Articles

Unexpected Reactions of Cationic Carbyne Complexes of Manganese and Rhenium with Mixed-Dimetal Carbonyl Anions. A New Route to Dimetal Bridging Carbyne Complexes

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The reaction of a cationic carbyne complex of manganese, [η-$C_5H_5(CO)_2Mn{\equiv}CC_6H_5$]$BBr_4$ (**1**), with $(Ph_3P)_2NFeCo(CO)_8$ (**3**) in THF at low temperature gave a heteronuclear dimetal bridging carbyne complex [$MnCo(\mu$-$CC_6H_5)(CO)_5(\eta$-$C_5H_5)$] (**5**) and a bridging carbene complex [$MnCo\{\mu$-$C(CO)C_6H_5\}(CO)_5(\eta$-$C_5H_5)$] (**6**). $Ph_3P)_2NWCo(CO)_9$ (**4**) also reacted with **1** to give the same products **5** and **6**. The analogous reaction of the cationic carbyne complex of rhenium, [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (**2**), with **3** or **4** afforded the corresponding bridging carbyne complex [$ReCo(\mu$-$CC_6H_5)(CO)_5(\eta$-$C_5H_5)$] (**7**) and bridging carbene complex [$ReCo\{\mu$-$C(CO)C_6H_5\}(CO)_5(\eta$-$C_5H_5)$] (**8**). **5** can convert to **6** by reaction with carbon monoxide gas. **5** or **6** reacted with $Fe_2(CO)_9$ to afford a trimetal bridging carbyne complex [$MnFeCo(\mu_3$-$CC_6H_5)$-(μ-$CO)(CO)_7(\eta$-$C_5H_5)$] (**9**). Analogous reaction of **7** or **8** with $Fe_2(CO)_9$ yielded the trimetal bridging carbyne complex [$ReFeCo(\mu_3$-$CC_6H_5)(CO)_8(\eta$-$C_5H_5)$] (**10**). The structures of **5**, **7**, **8**, **9** and **10** have been established by X-ray diffraction studies.

Introduction

The current interest in the synthesis, structure, and chemistry of dimetal bridging carbene and bridging carbyne complexes stems from the possible involvement of these species in some reactions catalyzed by organometallic compounds.[1,2] We have recently shown the reactions of a cationic carbyne complexes of rhenium and manganese, [η-$C_5H_5(CO)_2M{\equiv}CC_6H_5$]$BBr_4$ (M = Re, Mn), with the carbonyliron dianion such as $(NEt_4)_2$-$Fe_2(CO)_8$ and $Na_2Fe_3(CO)_{11}$, where the two metals are homonuclear, to yield dimetal bridging carbene complexes.[3,4] This represents a new route to dimetal bridging carbene complexes. We are now interested in examining the effect of different nucleophiles containing heteronuclear dimetal anions on the reactivities of the cationic carbyne complexes and the reaction products. Thus, we chose the mixed-dimetal carbonyl anions $Ph_3P)_2NFeCo(CO)_8$ (**3**) and $Ph_3P)_2NW{-}Co(CO)_9$ (**4**) as nucleophiles for the reactions with the cationic carbyne complexes of manganese and rhenium, [η-$C_5H_5(CO)_2$-$Mn{\equiv}CC_6H_5$]BBr_4 (**1**) and [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (**2**). These reactions afforded the unexpected heteronuclear dimetal bridging carbyne and bridging carbene complexes. These products reacted further with Fe_2-$(CO)_9$ to give the 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 by using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over the appropriate drying agents and storing over 4 Å molecular sieves under a N_2 atmosphere. The 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 SiO_2 (Scientific Adsorbents Inc., 40 μm Flash) used for chromatography was deoxygenated at room temperature under high vacuum for 12 h and stored under N_2. [η-$C_5H_5(CO)_2Mn{\equiv}CC_6H_5$]$BBr_4$ (**1**)[5] and [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (**2**)[6] were prepared as previously described. $Ph_3P)_2NFeCo(CO)_8$ (**3**) and $Ph_3P)_2NWCo(CO)_9$ (**4**) were prepared by literature methods.[7]

The IR spectra were measured on a Shimadzu-IR-440 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-

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Table 1. Crystal Data and Experimental Details for Complexes 5, 7, 8, 9, and 10

	5	7	8	9	10
formula	$C_{17}H_{10}O_5MnCo$	$C_{17}H_{10}O_5ReCo$	$C_{18}H_{10}O_6ReCo$	$C_{40}H_{20}O_{16}Mn_2Co_2Fe_2$	$C_{40}H_{20}O_{16}Re_2Co_2Fe_2$
fw	408.13	539.40	567.42	1096.02	1358.56
space group	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)	$P2_{1/}n$ (No. 14)	*Pnna* (No. 52)	$P2_1/n$ (No. 14)
a (Å)	7.717(3)	14.421(3)	8.514(1)	14.640(7)	13.540(2)
b (Å)	14.822(5)	14.966(2)	14.860(3)	26.229(6)	14.016(2)
c (Å)	14.366(8)	7.723(2)	14.093(2)	21.572(5)	22.211(4)
β (deg)	98.96(4)	98.78(2)	98.38(1)		93.03(1)
V (Å^3)	1623(1)	1647.3(5)	1763.9(5)	8283(7)	4209(1)
Z	4	4	4	8	4
d_{calcd} (g/cm^3)	1.670	2.175	2.076	1.758	2.144
cryst size (mm)	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.30 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.30 × 0.30
μ(Mo Kα) (cm^{-1})	18.22	83.75	78.35	21.27	72.43
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.716 09 Å)	Mo Kα (λ = 0.710 69 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)	24; 13.5−21.3	21; 14.4−21.2	24; 18.4−21.4	25; 14.1−21.0	24; 18.5−21.7
scan method	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ
data collection range, 2θ (deg)	5−50	5−50	5−50	5−50	5−50
no. of unique data,	2630	2759	2976	8003	7755
total with $I > 3.00\sigma(I)$	1038	1708	1976	3014	4978
no. of params refined	217	217	235	559	560
correction factors, max−min	0.8524−1.0000	0.7377−1.0000	0.8967−1.0828	0.6718−1.0000	0.8021−1.1125
R^a	0.056	0.039	0.029	0.058	0.031
$R_w{}^b$	0.057	0.045	0.030	0.051	0.033
quality-of-fit indicator^c	1.63	1.47	1.20	1.34	1.22
largest shift/esd. final cycle	0.00	0.00	0.00	0.00	0.11
largest peak, e$^-$/Å^3	0.59	0.84	0.46	0.54	0.55
minimum peak, e$^-$/Å^3	−0.46	−0.95	−0.61	−0.48	−0.69

