ELSEVIER

Journal of Organometallic Chemistry 568 (1998) 157–163

Journal of Organo metallic Chemistry

Study on the reactivity of $RuCo_2(\mu_3{-}S)(CO)_9$: synthesis and characterization of the cluster complexes containing the tetrahedral core MRuCoS (M=Mo, W) and the two tetrahedral core MRuCoS clusters

Er-Run Ding, Shu-Lin Wu, Chun-Gu Xia, Yuan-Qi Yin *

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, People's Republic of China

Received 1 April 1998

Abstract

New clusters $MRuCo(CO)_8(\mu_3\text{-}S)[\eta^5\text{-}C_5H_4C(O)CH_3]$ (M=Mo **2**, W **3**) and $[MRuCo(CO)_8(\mu_3\text{-}S)]_2[\eta^5\text{-}C_5H_4C(O)C_6H_4C(O)C_5H_4\text{-}\eta^5]$[M=Mo **4**, W **5**] have been isolated from the reaction of $RuCo_2(\mu_3\text{-}S)(CO)_9$ **1** with $[\eta^5\text{-}C_5H_4C(O)CH_3(CO)_3M]^-$ (M=Mo, W) and $^-[M(CO)_3\{\eta^5\text{-}C_5H_4C(O)C_6H_4C(O)C_5H_4\text{-}\eta^5\}(CO)_3M]^-$ [M=Mo, W], respectively. Clusters **2** and **5** have been established by single crystal X-ray diffraction methods. The crystals of cluster **2** are orthorhombic with space group *Pbca*, $a = 26.229(7)$, $b = 18.200(3)$, $c = 15.929(4)$ Å, $V = 7604(6)$ Å^3 and $Z = 18$; final $R = 0.033$, $R_w = 0.045$. The crystals of cluster **5** are triclinic space group $P\bar{1}$, $a = 12.688(4)$, $b = 20.290(7)$, $c = 9.429(3)$ Å, $\alpha = 99.78(3)$, $\beta = 90.64(2)$, $\gamma = 78.28(3)°$, $V = 2341(1)$ Å^3 and $Z = 4$; final $R = 0.042$, $R_w = 0.063$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; Transition metal; Carbonyl; Cluster; Cyclopentadienyl

---

1. Introduction

The chemistry of transition metal cluster has enjoyed an exponential growth since the mid 1970s [1–4]. In recent years the structural and bonding aspects of mixed-metal tetrahedral skeleton clusters have been extensively studied [5–7]. A large number of these clusters are known now, among them the clusters with a tetrahedral skeleton comprised by four different metal atoms have become a more and more interesting area. One of the main motivations for the synthesis of skeletal chiral clusters was to provide unambiguous evidence for cluster catalysis through asymmetric induction. The pioneering work of Vahrenkamp et al. [8] has proved this to be the case.

Our interest in the reactivity of chiral clusters prompted us to prepare clusters that contain a M_1M_2CoS skeleton. We have reported the synthesis and characterization of the some chiral clusters recently: $FeCoM(CO)_8(\mu_3\text{-}S)RC(O)C_5H_4$, $FeCoM(\mu_3\text{-}CPh)(CO)_8[RC(O)C_5H_4]H$ (R=H, CH_3, CH_3O; M=Mo, W) [9,10]. Considering the special catalytic activity of the ruthenium atom, we introduced it into the chiral cluster skeleton RuCoMS.

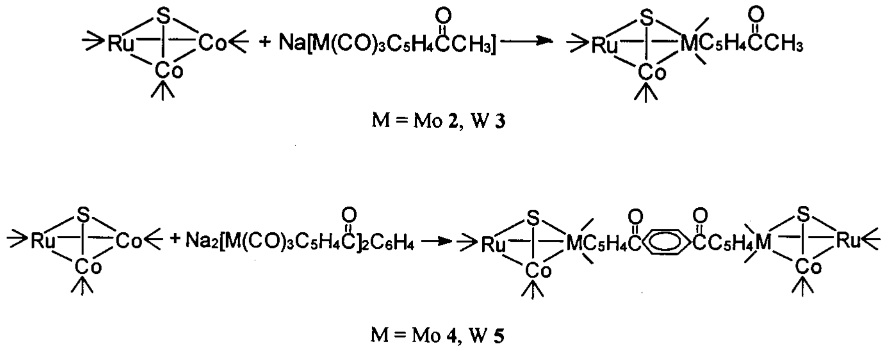
2. Results and discussion

Sulfur has always played an important role in the chemistry of the transition elements. The sulfido ligand is probably one of the most versatile of all known ligands. It exhibits a wide variety of structural configurations and electron-donating capabilities [11–15].

---

* Corresponding author. Fax: +86 931 8417088; e-mail: hcom@ns.lzb.ac.cn

0022-328X/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S0022-328X(98)00757-8



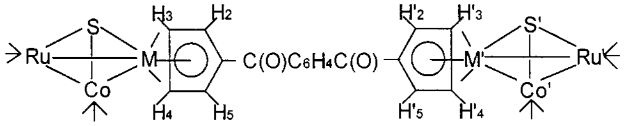
Scheme 1.

Some of those possess unusually high reactivities that would have implication for catalysis [18,19]. However these are few reports on the reaction of cluster $RuCo_2(\mu_3\text{-}S)(CO)_9$, which was first reported in 1980 by H. Vahrenkamp et al. [16,17]. Now the new tetrahedral core MRuCoS (M=Mo, W) cluster complexes and two unusual tetrahedral MRuCoS (M=Mo, W) clusters have been prepared by the reaction of $RuCo_2(\mu_3\text{-}S)(CO)_9$ with functionally cyclopentadienyl tricarbonyl Group 6 metal anions $[\{\eta^5\text{-}C_5H_4C(O)Me(CO)_3\}M]^-$ [M=Mo or W] and the bridged dianion $^-[M(CO)_3\{\eta^5\text{-}C_5H_4C(O)C_6H_4C(O)C_5H_4\text{-}\eta^5\}(CO)_3M]^-$ [M=Mo, W] in refluxing THF.

