Pergamon

*Polyhedron* Vol. 16, No. 14, pp. 2387–2391, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277–5387/97 \$17.00+0.00

PII: S0277–5387(96)00579–7

# Synthesis and reduction of [RuCoMo ($\mu_3$-S)(CO)$_8$(RC$_5$H$_4$)] [R = HC(O) (2), CH$_3$C(O) (3), C$_6$H$_5$C(O) (4), CH$_3$OC(O)C$_6$H$_4$C(O) (5)] heterometal clusters and structure of [RuCoMo ($\mu_3$-S)(CO)$_8$C$_5$H$_4$C(O)C$_6$H$_4$C(O)OCH$_3$]

Er-Run Ding,[a] Sheng-Min Liu,[a] Zhuan-Yun Zhao,[a] Yuan-Qi Yin[a]*
and Jie Shun[b]

[a]Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, P.R. China

[b]Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai 200032, P.R. China

(Received 28 October 1996; accepted 20 November 1996)

**Abstract**—The heterometal clusters [SRuCoMo(CO)$_8$C$_5$H$_4$R][R = HC(O) (**2**), CH$_3$C(O) (**3**), C$_6$H$_5$C(O) (**4**), CH$_3$OC(O)C$_6$H$_4$C(O) (**5**)] were synthesized by refluxing a solution of the cluster **1** [RuCo$_2$($\mu_3$-S)(CO)$_9$] and monoanions [$\eta^5$-RC$_5$H$_4$(CO)$_3$Mo] [R = HC(O), CH$_3$C(O), C$_6$H$_5$C(O), CH$_3$OC(O)C$_6$H$_4$C(O)]. Cluster **3** reacted with NaBH$_4$ in MeOH giving the secondary alcohol cluster RuCoMo($\mu_3$-S)(CO)$_8$ [$\eta^5$-C$_5$H$_4$CH(OH)CH$_3$]. All clusters were characterized by C, H analysis, IR and $^1$H NMR. Some were characterized by MS and $^{13}$C NMR. The results showed that the metal fragment Co(CO)$_3$ in RuCo$_2$($\mu_3$-S)(CO)$_9$ could be exchanged by Mo(CO)$_2$(C$_5$H$_4$R). Cluster **5** has been structurally determined by single-crystal X-ray diffraction. © 1997 Elsevier Science Ltd

*Keywords*: heterometal cluster; carbonyl; single crystal XRD.

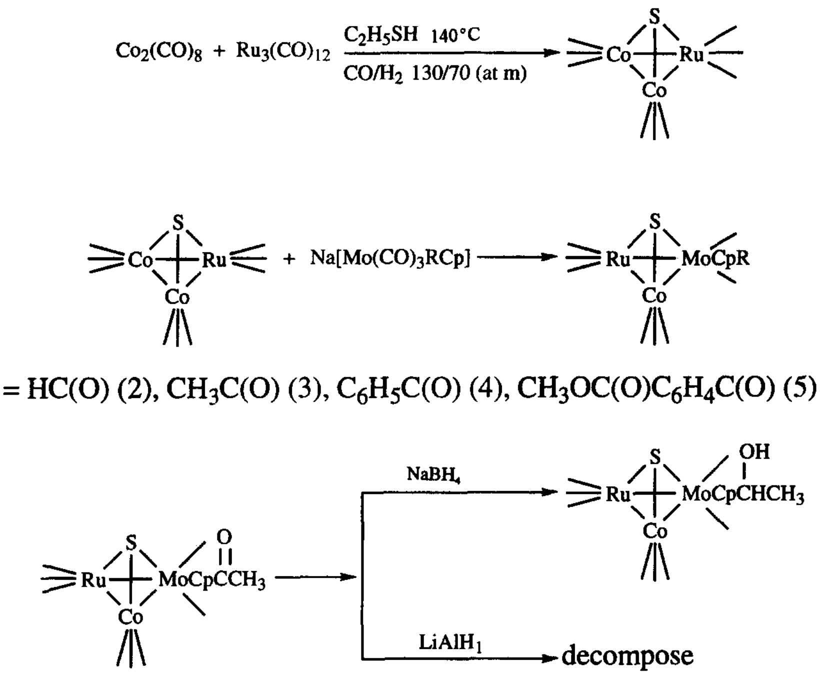
Organometallic cluster compounds [1–3] containing *p*-block nonmetals have come under increasing investigation because of their interesting structure and reactivity patterns [4]. Sulfur has always played an important role in the chemistry of the transition elements. The sulfido ligand is probably one of the most versatile of all known ligands. It exhibits a wide variety of geometries and electron-donating capabilities [5–7]. We have recently synthesized some sulfidometal clusters: SFeCoM(CO)$_8$RC(O)Cp (R = H, CH$_3$, C$_2$H$_5$O; M = Mo, W) [8–9]. Considering the special catalytic activity of the ruthenium atom, we introduced it into the chiral cluster skeleton RuCo MoS. In this paper, we report the reaction of the prochiral cluster RuCo$_2$($\mu_3$-S)(CO)$_9$ with Na[Mo (CO)$_3$C$_5$H$_4$R] forming the four new tetrahedral clusters (**2**–**5**). The reduction of cluster **3** with NaBH$_4$ gave cluster **6**. This type of complex has featured very little in the literature [10]. We have found no report of an X-ray structure of clusters containing the tetrahedral core RuCoMoS before our works.

