Unusual Reactions of Cationic Carbyne Complexes of Manganese and Rhenium with Reactive Salts $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$. A Route to Dimetal Bridging Carbene Complexes

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Received July 22, 1997

The reaction of a cationic carbyne complex of manganese, $[\eta\text{-}C_5H_5(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**), with the reactive salt $[Et_3NH][(\mu\text{-CO})(\mu\text{-}n\text{-}C_4H_9S)Fe_2(CO)_6]$ (**3**) in THF at low temperature gave the dimetal bridging carbene complex $[MnFe\{\mu\text{-C}(n\text{-}C_4H_9S)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (**8**) and $[Fe(CO)_3(n\text{-}C_4H_9S)]2$ (**7**). **1** reacted with $[Et_3NH][(\mu\text{-CO})(\mu\text{-}C_6H_5S)Fe_2(CO)_6]$ (**4**) to give the bridging carbene complex $[MnFe\{\mu\text{-C}(C_6H_5S)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (**11**) and the manganese phenylthiocarbene complex $[\eta\text{-}C_5H_5(CO)_2MnC(C_6H_5S)C_6H_5]$ (**12**), besides $[Fe(CO)_3C_6H_5S]_2$ (**10**). **1** also reacted with $[Et_3NH][(\mu\text{-CO})(\mu\text{-}p\text{-}CH_3C_6H_4S)Fe_2(CO)_6]$ (**5**) to yield $[Fe(CO)_3(p\text{-}CH_3C_6H_4S)]_2$ (**13**) and the bridging carbene complex $[MnFe\{\mu\text{-C}(p\text{-}CH_3C_6H_4S)C_6H_5\}(CO)_5\text{-}(\eta\text{-}C_5H_5)]$ (**14**). Analogous reactions of the cationic rhenium carbyne complex $[\eta\text{-}C_5H_5(CO)_2\text{-}Re{\equiv}CC_6H_5]BBr_4$ (**2**) with **3** and **4** gave the corresponding bridging carbene complexes $[ReFe\{\mu\text{-C}(n\text{-}C_4H_9S)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (**16**) and $[ReFe\{\mu\text{-C}(C_6H_5S)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (**17**) and the phenylthiocarbene complex $[\eta\text{-}C_5H_5(CO)_2ReC(C_6H_5S)C_6H_5]$ (**18**), respectively. The structures of **8**, **11**, **12**, **16**, and **18** have been established by X-ray diffraction studies.

Introduction

Transition metal cluster complexes are important intermediates in some catalytic reactions. Since many transition metal bridging carbene and carbyne complexes are transition metal clusters or the precursors of transition metal cluster complexes, the chemistry of transition metal bridging carbene and carbyne complexes are one area of current interest. Recently, we have shown that the reactions of the cationic carbyne complex of rhenium or manganese, $[\eta\text{-}C_5H_5\text{-}(CO)_2M{\equiv}CC_6H_5]BBr_4$ (M = Re, Mn), with the carbonyliron dianions gave unexpected dimetal bridging carbene complexes.[1,2] This represents a new route to dimetal bridging carbene complexes.

In the meantime, we have noted the chemistry of the reactive salts $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$, developed by Seyferth and co-workers in the late 1980s.[3,4] In their reactions, the Fe−Fe bond and RS−Fe bond are retained and the bridging CO is usually replaced by another bridging ligand. Although these reactive salts have been extensively investigated, their reactions with cationic transition metal carbyne complexes have not been reported. 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 $[\eta\text{-}C_5H_5(CO)_2\text{-}Re{\equiv}CC_6H_5]BBr_4$ (**2**), with the reactive $[Et_3NH][(\mu\text{-CO})\text{-}(\mu\text{-RS})Fe_2(CO)_6]$ salts, which afforded the novel heteronuclear dimetal bridging carbene complexes. In this paper, we describe these reactions and the structures of the resulting products.

Experimental Section

All procedures 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 the appropriate drying agents and stored over 4 Å molecular sieves under a N_2 atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl, while petroleum ether (30−60 °C) was distilled from CaH_2 and CH_2Cl_2 from P_2O_5. The neutral alumina (Al_2O_3) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water, and stored under N_2. $[\eta\text{-}C_5H_5(CO)_2\text{-}Mn{\equiv}CC_6H_5]BBr_4$ (**1**)[5] and $[\eta\text{-}C_5H_5(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**)[6] were prepared as previously described. $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})\text{-}Fe_2(CO)_6]$ (**3**, R = $n\text{-}C_4H_9$; **4**, R = C_6H_5; **5**, R = $p\text{-}CH_3C_6H_4$) were prepared by a literature method.[3a]

IR spectra were measured on a Shimadzu IR-440 spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature in acetone-d_6 solution with TMS as the internal

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S0276-7333(97)00626-2 CCC: $15.00
Publication on Web 01/28/1998

