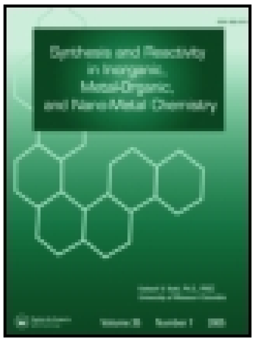

Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

ISSN: 0094-5714 (Print) 1532-2440 (Online) Journal homepage: http://www.tandfonline.com/loi/lsrt19

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To cite this article: Jie Zhang , Er-Run Ding , Xue-Nian Chen , Yu-Hua Zhang , Cui-Ping Song , Yuan-Qi Yin & Jie Sun (1999) Synthesis and Reaction of New Metal Cluster Complexes Containing a Wrucose Core, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 29:8, 1315-1329, DOI: 10.1080/00945719909351701

To link to this article: http://dx.doi.org/10.1080/00945719909351701

SYNTH. REACT. INORG. MET.-ORG. CHEM., 29(8), 1315-1329 (1999)

SYNTHESIS AND REACTION OF NEW METAL CLUSTER COMPLEXES CONTAINING A WRuCoSe CORE

Jie Zhang[a], Er-Run Ding[a], Xue-Nian Chen[a], Yu-Hua Zhang[a],
Cui-Ping Song[a], Yuan-Qi Yin[a]* and Jie Sun[b]

[a]State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou
Institute of Chemical Physics, Chinese Academy of Sciences,
Lanzhou 730000, China
[b]Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
Shanghai 200032, China

ABSTRACT

Several chiral cluster derivatives, $RuCoW(\mu_3\text{-}Se)(CO)_8\{\eta^5\text{-}C_5H_4C(O)R\}$ [R = H (**2**), CH_3 (**3**), C_6H_5 (**4**), $C_6H_4C(O)OCH_3$ (**5**)], were synthesized by reaction of the precursor $(\mu_3\text{-}Se)RuCo_2(CO)_9$ (**1**) with the functionally substituted cyclopentadienyl tricarbonyl metal complex anions $[W(CO)_3\{\eta^5\text{-}C_5H_4C(O)R\}]^-$ without using benzophenone ketyl. A new double-tetrahedral cluster compound, *p*-$[(\mu_3\text{-}Se)(CO)_8RuCoW(\eta^5\text{-}C_5H_4C(O))]_2C_6H_4$ (**6**), was obtained by treating (**1**) with a metal exchange reagent, $Na_2[W(CO)_3(\eta^5\text{-}C_5H_4)C(O)C_6H_4C(O)(\eta^5\text{-}C_5H_4)\}(CO)_3W]$. Cluster (**3**) reacted with $NaBH_4$ in

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MeOH to give the secondary alcohol cluster RuCoW(μ_3-Se)(CO)$_8${η^5-C$_5$H$_4$CH(OH)CH$_3$} (7). The cluster (3) reacted with Na$_2$Fe(CO)$_4$ in refluxing THF followed by the treatment of 40% H$_3$PO$_4$ to yield the new cluster HRuFeW(μ_3-Se)(CO)$_8${η^5-C$_5$H$_4$C(O)CH$_3$} (8). The structure of cluster (3) has been determined by single-crystal X-ray diffraction. Crystal data for cluster (3) give an orthorhombic space group *P*bca, $a = 26.326(4)$ Å, $b = 18.231(4)$ Å, $c = 15.956(3)$ Å, $V = 7658(4)$ Å^3, $Z = 16$, $R = 0.029$ and $R_W = 0.036$.

INTRODUCTION

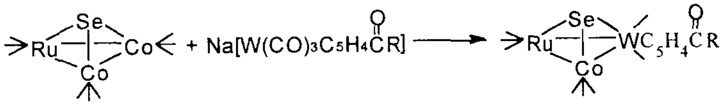
It is now well established that bridging ligands can play an important role in both the stabilization and the formation of metal cluster complexes[1-4]. Selenium-containing transitionmetal carbonyl clusters have attracted great attention due to their interesting bonding modes and versatile structural features[5,6]. Recently, a number of anionic selenium-iron carbonyl clusters have been structurally characterized. Examples[7-9] include [SeFe$_3$(CO)$_9$]$^{2-}$, [Se$_2$Fe$_5$(CO)$_{14}$]$^{2-}$ and [{Fe$_2$Se(CO)$_6$}$_2$(Se$_2$)]$^{2-}$. However, surprisingly few neutral selenium-ruthenium-tungsten carbonyl clusters have been structurally characterized.