## RESULTS AND DISCUSSION

In the presence of the ethanethiol Co$_2$(CO)$_8$ reacted with Ru$_3$(CO)$_{12}$ in hexane giving the cluster **1** [RuCo$_2$($\mu_3$-S)(CO)$_9$] (80%) [11]. Refluxing the solution of [NaMo(CO)$_3$(C$_5$H$_4$)R] [R = HC(O), CH$_3$C(O), C$_6$H$_5$C(O), CH$_3$OC(O)C$_6$H$_4$C(O)] with cluster **1** in THF gave the titled clusters **2**–**5** in moderate yield, which also can be prepared at ambient

---

*Author to whom correspondence should be addressed.



R = HC(O) (2), $CH_3C(O)$ (3), $C_6H_5C(O)$ (4), $CH_3OC(O)C_6H_4C(O)$ (5)

Scheme 1.

temperature, but in low yield and long reaction times (Scheme 1). Reduction of the cluster **3** by $NaBH_4$ in methanol at room temperature gave the cluster **6**. However, we could not reduce it using $LiAlH_4/AlCl_3$. This stronger reduction agent can decompose the tetrahedral skeleton of cluster **3**. All of the clusters are air-stable solids, but they are slightly air-sensitive in solution.

### *Spectra*

The IR spectra of all these clusters exhibited a large number of absorption bands between 1856 and 2087 $cm^{-1}$, which were assigned to terminal carbonyl vibrations. The spectra of cluster **6** revealed an OH absorption peak at 3383 $cm^{-1}$. These results are consistent with the reduction of the C=O groups (1686 $cm^{-1}$) in cluster **2** by the action of $NaBH_4$. For $^1H$ NMR assignment of the clusters, chemical shifts of the substituted cyclopentadienyl in clusters **2**–**5** appeared at lower fields than that in unsubstituted cyclopentadienyl because of their electron-withdrawing groups. It is interesting that the $^1H$ NMR spectra of the cyclopentadienyl protons of these clusters show four triplets ($A_2B_2$ type). This is due to the chiral skeleton RuCoMoS in these clusters [12]. Proton chemical shifts on the cyclopentadienyl in cluster **6** appeared at higher field than that in the cluster **2**, because the shielding of substituent —CH(OH)— to the protons of cyclopentadienyl is larger than that of —C=O—. The chemical shift of the proton of OH in cluster **6** appears at 2.10 ppm.

