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Remarkable Reactions of Cationic Carbyne Complexes of Manganese and Rhenium with Diiron Anions $[Fe_2(\mu\text{-}CO)(\mu\text{-}SeR)(CO)_6]^-$. A Route to RSe-Bridged Dimetal Bridging Carbene Complexes

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The reactions of 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), with diiron anionic compounds $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}SeR)(CO)_6]$ (**3**, R = C_6H_5; **4**, R = $p\text{-}CH_3C_6H_4$) in THF at low temperature gave the dimetal bridging carbene complexes $[MFe\{\mu\text{-}C(SeR)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (**10**, M = Mn, R = C_6H_5; **11**, M = Mn, R = $p\text{-}CH_3C_6H_4$; **13**, M = Re, R = C_6H_5; **14**, M = Re, R = $p\text{-}CH_3C_6H_4$), $[\eta\text{-}C_5H_5M(CO)_3]$ (**7**, M = Mn; **12**, M = Re), and $[Fe_2(\mu\text{-}SeR)_2(CO)_6]$ (**8**, R = C_6H_5; **9**, R = $p\text{-}CH_3C_6H_4$). Complexes **1** and **2** also react with $[MgBr][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_2H_5)(CO)_6]$ (**5**) to produce $[Fe_2(\mu\text{-}SeC_2H_5)_2(CO)_6]$ (**15**) and dimetal bridging carbene complexes $[MnFe\{\mu\text{-}C(SeC_2H_5)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (**17**) and $[ReFe\{\mu\text{-}C(SeC_2H_5)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (**18**), respectively. **2** reacts similarly with $[MgBr][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_4H_9\text{-}n)(CO)_6]$ (**6**) to give $[Fe_2(\mu\text{-}SeC_4H_9\text{-}n)_2(CO)_6]$ (**16**) and a Re−Fe bridging carbene complex $[ReFe\{\mu\text{-}C(SeC_4H_9\text{-}n)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (**19**), while the analogous reaction of **1** with **6** produced an unexpected trimetal bridging carbyne complex $[MnFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)CO)_6(\eta\text{-}C_5H_5)]$ (**20**). The structures of complexes **9**, **10**, **13**, **18**, and **20** have been established by X-ray diffraction studies.

Introduction

In view of the fact that metal−metal bonded cluster complexes are well known to play an important role in many catalytic reactions[1,2] and that many dinuclear and polynuclear metal complexes with a bridging carbene and carbyne ligand are themselves metal clusters or the precursors of metal cluster complexes, the chemistry of transition metal bridging carbene and carbyne complexes is an area of current interest. In this regard, we are interested in developing the methodologies for the synthesis of such complexes. Many dimetal bridging carbene and carbyne complexes have been synthesized by Stone and co-workers by reactions[3,4] of carbene or carbyne complexes with low-valent metal species or by reactions[5,6] of neutral or anionic carbyne complexes with metal hydrides or cationic metal compounds. In our laboratory, one of the methods for the preparation of bridging carbene and carbyne complexes has used the reactions of the highly electrophilic cationic carbyne complexes of manganese and rhenium, $[\eta\text{-}C_5H_5(CO)_2M{\equiv}CC_6H_5]BBr_4$ (M = Mn, Re), with anionic carbonylmetal compounds.[7,8] We have recently also shown the novel reaction of the reactive salts $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}RS)(CO)_6]$, developed by Seyferth and co-workers in the late 1980s, with $[\eta\text{-}C_5H_5(CO)_2M{\equiv}CC_6H_5]BBr_4$ (M = Mn, Re) to give RS-bridged dimetal bridging carbene complexes (eq 1).[9] This offers a possibility for the preparation of heteroatom-bridged bridging carbene complexes.

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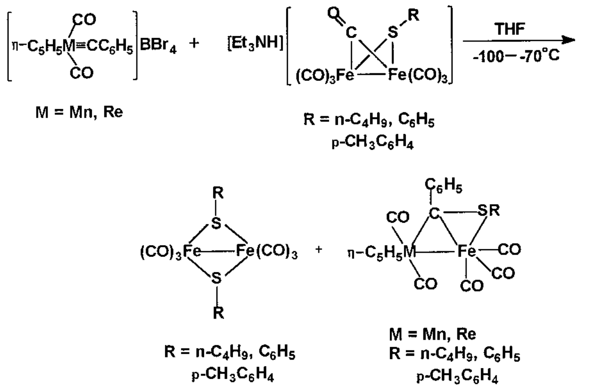

(1)

In the meantime, we have noted the applications of the $[Fe_2(\mu\text{-}CO)(\mu\text{-}SeR)(CO)_6]^-$ anions, the selenium analogue of reactive $[Fe_2(\mu\text{-}CO)(\mu\text{-}SR)(CO)_6]^-$ anions, in organometallic chemistry.[10,11] In their reactions the Fe−Fe and Fe−Se bonds are retained, and the bridging CO usually is replaced by an another bridging ligand. Although these reactive $[Fe_2(\mu\text{-}CO)(\mu\text{-}SeR)(CO)_6]^-$ anions have been extensively investigated, their reactions with cationic carbyne complexes have not been reported. To explore and compare the reactivity of the $[Fe_2(\mu\text{-}CO)(\mu\text{-}SeR)(CO)_6]^-$ anions toward the cationic carbyne complexes of manganese and rhenium, and to further examine the scope of the new method for preparation of dimetal bridging carbene and bridging carbyne complexes, we have studied the reactions of cationic carbyne complexes of manganese and rhenium, $[\eta\text{-}C_5H_5(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**) and $[\eta\text{-}C_5H_5(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**), with the diiron $[Fe_2(\mu\text{-}CO)(\mu\text{-}SeR)(CO)_6]^-$ anions, which afforded a series of novel RSe-bridged heteronuclear dimetal bridging carbene or a trimetal bridging carbyne complexes. We describe in this paper 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 (THF) and diethyl ether (Et_2O) 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. Complexes $[\eta\text{-}C_5H_5(CO)_2Mn{\equiv}C\ C_6H_5]BBr_4$ (**1**)[12] and $[\eta\text{-}C_5H_5(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**)[13] were prepared as previously described. Compounds $Fe_3(CO)_{12}$,[14] benzeneselenol,[15] 4-methylbenzeneselenol,[15] $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_6H_5)(CO)_6]$ (**3**),[11b] $[X][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_6H_4CH_3\text{-}p)(CO)_6]$ (**4**, X = Et_3NH or MgBr),[11b,16] $[MgBr][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_2H_5)(CO)_6]$ (**5**),[11b] and $[MgBr][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_4H_9\text{-}n)(CO)_6]$ (**6**)[16] 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 $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_6H_5)(CO)_6]$ (3) To Give $[\eta\text{-}C_5H_5Mn(CO)_3]$ (7), $[Fe_2(\mu\text{-}SeC_6H_5)_2(CO)_6]$ (8), and $[MnFe\{\mu\text{-}C(SeC_6H_5)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (10). To a solution of 0.81 g (1.61 mmol) of $Fe_3(CO)_{12}$ in 50 mL of THF was added 0.17 mL (1.60 mmol) of C_6H_5SeH and 0.25 mL (1.79 mmol) of Et_3N with stirring. The mixture was stirred at room temperature for 10 min, during which time the green solution turned brown-red. The resulting solution of $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_6H_5)(CO)_6]$ (**3**)[11b] was cooled to −100 °C and then poured rapidly onto 0.95 g (1.60 mmol) of freshly prepared **1** previously cooled to −100 °C with stirring. The reaction mixture was slowly warmed to −80 °C and then stirred at −80 to −50 °C for 7 h, during which time the brown-red solution turned dark brown. The resulting mixture was evaporated to dryness under vacuum at −50 to −40 °C, and the dark purple-red residue was chromatographed on an alumina (neutral, 200−300 mesh) column (1.6 × 15−25 cm) at −25 °C with petroleum ether as the eluant. The orange band which eluted first was collected, then a purple-red band was eluted with petroleum ether/CH_2Cl_2 (20:1). A third dark green band was eluted with petroleum ether/CH_2Cl_2/Et_2O (10:1:1). The solvents were removed from the above three eluates under vacuum, and the residues were recrystallized from petroleum ether/CH_2Cl_2 at −80 °C. From the first fraction, 0.016 g (5%, based on **1**) of yellow crystals of **7**[17] was obtained. **7** is a known compound and was identified by comparison of its melting point and IR and ^1H NMR spectra with those of an authentic sample.[17] From the second fraction, 0.23 g (24%, based on **1**) of red crystals of **8**[18] was obtained: mp 104 °C dec (lit.[18] 94−96 °C dec); IR (CH_2Cl_2) ν(CO) 2067 (s), 2031 (vs), 1993 (vs) cm^{-1} (lit.[18] (cyclohexane) 2061, 2031, 1998, 1991 cm^{-1}); ^1H NMR (CD_3COCD_3) δ 7.49−7.14 (m, 10H, C_6H_5); MS *m/e* 594 (M^+), 566 [M^+ − CO], 538 [M^+ − 2CO], 510 [M^+ − 3CO], 482 [M^+ − 4CO], 454 [M^+ − 5CO], 426 [M^+ − 6CO]. Anal. Calcd for $C_{18}H_{10}O_6Se_2Fe_2$: C, 36.53; H, 1.70. Found: C, 36.53; H, 1.90. From the third fraction, 0.59 g (66%, based on **1**) of **10** as blackish green crystals was obtained: mp 82 °C dec; IR (CH_2Cl_2) ν(CO) 2042 (vs), 1978 (s), 1940 (vs, br), 1888 (m), 1788 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.80−7.09 (m, 10H, C_6H_5), 4.65 (s, 5H, C_5H_5); MS *m/e* 562 [M^+], 534 [M^+ − CO], 506 [M^+ − 2CO], 478 [M^+ − 3CO], 450 [M^+ − 4CO], 422 [M^+ − 5CO], 158 [$C_6H_5SeH^+$]. Anal. Calcd for $C_{23}H_{15}O_5SeMnFe$: C, 49.23; H, 2.69. Found: C, 49.56; H, 2.72.

