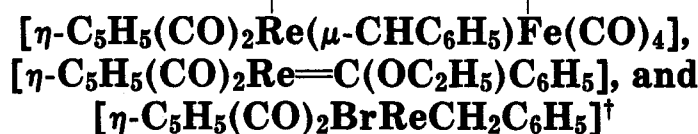


Unusual Reaction between a Cationic Carbyne Complex of Rhenium and Nucleophiles Containing a Carbonyliron Dianion To Form a Dimetal Complex with a Bridging Carbene Ligand. Syntheses and Crystal Structures of



Jiabi Chen,^{*1a} Yong Yu,^{1a} Kun Liu,^{1b} Guang Wu,^{1b} and Peiju Zheng^{1b}

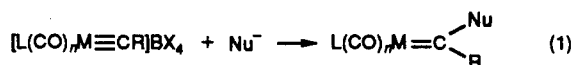
Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China, and Research Center of Analysis and Measurement, Fudan University, Shanghai 200433, China

Received October 19, 1992

The reaction of $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{CC}_6\text{H}_5]\text{BBr}_4$ (1) with $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$ in THF at low temperature gave dimetal complexes with bridging carbene ligands, $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}(\mu\text{-CHC}_6\text{H}_5)\text{Fe}(\text{CO})_4]$ (3), and $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5]$ (2), and $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{BrReCH}_2\text{C}_6\text{H}_5]$ (4). The same products, 2 and 3, were obtained from the reaction of 1 with $\text{Na}_2\text{Fe}(\text{CO})_4$ and $\text{Na}_2\text{Fe}_3(\text{CO})_{11}$. At low temperature complex 3 in toluene solution transformed into the complex $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{C}(\text{H})\text{C}_6\text{H}_5]$ (5). The structures of complexes 2, 3, 4, and 5 were established by X-ray crystallographic studies.

Introduction

We have previously shown that several carbene complexes containing a special substituent bonded to the carbene carbon atom have been synthesized by the reactions of cationic carbyne complexes of transition metals with nucleophiles.²⁻⁵ However, only a few carbene complexes with a transition metal or a metal group bonded to the carbene carbon atom through the metal atom are known^{2,6,7} (eq 1). Therefore, an attempt was made to



L = CO, C₅H₅, C₅MeH₄; R = NEt₂, C₆H₅; X = F, Cl, Br; M = Cr, Mn, Re; Nu = Sn(C₆H₅)₃, Pb(C₆H₅)₃, TeC₆H₅, Co(CO)₄

synthesize a carbene complex with a carbonyliron group on the carbene carbon by reaction of a cationic carbyne complex of rhenium, $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{CC}_6\text{H}_5]\text{BBr}_4$ (1), with nucleophiles containing a carbonyliron dianion to

examine the effect of the electronegative group of the carbonyliron dianion on the carbene complexes.

Unexpectedly, $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{CC}_6\text{H}_5]\text{BBr}_4$ (1) reacted with carbonyliron salts $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$, $\text{Na}_2\text{Fe}(\text{CO})_4$, and $\text{Na}_2\text{Fe}_3(\text{CO})_{11}$ in THF at low temperature to afford a dimetal complex with a bridging carbene ligand, $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}(\mu\text{-CHC}_6\text{H}_5)\text{Fe}(\text{CO})_4]$ (3), instead of the expected nonbridging carbene complex. The complexes $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5]$ (2) and $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{BrReCH}_2\text{C}_6\text{H}_5]$ (4) were also obtained as byproducts in this reaction. Herein we report the details of these reactions of complex 1 and the structural characterizations of the products.

Experimental Section

All manipulations were carried out under an N₂ atmosphere using standard Schlenk techniques. All solvents employed were dried by reflux over appropriate drying agents and stored over 4-Å molecular sieves under an N₂ atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl, petroleum ether (30–60 °C) from CaH₂, and CH₂Cl₂ from P₂O₅, while toluene was distilled from sodium. The neutral alumina (Al₂O₃) used for chromatography was deoxygenated at room temperature in high vacuum for 16 h, deactivated with 5% w/w N₂-saturated water, and stored under N₂. $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{CC}_6\text{H}_5]\text{BBr}_4$ (1) was prepared as previously described.⁹ $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$,¹⁰ $\text{Na}_2\text{Fe}(\text{CO})_4$,¹¹ and $\text{Na}_2\text{Fe}_3(\text{CO})_{11}$ ¹¹ were prepared by literature methods.

(8) Fischer, E. O.; Wenner, J. K. R.; Müller, G.; Riede, J. *Chem. Ber.* 1985, 118, 3311.

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

(10) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* 1982, 1, 1350.

(11) Strong, H.; Krusic, P. J.; Filippo, J. S., Jr. *Inorg. Synth.* 24, 157.

[†] Dedicated to Professor Yao-Zeng Huang on the occasion of his 80th birthday and in recognition of his many research contributions in organometallic chemistry.

(1) (a) Shanghai Institute of Organic Chemistry. (b) Fudan University, X-ray structure analysis.

(2) Fischer, E. O.; Chen, J.-B. *Acta Chim. Sin. (Chin. Ed.)* 1985, 43, 257.

(3) Chen, J.-B.; Lei, G.-X.; Zhang, Z.-Y.; Tang, Y.-Q. *Acta Chim. Sin. (Engl. Ed.)* 1986, 4, 311.

(4) Chen, J.-B.; Lei, G.-X.; Xu, W.-H.; Zhang, Z.-Y.; Xu, X.-J.; Tang, Y.-Q. *Sci. Sin. B*, 1987, XXX, 24.

(5) Chen, J.-B.; Lei, G.-X.; Zhang, Z.-Y.; Tang, Y.-Q. *Acta Chim. Sin. (Chin. Ed.)* 1989, 47, 31.

(6) Fischer, E. O.; Pardy, R. B. A.; Schubert, U. J. *Organomet. Chem.* 1979, 181, 37.

(7) (a) Fischer, H.; Fischer, E. O.; Cai, R.-F. *Chem. Ber.* 1982, 115, 2707. (b) Fischer, E. O.; Cai, R.-F.; Himmreich, D. *Chem. Ber.* 1983, 116, 1009.

Table I. Crystal Data and Experimental Details for X-ray Diffraction Studies of Complexes 2, 3, 4, and 5

	2	3	4	5
formula	ReO ₃ C ₁₃ H ₁₅	ReFeO ₆ C ₁₈ H ₁₁	ReBrO ₂ C ₁₄ H ₁₂	ReO ₂ C ₁₄ H ₁₁
formula wt	441.50	565.34	478.36	397.45
space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ /n	P2 ₁ /c
a, Å	10.088(2)	7.093(1)	10.399(2)	9.346(1)
b, Å	11.416(3)	29.912(3)	12.148(1)	7.278(1)
c, Å	12.813(3)	8.856(3)	10.928(3)	18.140(2)
β, deg	90.55(2)	110.21(2)	103.32(1)	97.85(1)
V, Å ³	1475.5	1763.3(1)	1343.5(8)	1222.5(2)
Z	4	4	4	4
D _{calc} , g/cm ³	1.987	2.130	2.365	1.080
crystal size, mm	0.20 × 0.10 × 0.20	0.20 × 0.25 × 0.20	0.07 × 0.15 × 0.20	0.07 × 0.55 × 0.20
Mo Kα, cm ⁻¹	83.499	78.06	121.05	50.30
data collectn instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiatn (monochromated in incident beam)	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)
orientatn rflctns, no., range (2θ)	25, 24–31°	25, 22–30°	25, 24–32°	25, 24–30°
temp, °C	25	25	25	25
scan method	ω-2θ	ω-2θ	ω-2θ	ω-2θ
data col. range, 2θ, deg	2–50	2–50	2–50	2–50
no. unique data, total	2746	3190	2224	2332
with F _o ² > 3σ(F _o ²)	2107	2315	1512	1437
no. of params refined	181	235	164	155
trans. factors, max, min (psi-scans)	0.999, 0.466	0.999, 0.673	1.044, 0.945	0.998, 0.550
correctns factors, max, min (numerical)	1.041, 0.961	1.064, 0.996	1.031, 0.999	1.027, 0.981
R ^a	0.030	0.0282	0.0206	0.0381
R _w ^b	0.039	0.0336	0.0233	0.0438
quality-of-fit indicator ^c	2.789	2.675	2.068	3.478
largest shift/essd, final cycle	0.03	<0.01	0.01	<0.01
largest peak, e/Å ³	1.383	0.975	0.417	0.767