### *Structure of the complex* 5

The structure of cluster **5** was determined by X-ray structure analysis. The molecule crystallizes in the triclinic crystal system, in the space group $P\bar{1}$. A diagram showing the structure and labeling for cluster **5** is shown in Fig. 1. Tables 1 and 2 give the selected bond distances and bond angles of cluster **5**, respectively. This compound contains a tetrahedral skeleton formed by Ru, Co, Mo and S, the slightly distanced triangular Ru—Co—Mo capped by a sulfido ligand. This is the first example for the structure of a complex containing the tetrahedral skeleton RuCoMoS. The acute angles in the tetrahedral core of cluster **5** about the basal atoms range from 55.69 to 64.71° and those about the sulfur atom average 72.7°, which deviate considerably from a perfect tetrahedral geometry. The distances from the sulfur atom to these metals are not equal [Ru—S = 2.351(3), Co—S = 2.190(3), Mo—S = 2.415(3) Å]. The bond length of Ru—S is similar to that of a known complex $[Ru_3(CO)_7(pph_3)(\mu_2\text{-}\eta^2\text{-}C_6H_5)(\mu_2\text{-}pph_2)(\mu_3\text{-}S)]$ (Ru—S = 2.365 Å), but shorter than that of the typical Ru—S bond length [13]. The distance of the Mo atom to the Cp ring center is 1.992 Å, which is much shorter than that of the Mo—Cp (2.227 Å) in the cluster $[FeCoMoS(CO)_8(CpR)]$ [8]. Since the $\pi$-system of the benzene derivative $—C(O)C_6H_5C(O)—$ would be quite well conjugated with the Cp ring, the bond lengths C(13)—C(14) (1.49 Å), C(14)—C(15) (1.49 Å) and C(18)—C(21) (1.50 Å) became shorter than that of a normal C—C single bond (1.54 Å), but longer than that of a C=C double bond (1.34 Å). Treating $\mu_3$-

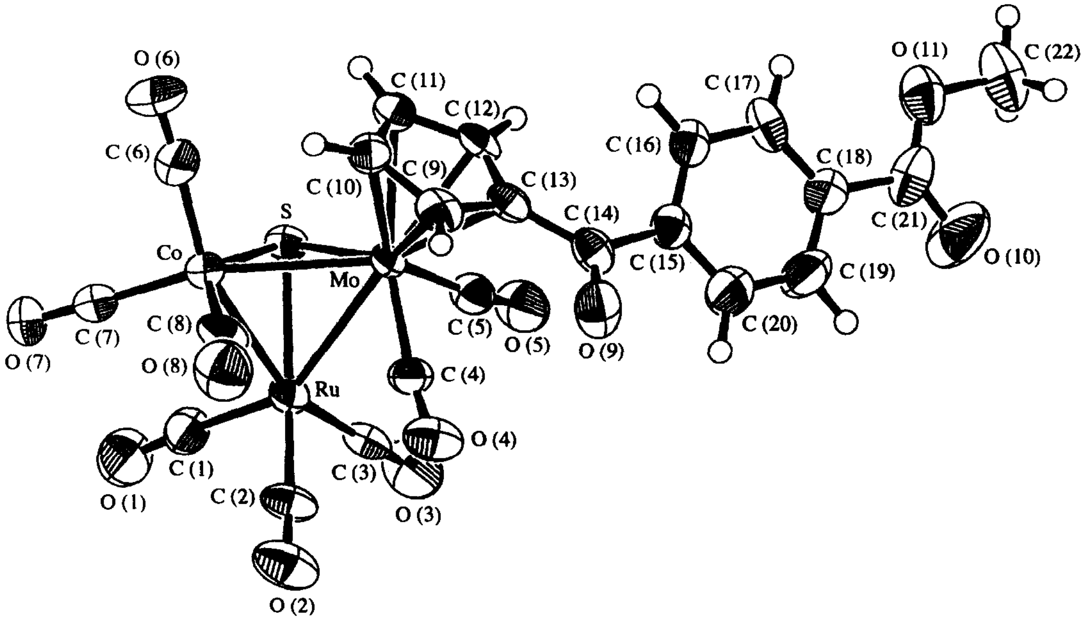


Fig. 1. Perspective view of the molecular structure of cluster **5**.