Reaction of 1 with $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_6H_4CH_3\text{-}p)(CO)_6]$ (4) To Give 7, $[Fe_2(\mu\text{-}SeC_6H_4CH_3\text{-}p)_2(CO)_6]$ (9), and $[MnFe\{\mu\text{-}C(SeC_6H_4CH_3\text{-}p)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (11). Compound **1** (0.95 g, 1.60 mmol) was treated, as used in the reaction of **1** with **3**, with $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_6H_4CH_3\text{-}p)(CO)_6]$ (**4**)[11b] prepared (in situ) by reaction of 0.880 g (1.75 mmol) of $Fe_3(CO)_{12}$ in 50 mL of THF with 0.302 g (1.76 mmol)

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of p-$CH_3C_6H_4SeH$ and 0.26 mL (1.83 mmol) of Et_3N, at −100 to −45 °C for 7−8 h. Further treatment as in the reaction of **1** with **3** gave 0.019 g (6%, based on **1**) of yellow crystals of **7**, 0.25 g (25%, based on **1**) of red crystals of **9**,[11a] and 0.58 g (63%, based on **1**) of blackish green crystals of **11**. **7** was identified by comparison of its mp and IR and ^1H NMR spectra. **9**: mp 122−123 °C; IR (CH_2Cl_2) ν(CO) 2066 (s), 2030 (vs), 1992 (vs) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.36−7.07 (m, 8H, $C_6H_4CH_3$), 2.28 (s, 3H, $C_6H_4CH_3$), 2.06 (s, 3H, $C_6H_4CH_3$); MS *m/e* 622 (M^+), 566 [M^+ − 2CO], 538 [M^+ − 3CO], 510 [M^+ − 4CO], 482 [M^+ − 5CO], 454 [M^+ − 6CO]. Anal. Calcd for $C_{20}H_{14}O_6Se_2Fe_2$: C, 38.75; H, 2.28. Found: C, 38.95; H, 2.32. **11**: mp 101−102 °C dec; IR (CH_2Cl_2) ν(CO) 2042 (vs), 1978 (s), 1937 (s, br), 1882 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.80−6.90 (m, 9H, C_6H_5 + $C_6H_4CH_3$), 4.64 (s, 5H, C_5H_5), 2.18 (s, 3H, $C_6H_4CH_3$); MS *m/e* 576 [M^+], 548 [M^+ − CO], 520 [M^+ − 2CO], 492 [M^+ − 3CO], 464 [M^+ − 4CO], 436 [M^+ − 5CO], 172 [$C_6H_5SeH^+$]. Anal. Calcd for $C_{24}H_{17}O_5SeMnFe$: C, 50.12; H, 2.98. Found: C, 50.19; H, 2.96.

Reaction of [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (2) with 3 To Give 8, [η-C_5H_5-$Re(CO)_3$] (12), and [ReFe{μ-C(SeC_6H_5)C_6H_5}$(CO)_5$(η-C_5H_5)] (13). Similar to the procedures used in the reaction of **1** with **3**, compound **2** (0.70 g, 0.963 mmol) was treated with **3** prepared (in situ) by the reaction of $Fe_3(CO)_{12}$ (0.540 g, 1.07 mmol) with 0.12 mL (1.13 mmol) of C_6H_5SeH and 0.18 mL (1.22 mmol) of Et_3N at −100 to −50 °C for 7−8 h. Further treatment of the resulting mixture as in the reaction of **1** with **3** afforded 0.014 g (4%, based on **2**) of gray crystals of **12**,[19] 0.125 g (22%, based on **2**) of red crystals of **8**, and 0.470 g (70%, based on **2**) of blackish green crystals of **13**. **8** was identified by its melting point and IR and ^1H NMR spectra. **12** is a known compound which was identified by comparison of its mp and IR and ^1H NMR spectra with those of an authentic sample. **13**: mp 112 °C dec; IR (CH_2Cl_2) ν(CO) 2040 (vs), 1974 (s), 1940 (s, br), 1882 (m), 1788 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.67−7.05 (m, 10H, C_6H_5), 5.26 (s, 5H, C_5H_5); MS *m/e* 694 [M^+], 666 [M^+ − CO], 638 [M^+ − 2CO], 610 [M^+ − 3CO], 582 [M^+ − 4CO], 554 [M^+ − 5CO],158 [$C_6H_5SeH^+$]. Anal. Calcd for $C_{23}H_{15}O_5SeReFe$: C, 39.90; H, 2.18. Found: C, 40.05; H, 2.33.

