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Syntheses, Reactions, and Structures of Dioxycarbene Complexes of Rhenium

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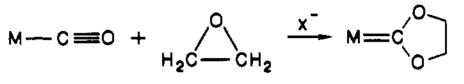
The cyclic dioxycarbene complex $Re(CO)_4Br(\overline{COCH_2CH_2O})$ (I) reacts with PPh_3 to give initially *fac*-$Re(CO)_3(PPh_3)Br(\overline{COCH_2CH_2O})$ (II) and upon further reaction $Re(CO)_2(PPh_3)_2Br(\overline{COCH_2CH_2O})$ (III). The reaction of I with the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 2$) gives the diphosphine-bridged complexes $[Re(CO)_3Br(\overline{COCH_2CH_2O})]_2(Ph_2P(CH_2)_nPPh_2)$ (IV, $n = 1$; V, $n = 2$). The structures of I and V were established by X-ray diffraction studies. The crystals of I are orthorhombic, space group *Pbca*, with $a = 11.764$ (2) Å, $b = 17.579$ (4) Å, $c = 10.658$ (2) Å, and $Z = 8$, while those of V are triclinic, space group $P\bar{1}$, with $a = 11.160$ (2) Å, $b = 11.369$ (3) Å, $c = 10.090$ (3) Å, $\alpha = 111.58$ (3)°, $\beta = 95.40$ (2)°, $\gamma = 92.78$ (2)°, $Z = 1$, and two acetones ($(CH_3)_2CO$) of crystallization. The dimethyldithiocarbamate ion, $^-S_2CN(CH_3)_2$, reacts with I to remove in effect ethylene oxide from the carbene ligand, giving $Re(CO)_5Br$ and $HOCH_2CH_2SC(=S)N(CH_3)_2$.

Introduction

Recently our group reported the synthesis of a number of transition-metal complexes containing cyclic dioxycarbene ligands, as well as cyclic aminooxy-, aminothio-, and dithiocarbene ligands.[2-5] The dioxycarbene complexes were prepared by the halide-catalyzed reaction of cationic and neutral metal carbonyl complexes with ethylene oxide according to eq 1. In order to



(1)

M = $CpFe(CO)_2^+$, $CpRu(CO)_2^+$, $CpMn(CO)(NO)^+$, $CpFe(CO)(PPh_3)^+$, $Mn(CO)_4Cl$, $Mn(CO)_4Br$, $Mn(CO)_4I$, $Re(CO)_4Cl$, $Re(CO)_4Br$, $Re(CO)_4I$, $Fe(CO)_4$, $Mn_2(CO)_9$, $Re_2(CO)_9$, $Ru_3(CO)_{11}$

explore the chemistry of complexes containing the dioxycarbene ligand $=\overline{COCH_2CH_2O}$, we have studied reactions of the complex $Re(CO)_4Br(\overline{COCH_2CH_2O})$ with a variety of phosphines, bipyridine, *o*-phenanthroline, and the dimethyldithiocarbamate ion. Reactions with phosphines lead to new compounds containing both phosphine and the dioxycarbene ligands, while reactions with the other ligands cause loss of the carbene from the metal. In this paper we describe the results of these studies and discuss the spectroscopic characterization of the new dioxycarbene complexes formed. We also present the X-ray crystallographic characterization of $Re(CO)_4Br(\overline{COCH_2CH_2O})$ and the dppe-bridged complex (dppe = 1,2-bis(diphenylphosphino)ethane) $[Re(CO)_3Br(\overline{COCH_2CH_2O})]_2(Ph_2PCH_2CH_2PPh_2)$.

Experimental Section

General Procedures. All reactions and manipulations were performed by using standard Schlenk techniques, except where noted otherwise. $Re(CO)_5Br$ was prepared as reported in the literature.[4,6] Methylene chloride was dried over CaH_2 and distilled under N_2. Hexane was distilled from CaH_2 and stored under N_2 over type 4A molecular sieves. Reagent grade $CHCl_3$ was passed down a column of basic alumina immediately before use. All other materials were reagent grade and were used without further purification. All of the new complexes reported in this paper are air-stable. Infrared spectra were recorded on a Perkin-Elmer 681 instrument, using the fine structure of gaseous CO in the 2050–2200-cm^{-1} range for calibration. ^1H and ^{13}C NMR spectra were obtained on a Nicolet NT-300 spectrometer; $Cr(acac)_3$ was added to reduce data collection time for the ^{13}C spectra. ^{31}P NMR spectra were recorded on a Bruker WM-300 instrument. Tetramethylsilane was employed as an internal standard for the ^1H and ^{13}C spectra; 85% H_3PO_4 was used as an external standard for the ^{31}P measurements. ^{13}C and ^{31}P spectra were proton-decoupled. Electron impact mass spectra were obtained with a Finnegan 4000GC-MS equipped with an INCOS data system; fast atom bombardment (FAB) spectra were obtained on a Kratos MS-50 mass spectrometer. A 5:1 (w/w) mixture of dithiothreitol and dithioerythritol was used as the matrix for the FAB spectra. Melting points (uncorrected) were determined in air on a Thomas melting point apparatus. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Syntheses of Complexes. $Re(CO)_4Br(\overline{COCH_2CH_2O})$ (I). This complex was prepared by the following modification of the original synthesis.[4] A mixture of 0.40 g (0.99 mmol) of $Re(CO)_5Br$, 2 mL of $BrCH_2CH_2OH$, 10 mL of ethylene oxide, and 0.10 g (1.0 mmol) of finely ground NaBr was stirred at 0 °C for 6 h and then allowed to stand at 0 °C for 48 h. All of the $Re(CO)_5Br$ had reacted (determined by IR), and the reaction mixture was taken to dryness under vacuum. The residue was extracted with $CHCl_3$, the extract filtered through anhydrous $MgSO_4$, and the solvent removed under vacuum, yielding a white solid. To this solid was added enough $CHCl_3$ to dissolve most, but not quite all, of the solid; $Re(CO)_3Br(\overline{COCH_2CH_2O})_2$, present in small amounts as an impurity, is substantially less soluble in $CHCl_3$ than is I. The $CHCl_3$ solution was filtered, 10–15 mL of hexane was added, and the mixture was allowed to stand at −20 °C overnight. The colorless crystals that formed were washed with hexane and vacuum-dried. This procedure gave 0.30 g (67% yield) of product containing 99.1% of I and 0.9% of $Re(CO)_3Br(\overline{COCH_2CH_2O})_2$ (determined by ^1H NMR). Repeating the recrystallization with $CHCl_3$ and hexane gave a product that showed no $Re(CO)_3Br(\overline{COCH_2CH_2O})_2$ contaminant. The compound was identified by its spectra. IR (CH_2Cl_2): 2116 m, 2016 vs, 1950 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.83 s. ^{13}C NMR (CD_3CN): δ 224.31 (carbene C); δ 187.21, 185.39, 184.01 (CO); δ 73.33 ($-CH_2CH_2-$).