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

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 $Ph_3P)_2NFeCo(CO)_8$ (3) to give [MnCo{μ-CC_6H_5}$(CO)_5(\eta$-C_5H_5)] (5) and [MnCo{μ-C(CO)C_6H_5}$(CO)_5(\eta$-$C_5H_5)$] (6). To 0.52 g (0.87 mmol) of **1** dissolved in 50 mL of THF at −90 °C was added 0.76 g (0.87 mmol) of $Ph_3P)_2NFeCo(CO)_8$ with vigorous stirring. Immediately, the brick-red solution turned dark red. The reaction mixture was stirred at −90 to −45 °C for 3−4 h, during which time the dark red solution gradually turned blackish-green. After the resulting solution was evaporated in high vacuum at −45 to −40 °C to dryness, the dark green residue was chromatographed on a silica gel column (1.6 × 15 cm) at −25 °C with petroleum ether as the eluant. After the light yellow band containing $Fe(CO)_5$ (caution) was eluted from the column, the blackish-green band was eluted with petroleum ether/CH_2Cl_2 (10:1) and was collected, and then the brown-red band was eluted with petroleum ether/CH_2Cl_2 (5:1). The solvents were removed from the above two eluates under vacuum, and the residues were recrystallized from petroleum ether or petroleum ether/CH_2Cl_2 solution at −80 °C. From the first fraction, 0.291 g (81%, based on **1**) of blackish-green crystals of **5** were obtained: mp 80−82 °C (dec); IR (νCO) (CH_2Cl_2) 2054 (s), 2022 (w), 1990 (vs), 1970 (s), 1889 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3) δ 7.82 (m, 2H, C_6H_5), 7.55 (m, 3H, C_6H_5), 5.07 (s, 5H, C_5H_5); MS *m/e* 408 (M$^+$), 380 (M$^+$ − CO), 352 (M$^+$ − 2CO), 324 (M$^+$ − 3CO), 296 (M$^+$ − 4CO), 268 (M$^+$ − 5CO). Anal. Calcd for $C_{17}H_{10}O_5MnCo$: C, 50.03; H, 2.47. Found: C, 49.91; H, 2.40. From the second fraction, 0.040 g (11%, based on **1**) of brown-red crystals of **6** were obtained: mp 109−110 °C (dec); IR (νCO) (CH_2Cl_2) 2054 (vs), 2022 (w), 1991 (vs), 1969 (s), 1891 (w), 1845 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.81 (m, 2H, C_6H_5), 7.55 (m, 3H, C_6H_5), 5.06 (s, 5H, C_5H_5); MS *m/e* 436 (M$^+$), 408 (M$^+$ − CO), 380 (M$^+$ − 2CO), 352 (M$^+$ − 3CO), 324 (M$^+$ − 4CO), 268 (M$^+$ − 6CO). Anal. Calcd for $C_{18}H_{10}O_6MnCo$: C, 50.55; H, 2.65. Found: C, 50.10; H, 2.30.

Reaction of [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (2) with 3 To Give [ReCo{μ-CC_6H_5}$(CO)_5(\eta$-$C_5H_5)$] (7) and [ReCo{μ-C(CO)C_6H_5}$(CO)_5(\eta$-$C_5H_5)$] (8). Compound **2** (0.31 g, 0.43 mmol) was treated, in a manner similar to that described above for the reaction of **1** with **3**, with $Ph_3P)_2NFeCo(CO)_8$ (0.38 g, 0.43 mmol). Immediately, the orange solution turned red. The reaction mixture was stirred at −90 to −45 °C for 4−5 h, during which time the solution gradually turned purple-red until blackish-green. Further treatment of the resulting solution similar to that in the reaction of **1** with **3** afforded 0.183 g (80%, based on **2**) of blackish-green crystals of **7** and 0.032 g (13%, based on **2**) of **8** as brown-red crystals. **7**: mp 68−70 °C (dec); IR (νCO) (CH_2Cl_2) 2050 (s), 2020 (vs), 1998 (s), 1978 (w), 1931 (s, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.87 (m, 2H, C_6H_5), 7.60 (m, 1H, C_6H_5), 7.50 (m, 2H, C_6H_5), 5.70 (s, 5H, C_5H_5); MS *m/e* 512 (M$^+$ − CO), 484 (M$^+$ − 2CO), 456 (M$^+$ − 3CO), 400 (M$^+$ − 5CO). Anal. Calcd for $C_{17}H_{10}O_5ReCo$: C, 37.85; H, 1.77. Found: C, 37.86; H, 1.96. **8**: mp 76−78 °C (dec); IR (νCO) (CH_2Cl_2) 2006(vs), 2000 (vs), 1998 (w), 1983 (m), 1923 (s), 1850 (s) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.35 (m, 5H, C_6H_5), 5.70 (s, 5H, C_5H_5); MS *m/e* 568 (M$^+$), 540 (M$^+$ − CO), 484 (M$^+$ − 3CO), 456 (M$^+$ − 4CO), 428 (M$^+$ − 5CO), 400 (M$^+$ − 6CO). Anal. Calcd for $C_{18}H_{10}O_6ReCo$: C, 38.10; H, 1.78. Found: C, 38.15; H, 1.84.

Reaction of 1 with $(Ph_3P)_2NWCo(CO)_9$ (4) To Give 5 and 6. Similar to the procedure for the reaction of **1** with **3**, compound **1** (0.52 g, 0.87 mmol) was treated with 0.90 g (0.87 mmol) of $(Ph_3P)_2NWCo(CO)_9$ at −90 to −45 °C for 4 h, during which time the orange-yellow solution gradually turned blackish-green. The solvent was removed at −45 to −40 °C in vacuo. The dark red residue was chromatographed on SiO_2 at −25 °C with petroleum ether/CH_2Cl_2 (10:1) as the eluant. After the light yellow band containing $W(CO)_6$ was eluted from the column, the blackish-green band was eluted with petroleum ether/CH_2Cl_2/Et_2O (10:1:1), and then the brown-red band was eluted with petroleum ether/CH_2Cl_2/Et_2O (5:1:1). The solvents were removed from the above two eluates under