Table 1. Selected interatomic distances (Å) of cluster **5**

| | | | | | |
|---|---|---|---|---|---|
| Ru—Mo | 2.879(1) | Ru—Co | 2.631(2) | Ru—S | 2.351(3) |
| Ru—C(1) | 1.89(1) | Ru—C(2) | 1.91(1) | Ru—C(3) | 1.88(1) |
| Mo—Co | 2.747(2) | Mo—S | 2.415(3) | Mo—C(4) | 1.95(1) |
| Mo—C(5) | 2.01(1) | Mo—C(9) | 2.33(1) | Mo—C(10) | 2.38(1) |
| Mo—C(11) | 2.35(1) | Mo—C(12) | 2.28(1) | Mo—C(13) | 2.31(1) |
| Co—S | 2.190(3) | Co—C(6) | 1.80(1) | Co—C(7) | 1.80(1) |
| Co—C(8) | 1.70(1) | O(1)—C(1) | 1.15(1) | O(2)—C(2) | 1.10(1) |
| O(3)—C(3) | 1.15(1) | O(4)—C(4) | 1.17(1) | O(5)—C(5) | 1.14(1) |
| O(6)—C(6) | 1.13(2) | O(7)—C(7) | 1.13(2) | O(8)—C(8) | 1.21(1) |
| O(9)—C(14) | 1.22(1) | O(10)—C(21) | 1.20(2) | O(11)—C(21) | 1.29(2) |
| O(11)—C(22) | 1.44(2) | C(9)—C(10) | 1.43(2) | C(9)—C(13) | 1.42(2) |
| C(10)—C(11) | 1.40(2) | C(11)—C(12) | 1.40(2) | C(12)—C(13) | 1.43(2) |
| C(13)—C(14) | 1.49(2) | C(14)—C(15) | 1.49(2) | C(15)—C(16) | 1.39(2) |
| C(15)—C(20) | 1.36(2) | C(16)—C(17) | 1.38(2) | C(17)—C(18) | 1.40(2) |
| C(18)—C(19) | 1.37(2) | C(18)—C(21) | 1.50(2) | C(19)—C(20) | 1.41(2) |

Table 2. Selected bond angles (°) of cluster **5**

| | | | | | |
|---|---|---|---|---|---|
| Mo—Ru—Co | 59.60(4) | Mo—Ru—S | 53.86(8) | Mo—Ru—C(1) | 150.1(4) |
| Mo—Ru—C(2) | 109.1(4) | Mo—Ru—C(3) | 105.9(3) | Co—Ru—S | 51.79(8) |
| Co—Ru—C(1) | 94.6(4) | Co—Ru—C(2) | 109.3(4) | Co—Ru—C(3) | 155.7(3) |
| S—Ru—C(1) | 99.2(4) | S—Ru—C(2) | 158.1(4) | S—Ru—C(3) | 104.0(3) |
| Ru—Mo—Co | 55.69(5) | Ru—Mo—S | | Ru—Mo—C(4) | 69.5(4) |
| Ru—Mo—C(5) | 77.8(3) | Co—Mo—S | 49.70(8) | Co—Mo—C(4) | 97.6(4) |
| Co—Mo—C(5) | 126.9(3) | S—Mo—C(4) | 121.3(4) | S—Mo—C(5) | 82.7(4) |
| Ru—Co—Mo | 64.71(5) | Ru—Co—S | 57.50(9) | Ru—Co—C(6) | 156.4(5) |
| Ru—Co—C(7) | 93.9(4) | Ru—Co—C(8) | 86.2(5) | Mo—Co—S | 57.25(9) |
| Mo—Co—C(6) | 99.8(4) | Mo—Co—C(7) | 157.5(4) | Mo—Co—C(8) | 81.6(4) |
| S—Co—C(6) | 99.5(5) | S—Co—C(7) | 106.2(5) | S—Co—C(8) | 133.0(5) |
| Ru—S—Mo | 74.33(9) | Ru—S—Co | 70.71(9) | Mo—S—Co | 73.0(1) |
| Ru—C(1)—O(1) | 176(1) | Ru—C(2)—O(2) | 176(1) | Ru—C(3)—O(3) | 178(1) |
| Mo—C(4)—O(4) | 169(1) | Mo—C(5)—O(5) | 174(1) | Co—C(6)—O(6) | 176(1) |
| Co—C(7)—O(7) | 178(1) | Co—C(8)—O(8) | 168(1) | | |

S as a four-electron donor and the cyclopentadienyl group as a five-electron donor, cluster **5** contains a total of 48 electrons and is electronically saturated.

