups are on the opposite side of the two Re atoms. The C(15)−C(16) distance between the two bridging carbons is 1.36-(2) Å, which is between normal C−C double- and triple-bond distances, indicating that the two bridging carbons have strong interactions. The μ-C−Re distance (average 2.27 Å) is very close to that found in the analogous dirhenium complex $[Re_2(\mu\text{-}H)\{\mu\text{-}C(SiPh_3)CO\}(CO)_8]$ (average 2.28 Å), reported by Fischer et al.[24]

The dihedral angle between the plane defined by Re-(1), C(15), and C(16) and the plane comprised of Re(2), C(15), and C(16) is 121.58°. The angles between the two cyclopentadienyl ring planes and the two benzene ring planes are 49.31 and 43.97°, respectively.
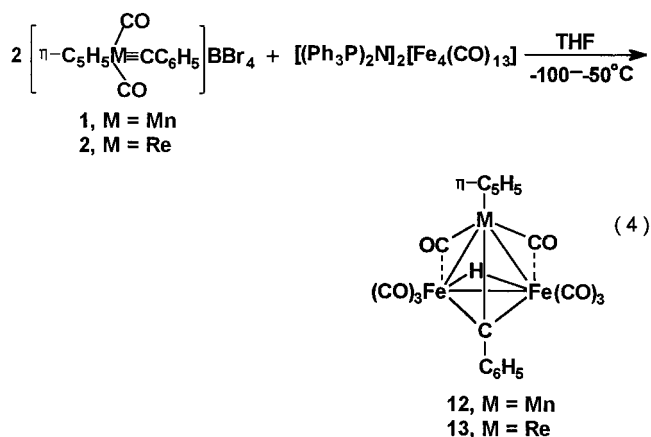
Complexes **7**, **8**, and **10** might be produced by loss of a $M'(CO)_5$ (M = Ru, Os) moiety from the $[M'_3(CO)_{11}]^{2-}$ (M' = Ru, Os) anion or by cleavage of the formed carbene intermediate $[(\eta\text{-}C_5H_5)(CO)_2M=C(C_6H_5)M'_3(CO)_{11}]$ (M = Mn, Re, M' = Ru, Os) to generate a $[M'_2(CO)_6H]^-$ species, which then becomes bonded to the carbyne or carbene carbon through the two Ru or Os atoms with bonding of the Mn or Re atom to the two Ru or Os atoms to give complexes **7** or **8** and **10**. This reaction pathway to complexes **7**, **8**, and **10** is rather analogous to that of the reaction[13] of reactive $[Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_4H_9\text{-}n)(CO)_6]^-$ anion with complex **1**. The latter was assumed to proceed via a $[Fe_2(CO)_6H]^-$ species, which attacks the carbyne carbon of cationic **1** to afford the bridging carbyne complex $[MnFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$. The origin of the H^- in these reactions could be THF solvent or water, which is a trace contaminant in the solvent THF or from glassware.

The reaction pathway to complexes **9** and **11** is presumed to be via the neutral carbyne intermediate $[(\eta\text{-}C_5H_5)(CO)_2M\equiv CC_6H_5]$ (M = Mn, Re), arising from the reduction of the carbyne cation **1** or **2**. Two $[(\eta\text{-}C_5H_5)(CO)_2M\equiv CC_6H_5]$ fragments could form the neutral carbyne dimer **9** or **11** by their dimerization. To our

knowledge, no such dimerization of carbyne species in reactions of transition-metal carbyne complexes has been reported.

Not all trimetal carbonyl anions can react with cationic carbyne complexes **1** and **2** to give trimetal bridging carbyne complexes, since the triiron carbonyl anion $[Fe_3(CO)_{11}]^{2-}$ reacted only with complex **2** to give not the trimetal bridging carbyne complex but rather the dimetal bridging carbene complex $[ReFe\{\mu\text{-}C(H)\text{-}C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$, the same product[6a] as that of the reaction of **2** with $[Fe(CO)_4]^{2-}$ or $[Fe_2(CO)_8]^{2-}$.