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 5, 7, and 8

Compound **5**

Mn−Co	2.608(3)	Co−C(3)	1.80(1)
Mn−C(8)	1.85(1)	Co−C(4)	1.76(2)
Co−C(8)	1.77(1)	Co−C(5)	1.76(2)
Mn−C(1)	1.77(2)	C(8)−C(14)	1.50(2)
Mn−C(2)	1.78(2)		
Co−Mn−C(8)	42.9(4)	Mn−Co−C(4)	118.4(5)
Mn−Co−C(8)	45.2(4)	Mn−Co−C(5)	123.8(6)
Mn−C(8)−Co	91.9(6)	Mn−C(8)−C(14)	135.3(10)
Co−Mn−C(1)	68.8(5)	Co−C(8)−C(14)	132.8(10)
Co−Mn−C(2)	111.8(5)	C(8)−C(14)-C(15)	121(1)
Mn−Co−C(3)	100.1(5)	C(8)−C(14)-C(19)	121(1)

	7	**8**		**7**	**8**
Re−Co	2.710(2)	2.720(1)	Co−C(4)	1.83(2)	1.800(1)
Re−C(8)	2.01(1)	2.121(8)	Co−C(5)	1.78(2)	1.77(1)
Co−C(8)	1.82(1)	2.021(8)	Co−C(7)		1.987(8)
Re−C(1)	1.91(2)	1.95(1)	C(8)−C(14)	1.45(2)	1.46(1)
Re−C(2)	1.92(2)	1.89(1)	C(7)−C(8)		1.40(1)
Co−C(3)	1.79(2)	1.838(10)	C(7)−O(7)		1.194(9)
Re−Co−C(8)	48.0(4)	50.5(2)	C(7)−Co-C(8)		40.9(3)
Co−Re−C(8)	42.2(4)	47.4(2)	Co−C(7)−C(8)		70.8(5)
Re−C(8)−Co	89.9(5)	82.1(3)	Re−C(8)−C(7)		104.0(5)
Co−Re−C(1)	110.4(5)	78.6(3)	Re−C(8)−C(14)	136(1)	133.2(6)
Co−Re−C(2)	70.3(4)	111.9(3)	Co−C(8)−C(7)		68.2(5)
Re−Co−C(3)	97.0(5)	94.2(3)	Co−C(8)−C(14)	133(1)	125.2(6)
Re−Co−C(4)	118.8(5)	93.5(3)	C(8)−C(14)-C(15)	118(1)	123.0(7)
Re−Co−C(5)	124.3(5)	160.1(3)	C(8)−C(14)-C(19)	122(1)	119.8(7)
Re−Co−C(7)		71.4(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 Complexes 9 and 10

	9, M = Mn	**10**, M = Re		**9**, M = Mn	**10**, M = Re
M(1)−Co(1)	2.575(3)	2.707(1)	M(1)−C(2)	1.83(1)	1.922(10)
M(1)−Fe(1)	2.570(2)	2.707(2)	Fe(1)−C(2)	2.26(1)	2.504(9)
Co(1)−Fe(1)	2.549(3)	2.542(2)	Co(1)−C(3)	1.80(1)	1.834(10)
M(1)−C(8)	1.94(1)	2.052(8)	Co(1)−C(4)	1.79(1)	1.79(1)
Fe(1)−C(8)	1.91(1)	1.936(8)	Co(1)−C(5)	1.83(2)	1.791(10)
Co(1)−C(8)	1.94(1)	1.922(7)	Fe(1)−C(20)	1.75(2)	1.81(1)
C(8)−C(9)	1.51(1)	1.48(1)	Fe(1)−C(21)	1.80(2)	1.78(1)
M(1)−C(1)	1.82(1)	1.941(10)	Fe(1)−C(22)	1.81(1)	1.77(1)
Co(1)−C(1)	2.32(1)	2.539(10)			
Fe(1)−Co(1)−M(1)	60.21(7)	62.00(4)	Co(1)−Fe(1)−C(8)	49.1(3)	48.5(2)
Co(1)−Fe(1)−M(1)	60.41(7)	61.99(4)	M(1)−Fe(1)−C(8)	48.6(3)	49.1(2)
Co(1)−M(1)−Fe(1)	59.38(7)	56.01(4)	Fe(1)−M(1)−C(8)	47.6(3)	45.5(2)
Co(1)−C(8)−M(1)	83.2(4)	85.8(3)	Fe(1)−C(2)−M(1)	77.2(5)	74.1(3)
Fe(1)−C(8)−M(1)	83.9(4)	85.4(3)	Co(1)−C(1)−M(1)	76.0(5)	73.0(3)
Co(1)−C(8)−Fe(1)	83.0(4)	82.4(3)	M(1)−C(8)−C(9)	132.8(8)	129.4(6)
Co(1)−M(1)−C(8)	48.4(3)	45.1(2)	Fe(1)−C(8)−C(9)	130.7(8)	130.0(6)
M(1)−Co(1)−C(8)	48.4(3)	49.1(2)	Co(1)−C(8)−C(9)	125.7(8)	127.5(5)
Fe(1)−Co(1)−C(8)	48.0(3)	49.0(2)			

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

vacuum, and the residues were recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C. From the first fraction, 0.275 g (76%, based on **1**) of blackish-green crystals of **5** were obtained, which was identified by its mp and IR, ^{1}H NMR, and mass spectra. From the second fraction, 0.055 g (14%, based on **1**) of brown-red crystals of **6** were obtained, which was identified by its mp and IR, ^{1}H NMR, and mass spectra.

Reaction of 2 with 4 To Give 7 and 8. As described above for the reaction of **1** with **3**, compound **2** (0.23 g, 0.32 mmol) was treated with 0.33 g (0.32 mmol) of **4** at −90 to −70 °C for 5 h, during which time the orange-red solution gradually turned dark purple. Further treatment of the resulting solution in a manner similar to that described in the reaction of **1** with **4** afforded 0.064 g (37%, based on **2**) of blackish-green crystalline **7** and 0.103 g (57%, based on **2**) of brown-red crystals of **8**, which were identified by their mp and IR, ^{1}H NMR, and mass spectra.

Reaction of 5 with CO To Give 6. Carbon monoxide gas was bubbled though a solution of 0.025 g (0.06 mmol) of **5** in 30 mL of THF at −50 to −40 °C for 6 h, during which time the blackish-green solution gradually turned brown green. After removal of the solvent in vacuo, the residue was chromatographed on SiO_2 with petroleum ether/CH_2Cl_2 (10:1) as the eluant. The brown band was eluted and collected. The solvent was removed, and the residue was recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C to give 0.019 g (70%, based on **5**) of brown-red crystals of **6**, which was identified by its mp and IR, ^{1}H NMR, and mass spectra.