^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/σ²(|F_o|). ^c Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations^a for 2 and 3

atom	2				3			
	x	y	z	B (Å ²)	x	y	z	B (Å ²)
Re	0.14344(4)	0.17388(3)	0.76296(3)	3.072(7)	0.15921(5)	0.11616(1)	0.57482(4)	2.717(6)
Fe					0.2778(2)	0.06903(4)	0.8601(1)	2.88(2)
O(1)	0.4071(8)	0.2525(9)	0.6711(8)	7.8(2)	-0.1493(9)	0.0409(3)	0.5302(8)	5.1(2)
O(2)	0.366(1)	0.4821(8)	0.9027(6)	7.7(2)	-0.159(1)	0.1822(3)	0.585(1)	7.7(3)
O(3)	0.5303(7)	0.1752(7)	0.0839(5)	4.9(1)	0.572(1)	0.0817(3)	1.1821(8)	5.5(2)
O(4)					-0.0817(9)	0.1046(2)	0.9105(7)	4.9(2)
O(5)					0.099(1)	-0.0185(3)	0.8741(9)	6.2(2)
O(6)					0.562(1)	0.0239(3)	0.7343(8)	6.4(2)
C(1)	0.306(1)	0.225(1)	0.7039(9)	4.7(2)	-0.031(1)	0.0688(3)	0.558(1)	3.5(2)
C(2)	0.637(1)	0.440(1)	0.1556(8)	4.4(2)	-0.036(1)	0.1568(3)	0.590(1)	4.5(2)
C(3)					0.458(1)	0.0766(3)	1.0592(9)	3.5(2)
C(4)					0.060(1)	0.0925(3)	0.892(1)	3.6(2)
C(5)					0.169(1)	0.0150(3)	0.865(1)	4.0(2)
C(6)					0.453(1)	0.0425(3)	0.778(1)	3.7(2)
C(7)	0.5372(9)	0.2085(8)	0.1837(7)	3.2(2)	0.366(1)	0.1322(3)	0.8059(9)	3.1(2)
C(8)	0.213(2)	0.192(2)	0.935(1)	8.1(4)	0.429(1)	0.1074(4)	0.487(1)	4.9(2)
C(9)	0.587(2)	0.265(1)	0.4304(9)	9.2(5)	0.374(1)	0.1532(4)	0.470(1)	5.1(2)
C(10)	0.502(1)	0.353(2)	0.4016(9)	8.7(4)	0.176(2)	0.1573(5)	0.362(1)	6.9(3)
C(11)	0.580(2)	0.456(1)	0.3918(9)	8.8(4)	0.104(2)	0.1143(6)	0.307(1)	7.3(3)
C(12)	0.715(1)	0.420(1)	0.415(1)	7.8(4)	0.262(2)	0.0817(4)	0.385(1)	6.3(3)
C(13)	0.4335(9)	0.1347(8)	0.2363(7)	3.2(2)	0.378(1)	0.1698(3)	0.921(1)	3.8(2)
C(14)	0.474(1)	0.042(1)	0.3026(9)	4.9(3)	0.207(2)	0.1913(4)	0.938(1)	5.5(2)
C(15)	0.623(1)	0.025(1)	0.647(1)	5.9(3)	0.233(2)	0.2254(4)	1.054(1)	7.8(3)
C(16)	0.245(1)	-0.002(1)	0.341(1)	5.9(3)	0.432(3)	0.2379(4)	1.152(1)	9.1(5)
C(17)	0.206(1)	0.089(1)	0.274(1)	5.8(3)	0.591(3)	0.2174(4)	1.130(2)	8.8(5)
C(18)	0.300(1)	0.158(1)	0.2210(9)	4.4(2)	0.572(2)	0.1844(4)	1.017(1)	5.7(3)
C(19)	0.615(1)	0.228(1)	0.0046(7)	5.5(3)				
C(20)	0.603(1)	0.150(1)	0.9113(8)	5.2(3)				

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(1/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

The IR spectra were measured on a Zeiss Specord-75 spectrophotometer. All ¹H NMR spectra were recorded at ambient temperature in acetone-d₆ solution with TMS as the internal reference using a Varian-200 spectrometer. Electron ionization mass spectra (EIMS) were run on a Finnigan 4021 GC/MS/DS spectrometer. The melting points were determined in sealed, nitrogen-filled capillaries and are not corrected.

Reaction of $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{CC}_6\text{H}_5]\text{BBR}_4$ (1) with $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$ To Give $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{C}(\text{OC}_2\text{H}_5)_2\text{C}_6\text{H}_5]$ (2),

$[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}(\mu\text{-CHC}_6\text{H}_5)_2\text{Fe}(\text{CO})_4]$ (3), and $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{BrReCH}_2\text{C}_6\text{H}_5]$ (4). To 0.94 g (1.29 mmol) of 1 dissolved in 50 mL of THF at -90 °C was added 0.42 g (0.70 mmol) of $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$ portionwise with vigorous stirring. Immediately the brick-red solution turned purple-red. The reaction mixture was stirred at -90 to -50 °C for 4 h. After the solution was evaporated in high vacuum at -40 °C to dryness, the dark purple residue was chromatographed on an alumina (neutral, 100–200 mesh) column

Table III. Positional Parameters and Their Estimated Standard Deviations^a for 4 and 5

atom	4				5			
	x	y	z	B (Å ²)	x	y	z	B (Å ²)
Re	0.22510(3)	0.17281(3)	0.32401(3)	2.735(5)	0.67451(6)	0.02369(7)	0.13610(4)	3.22(1)
Br	0.29157(9)	0.26873(8)	0.13450(8)	4.70(2)				
O(1)	0.0407(6)	0.3733(5)	0.2951(6)	5.7(2)	0.902(1)	0.319(1)	0.1804(6)	5.3(3)
O(2)	0.1211(7)	0.0092(6)	0.1104(6)	5.8(2)	0.481(1)	0.337(2)	0.0739(7)	6.2(3)
C(1)	0.1043(8)	0.2968(7)	0.3021(7)	4.0(2)	0.811(2)	0.207(2)	0.1641(8)	3.9(3)
C(2)	0.1539(8)	0.0724(7)	0.1886(7)	3.8(2)	0.556(2)	0.219(2)	0.0985(9)	4.5(4)
C(3)	0.0495(8)	0.1025(9)	0.3964(8)	4.9(2)	0.745(2)	-0.014(2)	0.041(1)	5.3(4)
C(4)	-0.0833(8)	0.0943(8)	0.3079(7)	4.2(2)	0.798(2)	0.093(2)	-0.0178(8)	3.9(3)
C(5)	-0.1778(7)	0.1755(9)	0.3051(7)	4.4(2)	0.811(2)	0.284(2)	-0.0146(9)	4.8(4)
C(6)	-0.3045(8)	0.170(1)	0.2263(9)	5.5(2)	0.866(2)	0.383(2)	-0.0694(9)	5.3(4)
C(7)	-0.3366(9)	0.079(1)	0.1524(9)	6.4(3)	0.904(2)	0.293(3)	-0.130(1)	5.5(4)
C(8)	-0.248(1)	-0.0030(9)	0.153(1)	6.6(3)	0.893(2)	0.105(2)	-0.1356(9)	5.0(4)
C(9)	-0.1230(9)	0.0042(8)	0.231(1)	5.4(2)	0.840(1)	0.004(2)	-0.0797(8)	4.5(3)
C(10)	0.3111(9)	0.1379(8)	0.5292(7)	4.7(2)	0.627(2)	-0.086(2)	0.253(1)	5.5(4)
C(11)	0.3689(8)	0.2362(8)	0.5049(7)	4.1(2)	0.505(2)	-0.144(3)	0.202(1)	6.3(5)
C(12)	0.4419(8)	0.2152(8)	0.4152(8)	4.2(2)	0.540(2)	-0.237(2)	0.144(1)	6.8(4)
C(13)	0.4296(8)	0.1012(9)	0.3837(8)	4.8(2)	0.685(2)	-0.286(2)	0.161(1)	5.5(4)
C(14)	0.3482(9)	0.0524(8)	0.4533(9)	5.1(2)	0.740(2)	-0.189(2)	0.229(1)	6.2(4)
H					0.250	0.332	0.465	4.0

^a See footnote a in Table II.