The useful mixed selenium-ruthenium-cobalt complexes for cluster building reactions is SeRuCo$_2$(CO)$_9$ that was first reported in 1983 by Vahrenkamp and co-workers[10]. Here, we wish to report the preparation and characterization of the mixed cluster compounds containing a SeRuCoW core from the cluster SeRuCo$_2$(CO)$_9$ (1).

RESULTS AND DISCUSSION

Clusters (2)–(5)

The compounds [W(CO)$_3${η^5-C$_5$H$_4$CR}]$^-$ [R = H, Me] have proved to be important in the synthesis of organometallic and metal cluster complexes containing the structure unit [W(CO)$_2${η^5-C$_5$H$_4$R}][11]. Now we have found an additional use of the monoanions in the synthesis of tetrahedral RuCoWSe cluster complexes. The reaction of cluster (**1**) with $[W(CO)_3\{\eta^5\text{-}C_5H_4C(O)R\}]^-$ [R = H, CH_3, C_6H_5, $C_6H_4C(O)OCH_3$] in refluxing THF afforded a moderate yield of $RuCoW(\mu_3\text{-}Se)(CO)_8\{\eta^5\text{-}C_5H_4C(O)R\}$ [R = H (**2**), CH_3 (**3**), C_6H_5 (**4**), $C_6H_4C(O)OCH_3$ (**5**)] as shown in eq. (1). These air-stable clusters are black in the solid state and red-purple in solution. The data of C/H analyses, IR spectra, ^1H NMR spectra and MS spectra of these compounds are consistent with the expected structure presented in FIG. 1. The results show that one of the $Co(CO)_3$ units in cluster (**1**) can be exchanged by an isoelectronic $W(CO)_2\{\eta^5\text{-}C_5H_4C(O)R\}$ unit to give the new chiral skeleton clusters (**2**)–(**5**).



(1)

R = H (**2**), CH_3 (**3**), C_6H_5 (**4**), $C_6H_4C(O)OCH_3$ (**5**)

Performance of Cluster (3)

Cluster (**3**) can be reduced with $NaBH_4$ in methanol at room temperature to give the secondary alcohol cluster $RuCoW(\mu_3\text{-}Se)(CO)_8\{\eta^5\text{-}C_5H_4CH(OH)CH_3\}$ (**7**) in high yield. We attempted to reduce cluster (**3**) with $LiAlH_4/AlCl_3$ in CH_2Cl_2 but failed because of it being decomposed by this stronger reduction agent. The reaction of cluster (**3**) with $Na_2[Fe(CO)_4]$ in refluxing THF, followed by acidic treatment of the reaction mixture using deoxygenated 40% H_3PO_4, gave the new air-sensitive cluster $HRuFeW(\mu_3\text{-}Se)(CO)_8\{\eta^5\text{-}C_5H_4C(O)CH_3\}$ (**8**) in low yield. Cluster (**8**) was confirmed by MS (FAB) spectra, C/H analyses, IR spectra and ^1H NMR spectra. The results show that the metal fragment $Co(CO)_3$ in cluster (**3**) could be exchanged by $HFe(CO)_3$ by a thermal method. The H atom in cluster (**8**) may be bonded to the RuFeCo triangular metal base as a face bridging position as described previously[12].