Reaction of 5 with $Fe_2(CO)_9$ To Give [MnFeCo(μ_3-CC_6H_5)(μ-CO)2$(CO)_6$(η-C_5H_5)] (9). To 27 mg (0.066 mmol) of **5** dissolved in 50 mL of THF at −40 °C was added 90 mg (0.247 mmol) of $Fe_2(CO)_9$. The mixture was stirred at −40 to 0 °C for 10 h, during which time the dark green solution gradually turned brown-red. After the solution was evaporated at 0 °C under vacuum to dryness, the residue was chromatographed on SiO_2 at −15 to −20 °C with petroleum ether/CH_2Cl_2 (10:1) as the eluant. The purple-red band was eluted and collected. The solvent was removed from the red eluate in vacuo, and the crude product was recrystallized from petroleum ether/CH_2Cl_2 at −80 °C to give 26 mg (72%, based on **5**) of purple-red crystals of **9**: mp 91−92 °C (dec); IR (νCO) (CH_2Cl_2) 2078 (vs), 2054 (w), 2031 (vs), 1984 (w), 1964 (m), 1889 (s), 1831 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.72 (m, 2H, C_6H_5), 7.51 (m, 2H, C_6H_5), 7.33 (m, 1H, C_6H_5), 4.90 (s, 5H, C_5H_5); MS *m/e* 548 (M^+), 464 ($M^+ - 3CO$), 408 ($M^+ - 5CO$), 380 ($M^+ - 6CO$), 324 ($M^+ - 8CO$). Anal. Calcd for $C_{20}H_{10}O_8$-MnFeCo: C, 43.83; H, 1.84. Found: C, 43.78; H, 1.83.

Reaction of 6 with $Fe_2(CO)_9$ To Give 9. To 25 mg (0.057 mmol) of **6** dissolved in 40 mL of THF at −40 °C was added 93 mg (0.256 mmol) of $Fe_2(CO)_9$. The mixture was stirred at −20 to 5 °C for 8 h, during which time the brown-green solution gradually turned brown-red. Further treatment of the resulting solution in a manner similar to that described in the reaction of **5** with $Fe_2(CO)_9$ afforded 22 mg (71%, based on **6**) of purple-red crystalline **9**, which was identified by its mp and IR, ^{1}H NMR, and mass spectra.

Reaction of 7 with $Fe_2(CO)_9$ To Give [ReFeCo(μ_3-CC_6H_5)(μ-CO)$_2$(CO)$_6$-(η-C_5H_5)] (10). To 28 mg (0.052 mmol) of **7** dissolved in 50 mL of THF at −40 °C was added 75 mg (0.206 mmol) of $Fe_2(CO)_9$. The mixture was stirred at −20 to 0 °C for 10 h, during which time the dark green solution gradually turned brown-red. Further treatment of the resulting solution as described above in the reaction of **5** with Fe_2-$(CO)_9$ yielded 26 mg (74%, based on **7**) of black-red crystalline **10**: mp 86−88 °C dec; IR (νCO) (CH_2Cl_2) 2074 (vs), 2054 (w), 2025 (vs), 1970 (w), 1954 (w), 1909 (s), 1854 (m, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.53 (m, 2H, C_6H_5), 7.45 (m, 2H, C_6H_5), 7.22 (m, 1H, C_6H_5), 5.62 (s, 5H, C_5H_5). Anal. Calcd for $C_{20}H_{10}O_8$ReFeCo: C, 35.36; H, 1.48. Found: C, 35.60; H, 1.59.

Reaction of 8 with $Fe_2(CO)_9$ To Give 10. To 23 mg (0.041 mmol) of **8** dissolved in 40 mL of THF at −40 °C was added 65 mg (0.179 mmol) of $Fe_2(CO)_9$. The mixture was stirred at −20 to 5 °C for 8 h, during which time the orange-red solution gradually turned dark red. Further treatment as described above in the reaction of **5** with $Fe_2(CO)_9$ gave 21 mg (75%, based on **8**) of black-red crystalline **10**, which was identified by its mp and IR and ^{1}H NMR spectra.

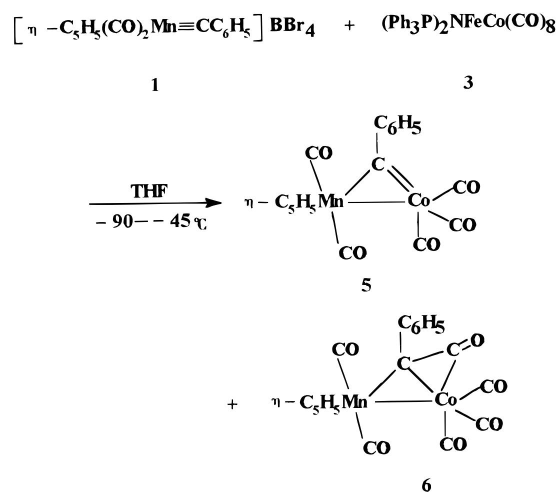
X-ray Crystal Structure Determinations of Complexes 5, 7, 8, 9, and 10. Single crystals of **5**, **7**, **8**, **9**, and **10** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH_2Cl_2 solution at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 2630, 2759, 2976, 8003, and 7755 independent reflections, of which 1038, 1708, 1976, 3014, and 4978 with $I > 3.00\,\sigma(I)$ were observable, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo Kα radiation with a $\omega-2\theta$ scan mode within the ranges $5° \leq 2\theta \leq 50°$ for **5**, **7**, **8**, **9**, and **10**, respectively.

The structures of **5**, **7**, **8**, and **9** 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 based on 1038, 1708, 1976, and 3014 observed reflections ($I > 3.00\sigma(I)$) and 217, 217, 235, and 559 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.056$ and $R_w = 0.057$ for 5, $R = 0.039$ and $R_w = 0.045$ for **7**, $R = 0.029$ and $R_w = 0.030$ for **8**, and $R = 0.058$ and $R_w = 0.051$ for **9**. For **10**, the structure was solved by 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 4978 observed reflections ($I > 3.00\sigma(I)$) and 560 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.031$ and $R_w = 0.033$. All of 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 **5**, **7**, **8**, **9**, and **10** are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3. Atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **5**, **7**, **8**, **9**, and **10** are given in the Supporting Information. The molecular structures of **5**, **7**, **8**, **9**, and **10** are given in Figures 1, 2, 3, 4, and 5, respectively.