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 [η-$C_5H_5(CO)_2Mn{\equiv}CC_6H_5$]$BBr_4$ (1) with [Et_3NH][(μ-CO)(μ-n-C_4H_9S)$Fe_2(CO)_6$] (3) To Give [η-$C_5H_5Mn(CO)_3$] (6), [$Fe(CO)_3(n$-$C_4H_9S)]_2$ (7), [MnFe{μ-C(n-C_4H_9S)C_6H_5}$(CO)_5$(η-C_5H_5)] (8), and [(η-C_5H_5)-$(CO)_2MnC(C_6H_5)Fe(CO)_3(n$-$C_4H_9S)$] (9). To a solution of 1.60 g (3.20 mmol) of $Fe_3(CO)_{12}$ in 50 mL of THF was added 0.35 mL (3.20 mmol) of n-C_4H_9SH and 0.44 mL (3.20 mmol) of Et_3N with stirring. The mixture was stirred at room temperature for 40 min. The resulting brown-red solution of **3** was cooled to −90 °C, and then 1.90 g (3.20 mmol) of **1** was added portionwise with vigorous stirring. The mixture was stirred at −90 to −70 °C for 3 h, during which time the brown-red solution gradually turned deep red and finally dark red. The resulting mixture was evaporated to dryness under high vacuum from −50 to −40 °C. The dark red residue was chromatographed on an alumina (neutral, 200−300 mesh) column (1.6 × 15 cm) at −25 °C with petroleum ether as the eluant. The orange band which eluted first was collected, then a green band was eluted with petroleum ether/CH_2Cl_2 (20:1). A third brown 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, yellow crystals of **6** and red crystals of **7** were obtained. The first fraction, a mixture of **6** and **7**, was again chromatographed in the same manner as described above to give yellow and orange fractions. The solvent was removed from each fraction in vacuo, and the residues were recrystallized from petroleum ether or petroleum ether/CH_2Cl_2 at −80 °C. This gave yellow crystals of **6**[7] (0.020 g, 3% based on **1**) and red crystals of **7**[8] (0.053 g, 4% based on **1**). **6** is a known compound and was identified by comparison of its melting point and IR and ^{1}H NMR spectra with those of an authentic sample.[7] **7**: mp 38−40 °C (dec); IR (νCO) (hexane) 2050 (s), 1959 (vs), 1920 (m) cm^{-1} (lit.[8] (KBr) 2080, 2035, 1999, 1986 cm^{-1}); ^{1}H NMR (CD_3COCD_3) δ 2.52 (t, 2H), 1.62 (m, 2H), 1.44 (m, 2H), 0.90 (t, 3H); MS *m/e* 458 (M^+), 430 (M^+ − CO), 402 (M^+ − 2CO), 374 (M^+ − 3CO), 346 (M^+ − 4CO), 318 (M^+ − 5CO), 290 (M^+ − 6CO), 234 (M^+ − 6CO − Fe). Anal. Calcd for $C_{14}H_{18}O_6S_2Fe_2$: C, 31.46; H, 3.96. Found: C, 31.68; H, 3.94. From the second fraction, 1.50 g (85%, based on **1**) of dark green crystals of **8** were obtained: mp 68−70 °C dec; IR (νCO) (hexane) 2050 (m), 1986 (s), 1962 (s), 1956 (s), 1908 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.65 (d, 2H, C_6H_5), 7.46 (t, 2H, C_6H_5), 7.29 (t, 1H, C_6H_5), 4.61 (s, 5H, C_5H_5), 2.19 (m, 1H, C_4H_9), 1.68 (m, 1H, C_4H_9), 1.48 (m, 2H, C_4H_9), 1.24 (m, 2H, C_4H_9), 0.77 (t, 3H, C_4H_9); MS m/e 494 (M^+), 438 (M^+ − 2CO), 410 (M^+ − 3CO), 382 (M^+ − 4CO), 354 (M^+ − 5CO), 298 (M^+ − 5CO − Fe). Anal. Calcd for $C_{21}H_{19}O_5SMnFe$: C, 51.04; H, 3.87. Found: C, 51.22; H, 4.00. From the third fraction, 0.092 g (6%, based on **1**) of **9** as reddish-brown crystals were obtained: mp 100−101 °C (dec); IR (νCO) (hexane) 2040 (m), 1982 (s), 1960 (s), 1958 (s), 1902 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.70−7.00 (m, 5H, C_6H_5), 4.58 (s, 5H, C_5H_5), 2.08 (m, 1H, C_4H_9), 1.64 (m, 1H, C_4H_9), 1.45 (m, 2H, C_4H_9), 1.20 (m, 2H, C_4H_9), 0.79 (t, 3H, C_4H_9); MS *m/e* 494 (M^+), 438 (M^+ − 2CO), 410 (M^+ − 3CO), 382 (M^+ − 4CO), 354 (M^+ − 5CO), 298 (M^+ − 5CO − Fe). Anal. Calcd for $C_{21}H_{19}O_5SMnFe$: C, 51.04; H, 3.87. Found: C, 50.72; H, 3.97.

Reaction of 1 with [Et_3NH][(μ-CO)(μ-C_6H_5S)$Fe_2(CO)_6$] (4) To Give [$Fe(CO)_3C_6H_5S]_2$ (10), [MnFe{μ-C(C_6H_5S)-C_6H_5}$(CO)_5$(η-C_5H_5)] (11), and [η-$C_5H_5(CO)_2MnC(C_6H_5S)$-C_6H_5] (12). To a solution of 1.60 g (3.20 mmol) of $Fe_3(CO)_{12}$ in 50 mL of THF was added 0.32 mL (3.20 mmol) of C_6H_5SH and 0.44 mL (3.20 mmol) of Et_3N with stirring. The mixture was stirred at room temperature for 40 min. The resulting brown-red solution of **4** was cooled to −90 °C and then treated, in a manner similar to that described above, with 1.90 g (3.20 mmol) of **1** at −90 to −70 °C for 3.5 h, during which time the brown-red solution gradually turned deep red to dark red. The solvent was removed from −45 to −40 °Cin vacuo. The dark red residue was chromatographed on alumina at −25 °C with petroleum ether followed by petroleum ether/CH_2Cl_2 (20:1) as the eluant. The brown-red band which eluted first was collected, and then the green band was eluted with petroleum ether/CH_2Cl_2 (5:1). A third brown-yellow 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 solution at −80 °C. From the first fraction, 0.080 g (5%, based on **1**) of orange-red crystals of **10**[9] were obtained: mp 150 °C (dec) (lit.[9] 153 °C); IR (νCO) (hexane) 2080 (m), 2050 (s), 2005 (vs), 1998 (m), 1965 (w), 1950 (s) cm^{-1} (lit.[9] (CCl_4) 2073 (s), 2038 (vs), 2003 (vs), 1957 (w) cm^{-1}); MS *m/e* 498 (M^+), 470 (M^+ − 2CO), 442 (M^+ − 3CO), 414 (M^+ − 4CO), 386 (M^+ − 5CO), 358 (M^+ − 6CO). From the second fraction, 1.40 g (84%, based on **1**) of dark green crystals of **11** were obtained: mp 85−86 °C (dec); IR (νCO) (hexane) 2050 (m), 1992 (s), 1962 (s), 1958 (s), 1902 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.75−7.05 (m, 10H, C_6H_5), 4.65 (s, 5H, C_5H_5); MS *m/e* 486 (M^+− CO), 402 (M^+ − 4CO), 374 (M^+ − 5CO), 318 (M^+ −5CO − Fe). Anal. Calcd for $C_{23}H_{15}O_5SMnFe$: C, 53.72; H, 2.94. Found: C, 53.44; H, 2.86. From the third fraction, 0.110 g (9%, based on **1**) of **12** as orange-red crystals were obtained: mp 69−70 °C (dec); IR (νCO) (hexane) 1982 (s), 1928 (s) cm^{-1}; ^{1}H NMR (CD_3-$COCD_3$) δ 7.10−6.60 (m, 10H, C_6H_5), 4.89 (s, 5H, C_5H_5); MS *m/e* 744 (M^+), 346 (M^+ − CO), 318 (M^+ − 2CO). Anal. Calcd for $C_{20}H_{15}O_2SMn$: C, 64.17; H, 4.04. Found: C, 64.30; H, 3.95.