***fac*-$Re(CO)_3(PPh_3)Br(\overline{COCH_2CH_2O})$ (II).** A solution of PPh_3 (0.026 g, 0.10 mmol) and I (0.045 g, 0.10 mmol) in 10 mL of toluene was heated under a slow stream of N_2 until reflux began, and reflux was continued for 15 min. The solvent was removed under vacuum, and the colorless residue was washed with hexane several times. The product was dissolved in CH_2Cl_2, and hexane was added until the solution began to get cloudy. The solution was stored overnight at −20 °C to give colorless crystals: yield 0.059 g (87%); mp 188 °C. Anal. Calcd for $C_{24}H_{19}BrO_5PRe$: C, 42.11; H, 2.80. Found: C, 42.06; H, 2.77. IR (CH_2Cl_2): 2038 s, 1958 s, 1906 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.62 m, 7.41 m (15 H, C_6H_5); δ 4.19 m (4 H, $-CH_2CH_2-$). ^{13}C NMR (acetone-d_6): δ 231.02 (carbene C); δ 194.98, 189.92, 188.98 (CO); δ 134.71, 134.57, 131.18, 129.15, 129.03 (C_6H_5); δ 72.26 ($-CH_2CH_2-$). ^{31}P NMR ($CDCl_3$): δ 6.73. Mass spectrum (*m/e* (relative intensity, probable assignment)): 684 (0.1, M^+); 656 (0.2, $(M - CO)^+$); 628 (0.3, $(M - 2\ CO)^+$); 584 (0.9, $ReBr(CO)_2(PPh_3)^+$); 528 (1.1, $ReBr(PPh_3)^+$); 422 (0.8, $ReBr(COCH_2CH_2O)(CO)_3^+$); 394 (0.8, $ReBr(COCH_2CH_2O)(CO)_2^+$); 262 (100, PPh_3^+).

$Re(CO)_2(PPh_3)_2Br(\overline{COCH_2CH_2O})$ (III). A solution of PPh_3 (0.157 g, 0.60 mmol) and I (0.094 g, 0.21 mmol) in 25 mL of toluene was refluxed under a slow flow of N_2 for 10 h. The solvent was removed under vacuum. The white residue was washed three times with hexane and then dissolved in CH_2Cl_2. Hexane was added until the solution began to get cloudy, and the mixture was allowed to stand at −20 °C overnight. The colorless crystals that formed were washed with hexane and dried under vacuum: yield 0.15 g (78%); mp 202 °C. Anal. Calcd for $C_{41}H_{34}BrP_2O_4Re$: C, 53.60; H, 3.73. Found: C, 53.28; H, 3.84. IR (CH_2Cl_2): 1944 s, 1860 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.70 m, 7.32 m

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Table I. Summary of Crystal Data and Intensity Data Collection for $\mathrm{Re(CO)_4Br(\overline{COCH_2CH_2O})}$ (I) and $\mathrm{[Re(CO)_3Br(\overline{COCH_2CH_2O})]_2(dppe)\cdot 2(CH_3)_2CO}$ ($\mathrm{V\cdot 2(CH_3)_2CO}$)

	I	V
formula unit	$\mathrm{C_7H_4O_6BrRe}$	$\mathrm{C_{44}H_{44}O_{12}Br_2P_2Re_2}$
mol wt	450.21	1359.02
space group	*Pbca*	$P\bar{1}$
a, Å	11.764 (2)	11.160 (2)
b, Å	17.579 (4)	11.369 (3)
c, Å	10.658 (2)	10.090 (3)
α, deg	90	111.58 (3)
β, deg	90	95.40 (2)
γ, deg	90	92.78 (2)
vol, Å^3	2204.0 (7)	1180.4 (5)
no. of reflecns used in lattice param determn[f]	18	14
no. of molecules per cell	8	1
calcd density, g/cm^3	2.713	1.912
cryst dimens, cm	0.015 × 0.01 × 0.01	0.015 × 0.01 × 0.01
abs coeff, cm^{-1} [g]	155.07	73.41
ratio of min/max transmission factor	0.54	0.72
wavelength, Å	0.709 26	0.709 66
monochromator	oriented graphite cryst	
scan mode	ω-step scan (0.5 s/0.01° step)	
scan width, deg	1.2	
bkgd	5 s at each side of scan	
$2\theta_{\max}$, deg	50	50
reflecns measd	4426	4948
reflecns obsd ($I \geq 3\sigma_I$)	2045	4291
unique reflecns	1201	3619
internal consistency factor[a]	0.033	0.030
R[b]	0.034	0.035
R_w[c]	0.047	0.049
S[d]	1.655	1.819
secondary extinction param[e]	0.074 (22) × 10^4	none

[a] Agreement between symmetry-related or multiply measured reflections defined as $R_I = \sum|I - \langle I\rangle|/\sum I$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma_F^2$. [d] $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, N_o and N_v being numbers of observations and varied parameters, respectively. [e] Isotropic parameter applied onto F_c, on the basis of the method of P. Coppens and W. C. Hamilton[8] with a polarization factor in the case of a monochromator in the diffracted beam. [f] 2θ was the sum of $|\omega_+|$ and $|\omega_-|$. [g] Empirical correction applied.

(30 H, $\mathrm{C_6H_5}$); δ 3.49 s (4 H, $\mathrm{-CH_2CH_2-}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 237.19 (carbene C); δ 201.85, 193.83 (CO); δ 134.08, 129.33, 127.75 ($\mathrm{C_6H_5}$); δ 68.80 ($\mathrm{-CH_2CH_2-}$). ^{31}P NMR ($\mathrm{CDCl_3}$): δ 12.49. Mass spectrum (*m*/*e* (relative intensity, probable assignment)): 846 (0.1, $\mathrm{ReBr(CO)_2(PPh_3)_2^+}$); 818 (0.2, $\mathrm{ReBr(CO)(PPh_3)_2^+}$); 528 (0.3, $\mathrm{ReBr(PPh_3)^+}$); 262 (100, $\mathrm{PPh_3^+}$). Compound III can also be prepared in 90% yield from equimolar amounts of II and $\mathrm{PPh_3}$ by using the procedure described above.