Reaction of 2 with [MgBr][Fe_2(μ-CO)(μ-$SeC_6H_4CH_3$-p)$(CO)_6$] (4) To Give 9, 12, and [ReFe{μ-C($SeC_6H_4CH_3$-p)C_6H_5}$(CO)_5$(η-C_5H_5)] (14). A Schlenk flask was charged with 0.079 g (1.00 mmol) of selenium powder, 20 mL of THF, and 1.01 mmol of Grignard reagent p-$CH_3C_6H_4MgBr$ in THF. The mixture was stirred at room temperature for 20 min, and at this time the selenium powder completely disappeared to give a colorless solution. To this solution was added 0.500 g (0.991 mmol) of $Fe_3(CO)_{12}$, and the mixture was stirred at room temperature for 30 min, resulting in formation of a brown-red solution of the salt [MgBr][Fe_2(μ-CO)(μ-$SeC_6H_4CH_3$-p)$(CO)_6$] (**4**),[11b,16] which was cooled to −100 °C and then poured rapidly onto 0.65 g (0.89 mmol) of freshly prepared **2** previously cooled to −100 °C with vigorous stirring. Immediately the brown-red solution turned dark brown. The reaction mixture was slowly warmed to −80 °C and then stirred at −80 to −50 °C for 6 h. Further treatment of the resulting mixture as in the reaction of **1** with **3** afforded 0.014 g (5%, based on **2**) of gray crystals of **12**, 0.055 g (10%, based on **2**) of red crystals of **9**, and 0.51 g (82%, based on **2**) of deep purple-red crystals of **14**. Products **9** and **12** were identified by their mp and IR and ^1H NMR spectra. **14**: mp 82−83 °C dec; IR (CH_2Cl_2) ν(CO) 2076 (vs), 2047 (vs), 2013 (vs),1987 (s), 1864 (s), 1827 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.65−6.96 (m, 9H, C_6H_5 + $C_6H_4CH_3$), 5.29 (s, 5H, C_5H_5), 2.17 (s, 3H, $C_6H_4CH_3$); MS *m/e* 706 [M^+], 678 [M^+ − CO], 650 [M^+ − 2CO], 622 [M^+ − 3CO], 594 [M^+ − 4CO], 566 [M^+ − 5CO], 186 [$CH_3C_6H_4SeH^+$]. Anal. Calcd for $C_{24}H_{17}O_5SeReFe$: C, 40.81; H, 2.43. Found: C, 40.74; H, 2.55.

Reaction of 1 with [MgBr][Fe_2(μ-CO)(μ-SeC_2H_5)$(CO)_6$] (5) To Give [Fe_2(μ-SeC_2H_5)$_2$$(CO)_6$] (15) and [MnFe{$\mu$-C($SeC_2H_5$)$C_6H_5$}$(CO)_5$($\eta$-$C_5H_5$)] (17). A Schlenk flask was charged with 0.140 g (1.77 mmol) of selenium powder, 20 mL of THF, and 1.80 mmol of Grignard reagent C_2H_5MgBr in THF. The mixture was stirred at room temperature for 20 min, and at this time the selenium powder completely disappeared to give a colorless solution. To this solution was added 0.888 g (1.76 mmol) of $Fe_3(CO)_{12}$, and the mixture was stirred at room temperature for 30 min, resulting in formation of a brown-red solution of the salt [MgBr][Fe_2(μ-CO)(μ-SeC_2H_5)$(CO)_6$] (**5**),[11b] which was cooled to −100 °C and then poured rapidly onto 0.95 g (1.60 mmol) of freshly prepared **1** previously cooled to −100 °C with vigorous stirring. Immediately the brown-red solution turned dark brown. The reaction mixture was slowly warmed to −80 °C and then stirred at −80 to −50 °C for 6−7 h. Further treatment of the resulting mixture as in the reaction of **1** with **3** gave 0.150 g (19%, based on **1**) of red crystals of **15**[20] and 0.585 g (72%, based on **1**) of **17**. Product **15** is a red viscous oil at room temperature: IR (CH_2Cl_2) ν(CO) 2061 (s), 2025 (vs), 1985 (vs) cm^{-1} (lit.[20] (KBr) 2060 (vs), 2020 (vs), 1985 (vs) cm^{-1}); ^1H NMR (CD_3COCD_3) δ 2.75 (m, 4H, CH_3CH_2), 1.48 (m, 6H, CH_3CH_2); MS *m/e* 498 (M^+), 442 [M^+ − 2CO], 414 [M^+ − 3CO], 386 [M^+ − 4CO], 358 [M^+ − 5CO], 330 [M^+ − 6CO]. **17**: mp 106−108 °C dec; IR (CH_2Cl_2) ν(CO) 2038 (vs), 1971 (s), 1936 (vs, br), 1881 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.65 (d, 2H, C_6H_5), 7.42 (t, 2H, C_6H_5), 7.25 (t, 1H, C_6H_5), 4.62 (s, 5H, C_5H_5), 1.89 (q, 2H, CH_3CH_2), 1.17 (t, 3H, CH_3CH_2); MS *m/e* 514 [M^+], 458 [M^+ − 2CO], 430 [M^+ − 3CO], 402 [M^+ − 4CO]. Anal. Calcd for $C_{19}H_{15}O_5SeMnFe$: C, 44.48; H, 2.95. Found: C, 44.28; H, 2.97.

Reaction of 2 with 5 To Give 15 and [ReFe{μ-C(SeC_2H_5)C_6H_5}$(CO)_5$(η-C_5H_5)] (18). As used in the reaction of **1** with **5**, **2** (0.65 g, 0.90 mmol) was treated with **5** prepared (in situ) by the reaction of 0.085 g (1.07 mmol) of selenium powder, 1.08 mmol of C_2H_5MgBr, and 0.537 g (1.06 mmol) of $Fe_3(CO)_{12}$ at −100 to −50 °C for 7 h. Further treatment as in reaction of **1** with **5** yielded 0.080 g (18%, based on **2**) of red viscous oil of **15** and 0.420 g (73%, based on **2**) of blackish red crystals of **18**. **15** was identified by its melting point and IR, ^1H NMR, and mass spectra. **18**: mp 114−116 °C dec; IR (CH_2Cl_2) ν(CO) 2036 (vs), 1967 (s), 1939 (s, br), 1879 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.54 (d, 2H, C_6H_5), 7.40 (t, 2H, C_6H_5), 7.36 (t, 1H, C_6H_5), 5.25 (s, 5H, C_5H_5), 1.85 (q, 2H, CH_3CH_2), 1.20 (t, 3H, CH_3CH_2); MS *m/e* 644 [M^+], 616 [M^+ − CO], 588 [M^+ − 2CO], 560 [M^+ − 3CO], 532 [M^+ − 4CO], 504 [M^+ − 5CO]. Anal. Calcd for $C_{19}H_{15}O_5SeReFe$: C, 35.42; H, 2.35. Found: C, 35.52; H, 2.33.

Reaction of 2 with [MgBr][Fe_2(μ-CO)(μ-SeC_4H_9-n)$(CO)_6$] (6) To Give [Fe_2(μ-SeC_4H_9-n)$_2$$(CO)_6$] (16) and [ReFe{$\mu$-C($SeC_4H_9$-n)$C_6H_5$}$(CO)_5$($\eta$-$C_5H_5$)] (19). In a manner similar to the procedure for the reaction of **1** with **5**, **2** (0.70 g, 0.963 mmol) was treated with [MgBr][Fe_2(μ-CO)(μ-SeC_4H_9-n)$(CO)_6$] (**6**)[16] prepared (in situ) by the reaction of 0.089 g (1.13 mmol) of selenium powder, 1.13 mmol of n-C_4H_9MgBr, and 0.562 g (1.12 mmol) of $Fe_3(CO)_{12}$ at −100 to −50 °C for 7 h. Further treatment of the resulting mixture as in the reaction of **1** with **3** afforded 0.085 g (16%, based on **2**) of red viscous oil of **16** and 0.390 g (60%, based on **2**) of purple-red crystalline **19**. **16**: IR (CH_2Cl_2) ν(CO) 2060 (s), 2045 (m), 2026 (vs), 1982 (vs, br), 1935 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 2.77 (m, 4H, $(CH_2)_3CH_3$), 1.71 (m, 4H, $(CH_2)_3CH_3$), 1.47 (m, 4H, $(CH_2)_3CH_3$), 0.94 (m, 6H, $(CH_2)_3CH_3$); MS *m/e* 552 (M^+), 524 [M^+ − CO], 496 [M^+ − 2CO], 468 [M^+ − 3CO] 440 [M^+ − 4CO], 412 [M^+ − 5CO], 384 [M^+ − 6CO]. Anal. Calcd for $C_{14}H_{18}O_6Se_2Fe_2$: C, 30.47; H, 3.29. Found: C, 30.59; H, 3.23. **19**: mp 56−57 °C dec; IR (CH_2Cl_2) ν(CO) 2037 (vs), 1966 (s), 1942 (s, br), 1878 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.42 (d, 2H, C_6H_5), 7.35 (t,