Reaction of 1 with [Et_3NH][(μ-CO){μ-p-$CH_3C_6H_4S$}Fe_2-$(CO)_6$] (5) To Give [$Fe(CO)_3(p$-$CH_3C_6H_4S)]_2$ (13) and [MnFe{μ-C(p-$CH_3C_6H_4S$)C_6H_5}$(CO)_5$(η-C_5H_5)] (14). Compound 1 (1.90 g, 3.20 mmol) was treated, in a manner similar to that described in the reaction of **1** with **4**, with **5**, prepared (in situ) by the reaction of 1.60 g (3.20 mmol) of $Fe_3(CO)_{12}$ in 50 mL of THF with 0.34 mL (3.20 mmol) of p-$CH_3C_6H_4SH$ and 0.44 mL (3.20 mmol) of Et_3N at −90 to −70 °C for 3.5 h, during which time the brown-red solution gradually turned dark red. Further treatment as described above in the reaction of **1** with **4** gave 0.050 g (3%, based on **1**) of orange-red crystals of **13**[10] and 1.48 g (88%, based on **1**) of dark green crystalline **14**. **13**: mp 102−104 °C (dec) (lit.[10] 105 °C); IR (νCO) (hexane) 2050 (w), 2000 (m), 1998 (s), 1980 (w) cm^{-1} (lit.[10] (CH_2Cl_2) 2065 (s), 2030 (s), 1995 (s) cm^{-1}); ^{1}H NMR (CD_3COCD_3) δ 7.30 (m, 4H, $C_6H_4CH_3$), 7.13 (m, 4H, $C_6H_4CH_3$), 2.27 (s, 3H, $C_6H_4CH_3$), 2.23 (s, 3H, $C_6H_4CH_3$) (lit.[10] ($CDCl_3$) δ 7.16 (d, 2H), 7.14 (d, 2H), 6.96 (d, 4H), 2.21 (s, 6H)); MS *m/e* 526 (M^+), 470 (M^+ − 2CO), 442 (M^+ − 3CO), 414 (M^+ − 4CO), 386 (M^+ − 5CO), 358 (M^+ − 6CO). Anal. Calcd for $C_{20}H_{14}O_6S_2Fe_2$: C, 45.66; H, 2.68. Found: C, 45.31; H, 2.90. **14**: mp 90 °C (dec); IR (νCO) (hexane) 2040 (m), 1988 (s), 1960 (s), 1958 (s), 1902 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.70−6.90 (m, 9H, C_6H_5 and C_6H_4-CH_3), 4.61 (s, 5H, C_5H_5), 2.16 (s, 3H, $C_6H_4CH_3$); MS *m/e* 472 (M^+ − 2CO), 444 (M^+ − 3CO), 416 (M^+− 4CO), 388 (M^+ − 5CO), 332 (M^+ − 5CO − Fe). Anal. Calcd for $C_{24}H_{17}O_5$-SMnFe: C, 54.57; H, 3.24. Found: C, 54.55; H, 3.26.

Reaction of [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (2) with 3 To Give [η-$C_5H_5Re(CO)_3$] (15) and [ReFe{μ-C(n-C_4H_9S)C_6H_5}-$(CO)_5$(η-C_5H_5)] (16). Similar to the procedures for the reaction of **1** with **3**, compound **2** (0.50 g, 0.68 mmol) was treated with **3**, prepared (in situ) by the reaction of $Fe_3(CO)_{12}$ (0.382

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Table 1. Crystal Data and Experimental Details for Complexes 8, 11, 12, 16, and 18

	8	11	12	16	18
formula	$C_{21}H_{19}O_5SFeMn$	$C_{23}H_{15}O_5SFeMn$	$C_{20}H_{15}O_2SMn$	$C_{21}H_{19}O_5SReFe$	$C_{20}H_{15}O_2SRe$
fw	494.22	514.21	748.67	625.49	505.60
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No.1)	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
a (Å)	8.739(4)	7.156(3)	10.459(5)	10.426(2)	23.291(6)
b (Å)	23.057(9)	17.637(5)	10.687(6)	24.127(6)	12.555(2)
c (Å)	10.589(6)	17.169(4)	8.417(4)	8.852(2)	12.2817(8)
α (deg)			92.59(5)	94.90(2)	90
β (deg)	91.67(5)	96.86(3)	106.92(4)	90.50(2)	90
γ (deg)			77.30(4)	94.79(2)	90
V (Å^3)	2132(1)	2151(1)	877.8(8)	2210.5(8)	3591(2)
Z	4	4	1	4	8
d_{calcd} (g/cm^3)	1.539	1.587	1.416	1.879	1.870
cryst size (mm)	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.30 × 0.30	0.20 × 0.20 × 0.40
μ(Mo Kα) (cm^{-1})	13.98	13.89	8.78	62.52	68.94
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 69)	Mo Kα (λ = 0.710 69)	Mo Kα (λ = 0.710 69)	Mo Kα (λ = 0.710 69)	Mo Kα (λ = 0.710 69)
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
temperature (°C)	20.0	20.0	20.0	20.0	20.0
orientation of reflns [no.; range (2θ) (deg)	18; 18.7−22.6	14; 18.5−26.5	19; 14.5−19	15; 18.6−21.8	17; 24.0−26.4
scan method	ω−2θ	ω−2θ	ω−2θ	ω−2θ	ω−2θ
data collection range, 2θ (deg)	5−45.1	5−45	5−45	5−45	5−45
no. of unique data	2430	2931	2290	4964	2680
total no. of data with $I > 3.00\sigma(I)$	1100	1293	1867	3727	1622
no. of params refined	263	280	430	523	217
correction factors, max, min	1.1228, 0.8064	1.000, 0.8954	0.9988, 0.7685	1.0000, 0.7869	1.0937, 0.9482
R^a	0.056	0.042	0.051	0.029	0.028
$R_w{}^b$	0.059	0.035	0.063	0.033	0.034
quality-of-fit indicator^c	1.74	1.25	1.93	1.40	1.34
largest shift/esd. final cycle	0.09	0.00	0.07	0.01	0.04
largest peak, e$^-$/Å^3	0.36	0.38	0.69	0.52	0.63
minimum peak, e$^-$/Å^3	−0.37	−0.30	−0.40	−0.46	−0.59