[*fac*-$\mathbf{Re(CO)_3Br(\overline{COCH_2CH_2O})]_2(Ph_2PCH_2PPh_2)}$ (IV). A solution of $\mathrm{Ph_2PCH_2PPh_2}$ (0.031 g, 0.08 mmol) and I (0.072 g, 0.16 mmol) in 15 mL of toluene was refluxed under a slow flow of $\mathrm{N_2}$ for 45 min. The solvent was removed under vacuum, and the white residue was washed several times with hexane. Following dissolution of the product in $\mathrm{CH_2Cl_2}$, hexane was added until the solution began to get cloudy, and the resulting mixture was stored at −20 °C overnight. White crystals of IV were obtained by filtration, washed with hexane, and dried under vacuum: yield 0.080 g (81%); mp 158 °C. Anal. Calcd for $\mathrm{C_{37}H_{30}Br_2O_{10}P_2Re_2}$: C, 36.16; H, 2.46. Found: C, 35.87; H, 2.73. IR ($\mathrm{CH_2Cl_2}$): 2036 s, 1959 s, 1914 s cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.73 m, 7.38 m, 7.12 m (20 H, $\mathrm{C_6H_5}$); δ 5.01 m (8 H, $\mathrm{-CH_2CH_2-}$); δ 4.19 t (2 H, $\mathrm{PCH_2P}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 135.89, 132.86, 131.15, 130.08, 129.26, 127.24 ($\mathrm{C_6H_5}$); δ 71.27 ($\mathrm{-CH_2CH_2-}$) (carbene C and CO peaks were not observed due to low solubility). ^{31}P NMR ($\mathrm{CDCl_3}$): δ 4.04. Mass spectrum (FAB *m*/*e* (relative intensity, probable assignment)): 1228 (5, M$^+$); 1149 (95, (M − Br)$^+$); 1121 (9, (M − Br − CO)$^+$); 727 (100, $\mathrm{Re(CO)_3(COCH_2CH_2O)(Ph_2PCH_2PPh_2)^+}$).

[*fac*-$\mathbf{Re(CO)_3Br(\overline{COCH_2CH_2O})]_2(Ph_2PCH_2CH_2PPh_2)\cdot 2(CH_3)_2CO}$ ($\mathbf{V\cdot 2(CH_3)_2CO}$). In a manner similar to the preparation of IV, 0.018 g of $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (0.045 mmol) and 0.040 g of I (0.089 mmol) in 15 mL of toluene were heated at 80 °C for 60 min. The solvent was removed under vacuum, leaving a white residue, which was stirred with hexane overnight, filtered, and rinsed with additional portions of hexane. After the solid was dried under vacuum, the residue was dissolved in 2 mL of acetone. Initially all the product appeared to dissolve, but within minutes tiny, colorless crystals began to form. These crystals were removed by filtration and rinsed with cold acetone. One of these crystals was subsequently used for characterization by X-ray crystallography: yield 30 mg (50%); mp 174 °C, dec pt 185 °C. IR ($\mathrm{CH_2Cl_2}$): 2039 s, 1959 s, 1908 s, 1710 m (acetone) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.37 m (20 H, $\mathrm{C_6H_5}$); δ 4.59 m, 4.33 m (8 H, $\mathrm{-OCH_2CH_2O-}$); δ 2.59 broad m (4 H, $\mathrm{-PCH_2CH_2P-}$). ^{13}C NMR (acetone-d_6): δ 133.67, 131.29, 129.40 ($\mathrm{C_6H_5}$); δ 72.28 ($\mathrm{-OCH_2CH_2O-}$); other peaks not observed due to low solubility. ^{31}P NMR (acetone-d_6): δ 4.49, 2.19.

Table II. Atomic Parameters[a] for $\mathrm{Re(CO)_4Br(\overline{COCH_2CH_2O})}$ (I)

atom	x[b]	y	z	U_{eq},[c] Å^2
Re	3748.9 (4)	1624.7 (3)	4325.3 (5)	43.3 (1)
Br	3865 (1)	799 (1)	6353 (2)	72.5 (6)
C(1)	3755 (17)	−245 (12)	1679 (19)	97 (7)
C(2)	3050 (17)	−588 (10)	2680 (20)	87 (7)
C(3)	3664 (13)	2193 (7)	2836 (14)	53 (4)
C(4)	5458 (13)	1589 (8)	4243 (12)	52 (5)
C(5)	3804 (15)	2546 (11)	5383 (16)	69 (6)
C(6)	2092 (12)	1579 (8)	4442 (14)	52 (5)
C(7)	3629 (10)	589 (7)	3287 (12)	43 (3)
O(1)	4105 (8)	522 (6)	2189 (11)	63 (3)
O(2)	3033 (8)	35 (6)	3606 (11)	66 (3)
O(3)	3661 (11)	2558 (7)	1918 (11)	81 (4)
O(4)	6408 (8)	1560 (7)	4210 (11)	77 (4)
O(5)	3790 (11)	3086 (9)	5963 (14)	104 (5)
O(6)	1135 (9)	1535 (7)	4494 (11)	76 (4)

[a] The estimated standard deviations in the parentheses are for the least significant digits. [b] Fractional atomic coordinates ×10^4. [c] $U_{iso} \equiv 10^3[{}^1/_3\sum U_{ij}\vec{a}_i^*\cdot\vec{a}_j^* a_i a_j]$, where the temperature factors are defined as $\exp(-2\pi^2\sum h_i h_j a_i^* a_j^* U_{ij})$.

When these crystals were vacuum-dried, they converted to a white solid showing no peaks due to acetone by IR or ^{1}H NMR. Anal. Calcd for $\mathrm{C_{38}H_{32}Br_2P_2O_{10}Re_2}$: C, 36.72; H, 2.59. Found: C, 36.58; H, 2.66. Mass spectrum (FAB, *m*/*e* (relative intensity, probable assignment)): 1242 (0.5, M$^+$); 1186 (1, (M − 2 CO)$^+$); 1163 (9, (M − Br)$^+$); 713 (100, $\mathrm{Re(CO)_2(COCH_2CH_2O)(Ph_2PCH_2CH_2PPh_2)^+}$).

Structure Determinations

General Procedures. Details of experimental procedures and data processing are given in Table I, with relevant crystallographic data. Crystals were mounted on the end of glass fibers with glue and attached to standard goniometer heads. The crystals were aligned in a four-circle X-ray diffractometer (DATEX), designed and built in the Ames Laboratory, controlled by an LSI-11 computer that in turn was interfaced to a VAX 11/730 computer. Preliminary ω-oscillation photographs were taken at various ϕ settings. The approximate positions of 12 reflections were selected from these photographs and used as input into an automatic indexing program. The resulting cell dimensions and symmetries were confirmed by examining axial photographs.

The intensity data were corrected for Lorentz–polarization and absorption effects. The estimated variance in each intensity was calculated by $\sigma_I^2 = C_T + C_B + (0.03C_T)^2 + (0.03C_B)^2 + (0.03I)^2$, where C_T and C_B represent the total and background counts, respectively, and the last three terms represent uncertainties in C_T and C_B due to primary beam fluctuation and nonstatistical errors and in absorption correction, respectively. Computer programs used in this study are listed in ref 7.