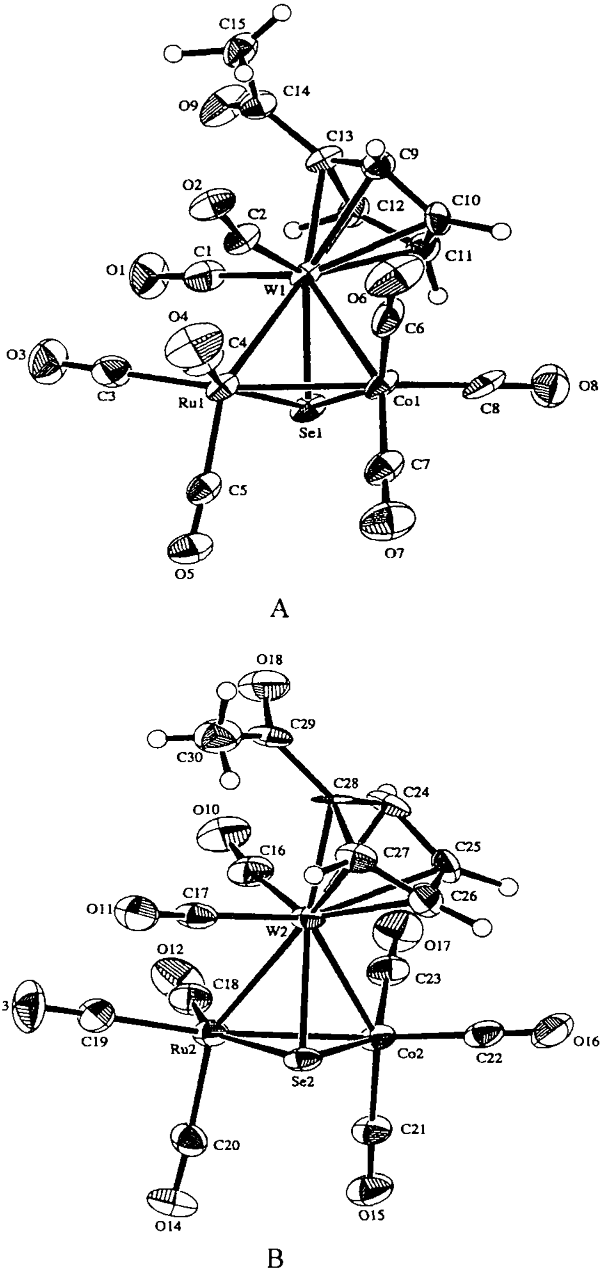
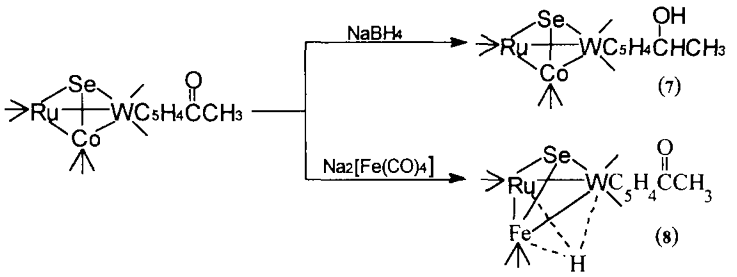


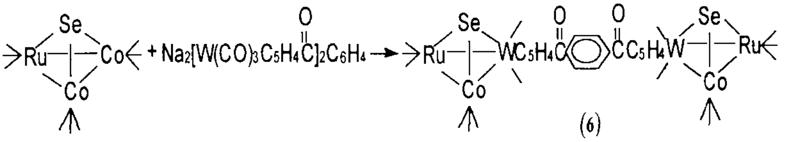
FIG. 1 Perspective View of the Molecular Unit of Cluster (**3**)
(A and B are the two Isomeric Molecules in an Unit Cell)



(2)

Cluster (6)

The reaction of two molecules of cluster (**1**) with $[W(CO)_3(\eta^5\text{-}C_5H_4)C(O)\text{-}C_6H_4C(O)(\eta^5\text{-}C_5H_4)(CO)_3W]^{2-}$ in refluxing THF gave the new double-tetrahedral cluster compound $(\mu_3\text{-Se})(CO)_8RuCoW(\eta^5\text{-}C_5H_4)C(O)C_6H_4C(O)(\eta^5\text{-}C_5H_4)RuCo\text{-}W(CO)_8(\mu_3\text{-Se})$ (**6**). The formula was confirmed by elemental analysis and FAB MS spectra. Cluster (**6**) is believed to be isostructural with the cluster *p*-$[RuCoW(\mu_3\text{-S})(CO)_8(\eta^5\text{-}C_5H_4)C(O)]_2C_6H_4$ based on their similar ^{1}H NMR and IR spectral patterns and the structure of the latter has been determined by X-ray diffraction[14]. Cluster (**6**) is made of two identical tetrahedral subclusters RuCoWSe, which are connected by a $\{\eta^5\text{-}C_5H_4C(O)C_6H_4C(O)C_5H_4\text{-}\eta^5\}$ bridge ligand through W atoms. No cluster complex containing two of the subcluster cores RuCoWSe have been reported, though a few such single cluster complexes have appeared in the literature[10].