Like the trimetal carbonyl anions **3** and **4**, the tetrametal carbonyl anionic compound $[(PPh_3)_2N]_2[Fe_4(CO)_{13}]$ (**5**) can also react with cationic carbyne complexes **1** and **2** under the same conditions to afford the analogous trimetal bridging carbyne complexes $[MnFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (**12**) and $[ReFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)CO)_6(\eta\text{-}C_5H_5)]$ (**13**) (eq 4) in high

$$2\left[\eta\text{-}C_5H_5\overset{CO}{\underset{CO}{M\equiv CC_6H_5}}\right]BBr_4 + [(Ph_3P)_2N]_2[Fe_4(CO)_{13}] \xrightarrow[-100--50°C]{THF}$$

1, M = Mn
2, M = Re

(4)

12, M = Mn
13, M = Re

yields (>85%), respectively, among which product **12** is a known compound obtained from the reaction of **1** with reactive $[Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_4H_9\text{-}n)(CO)_6]^-$ anion and has been characterized by X-ray crystallography.[13]

The formation pathway of complexes **12** and **13** could proceed via a $[Fe_2(CO)_6H]^-$ species derived from cleavage of the $[Fe_4(CO)_{13}]^{2-}$ anion, analogous to that of ruthenium and osmium complexes **7**, **8**, and **10**, which was assumed to be via an $[M'_2(CO)_6H]^-$ (M' = Ru, Os) species.

A number of trimetal bridging carbyne complexes have been prepared by Stone et al. and by us, as mentioned in the Introduction. However, complexes **7**, **8**, **10**, **12**, and **13**, as heteronuclear trimetal bridging carbyne complexes, were synthesized first by the reaction of the cationic carbyne complexes with the polymetal carbonyl anions in one step. Undoubtedly, this is a new and convenient method for preparation of such trimetal bridging carbyne complexes.

It is equally interesting that complex **13**, when treated with an excess of PPh_3 in THF at 0 to 5 °C for 24 h, gave the PPh_3-substituted bridging carbyne complex $[ReFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_5(PPh_3)(\eta\text{-}C_5H_5)]$ (**14**) (eq 5) in 91% yield.

Unexpectedly, the Mn−Fe_2 trimetal bridging carbyne complex **12** does not react with PPh_3 under the same conditions to afford the analogous PPh_3-substituted complex, even at room temperature for 48 h.

The formulas of complexes **12**−**14** were also supported by microanalytical and spectroscopic data (Experimental

(20) Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Steinmetz, G. R.; Rosen, R. P.; Gladfelter, W. L.; Geoffroy, G. L.; Bruck, M. A.; Bau, R. *Inorg. Chem.* **1981**, *20*, 3823.

(21) (a) Haines, R. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 7, p 633. (b) Field, J. S.; Haines, R. J.; Stewart, M. W.; Woollam, S. F. *S. Afr. J. Chem.* **1993**, *46*, 45.

(22) (a) Field, J. S.; Haines, R. J.; Sundermeyer, J.; Woollam, S. F. *J. Chem. Soc., Chem. Commun.* **1991**, 1382. (b) Field, J. S.; Haines, R. J.; Stewart, M. W.; Sundermeyer, J.; Woollam, S. F. *J. Chem. Soc., Dalton Trans.* **1993**, 947.

(23) Busetto, L.; Green, M.; Howard, J. A. K.; Hessner, B.; Jeffery, J. C.; Mills, R.M.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 1101.

(24) Fischer, E. O.; Rustemeyer, P.; Orama, O.; Neugebauer, D.; Schubert, U. *J. Organomet. Chem.* **1983**, *247*, 7.

(5)
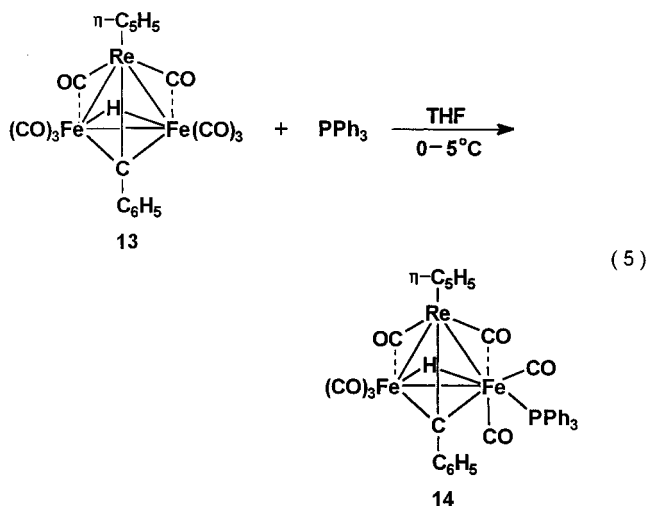
Section). Their ^{1}H NMR spectra had resonances at −23.80, −23.09, and −22.06 ppm, respectively. These resonances have undergone remarkable upfield shifts, as compared with those of the analogous bridging carbyne complexes **7**, **8**, and **10**. Their structures were further confirmed by X-ray diffraction determinations of **13** and **14**.