(1.6 × 15 cm) at -25 °C with petroleum ether/CH₂Cl₂ (20:1) as the eluant. The yellow band which eluted first was collected, and then a purple-red band was eluted with petroleum ether/CH₂Cl₂ (10:1). A third band (deep-red) was eluted with petroleum ether/CH₂Cl₂/Et₂O (10:1:1). The solvents were removed from the above three eluates in vacuo, and the residues were recrystallized from the petroleum ether/CH₂Cl₂ solution at -80 °C. From the first fraction, 0.10 g (36%, based on 1) of orange-yellow crystals of 2 was obtained (mp 94–96 °C dec). IR (ν_{CO}): (CH₂Cl₂) 1955 vs, 1875 vs cm⁻¹; (hexane) 1975 vs, 1900 vs cm⁻¹. ¹H NMR (CD₃COCD₃): δ 7.30 (m, 3 H, C₆H₅), 7.02 (m, 2 H, C₆H₅), 5.30 (s, 5 H, C₅H₅), 4.62 (q, 2 H, OCH₂CH₃), 1.50 (s, 3 H, OCH₂CH₃). MS: m/e 440 (M⁺, based on ¹⁸⁵Re), 442 (M⁺, based on ¹⁸⁷Re). Anal. Calcd for C₁₆H₁₅O₃Re: C, 43.53; H, 3.42. Found: C, 43.72; H, 3.41. From the second fraction was separated 0.15 g (41%, based on 1) of brick-red crystals of 3 (mp 84–86 °C dec). IR (ν_{CO}): (CH₂Cl₂) 2015 s, 1995 vs, 1950 s br, 1890 vs br cm⁻¹; (hexane) 2075 s, 1998 vs, 1982 vs, 1962 s br, 1915 vs cm⁻¹. ¹H NMR (CD₃COCD₃): δ 9.03 (s, 1 H, CH-), 7.40 (m, 2 H, C₆H₅), 7.20 (m, 2 H, C₆H₅), 7.02 (m, 1 H, C₆H₅), 5.68 (s, 5 H, C₅H₅). MS: m/e 566 (M⁺, based on ¹⁸⁷Re, ⁵⁶Fe), 538 (M⁺ - CO), 510 (M⁺ - 2 CO), 482 (M⁺ - 3 CO), 454 (M⁺ - 4 CO), 426 (M⁺ - 5 CO), 398 (M⁺ - 6 CO), 342 (C₅H₅ReCHC₆H₅⁺), 252 (C₅H₅Re⁺), 90 (CHC₆H₅⁺). Anal. Calcd for C₁₈H₁₁O₃Re: C, 38.24; H, 1.96. Found: C, 38.18; H, 2.14. From the third fraction, 0.08 g (25%, based on 1) of 4 as red crystals was obtained (mp 96–98 °C dec). IR (ν_{CO}): (CH₂Cl₂) 2020 s, 1960 vs cm⁻¹; (hexane) 2080 s, 1958 vs br cm⁻¹. ¹H NMR (CD₃COCD₃): δ 7.28 (m, 4 H, C₆H₅), 7.08 (m, 1 H, C₆H₅), 5.50 (s, 5 H, C₅H₅), 3.62 (s, 2 H, CH₂-). MS: m/e 478 (M⁺, based on ¹⁸⁷Re), 450 (M⁺ - CO), 422 (M⁺ - 2 CO), 343 (M⁺ - 2 CO - Br), 342 (C₅H₅ReCHC₆H₅⁺), 252 (C₅H₅Re⁺), 91 (CH₂C₆H₅⁺). Anal. Calcd for C₁₄H₁₂O₂BrRe: C, 35.15; H, 2.53. Found: C, 34.97; H, 2.52.

Reaction of 1 with Na₂Fe(CO)₄ To Give 2 and 3. To a stirred solution of 1 (0.78 g, 1.07 mmol) in 40 mL of THF at -90 °C was added 0.15 g (0.61 mmol) of Na₂Fe(CO)₄. Immediately the yellow solution became bright red in color. The reaction mixture was stirred for 3.5 h at -70 to -60 °C. After removal of the solvent in vacuo at -50 °C, the dark purple-red residue was chromatographed on Al₂O₃ (neutral) at -25 °C with petroleum ether/CH₂Cl₂ (15:1) as the eluant. The yellow band which eluted first was collected and then the second purple-red band was eluted with petroleum ether/CH₂Cl₂/Et₂O (15:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from petroleum ether/CH₂Cl₂ at -80 °C. From the first fraction, 0.09 g (38%, based on 1) of orange-yellow crystals of 2 was obtained (mp 94–96 °C dec). IR (ν_{CO}): (CH₂Cl₂) 1955 vs, 1875 vs cm⁻¹. ¹H NMR (CD₃COCD₃): δ 7.30 (m, 3 H, C₆H₅), 7.03 (m, 2 H, C₆H₅), 5.30 (s, 5 H, C₅H₅), 4.62 (q, 2 H, OCH₂CH₃),

1.50 (s, 3 H, OCH₂CH₃). MS: m/e 442 (M⁺, based on ¹⁸⁷Re). From the second fraction, 0.16 g (53%, based on 1) of 3 as brick-red crystals was obtained (mp 84–86 °C dec). IR (ν_{CO}) (CH₂Cl₂) 2015 s, 1995 vs, 1950 s br, 1890 vs br cm⁻¹. ¹H NMR (CD₃COCD₃): δ 9.03 (s, 1 H, CH-), 7.40 (m, 2 H, C₆H₅), 7.20 (m, 2 H, C₆H₅), 7.03 (m, 1 H, C₆H₅), 5.68 (s, 5 H, C₅H₅). MS: m/e 566 (M⁺, based on ¹⁸⁷Re).

Reaction of 1 with Na₂Fe₃(CO)₁₁ To Give 2 and 3. Similar to the procedures described above for the reaction of 1 with Na₂Fe(CO)₄, a stirred yellow solution of 1 (0.78 g, 1.07 mmol) in THF (40 mL) at -90 °C was treated with Na₂Fe₃(CO)₁₁ (0.30 g, 0.58 mmol). The yellow solution turned dark purple-red quickly. The mixture was stirred at -70 to -60 °C for 4 h. After vacuum removal of the solvent, further treatment of the dark purple-red residue as described for the reaction of 1 with Na₂Fe(CO)₄ gave 0.10 g (42%, based on 1) of orange-yellow crystalline 2 and 0.14 g (47%, based on 1) of brick-red crystals of 3. The two products were identified by comparison of their melting points and infrared, ¹H NMR, and mass spectra with those of the same compounds characterized above.

Conversion of [η-C₅H₅(CO)₂Re(μ-CHC₆H₅)Fe(CO)₄] (3) to η-C₅H₅(CO)₂ReC(OC₂H₅)C₆H₅ (2). Brick-red crystals of 3 (0.10 g) were dissolved in 15 mL of THF/petroleum ether (1:10) at -10 °C. The solution cooled from -10 to -80 °C within 24–48 h. After the solution was kept at -80 °C for an additional 48 h, 0.037 g (47%) of orange-yellow crystals of 2 was obtained (mp 94–96 °C dec). IR (ν_{CO}): (CH₂Cl₂) 1955 vs, 1875 vs cm⁻¹. ¹H NMR (CD₃COCD₃): δ 7.30 (m, 3 H, C₆H₅), 7.02 (m, 2 H, C₆H₅), 5.30 (s, 5 H, C₅H₅), 4.62 (q, 2 H, OCH₂CH₃), 1.50 (s, 3 H, OCH₂CH₃). MS: m/e 442 (M⁺, based on ¹⁸⁷Re). Anal. Calcd for C₁₆H₁₅O₃Re: C, 43.53; H, 3.42. Found: C, 43.67; H, 3.37.