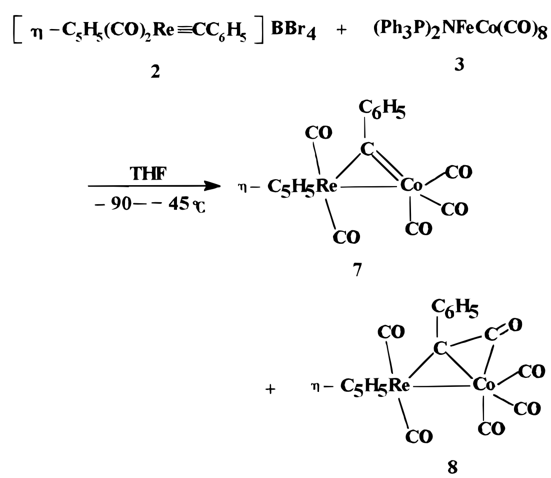
Results and Discussion

[η-$C_5H_5(CO)_2Mn{\equiv}CC_6H_5$]$BBr_4$ (**1**) was treated with an equimolecular amount of $Ph_3P)_2NFeCo(CO)_8$ (**3**) in THF at low temperature (−90 to −45 °C) for 3−4 h. After removal of the solvent under high vacuum, the residue was chromatographed on a SiO_2 column at low temperature and the crude products were recrystallized from petroleun ether/CH_2Cl_2 at −80 °C to give blackish-green complex **5**, [MnCo{μ-CC_6H_5}(CO)$_5$(η-C_5H_5)], and brown-red complex **6**, [MnCo{μ-C(CO)C_6H_5}(CO)$_5$(η-C_5H_5)] (eq 1), in 81% and 11% isolated yields, respectively.



(1)

Analogous reaction of [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (**2**) with **3** under the same conditions afforded blackish-green crystalline **7**, [ReCo{μ-CC_6H_5}(CO)$_5$(η-C_5H_5)], and brown-red crystalline **8**, [ReCo{μ-C(CO)C_6H_5}(CO)$_5$(η-C_5H_5)] (eq 2), in 80% and 13% yields, respectively.



(2)

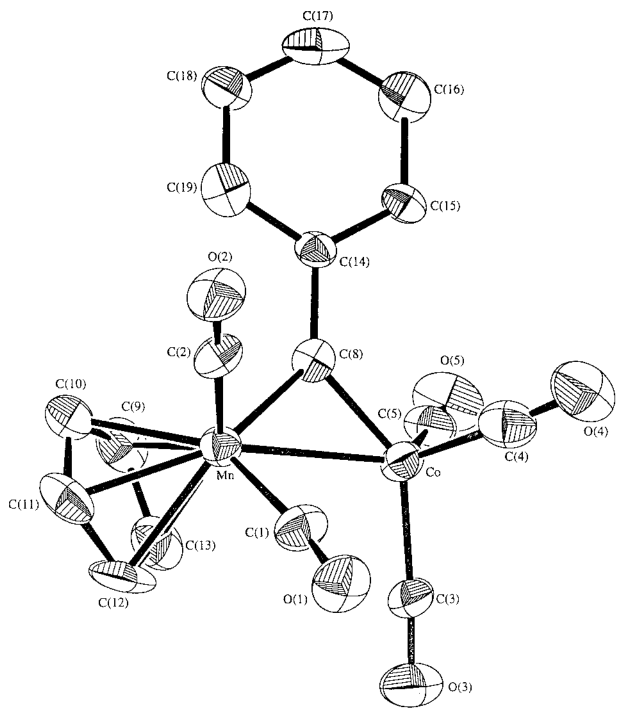


Figure 1. Molecular structure of **5**, showing the atom-numbering scheme.

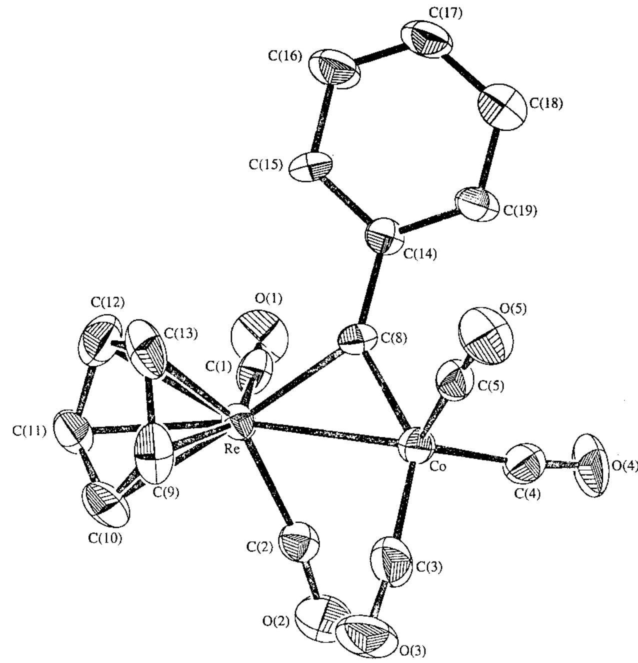


Figure 2. Molecular structure of **7**, showing the atom-numbering scheme.

Compound **1** also reacted with $Ph_3P)_2NWCo(CO)_9$ (**4**) under the same conditions to produce products **5** and **6** (eq 3) in similar yield. Complex **2** reacted similarly with **4** under the same conditions (eq 4), however, the main product was complex **8** (57%) instead of complex **7** (37%).

$$1 + \underset{4}{(Ph_3P)_2NWCo(CO)_9} \xrightarrow[-90\ \text{to}\ -45\ ^\circ C]{THF} 5 + 6 \quad (3)$$

$$2 + \underset{4}{(Ph_3P)_2NWCo(CO)_9} \xrightarrow[-90\ \text{to}\ -45\ ^\circ C]{THF} 7 + 8 \quad (4)$$

On the basis of elemental analyses, spectroscopic evidence, and X-ray crystallography, complexes **5** and **7** are formulated as heteronuclear dimetal bridging carbyne complexes, and complexes **6** and **8** are formulated as heteronuclear dimetal bridging carbene complexes with a CO group bonded to the bridging carbene carbon and a Co atom through the carbon atom.

Complexes **5**−**8** are readily soluble in polar organic solvents but sparingly soluble in nonpolar solvents. They are sensitive to air and temperature in solution but relatively stable as the solid. The compositions of complexes **5**−**8** were established by elemental analysis and IR, ^{1}H NMR, and mass spectroscopy (see Experimental Section), all of which are consistent with the structures shown. The X-ray diffraction studies for complexes **5**, **7**, and **8** were carried out in order to firmly establish their structures.