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Table 1. Crystal Data and Experimental Details for Complexes 9, 10, 13, 18, and 20

	9	**10**	**13**	**18**	**20**
formula	$C_{20}H_{14}O_6Se_2Fe_2$	$C_{23}H_{15}O_5SeMnFe$	$C_{23}H_{15}O_5SeReFe$	$C_{19}H_{15}O_5SeReFe$	$C_{20}H_{11}O_8MnFe_2$
fw	619.94	561.11	692.38	644.34	545.93
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	12.395(2)	9.632(5)	10.929(4)	9.137(2)	8.169(3)
b (Å)	17.293(4)	16.174(5)	11.639(2)	13.923(2)	9.038(2)
c (Å)	22.150(3)	7.273(3)	9.017(2)	8.734(2)	27.434(9)
α (deg)		96.69(3)	97.95(2)	103.06(2)	
β (deg)	104.19(1)	93.24(4)	91.18(2)	113.04(1)	91.35(3)
γ (deg)		102.63(3)	75.68(2)	80.22(2)	
V (Å^3)	4603(1)	1094.2(8)	1100.6(5)	991.9(3)	2025(1)
Z	8	2	2	2	4
d_{calcd} (g /cm^3)	1.789	1.703	1.508	2.157	1.791
F(000)	2416.00	556.00	656.00	608.00	1088.00
μ(Mo Kα) (cm^{-1})	44.54	29.34	78.41	86.91	20.72
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
temperature (°C)	20	20	20	20	20
orientation reflections: no.; range (2θ) (deg)	20; 13.7−21.5	19; 12.7−22.5	19; 18.5−21.4	19; 18.3−25.6	15; 11.1−18.1
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
data coll. range, 2θ (deg)	5−50	5−50	5−50	5−50	5−51
no. of unique data,	6356	3861	3427	2871	3775
total with $I > 2.50\sigma(I)$	3645 ($I > 2.00\sigma(I)$)	1467	3028	2586 ($I > 3.00\sigma(I)$)	1449
no. of params refined	541	280	280	245	280
corr factors, max., min.	0.8068−1.0000	0.7493−1.0786	0.9010−1.0642	0.7418−1.2593	0.8169−1.0706
R^a	0.040	0.065	0.028	0.038	0.059
$R_w{}^b$	0.041	0.065	0.036	0.049	0.065
quality-of-fit indicator^c	1.17	1.59	1.55	2.15	1.53
largest shift/esd. final cycle	0.00	0.00	0.00	0.03	0.01
max. peak, e$^-$/Å^3	0.44	0.59	1.03	1.18	0.54
min. peak, e$^-$/Å^3	−0.39	−0.73	−1.03	−1.43	−0.60

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

2H, C_6H_5), 7.12 (d, 1H, C_6H_5), 5.27 (s, 5H, C_5H_5), 0.86 (m, 1H, $(CH_2)_3CH_3$), 1.70 (m, 1H, $(CH_2)_3CH_3$), 1.51 (m, 2H, $(CH_2)_3CH_3$), 1.19 (q, 2H, $(CH_2)_3CH_3$), 0.74 (t, 3H, $(CH_2)_3CH_3$); MS *m/e* 672 [M$^+$], 618 [M$^+$ − 2CO], 590 [M$^+$ − 3CO], 534 [M$^+$ − 5CO]. Anal. Calcd for $C_{21}H_{19}O_5SeReFe$: C, 37.51; H, 2.85. Found: C, 37.68; H, 2.81.

Reaction of 1 with 6 To Give 16 and [MnFe$_2$(μ-H)(μ-CO)$_2$(μ_3-CC$_6$H$_5$)(CO)$_6$(η-C$_5$H$_5$)] (20). The reaction of **1** (0.880 g, 1.48 mmol) with **6** prepared (in situ) by the reaction of 0.130 g (1.65 mmol) of selenium powder, 1.65 mmol of n-C_4H_9MgBr, and 0.822 g (1.63 mmol) of $Fe_3(CO)_{12}$ was as in the reaction of **1** with **5** at −100 to −50 °C for 7 h, during which time the dark brown solution turned dark purple-red. Further treatment in a manner similar to that in the reaction of **2** with **6** yielded 0.150 g (18%, based on **1**) of red viscous oil of **16** and 0.370 g (47%, based on **1**) of blackish red crystalline **20**. Product **16** was identified by its mp and IR, ^{1}H NMR, and mass spectra. **20**: mp 140 °C dec; IR (CH_2Cl_2) ν(CO) 2076 (s), 2039 (vs), 2012 (w),1975 (vs), 1942 (s, br), 1879 (s), 1870 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 8.02 (m, 2H, C_6H_5), 7.98 (m, 2H, C_6H_5), 7.53 (m, 1H, C_6H_5), 4.79 (s, 5H, C_5H_5), −23.84 (s, 1H, μ-H); MS *m/e* 546 [M$^+$], 545 [M$^+$ − H], 517 [M$^+$ − H − CO], 489 [M$^+$ − H − 2CO], 433 [M$^+$ − H − 5CO], 405 [M$^+$ − H − 6CO], 349 [M$^+$ − H − 8CO]. Anal. Calcd for $C_{20}H_{11}O_8MnFe_2$: C, 44.00; H, 2.03. Found: C, 43.83; H, 2.40.

X-ray Crystal Structure Determinations of Complexes 9, 10, 13, 18, and 20. The single crystals of complexes **9**, **10**, **13**, **18**, and **20** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether or petroleum ether/CH_2Cl_2 at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 6356, 3861, 3427, 2871, and 3775 independent reflections, of which 3645 with $I > 2.00\sigma(I)$ for **9**, 1467, 3028, and 1449 with $I > 2.50\sigma(I)$ for **10, 13**, and **20**, and 2586 with $I > 3.00\sigma(I)$ for **18** were observable, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo Kα radiation with an $\omega-2\theta$ scan mode within the range 5° ≤ $2\theta \leq 50°$.

The structures of **9**, **10**, **13**, **18**, and **20** were solved by the direct methods and expanded using Fourier techniques. For all five complexes, the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was respectively based on 3645, 1467, 3208, 2586, and 1449 observed reflections and 541, 280, 280, 245, and 280 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.040$ and $R_w = 0.041$ for **9**, $R = 0.065$ and $R_w = 0.065$ for **10**, $R = 0.028$ and $R_w = 0.036$ for **13**, $R = 0.038$ and $R_w = 0.049$ for **18**, and $R = 0.059$ and $R_w = 0.065$ for **20**, respectively. All the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

The details of the crystallographic data and the procedures used for data collection and reduction information for **9**, **10**, **13**, **18**, and **20** are given in Table 1. The selected bond lengths and angles are listed in Tables 2 and 3, respectively. The atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, least-squares planes for **9**, **10**, **13**, **18**, and **20**, and the molecular structures of **9** and **13** are given in the Supporting Information. The molecular structures of **10**, **18**, and **20** are given in Figures 1, 2, and 3, respectively.