## EXPERIMENTAL

All reactions were performed under pure nitrogen using standard Schlenk and vacuum-line techniques. Solvents were purified, dried and distilled under nitrogen prior to use. Column chromatography was carried out by using silica gel of $\rho$ 300–400 mesh. $Co_2(CO)_8$ [14], $Ru_3(CO)_{12}$ [15] and $RC_5H_4Na$ [R = HC(O), MeC(O), $C_6H_5C(O)$, $CH_3OC(O)C_6H_4C(O)$] [16] were prepared according to the literature. IR spectra were recorded on a Nicolet F7-IR 10DX spectrophotometer; $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Am-300 MHz spectrometer; CH analyses and MS determination were performed on a 1106-type analyzer and Finnigan MAT 8430 (FAB) or HP 5985 (EI).

### *Preparation of cluster* **2**

$[RuCoMo(\mu_5S)(CO)_8C_5H_4C(O)H]$: A 50 cm$^3$ three-necked flask with a magnetic bar, a rubber tube septum and reflux condenser topped with a nitrogen inlet tube was charged with 264 mg (1.0 mmol) of $Mo(CO)_6$, 116 mg (1.0 mmol) of $NaC_5H_4C(O)H$ and 20 cm$^3$ THF. The mixture was refluxed for 12 h. Upon cooling to room temperature, 503 mg (1.0 mmol) $RuCoMo(\mu_5\text{-}S)(CO)_9$ was added and the mixture was heated to reflux for 2 h. The solvent was evaporated *in vacu.* The residue was dissolved in a minimal amount of $CH_2Cl_2$ and was subjected to chromatographic separation on a silica gel column. Elution with a mixture of hexane/$CH_2Cl_2$ (3 : 1) yielded the following bands in order of elution: a small amount of unreacted **1**, a trace of $Ru_3(CO)_{12}$ and the main black product 272.7 mg (45%). Cluster **2**. Found: C, 27.6; H, 1.0%. Calc. for $C_{14}H_5O_9Ru$ CoMoS: C, 27.8; H, 0.83%. IR (KBr disc): $\nu$(co) 2087vs, 2080vs, 2040vs, 1996vs, 1985vs, 1974vs, 1948s, 1905m, 1868s cm$^{-1}$, 1687s, (C=O) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 9.68 (s, 1H, CHO), $\delta$5.99, 5.93, 5.65, 5.59 (q, 4H, $C_5H_4$), $^{13}$C NMR ($CDCl_3$): 98.94, 95.76, 95.57, 91.40, 90.23 ($C_5H_4$); 184.70 (COH); 229.26 (t-CO) ppm. MS (FAB, Ru$^{102}$): 606 (M$^+$), 578 (M$^+$-CO), 522 (M$^+$-3CO), 494 (M$^+$-4CO), 438 (M$^+$-6CO).

### *Preparation of the cluster* **3**

$[RuCoMo(\mu_3\text{-}S)(CO)_8C_5H_4C(O)CH_3]$: To the flask described above was added 264 mg (1.0 mmol) of $Mo(CO)_6$, 130 mg (1.0 mmol) of $[NaC_5H_4C(O)CH_3]$ and 20 cm$^3$ of THF. The workup was similar to that for the preparation of cluster **2**. A black solid was obtained. Cluster **3**: m.p., 102–103°C. Found: C, 29.2; H, 1.1%. Calc. for $C_{15}H_7O_9RuCoMoS$: C, 29.0; H, 1.1%. IR (KBr disc): v (co) 2081vs, 2042vs, 2010vs, 1994vs, 1987vs, 1979vs, 1894s, 1856s cm$^{-1}$. $\nu$(C=O) 1686m cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$2.39 (s, 3H, $CH_3$), $\delta$5.50–5.95 (q, 4H, $C_5H_4$). MS (EI, Ru$^{101}$): 591 (M$^+$-CO), 423 (M$^+$-7CO), 395 (M$^+$-8CO).