The results of the X-ray diffraction work of complex **5** are summarized in Table 1, and the structure is shown in Figure 1. In **5** the Mn−Co bond is bridged by CC_6H_5, giving a dimetallacyclopropene ring. The dimensions of the dimetallacyclopropene ring are: Mn−Co 2.608(3), C(8)−Mn 1.85(1), and C(8)−Co 1.77(1) Å. Since the radii of coblt and iron are nearly the same, it is interesting to compare the metal−metal bond distance in **5** with the shorter Mn−Fe separation (2.572(1) Å) found in analogous bridging carbyne complex [(CO)(η-C_5H_5)Fe(μ-COEt)(μ-CO)Mn(η-C_5H_4Me)(CO)].[8] But the Mn−Co bond in **5** is slightly shorter than the similar bond in the bridging carbene complex [MnFe(μ-C(COEt)Ph}(η-C_5H_5)$(CO)_5$] (2.6929(8) Å).[4] The C(8)−Mn linkage in **5** is slightly longer than the corresponding distance (1.839(4) Å) in [(CO)(η-C_5H_5)Fe(μ-COEt)(μ-CO)Mn(η-C_5H_4Me)(CO)][8] but is significantly shorter than that in [MnFe(μ-C(COEt)Ph}(η-C_5H_5)$(CO)_5$] (2.021(4) Å).[4] The C(8)−Co distance in **5** (1.77(1) Å) is as expected for a C=Co bond, which is obviously shorter than corresponding distance in [(CO)(η-C_5H_5)Fe(μ-COEt)(μ-CO)Mn(η-C_5H_4Me)(CO)] (1.843(4) Å)[8] and [MnFe(μ-C(COEt)Ph}(η-C_5H_5)$(CO)_5$] (2.020(4) Å).[4]

The molecular structure of complex **7** shown in Figure 2 resembles that of complex **5**, as can be visualized in the ORTEP diagrams of **5** and **7** represented in Figures 1 and 2. This investigation was carried out in order to extend the scope of the structural data available for heteronuclear dimetal bridging carbyne complexes. In **7** the dimensions of the dimetallacyclopropene ring are Re−Co 2.710(2), C(8)−Re 2.01(1), and C(8)−Co 1.82(1) Å. Since the radii of Re and W are approximately the same, we can compare the metal−metal bond distance in **7** with the slightly longer Co−W separation (2.758(1) Å) found in analogous carbyne complex [CoW(μ-$CC_6H_4Me_4$)$(CO)_3$(η-C_5H_5)(η-C_5Me_5)].[9] The Re−Co bond length in **7** is somewhat longer than the similar bonds found in [ReFe(μ-CC_6H_5)(μ-CO)$(CO)_3$-(η-C_5H_5)($COC_2B_{10}H_{10}$)] (Re−Fe = 2.682(2) Å).[10] The C(8)−Re bond distance in **7** is significantly longer than the corresponding distance (1.86(4) Å) in [ReFe(μ-CC_6H_5)(μ-CO)-

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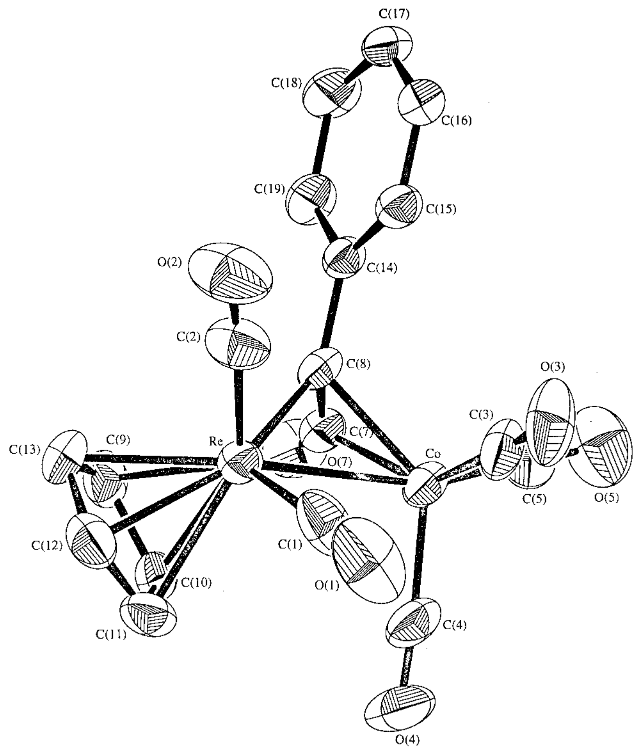

Figure 3. Molecular structure of **8**, showing the atom-numbering scheme.

$(CO)_3(\eta\text{-}C_5H_5)(COC_2B_{10}H_{10})]$[10] but somewhat shorter than the corresponding distance in $[ReFe(\mu\text{-}CHC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (2.120(5) Å).[3] The C(8)−Co distance (1.82(1) Å) in **7** is also as expected for a C═Co bond based on the comparable μ-C═Co separation (1.77(1) Å) found in **5**.

The structure of complex **8** (Figure 3) resembles that of $[ReFe\{\mu\text{-}C(n\text{-}C_4H_9S)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$,[11] except that the substituent on the bridging carbene carbon is a bridged CO group in **8** but a bridged $n\text{-}C_4H_9S$ group in the latter. The Re−Co bond is bridged by $C(CO)C_6H_5$, giving a dimetallacyclopropane ring, and the CO group is bridged to a μ-C−Co bond through the C(7) atom, thus giving the Co an 18-electron configuration. The C(8)−C(7) bond distance is only 1.40(1) Å. The Co−C(7) distance of 1.987(8) Å is close in value to the similar bond in $[Fe(COC_6H_4CF_3\text{-}p)(\eta\text{-}C_5H_5)(CO)_2]$ (1.972(4) Å).[12] The bond length of C(7)−O(7) (1.194(9) Å) is slightly shorter than that in $[Fe(COC_6H_4CF_3\text{-}p)(\eta\text{-}C_5H_5)(CO)_2]$ (1.217(6) Å).[12] In **8** the dimensions of the dimetallacyclopropane ring are Re−Co 2.720(1), C(8)−Re 2.121(8), and C(8)−Co 2.021(8) Å. The Re−Co bond length in **8** is slightly shorter than the similar bonds found in $[ReFe(\mu\text{-}CHC_6H_5)(CO)_6(\eta\text{-}C_5H_5)]$ (2.7581(8) Å)[3] and $[ReFe(\mu\text{-}C(n\text{-}C_4H_9S)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (2.784(2) Å)[11] but is nearly the same as that of **7**. The C(8)−Re bond distance in **8** is the same within experimental error as the corresponding distance in $[ReFe(\mu\text{-}C(n\text{-}C_4H_9S)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ (2.128(10) Å)[11] but is somewhat longer than that in **7** (2.01(1) Å). The C(8)−Co distance (2.021(8) Å) is markedly longer than that (1.82(1) Å) in **7**.