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(7) Calculations were carried out on a VAX 11/780 computer. Indexing of the crystals was done by using the program BLIND (Jacobson, R. A. *J. Appl. Crystallogr.* **1976**, *9*, 115). Structure factor calculations and least-squares refinements were done by using the block-matrix/full-matrix program ALLS (Lapp, R. L.; Jacobson, R. A. U.S. Department of Energy Report IS-4708; Iowa State University: Ames, IA, 1979). Fourier series calculations were done by using the program FOUR (Powell, D. R.; Jacobson, R. A. U.S. Department of Energy Report IS-4737; Iowa State University: Ames, IA, 1980), and for molecular drawings the program ORTEP (Johnson, C. K. U.S. Atomic Energy Commission Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1970) was used. An empirical absorption correction was carried out by using diffractometer ϕ-scan data and the program ABSN (Karcher, B. A. Ph.D. Dissertation, Iowa State University, 1981).

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Table III. Atomic Parameters[a] for $[Re(CO)_3Br(COCH_2CH_2O)]_2(dppe)\cdot 2(CH_3)_2CO$ ($V\cdot 2(CH_3)_2CO$)

atom	x^b	y	z	U_{eq},[c] Å^2
Re	-2702.0 (2)	-2815.2 (2)	-2869.2 (3)	37.2 (1)
Br	-1344 (1)	-3859 (1)	-1417 (1)	52.7 (3)
Br′	-3952 (4)	-2061 (4)	-4663 (4)	56 (1)
P	-1932 (1)	-692 (2)	-1083 (2)	33.2 (6)
C(1)	169 (8)	-1923 (10)	-5059 (10)	72 (4)
C(2)	492 (8)	-3200 (11)	-5089 (11)	73 (4)
C(3)	-3623	-2158	-4066	47
C(3)′	-1875	-3438	-1563	63
C(5)	-4072 (7)	-2850 (7)	-1783 (9)	51 (3)
C(6)	-3212 (8)	-4541 (7)	-4246 (9)	58 (3)
C(7)	-1184 (6)	-2694 (7)	-3945 (7)	43 (2)
C(8)	-274 (6)	-539 (6)	-698 (7)	37 (2)
C(9)	2409 (10)	4491 (10)	-2000 (10)	74 (4)
C(10)	3566 (10)	4395 (12)	-1253 (16)	106 (6)
C(11)	2058 (11)	5770 (11)	-1852 (14)	95 (5)
C(111)	-2283 (6)	642 (6)	-1600 (7)	38 (2)
C(112)	-1414 (8)	1524 (7)	-1674 (8)	53 (2)
C(113)	-1766 (9)	2532 (8)	-2051 (10)	63 (3)
C(114)	-2963 (10)	2633 (9)	-2376 (11)	71 (4)
C(115)	-3828 (8)	1756 (9)	-2324 (10)	64 (3)
C(116)	-3504 (7)	778 (8)	-1920 (8)	53 (3)
C(121)	-2441 (6)	-259 (6)	710 (7)	36 (2)
C(122)	-2959 (7)	846 (7)	1367 (8)	48 (2)
C(123)	-3321 (8)	1129 (8)	2727 (9)	55 (3)
C(124)	-3175 (8)	307 (8)	3412 (8)	55 (3)
C(125)	-2657 (8)	-801 (8)	2775 (9)	54 (3)
C(126)	-2296 (7)	-1102 (7)	1413 (8)	48 (2)
O(1)	-886 (5)	-1719 (5)	-4269 (6)	57 (2)
O(2)	-457 (5)	-3582 (6)	-4389 (6)	63 (2)
O(3)	-4212	-1696	-4778	94
O(3)′	-1268	-3730	-826	63
O(5)	-4848 (6)	-2845 (7)	-1153 (8)	76 (3)
O(6)	-3530 (7)	-5502 (7)	-5022 (8)	94 (3)
O(7)	1741 (10)	3552 (8)	-2670 (13)	152 (5)

[a] The estimated standard deviations in the parentheses are for the least significant digits. Primed atoms represent the minor positions of the disordered atoms. [b] Positional parameters $\times 10^4$. [c] $U_{iso} = 10^3 \times [{}^1/_3 \sum U_{ij} \vec{a}_i^* \cdot \vec{a}_j^* a_i a_j]$, where the temperature factors are defined as $\exp(-2\pi^2 \sum h_j a_i^* a_j^* U_{ij})$.

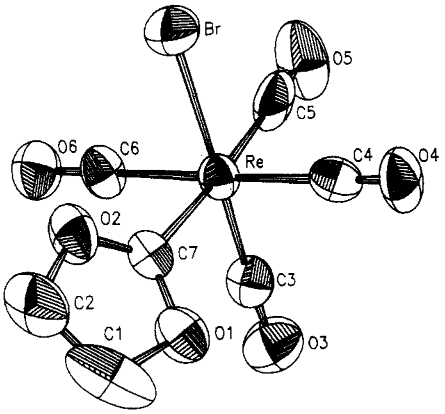

Figure 1. ORTEP drawing of $Re(CO)_4Br(COCH_2CH_2O)$ (I). Thermal ellipsoids are drawn at the 50% probability level.

Table IV. Selected Bond Distances (Å) for $Re(CO)_4Br(COCH_2CH_2O)$ (I) and $[Re(CO)_3Br(COCH_2CH_2O)]_2(dppe)\cdot 2(CH_3)_2CO$ ($V\cdot 2(CH_3)_2CO$)

(a) Comparison of Bond Distances around Re Atom

	I	$V\cdot 2(CH_3)_2CO$[a]
Re–Br	2.606 (2)	2.624 (1)
Re–P		2.474 (1)
Re–C(3)	1.878 (14)	1.892
Re–C(4)	2.014 (14)	
Re–C(5)	1.974 (18)	1.970 (7)
Re–C(6)	1.954 (14)	1.960 (7)
Re–C(7)	2.135 (13)	2.122 (6)
C(1)–C(2)	1.480 (28)	1.503 (12)
C(1)–O(1)	1.510 (23)	1.464 (10)
C(2)–O(2)	1.474 (22)	1.460 (10)
C(3)–O(3)	1.171 (19)	1.202
C(4)–O(4)	1.119 (18)	
C(5)–O(5)	1.133 (23)	1.120 (9)
C(6)–O(6)	1.130 (18)	1.102 (10)
C(7)–O(1)	1.303 (16)	1.302 (8)
C(7)–O(2)	1.247 (16)	1.302 (8)

(b) Bond Distances in dppe and Acetone Portions of $V\cdot 2(CH_3)_2CO$

P–C(8)	1.841 (6)	C(9)–C(10)	1.462 (14)
P–C(111)	1.824 (6)	C(9)–C(11)	1.482 (14)
P–C(121)	1.844 (6)	C(9)–O(7)	1.204 (13)
C(111)–C(112)	1.388 (9)	C(121)–C(122)	1.373 (8)
C(111)–C(116)	1.399 (9)	C(121)–C(126)	1.394 (8)
C(112)–C(113)	1.396 (11)	C(122)–C(123)	1.393 (10)
C(113)–C(114)	1.366 (12)	C(123)–C(124)	1.359 (10)
C(114)–C(115)	1.373 (12)	C(124)–C(125)	1.371 (10)
C(115)–C(116)	1.370 (10)	C(125)–C(126)	1.392 (10)
C(8)–C(8)[b]	1.535 (8)		

[a] For the disordered atoms the distances in the minor image are Re–Br = 2.596 (4) Å, Re–C(3) = 1.900 Å and C(3)–O = 1.109 Å. [b] Symmetry code $-x, -y, -z$.