(3)

Characterization

The IR spectra of all clusters exhibit strong absorption bands between 2085 and 1847 cm^{-1} which are assigned to ν(C≡O) in terminal carbonyl ligands. The IR spectra of clusters (**2**)–(**5**) and cluster (**8**) also show corresponding ν(C=O) absorption bands in the range 1658–1687 cm^{-1} and the hydroxyl group in cluster

(7) is seen at about 3381 cm^{-1}. For the ^1H NMR assignments of the clusters, the proton chemical shifts of substituted cyclopentadienyl groups appear at a more downfield position than those of the unsubstituted one[13], since formyl, acetyl and ester carbonyls are well known electron-withdrawing groups. The proton bonded to the metal atoms in cluster (**8**) appears at -17.84 ppm. The FAB MS spectra of clusters (**2**), (**3**) and (**5**) exhibit the loss of carbonyls from the molecular ions.

Structure of Cluster (3)

The structure of cluster (**3**) was determined by X-ray structure analysis. Crystal data are collected in TABLE I. TABLES II and III give selected bond lengths and angles and non-hydrogen atomic coordinates, isotropic thermalparameters for cluster (**3**) are listed in TABLE IV. The structure of cluster (**3**) is revealed by the presence of two isomeric molecules (A and B) in an unit cell (see FIG. 1) and the tetrahedral core of each molecule in cluster (**3**) is composed of four different atoms (Ru, Co, W and Se). Both the Ru and the Co atoms bear three terminal carbonyl ligands and the W atom is coordinated by two terminal carbonyl ligands and one substituted cyclopentadienyl ligand. The slightly distorted triangular RuCoW [Ru-Co = 2.647 Å, Co-W = 2.764 Å, Ru-W =2.881 Å] is capped by a selenium atom ligand and the RuCoWSe core deviates a bit from a perfect tetrahedral geometry. The distance of the W atom to the Cp ring center (1.993 Å) is very similar to that of W-Cp (1.990 Å) in the known cluster $FeCoMoS(CO)_8C_5H_4C(O)C_6H_4C(O)OCH_3$[15]. Cluster (**3**) is isostructural and isoelectronic with the known cluster $SRuCoMoC_5H_4C(O)C_6H_4C(O)OCH_3$[16].

EXPERIMENTAL

All reactions were carried out under an atmosphere of pure nitrogen by using standard Schlenk techniques. All solvents were thoroughly dried and distilled immediately before use. IR spectra were recorded on a Nicolet FT-IR

TABLE I. X-Ray Crystallographic Data and Processing Parameters for Cluster (**3**)

Formula	$C_{15}H_7O_9RuCoWSe$
Mr	754.03
System	Orthorhombic
space group	*P*bca
F(000)	5568.00
a (Å)	26.326(4)
b (Å)	18.231(4)
c (Å)	15.956(3)
V (Å^3)	7658(4)
Z	16
D_c (g/cm^3)	2.616
μ(MoK_α) (cm^{-1})	95.83
Crystal dimensions (mm^3)	0.20×0.20×0.30
Temperature (℃)	20.0
Scan type	ω-2θ
$2\theta_{max}$ (deg)	45
No. of Reflections Measured	Total 4890
No. Observations [I>3.00σ(I)]	3492
No. Variables	505
Reflection/Parameter Ratio	6.91
R^a, $R_w{}^b$	0.029, 0.036

$^a R = \Sigma \| Fo | - | Fc \| / \Sigma | Fo |$ $^b R_w = [\Sigma\omega(| Fo | - | Fc |)^2/\Sigma\omega Fo^2]^{1/2}$