2.1. Synthesis and characterization of clusters 2–5

Reaction of $RuCo_2(\mu_3\text{-}S)(CO)_9$ with $Na[M(CO)_3C_5H_4C(O)CH_3]$ [M=Mo or W] in refluxing THF formed two new tetrahedral mixed metal clusters $RuCoM(\mu_3\text{-}S)(CO)_8C_5H_4C(O)CH_3$ (M=Mo **2**, W **3**), respectively (Scheme 1). The infrared spectra of clusters **2** and **3** show very similar characteristic absorption of the terminal carbonyl ligand in the region 2081–1856 cm^{-1}. The ^1H-NMR assignment of clusters **2** and **3** shows proton chemical shifts of substituted cyclopentadienyls which appeared downfield relative to that of unsubstituted cyclopentadienyl [20] since the acetyl is a well known electron-withdrawing group. The crystal structure of cluster **2** was determined.

Reaction of $RuCo_2(\mu_3\text{-}S)(CO)_9$ with $Na_2[M(CO)_3\text{-}C(O)C_5H_4]_2C_6H_4$ (M=Mo, W) in refluxing THF formed two of new novel clusters **4** and **5** in moderate yield (Scheme 1). The IR spectra of these show absorption characteristic of terminal CO ligand in the region 2085–1899 cm^{-1}. The vibrational frequency of C=O in **4**, **5** appears at about 1661 cm^{-1} and 1659 cm^{-1}, which is much lower than that of the RC=O in known clusters $FeCoM(CO)_8(\mu_3\text{-}CPh)C_5H_4C(O)R$ [10]. It should be mentioned that molecule structure of **5** is an achiral molecule containing a crystallographic symmetric center, this is meso form, however the ^1H-NMR spectra of the cyclopentadienyl protons of **4** and **5** show an A_2BB' pattern in stead of A_2B_2 pattern, of which the two upfield sets of quartets are assigned to H^3 and H^4 and the downfield triplet or multiplet are assigned to H^2 and H^5 close to the bridge of the electron-withdrawing group $-C(O)C_6H_4C(O)-$. This is due to a chiral tetrahedral subcluster $RuCoMo(\mu_3\text{-}S)(CO)_8$ in these clusters [21–24]. All of the clusters **2–5** are air stable black or red solid. They are soluble in polar solvents such as THF, toluene, and chloroform. All of them can be prepared at ambient temperature but in low yield.



Cluster **4** (M = Mo) and **5** (M = W)

Table 1
Summary of crystal and intensity data for the complexes **2** and **5**

Complexes	**2**	**5**
Empirical formula	$C_{15}H_7O_9SRuCoMo$	$C_{34}H_{12}O_{18}S_2Ru_2Co_2W_2$
Formula weight	619.22	1460.28
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
a (Å)	26.229(7)	12.688(4)
b (Å)	18.200(6)	20.290(7)
c (Å)	15.929(4)	9.429(3)
α (°)		99.78(3)
β (°)		90.64(2)
γ (°)		78.28(3)
Z	16	4
V (Å^3)	7604(6)	2341(1)
$D_{calc.}$ (g cm^{-3})	2.163	2.071
Radiation (Å)	0.71069	0.71069
Temperature (°C)	20	20
μ (Mo–K_α) cm^{-1}	24.51	63.73
F (000)	4768.00	1364.00
Number of observations [$I > 3.00\sigma(I)$]	3343	4618
Total number of reflections	4883	6460
Residuals: R, R_w	0.033, 0.045	0.042, 0.063