Structure Determination for I. The structure of I was determined by using Patterson, structure factor, and electron density function calculations. The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined, along with hydrogen atoms included at the ideal positions with fixed isotropic temperature factors (B = 7 Å^2). The final difference electron density map was featureless.

The final positional and thermal parameters are listed in Table II, while bond lengths and bond angles are given in Tables IV and V, respectively. An ORTEP drawing of the molecule is given in Figure 1.

Structure Determination for V. Initial positions for the heavy atoms were obtained from an analysis of the Patterson function, and the remaining atoms were located from structure factor and electron density function calculations. Both centrosymmetric and noncentrosymmetric models were tested. The noncentrosymmetric model gave a higher residual index (R_w = 6.1%) than the centrosymmetric one (R_w = 4.9%); hence, the latter was chosen. Difference electron density maps for the centrosymmetric model showed four peaks away from the complex molecule; these peaks were assigned as an acetone in view of the solvent used in the crystallization. It was also found that Br, C(3), and O(3) were disordered over two possible configurations with a refined occupancy ratio of 0.815 (3):0.185. Since the Br position of one configuration was very close to the middle of C(3) and O(3) of the other, the positional and isotropic thermal parameters of C(3) and O(3) in the major configuration were refined together with the parameters of only the Re atoms to reduce correlation effects. After chemically reasonable parameters were obtained, they were kept fixed in the rest of the calculations. No attempt was made to refine parameters of C(3) and O(3) in the minor configuration. In the final stages of the refinement, the occupancy factor and two sets of positional and anisotropic thermal parameters for the Br atoms were refined along with the positional and anisotropic thermal parameters of the remaining non-hydrogen atoms. Hydrogen atoms were included at the ideal positions with fixed isotropic temperature factors (B = 5–9 Å^2, depending on the magnitude of the thermal motion of the carbon atom to which each hydrogen atom is bonded). The final difference electron density map was featureless.

The final positional and thermal parameters are listed in Table III, while bond lengths and bond angles are given in Tables IV and V, respectively. An ORTEP drawing of the molecule is given in Figure 2.

Results and Discussion

Reactions of $Re(CO)_4Br(COCH_2CH_2O)$ (I) with Phosphines. The reaction (eq 2) of I with an equimolar amount of PPh_3 in refluxing toluene gives *fac*-$Re(CO)_3(PPh_3)Br(COCH_2CH_2O)$, in 87% yield, within 30 min. The three equally intense ν(CO) absorptions in II are characteristic of facial tricarbonyl complexes[9]

$$\underset{\text{I}}{Re(CO)_4Br(COCH_2CH_2O)} + PPh_3 \rightarrow \underset{\text{II}}{Re(CO)_3(PPh_3)Br(COCH_2CH_2O)} + CO \quad (2)$$

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Table V. Selected Bond Angles (deg) for $Re(CO)_4Br(\overline{COCH_2CH_2O})$ (I) and $[Re(CO)_3Br(\overline{COCH_2CH_2O})]_2(dppe)\cdot 2(CH_3)_2CO$ ($V\cdot 2(CH_3)_2CO$)

(a) Comparison of Bond Angles around Re Atom

	I	$V\cdot 2(CH_3)_2CO$
Br–Re–P		89.5 (1)
P–Re–C(3)		93.9
P–Re–C(5)		90.3 (2)
P–Re–C(6)		176.0 (2)
P–Re–C(7)		86.7 (2)
Br–Re–C(3)	178.1 (4)	174.8
Br–Re–C(4)	88.1 (4)	
Br–Re–C(5)	88.9 (5)	92.1 (2)
Br–Re–C(6)	88.7 (4)	87.0 (2)
Br–Re–C(7)	87.7 (3)	87.2 (2)
C(3)–Re–C(4)	91.9 (6)	
C(3)–Re–C(5)	92.7 (7)	91.8
C(3)–Re–C(6)	91.3 (6)	89.5
C(3)–Re–C(7)	90.7 (6)	89.1
C(4)–Re–C(5)	91.0 (7)	
C(4)–Re–C(6)	175.7 (6)	
C(4)–Re–C(7)	91.0 (5)	
C(5)–Re–C(6)	91.7 (7)	91.4 (3)
C(5)–Re–C(7)	176.0 (6)	176.9 (3)
C(6)–Re–C(7)	86.1 (5)	91.5 (3)
C(2)–C(1)–O(1)	104.9 (15)	102.5 (6)
C(1)–C(2)–O(2)	100.8 (15)	103.3 (6)
Re–C(3)–O(3)	176.5 (13)	177.2
Re–C(4)–O(4)	177.9 (13)	
Re–C(5)–O(5)	176.7 (16)	180.0 (6)
Re–C(6)–O(6)	179.2 (13)	177.9 (7)
Re–C(7)–O(1)	121.0 (9)	123.4 (4)
Re–C(7)–O(2)	124.2 (9)	124.7 (4)
O(1)–C(7)–O(2)	114.6 (12)	111.8 (5)
C(1)–O(1)–C(7)	106.7 (12)	111.3 (5)
C(2)–O(2)–C(7)	112.9 (12)	111.0 (6)

(b) Selected Bond Angles of dppe and Acetone in $V\cdot 2(CH_3)_2CO$

Re–P–C(8)	111.6 (2)	C(8)–P–C(111)	105.1 (3)
Re–P–C(111)	115.4 (2)	C(8)–P–C(121)	103.3 (2)
Re–P–C(121)	116.3 (2)	C(111)–P–C(121)	103.8 (3)
C(10)–C(9)–C(11)	118.5 (9)	C(10)–C(9)–O(7)	120.3 (9)
C(11)–C(9)–O(7)	121.1 (9)	P–C(8)–C(8)[a]	116.1 (4)

[a] Symmetry code −x, −y, −z.