Conversion of [η-C₅H₅(CO)₂Re(μ-CHC₆H₅)Fe(CO)₄] (3) into [η-C₅H₅(CO)₂ReC(H)C₆H₅] (5). Brick-red crystals of 3 (0.10 g) were dissolved in 15 mL of toluene/petroleum ether (1:10) at -10 °C. The solution was cooled from -10 to -80 °C within 24–48 h and kept at -80 °C for another 48 h to afford 0.052 g (70%) of deep red crystals of 5: mp 148–149 °C dec, lit.¹² mp 148.5 °C. IR (ν_{CO}): (CH₂Cl₂) 1968 vs, 1888 vs cm⁻¹. ¹H NMR (CD₃COCD₃): δ 7.52 (m, 2 H, C₆H₅), 7.20 (m, 2 H, C₆H₅), 7.04 (m, 1 H, C₆H₅), 5.76 (s, 5 H, C₅H₅), 16.0 (s, 1 H, CH). MS: m/e 398 (M⁺, based on ¹⁸⁷Re). Anal. Calcd for C₁₄H₁₁O₂Re: C, 42.31; H, 2.79. Found: C, 42.67; H, 2.89.

X-ray Crystal Structure Determinations of Complexes 2, 3, 4, and 5. The crystals of complexes 2, 3, 4, and 5 suitable for X-ray diffraction were obtained by recrystallization from

Table IV. Bond Distances (Å)^a for 2, 3, 4, and 5

	2	3	4	5		2	3	4	5
Re-Fe		2.7581(8)			O(2)-C(2)	1.160(8)	1.151(7)	1.141(7)	1.16(1)
Re-Br			2.6047(6)		O(3)-C(3)		1.118(6)		
Re-C(1)	1.900(7)	1.924(7)	1.941(7)	1.866(8)	O(3)-C(7)	1.335(6)			
Re-C(2)	1.895(8)	1.880(7)	1.930(6)	1.874(9)	O(3)-C(19)	1.464(7)			
Re-C(3)			2.315(6)	1.95(2)	O(4)-C(4)		1.128(6)		
Re-C(7)	1.990(5)	2.120(5)			O(5)-C(5)		1.133(7)		
Re-C(8)	2.315(9)	2.316(6)			O(6)-C(6)		1.123(7)		
Re-C(9)	2.330(8)	2.322(6)			C(3)-H				1.124(8)
Re-C(10)	2.308(8)	2.291(7)	2.255(6)	2.37(5)	C(3)-C(4)			1.496(8)	1.47(1)
Re-C(11)	2.311(7)	2.269(7)	2.319(6)	2.35(5)	C(4)-C(5)			1.389(9)	1.398(9)
Re-C(12)	2.335(8)	2.291(6)	2.304(6)	2.29(2)	C(4)-C(9)			1.382(9)	1.40(4)
Re-C(13)			2.251(6)	2.30(2)	C(5)-C(6)			1.400(8)	1.39(6)
Re-C(14)			2.224(7)	2.31(4)	C(6)-C(7)			1.36(1)	1.36(6)
Fe-C(3)		1.800(6)			C(7)-C(8)			1.36(1)	1.375(7)
Fe-C(4)		1.809(6)			C(7)-C(13)	1.508(8)	1.504(7)		
Fe-C(5)		1.798(7)			C(8)-C(9)	1.36(2)	1.43(1)	1.38(2)	1.40(5)
Fe-C(6)		1.823(6)			C(8)-C(12)	1.30(1)	1.44(1)		
Fe-C(7)		2.097(5)			C(9)-C(10)	1.36(2)	1.40(1)		
O(1)-C(1)	1.155(8)	1.151(7)	1.133(7)	1.186(9)	C(10)-C(11)	1.42(2)	1.141(1)	1.391(9)	1.39(4)
C(10)-C(14)			1.436(9)	1.43(4)	C(15)-C(16)	1.37(2)	1.43(1)		
C(11)-C(12)	1.45(1)	1.46(1)	1.394(8)	1.45(6)	C(16)-C(17)	1.40(1)	1.36(2)		
C(12)-C(13)			1.426(9)	1.39(3)	C(17)-C(18)	1.414(9)	1.37(2)		
C(13)-C(14)	1.417(9)	1.425(9)	1.39(1)	1.45(1)	C(19)-C(20)	1.49(1)			
C(13)-C(18)	1.382(8)	1.412(9)			Re-C(cen) ^b	2.0016	1.9524	1.9293	1.98
C(14)-C(15)	1.404(9)	1.41(1)							

^a Numbers in parentheses are estimated standard deviations in the least significant digits. ^b C(cen) denotes the centroid of the cyclopentadienyl.

petroleum ether/CH₂Cl₂ at -80 °C. For each complex, a single crystal was carefully sealed in a nitrogen-filled capillary. The X-ray diffraction intensity data were collected on an Enraf-Nonius CAD4 diffractometer at room temperature.

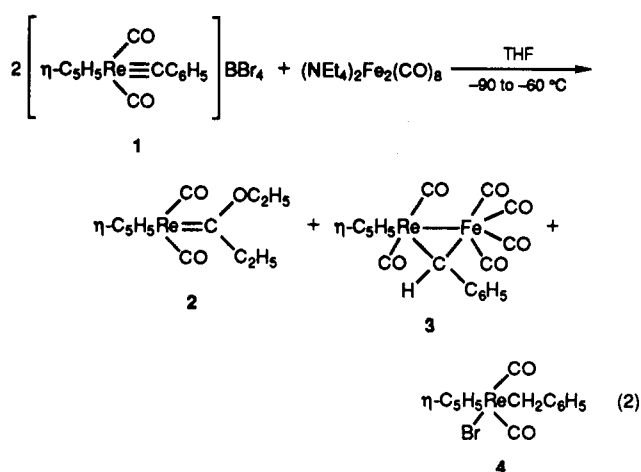
The cell constants were determined from a list of reflections found by an automated search routine. Relevant crystal data and details of the parameters associated with the data collection for 2, 3, 4, and 5 are given in Table I.

After correction for the LP factor and the empirical absorption factor, the intensity data were placed on an approximately absolute scale by the Wilson statistical. The structures of 2 and 5 were solved by heavy-atom methods. The structures of 3 and 4 were solved by direct methods. All non-hydrogen atoms except Re were located by difference Fourier techniques and refined with the anisotropic thermal parameters. The positional parameters of the hydrogen atom of the carbene carbon atom of 3 were obtained from a D map. Hydrogen atoms were not included in other structures. The final *R* values of the four structures are listed in Table I.

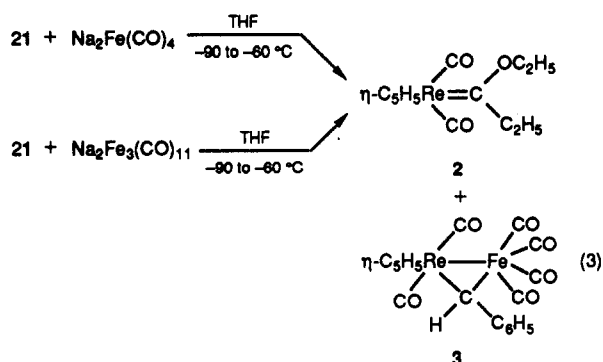
Fractional coordinates and equivalent temperature factors of the non-hydrogen atoms for 2 and 3 are listed in Table II and those for 4 and 5 are in Table III. Bond lengths for all four structures are given in Table IV. Selected bond angles for 2 and 3 are given in Table V and for 4 and 5, in Table VI. ORTEP drawings for 2, 3, 4, and 5 are given in Figures 1, 2, 3, and 4, respectively. Computations were performed on a MICRO-VAX II computer with the SDP-PLUS program.

