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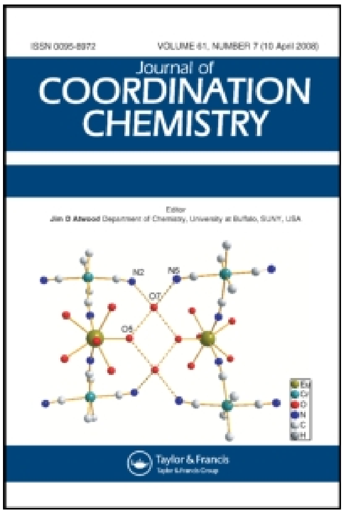

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PREPARATION AND CHARACTERIZATION OF CLUSTERS CONTAINING THE CoMRuS (M=Mo OR W) CORE

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PREPARATION AND CHARACTERIZATION OF CLUSTERS CONTAINING THE CoMRuS (M=Mo OR W) CORE

YU-HUA ZHANG[a], BAO-HAN XIE[a], YUE-QI LIU[a],
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(Received 20 April 2000)

The reaction of $(\mu_3\text{-S})RuCo_2(CO)_9$ with functionally substituted cyclopentadienyl tricarbonyl metal anions $M(CO)_3(C_5H_4C(O)R)$ (M = Mo, W; R = OEt, CH_2CH_2COOMe) in THF under reflux gave new chiral skeleton clusters $(\mu_3\text{-S})RuCoM(CO)_8(C_5H_4C(O)R)$ [M = Mo, R = OEt (1); M = W, R = OEt (2); M = Mo, R = CH_2CH_2COOMe (3); M = W, R = CH_2CH_2COOMe (4)]. These complexes were characterized by elemental analysis, IR and ^1H NMR spectra. The molecular structure of compound (1) was determined by single-crystal X-ray diffraction methods.

Keywords: Chiral cluster; Crystal structure; Synthesis; Cobalt; Molybdenum; Tungsten; Sulfur

INTRODUCTION

Asymmetric catalysis induced by a metal cluster which contains a chiral metal framework would be the strongest evidence for the catalysis by the intact cluster [1]. Considerable efforts have been directed to the synthesis of chiral tetrahedral clusters containing four different atoms at the vertices of

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the tetrahedron during the past years. However, there remains the major problem of enantiomer separation [2]. Although Vahrenkamp had achieved some pioneering results in this area before 1990 [1], few pure enantiomers of chiral clusters have been obtained until now. Recently, we described the synthesis and structure of chiral clusters containing organic groups such as aldehydes, ketones or esters [3–8]. It is possible to obtain pure enantiomers of chiral clusters by separating enantiomers of the aldehyde, ketone or ester. As part of this work, we report the synthesis and characterization of four tetrahedral clusters containing an ester group.

EXPERIMENTAL

All reactions were carried out under nitrogen of high purity using standard Schlenk techniques. All solvents were dried according to standard procedures before use. Chromatographic separations and purifications were performed on 160–200 mesh silica gel. $Mo(CO)_6$ and $W(CO)_6$ were purchased from Fluka and Aldrich. $(\mu_3\text{-S})RuCo_2(CO)_9$ [9] and $Na(C_5H_4COOEt)$ [10] were prepared according to published methods. IR spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer, and ^1H NMR on a Bruker-AM 400 MHz spectrometer; C/H determinations were performed using a Carlo-Erba 1160 microanalyser.

Preparation of $Na(C_5H_4C(O)CH_2CH_2COOMe)$

Freshly cracked cyclopentadiene (5 cm^3, 60 mmol) was added to a slurry of sodium sand (1.0 g, 44 mmol) in 25 cm^3 of THF at 0°C in a Schlenk flask. The flask was fitted with a gas outlet tube connected to a mercury overpressure valve allowing the evolution of hydrogen. The mixture was stirred until the sodium had completely reacted. To the resulting pink solution of sodium cyclopentadiene, dimethyl succinate (6 cm^3, 46 mmol) was added. The reaction mixture was heated under reflux overnight and then the solvent was removed *in vacuo*. The resulting solid was washed with diethylether until the filtrate became white. After drying, the hygroscopic, slightly air-sensitive solid could be used directly in the following experiments.