The structure of **13** shown in Figure 3 is very similar to that of the analogous bridging carbyne complex [MnFe$_2$(μ-H)(μ-CO)$_2$(μ_3-CC$_6$H$_5$)(CO)$_6$(η-C$_5$H$_5$)],[13] except that the Re atom in **13** is displaced by the Mn atom in the latter. The Re−Fe distances (Re−Fe(1) = 2.709(2) Å, Re−Fe(2) = 2.715(2) Å) are somewhat longer than the corresponding distances in [MnFe$_2$(μ-H)(μ-CO)$_2$(μ_3-CC$_6$H$_5$)(CO)$_6$(η-C$_5$H$_5$)] (Mn−Fe(1) = 2.606(3) Å, Mn−Fe(2) = 2.612(3) Å).[13] The μ-C(6)−Re distance of 2.062(12) Å and the average μ-C(6)−Fe distance of 1.970 Å are both slightly longer than those found in [MnFe$_2$(μ-H)-(μ-CO)$_2$(μ_3-CC$_6$H$_5$)(CO)$_6$(η-C$_5$H$_5$)] (μ-C(6)−Mn = 2.00(1) Å, average μ-C(6)−Fe = 1.94 Å),[13] while the average Fe−H bond length (1.68 Å) is somewhat shorter than that in [MnFe$_2$(μ-H)(μ-CO)$_2$(μ_3-CC$_6$H$_5$)(CO)$_6$(η-C$_5$H$_5$)] (1.77 Å).[13]

The X-ray structure study of complex **14** (Figure 4) confirmed the presence of the PPh$_3$ ligand in **14**. Its structure resembles that of **13**, except that a terminal CO ligand in the latter is displaced by PPh$_3$ in **14**. Many structural features of the principal [ReFe$_2$(μ-H)(μ-CO)$_2$-(μ_3-CC$_6$H$_5$)(CO)$_6$(η-C$_5$H$_5$)] moiety in **14** are nearly the same as those of **13**: the two Re−Fe distances, the Fe−Fe distance, the μ-C−Re distance, the two μ-C−Fe distances, and the average Re−C(Cp) distance. An apparent difference in the structures of **14** and **13** is the longer Fe−H bond length in **14** (average 1.80(2) Å), as compared to **13** (average 1.68(2) Å), and the larger angles between the benzene ring plane defined by C(7) through C(12) and the cyclopentadienyl ring plane in **14** (28.89°) as compared to **13** (23.15°), arising from the steric hindrance of the bulky PPh$_3$ group on the Fe(2) atom.

Of particular interest are the reactions of the novel trimanganese tetrathiolated incomplete cubane [Mo(η-C$_5$H$_5$)$_2$(H)CO][Mn$_3$(CO)$_9$(μ-SC$_6$H$_5$)$_4$] (**6**), reported most recently by Dias et al.[12] The freshly prepared **6** was treated with an equimolar quantity of cationic **1** in THF at low temperature (−100 to −50 °C) for 4−5 h. After

workup as described in the Experimental Section, no expected trimetal bridging carbyne complex but the (phenylthio)carbene complex [(η-C$_5$H$_5$)(CO)$_2$Mn=C-(SC$_6$H$_5$)C$_6$H$_5$] (**15**) and thiolato-bridged Mo−Mn carbonyl complex [Mo(η-C$_5$H$_5$)(CO)$_2$(μ-SC$_6$H$_5$)$_2$Mn(CO)$_3$] (**16**) (eq 6) were obtained in 50% and 30% yields, respectively, of which product **15** is a known compound and was characterized by an X-ray diffraction analysis.[14]

(6)
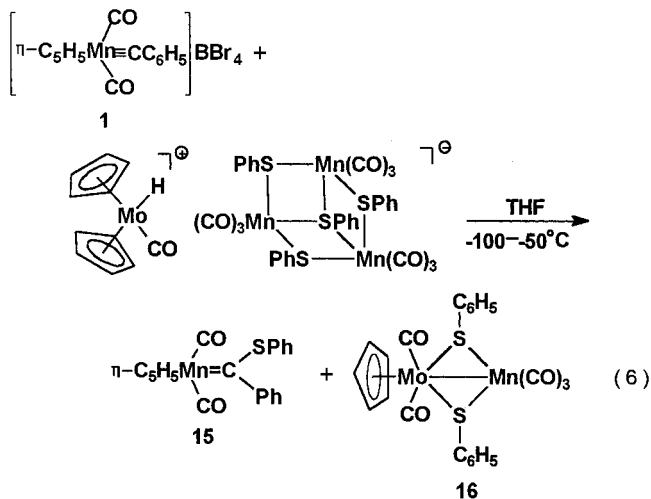
Like **1**, cationic carbyne complex **2** also reacts with anion **6**; however, the products are different. The reaction of **2** with **6** under the same conditions as those for **1** yields only the known mercaptocarbene complex [(η-C$_5$H$_5$)(CO)$_2$Re=C(SC$_6$H$_5$)C$_6$H$_5$] (**17**)[14] and phenyl-carbene complex [(η-C$_5$H$_5$)(CO)$_2$Re=C(H)C$_6$H$_5$] (**18**)[6a,15] (eq 7) in 47% and 26% yields, respectively. The forma-