^{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 $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

g, 0.76 mmol) with 0.08 mL (0.76 mmol) of n-C_4H_9SH and 0.10 mL (0.76 mmol) of Et_3N at −90 to −70 °C for 3.5 h, during which time the orange-red solution gradually turned deep red until it finally turned dark red. Further treatment of the resulting mixture as described in the reaction of **1** with **3** afforded 0.015 g (6%, based on **2**) of yellow crystals of **15**[11] and 0.170 g (40%, based on **2**) of orange-red crystals of **16**. **15** is a known compound and was identified by comparison of its melting point and IR and ^{1}H NMR spectra with those of an authentic sample. **16**: mp 70 °C (dec); IR (νCO) (hexane) 2020 (m), 1990 (w), 1980 (vs), 1966 (m), 1960 (s), 1950 (s), 1904 (s), 1898 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.60−6.80 (m, 10H, C_6H_5), 5.40 (s, 5H, C_5H_5), 5.26 (s, 5H, C_5H_5), 2.49 (m, 2H, C_4H_9), 1.62 (m, 2H, C_4H_9), 1.47 (m, 4H, C_4H_9), 1.22 (m, 4H, C_4H_9), 0.76 (m, 6H, C_4H_9); MS *m/e* 625 (M^+), 597 (M^+ − CO), 569 (M^+ − 2CO), 542 (M^+ − 3CO), 514 (M^+ − 4CO), 486 (M^+ − 5CO), 430 (M^+ − 5CO − Fe). Anal. Calcd for $C_{21}H_{19}O_5SReFe$: C, 40.32; H, 3.06. Found: C, 40.51; H, 3.02.

Reaction of 2 with 4 To Give 10, [ReFe{μ-C(C_6H_5S)C_6H_5}(CO)$_5$(η-C_5H_5)] (17), and [η-C_5H_5(CO)$_2$ReC(C_6H_5S)C_6H_5] (18). As described above for the reaction of **1** with **4**, compound **2** (0.47 g, 0.66 mmol) was treated with **4**, prepared (in situ) by the reaction of 0.37 g (0.73 mmol) of $Fe_3(CO)_{12}$ with 0.075 mL (0.73 mmol) of C_6H_5SH and 0.10 mL (0.73 mmol) of Et_3N at −90 to −70 °C for 3.5 h, during which time the orange-red solution gradually turned dark red. Further treatment in a manner similar to that described in the reaction of **1** with **4** yielded 0.020 g (6%, based on **2**) of orange-red crystals of **10**, 0.142 g (32%, based on **2**) of red crystals of **17**, and 0.053 g (16%, based on **2**) of **18** as gold-yellow crystals. **10** was identified by its melting point and IR and ^{1}H NMR spectra. **17**: mp 86−88 °C (dec); IR (νCO) (hexane) 2000 (m), 1988 (s), 1979 (s), 1962 (m), 1958 (s), 1912 (m), 1900 (s), 1892 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.61−6.70 (m, 10H, C_6H_5), 5.30 (s, 5H, C_5H_5); MS *m/e* 589 (M^+ − 2CO), 505 (M^+ − 5CO), 449 (M^+ − 5CO − Fe). Anal. Calcd for $C_{23}H_{15}O_5SReFe$: C, 42.80; H, 2.34. Found: C, 43.11; H, 2.55. **18**: mp 156 °C (dec); IR (νCO) (hexane) 1980 (s), 1908 (s) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.20−6.72 (m, 10H, C_6H_5), 5.49 (s, 5H, C_5H_5); MS *m/e* 506 (M^+), 478 (M^+ − CO), 450 (M^+ − 2CO). Anal. Calcd for $C_{20}H_{15}O_2SRe$: C, 47.51; H, 2.99. Found: C, 47.65; H, 2.94.

Reaction of 11 with PPh_3 To Give 12. A solution of PPh_3 (0.031 g, 0.12 mmol) in 10 mL of petroleum ether was added dropwise to a solution of **11** (0.050 g, 0.097 mmol) in 40 mL of petroleum ether at −55 °C. The reaction mixture was stirred at −55 to −10 °C for 6 h. The solvent was removed under vacuum, and the residue was chromatographed on alumina at −25 °C with petroleum ether followed by petroleum ether/CH_2Cl_2 (20:1) as the eluant. After elution of the green band which contains unreacted **11**, the brown-yellow band was eluted with petroleum ether/CH_2Cl_2/Et_2O (10:1:1). The solvent was removed in vacuo, and the residue was recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C to give 0.014 g (39%, based on **11**) of orange crystals of **12**, which was identified by its melting point and IR, ^{1}H NMR, and mass spectra.

X-ray Crystal Structure Determinations of Complexes 8, 11, 12, 16, and 18. The single crystals of **8**, **11**, **12**, **16**, and **18** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH_2Cl_2 solution at −80 °C. Single crystals of **8**, **11**, **12**, **16**, and **18** were sealed in capillaries under an N_2 atmosphere. The X-ray diffraction intensity data for **8**, **11**, **12**, **16**, and **18** were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo Kα radiation with an ω−2θ scan mode within the ranges 5° ≤ 2θ ≤ 45°.