Synthesis of Cluster (1) and (3)

To a solution of $Na(C_5H_4COOEt)$ (0.160 g, 1.0 mmol) in THF (25 cm^3), $Mo(CO)_6$ (0.264 g, 1.0 mmol) was added. After the mixture was heated

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under reflux for 14 h and cooled to room temperature, (μ_3-S)RuCo$_2$(CO)$_9$ (0.503 g, 1.0 mmol) was added and stirred at 60°C for 1.5 h. The solvent was then removed under vacuum. The residue was chromatographed on a 2.5 × 25 cm silica gel column. Petroleum ether (60 – 90°C) – CH$_2$Cl$_2$ (4 : 1) used as eluant gave unreacted material and a yellow band. Petroleum ether (60 – 90°C) – CH$_2$Cl$_2$ (1 : 1) gave a dark red band from which compound (1) was obtained as a dark red solid; 0.265 g, 40.0% yield. Calcd. for $C_{16}H_9O_{10}$CoMoRuS (%): C, 29.60; H, 1.40. Found: C, 29.72; H, 1.38. IR (KBr disk): $\nu(C{\equiv}O)$2081.6 vs, 2038.5 vs, 2002.6 vs, 1971.4 vs, 1879.4 s cm^{-1}, $\nu(C{=}O)$1722.6 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ5.98 – 5.47(*q*, 4H, C$_5$H$_4$), 4.34 – 4.29(*q*, 2H, CH$_2$), 1.33(*t*, 3H, CH$_3$).

Compound (3) was prepared using the same procedure as that for (1), except that Na[C$_5$H$_4$C(O)CH$_2$CH$_2$COOMe] was used instead of Na(C$_5$H$_4$COOEt). With CH$_2$Cl$_2$ a dark red band was eluted, from which 0.185 g of (3) as a dark red solid was obtained; 26.8% yield. Calcd. for $C_{18}H_{11}O_{11}$ CoMoRuS (%): C, 31.28; H, 1.60. Found: C, 31.35; H, 1.46. IR (KBr disk): $\nu(C{\equiv}O)$2081.3 vs, 2042.8 vs, 2006.1 vs, 1986.8 vs, 1965.6 s, 1919.3 m, 1846.0s cm^{-1}, $\nu(C{=}O)$1738.0 s, 1691.7s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ5.92 – 5.48(*q*, 4H, C$_5$H$_4$), 3.69(*s*, 3H, CH$_3$), 3.02(*s*, 2H, CH$_2$), 2.73(*s*, 2H, CH$_2$).

Synthesis of Cluster (2) and (4)

Some 0.352 g (1.0 mmol) of W(CO)$_6$ was added to a solution of 25 cm^3 of DMF containing 1.0 mmol of Na(C$_5$H$_4$COOEt). The mixture was heated at 120°C with stirring for 14 h. After cooling the mixture to room temperature, 0.503 g (1.0 mmol) of (μ_3-S)RuCo$_2$(CO)$_9$ was added and the reaction mixture was stirred at 60°C for 1.5 h. The solvent was removed under reduced pressure and the residue was loaded on a 2.5 × 25 cm silica gel column. Elution with petroleum (60 – 90°C) – CH$_2$Cl$_2$ (4 : 1) produced a small amount of (μ_3-S)RuCo$_2$(CO)$_9$ and a yellow band. Petroleum (60 – 90°C) – CH$_2$Cl$_2$ (1 : 1) yielded the product (2); 0.265 g, 36.0% yield. Calcd. for $C_{16}H_9O_{10}$CoRuSW (%): C, 26.07; H, 1.23. Found: C, 26.17; H, 1.27. IR (KBr disk): $\nu(C \equiv O)$2079.4 vs, 2037.0 vs, 1998.4 vs, 1965.6 vs, 1882.7s cm^{-1}, $\nu(C{=}O)$1722.6 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ5.96 – 5.55(*t*, 4H, C$_5$H$_4$), 4.33(*s*, 2H, CH$_2$), 1.33(*s*, 3H, CH$_3$).