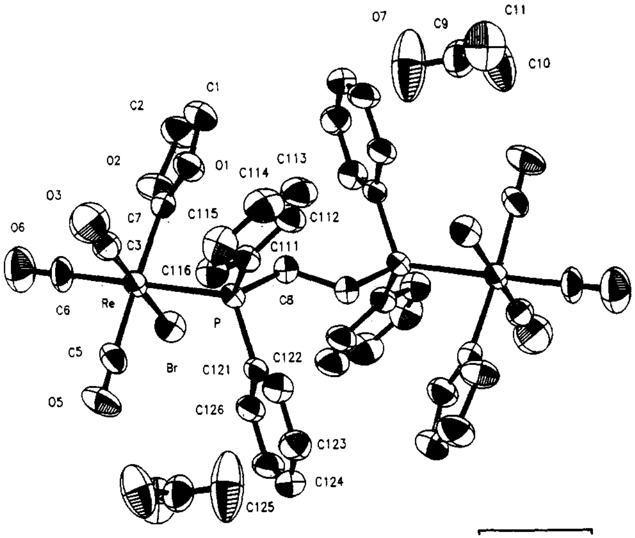


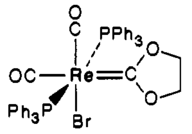
Figure 2. ORTEP drawing of $[Re(CO)_3Br(\overline{COCH_2CH_2O})]_2(Ph_2PCH_2CH_2PPh_2)\cdot 2(CH_3)_2CO$ ($V\cdot 2(CH_3)_2CO$).

and are comparable to those reported previously for *fac*-$Mn(CO)_3(PPh_3)Cl(\overline{COCH_2CH_2O})$ at 2036, 1967, and 1923 cm^{-1}.[10] Due to the presence of the asymmetric Re center in II, the protons in the carbene ligand are diastereotopic and occur as a multiplet at δ 4.19. Similar multiplets are observed for the carbene protons in IV and V below. However, in I, where there is no asymmetric center, the carbene resonance is a singlet.

If II is heated with an additional 1 mol of PPh_3 in toluene, a much slower reaction (eq 3) occurs (~10 h) to give $Re(CO)_2(PPh_3)_2Br(\overline{COCH_2CH_2O})$ (III) in 90% yield. The presence of

$$\underset{\text{II}}{Re(CO)_3(PPh_3)Br(\overline{COCH_2CH_2O})} + PPh_3 \rightarrow \underset{\text{III}}{Re(CO)_2(PPh_3)_2Br(\overline{COCH_2CH_2O})} + CO \quad (3)$$

two ν(CO) bands of approximately equal intensity at 1944 and 1860 cm^{-1} indicates that the CO ligands are cis to each other.[6] The ^{31}P NMR spectrum shows a single resonance at δ 12.49, and the ^{13}C NMR spectrum shows two signals in the carbonyl region at δ 193.83 and 201.85. These data are consistent only with the isomeric structure



III

Compound III was also prepared from I and ≥2 mol of PPh_3 in refluxing toluene, as described in the Experimental Section. Both II and III were formed in low yields by photolyzing I and II, respectively, in CH_2Cl_2 solutions containing 1 mol of PPh_3/mol of Re complex. Small amounts of other photolysis products were observed by ^1H NMR, but these compounds were not identified.

The diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2) react with I to give dinuclear products in which two $Re(CO)_3Br(\overline{COCH_2CH_2O})$ groups are bridged by a single diphosphine ligand (eq 4). These reactions are performed in highest yield if exactly $^1/_2$ mol of diphosphine ligand/mol of I is used. If less than $^1/_2$ mol of diphosphine is used, the reaction does not proceed to completion, and unreacted I remains. If more than $^1/_2$ mol of diphosphine is used, excess diphosphine ligand remains; over a period of hours in refluxing toluene the excess diphosphine appears to react slowly to give other, as yet unidentified, products. The reaction of I with $^1/_2$ mol of $Ph_2PCH_2PPh_2$ (dppm) in refluxing toluene yields [*fac*-$Re(CO)_3Br(\overline{COCH_2CH_2O})]_2$(dppm) (IV), whose FAB mass spectrum shows a parent ion for this dinuclear composition. The IR spectrum of IV in CH_2Cl_2 solution exhibits three strong bands of approximately equal intensity at 2036, 1959, and 1914 cm^{-1}; as in II, the positions and intensities of these bands are consistent with a facial arrangement of the three CO ligands on each metal. A single resonance is observed in the ^{31}P NMR spectrum of IV, suggesting magnetically equivalent environments for the two phosphorus atoms. Since the two Re atoms are asymmetric centers, it is possible for IV to exist as two diastereomers: one in which the chirality is the same at both Re atoms and the other in which they are different. The presence of only one ^{31}P signal suggests that only one of these diasteromers is isolated.

$$2Re(CO)_4Br(\overline{COCH_2CH_2O}) + Ph_2P(CH_2)_nPPh_2 \rightarrow \underset{\substack{\text{IV } (n = 1) \\ \text{V } (n = 2)}}{[Re(CO)_3Br(\overline{COCH_2CH_2O})]_2(Ph_2P(CH_2)_nPPh_2)} + 2CO \quad (4)$$

The reaction of $^1/_2$ mol of $Ph_2P(CH_2)_2PPh_2$ (dppe) with I gives the dppe-bridged, dinuclear complex [*fac*-$Re(CO)_3Br(\overline{COCH_2CH_2O})]_2$(dppe) (V), which was isolated from acetone as the disolvate as colorless crystals suitable for X-ray diffraction study (see below). The FAB mass spectrum confirmed the dinuclear formulation of the compound. With ν(CO) bands at 2039, 1959, and 1908 cm^{-1}, V has an IR spectrum very similar to that of II and IV.