The possible reaction pathway to complexes **5** and **7** (eqs 1−4) could proceed via a synthon for $Co(CO)_3^-$, which attacked on the carbyne carbon of cationic carbyne complex **1** or **2** with bonding of the Co atom to the Mn or Re atom to construct a dimetallacyclopropene ring, since the analogous reaction[13] of the $Co(CO)_4^-$ anion with complex **1** or **2** under the same conditions gave no bridging carbyne complex **5** or **7** but bridging carbene complex **6** or **8**. The clever synthon of $Co(CO)_3^-$ could come from either expulsion of $Fe(CO)_5$ or $W(CO)_6$ directly from the $FeCo(CO)_8^-$ or $WCo(CO)_9^-$ anion in the presence of complex **1** or **2** or a carbene intermediate $[\eta\text{-}C_5H_5(CO)_2M{=}C(C_6H_5)M'Co(CO)_n]$ (M = Mn or Re, M′ = Fe or W, n = 8 or 9) formed by attack of the $[M'Co(CO)_n]^-$ anion on the carbyne carbon of **1** or **2**. The carbene intermediate then underwent expulsion of $Fe(CO)_5$ or $W(CO)_6$ to generate the $Co(CO)_3^-$ moiety. We have indeed isolated $Fe(CO)_5$ and $W(CO)_6$ in the course of the column chromatography (Experimental Section). The formation of **6** or **8** could proceed via intermediate complex **5** or **7**. To explore this possibility, we investigated the reaction of CO gas with complex **5**. This reaction gave complex **6** in 70% yield (eq 5). This result

$$5 + CO \xrightarrow[-50\text{ to }-40\ ^\circ C]{THF} 6 \qquad (5)$$

shows that complex **5** can indeed convert to complex **6** and suggests that **6** was derived from **5** by addition of one CO molecule generated by cleavage of the dimetal carbonyl anions or other species.

A number of dimetal bridging carbyne complexes have prepared by Stone et al. by reactions[14] of alkylidyne complexes with low-valent metal species or by reactions[15] of anionic carbyne complexes with cationic metal compounds. Complexes **5** and **7**, as heteronuclear dimetal bridging carbyne complexes, were synthesized first by reactions of the cationic carbyne complexes with the mixed-dimetal carbonyl anions. Undoubtedly, this is a new, direct, and convenient method for the synthesis of dimetal bridging carbyne complexes.

Interestingly, complex **5** reacted with an excess of $Fe_2(CO)_9$ in THF at −40 to 0 °C for 10 h. After workup as described in the Experimental Section, the purple-red compound **9**, $[MnFeCo(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)]$, was isolated in 72% yield (eq 6). Surprisingly, complex **6** can also react with $Fe_2(CO)_9$ under similar conditions to give the same product **9** (eq 7) in nearly the same yield.

Complex **7** or **8** reacted similarly with $Fe_2(CO)_9$ under similar conditions to give blackish-red crystalline compound **10**, $[ReFeCo(\mu_3\text{-}CC_6H_5)(CO)_8(\eta\text{-}C_5H_5)]$, in 74−75% yields (eqs 8 and 9).

Complexes **9** and **10** are formulated as the hetero-

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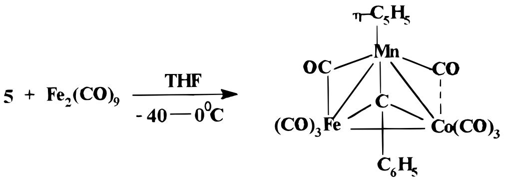

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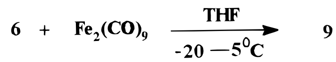
9



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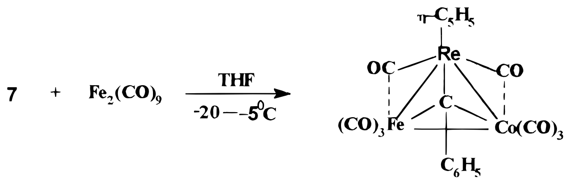

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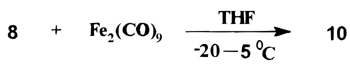

(9)

nuclear trimetal bridging carbyne complexes whose structures have been established by X-ray diffraction studies.

The molecular structure of **9** is shown in Figure 4. It is very interesting that complex **9** crystallizes with two independent molecules in the asymmetric unit. However, its ^1H NMR spectrum showed that the two molecules are separated in solution, giving a single normal molecule. Although two independent molecules in an asymmetric unit is not unusual in crystallography, this structure was observed in the trimetal bridging carbyne complexes for first time.

In **9** the triangular MnFeCo arrangement with a capping μ_3-CC_6H_5 ligand is confirmed. The three metal atoms construct an approximate isosceles triangle (Mn(1)−Fe(1) = 2.570(2) Å, Mn(1)−Co(1) = 2.575(3) Å, and Fe(1)−Co(1) = 2.549(3) Å). The μ-C(8)−Mn(1), μ-C(8)−Fe(1), and μ-C(8)−Co(1) distances are 1.94(1), 1.91(1), and 1.94(1) Å, respectively. Compound **9** appears to be the first example of a species with Mn−Co, Mn−Fe, and Fe−Co bonds studies by X-ray crystallography, and hence, comparison of these metal−metal bond distances with others involving these elements is not possible.

In **9**, the Fe and Co atoms each carry three terminal carbonyl groups and the Mn atom carries one bridged carbonyl group to Fe, with a second CO on Mn being semi-bridging to Co (Mn(1)−C(2)−O(2) = 155(1)°, Fe(1)−C(2) = 2.26(1) Å; Mn(1)−C(1)−O(1) = 160(1)°, Co(1)−C(1) = 2.32(1) Å), thus giving each metal atom an 18-electron configuration.