Results and Discussion

Two molar equivalents of [η -C₅H₅(CO)₂Re≡CC₆H₅]-BBR₄ (1) reacted with one of [NEt₄]₂[Fe₂(CO)₈] in THF at low temperature (-90 to -60 °C) for 3–4 h. The resulting mixture was chromatographed on an alumina column at low temperature and the crude products were recrystallized from the petroleum ether/CH₂Cl₂ solution at -80 °C to give orange-yellow crystalline 2, brick-red crystals of 3, and red crystals of 4 (eq 2) in 36, 41, and 25% isolated yields, respectively.



The complex 1 also reacted with Na₂Fe(CO)₄ and Na₂-Fe₃(CO)₁₁ under the same conditions to afford products 2 and 3 (eq 3) in similar yields, but no product 4 was produced.



The formulations of complexes 2, 3, and 4 were supported by elemental analyses and spectroscopic data (see Experimental Section).

Complex 3 is a heteronuclear dimetal complex with a bridging carbene ligand. It is soluble in polar organic

Table V. Selected Bond Angles (deg)^a for 2 and 3

	2	3		2	3
Re-C(1)-O(1)	176.9(6)	172.5(6)	C(2)-Re-C(10)	116.8(5)	87.9(4)
Re-C(2)-O(2)	173.4(6)	173.9(7)	C(2)-Re-C(11)	94.0(3)	103.2(4)
Re-C(7)-O(3)	134.7(4)		C(2)-Re-C(12)	107.4(4)	140.5(3)
Re-C(7)-Fe		81.7(2)	C(7)-Re-C(8)	125.6(5)	88.5(2)
Re-C(7)-C(13)	121.5(4)	133.2(5)	C(7)-Re-C(9)	97.7(3)	87.1(2)
Re-Fe-C(3)		136.2(2)	C(7)-Re-C(10)	98.5(3)	117.2(3)
Re-Fe-C(4)		86.5(2)	C(7)-Fe-C(11)	130.2(5)	145.7(2)
Re-Fe-C(5)		119.1(2)	C(7)-Re-C(12)	153.8(4)	121.4(3)
Re-Fe-C(6)		83.7(2)	C(8)-Re-C(9)	34.0(4)	35.7(2)
Re-Fe-C(7)		49.5(1)	C(8)-Re-C(10)	57.4(4)	59.9(3)
Fe-Re-C(1)		71.2(2)	C(8)-Re-C(11)	57.3(4)	60.5(3)
Fe-Re-C(2)		105.2(3)	C(8)-Re-C(12)	32.6(4)	36.4(2)
Fe-Re-C(7)		48.9(1)	C(9)-Re-C(10)	34.2(4)	35.3(2)
Fe-Re-C(8)		103.0(2)	C(9)-Re-C(11)	57.5(4)	59.4(3)
Fe-Re-C(9)		125.2(2)	C(9)-Re-C(12)	56.2(4)	60.2(3)
Fe-Re-C(10)		160.5(3)	C(10)-Re-C(11)	35.9(4)	35.9(3)
Fe-Re-C(11)		146.4(3)	C(10)-Re-C(12)	59.0(3)	61.1(3)
Fe-Re-C(12)		111.6(2)	C(11)-Re-C(12)	36.4(4)	37.4(3)
C(1)-Re-C(2)	86.9(3)	88.2(2)	C(3)-Fe-C(4)		99.0(2)
C(1)-Re-C(7)	93.0(3)	118.2(2)	C(3)-Fe-C(5)		104.6(3)
C(1)-Re-C(8)	95.7(4)	121.8(2)	C(3)-Fe-C(6)		95.4(3)
C(1)-Re-C(9)	119.6(5)	149.1(2)	C(3)-Fe-C(7)		86.8(2)
C(1)-Re-C(10)	152.5(5)	124.5(3)	C(4)-Fe-C(5)		87.1(3)
C(1)-Re-C(11)	136.4(5)	92.2(3)	C(4)-Fe-C(6)		165.6(3)
C(1)-Re-C(12)	102.3(3)	90.2(2)	C(4)-Fe-C(7)		91.4(2)
C(2)-Re-C(7)	94.5(2)	93.7(2)	C(5)-Fe-C(6)		88.6(3)
C(2)-Re-C(8)	139.5(4)	144.2(3)	C(5)-Fe-C(7)		168.7(2)
C(2)-Re-C(9)	150.0(4)	108.7(3)	C(6)-Fe-C(7)		90.1(2)
Fe-C(3)-O(3)		179.1(5)	C(7)-C(13)-C(14)	119.2(5)	123.9(6)
Fe-C(4)-O(4)		175.6(6)	C(7)-C(13)-C(18)	120.5(5)	117.1(6)
Fe-C(5)-O(5)		177.3(6)	C(14)-C(13)-C(18)	120.3(6)	119.1(7)
Fe-C(6)-O(6)		175.2(6)	C(13)-C(14)-C(15)	119.0(6)	119.7(8)
Fe-C(7)-C(13)		118.0(4)	C(14)-C(15)-C(16)	121.5(7)	119.3(9)
C(7)-O(3)-C(19)	121.5(5)		C(15)-C(16)-C(17)	119.0(7)	119.0(8)
C(9)-C(8)-C(12)	111(1)	108.2(7)	C(16)-C(17)-C(18)	121.1(6)	124(1)
C(8)-C(9)-C(10)	109(2)	109.2(8)	C(13)-C(18)-C(17)	119.0(6)	119.3(8)
C(9)-C(10)-C(11)	106.4(9)	108.5(9)	Fe-Re-C(cen) ^b		133.78
O(3)-C(7)-C(13)	103.8(4)		C(1)-Re-C(cen)	124.02	113.18
O(3)-C(19)-C(20)	105.7(5)		C(2)-Re-C(cen)	124.59	119.59
C(10)-C(11)-C(12)	106(1)	108.5(7)	C(7)-Re-C(cen)	123.93	113.79
C(8)-C(12)-C(11)	107(1)	105.7(7)			

^a Numbers in parentheses are estimated standard deviations in the least significant digits. ^b C(cen) denotes the centroid of the cyclopentadienyl.

solvents but only slightly soluble in nonpolar solvents. It is air stable in the solid state for a short period but very sensitive to air and temperature in solution. Its IR spectrum (in hexane) showed CO stretching vibration bands at 2075 s, 1998 vs, 1982 vs, 1962 s br, and 1915 vs cm^{-1} . The ^1H NMR spectrum of **3** showed a resonance at δ 9.03 in the region expected for a μ -CHR ligand¹³ which may be compared with that (8.09 ppm) in the heteronuclear dimetal bridging carbene complex $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]$.¹⁴ An X-ray diffraction study was carried out in order to establish firmly its structure. The results are summarized in Tables II, IV, and V, and the structure is shown in Figure 2. As expected, four terminal carbonyl groups are attached to the iron and two to the rhenium. The metal-metal bond of $\text{Re}^{\text{II}}\text{-Fe}$ is bridged by the CHC_6H_5 group. The coordination geometry of the Re atom is that of a pseudo-trigonal bipyramid if the $\text{C}(\eta^5)$ -bonded cyclopentadienyl is regarded as occupying a single polyhedral vertex. The Re atom is nearly coplanar with C(2), Fe, and C(cen) (C(cen) denotes centroid of the cyclopentadienyl) which define the "equatorial" plane of the trigonal bipyramid. The C(1) and C(7) atoms form the two vertices of the bipyramid. The Fe atom is in an approximately octahedral environment. The Re-Fe distance of 2.7581(8) Å in complex **3** is much shorter than

that found in the dimetal bridging carbene complex $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]$ (3.033(1) Å)¹⁴ and slightly shorter than that found in the bridging carbyne complex $[\text{MoFe}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ (2.823(1) Å).¹⁵ The alkylidene carbon asymmetrically bridges the metal-metal bond (C-Re 2.120(5), C-Fe 2.097(5) Å), but this asymmetry is less marked than that in $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]$ (C-Re 2.155(8), C-W 2.404-(6) Å).¹⁴ The $\mu\text{-C-Re}$ distance of **3** is comparable with that (2.13 (3) Å) in the complex $[\text{Re}_2(\mu\text{-H})_2(\mu\text{-CHBu}^t)(\eta\text{-C}_6\text{H}_6)_2]$.¹⁶ The $\mu\text{-C-Fe}$ distance in **3** is comparable with that in complex $[\text{WFe}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})(\text{CO})\text{O}\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (2.054(4) Å)¹⁷ and complex $[\text{MoFe}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ (2.008(5) Å).¹⁵

The C(7) atom showed the semibringing character with the angle of Fe-C(7)-C(13) (118.0(4)°) conforming to that expected for an sp^2 hybridized carbon atom. The C(7) atom lies essentially in the plane of the benzene ring (± 0.025 Å). The benzene ring plane is at an angle of 84.4-(3)° to the plane comprised of Re, Fe, and C(7).