TABLE II. Selected Bond Lengths (Å) of Cluster (**3**)

		Molecular A	
W(1)-Ru(1)	2.881(1)	W(1)-Se(1)	2.503(1)
W(1)-Co(1)	2.764(1)	W(1)-C(Cp, ave)	2.34
Ru(1)-Se(1)	2.453(2)	Ru(1)-Co(1)	2.647(2)
Se(1)- Co(1)	2.320(2)	C-O(t-co, ave)	1.13
C(13)-C(14)	1.49(1)	C(14)-C(15)	1.50(1)
		Molecular B	
W(2)-Ru(2)	2.889(1)	W(2)-Se(2)	2.496(1)
W(2)-Co(2)	2.772(1)	W(2)-C(Cp, ave)	2.32
Ru(2)-Se(2)	2.443(2)	Ru(2)-Co(2)	2.646(2)
C-O(t-co, ave)	1.13	C(28)-C(29)	1.48(2)
C(29)-C(30)	1.49(2)		

TABLE III. Selected Bond Angles (°) of Cluster (**3**)

		Molecular A	
Ru(1)-W(1)-Se(1)	53.64(3)	Ru(1)-W(1)-Co(1)	55.89(5)
Se(1)-W(1)-Co(1)	51.99(4)	W(1)-Ru(1)-Se(1)	55.27(3)
W(1)-Ru(1)-Co(1)	59.81(4)	Se(1)-Ru(1)-Co(1)	53.97(4)
W(1)-Se(1)-Ru(1)	71.09(4)	W(1)-Se(1)-Co(1)	69.80(5)
Ru(1)-Se(1)-Co(1)	67.30(5)	W(1)-Co(1)-Ru(1)	64.30(4)
W(1)-Co(1)-Se(1)	58.21(4)	Ru(10-Co(1)-Se(1)	58.74(5)
W(1)-C-O(ave)	169.5	Ru-C-O(ave)	177
Co-C-O(ave)	176.7		
		Molecular B	
Ru(2)-W(2)-Se(2)	53.36(3)	Ru(2)-W(2)-Co(2)	55.68(4)
Se(2)-W(2)-Co(2)	51.94(4)	W(2)-Ru(2)-Se(2)	55.05(3)
W(2)-Ru(2)-Co(2)	59.91(4)	Se(2)-Ru(2)-Co(2)	54.06(5)
W(2)-Se(2)-Ru(2)	71.59(4)	W(2)-Se(2)-Co(2)	70.17(5)
Ru(2)-Se(2)-Co(2)	67.43(5)	W(2)-Co(2)-Se(2)	57.90(4)
W(2)-Co(2)-Ru(2)	64.41(4)	Ru(2)-Co(2)-Se(2)	58.52(5)
W-C-O(ave)	172.5	Ru-C-O(ave)	177.7
Co-C-O(ave)	177.7		

10DX spectrophotometer. ^{1}H NMR spectra were recorded on a Brucker AM-300 MHz spectrometer. Elemental analyses and FAB MS spectra were performed on a Carlo Erba 1106-type analyzer and a Finnigan MAT 8430 spectrometer, respectively. $W(CO)_6$ was bought from Aldrich Chem. Co. $Co_2(CO)_8$[17], $Ru_3(CO)_{12}$[18], $(\mu_3\text{-}Se)RuCo_2(CO)_9$[19], $RC(O)C_5H_4Na$ [R = H, CH_3, C_6H_5, $C_6H_4C(O)OCH_3$][20] and $Na_2[W(CO)_3(\eta^5\text{-}C_5H_4)C(O)C_6H_4C(O)(\eta^5\text{-}C_5H_4)(CO)_3W]$[21] were prepared according to the literature.