(7)
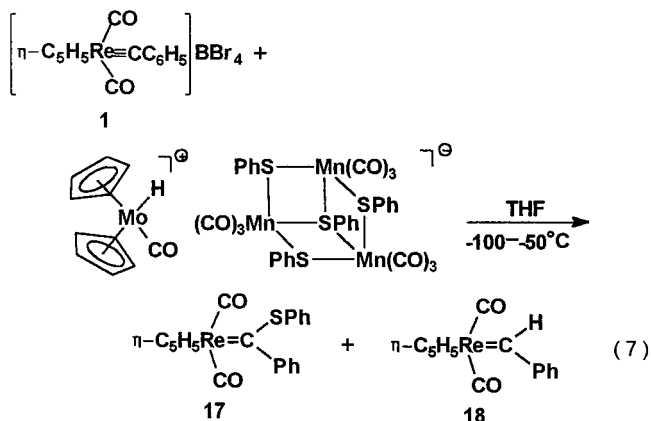
tion of products **15**−**18** is unexpected, and we do not know the chemistry involved.

The structure of complex **16** (Figure 5) was established by single-crystal X-ray diffraction. The Mo−Mn distance of 2.786(3) Å is somewhat longer than that found in the analogous compound [MoMn(CO)(η-C$_5$H$_5$)-{μ-(η^5:η^1-C$_5$H$_4$)}] (2.7605(8) Å).[25] The Mo−μ-S(1) and Mo−μ-S(2) bond lengths are 2.491(4) and 2.507(5) Å, respectively, which are nearly the same as those in the thiolato-bridged molybdenum compound [Et$_3$NH]$_2$-[Mo$_2$(NNHPh)(NNPh)(SCH$_2$CH$_2$S)$_3$(SCH$_2$CH$_2$SH)] (av-

(25) Hoxmeier, R. J.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1979**, *18*, 3462.

erage Mo$-\mu$-S = 2.501(6) Å),[26] while the distances of Mn$-\mu$-S(1) and Mn$-\mu$-S(2), 2.349(5) and 2.344(5) Å, respectively, are significantly longer than the corresponding bonds in the analogous thiolato-bridged manganese carbonyl complex [MnCr$_2$(μ-SCMe$_3$)(μ_3-S)$_2$(CO)$_3$] (Mn$-$S(1) = 2.272(2) Å, Mn$-$S(2) = 2.297(2) Å).[27]

The dihedral angle between the plane defined by Mo, Mn, and S(1) and the plane comprised of Mo, Mn, and S(2) is 91.04°. The angle between the two benzene ring planes is 140.47°. The benzene ring plane defined as C(11) through C(16) is respectively oriented 120.39 and 35.45° with respect to the MoMnS(1) plane and MoMnS-(2) plane, while the benzene ring C(17)C(18)C(19)C-(20)C(21)C(22) plane is oriented 33.35 and 121.71°, respectively, with respect to the MoMnS(1) and MoMnS-(2) planes.

The title reaction shows the novel reactions of the tri- and tetrametal carbonyl anions with cationic carbyne

complexes of manganese and rhenium, **1** and **2**, to give a series of heteronuclear trimetal bridging carbyne complexes. The reaction results indicate that the different center metals in the cationic carbyne complexes and the different carbonylmetal anions exert great influence on the reactivity of the cationic carbyne complexes and the resulting products. The title reaction may offer a convenient and useful method for preparation of trimetal bridging carbyne complexes.

Supporting Information Available: Tables of the positional parameters and B_{iso}/B_{eq} values, H atom coordinates, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **7**, **9**, **13**, **14,** and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0201359

(26) Hsieh, T.-C.; Gebreyes, K.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1172.

(27) Pasynkii, A. A.; Eremenko, I. L.; Orezsakhatov, B.; Casanov, G. S. *J. Organomet. Chem.* **1984**, *270*, 53.