Compound (4) was prepared using the same procedure as that for (2), except Na[C$_5$H$_4$C(O)CH$_2$CH$_2$COOMe] was used instead of Na(C$_5$H$_4$COOEt). CH$_2$Cl$_2$ as the eluant gave a dark red band, from which 0.341 g of (4) as dark red solid was obtained; 43.8% yield. Calcd.

for $C_{18}H_{11}O_{11}CoRuSW$ (%): C, 27.75; H, 1.42. Found: C, 27.76; H, 1.50. IR (KBr disk): $\nu(C \equiv O)$2086.1 vs, 2045.0 vs, 2022.2 vs, 1991.8 vs, 1960.5 s, 1909.0 s cm^{-1}, $\nu(C{=}O)$1726.4 s, 1681.0 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ5.97 – 5.59(*q*, 4H, C_5H_4), 3.89(*s*, 3H, CH_3), 3.00(*s*, 2H, CH_2), 2.75(*s*, 2H, CH_2).

Crystallography of (1)

A single crystal of dimensions 0.20 × 0.20 × 0.30 mm was obtained by slowly cooling a hexane/dichloromethane solution containing compound (**1**) to −18°C. The determination of unit cell parameters and the collection of intensity data were performed on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoKα ($\lambda = 0.71069$ Å) radiation at 23 ± 1°C. A total of 4476 reflections, of which 4378 were unique, were collected in the range $0 < \theta < 26°$ using the $\omega/2\theta$ scan technique. An *Lp* correction was applied to the data. The structure was solved by direct methods using 3686 independent reflections with $I > 2.0\sigma(I)$ followed by succeeding difference Fourier synthesis. All non-hydrogen and hydrogen atoms were found in the difference maps. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in final calculations but were not refined. Calculations were performed on a VAX-II computer using TEXSAN program system.

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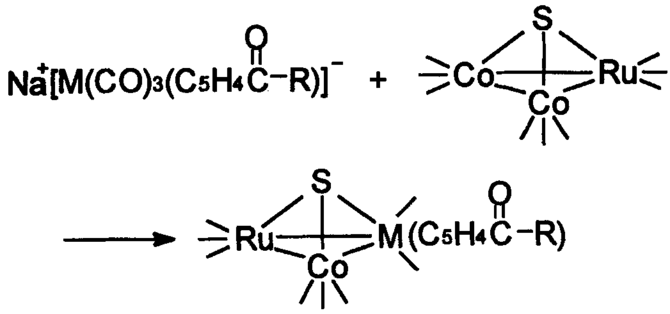
RESULTS AND DISCUSSION

The reactions described in this work are summarized in Scheme 1. The sodium salts of substituted cyclopentadienyl tricarbonylmolybdenum (tungsten), $\{M(CO)_3\ [C_5H_4C(O)R]\}^-$ (R = OEt or CH_2CH_2COOMe) (M = Mo or W) prepared from $M(CO)_6$ and the corresponding substituted sodium cyclopentadienyl, reacted *in situ* with (μ_3-S)$RuCo_2(CO)_9$ to give the expected compounds (**1**)–(**4**) in 43.8–26.8% yield. This could be regarded as a result of the displacement of $Co(CO)_3$ (d^9 ML_3) in (μ_3-S)$RuCo_2(CO)_9$ by isoloble metal fragments $M(CO)_2[C_5H_4C(O)R]$ (d^5 ML_5). Further consideration of the structures of (**1**)–(**4**) reveals that this general class of compounds becomes chiral around the SRuCoM core.

Clusters (**1**)–(**4**) are air-stable solids with deep colour; they are not stable in solvents such as THF and CH_2Cl_2. The clusters have been characterized by elemental analysis and spectroscopic techniques. IR spectra of clusters (**1**)–(**4**) showed several strong absorption bands in the region 2086–1846 cm^{-1}, characteristic of carbonyl ligands attached to transition metals.



