SHORT PAPER

J. Chem. Research (S),
2002, 194–195

Synthesis of cluster derivatives containing the NiRuMoS core[†]

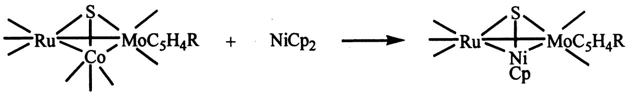
Zhi-Guo Bian,[a] Yu-Hua Zhang,[a] Bin Hu,[a] Wei-Qiang Zhang,[a] Bao-Hua Zhu,[a] Yuan-Qi Yin*[a] and Jie Sun[b]

[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

The new clusters [NiRuMo(CO)$_5$(μ_3-S)(η^5 –C$_5$H$_5$)(η^5 –C$_5$H$_4$R)](R = H **3** or COCH$_3$ **4**) were isolated from the reaction of [CoRuMo(CO)$_8$(μ_3-S) (η^5 –C$_5$H$_4$R)](R = H **1** or COCH$_3$ **2**) with NiCp$_2$, and the structure of cluster **4** has been established by single crystal X-ray diffraction method.

Keywords: cluster derivatives, NiRuMoS

The chemistry of transition metal clusters has enjoyed an exceptional growth since the mid 1970s,[1–3] especially in recent years the structural and bonding aspects of mixed-metal tetrahedral skeleton clusters have been extensively studied.[4–5] In our research group, considerable efforts have been directed to the synthesis of chiral tetrahedral clusters containing four different atoms at the verticals of the tetrahedron because the chiral cluster can induce an asymmetric catalysis potentially. Recently we have described the synthesis and structure of chiral clusters containing the core {MoRuCoS}.[6–7] Here we wish to report two other novel chiral cluster derivatives [NiRuMo(CO)$_5$(μ_3-S)(η^5 –C$_5$H$_5$)(η^5 –C$_5$H$_4$R)](R = H **3** or COCH$_3$ **4**),which have been obtained from the reaction of [CoRuMo(CO)$_8$(μ_3-S) (η^5 –C$_5$H$_4$R)])J(R = H **1** or COCH$_3$ **2**) with NiCp$_2$ in refluxing THF (Scheme 1). Both **3** and **4** are air-stable black crystals and soluble in polar solvents. Satisfactory C, H analyses were obtained for the two compounds.



1 R=H
2 R=COCH$_3$

3 R=H
4 R=COCH$_3$

Scheme 1
Synthesis of compounds **3** and **4**.

The similar spectral feature of **3** and **4** suggest that they have the same configuration. The IR spectra of **3** and **4** show intense terminal carbonyl absorption bands in the range 1915–2072 cm^{-1} and in the IR spectrum of **4** show one additional absorption band at 1666.6 cm^{-1} for the ketonic carbonyl. The ^{1}H NMR spectra of **3** and **4** show one single peak at δ 5.33ppm and δ 5.35ppm, respectively, assigned to the protons on the cyclopentadienyl ring attached to the Ni atom. In addition, the ^{1}H spectrum of **3** shows one singlet at δ5.48ppm for the cyclopentadienyl protons attached to the Mo atom, however, that of **4** exhibits one multiplet at δ 5.54–6.01ppm because of electron-withdrawing effect of acetyl group and a singlet at δ2.37ppm for the methyl group.

In order to unambiguously conform the structure of cluster **4**, an X-ray diffraction analysis was undertaken. The molecular structure of **4** is shown in Fig.l. As shown in Fig.1, cluster **4** consists of a distorted tetrahedral core {MoNiRuS}, which carries two carbonyl on the Mo atom, three on the Ru atom, one cyclopentadienyl ligand attached to the Ni atom, and one cyclopentadienyl ligand coordinated to the Mo atom. The distance from Mo atom to the centroid of the cyclopentadienyl ring denoted as Mo–Cp$_{\text{cent}}$ (1.9914 Å) is longer than the Ni–Cp$_{\text{cent}}$ (l.7178 Å) distance. The acute angles in the tetrahedral core of cluster **4** about the basal atoms range from 49.86° to 66.19°, and those about the sulfur atom average 72.25°, which deviate considerably from perfect tetrahedral geometry. This is due to the metal–metal bonded RuNiMo triangle restricting the angles around the sulfur atom.