(14) Jeffery, J. C.; Orpen, A. G.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Dalton Trans.* 1986, 173.

(15) Garcia, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1987, 1209.

(16) Bandy, J. A.; Cloke, F. G. N.; Green, M. L. H.; O'Hare, D.; Prout, K. *J. Chem. Soc., Chem. Commun.* 1984, 240.

(17) Delgado, E.; Hein, J.; Jeffery, J. C.; Ratermann, A. L.; Stone, F. G. A.; Farregia, L. J. *J. Chem. Soc., Dalton Trans.* 1987, 1191.

(13) Herrmann, W. A. *Adv. Organomet. Chem.* 1982, 20, 159; *J. Organomet. Chem.* 1983, 250, 319.

Table VI. Bond Angles (deg)^a for 4 and 5

	4	5		4	5
Re-C(1)-O(1)	175.1(6)	177.1(8)	C(3)-Re-C(12)	134.9(2)	101(2)
Re-C(2)-O(2)	174.8(6)	178.2(9)	C(3)-Re-C(13)	121.8(3)	91(1)
Re-C(3)-C(4)	119.2(4)	139.4(6)	C(3)-Re-C(14)	85.7(3)	117(1)
Re-C(3)-H		104.6(6)	C(10)-Re-C(11)	35.4(2)	34(1)
Br-Re-C(1)	80.6(2)		C(10)-Re-C(12)	59.2(2)	59(2)
Br-Re-C(2)	78.3(2)		C(10)-Re-C(13)	60.5(2)	60(1)
Br-Re-C(3)	144.3(2)		C(10)-Re-C(14)	37.5(2)	35(1)
Br-Re-C(10)	139.3(2)		C(11)-Re-C(12)	35.1(2)	36(2)
Br-Re-C(11)	107.0(2)		C(11)-Re-C(13)	60.0(2)	60(1)
Br-Re-C(12)	80.3(2)		C(11)-Re-C(14)	60.8(2)	58(2)
Br-Re-C(13)	89.8(2)		C(12)-Re-C(13)	36.5(2)	35.4(6)
Br-Re-C(14)	125.5(2)		C(12)-Re-C(14)	60.6(2)	59(1)
C(1)-Re-C(2)	105.9(3)	84.5(3)	C(13)-Re-C(14)	36.3(3)	37(2)
C(1)-Re-C(3)	77.8(2)	92.4(4)	C(4)-C(3)-H		115.9(8)
C(1)-Re-C(10)	111.5(3)	101.6(6)	C(3)-C(4)-C(5)	120.7(6)	122(2)
C(1)-Re-C(11)	96.8(2)	131(2)	C(3)-C(4)-C(9)	123.2(7)	121(2)
C(1)-Re-C(12)	114.9(3)	159(1)	C(5)-C(4)-C(9)	116.0(6)	117(2)
C(1)-Re-C(13)	151.3(3)	129.7(8)	C(4)-C(5)-C(6)	122.6(8)	122(3)
C(1)-Re-C(14)	148.3(3)	100.3(6)	C(5)-C(6)-C(7)	118.3(8)	119(2)
C(2)-Re-C(3)	80.5(3)	92.4(4)	C(6)-C(7)-C(8)	121.2(8)	121(4)
C(2)-Re-C(10)	129.7(3)	114.1(5)	C(7)-C(8)-C(9)	119.6(8)	120(4)
C(2)-Re-C(11)	157.3(2)	96.0(6)	C(4)-C(9)-C(8)	122.3(7)	120(1)
C(2)-Re-C(12)	129.6(2)	110.5(5)	C(11)-C(10)-C(14)	109.0(6)	108(4)
C(2)-Re-C(13)	98.5(3)	145.4(6)	C(10)-C(11)-C(12)	107.9(6)	109(2)
C(2)-Re-C(14)	97.7(3)	149(2)	C(11)-C(12)-C(13)	108.3(6)	108(3)
C(3)-Re-C(10)	75.8(2)	151.0(4)	C(12)-C(13)-C(14)	108.3(6)	107(4)
C(3)-Re-C(11)	103.7(2)	137(2)	C(10)-C(14)-C(13)	106.6(7)	109(6)
Br-Re-C(cen) ^b	109.88		C(2)-Re-C(cen)	126.08	126.5
C(1)-Re-C(cen)	127.99	127.4	C(3)-Re-C(cen)	105.85	122.5

^a Numbers in parentheses are estimated standard deviations in the least significant digits. ^b C(cen) denotes the centroid of the cyclopentadienyl.

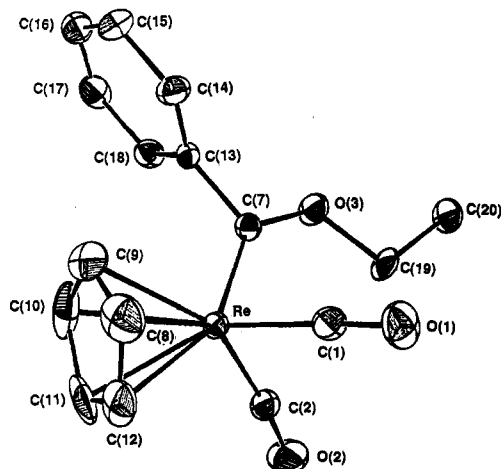


Figure 1. Molecular structure for 2.

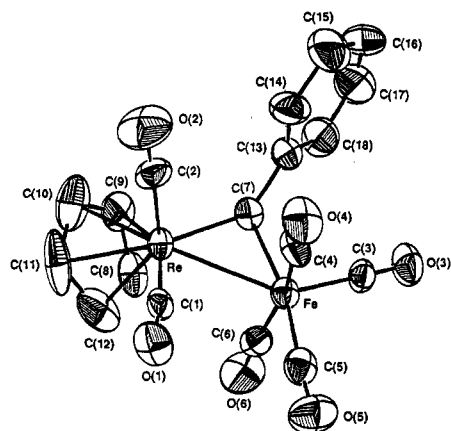


Figure 2. Molecular structure for 3.

Complex 2 is an alkoxycarbene complex which can be readily prepared by the reaction of $C_5H_5Re(CO)_3$ with C_6H_5Li in ether at 0 °C and subsequent alkylation with

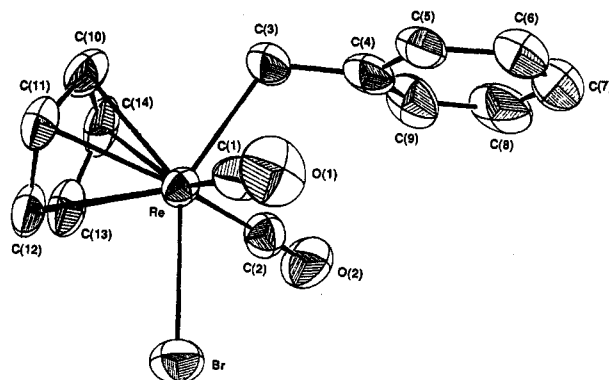


Figure 3. Molecular structure for 4.

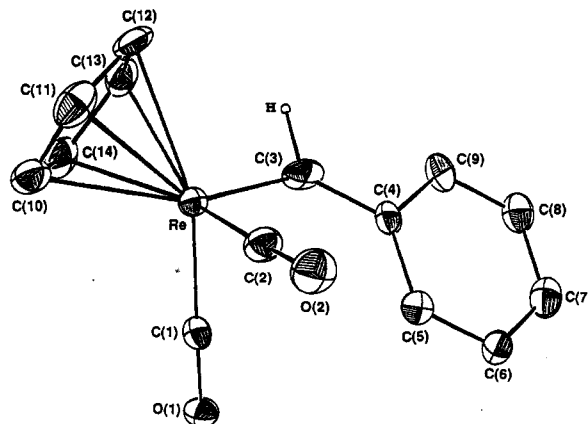


Figure 4. Molecular structure for 5.