Table 2
Atomic coordinates and B_{iso}/B_{eq} for cluster **2**

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Ru(1)	0.00817(3)	0.19716(5)	0.62084(5)	2.71(2)	Ru(2)	0.77478(3)	−0.02623(5)	0.29369(5)	2.70(2)
Mo(1)	0.00418(3)	0.0856(5)	0.47939(5)	2.41(2)	Mo(2)	0.77193(3)	0.12364(5)	0.23728(5)	2.25(2)
Co(1)	−0.04353(4)	0.07548(7)	0.59539(7)	2.58(3)	Co(2)	0.79384(5)	0.08156(8)	0.39876(7)	2.78(3)
S(1)	0.03987(8)	0.0778(1)	0.6126(1)	2.69(5)	S(2)	0.84273(8)	0.0564(1)	0.2906(1)	2.70(5)
O(1)	0.1058(3)	0.1641(5)	0.7979(4)	5.3(2)	O(2)	−0.0598(3)	0.2196(4)	0.8129(5)	5.2(2)
O(3)	0.0896(3)	0.3019(5)	0.6832(6)	6.7(3)	O(4)	−0.0778(3)	0.3088(4)	0.6420(5)	5.8(2)
O(5)	0.0313(3)	0.2388(4)	0.4402(5)	5.2(2)	O(6)	−0.1379(3)	0.1264(4)	0.6712(5)	5.1(2)
O(7)	−0.0569(3)	0.1132(4)	0.4171(4)	4.4(2)	O(8)	−0.0659(3)	−0.0827(4)	0.5953(5)	4.4(2)
O(9)	−0.0088(3)	0.1101(5)	1.0022(5)	5.7(2)	O(10)	0.6639(2)	0.0552(4)	0.2243(4)	3.9(2)
O(11)	0.8034(3)	0.0532(5)	0.0637(5)	5.8(2)	O(12)	0.6721(3)	−0.0804(5)	0.3618(5)	5.9(2)
O(13)	0.7683(3)	−0.1085(5)	0.1265(5)	6.0(2)	O(14)	0.8379(3)	−0.1484(4)	0.3735(4)	4.1(2)
O(15)	0.8196(3)	−0.0219(5)	0.5322(5)	6.1(2)	O(16)	0.8470(3)	0.2108(5)	0.4658(5)	5.9(2)
O(17)	0.6868(3)	0.1125(5)	0.4346(5)	6.7(3)	O918)	0.7434(3)	0.2083(5)	0.0111(4)	4.9(2)
C(1)	0.0678(4)	0.1385(6)	0.7779(6)	3.5(3)	C(2)	−0.0348(4)	0.1756(6)	0.7825(6)	3.6(3)
C(3)	0.0590(4)	0.2624(6)	0.6611(7)	4.1(3)	C(4)	−0.0454(4)	0.2683(6)	0.6339(6)	3.3(3)
C(5)	0.0219(4)	0.2225(6)	0.5070(7)	3.5(5)	C(6)	−0.1002(4)	0.1073(6)	0.6432(6)	3.3(3)
C(7)	−0.0519(3)	0.0985(6)	0.4866(7)	3.3(3)	C(8)	−0.0564(3)	−0.0224(7)	0.5949(6)	3.3(3)
C(9)	−0.0432(4)	0.0296(6)	0.8559(6)	3.6(3)	C(10)	−0.0440(4)	−0.0210(6)	0.7888(7)	4.2(3)
C(11)	0.0075(5)	−0.0424(6)	0.7720(6)	3.9(3)	C(12)	0.0386(4)	−0.0068(5)	0.8301(6)	3.3(2)
C(13)	0.0081(3)	0.0383(5)	0.8824(6)	2.9(2)	C(14)	0.0240(4)	0.0803(6)	0.9605(6)	4.0(3)
C(15)	0.0786(4)	0.0820(7)	0.9820(7)	5.2(3)	C(16)	0.7061(4)	0.0718(5)	0.2335(6)	2.9(2)
C(17)	0.7919(4)	0.0773(6)	0.1279(6)	3.8(3)	C(18)	0.7096(4)	−0.0610(6)	0.3334(7)	3.9(3)
C(19)	0.7706(4)	−0.0796(6)	0.1905(7)	3.7(3)	C(20)	0.8135(4)	−0.1035(6)	0.3457(6)	3.2(3)
C(21)	0.8104(4)	0.0157(6)	0.4787(6)	3.9(3)	C(22)	0.8261(4)	0.1627(6)	0.4398(6)	3.4(3)
C(23)	0.7287(4)	0.1009(6)	0.4176(6)	4.2(3)	C(24)	0.7981(3)	0.2280(5)	0.1680(6)	3.2(2)
C(25)	0.8082(4)	0.2405(5)	0.2535(6)	3.5(3)	C(26)	0.7602(4)	0.2416(5)	0.2961(6)	3.4(2)
C(27)	0.7207(3)	0.2287(5)	0.2383(6)	2.8(2)	C(28)	0.7437(3)	0.2201(5)	0.1583(6)	2.6(2)
C(29)	0.7177(4)	0.2115(5)	0.0744(7)	3.3(3)	C(30)	0.6617(4)	0.2090(6)	0.0729(7)	4.4(3)

2.2. *Structure of clusters **2** and **5***

The structure of cluster **2** was determined by X-ray structure analysis. The molecule crystallizes in the orthorhombic crystal system, in the space group Pbca. Cluster **2** displays a RuCoMoS tetrahedral geometry. Crystal data collected in Tables 1, 2 and 4 give the atomic coordinates and selected bonds distance and angles for **2**. The structure of cluster **2** unexpectedly reveals the presence of two isomeric molecules in the unit cell, which are respectively in Fig. 1 (**A** and **B**). The two independent molecular units are almost identical, and the very slight structural differences between them are just reflecting the influence of packing forces. Each unit displays a RuCoMoS tetrahedral geometry. The acute angles in tetrahedral geometry of **2** about the basal atoms range from 50.12 to 64.09° and those about the sulfur atom average 73.46°, which deviates considerably from a perfect tetrahedral geometry. This results because the metal-metal bonded RuCoMo triangle restricts the angles around the sulfur atom. The bond length of Ru–S (2.330 Å) is roughly equal with a known complex $HRu_3(CO)_9[(\mu_3\text{-}S)Mo(CO)_3(NCCH_3)_2]$ [25] [Ru–S = 2.365 Å] but short than that of the typical Ru–S bond length (2.441 Å) [26].