### *Preparation of the cluster* **4**

$[RuCoMo(\mu_3\text{-}S)(CO)_8C_5H_4C(O)C_6H_5]$: To the flask described above were added 264 mg (1.0 mmol) of $Mo(CO)_6$, 192 mg (1.0 mmol) of $[NaC_5H_4C(O)C_6H_5]$ and 20 cm$^3$ of THF. The workup was similar to that of the preparation of cluster **2**. 220 mg (32%) of the black solid was obtained. Found: C, 35.4; H, 1.4. Calc. for $C_{20}H_9O_9RuCoMoS$: C, 35.2; H, 1.3%. IR(KBr disc): $\nu$(co) 2080vs, 2043vs, 2003vs, 1979s, 1885s cm$^{-1}$, $\nu$(C=O) 1665m cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$5.55–6.05 (4H, $C_5H_4$), $\delta$7.47–7.82 (5H, $C_6H_5$). MS (FAB, Ru$^{102}$): 682 (M$^+$), 579 (M$^+$-3CO), 459 (M$^+$-8CO).

### *Preparation of cluster* **5**

$[RuCoMo(\mu_3\text{-}S)(CO)_8C_5H_4C(O)C_6H_5C(O)OCH_3]$: To the flask described above were added 264 mg (1.0 mmol) of $Mo(CO)_6$, 239 mg (1.0 mmol) of $[NaC_5H_4C(O)C_6H_4C(O)OCH_3]$ and 20 cm$^3$ of THF. The workup was similar to that of the preparation of cluster **2**. 240 mg (33%) of the black solid was obtained. m.p. 98°C. Found: C, 35.5; H, 1.5. Calc. for $C_{22}H_{11}O_{11}RuCoMoS$: C, 35.7; H, 1.6%. IR (KBr disc): 2079vs, 2043vs, 1990vs; 1915s cm$^{-1}$. $\nu$(C=O) 1726s, 1656m cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$7.76–8.10 (q, 4H, $C_6H_4$), $\delta$5.52–5.97 (q, 4H, $C_5H_4$), $\delta$3.89 (s, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$52.55 ($CH_3$), 91.68, 93.82, 94.62, 95.15, 99.67 ($C_5H_4$); $\delta$128.19, 129.99, 133.87, 141.27 ($C_6H_4$); 166.10, 189.12 (C=O); $\delta$223.43, 229.61 (t-co).

### *The reduction of the cluster $[RuCoMoS(CO)_8C_5H_4C(O)CH_3]$*

7.6 mg (0.2 mmol) of $NaBH_4$ were added to a solution of cluster **3** (62 mg, 0.1 mmol) in 8 cm$^3$ of MeOH. The mixture was stirred at room temperature for 9 h. Solvent was removed under reduced pressure and the residue extracted with $CH_2Cl_2$, then separated on a silica gel column. 49 mg (80%) of cluster **6** as a brown-red solid was obtained. Found: C, 29.1; H, 1.4. Calc. for cluster **6**: C, 29.0; H, 1.3%. IR (Kbr disc): 3383w (OH), 2080vs, 2027vs, 1991vs, 1972vs, 1894s cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$1.43 (3H, $CH_3$), 2.10 (1H, OH), 4.63 (CH), 5.24–5.53 (4H, $C_5H_4$)