Results and Discussion

The complex [η-$C_5H_5(CO)_2Mn{\equiv}CC_6H_5$]$BBr_4$ (**1**) was treated, in separate experiments, with an equimolar quantity of freshly prepared (in situ) [Et_3NH][Fe_2(μ-CO)(μ-SeC_6H_5)$(CO)_6$] (**3**) and [Et_3NH][Fe_2(μ-$SeC_6H_4CH_3$-p)$(CO)_6$] (**4**) in THF at low temperature (−100 to −50 °C) for 7−8 h. After vacuum removal of the solvent, the residue was chromatographed on an alumina column at low temperature, and the crude products were

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 10, 13, and 18

	10 M = Mn	**13** M = Re	18 M = Re		**10** M = Mn	**13** M = Re	**18** M = Re
M−Fe	2.697(3)	2.7731(9)	2.782(1)	M−C(1)	1.77(2)	1.874(8)	1.883(9)
M−C(6)	2.00(2)	2.118(6)	2.130(9)	M−C(2)	1.79(2)	1.877(9)	1.90(1)
Fe−C(6)	1.86(2)	1.918(6)	1.927(9)	Fe−C(3)	1.75(2)	1.761(8)	1.77(1)
Fe−Se	2.398(3)	2.397(1)	2.395(2)	Fe−C(4)	1.77(2)	1.818(7)	1.77(1)
Se−C(6)	1.99(2)	1.965(6)	1.964(8)	Fe−C(5)	1.78(2)	1.791(8)	1.84(1)
Se−C(18)	1.92(2)	1.938(7)	1.97(1)	M−C(Cp) (av)	2.144	2.302	2.286
C(6)−C(7)	1.54(2)	1.488(8)	1.46(1)				
M−Fe−C(6)	47.7(5)	49.7(2)	49.9(3)	Se−Fe−C(6)	54.1(5)	52.8(2)	52.7(2)
Fe−M−C(6)	43.4(4)	43.7(2)	43.7(2)	Fe−C(6)−Se	77.0(6)	76.3(2)	76.0(3)
M−C(6)−Fe	88.9(7)	86.6(2)	86.4(4)	M−C(6)−C(7)	122(1)	120.4(4)	122.7(6)
M−Fe−Se	76.8(1)	79.96(4)	80.48(4)	Fe−C(6)−C(7)	137(1)	136.9(4)	135.3(7)
M−C(6)−Se	105.5(7)	109.4(3)	110.1(4)	C(6)−Se−C(18)	112.8(7)	108.5(3)	105.5(4)
Fe−Se−C(6)	48.9(4)	51.0(2)	51.3(3)	Fe−Se−C(18)	104.7(5)	103.9(2)	106.3(3)

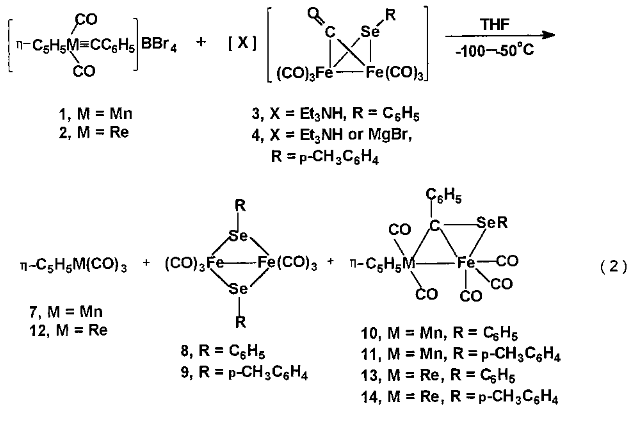
[a] Estimated standard deviations in the least significant figure are given in parentheses.

Table 3. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complex 20

Mn−Fe(1)	2.606(3)	Fe(2)−C(2)	2.33(2)
Mn−Fe(2)	2.612(3)	Fe(1)−C(3)	1.80(1)
Fe(1)−Fe(2)	2.640(5)	Fe(1)−C(4)	1.78(2)
Mn−C(6)	2.00(1)	Fe(1)−C(5)	1.81(2)
Fe(1)−C(6)	1.94(1)	Fe(2)−C(18)	1.76(2)
Fe(2)−C(6)	1.95(1)	Fe(2)−C(19)	1.78(2)
C(6)−C(7)	1.47(2)	Fe(2)−C(20)	1.85(2)
Mn−C(1)	1.84(2)	Mn−C(Cp) (avg.)	2.11
Fe(1)−C(1)	2.37(2)	Fe(1)−H(11)	1.74
Mn−C(2)	1.80(2)	Fe(2)−H(11)	1.80
Fe(1)−Mn−Fe(2)	60.77(8)	Mn−Fe(2)−C(6)	49.4(4)
Mn−Fe(1)−Fe(2)	59.74(8)	Fe(1)−Fe(2)−C(6)	47.0(4)
Mn−Fe(2)−Fe(1)	59.49(8)	Mn−C(1)−Fe(1)	75.4(6)
Mn−C(6)−Fe(1)	83.0(5)	Mn−C(2)−Fe(2)	77.2(6)
Mn−C(6)−Fe(2)	82.7(5)	Mn−C(6)−C(7)	130(1)
Fe(1)−C(6)-Fe(2)	85.5(5)	Fe(1)−C(6)−C(7)	129(1)
Fe(1)−Mn−C(6)	47.5(4)	Fe(2)−C(6)−C(7)	128(1)
Fe(2)−Mn−C(6)	47.9(4)	Mn−C(1)−O(1)	158(1)
Mn−Fe(1)−C(6)	49.6(4)	Mn−C(2)−O(2)	158(1)
Fe(2)−Fe(1)−C(6)	47.6(4)		

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

recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C to give yellow crystals of [η-$C_5H_5Mn(CO)_3$] (**7**), red selenolato-bridged iron carbonyl compounds [Fe_2(μ-$SeC_6H_5)_2(CO)_6$] (**8**) and [Fe_2(μ-$SeC_6H_4CH_3$-*p*$)_2(CO)_6$] (**9**), and blackish green Mn−Fe dimetal bridging carbene complexes [MnFe{μ-C(SeC_6H_5)C_6H_5}$(CO)_5$(η-C_5H_5)] (**10**) (from **3**) and [MnFe{μ-C($SeC_6H_4CH_3$-*p*)C_6H_5}$(CO)_5$(η-C_5H_5)] (**11**) (from **4**) (eq 2) in 5−6%, 24−25%, and 63−66% yields, respectively, among which **7**[17] and **8**[18] are known compounds.



Like **1**, the cationic carbyne complex of rhenium, [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (**2**), also reacts with anionic compounds **3** and **4** under the same conditions to afford the Re−Fe dimetal bridging carbene complexes [ReFe{μ-C(SeC_6H_5)C_6H_5}$(CO)_5$(η-C_5H_5)] (**13**) and [ReFe{μ-C($SeC_6H_4CH_3$-p)C_6H_5}$(CO)_5$(η-C_5H_5)] (**14**) in 70% and 82% yield, respectively, in addition to [η-$C_5H_5Re(CO)_3$] (**12**) and **8** or **9** (eq 2).