1 M=Mo, R=OEt
2 M=W, R=OEt
3 M=Mo, $R=CH_2CH_2COOMe$
4 M=W, $R=CH_2CH_2COOMe$

SCHEME 1

The strong absorption band around 1730 cm^{-1} can be assigned to the ester carbonyl in each cluster. An additional band at 1691 cm^{-1} in (3) and 1681 cm^{-1} in (4) is characteristic of the ketonic carbonyl. ^{1}H spectra of all

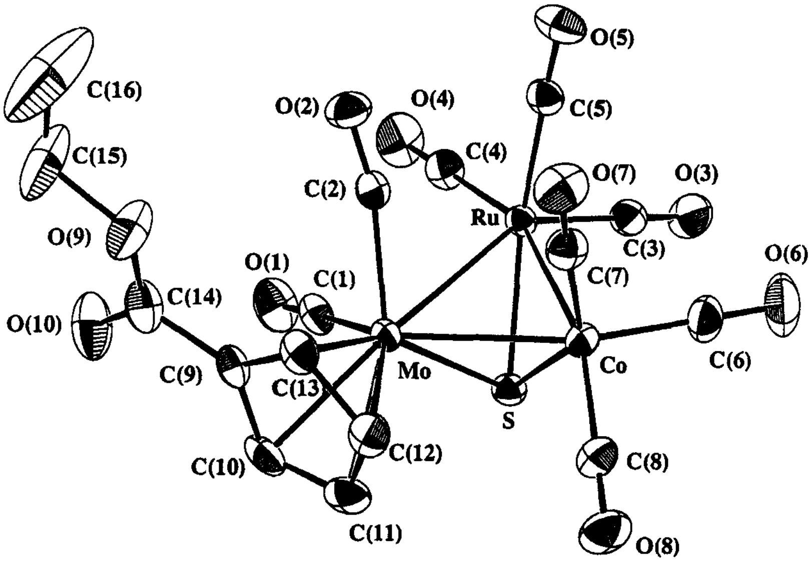


FIGURE 1 Molecular structure of compound (1). Hydrogen atoms have been omitted for clarity.

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these clusters exhibited a multiplet at $\delta 5.98 - 5.47$ for the four protons of the substituted cyclopentadienyl ligand. Because of the electron-withdrawing effect of the organic group attached to the cyclopentadienyl ring, the multiplet appeared downfield relative to that of unsubstituted cyclopentadienyl.

TABLE I Summary of crystal and intensity data for cluster (1)

Formula	$C_{16}H_9O_{10}CoMoRuS$
F.W.	649.24
Crystal System	Monoclinic
Space Group	$P2_1/n$
$F(000)$	1256
a(Å)	10.075(1)
b(Å)	9.034(2)
c(Å)	22.973(7)
β(°)	92.70(1)
V(Å^3)	2088.7(8)
Z	4
Dcalc (g cm^{-3})	2.064
μ(Mo-Kα) (cm^{-1})	22.07
Temperature (°C)	23
Scan type	$\omega/2\theta$
$2\theta_{max}$ (°)	51.9
No. observations	3686 ($I > 2.00\sigma(I)$)
No. Variables	271
R[a], Rw[b]	0.030, 0.042

[a] $R = (\Sigma||F_o| - F_c||)/\Sigma|F_o|$.
[b] $R = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega(F_o^2)]^{1/2}$.

TABLE II Selected bond lengths (Å) and angles (o) for cluster (1)