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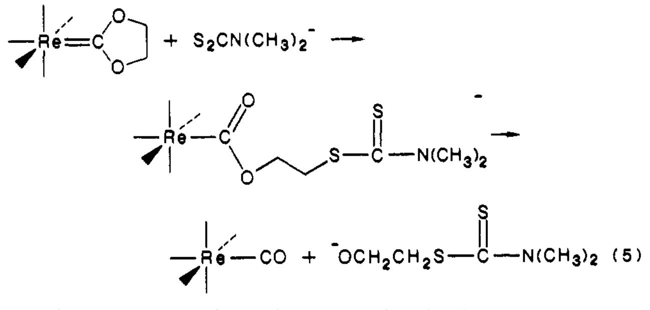
The ^{1}H NMR spectrum of V in $CDCl_3$ exhibits multiplets attributable to protons of the dioxycarbene ligands at δ 4.59 and 4.33; in addition, two signals are observed in the ^{31}P spectrum, at δ 4.49 and 2.19. Furthermore, the carbene multiplets at δ 4.59 and 4.33 and also the multiplets assigned to the ethylene protons of the dppe ligand at δ 2.59 change gradually with time. The changes involve small changes in the chemical shift (<0.05 ppm), and the patterns of intensity within the multiplets change significantly. However, integration of the multiplets indicates that the total area of the peaks near δ 4.59 and 4.33 remains approximately double the area of the multiplet near δ 2.59. All samples of V studied showed all three multiplets, including the sample from which crystals were taken for X-ray structure determination. The multiplets were also observed, but with slightly different chemical shifts and patterns, in acetone-d_6, CD_2Cl_2, and nitrobenzene-d_5. A variable-temperature experiment was conducted in which a solution of V in nitrobenzene-d_5 was heated from 21 to 127 °C and then cooled back to the original temperature. Spectra taken over this temperature range showed changes in chemical shifts and in the patterns of the multiplets in question, but there was no evidence for coalescence of the peaks. The final spectrum in this experiment was identical with the original spectrum at 21 °C. All of these observations are consistent with the presence of two diastereomers of V in solution: one in which the asymmetric Re centers both have the same chirality and the other in which the chiralities are different. Each diastereomer gives separate ^{31}P signals. The asymmetric Re centers also cause the carbene and dppe ethylene protons to be diastereotopic and, therefore, complex multiplets. The changes in the multiplets in different solvents and at different temperatures are presumably due to small changes in the chemical shifts of the protons. The observed changes in the ^{1}H NMR spectra with time suggest slow interconversion between the diastereomers.

Other Reactions of $Re(CO)_4Br(\overline{COCH_2CH_2O})$. Refluxing I with an equimolar amount of 2,2′-bipyridine (bpy) in toluene gives $Re(CO)_3Br(bpy)$ in 90% yield. The product has IR bands at 2027, 1923, and 1901 cm^{-1}, which are similar to those reported for $Re(CO)_3I(bpy)$.[11] The identity of the product has been substantiated by ^{1}H NMR and mass spectra and by independently synthesizing the compound from $Re(CO)_5Br$ and bpy.[11] Similarly, refluxing I with *o*-phenanthroline (*o*-phen) gives a product having IR, ^{1}H NMR, and mass spectra consistent with $Re(CO)_3Br$(*o*-phen). In the reactions of I with bpy and *o*-phen, we have also observed, in addition to the Re complex products, several ^{1}H NMR peaks near δ 3.64, a chemical shift that is similar to those reported for the methyl peaks of $(CH_3O)_2C{=}C(OCH_3)_2$ and $H_2C{=}C(OCH_3)_2$;[12] these peaks apparently correspond to organic products formed when the carbene ligand is lost in the reaction. Efforts to characterize them were unsuccessful.

In acetonitrile solution at 0 °C, I reacts rapidly with the dimethyldithiocarbamate ion, $S_2CN(CH_3)_2^-$, to give a mixture of products. In the ^{1}H NMR spectrum the principal change observed is the disappearance of the carbene peak of I and the appearance of new bands at δ 3.91 (t), 3.60 (t), 3.57 (s), 3.41 (s), and ca. 2.25 (t).[13] At the same time, the IR spectrum shows the appearance of bands matching those of $Re(CO)_5Br$[6] and bands of moderately strong intensity at 1500 and 977 cm^{-1}. Besides $Re(CO)_5Br$, the other major product was identified as $HOCH_2CH_2SC({=}S)N(CH_3)_2$; this product was prepared independently from $HOCH_2CH_2Br$ and $NaS_2CN(CH_3)_2{\cdot}H_2O$ in CH_3CN solution at 0 °C in a reaction that has been reported previously.[14] The ^{1}H NMR spectrum of the synthesized product was identical with that observed in the reaction, including the concentration-dependent triplet near δ 2.25. The 1500- and 977-cm^{-1} IR bands, characteristic of the C—N and C=S stretching modes, respectively, in dithiocarbamate compounds,[15] were also present in the IR spectrum of this compound.

As a possible route for the formation of $Re(CO)_5Br$ and $HOCH_2CH_2SC(S)N(CH_3)_2$ from $Re(CO)_4Br(\overline{COCH_2CH_2O})$ and dithiocarbamate ion, we suggest that a carbon of the $-CH_2CH_2-$ backbone of the dioxycarbene ligand undergoes nucleophilic attack by the dithiocarbamate, followed by elimination of the anion of the product thioester (eq 5). The anion formed



could gain a proton from the water of hydration accompanying the dithiocarbamate salt used. The first step of eq 5 is related to the ring opening observed when $Mn(CO)_5(\overline{COCH_2CH_2O})^+$ reacts with I$^-$.[10] Overall, the mechanism is very similar to the reverse of that proposed for the bromide-catalyzed cyclization reaction that gives $Re(CO)_4Br(\overline{COCH_2CH_2O})$ from $Re(CO)_5Br$ and oxirane, presumably involving the $BrCH_2CH_2O^-$ ion.[3,4]

The products $Re(CO)_5Br$ and $HOCH_2CH_2SC({=}S)N(CH_3)_2$ only account for about 70% of the products of reaction of I and dithiocarbamate. Small ^{1}H NMR and infrared peaks matching those of independently synthesized $Re(CO)_4[S_2CN(CH_3)_2]$[16] and $[Re(CO)_3(S_2CN(CH_3)_2)]_2$[16,17] were also observed, as well as several minor peaks, which remain unidentified. These products may be formed directly from I and $S_2CN(CH_3)_2^-$, or they may be secondary reaction products; we have observed that in CH_3CN solution $Re(CO)_5Br$ does react slowly with $S_2CN(CH_3)_2^-$ to give first $Re(CO)_4[S_2CN(CH_3)_2]$ and then $[Re(CO)_3(S_2CN(CH_3)_2)]_2$.

Discussion of Structures of I and V. In both I and V, the rhenium–carbene carbon (C(7)) distances are similar: 2.135 (13) Å for I and 2.122 (6) Å for V. These distances are considerably greater than the Re–CO distances (1.88–2.01 Å in I, 1.89–1.97 Å in V), which indicates weaker π bonding from the metal to the carbene than to the CO ligands in these complexes. The Re–C(7) distances are also longer than Re–carbene bonds in $(\eta\text{-Cp})Re(NO)(PPh_3)({=}CHPh)^+$ (1.949 (6) Å)[18] (Cp = cyclopentadienyl) and $(\eta\text{-}C_5Me_5)Re(NO)[P(OPh)_3]({=}CH_2)^+$ (1.898 (18) Å).[19] However, they are comparable to or slightly longer than Re–C bonds to oxygen-containing carbenes in $Re_2(CO)_9[{=}C(OMe)SiPh_3]$ (2.09 (2) Å)[20] and $MnRe(CO)_9[{=}C(OMe)Me]$ (2.094 (7) Å).[21] The Re–C(7) bond distance is clearly not as long as Re–C single-bond distances in $CH_3Re(CO)_5$ (2.308 Å),[22] $(CO)_5ReCH_2CH_2Re(CO)_5$ (2.304 (8) Å),[23] and $(\eta\text{-Cp})Re(NO)(PPh_3)(CH_2Ph)$ (2.203 (8) Å).[24] Thus, it appears that there is