$[Et_3O][BF_4]$ in aqueous solution at 0 °C analogous to the preparation of $[\eta-C_5H_5(CO)_2Re=C(OC_2H_5)C_6H_4CF_3-4]$.⁹ Complex 4 is a benzylrhenium bromide. Complexes 2 and 4 are soluble in both polar and nonpolar organic solvents and are air stable in the solid state. Their IR spectra (in hexane) show carbonyl stretching bands respectively at

1975 vs and 1900 vs, and 2080 s and 1958 vs cm^{-1} . The ^1H NMR spectra of 2 and 4 show respectively resonances at δ 1.50 and 4.62 attributed to the OCH_2CH_3 proton signals and at δ 3.62 attributed to the ReCH_2 - proton signal. The results of the structural determinations for 2 and 4 are summarized in Tables II-VI, and the molecules for 2 and 4 are presented in Figures 1 and 3, respectively.

In molecule 2, the central Re atom is bonded to C(1), C(2), C(7), C(8), C(9), C(10), C(11), and C(12) to satisfy the 18-electron rule. The bond parameters indicate that the Re atom has a deformed tetrahedral coordination geometry if the cyclopentadienyl is considered as occupying a single polyhedral vertex. The sum of the three bond angles around the C(7) atom ($\text{Re}-\text{C}(7)-\text{O}(3)$ $134.7(4)^\circ$, $\text{Re}-\text{C}(7)-\text{C}(13)$ $121.5(4)^\circ$, $\text{O}(3)-\text{C}(7)-\text{C}(13)$ $103.8(4)^\circ$) is exactly 360° , which indicates that the C(7) atom is coplanar strictly with the three bonding atoms (Re, C(13), and O(3)) by using its sp^2 hybridized orbitals to form three σ bonds and leaving its p_z orbital forming a π bond with the Re atom. According to the bond lengths of $\text{Re}-\text{C}(7)$ (1.990(5) Å), $\text{Re}-\text{C}(1)$ (1.900(3) Å), and $\text{Re}-\text{C}(2)$ (1.895(8) Å), we consider that there is a certain π bond character, besides σ bond character, in the three bonds.

In molecule 4, the central Re atom is bonded to C(1), C(2), C(3), C(10)-C(14), and Br to satisfy the 18-electron rule. The Re atom has a distorted trigonal-bipyramidal coordination environment if cyclopentadienyl is considered as occupying a single polyhedral vertex. C(1), C(2), and C(cen) define the "equatorial" plane, while Br and C(3) form the two vertices of the trigonal bipyramid. The Re atom is lying on the "equatorial" plane. As expected, the $\text{Re}-\text{CH}_2$ distance of 2.315(6) Å in 4 is much longer than the $\text{Re}-\text{C}(7)_{\text{carbene}}$ bond (1.990(5) Å) in 2 and $\text{Re}-\text{C}(3)_{\text{carbene}}$ bond (1.977(7) Å) in $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{C}(\text{H}-\text{C}_6\text{H}_5)]$ (5) (see below) and comparable with that (2.29(1) Å) found in complex $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{HReCH}_2\text{C}_6\text{H}_5]$.¹² This indicated that the $\text{CH}_2\text{C}_6\text{H}_5$ group is σ -bonded to the Re atom. As compared with complex 5, the bond angle of $\text{Re}-\text{C}(3)-\text{C}(4)$ ($119.2(4)^\circ$) in 4 is much less than that found ($136.1(5)^\circ$) in 5. The C(3) atom and C(4)-C(9) atoms of the benzene ring lie in a plane (± 0.01 Å). The plane defined by C(3) and C(4)-C(9) is essentially perpendicular to the plane comprised of C(3), Re, and Br since the angle between the planes is 90.86° .

The reaction pathways to complexes 2, 3, and 4 are not yet clear. However, the formation of 3 might involve initial formation of the " $\text{Fe}(\text{CO})_4^{2-}$ " species arising from $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$ which then attacks at the carbyne carbon atom of 1. This was confirmed by the reaction of 1 with $\text{Na}_2\text{Fe}(\text{CO})_4$, giving product 3, to generate an anionic carbene intermediate $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{ReC}(\text{C}_6\text{H}_5)\text{Fe}(\text{CO})_4]^{-(\text{NEt}_4)^+}$. There are analogous precedents for this type of intermediate in the literature.^{18,19} The protonation of the anionic carbene intermediate then affords the bridging carbene complex 3. The source of the H atom could be water which is a trace contaminant in solvent THF. It is not excluded that a possible alternative formation pathway might involve initial formation of the dimetal dicarbene intermediate complex $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{C}(\text{C}_6\text{H}_5)]_2\text{Fe}_2(\text{CO})_8$, which then could suffer heterolytic cleavage of the $\text{Re}-\text{Fe}$ bond to give the cationic carbyne complex $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{CC}_6\text{H}_5]^+$ and the binuclear anionic complex $[\eta\text{-C}_5\text{H}_5-$

$(\text{CO})_2\text{Re}(\mu\text{-CC}_6\text{H}_5)\text{Fe}(\text{CO})_4]^-$. The protonation of the latter finally affords complex 3. Stone et al. have provided numerous examples of dimetal species with a structure akin to the cation bridging carbyne intermediate.²⁰⁻²⁴

Stone et al. have extensively studied the chemistry of dimetal complexes with a bridging carbene or carbyne ligand. A series of dimetal bridging carbene complexes has been synthesized by reactions²⁵⁻²⁷ of carbene complexes such as $[(\text{CO})_5\text{M}=\text{C}(\text{OMe})\text{Ph}]$ ($\text{M} = \text{Cr}$ or W) and $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Mn}=\text{C}(\text{OMe})\text{Ph}]$ with low-valent metal species MLn such as $\text{Pt}(\text{COD})_2$, $\text{Ni}(\text{COD})_2$ ($\text{COD} = 1,5$ -cyclooctadiene), $\text{Pt}(\text{C}_2\text{H}_4)_3$, $\text{Pd}(\text{dba})_2$ ($\text{dba} = \text{dibenzylideneacetone}$), and $\text{Cp}^*\text{Cu}(\text{THF})$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) or by the reactions^{19,28} of neutral carbyne complexes such as $[\text{Cp}(\text{CO})_2\text{W}=\text{C}(\text{C}_6\text{H}_4\text{Me-4})]$ and $[\text{ReM}(\equiv\text{CR})(\text{CO})_3]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) with metal hydrides such as $[\text{N}(\text{PPh}_3)_2][\text{WH}(\text{CO})_5]$ and $[\text{K}[\text{BH}(\text{CHMeEt})_3]]$. However, complex 3 was the first dimetal complex with a bridging carbene ligand synthesized by the reaction of a cationic carbyne complex of a transition metal with the nucleophile containing a carbonylmetal anion. An analogous reaction of the cationic carbyne complex $[\text{MeCp}(\text{CO})_2\text{Mn}=\text{CR}]^-(\text{BCL}_4)$ ($\text{R} = \text{C}_6\text{H}_5$, CpFeCp) with the carbonylmetal salt $[\text{K}[\text{Mn}(\text{CO})_5]]$ led to the isomeric ketenyl complex $[\text{MeCp}(\text{CO})\text{Mn}(\mu\text{-CO})\{\mu\text{-}(\text{C}=\text{O})\text{R}\}\text{Mn}(\text{CO})_4]^8$ instead of the bridging carbene complex. Recently, Stone et al. reported that the analogous reaction of the cationic carbyne complex $[\text{Re}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me-4})(\text{BCL}_4)]$ with $[\text{NEt}_4][\text{Rh}(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ did not afford the expected bridging carbene or the carbyne complex) but rather the dimetal complex $[\text{ReRh}\{\mu\text{-}\sigma, \eta^5\text{-C}_2\text{B}_9\text{H}_7(\text{CH}_2\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_4(\eta\text{-C}_5\text{H}_4\text{Me-4})]$,¹⁹ in which the carbaborane cage carries a $(\eta\text{-C}_5\text{H}_4\text{Me-4})\text{Re}(\text{CO})_2$ substituent at the boron atom and the Re atom is linked to the Rh atom to form a $\text{BRe}(\eta\text{-C}_5\text{H}_4\text{Me-4})(\text{CO})_2\text{Rh}(\text{CO})_2$ bridge system.