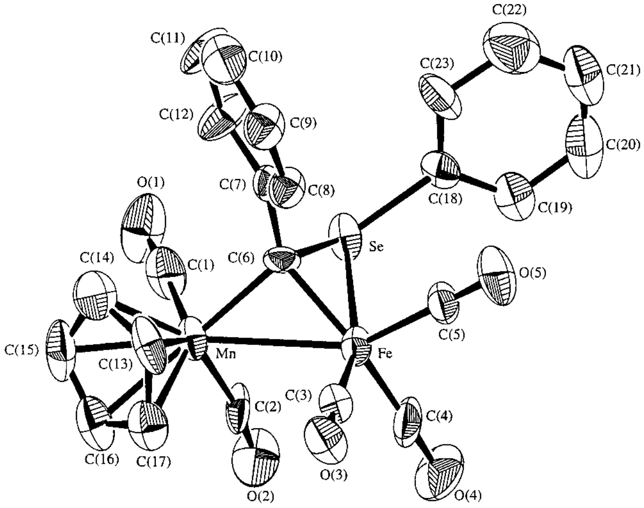


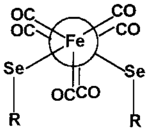
Figure 1. Molecular structure of **10**, showing the atom-numbering scheme with 40% thermal ellipsoids.

Compounds **10**, **11**, **13**, and **14** are readily soluble in polar organic solvents but only sparingly soluble in nonpolar solvents. They are very sensitive to air and temperature in solution but relatively stable as the solid. On the basis of elemental analyses, spectroscopic evidence, and X-ray crystallography, products **10**, **11**, **13**, and **14** are formulated as heteronuclear dimetal bridging carbene complexes possessing a SeR ligand bridged to the Fe atom and carbene carbon, similar to the complexes [MFe{μ-C(SR)C_6H_5}$(CO)_5$(η-C_5H_5)] shown in eq 1. The X-ray diffraction studies for complexes **10** and **13** were carried out in order to firmly establish their structures.

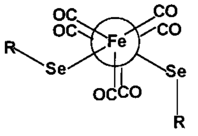
The molecular structure of complex **10** (Figure 1) confirmed that the SeR ligand bridges the carbene carbon (C(6)) and the Fe atom through the Se atom and provides two electrons for Fe to satisfy the 18-electron configuration. The Mn−Fe distance of 2.697(3) Å is approximately the same as that found in analogous bridging carbene complexes [MnFe{μ-C(SC_4H_9-n)C_6H_5}$(CO)_5$(η-C_5H_5)] (2.705(4) Å),[9] [MnFe{μ-C(SC_6H_5)C_6H_5}$(CO)_5$(η-C_5H_5)] (2.704(2) Å),[9] and [MnFe{μ-C(COEt)C_6H_5}$(CO)_5$(η-C_5H_5)] (2.6929(8) Å),[7b] but obviously longer than that in the bridging carbyne complex [(η-C_5H_5)(CO)Fe(μ-CO)(μ-COEt)Mn(CO)(η-MeC_5H_4)] (2.572(1) Å).[21] The μ-C−Mn distance of 2.00(2) Å is slightly shorter than that in the analogous complex [MnFe{μ-C(SC_6H_5)C_6H_5}$(CO)_5$(η-C_5H_5)] (2.057(9) Å).[9] The μ-C−Fe bond length of 1.86(2) Å is not only shorter than that in the bridging carbene complexes [MnFe{μ-C(COEt)C_6H_5}$(CO)_5$(η-C_5H_5)] (2.020(4) Å)[7b] and [Fe_2{μ-C(OC_2H_5)C_6H_4-CF_3-*p*}$(CO)_2$(C_8H_8)] (average 2.037 Å)[22] but also shorter than that in analogous complexes [MnFe{μ-C(SC_4H_9-*n*)C_6H_5}$(CO)_5$(η-C_5H_5)] (1.94(1) Å)[9] and [MnFe{μ-C(SC_6H_5)C_6H_5}$(CO)_5$(η-C_5H_5)] (1.897(9) Å)[9] and is comparable to that in the bridging carbyne complex [MnFe(μ-CC_6H_5)$(CO)_4$(NO)(η-C_5H_5)] (1.853(3) Å).[8f] This might be caused by bridging of the SeR group leading to the ring shrinkage. The Se−Fe bond length of 2.398(3) Å is somewhat longer than that found (average 2.363 Å) in [Fe_2(μ-Se)$_2$$(CO)_6$].[23] The C(6)−Se distance (1.99(2) Å) and Se−Fe distance in **10** are both obviously longer than the C(6)−S distance (1.799(9) Å) and S−Fe distance (2.279(3) Å), respectively, in [MnFe{μ-C(SC_6H_5)C_6H_5}$(CO)_5$(η-C_5H_5)].[9]

The structure of complex **13** (Supporting Information) resembles that of **10**. Both structures have many common features. The Re−Fe bond distance (2.7731(9) Å) in **13** is very close to that in analogous complexes [ReFe{μ-C(SC_4H_9-n)C_6H_5}$(CO)_5$(η-C_5H_5)] (2.784(2) Å)[9] and [ReFe{μ-C(H)C_6H_5}$(CO)_6$(η-C_5H_5)] (2.7581(8) Å)[7a] but is slightly longer than that found in [ReFe(μ-CC_6H_5)(μ-CO)$(CO)_3$(η-C_5H_5)(COC_2H−$B_{10}H_{10}$)] (2.682(6) Å).[24] The μ-C−Re distance (2.118(6) Å) is the same within experimental error as that in [ReFe{μ-C(SC_4H_9-*n*)C_6H_5}$(CO)_5$(η-C_5H_5)] (2.128(10) Å)[9] and [ReFe{μ-C(H)C_6H_5}$(CO)_6$(η-C_5H_5)] (2.120(5) Å),[7a] while the μ-C−Fe distance of 1.918(6) Å is somewhat shorter than that in [ReFe{μ-C(SC_4H_9-*n*)C_6H_5}$(CO)_5$(η-C_5H_5)] (1.951(1) Å)[9] and [ReFe{μ-C(H)C_6H_5}$(CO)_6$(η-C_5H_5)] (2.097(5) Å).[7a] The Se−Fe (2.397(1) Å) and Se−C(6) (1.965(6) Å) bond lengths are close to those of **10**.

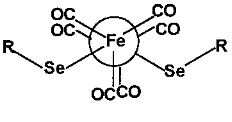
Complexes **8** and **9** are known bis[μ-(areneselenolato)]-hexacarbonyldiiron compounds, reported previously by Schermer[18] and Song,[11a] respectively. It is interesting to note that there are three possible steric configurations, A, B, and C, in the bis(μ-SeR)hexacarbonyldiiron compounds. The configuration A is unfavorable in steric effect because of the steric repelling action of the two neighboring R groups. For configuration C, the two R groups lie in cis position and have the same chemical environment; thus, its ^1H NMR spectrum should be a single signal for the R group. However, the ^1H NMR spectrum of **9** showed the two singlets of the methyl proton signals of the *p*-tolyl group respectively at 2.28 and 2.06 ppm, while the benzene ring proton showed two sets of A_2B_2 resonances at ca. 7.36−7.07 ppm. Hence, we consider that complex **9** adopts the B configuration, where the two R (*p*-$CH_3C_6H_4$) groups lie in trans position and have different chemical environments.



(A)



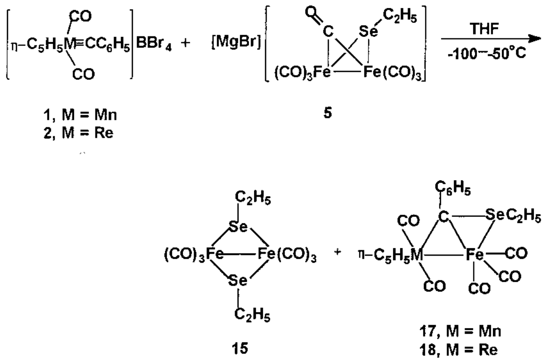
(B)



(C)

Althuogh several bis(μ-SeR)hexacarbonyldiiron compounds have been synthesized,[11a,18,20,25] no X-ray structure of such compounds is known. To firmly confirm their configuration and examine their structural features, a single-crystal X-ray diffraction study was carried out on complex **9**. The structural data and the molecular structure of **9** are given in the Supporting Information. The results of the X-ray diffraction of **9** confirmed its B configuration. Complex **9** appears to be the first example of a species with Fe−Fe and Fe−Se(R) bonds studied by X-ray crystallography.