The red prismatic crystal of cluster **5** suitable for structure determination was obtained from the solution of CH_2Cl_2. Crystal datas collected in Table 1. Table 3 gives the atomic coordinates, the relevant bond lengths and angles of **5** are summarized in Table 5. The asymmetric unit involves two equivalent cluster molecules as **2**, which are respectively represented in Figs. 2 and 3. The two independent molecular units are also almost identical, and the very slight structural differences between them are just reflecting the influence of packing forces. Each unit is made of two identical tetrahedral skeleton subclusters, RuCoWS, which connected with the bridge of $C_5H_4C(O)C_6H_4C(O)C_5H_4$ ligand through W atoms. Capping S atom is bonded to Ru, Co and W with bond lengths 2.310(4), 2.197(4) and 2.376(4) Å, respectively. The W atom–Cp ring center distance is 1.970 Å. The bond length of C(5)–C(6) (1.46 Å) and C(6)–C(7) (1.47 Å) are much shorter than that of the normal C–C single bond (1.54 Å) but longer than a C=C double bond (1.34 Å), because the π-system of the benzene derivation bridge –$C(O)C_6H_4C(O)$– would be quite well conjugated with that of Cp ring. Treating μ_3-S as a four-electron donor, the cyclopentadienyl group as a five-electron donor, cluster **5** contains a total of 2 × 48 electrons

Table 3
Atomic coordinates and B_{iso}/B_{eq} for cluster **5**

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
W(1)	0.10391(4)	0.23216(3)	−0.23857(6)	3.30(1)	W(2)	−0.39152(4)	0.23039(3)	−0.07354(6)	3.54(1)
Ru(1)	0.0935(1)	0.18291(8)	−0.5416(1)	4.81(3)	Ru(2)	−0.40314(10)	0.16158(8)	0.1649(1)	4.43(3)
Co(1)	0.1433(2)	0.0962(1)	−0.3610(2)	4.34(5)	Co(2)	−0.3507(1)	0.0909(1)	−0.0949(2)	4.04(5)
S(1)	−0.0140(3)	0.1652(2)	−0.3594(4)	4.19(9)	S(2)	−0.5093(3)	0.1572(2)	−0.0370(4)	4.05(9)
O(1)	0.2507(8)	0.3745(6)	−0.087(1)	5.4(3)	O(2)	−0.040(1)	0.3619(7)	−0.335(1)	7.0(4)
O(3)	0.2993(9)	0.2695(7)	−0.381(1)	6.5(4)	O(4)	−0.029(1)	0.3028(10)	−0.665(2)	9.3(5)
O(5)	0.306(1)	0.177(1)	−0.694(2)	11.0(6)	O(6)	0.032(1)	0.084(1)	−0.791(2)	11.4(6)
O(7)	0.3705(9)	0.1019(7)	−0.372(2)	7.7(4)	O(8)	0.131(1)	−0.0236(7)	−0.578(2)	8.1(4)
O(9)	0.118(1)	0.0288(8)	−0.116(2)	8.5(5)	O(10)	−0.245(1)	0.3793(7)	−0.066(2)	7.5(4)
O(11)	−2.005(9)	0.2560(7)	0.122(1)	6.2(3)	O(12)	−0.543(1)	0.3477(7)	0.132(1)	7.0(4)
O(13)	−0.191(1)	0.146(1)	0.325(2)	11.5(6)	O(14)	−0.524(1)	0.2745(9)	0.393(1)	8.2(4)
O(15)	−0.482(1)	0.0538(10)	0.291(2)	11.0(6)	O(16)	−0.347(1)	−0.0390(8)	−0.002(2)	9.4(5)
O(17)	−0.3816(10)	0.0478(8)	−0.405(1)	7.6(4)	O(18)	−0.1253(9)	0.0980(6)	−0.072(1)	5.7(3)
C(1)	0.212(1)	0.2478(8)	−0.042(2)	4.8(4)	C(2)	0.156(1)	0.1945(8)	−0.023(1)	4.7(4)
C(3)	0.047(1)	0.2207(7)	−0.012(2)	3.9(4)	C(4)	0.029(1)	0.2900(7)	−0.020(1)	3.8(3)
C(5)	0.130(1)	0.3086(8)	−0.041(1)	4.1(4)	C(6)	0.157(1)	0.3745(7)	−0.051(1)	3.9(4)
C(7)	0.075(1)	0.4383(8)	−0.024(2)	3.8(3)	C(8)	0.083(1)	0.4898(8)	−0.102(2)	4.5(4)
C(9)	−0.009(1)	0.4484(8)	0.078(2)	4.3(4)	C(10)	0.011(1)	0.3134(9)	−0.305(2)	4.5(4)
C(11)	0.223(1)	0.2537(9)	−0.346(2)	4.7(4)	C(12)	0.017(2)	0.259(1)	−0.617(2)	6.9(6)
C(13)	0.226(2)	0.181(1)	−0.638(2)	7.4(6)	C(14)	0.053(1)	0.125(1)	−0.701(2)	7.6(6)
C(15)	0.282(1)	0.1009(9)	−0.370(2)	5.5(5)	C(16)	0.135(1)	0.025(1)	−0.499(2)	7.3(6)
C(17)	0.128(1)	0.0575(9)	−0.206(2)	6.0(5)	C(18)	−0.465(1)	0.2988(9)	−0.232(2)	5.3(5)
C(19)	−0.444(1)	0.2320(10)	−0.312(2)	5.4(5)	C(20)	−0.328(1)	0.2091(9)	−0.317(2)	5.2(4)
C(21)	−0.283(1)	0.2582(9)	−0.240(2)	5.0(4)	C(22)	−0.363(1)	0.3174(9)	−0.185(2)	4.8(4)
C(23)	−0.337(1)	0.3807(9)	−0.096(2)	5.6(5)	C(24)	−0.425(1)	0.4417(8)	−0.049(2)	4.8(4)
C(25)	−0.411(1)	0.481(1)	0.076(3)	6.7(6)	C(26)	−0.516(2)	0.462(1)	−0.131(2)	7.0(6)
C(27)	−0.276(1)	0.2431(9)	0.055(2)	5.2(4)	C(28)	−0.488(1)	0.3024(9)	0.064(2)	4.5(4)
C(29)	−0.273(2)	0.152(1)	0.264(2)	7.2(6)	C(30)	−0.475(1)	0.229(1)	0.308(2)	6.0(5)
C(31)	−0.452(1)	0.094(1)	0.246(2)	6.2(5)	C(32)	−0.354(1)	0.0140(9)	−0.032(2)	5.5(5)
C(33)	−0.368(1)	0.066(1)	−0.288(2)	5.9(5)	C(34)	−0.211(1)	0.0975(9)	−0.076(2)	4.7(4)

and is electronically saturated for each of the two tetrahedral core respectively.