The molecular structure of complex **10** shown in Figure 5 has many common features with that of complex **9**. Similar to that found in **9**, there are two independent molecules in the asymmetric unit of **10**. The two molecules in the cell are the same. The molecule of **10** possesses a trimetalatetrahedrane CReFeCo core. The three metal atoms construct an approximate isosceles triangle (Re(1)−Fe(1) = 2.707(2) Å, Re(1)−Co(1) = 2.707(1) Å, and Fe(1)−Co(1) = 2.542(2) Å). The Re−Co bond length is closely related to that of known complexes [$Co_2Re(\mu_3$-CC_6H_4Me-4)$(CO)_{10}$] (average Re−Co = 2.70 Å)[16] and [$ReCo_2(\mu_3$-$CC_6H_5)(\mu$-$CO)_2(CO)_5(\eta$-$C_5H_5)(COC_2B_{10}H_{10})$] (2.669(3) Å).[10] The μ-C−Re, μ-C−Fe, and μ-C−Co distances are 2.052(8), 1.936(8), and 1.922(7) Å, respectively, of which the μ-C−Co bond length is comparable to that found in [$Co_2Re(\mu_3$-CC_6H_4-Me-4)$(CO)_{10}$] (average 1.89 Å)[16] and [$ReCo_2(\mu_3$-$CC_6H_5)(\mu$-$CO)_2(CO)_5(\eta$-$C_5H_5)(COC_2B_{10}H_{10})$] (average 1.93 Å),[10] while the μ-C−Re bond length is nearly the same as that in [$ReCo_2(\mu_3$-$CC_6H_5)(\mu$-$CO)_2(CO)_5(\eta$-$C_5H_5)(COC_2B_{10}H_{10})$] (2.01(1) Å)[10] but somewhat shorter than that in [$Co_2Re(\mu_3$-CC_6H_4Me-4)$(CO)_{10}$] (average 2.189(6) Å).[16]

In **10** the Co and Fe atoms each carry three terminal carbonyl groups and the Re atom carries two carbonyl groups being semibridging to the Co and Fe atoms,

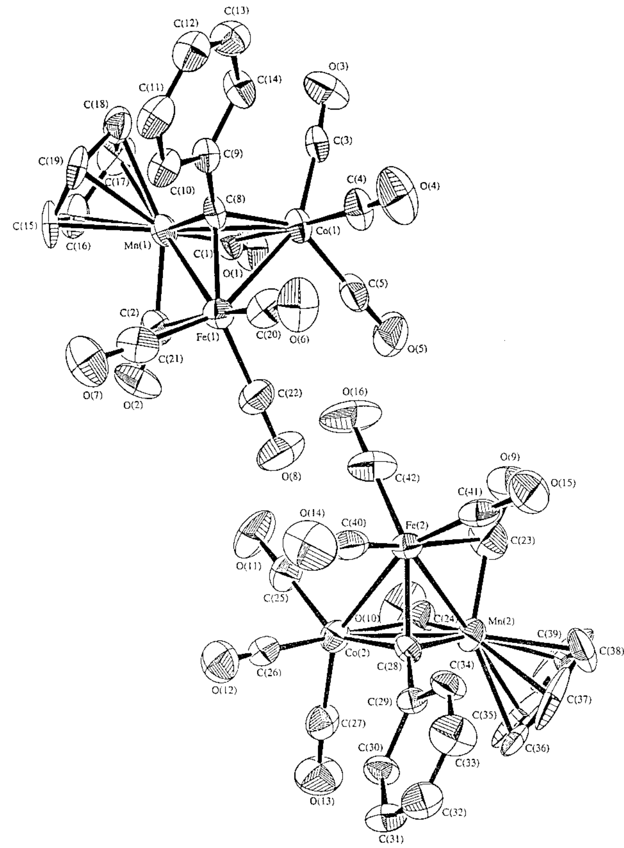

Figure 4. Molecular structure of **9**, showing the atom-numbering scheme.

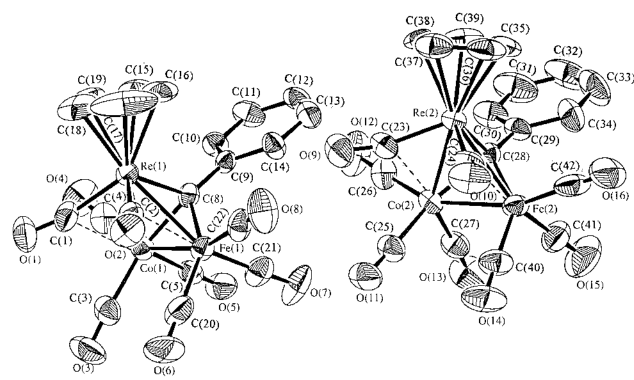

Figure 5. Molecular structure of **10**, showing the atom-numbering scheme.

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respectively (Re(1)−C(1)−O(1) = 166.8(9)°, Co(1)−C(1) = 2.539(10) Å; Re(1)−C(2)−O(2) = 165.2(9)°, Fe(1)−C(2) = 2.504(9) Å). Complex **10** is a 48 CVE (cluster valence electron) complex, where the Re and Fe atoms formally have 19 and 17 electrons, respectively, which probably accounts for the presence of the semibridging carbonyl. In **10** the semibridging CO ligand reveals itself in the IR spectrum with a band at 1854 cm^{-1}. The analogous 48-valence-electron structure was found in the complex $[MW_2\{\mu_3\text{-}C_2R_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ (M = Ru or Os).[17]

A series of trimetal bridging carbyne complexes have been synthesized by Stone et al. by reactions[14a,c,18] of alkylidyne complexes, such as $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, with low-valent metal species. Complexes **9** and **10**, as heteronuclear trimetal bridging carbyne complexes, were obtained by the reaction of dimetal bridging carbyne or bridging carbene complexes with $Fe_2(CO)_9$. Only one analogous reaction is known.[14c] Stone et al. reported that the carbyne complex $[M(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W) reacted with an excess of $Fe_2(CO)_9$ to afford a trimetal bridging carbyne complex, $[MFe_2\{\mu_3\text{-}C(C_6H_4Me\text{-}4)\}(CO)_9(\eta\text{-}C_5H_5)]$ (M = Mo, W).[14c] In this reaction, the initially formed dimetal bridging carbyne intermediate $[MFe(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(\eta\text{-}C_5H_5)(CO)_6]$ reacted further with $Fe_2(CO)_9$ to give the trimetal species. The reaction of a dimetal bridging carbene complex with low-valent metal species giving a trimetal bridging carbyne complex is unusual. To our knowledge, no such reaction has been reported. The reaction of the dimetal bridging carbene complexes with $Fe_2(CO)_9$ afforded the heteronuclear trimetal bridging carbyne complexes, which may represent a new route to trimetal bridging carbyne complexes.

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Supporting Information Available: Tables of atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **5**, **7**, **8**, **9**, and **10** (58 pages). Ordering information is given on any current masthead page.

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