To explore the effect of different substituents on the Se atom on the reactivity of the reactive salts and reaction products, [MgBr][Fe_2(μ-CO)(μ-SeC_2H_5)$(CO)_6$] (**5**), where the substituent on Se is an ethyl group, and the *n*-butyl analogue were used in the reaction with **1** and **2** under the same conditions. The known bis(μ-SeC_2H_5)hexacarbonyldiiron compound **15** and bridging carbene complexes [MnFe{μ-C(SeC_2H_5)C_6H_5}$(CO)_5$(η-C_5H_5)] (**17**) and [ReFe{μ-C(SeC_2H_5)C_6H_5}$(CO)_5$(η-C_5H_5)] (**18**) were formed in 18−19% and 72−73% yield, respectively, in the case of [MgBr][Fe_2(μ-CO)(μ-SeC_2H_5)$(CO)_6$] (eq 3).



(3)

Analogous products [Fe_2(μ-SeC_4H_9-*n*)$_2$$(CO)_6$] (**16**) and [ReFe{$\mu$-C($SeC_4H_9$-*n*)$C_6H_5$}$(CO)_5$($\eta$-$C_5H_5$)] (**19**) in 16% and 60% yield, respectively, were obtained in the reaction of [MgBr][Fe_2(μ-CO)(μ-SeC_4H_9-*n*)$(CO)_6$] (**6**) with **2** (eq 4).

The structures of complexes **17**−**19** were supported by their elemental analyses and IR, ^1H NMR, and mass spectra, among which the structure of complex **18** has been further confirmed by its X-ray crystallography.

The molecular structure of **18** shown in Figure 2 resembles that of **13**, except that the substituent on the Se atom is an ethyl group instead of a phenyl group. The Re−Fe distance (2.782(1) Å) is nearly the same as that in **13**. The μ-C−Re distance of 2.130(9) Å and the

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[21] Fong, R. H.; Lin, C.-H.; Idmouaz, H.; Hersh, W. H. *Organometallics* **1993**, *12*, 503.

[22] Chen, J.-B.; Li, D.-S.; Yu, Y.; Jin, Z.-S.; Zhou, Q.-L.; Wei, G.-C. *Organometallics* **1993**, *12*, 3885.

[23] Campana, C. F.; Yip-Kwai Lo, F.; Dahl, L. F. *Inorg. Chem.* **1979**, *18*, 3060.

[24] Zhu, B.; Yu, Y.; Chen, J.-B.; Wu, Q.-J.; Liu, Q.-T. *Organometallics* **1995**, *14*, 3963.

[25] Rosenbuch, P.; Welcman, N. *J. Chem. Soc., Dalton Trans.* **1972**, 1963.

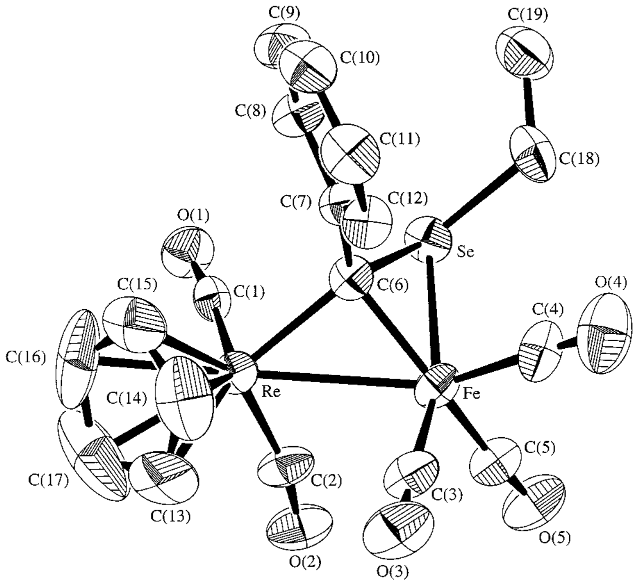
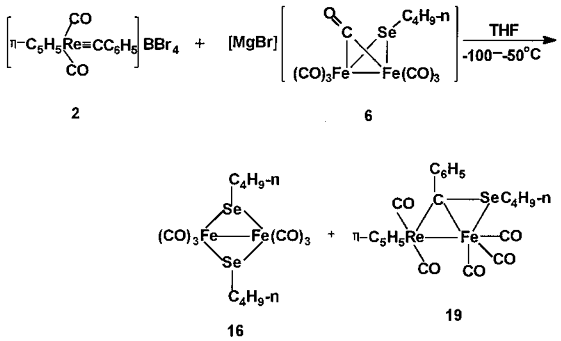


Figure 2. Molecular structure of **18**, showing the atom-numbering scheme with 40% thermal ellipsoids.



(4)

μ-C–Fe distance of 1.927(9) Å are both slightly longer than those found in **13**, while the Se–C(6) distance (1.963(8) Å) and Se–Fe distance (2.395(2) Å) are both the same within experimental error as those in **13**.

The reaction pathways to complexes **10**, **11**, **13**, **14**, and **17**–**19** are not clear. Presumably, their formation occurred via an $[Fe(CO)_3(SeR)]^-$ anion derived from dissociation of the $[X][Fe_2(\mu\text{-}CO)(\mu\text{-}SeR)(CO)_6]$ salt, a process involving the breaking of Fe–Fe and Fe–Se bonds. The anion might then attack the carbyne carbon of **1** or **2** with bonding of the Fe atom to the Mn or Re atom and the Se atom to the carbyne carbon to construct an RSe-bridged dimetallacyclopropane ring. Two $[Fe(CO)_3(SeR)]$ fragments could form a selenolato-bridged iron carbonyl compound $[Fe_2(\mu\text{-}SeR)_2(CO)_6]$ by their dimerization. To our knowledge, no such Fe–Se and Fe–Fe bond cleavage in the reactions of the $[Fe_2(\mu\text{-}CO)(\mu\text{-}SeR)(CO)_6]^-$ anions has been reported up to now. However, unlike $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}SPh)(CO)_6]$, the $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}SePh)(CO)_6]$ salt did not undergo cleavage to generate a $PhSe^-$ species, and formation of a phenylselenocarbene complex, an analogue of the phenylthiocarbene complex $[\eta\text{-}C_5H_5(CO)_2M{=}C(SPh)C_6H_5]$ (M = Mn or Re),[9] was not observed in the reaction of $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}SePh)(CO)_6]$ with **1** or **2**.

Surprisingly, the reaction of **1** with $[MgBr][Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_4H_9\text{-}n)(CO)_6]$ (**6**) under the same conditions gave no analogous dimetal bridging carbene complex but rather an unexpected trimetal bridging carbyne complex, $[MnFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (**20**), in reasonable yield, in addition to product **16** (eq 5).