The structures of **8**, **11**, **16**, and **18** were solved by direct methods and expanded using Fourier techniques. For the four complexes, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was, respectively, based on 1100, 1293, 3727, and 1622 observed reflections ($I > 3.00\sigma(I)$) and 263, 280, 523, and 217 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.056$ and $R_w = 0.059$ for **8**, $R = 0.042$

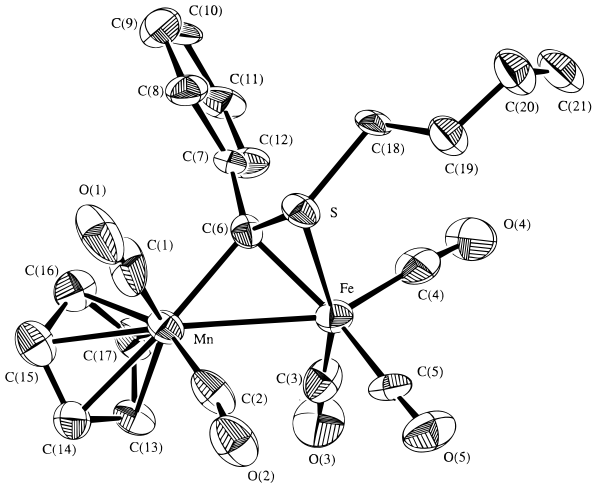


Figure 1. Molecular structure of **8** and the atom-numbering scheme.

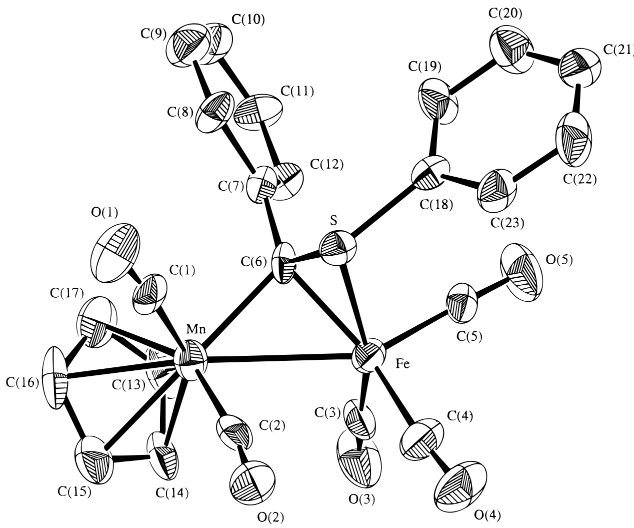


Figure 2. Molecular structure of **11** and the atom-numbering scheme.

and $R_w = 0.035$ for **11**, $R = 0.029$ and $R_w = 0.033$ for **16**, and $R = 0.028$ and $R_w = 0.034$ for **18**, respectively. While the structure of **12** was solved by the heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1867 observed reflections ($I > 3.00\sigma(I)$) and 430 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.051$ and $R_w = 0.063$. All the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

The details of the crystallographic data and the procedures used for data collection and reduction information for **8**, **11**, **12**, **16**, and **18** are given in Table 1. The positional parameters and temperature factors of the non-hydrogen atoms, H atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, the bond lengths and angles, and least-squares planes for **8**, **11**, **12**, **16**, and **18** are given in the Supporting Information. The molecular structures of **8**, **11**, **12**, **16**, and **18** are given in Figures 1−5, respectively.

Results and Discussion

Compound $[\eta\text{-}C_5H_5(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**) was treated with equimolecular amounts of freshly prepared

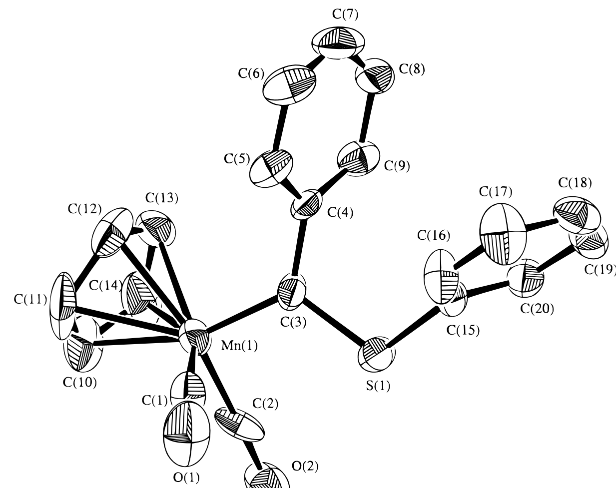
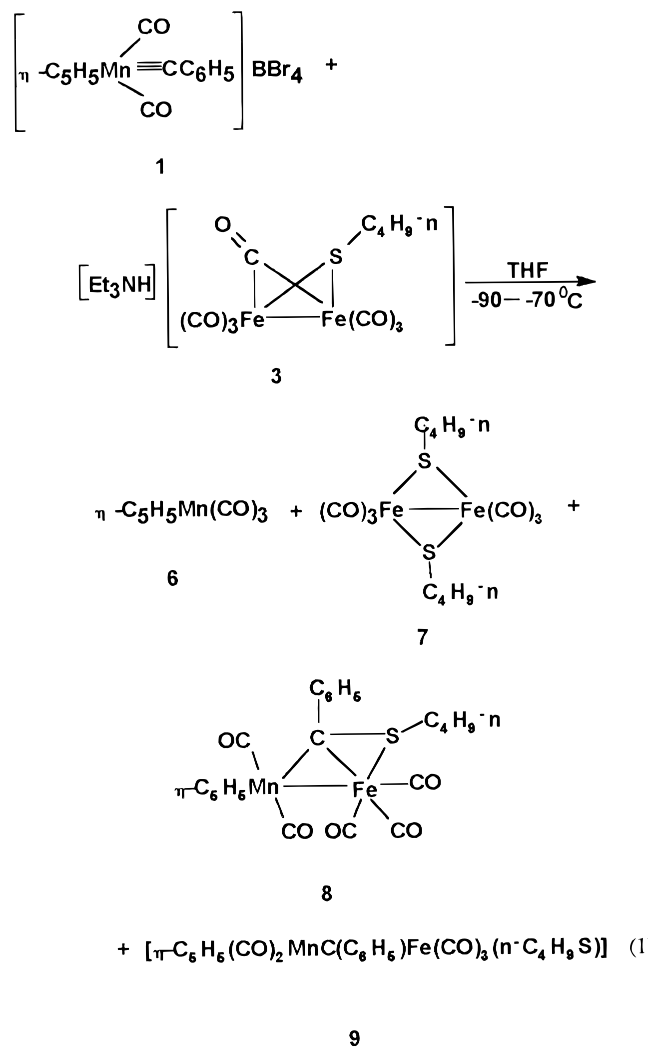