Ru—C(3)	1.896(4)	Mo—C(12)	2.380(4)	O(8)—C(8)	1.128(5)
Ru—C(4)	1.897(4)	Mo—Co	2.7440(6)	O(9)—C(14)	1.311(6)
Ru—C(5)	1.914(4)	Co—C(7)	1.771(5)	O(9)—C(15)	1.469(7)
Ru—S	2.324(1)	Co—C(6)	1.784(5)	O(10)—C(14)	1.197(6)
Ru—Co	2.6061(7)	Co—C(8)	1.806(4)	C(9)—C(13)	1.410(6)
Ru—Mo	2.8631(7)	Co—S	2.199(1)	C(9)—C(10)	1.440(6)
Mo—C(2)	1.978(4)	O(1)—C(1)	1.139(5)	C(9)—C(14)	1.476(6)
Mo—C(1)	1.994(4)	O(2)—C(2)	1.144(5)	C(10)—C(11)	1.388(7)
Mo—C(9)	2.280(4)	O(3)—C(3)	1.132(5)	C(11)—C(12)	1.414(7)
Mo—C(10)	2.293(4)	O(4)—C(4)	1.120(5)	C(12)—C(13)	1.409(6)
Mo—C(13)	2.331(4)	O(5)—C(5)	1.128(5)	C(15)—C(16)	1.37(2)
Mo—C(11)	2.346(4)	O(6)—C(6)	1.137(6)	Ru—C(2)	2.746(4)
Mo—S	2.380(1)	O(7)—C(7)	1.144(5)		
C(3)—Ru—S	95.6(1)	C(2)—Mo—S	117.8(1)	C(6)—Co—S	104.1(2)
C(3)—Ru—Co	99.8(1)	C(2)—Mo—Co	95.3(1)	C(6)—Co—Ru	90.1(1)
C(3)—Ru—Mo	148.7(1)	C(2)—Mo—Ru	66.2(1)	C(6)—Co—Mo	153.5(2)
C(4)—Ru—S	111.1(1)	S—Mo—Co	50.21(3)	C(8)—Co—S	102.6(1)
C(4)—Ru—Co	160.0(1)	S—Mo—Ru	51.64(3)	C(8)—Co—Ru	159.1(1)
C(4)—Ru—Mo	101.8(1)	Co—Mo—Ru	55.34(2)	C(8)—Co—Mo	101.1(1)
C(5)—Ru—S	151.1(1)	C(1)—Mo—S	83.6(1)	S—Co—Ru	57.11(3)
C(5)—Ru—Co	99.2(1)	C(1)—Mo—Co	128.5(1)	S—Co—Mo	56.27(3)
C(5)—Ru—Mo	110.3(1)	C(1)—Mo—Ru	79.5(1)	Ru—Co—Mo	64.65(2)
S—Ru—Co	52.59(3)	C(7)—Co—S	139.0(1)	Co—S—Ru	70.30(3)
S—Ru—Mo	53.39(3)	C(7)—Co—Ru	92.6(1)	Ru—S—Mo	74.97(3)
Co—Ru—Mo	60.01(2)	C(7)—Co—Mo	87.1(1)	Co—S—Mo	73.52(4)

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For (1) and (2), signals at δ4.34–4.29 and 1.33 correspond to the protons on CH_2 and CH_3 units in the ethyl ester group, respectively. For clusters (3) and (4), the singlet at δ3.69 in (3) and 3.89 in (4) is assigned to the methyl protons, and signals at δ3.02–2.72 are assigned to the protons on the two CH_2 units between the ketonic and ester groups.

The molecular structure of cluster (1) was determined by X-ray crystallography. Results show that one of the $Co(CO)_3$ units in the cluster $(\mu_3\text{-}S)RuCo_2(CO)_9$ may be exchanged by the $Mo(CO)_2(C_5H_4COOEt)$ group to give the new chiral skeleton cluster shown in Figure 1. Thus an ester group has been attached to the cluster.

Crystal data for cluster (1) are collected in Table I. Table II gives selected bond lengths and angles and final atomic coordinates are listed in Table III. As seen in Figure 1, this cluster contains a chiral tetrahedron-type framework, composed of four different atoms (Ru, Co, Mo and S), which deviates somewhat from perfect tetrahedral geometry. The acute angles in the tetrahedron about the basal metal atoms range from 50.21(3) to

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TABLE III Final atomic coordinates and equivalent thermal parameters (Å^2) for the heavy atoms in (1)