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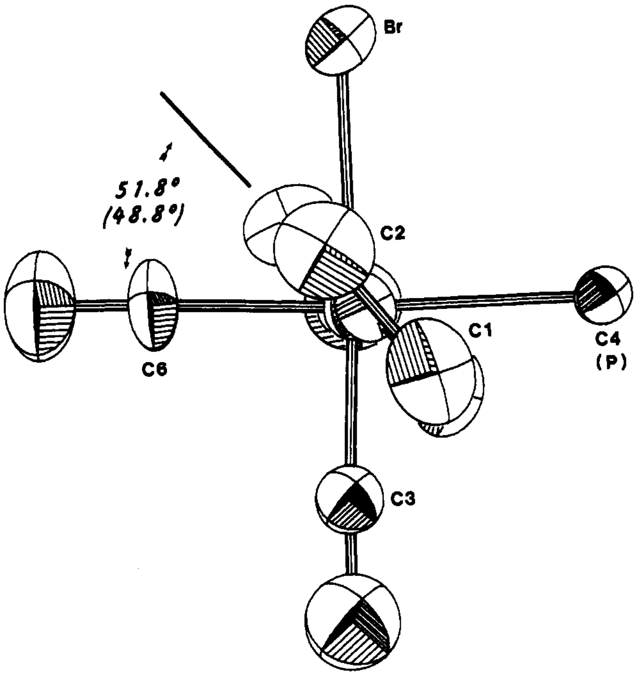

Figure 3. View down C(7)–Re–C(5) axis. Angle is between plane of carbene ligand and plane defined by C(4), C(5), C(6), and C(7): 51.8° for I and 48.8° for V.

some π bonding between Re and the carbene ligand in I and V.

Within the carbene ligand, there is considerable π interaction between C(7) and its neighboring oxygens. In V, for example, the C(7)–oxygen distance is approximately 0.16 Å shorter than the C(1)–O(1) and C(2)–O(2) distances of 1.46 Å, which are typical of single carbon–oxygen bonds.[25] In both I and V the dimensions of the dioxycarbene ligand are similar to those reported for $\mathrm{Mn(CO)_4Cl(\overline{COCH_2CH_2O})}$.[26] The dioxycarbene ligands are very nearly planar; in both I and V all five atoms are within 0.018 Å of their least-squares plane. In I, the least-squares plane of the carbene ligand makes an angle of 51.8° with the least-squares plane defined by C(4), C(5), C(6), and C(7); the corresponding angle for V is 48.8°. A perspective view illustrating these angles is given in Figure 3. These values are similar to the angle of 49° reported between comparable planes of $\mathrm{Mn(CO)_4Cl(\overline{COCH_2CH_2O})}$.[26] Frontier orbital arguments predict that the favored orientation of the plane of the carbene ligand should be perpendicular to the M–L bond for complexes of formula $\mathrm{M(CO)_4L(carbene)}$ where L is a pure σ donor or weak π acceptor.[27] The deviation of I, V, and $\mathrm{Mn(CO)_4Cl(\overline{COCH_2CH_2O})}$ from this predicted structure suggests that Re to carbene π bonding is relatively weak as also indicated by the Re–C(7) bond distance and that steric or possibly crystal-packing forces determine the orientation of the carbene ligand.

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Supplementary Material Available: Listings of thermal parameters and hydrogen atom positions (4 pages); listings of calculated and observed structure factors (18 pages). Ordering information is given on any current masthead page.

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Synthesis, Reactivity, and Simultaneous Two-Electron Electrochemistry of Trinuclear Iron–Molybdenum and Cobalt–Molybdenum Carbonyl Thiolate Complexes†

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The new heterometallic trinuclear species $[\mathrm{M(SR)_4\{Mo(CO)_4\}_2}]^{2-}$ (M = Fe, Co; R = Ph, Bz) have been prepared by three distinct methods: (a) reaction of $[\mathrm{Mo(CO)_4(SR)_2}]^{2-}$ with $\mathrm{MX_2}$ or $[\mathrm{MX_4}]^{2-}$ (X = halide); (b) reaction of $[\mathrm{Mo(CO)_4(norbornadiene)}]$ with $[\mathrm{M(SR)_4}]^{2-}$; (c) reaction of $[\mathrm{Mo_2(CO)_8(SR)_2}]^{2-}$ with $\mathrm{MX_2}$ or $[\mathrm{MX_4}]^{2-}$. All complexes have been characterized by IR and electronic spectroscopy, elemental analysis, and CO evolution studies. The Co complexes have been further characterized by EPR spectroscopy and shown to exhibit spectra consistent with the presence of three unpaired electrons from Co(II) in a tetrahedral environment. The trinuclear Fe– and Co–SPh species react with organic isocyanides to yield products that are postulated to be $[\mathrm{M(SR)_4(CyNC)_2\{Mo(CO)_4\}_2}]^{2-}$ but whose IR spectra unexpectedly contain a carbonyl pattern significantly different from that of their precursors, leaving some doubt as to their structures. $[\mathrm{M(SR)_4\{Mo(CO)_4\}_2}]^{2-}$ (M = Fe, Co; R = Ph) also react with 2,2′-bipyridine and *o*-phenanthroline (L) producing the dinuclear, neutral complexes $[\mathrm{(CO)_4Mo(SR)_2ML_2}]$. Cyclic voltammetry studies of $[\mathrm{M(SR)_4\{Mo(CO)_4\}_2}]^{2-}$ (M = Fe, Co; R = Ph, Bz) show that the complexes are oxidized at ca. 0 V by two electrons in a single step, a phenomenon attributed to the formation of two Mo–Fe(Co) metal–metal bonds in the product. Consistent with this hypothesis, chemical oxidation of $[\mathrm{M(SR)_4\{Mo(CO)_4\}_2}]^{2-}$ (M = Fe, Co; R = Ph) with $\mathrm{I_2}$ yields the neutral trinuclear complexes $[\mathrm{M(SR)_4\{Mo(CO)_4\}_2}]$ (M = Fe, Co; R = Ph).

Introduction

As part of our efforts to better understand the chemistry of low-valent metal carbonyl thiolate species, we have recently reported the preparation of mononuclear[3] molybdenum complexes containing cis terminal thiolate groups and dinuclear[4–6] molybdenum and tungsten species with bridging thiolate moieties. One goal of this work was to generate starting materials for the syn-

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