3. Experimental

All reactions were performed under an atmosphere of pure nitrogen by using standard schlenck or vacuum line techniques. Solvents were purified, dried, and distilled under nitrogen prior to use. Column chromatography were carried out by using silica gel of ρ 300–400 mesh. $Mo(CO)_6$, $W(CO)_6$ were purchased from Fluka and Aldrich. $Co_2(CO)_8$ [27], $Ru_3(CO)_{12}$ [28], RC_5H_4Na [R=MeC(O), $C_6H_5C(O)$] [29], and $[NaC_5H_4C(O)]_2C_6H_4$ [30]were prepared according to the literature. IR. spectra were recorded on a Nicolet FT-IR. 10 DX spectrophotometer; ^{1}H-NMR spectra were recorded on Bruker AM-300 MHz spectrometer; C\H analyses and MS determinations were performed on a Carlo Erba 1106-type analyzer and Finnigan MAT 8430.

3.1. Preparation of 2–5

3.1.1. Cluster 2

A 50 ml two-necked flask with a magnetic bar, a rubber septum, and reflux condenser topped with a nitrogen inlet tube was charged with 264 mg (1.0 mmol) of $Mo(CO)_6$, 130 mg (1.0 mmol) of $NaC_5H_4C(O)CH_3$, and 20 ml THF. The mixture was refluxed for 12 h. Upon cooling to room temperature, 503 mg (1.0 mmol) of $RuCo_2(\mu_3{-}S)(CO)_9$ was added and the mixture was stirred at ambient temperature for 1 h then it was heated to reflux for 1 h. The solvent was evaporated in vacuum. The residue was dissolved in a minimal amount of CH_2Cl_2 and was subjected to chromatographic, separation on silica gel column. Elution with a mixture of hexane/CH_2Cl_2 (3:1) yield the following brands in order of elution: a small amount of unreacted cluster **1**, a trace of $Ru_3(CO)_{12}$, and the main black product **2** 260 mg (42%). Cluster **2**: m.p., 102–103°C; Anal. Calc. for $C_{15}H_7O_9RuCoMoS$: C, 29.05; H, 1.13. Found: C, 29.16; H, 1.14%. IR (KBr disk) v(CO) 2081 vs, 2042 vs, 2010 vs, 1994 vs, 1987 vs, 1979 vs, 1894 s, 1856s, v(C=O) 1686 m cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.39 (s, 3H, CH_3), 5.95–5.50 (m, 4H, C_5H_4). MS (FAB, Mo^{96}) 591 ($M^+ - CO$), 423 ($M^+ - 7CO$), 395 ($M^+ - 8CO$). The workup for **3**–**5** was similar to that of the preparation **2**.