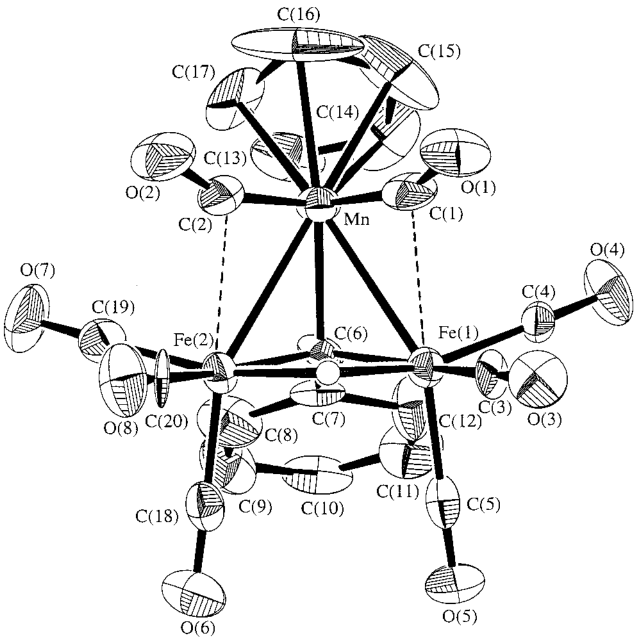
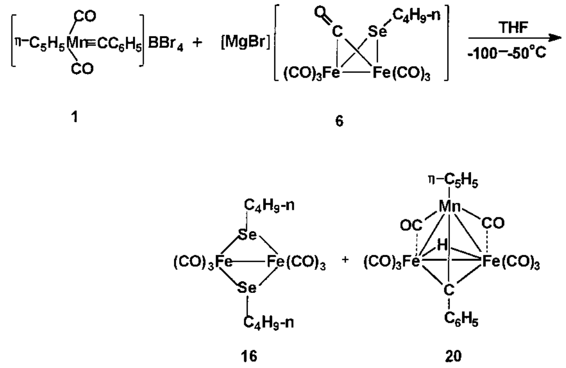


Figure 3. Molecular structure of **20**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability.



(5)

Complex **20** is formulated as a μ-H-bridged heteronuclear trimetal bridging carbyne complex whose structure has been established by its ^1H NMR spectrum and X-ray diffraction study. The existence of the bridging H atom in **20** was initially revealed by its ^1H NMR spectrum, which showed a high-field resonance at δ −23.84, characteristic for an Fe–H–Fe species.

The structure of **20** has been further confirmed by its X-ray crystallography; its molecular structure is shown in Figure 3. In **20**, the triangular MnFeFe arrangement with a capping μ_3-CC_6H_5 ligand is confirmed. The three metal atoms construct an approximate isosceles triangle (Mn–Fe(1) = 2.606(3) Å, Mn–Fe(2) = 2.612 (3) Å, and Fe(1)–Fe(2) = 2.640(5) Å). While an analogous bridging carbyne complex with a trimetalatetrahedrane CMnFeFe core has been synthesized by reaction[26] of $[Mn_3(\mu\text{-}H)_3(CO)_{12}]$ with *trans*-$[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$, compound **20** appears to be the first example

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[26] Brun, P.; Dawkins, G. M.; Green, M.; Mills, R. M.; Salauen, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 1357.

of a species with Mn−Fe, Mn−Fe, and Fe−Fe bonds studied by X-ray crystallography. The Mn−Fe bond lengths (average 2.609 Å) in **20** are slightly longer than that in the analogous complex [MnFeCo(μ_3-CC$_6$H$_5$)(μ-CO)(CO)$_7$(η-C$_5$H$_5$)] (2.570(2) Å).[8e] The Fe(1)−Fe(2) bond length is somewhat longer than that of the similar complex [WFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)] (2.538-(2) Å).[4d] The μ-C(6)−Mn, μ-C(6)−Fe(1), and μ-C(6)−Fe(2) distances are 2.00(1), 1.94(1), and 1.95(1) Å, respectively, of which the μ-C−Mn bond length is closely related to that found in complex [MnFeCo(μ_3-CC$_6$H$_5$)-(μ-CO)(CO)$_7$(η-C$_5$H$_5$)] (1.94(1) Å),[8e] while the μ-C−Fe bond length (average 1.945 Å) is nearly the same as that in [MnFeCo(μ_3-CC$_6$H$_5$)(μ-CO)(CO)$_7$(η-C$_5$H$_5$)] (1.91(1) Å)[8e] but slightly shorter than that in [WFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)] (average 2.003 Å).[4d]

In **20** the Fe(1) and Fe(2) atoms are bridged by a hydrogen, the average Fe−H distance being 1.77 Å. The two Fe atoms each carry three terminal CO groups, and the Mn atom carries two CO groups, being semibridging to the two Fe atoms, respectively (Mn−C(1)−O(1) = 158-(1)°, Fe(1)−C(1) = 2.37(2) Å; Mn−C(2)−O(2) = 158(1)°, Fe(2)−C(2) = 2.33(2) Å). Complex **20** is a 48 CVE (cluster valence electron) complex, where the Mn and Fe atoms formally have 19 and 17 electrons, respectively, which probably accounts for the presence of the semibridging carbonyl and bridging hydrogen. In **20**, the semibridging CO ligands reveal themselves in the IR spectrum with the two bands at 1879 and 1870 cm^{-1}, respectively. The analogous 48-valence-electron structure was found in the complexes [MW$_2$(μ_3-C$_2$R$_2$)(CO)$_7$-(η-C$_5$H$_5$)$_2$] (M = Ru or Os)[27] and [ReFeCo(μ_3-CC$_6$H$_5$)-(CO)$_8$(η-C$_5$H$_5$)].[8e]

Complex **20** might be produced by loss of a μ-CO and a μ-SeC$_4$H$_9$-*n* moiety from the [Fe$_2$(μ-CO)(μ-SeC$_4$H$_9$-*n*)-(CO)$_6$]$^-$ anion involving the breaking of Fe−C (μ-CO) and Fe−Se bonds or by cleavage of the formed carbene intermediate [(η-C$_5$H$_5$)-Mn=C(C$_6$H$_5$){Fe$_2$(μ-CO)(μ-SeC$_4$H$_9$-*n*)(CO)$_6$}] to generate a [Fe$_2$(CO)$_6$H]$^-$ species, which then becomes bonded to the carbyne or carbene carbon through the two Fe atoms with bonding of the Mn atom to the two Fe atoms to afford complex **20**. The origin of the H$^-$ in this reaction could be THF solvent or water, which is a trace contaminant in the solvent THF or from glassware. To our knowledge, no such Fe−C and Fe−Se bond cleavage (namely, the bridging CO and SeR groups were simultaneously replaced by another bridging ligand in the reaction of the [X][Fe$_2$(μ-CO)(μ-SeR)-(CO)$_6$] salt) has been reported.

A series of trimetal bridging carbyne complexes have been synthesized by Stone et al. and by us by reactions[4c,d,8e,f,24,28] of alkylidyne complexes with low-valent metal species. However, complex **20**, as a trimetal bridging carbyne complex, was synthesized by the reaction of a transition metal cationic carbyne complex with a carbonylmetal anion for the first time. Such reaction of a cationic carbyne complex with a [X][Fe$_2$-(μ-CO)(μ-SeR)(CO)$_6$] salt producing a trimetal bridging carbyne complex is quite unusual.

In conclusion, the title reaction shows unusual reactions between the diiron anions and the cationic carbyne complexes of manganese and rhenium. The reaction results indicate that the different diiron anions exert a great influence on the reactivity of the cationic carbyne complexes and reaction products and that the different cationic carbyne complexes exhibit certain influences on the resulting products. This offers a useful method for the preparation of the heteroatom-bridged dimetal bridging carbene and trimetal bridging carbyne complexes.

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Supporting Information Available: Tables of the positional parameters and B_{iso}/B_{eq}, H atom coordinates, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **9**, **10**, **13**, **18**, and **20** and molecular structural figures for **9** (Figure 4) and **13** (Figure 5). This material is available free of charge via the Internet at http://pubs.acs.org.

OM001035A

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