Figure 3. Molecular structure of **12** and the atom-numbering scheme, showing only one of the two independent molecules for clarity.

(in situ) $[(\mu\text{-}CO)(\mu\text{-}n\text{-}C_4H_9S)Fe_2(CO)_6][Et_3NH]$ (**3**) in THF at −90 to −70 °C for 3 h. Yellow crystals of **6**, red crystals of **7**, dark green crystals of **8**, and reddish-brown crystalline **9** (eq 1) were isolated in 3, 4, 85, and 6% yields, respectively, on workup, among which **6**[7] and **7**[8] are known compounds.



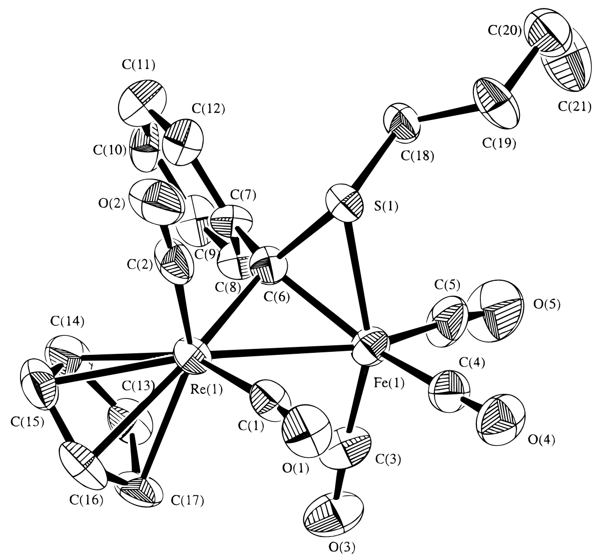


Figure 4. Molecular structure of **16** and the atom-numbering scheme, showing only one of the two independent molecules for clarity.

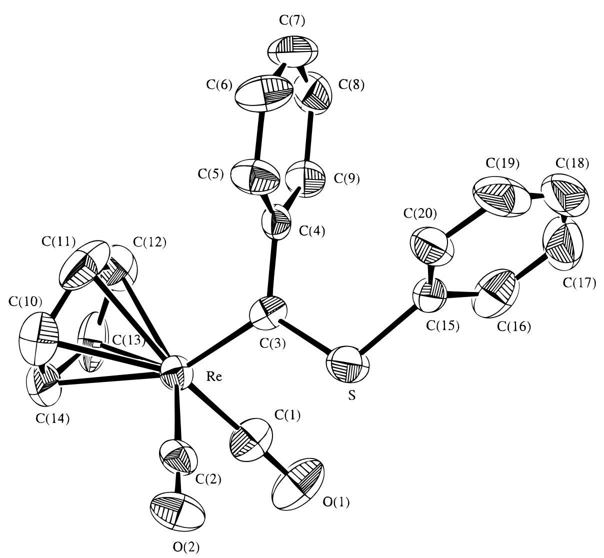
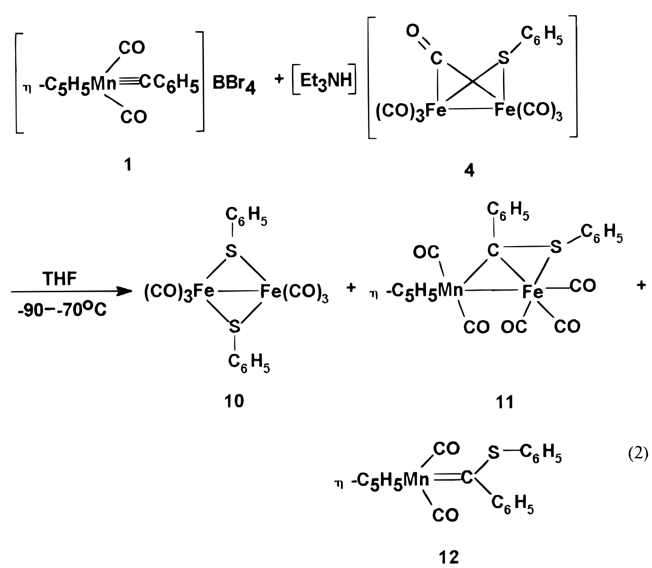


Figure 5. Molecular structure of **18** and the atom-numbering scheme.

Complex **8** is formulated as a dimetal bridging carbene complex, which has been confirmed by its single-crystal X-ray diffraction study. The structure of complex **9** is not known since we were unable to obtain crystals suitable for an X-ray study and spectroscopic studies did not result in an unambiguous proof of structure. In solution, complex **9** was transformed into complex **8**, as observed by ^{1}H NMR spectroscopy. The acetone-d_6 solution of **9** whose NMR spectrum had been measured was kept at room temperature for about 0.5 h, during which time the solution changed from red-brown to dark green. Its ^{1}H NMR spectrum now showed only the proton signals attributable to the phenyl, cyclopentadienyl, and butyl protons of **8** but none of the original proton signals assigned to **9**, confirming the transformation of **9** into **8**. Further evidence for this transformation came from the recrystallization of complex **9**. In order to obtain X-ray quality crystals, recrystallization of complex **9** was attempted from petroleum ether/CH_2Cl_2 solution at −80 °C for 72−96 h. However, only dark green crystals of **8** were obtained in 95% yield. The parent ion (M^+) and the principal fragment ions in the mass spectrum and C,H elemental analyses of **9** indicate the same composition, (η-C_5H_5)$(CO)_2$MnC(C_6H_5)Fe$(CO)_3$(n-C_4H_9S), as that of **8**. The phenyl signals (δ 7.70−7.00) and the Cp signal (δ 4.58) in its ^{1}H NMR spectrum are different from those of **8** (δ 7.65−7.29 for phenyl and δ 4.61 for Cp). The ν(CO) absorptions of **9** are similar to those of **8**. At present, there is not sufficient evidence to assign a structure to **9**.