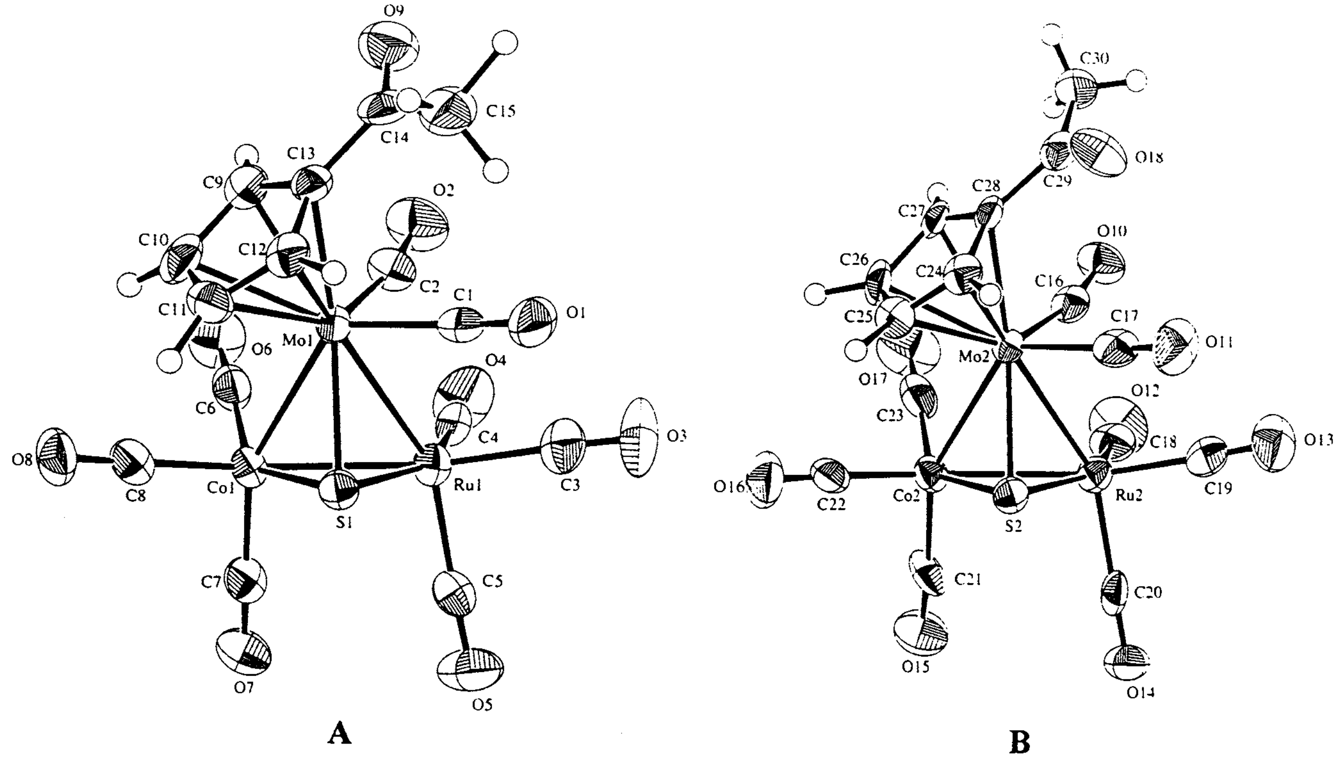


Fig. 1. Perspective view of the first and second molecular unit of the complex **2** (**A** and **B**).

3.1.2. Cluster *3*

Yield, 44%. m.p., 112–113°C. Anal. Calc. for $C_{15}H_7O_9RuCoWS$: C, 25.43; H, 1.00. Found: C, 25.40; H, 1.10%. IR (KBr disk) υ(CO) 2080 vs, 2040 vs, 2016 vs, 2005 vs, 1989 vs, 1985 vs, 1976 vs, 1896 m, 1859, υ(C=O) 1688 m. ^{1}H-NMR($CDCl_3$) δ 2.40 (s, 3H, CH_3), 5.93–5.59 (m, 4H, C_5H_4). MS (FAB Ru^{102}) 708 (M^+), 680 ($M^+ - CO$), 652 ($M^+ - 2CO$), 484 ($M^+ - 8CO$)

3.1.3. Cluster *4*

Yield, 49%. Anal. Calc. for $S_2Ru_2Co_2Mo_2C_{34}H_{12}O_{18}$: C, 31.79; H, 0.94 Found: C, 31.66, H, 1.01%. IR (KBr disk) 2085 vs, 2008 vs, 1907 m, 1650 m (C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 6.02–5.85 [t, 4H, 2(H^2,H^5)], δ 5.60–5.32 [q, q, 4H, 2(H^3H^4)], δ 7.94 (s, 4H, C_6H_4). MS (FAB) 1228 ($M^+ - 2CO$) 1172 ($M^+ - 4CO$).

Table 4
Intramolecular distances (Å) and bond angles (°) for cluster **2**

Molecule A					
Ru(1)–Mo(1)	2.885(1)	Ru(1)–Co(1)	2.628(2)	Ru(1)–S(1)	2.330(3)
Mo(1)–Co(1)	2.760(1)	Mo(1)–S(1)	2.376(2)	Co(1)–S(1)	2.205(3)
Mo(1)–Cp	2.002				
Mo(1)–Ru(1)–Co(1)	59.87(4)	Mo(1)–Ru(1)-S(1)	52.92(6)	Co(1)–Ru(1)-S(1)	52.39(7)
Ru(1)-Mo(1)-Co(1)	55.44(4)	Ru(1)–Mo(1)-S(1)	51.47(6)	Co(1)-Mo(1)–S(1)	50.17(6)
Ru(1)–Co(1)–Mo(1)	64.69(4)	Ru(1)–Co(1)–S(1)	56.83(7)	Mo(1)–Co(1)–S(1)	55.85(7)
Ru(1)–S(1)–Mo(1)	75.61(7)	Ru(1)–S(1)–Co(1)	70.78(8)	Mo(1)–S(1)–Co(1)	73.99(8)
Molecule B					
Ru(2)–Mo(2)	2.873(1)	Ru(2)–Co(2)	2.627(2)	Ru(2)–S(2)	2.332(3)
Mo(2)–Co(2)	2.745(1)	Mo(2)–S(2)	2.381(2)	Co(2)–S(2)	2.196(3)
Mo(2)–Cp	1.985				
Mo(2)–Ru(2)–Co(2)	59.68(4)	Mo(2)–Ru(2)–S(2)	53.23(6)	Co(2)–Ru(2)–S(2)	52.15(6)
Ru(2)–Mo(2)–Co(2)	55.70(3)	Ru(2)–Mo(2)–S(2)	51.68(6)	Co(2)–Mo(2)–S(2)	50.11(6)
Ru(2)–Co(2)–Mo(2)	64.62(4)	Ru(2)–Co(2)–S(2)	57.00(7)	Mo(2)–Co(2)–S(2)	56.32(7)
Ru(2)–S(2)–Mo(2)	75.09(7)	Ru(2)–S(2)–Co(2)	70.84(8)	Mo(2)–S(2)–Co(2)	73.57(8)