Preparation of Clusters (2)–(5)

$W(CO)_6$ (352 mg, 1.0 mmol) was added to a solution of sodium formylcyclopentadienide (116 mg, 1.0 mmol) in diglyme (20 mL). The mixture was refluxed for 4 h with stirring. After the solvent was evaporated under reduced pressure, THF (20 mL) and cluster (**1**) $[(\mu_3\text{-}Se)RuCo_2(CO)_9]$ (550 mg, 1.0

TABLE IV Atomic Coordinates and Biso/Beq for Cluster (**3**)

Atom	x	y	z	B_{eq}
W(1)	0.77170(2)	0.12261(3)	0.73976(3)	2.39(1)
W(2)	0.50415(2)	0.08663(3)	0.24682(3)	2.52(1)
Ru(1)	0.77491(3)	-0.02776(6)	0.79507(5)	2.84(2)
Ru(2)	0.50977(3)	0.19752(6)	0.37583(5)	2.77(2)
Se(1)	0.84817(4)	0.05533(7)	0.79246(7)	2.89(3)
Se(2)	0.54429(4)	0.07356(7)	0.38773(6)	2.72(3)
Co(1)	0.79294(5)	0.07998(9)	0.90224(9)	2.94(4)
Co(2)	0.45659(5)	0.07644(9)	0.40133(9)	2.75(3)
O(1)	0.8023(4)	0.0529(5)	0.5663(5)	5.8(3)
O(2)	0.6638(3)	0.0548(5)	0.7278(5)	4.3(2)
O(3)	0.7671(4)	-0.1082(6)	0.6302(6)	6.7(3)
O(4)	0.6721(3)	-0.0779(6)	0.8628(6)	6.5(3)
O(5)	0.8358(3)	-0.1512(5)	0.8725(5)	4.4(2)
O(6)	0.6859(3)	0.1108(7)	0.9336(6)	6.8(3)
O(7)	0.8185(4)	-0.0248(6)	1.0324(6)	6.6(3)
O(8)	0.8447(4)	0.2088(6)	0.9717(6)	6.0(3)
O(9)	0.7441(3)	0.2081(6)	0.5135(5)	5.2(2)
O(10)	0.4421(3)	0.2206(6)	0.1840(5)	5.5(3)
O(11)	0.6063(3)	0.1639(6)	0.1986(5)	5.3(3)
O(12)	0.4236(3)	0.3065(5)	0.3546(6)	5.7(3)
O(13)	0.5896(4)	0.3025(5)	0.3125(6)	6.3(3)
O(14)	0.5329(3)	0.2399(5)	0.5558(5)	4.9(2)
O(15)	0.4443(3)	0.1183(5)	0.5774(5)	4.6(2)
O(16)	0.4340(3)	-0.0809(6)	0.4013(5)	4.7(2)
O(17)	0.3642(3)	0.1295(5)	0.3230(0)	5.3(3)
O(18)	0.4892(4)	0.1121(6)	-0.0046(5)	5.6(3)
C(1)	0.7904(5)	0.0752(7)	0.6300(8)	4.2(3)
C(2)	0.7057(5)	0.0701(7)	0.7352(6)	3.0(3)

(continued)

TABLE IV (continued)

Atom	x	y	Z	B_{eq}
C(3)	0.7694(5)	-0.0796(7)	0.6911(8)	3.9(3)
C(4)	0.7097(5)	-0.0597(7)	0.8357(7)	4.0(3)
C(5)	0.8127(5)	-0.1053(7)	0.8466(7)	3.4(3)
C(6)	0.7283(5)	0.0992(8)	0.9185(7)	4.5(4)
C(7)	0.8086(5)	0.0154(8)	0.9808(7)	4.0(3)
C(8)	0.8251(4)	0.1601(9)	0.9427(7)	4.1(3)
C(9)	0.7222(4)	0.2291(6)	0.7415(7)	3.3(3)
C(10)	0.7613(4)	0.2415(6)	0.8004(7)	3.2(3)
C(11)	0.8094(4)	0.2399(6)	0.7564(7)	3.6(3)
C(12)	0.7982(4)	0.2269(6)	0.6702(6)	3.0(3)
C(13)	0.7445(4)	0.2191(7)	0.6590(6)	2.8(3)
C(14)	0.7187(4)	0.2108(7)	0.5763(7)	3.2(3)
C(15)	0.6617(4)	0.2099(7)	0.5755(7)	4.3(3)
C(16)	0.4671(5)	0.1745(8)	0.2131(7)	4.0(3)
C(17)	0.5692(4)	0.1391(7)	0.2168(7)	3.5(3)
C(18)	0.4555(5)	0.2655(7)	0.3619(7)	3.8(3)
C(19)	0.5602(4)	0.2639(7)	0.3351(7)	3.7(3)
C(20)	0.5227(4)	0.2234(7)	0.4893(8)	3.6(3)
C(21)	0.4488(4)	0.1032(7)	0.5087(7)	3.4(3)
C(22)	0.4427(4)	-0.0197(9)	0.4019(7)	3.5(3)
C(23)	0.4006(5)	0.1100(7)	0.3517(4)	3.6(3)
C(24)	0.4551(4)	0.0326(7)	0.1409(7)	3.6(3)
C(25)	0.4560(5)	-0.0181(7)	0.2084(8)	4.1(3)
C(26)	0.5062(5)	-0.0399(7)	0.2237(8)	3.7(3)
C(27)	0.5373(4)	-0.0053(7)	0.1641(7)	3.3(3)
C(28)	0.5063(4)	0.0408(7)	0.1133(6)	2.8(3)
C(29)	0.5213(5)	0.0825(7)	0.0375(7)	3.7(3)
C(30)	0.5761(5)	0.0838(9)	0.0137(8)	5.3(4)