### *Crystallography of cluster* **5**

A red prismatic crystal of $RuCoMoSC_{22}H_{11}O_{11}$ was obtained from 1 : 1 hexane $CH_2Cl_2$ at −18°C. A crystal of approximate dimensions 0.20 × 0.20 × 0.30 mm$^3$

was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-$K_\alpha$ ($\lambda = 0.71069$ Å) radiation and a 12 kW rotating anode generator. A total of 3861 reflections were collected, 3570 were unique ($R_{\text{int}} = 0.029$). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 18 carefully centered reflections in the range $13.44 < 2\theta < 16.62°$ corresponded to a primitive triclinic cell with dimensions: space group $P\bar{1}$. $a = 8.174(3)$, $b = 19.45(4)$, $c = 8.04(2)$Å, $\alpha = 92.78(2)$, $\beta = 108.74(3)$, $\gamma = 88.71(3)°$, $V = 1209.5(7)$ Å$^3$, $Z = 2$, $Fw = 739.33$, $D_{\text{calc}} = 2.03$ g cm$^{-3}$, $F_{(000)} = 720.00$, $R = 0.056$, $Rw = 0.074$. The data were collected at a temperature of 20 ± 1°C using the $\omega$–$2\theta$ scan technique to a maximum $2\theta$ value of 47.0°. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. [17] The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2674 observed reflections [$I > 3.00\sigma(I)$] and 334 variable parameters and converged with unweighted and weighted agreement factor of: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.056$. $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2} = 0.074$. Neutral atoms scattering factors were taken from Cromer and Waber [18]. All calculation were performed using the TEXSAN [19] crystallographic software package of Molecular Structure Corporation.

*Acknowledgment*—This work was supported by the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry of the Chinese Academy of Sciences.

## REFERENCES

1. Johnson, B. F. G., *Transition Metal Clusters*; John Wiley and Sons, New York, 1980.
2. Shriver, D. F., Kaesz, H. D. and Adams, R. D., *The Chemistry of Metal Cluster Complexes*, VCH Publishers, Inc., New York, 1990.
3. Mingos, D. M. P. and Wales, D. J., *Introduction to Cluster Chemistry*. Prentice Hall, Englewood Cliffs, NJ, U.S.A., 1990.
4. Whitmire, K. H., *J. Coord. Chem. B* 1988, **17,** 95.
5. Adams, R. D. and Foust, D. F., *Organometallics* 1983, **2,** 323, and refs therein.
6. Adams, R. D., Babin, J. E. and Natarajan, K., *J. Am. Chem. Soc.* 1986, **108,** 3518.
7. Adams, R. D. and Hor, Ros. A., *Organometallics* 1984, **3,** 1915.
8. Wu, H. P. and Yuan, Y. Q., *Polyhedron* 1996, **1,** 43.
9. Wu, H. P., Yuan, Y. Q. and Yang, Q. C., *Inorg. Chim. Acta* 1996, **245,** 143.
10. Roland, E. and Vahrenkamp, H., *Chem. Ber.* 1984, **117,** 1039.
11. Roland, E., Bernhardt, W. and Vahrenkamp, H., *Chem. Ber.* 1986, **119,** 2566.
12. Beurich, H. and Vahrenkamp, H., *Angew. Chem., Int. Ed Engl.* 1978, **17,** 863.
13. Hoferkamp, L. A., Rhenwald, G., Stoeckli-Evans, H. and Suss-Fink, G., *Organometallics* 1996, **15,** 704.
14. King, P. B., *Organometallic Syntheses*, Vol. 1 *Transition-Metal Compounds*. New York and London, Academic Press, 1965, p. 98.
15. Bruce, M. I., Jensen, C. M. and Jones, N. L., *Inorg. Synth.* 1989, **26,** 259.
16. Seyferth, D., Hallgren, J. E. and Hung, P. L. K., *J. Organomet. Chem.* 1973, **50,** 265.
17. DIRDIF92, Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. and Smykalla, C., The DIRDIF program system. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
18. Cromer, D. T. and Waber, J. T., *International Tables for X-ray Crystallography*, Vol. IV. The Kynoch Press, Birmingham, England, 1979, Table 2.2 A.
19. *TEXSAN. Crystal Structure Analysis Package*. Molecular Structure Corporation, Texas, U.S.A. 1985 and 1992.