In order to examine the effect of different substituents on the RS group on the reactivity of the reactive salts and on the reaction products, [Et_3NH][(μ-CO)(μ- C_6H_5S)$Fe_2(CO)_6$] (**4**), where the substituent on RS is a phenyl group, and the *p*-tolyl analog were used in the reaction with **1** under the same conditions. The known thiolato-bridged iron carbonyl compound **10**,[9] bridging carbene complex **11**, and phenylthiocarbene complex **12** (eq 2) were formed in 5, 84, and 9% yields, respectively, in the case of [Et_3NH][(μ-CO)(μ-C_6H_5S)$Fe_2(CO)_6$]. The structures of complexes **11** and **12** have been established by X-ray diffraction analyses.



Analogous products ([Fe$(CO)_3$(p-$CH_3C_6H_4S$)]$_2$ (**13**) and [MnFe{μ-C(p-$CH_3C_6H_4S$)C_6H_5}$(CO)_5$(η-C_5H_5)] (**14**)) were obtained in the reaction of [Et_3NH][(μ-CO)(μ-p-$CH_3C_6H_4S$)$Fe_2(CO)_6$] (**5**) with **1**.

The molecular structure of complex **8** (Figure 1) confirmed that it is a novel Mn−Fe dimetal bridging carbene complex. The S atom bridges the carbene carbon (C(3)) atom and the Fe atom and provides two electrons for Fe to satisfy the 18-electron configuration. The Mn−Fe distance of 2.705(4) Å is somewhat longer than that found in the analogous bridging carbene complex [MnFe{μ-C(COEt)Ph}(η-C_5H_5)$(CO)_5$] (2.6929-(8)Å)[2] but is obviously longer than that in the analogous carbyne complex [(η-C_5H_5)(CO)Fe(μ-CO)(μ-COEt)Mn-(CO)(η-MeC_5H_4)] (2.572(1) Å).[12] The μ-C−Fe distance-(1.94(1) Å) in **8** is not only shorter than that in the bridging carbene complexes [MnFe{μ-C(COEt)Ph}(η-

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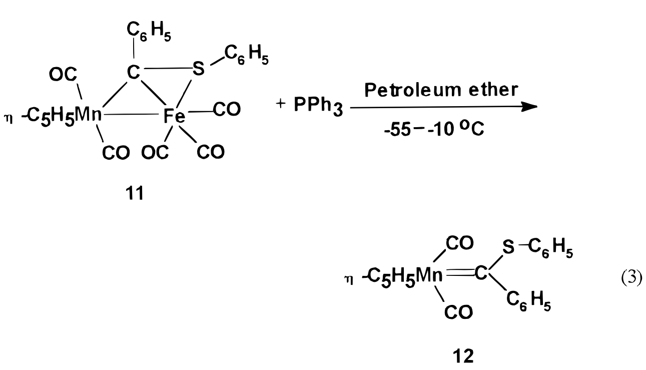
$C_5H_5)(CO)_5]$ (2.020(4) Å)[2] and $[C_8H_8(CO)_2Fe\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}Fe(CO)_2]$ (average 2.037 Å),[14] but is also shorter than that in the carbyne-bridged complex $[(CO)_2(\eta\text{-}C_5H_5)Mo(\mu\text{-}C(C_6H_4CH_3\text{-}4)Fe(CO)_4]$ (2.008(5) Å)[13] and is comparable to that in the iron carbene complex $[C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}o]$ (1.915(15) Å).[15] The S−Fe distance of 2.265(5) Å in **8** is the same as the normal distance of the S−Fe bond (2.270 Å) found in $[NEt_3H][(\mu\text{-}SO_2)(\mu\text{-}(CH_3)_3CS)Fe_2(CO)_6]$.[16] The C(6)−S distance of 1.76(1) Å is nearly the same as the C(3)−S(1) distance (1.74(1) Å) in carbene complex **12**.

The structure of complex **11** (Figure 2) resembles that of **8**, except that the substituent on the S atom is a phenyl group instead of a butyl group. The Mn−Fe bond length (2.704(2) Å) is the same within experimental error as that in **8**. The C(6)−Mn distance of 2.057(9) Å is slightly longer than that in **8**, but the C(6)−Fe distance of 1.897(9) Å is somewhat shorter. The S−C(6) distance of 1.799(9) Å and S−Fe distance of 2.279(3) Å are both slightly longer than those found in **8**.

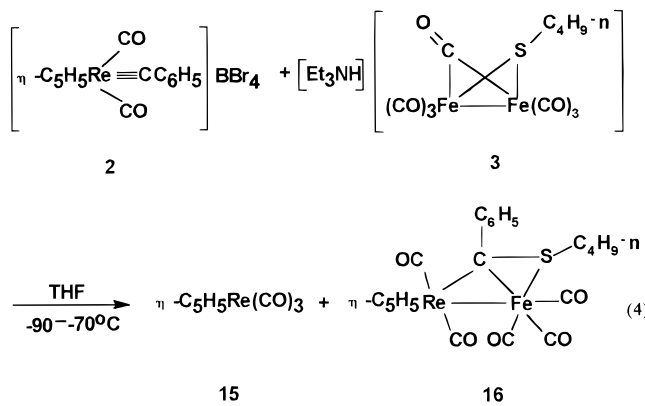
The molecular structure of complex **12** shown in Figure 3 has many common features of previously determined analogous alkoxycarbene complexes.[1,17] Interestingly, there are two independent molecules in the asymmetric unit of the complex **12**, which is similar to that found in complex **16** (below). However, its ^1H NMR spectrum showed that the two molecules are separated in solution, giving a single normal molecule. The two molecules in the unit cell are the same. The sum of the three angles around the C(3) atom is exactly 360°, which means that the Mn(1), C(3), C(4), and S atoms are in one plane. The $Mn-C_{carbene}$ distance of 1.84(1) Å in **12** is close to that in the analogous carbene complex $[CpMn(CO)_2C(OEt)Ph]$ (1.865(14) Å).[17]