Table 5
Selected bond distances (Å) and bond angles (°) for complex **5**

Molecule A					
W(1)–Ru(1)	2.873(1)	W(1)–Co(1)	2.750(2)	W(1)–S(1)	2.376(4)
Ru(1)–Co(1)	2.633(3)	Ru(1)–S(1)	2.325(4)	Co(1)–S(1)	2.191(4)
C(5)–C(6)	1.46(2)	C(6)–C(7)	1.47(2)	W(1)–Cp	1.970
Ru(1)–W(1)–Co(1)	55.80(6)	Ru(1)–W(1)–S(1)	51.52(10)	Co(1)–W(1)–S(1)	50.0(1)
W(1)–Ru(1)–Co(1)	59.73(5)	W(1)–Ru(1)–S(1)	53.13(9)	Co(1)–Ru(1)–S(1)	52.0(1)
W(1)–Co(1)–Ru(1)	64.47(6)	W(1)–Co(1)–S(1)	56.1(1)	Ru(1)–Co(1)–S(1)	56.7(1)
W(1)–S(1)–Ru(1)	75.4(1)	W(1)–S(1)–Co(1)	73.9(1)	Ru(1)–S(1)–Co(1)	71.3(1)
Molecule B					
W(2)–Ru(2)	2.861(1)	W(2)–Co(2)	2.744(2)	W(2)–S(2)	2.376(4)
Ru(2)–Co(2)	2.637(3)	Ru(2)–S(2)	2.320(4)	Co(2)–S(2)	2.197(4)
C(22)–C(23)	1.51(2)	C(23)–C(24)	1.49(2)	W(2)–Cp	1.980
Ru(2)–W(2)–Co(2)	56.10(6)	Ru(2)–W(2)–S(2)	51.58(9)	Co(2)–W(2)–S(2)	50.2(1)
W(2)–Ru(2)–Co(2)	59.70(5)	W(2)–Ru(2)–S(2)	53.35(10)	Co(2)–Ru(2)–S(2)	52.1(1)
W(2)–Co(2)–Ru(2)	64.20(6)	W(2)–Co(2)–S(2)	56.2(1)	Ru(2)–Co(2)–S(2)	56.5(1)
W(2)–S(2)–Ru(2)	75.1(1)	W(2)–S(2)–Co(2)	73.6(1)	Ru(2)–S(2)–Co(2)	71.4(1)

*3.1.4. Cluster **5***

Yield, 42%. Anal. Calcd for $S_2Ru_2Co_2W_2C_{34}H_{12}O_8$: C, 27.97; H, 0.8. Found: C, 28.02; H, 0.97%. IR (KBr disk) 2083 vs, 2040 vs, 2002 vs, 1899 vs, 1661 m (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$) δ 6.01–5.35 (m, 8H, 2 × C_5H_4),δ 7.92 (s, 4H, C_6H_4); MS (FAB Ru^{102}) 1433 ($M^+ - CO$).

3.2. Crystallographic analyses

Crystals of **2** suitable for diffraction analysis were grown from a solution in CH_2Cl_2/hexane (1:2) solvent mixture at −18°C. The red crystals of **5** were grown the solution in CH_2Cl_2 at −18°C. The data crystals were mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffrectormeter with graphite monochromated Mo–K_α radiation. Crystal data, data collection parameters and results of the analyses are listed in Table 1. All the data were collected at a temperature of 20 ± 1°C using the $w - 2\theta$ scan techniques. All the structures were solved by direct methods [31] and expanded using Fourier technique [32]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Full-matrix least-squares refinements minimized the function $\Sigma\omega(|F_o| - |F_c|)^2$ where $\omega = [\sigma^2(F_o)]^-1 = 4F_o^2[\sigma^2(F_o^2)]^{-2}$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]$ $[Lp]^{-2}$ Neutral atom scattering factors were taken from Cromer and Waber [33]. All calculations were performed using the TEXSAN [34] crystallographic software package of Molecular Structure Corporation.

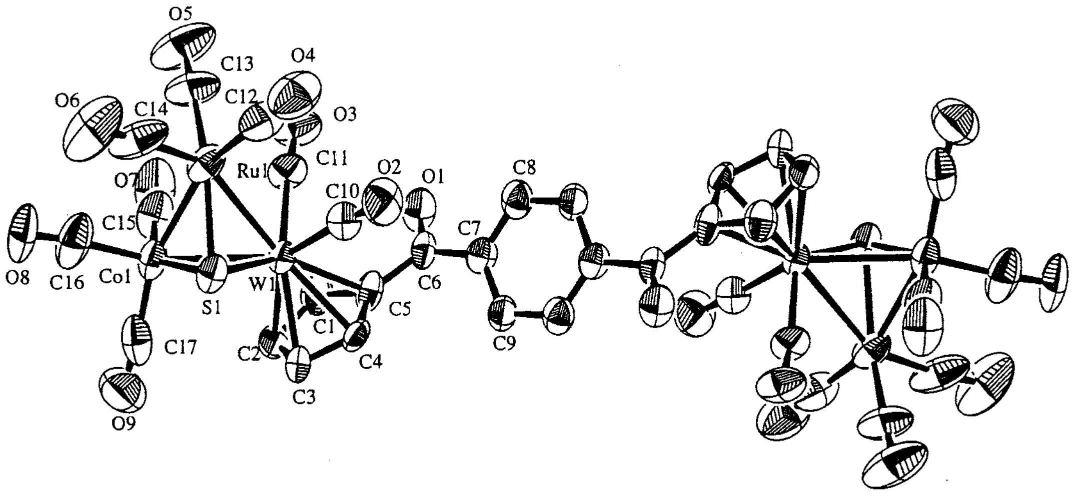


Fig. 2. Perspective view of the first molecular unit of the complex **5**.