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Ru	0.24987(3)	−0.05295(3)	0.145358(12)	2.74(1)
Mo	0.35513(3)	0.19301(3)	0.083852(13)	2.56(1)
Co	0.08969(5)	0.12876(6)	0.08875(2)	3.03(2)
S	0.23246(10)	−0.01276(11)	0.04535(4)	3.16(4)
O(1)	0.5976(3)	−0.0236(4)	0.08112(17)	5.8(2)
O(2)	0.4256(3)	0.2293 (4)	0.21604(12)	4.6(1)
O(3)	0.0802(4)	−0.3296(4)	0.14309(16)	6.2(2)
O(4)	0.4997(4)	−0.2222(4)	0.17943(19)	6.6(2)
O(5)	0.1904(4)	0.0402(4)	0.26864(13)	5.3(2)
O(6)	−0.1320(4)	−0.0702(5)	0.1091(2)	7.9(2)
O(7)	0.0796(4)	0.3325(4)	0.18677(16)	5.9(2)
O(8)	−0.0202(4)	0.3112(4)	−0.00760(15)	5.9(2)
O(9)	0.6350(3)	0.4581(4)	0.14711(19)	6.5(2)
O(10)	0.7323(4)	0.3215(5)	0.0801(2)	7.5(2)
C(1)	0.5081(4)	0.0531(5)	0.08286(19)	3.8(2)
C(2)	0.3891(4)	0.2030(4)	0.16928(17)	3.1(2)
C(3)	0.1425(4)	−0.2253(5)	0.14417(18)	4.0(2)
C(4)	0.4062(4)	−0.1606(5)	0.1668(2)	4.0(2)
C(5)	0.2141(4)	0.0032(4)	0.22339(17)	3.5(2)
C(6)	−0.0468(4)	0.0087(6)	0.1010(2)	4.7(2)
C(7)	0.0867(4)	0.2528(5)	0.1483(2)	4.1(2)
C(8)	0.0208(4)	0.2402(5)	0.02946(19)	4.1(2)
C(9)	0.5042(4)	0.3775(4)	0.06898(18)	3.6(2)
C(10)	0.4746(5)	0.3060(5)	0.01387(19)	4.3(2)
C(11)	0.3424(5)	0.3346(5)	−0.0019(2)	4.6(2)
C(12)	0.2884(5)	0.4236(5)	0.0418(2)	4.3(2)
C(13)	0.3876(4)	0.4484(4)	0.0860(2)	3.7(2)
C(14)	0.6370(5)	0.3808(5)	0.0989(2)	4.9(2)
C(15)	0.7610(7)	0.4635(11)	0.1819(4)	10.3(5)
C(16)	0.7391(12)	0.5251(16)	0.2350(6)	18(1)

64.65(2)° and that of the sulfido atom averages 72.93(3)°. Three terminal carbonyl ligands are bonded to Ru and Co atoms respectively, while the Mo atom is coordinated to two carbonyl ligands and a substituted cyclopentadienyl ligand. Because of the different sizes of the four metals, the distances from the sulfido atom to the three metals are different [Ru-S = 2.324(1), Co-S = 2.199(1), Mo-S = 2.380(1) Å].

The torsion angle C(13)—C(9)—C(14)—O(9) is 2.0(6)°, and the bond length C(9)—C(14) is 1.476 Å, shorter than a normal C—C bond (1.54 Å). All atoms in the cyclopentadienyl ligand together with C(14), O(10) and O(9) in the EtOOC group are located in a plane, and the π system of the EtOOC substituent is fully conjugated with the cyclopentadienyl π system. Finally, it is worth noting that the carbonyl C(2)—O(2) bound to Mo is semibridging, because the asymmetry parameter α(0.39) is well within the range for semibridging carbonyls [11].

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Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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[11] An asymmetric parameter is defined as $\alpha = (d_2 - d_1)/d_1$ where d_2 is the long M···C distance and d_1 is the short M—C distance. If $0.1 \le \alpha \le 0.6$, a semibridging carbonyl is designated according to Curtis' suggestion; M. D. Curtis, K. R. Han and W. M. Butler, *Inorg. Chem.* **19**, 2096 (1980).