The formation of complex 2 might proceed by the following pathway: loss of the " $\text{HFe}(\text{CO})_4$ " species from 3 and subsequent abstraction of the OC_2H_5 species from the reaction mixture leading to the isolation of ethoxy-carbene complex 2. It is not yet clear how the OC_2H_5 group is formed during the reaction. We tentatively speculate that it is derived from the solvent (THF). Evidence in favor of this is that when the brick-red crystals of 3 were recrystallized from the THF/petroleum ether (1:10) solution at -10 to -80°C for 96 h, orange-yellow crystals of 2 were obtained in 47% yield. It is also noted that when the NMR sample tube of 3 was allowed to stand at 0 to 10°C , the color of the solution of 3 in tetrahydrofuran- d_8 turned from brick-red to orange-red after standing for 24 h. The ^1H NMR spectrum of the resulting solution showed proton signals at δ 7.25 (m, 3 H), 6.95 (m,

(20) Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M. J.; Woodward, P. *Dalton Trans.* 1983, 101.

(21) Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Razay, H.; Stone, F. G. A. *Dalton Trans.* 1984, 1563.

(22) Abad, J. A.; Delgado, E.; Garcia, M. E.; Grosse-Ophoff, M. J.; Hart, I. J.; Jeffery, J. C.; Simmons, M. S.; Stone, F. G. A. *Dalton Trans.* 1987, 41.

(23) Green, M.; Howard, J. A. K.; James, A. P.; Nunn, C. M.; Stone, F. G. A. *Dalton Trans.* 1987, 61.

(24) Garcia, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *Dalton Trans.* 1987, 1209.

(25) Ashworth, T. V.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1980, 1593.

(26) Berry, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1980, 1601.

(27) Carriedo, G. A.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1984, 1555.

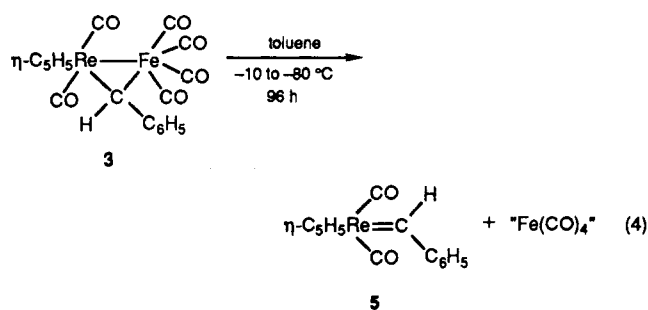
(28) Hodgson, D.; Howard, J. A. K.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Dalton Trans.* 1985, 1331.

(18) Pilotti, M. U.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1990, 2625.

(19) Pilotti, M. U.; Stone, F. G. A.; Topaloglu, L. *J. Chem. Soc., Dalton Trans.* 1991, 1621.

2 H), and 5.27 (s, 5 H) which could be assigned to the benzene ring protons and cyclopentadienyl protons of $\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{C}(\text{OC}_2\text{D}_5)\text{C}_6\text{H}_5$, respectively, together with the original proton signals of **3**. This suggested that a partial transformation of **3** into deuterated ethoxycarbene complex might have occurred. It is not excluded, however, that there is some other contaminant which is an ethoxy source in the solvent (THF) or reagents. However, neither ethanol or diethyl ether was detected in the solvent (THF) used before the reaction or recrystallization by chromatography. Also no trace of complex **2** was found by ^1H NMR spectral measurement (in CD_2Cl_2) in the starting material **1** before the reaction.

The mode of formation of complex **4** is not known but a reasonable pathway is via release of " $\text{Fe}(\text{CO})_4$ " species from **3** to generate an intermediate carbene complex, $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{C}(\text{H})\text{C}_6\text{H}_5]$ (**5**),¹² which could then abstract a hydrogen from the solvent THF and a bromide ion from the BBr_4^- species during the reaction, resulting in the formation of complex **4** in lower yield. Formation of the analogous compound was observed in the reaction of **5** with Et_2AlH leading to $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{HReCH}_2\text{C}_6\text{H}_5]$.¹² Direct evidence for the formation of the intermediate carbene complex **5** through initial loss of the $\text{Fe}(\text{CO})_4$ moiety from **3** is based on the following fact. When brick-red complex **3** was recrystallized from toluene/petroleum ether (1:10) at -10 to -80 °C for 96 h, deep red crystals of **5** were obtained in 70% yield (eq 4). However, recrystallization of **3** from CH_2Cl_2 /petroleum ether under the same conditions gave no **5**, only the brick-red crystals of **3** were obtained.



Complex **5** is a known compound, reported previously by Fischer et al.¹² Although several Fischer-type carbene complexes with a hydrogen atom on the carbene carbon

atom have been synthesized,^{12,29–33} only a few of them have been studied by X-ray diffraction.^{28–30} So a single-crystal X-ray diffraction study was carried out on complex **5** for comparison with alkoxycarbene complex **2** and analogues. The results are given in Table III, IV, and VI, and the molecule is illustrated in Figure 4.

In molecule **5**, the $\text{Re}-\text{C}(3)_{\text{carbene}}$ distance of 1.95 (2) Å is shorter than that found (2.032(7) Å) in $[\text{W}\{\text{C}(\text{H})\text{-C}_6\text{H}_4\text{Me-4}\}(\text{SnPh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ²⁸ and **2** ($\text{Re}-\text{C}(7)_{\text{carbene}}$ 1.990(5) Å) but significantly longer than that found (1.92-(2) Å) in $[(\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}=\text{C}(\text{H})\text{Si}(\text{C}_6\text{H}_5)_3)]$.²⁹ The bond angle of $\text{Re}-\text{C}(3)-\text{C}(4)$ ($139.4(6)^\circ$) is much larger than the corresponding angle ($\text{Re}-\text{C}(7)-\text{C}(13)$ $121.5(4)^\circ$) in **2** and may be compared with that ($137.7(5)^\circ$) found in $[\text{W}\{\text{C}(\text{H})\text{-C}_6\text{H}_4\text{Me-4}\}(\text{SnPh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$. The C(3) atom is coplanar with the benzene ring. The two CO groups on Re are essentially linear ($\text{Re}-\text{C}(1)-\text{O}(1)$ $177.1(8)^\circ$, $\text{Re}-\text{C}(2)-\text{O}(2)$ $178.2(9)^\circ$), and the Re atom and two CO groups lie in one plane. The plane of the benzene ring is essentially perpendicular to the plane of the cyclopentadienyl ring and the plane defined by Re, C(1), O(1), C(2), and O(2), since the angles between the planes of the benzene ring and the cyclopentadienyl ring, and the benzene ring and Re, C(1), O(1), C(2), and O(2), are 87.11° and 89.42° , respectively. The plane defined by C(1), O(1), Re, C(2), and O(2) is inclined at 57.82° to the plane of the cyclopentadienyl ring.

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

Supplementary Material Available: Tables of displacement parameters, least-squares planes, and additional bond angles for **2** and **3** (16 pages). Ordering information is given on any current masthead page.

OM920659G

(29) Fischer, E. O.; Rustemeyer, P.; Neugebauer, D. *Z. Naturforsch.* **1980**, *35b*, 1083.

(30) Fischer, E. O.; Rustemeyer, P.; Ackermann, K. *Chem. Ber.* **1982**, *115*, 3851.

(31) Clark, G. R.; Roper, W. R.; Wright, A. H. *J. Organomet. Chem.* **1984**, *273*, C17.

(32) Agüero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 793.

(33) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.