Complex **12** might be produced by loss of an $Fe(CO)_3$ moiety from the $Fe(CO)_3(SPh)^-$ anion involving the breaking of Fe−S bond of **4** or by cleavage of the carbene intermediate $[(\eta\text{-}C_5H_5)Mn{=}C(C_6H_5)Fe(CO)_3(C_6H_5S)]$ to generate a PhS^- species, which then becomes bonded to the carbene carbon to afford complex **12**. Both possibilities result from the stabilization of the negative charge on the S atom by the phenyl group. To our knowledge, no such Fe−S bond cleavage in reactions of the $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ salts has been reported. In order to explore this possibility, we investigated the reaction of PPh_3 with complex **11**. This reaction gave orange-red crystals of **12** in 39% yield (eq 3). This result shows that the S−Fe bond of **11** can

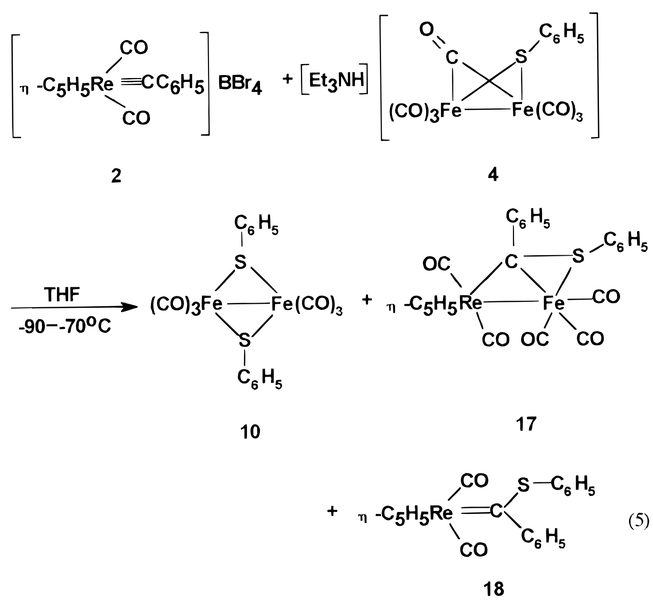


indeed be broken, since **11** was converted to complex **12** by loss of the $Fe(CO)_3$ moiety. However, complex **8** did not react with PPh_3 under the same conditions.

It is found that the central metal exerts a great affect on the reactivities of cationic transition metal carbyne complexes.[1,2,18,19] To further examine this effect, the cationic rhenium carbyne complex **2** was used in reactions with the reactive salts under the same conditions. Similar to the reaction of **1** with **3**, **2** was treated with **3** to afford yellow crystals of **15** and orange-yellow crystals of **16** (eq 4) in 6 and 40% yields, respectively, of which **15** is known[11] and **16** is a Re−Fe bridging carbene complex. Complex **2** reacted similarly with



reactive salt **4** under the same conditions to give **10**, the rhenium−iron bridging carbene complex **17**, and the rhenium phenyl−thiocarbene complex **18** (eq 5) in 6, 32, and 16% yields, respectively. The structures of products



16, **17**, and **18** were supported by their elemental analyses and IR, ^1H NMR, MS, and X-ray diffraction studies.

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It is very interesting that the bridging carbene complex **16** crystallizes with two independent molecules in the asymmetric unit. Although the two independent molecules in an asymmetric unit is not unusual in crystallograpy, this structure was observed in the bridging carbene complexes for the first time. The two molecules in the unit cell are nearly the same. The Re–Fe distance of 2.784(2) Å in **16** is very close to that in the analogous complex [ReFe{μ-C(H)C_6H_5}$(CO)_6$(η-C_5H_5)] (2.7581(8) Å)[1] but is slightly longer than that found in [ReFe(μ-CC_6H_5)(μ-CO)$(CO)_3$(η-C_5H_5)($COC_2HB_{10}H_{10}$)] (2.682(6) Å).[20] The μ-C–Re(1) distance (2.128(10) Å) is nearly the same as that in [ReFe{μ-C(H)C_6H_5}$(CO)_6$(η-C_5H_5)] (2.120(5) Å).[1] But the μ-C–Fe(1) distance of 1.951(1) Å is shorter than that found in [ReFe{μ-C(H)C_6H_5}$(CO)_6$(η-C_5H_5)] (2.097(5) Å).[1]

The molecular structure of complex **18**, shown in Figure 5, demonstrates that the coordination of the Re atom is that of a distorted tetrahedron. The apex of this tetrahedron is the Cp ring. The sum of the three angles around C(3) is 359.9°, the same as that in complex **12**. The Re–$C(3)_{carbene}$ distance of 1.966(9) Å is slightly shorter than that found in the analogous carbene complex [η-$C_5H_5(CO)_2Re{=}C(OC_2H_5)C_6H_5$] (1.990(5) Å).[1] The bond length of S–C(3) (1.749(9) Å) in **18** is close to that of S(1)–C(6) (1.785(9) Å) in complex **16**.

The title reaction demonstrates a novel and convenient route for the preparation of heteronuclear dimetal bridging carbene complexes.

Acknowledgment. Financial support from the National Natural Science Foundation of China and the Science Foundation of the Chinese Academy of Sciences is gratefully acknowledged.

Supporting Information Available: Tables of the positional parameters and temperature factors, H atom coordinates, anisotropic displacement parameters, bond lengths and angles, and least-squares planes for **8**, **11**, **12**, **16**, and **18** (53 pages). Ordering information is given on any current masthead page.

OM9706267

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