mmol) were added and the mixture was stirred at 60° C for another 2 h. After the solvent was removed in *vacuo*, the residue was extracted by a minimum amount of CH_2Cl_2 and the products were chromatographed on a 2.5 × 20 cm silica gel column using CH_2Cl_2/hexane (2:3) as an eluent. The main product (**2**) (300 mg, 41 %) was obtained as a black solid (m.p. 100–101° C). *Anal.* Calcd. for $C_{14}H_5O_9RuCoWSe$ (740.00): C, 22.72; H, 0.68 %. Found: C, 22.88; H, 0.74 %. IR (KBr disk): 2085 vs, 2037 vs, 2022 vs, 1976 vs, 1970 vs, 1946 vs, 1908 vs, 1867 s, 1687 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.53–5.91 ppm (m, 4H, C_5H_4), δ 9.72 ppm (s, 1H, CHO). MS (FAB): 740 (M^+), 684 (M^+-2CO), 656 (M^+-3CO).

The method of the preparation of clusters (**3**), (**4**) and (**5**) was similar to that of the preparation of cluster (**2**).

Cluster (**3**). (342 mg, 43 %), m.p. 123–124° C. *Anal.* Calcd. for $C_{15}O_9H_7RuCoWSe$ (754.03): C, 23.89; H, 0.94 %. Found: C, 24.01; H, 1.02 %. IR (KBr disk): 2077 vs, 2044 vs, 2036 vs, 2012 vs, 1984 vs, 1974 vs, 1892 m, 1857 s, 1687 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.41 ppm (s, 3H, CH_3), δ 5.51–5.87 ppm (m, 4H, C_5H_4). MS (FAB): 755 (M^+), 707 (M^+-CO), 699 (M^+-2CO), 671 (M^+-3CO).

Cluster (**4**). (302 mg, 36 %), *Anal.* Calcd. for $C_{20}H_9O_9RuCoWSe$ (816.10): C, 29.44; H, 1.11 %. Found: C, 29.68; H, 1.24 %. IR (KBr disk): 2083 vs, 2049 vs, 1977 vs, 1888 s, 1658 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.56–6.04 ppm (m, 4H, C_5H_4), δ 7.48–7.83 ppm (m, 5H, C_6H_5).

Cluster (**5**). (350 mg, 40 %), *Anal.* Calcd. for $C_{22}H_{11}O_{12}RuCoWSe$ (890.14): C, 29.69; H, 1.25 %. Found: C, 30.06; H, 1.19 %. IR (KBr disk): 2079 vs, 2038 vs, 1994 vs, 1915 m, 1726 m, 1661 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.96 ppm (s, 3H, CH_3), δ 5.60–5.96 ppm (m, 4H, C_5H_4), δ 7.82–8.18 ppm (m, 4H, C_6H_4). MS (FAB): 891 (M^+), 863 (M^+-CO), 835 (M^+-2CO), 807 (M^+-3CO).