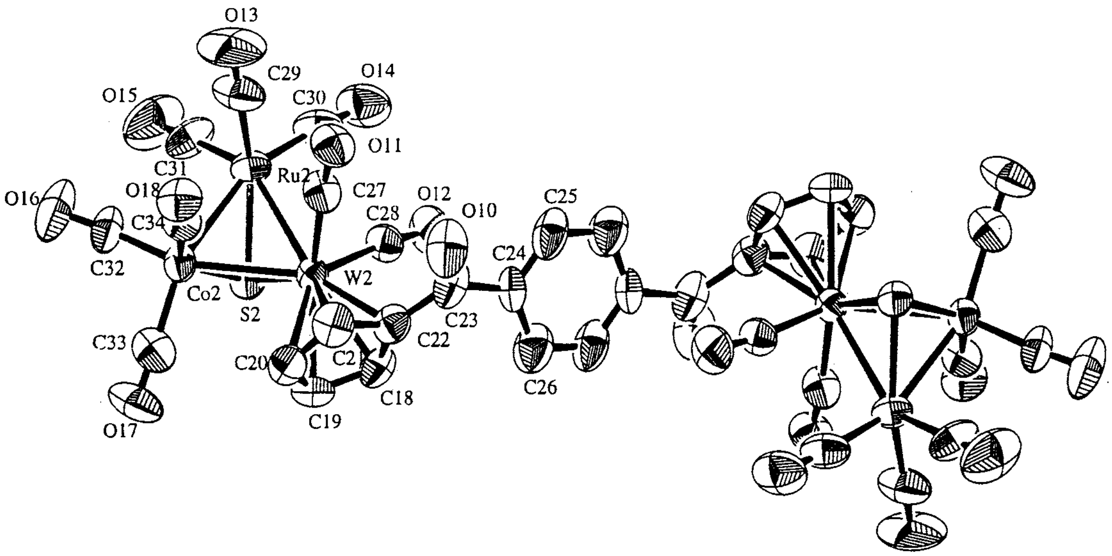


Fig. 3. Perspective view of the second molecular unit of the complex **5**.

Acknowledgements

This work was supported by the Laboratory of Organometallics Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences and the National Science Foundation of China.

References

[1] H. Vahrenkamp, Adv. Organomet. Chem. 22 (1983) 169.

[2] F.G.A. Stone, Angew. Chem. Int. Engl. 23 (1984) 89.

[3] M.L. Ziegler, H.P. Neumann, Chem. Ber. 122 (1989) 25.

[4] D.F. Shriver, H.D. Kaesz, R.D. Adams, The Chemistry of Metal Cluster Complex, VCH, Weinheim, 1990.

[5] T. Albiez, H. Bantel, H. Vahrenkamp, Chem. Ber. 123 (1990) 1805.

[6] F.G.A. Stone, M.L. Williomes, J. Chem. Soc. Dalton Trans. (1988) 2467.

[7] R.C. Lin, Y. Chi, S.M. Peng, G.H. Li, Inorg. Chem. 31 (1992) 3818.

[8] H. Vahrenkamp, J. Organomet. Chem. 65 (1989) 372.

[9] H.P. Wu, Y.Q. Yin, Q.C. Yang, Inorg. Chim. Acta. 245 (1996) 143.

[10] H.P Wu, Y.Q. Yin, X.Y Huang, K.B. Yu, J. Organomet. Chem. 498 (1995) 119.

[11] H. Bantel, W. Bernhardt, A.K. Powell, H. Vahrenkamp, Chem. Ber. 122 (1988) 1247.

[12] S. Luo, A.E. Ogilvy, T.B. Rauchfuss, A.L. Rheingold, S.R. Wilson, Organometallics 10 (1991) 1002.

[13] R.D. Adams, J.E. Babin, M. Tasi, Organometallics 2 (1983) 219.

[14] R.D. Adams, J.E. Babin, M. Tasi, Inorg. Chem. 27 (1988) 2618.

[15] E.W Abel, B.C. Crosse, Organomet. Chem. Rev. 2 (1967) 433.

[16] E. Roland, H. Vahrenkamp, Chem. Ber. 117 (1984) 1039.

[17] E. Roland, H. Vahrenkamp, Organometallics 2 (1983) 1048.

[18] R.D. Adams, L.W. Yang, J. Am. Chem. Soc. 105 (1983) 235.

[19] R.D. Adams, S. Wang, Organometallics 5 (1986) 1272.

[20] R. Blumhofer, K. Fischer, H. Vahrenkamp, Chem. Ber. 119 (1986) 194.

[21] L.C. Song, J.Y. Shen, Q.M. Hu, X.Y. Huang, Organometallics 14 (1995) 98.

[22] H. Beurich, H. Vahrenkamp, Angew. Chem. Int. Ed. Engl. 17 (1978) 863.

[23] E.R. Ding, X.M. Liu, Z.Y. Zhao, Y.Q. Yin, J. Sun, Polyhedron 16 (1997) 2387.

[24] E.R. Ding, X.M. Liu, Y.Q. Yin, J. Sun, Polyhedron 16 (1997) 3272.

[25] E.J. Voss, C.L. Stern, D.F. Shriver, Inorg. Chem. 33 (1994) 1087.

[26] L.A. Hoferkamp, G. Rheinwald, H. Stoeckli–Evens, G. Süss-Fink, Organometallics 15 (1996) 704.

[27] R.B. King, Organometallic Syntheses: Transition-Metal Compounds, vol. 1, Academic Press, New York, 1965, p. 98.

[28] A. Mantovani, S. Cenini, Inorg. Synth. 16 (1972) 47.

[29] D. Seyferth, J.E. Hallgren, P.L.K. Hung, J. Organomet. Chem. 50 (1973) 265.

[30] T.E. Bitterwolf, J. Organomet. Chem. 386 (1990) 9.

[31] G.M. Sheldrick, SHELXS86, in: G.M Sheldrick, C. Kruger, R. Goddard (Eds.), Crystallographic Computing 3, Oxford University Press, London, 1985.

[32] P.T. Beurskens, G. Admireal, G. Beurskens, et al., DIRDIF92, 1992.

[33] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, Table 2.2(A), vol. IV, Kynoch Press, Birmingham, 1974.

[34] TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.