Preparation of Cluster (6)

A mixture of $W(CO)_6$ (264 mg, 1.0 mmol) and $[NaC_5H_4C(O)]_2C_6H_4$ (153 mg, 0.5 mmol) was dissolved in diglyme (20 mL). The method was similar to that of the preparation of cluster (**2**) and the black solid cluster (**6**) (264 mg, 34 %) was obtained. *Anal.* Calcd. for $C_{34}H_{12}O_{18}Ru_2Co_2W_2Se_2$ (1554.08): C, 26.28; H, 0.78 %. Found: C, 26.38; H, 0.89 %. IR (KBr disk): 2081 vs, 2037 vs, 2002 vs, 1872 m, 1658 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.30–5.94 ppm (m, 8H, $2C_5H_4$), δ 7.88 ppm (s, br, 4H, C_6H_4). MS (FAB): 1554 (M^+), 1498 (M^+-2CO), 1470 (M^+-3CO).

Reactions of Cluster (3)

$NaBH_4$ (7.6 mg, 0.2 mmol) was added to a solution of cluster (**3**) (75 mg, 0.1 mmol) in MeOH (8 mL). The mixture was stirred at room temperature for 9 h, and then separated on a silica gel column. Cluster (**7**) (50 mg, 85 %) was obtained as brown-red solid. *Anal.* Calcd. for $C_{15}H_9O_9$RuCoWSe (756.04): C, 23.83; H, 1.20 %. Found: C, 23.78; H, 1.14 %. IR (KBr disk): 3381 m, 2081 vs, 2079 vs, 1993 vs, 1770 vs, 1894 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.48 ppm (s, br, 3H, CH_3), δ 2.16 ppm (s, 1H, OH), δ 4.61 ppm (s, br, 1H, CH), δ 5.24–5.52 ppm (m, 4H, C_5H_4). MS (FAB): 728 (M^+-CO), 700 (M^+-2CO), 672 (M^+-3CO).

$Na_2[Fe(CO)_4]$ (31.25 mg, 0.15 mmol) and cluster (**3**) (75.6 mg, 0.1 mmol) were dissolved in THF (20 mL). The mixture was refluxed for 6 h and cooled to room temperature. The solvent was removed in *vacuo* and the resulting residue was acidified with deoxygenated 40% H_3PO_4 (12 mL) for 10 min. The mixture was then extracted with CH_2Cl_2. The organic layer was concentrated in *vacuo* and then chromatographed on a 2.5×20 cm silica gel column using CH_2Cl_2/hexane (1:1) as an eluent. The main product was cluster (**8**) (black solid, 17 mg, 25 %) and a trace of $Fe_3(CO)_{12}$ was also obtained. *Anal.* Calcd. for $C_{15}H_8O_9$RuFeWSe (751.95): C, 23.96; H, 1.07 %. Found: C, 23.96; H, 1.07 %. IR (KBr disk): 2081 vs, 2068 vs, 2019 vs, 1999 vs, 1984 vs, 1847 vs, 1683 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.33 ppm (s, 3H, CH_3), δ 5.22–5.96 ppm (m, 4H, C_5H_4), δ -17.84 ppm (s, 1H, H-M). MS (FAB): 753 (M^+), 725 (M^+-CO), 669 (M^+-3CO).

Crystallography

Crystals of cluster (**3**), suitable for a diffraction analysis, were grown from hexane/CH_2Cl_2 (1:1) at -18° C. The crystals were mounted on a glass fibre. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K_α (λ = 0.71069 Å) radiation. A summary of selected crystallographic data for cluster (**3**) is given in TABLE I. All data were collected at the temperature of 20 ± 1° C using the ω-2θ scan techniques. The structure was solved by a direct method[22] and expanded using the Fourier technique[23]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3492 observed reflections [$I > 3.00\sigma(I)$] and 505 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber[24]. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation.

ACKNOWLEDGMENT

We are grateful for financial support of this work by the National Natural Foundation of China and the Foundation of Chinese Academy of Sciences.

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Received: 21 October 1998
Accepted: 15 March 1999

Referee I: M. Mikuriya
Referee II: K. Sakata