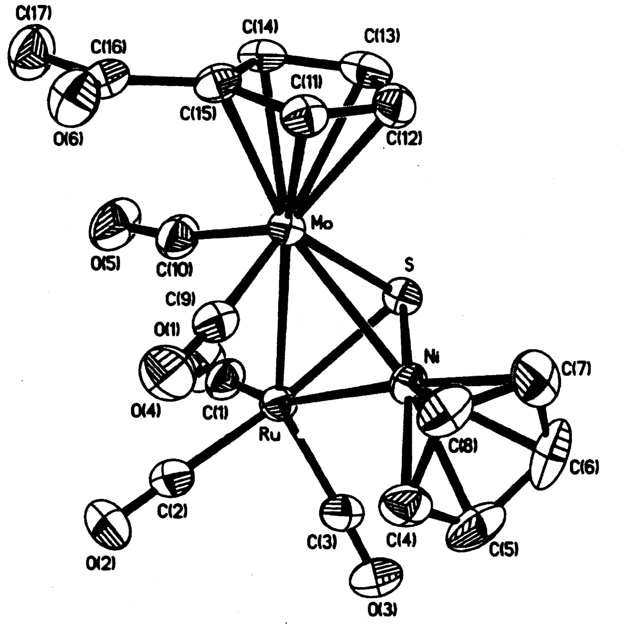


Fig. 1 Crystal structure of the cluster **4**. Selected bond distances (Å) and angles (°):Ru-S 2.3138(13), Ru-Mo 2.8498(6), Ru-Ni 2.5699(8), Mo-S 2.3819(13), Mo-Ni 2.6479(7), Ni-S 2.1337(14), Ni-C$_{CP}$ 2.088, Mo-C$_{CP}$ 2.328, S-Mo-Ni 49.86(3), S-Mo-Ru 51.55(3), Ni-Mo-Ru 55.592(18), S-Ni-Ru 58.05(4), S-Ni-Mo 58.58(4), Ru-Ni-Mo 66.19(2), S-Ru-Ni 51.49(4), S-Ru-Mo 53.73(3), Ni-Ru-Mo 58.218(19), Ni-S-Ru 70.46(4), Ni-S-Mo 71.56(4), Ru-S-Mo 74.72(4)

Experimental

All reactions were carried out under a highly pure nitrogen atmosphere using standard Schlenk and vacuum techniques. Petroleum ether was distilled over sodium-benzophenone while CH$_2$Cl$_2$ was dis-

---

* To receive any correspondence. E-mail: hcom@ns.lzb.ac.cn
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

tilled over CaH_2 Column chromatography was carried out using 160-200 mesh silica gel. Compound $Mo(CO)_6$ were purchased from Fluka Chem.Co. Compounds **1** and **2** were prepared according to literature methods.[6] IR spectra were recorded on a Nicolet FT-IR 10 DX spectrometer; ^1H NMR spectra on a Bruker AM-400 MHz spectrometer; analyses(C, H) were performed on an 1106-type analyser.

Preparation of **3**: The cluster **1** (260 mg, 0.45 mmol) and $NiCp_2$ (200 mg, 1.06 mmol) were dissolved in THF (25 ml). The mixture was refluxed for 18 h. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (5 ml). Then the extract was subjected to column chromatographic separation using 1:10 CH_2Cl_2/petroleum ether as eluent. Several small bands with a major one were developed. From the main black band was obtained **3** 40 mg (16.0%) as a black solid. (Calc. for $C_{15}H_{10}O_5MoNiRuS$: C, 32.28; H, 1.81; Found: C, 32.26; H, 1.80). IR (KBr disk): 2048.5vs, 2027.3s, 1975.2vs, 1915.4s, 1859.5s ($C \equiv O$). δ_H ($CDCl_3$): 5.33(s, 5H,C_5H_5), 5.48(s, 5H C_5H_5).

Preparation of **4**: The cluster **2** (450 mg, 0.73 mmol) and $NiCp_2$ (200 mg, 1.06 mmol) were dissolved in THF (25 ml). After the mixture was refluxed for 30 h, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (5 ml). Then the extracts were subjected to column chromatographic separation using 1:2 CH_2Cl_2/petroleum ether as eluent. Several small bands with a major one were developed. From the main black band was obtained **4** 110 mg (25.0%) as a black solid. (Calc. for $C_{17}H_{12}O_6MoNiRuS$: C, 34.03; H, 2.02; Found: C, 34.05; H, 2.02), IR (KBr disk): 2071.7vs, 2010.0s, 1986.8vs, 1930.9s, 1871.ls ($C \equiv O$), 1666.6s ($C = O$). δ_H($CDCl_3$): 5.35 (s, 5H, C_5H_5), 5.54–6.01 (t, 5H, C_5H_4), 2.37 (s,3H, CH_3).

Crystal data for **4**: A crystal of compound **4** $C_{17}H_{12}O_6MoNiRuS$, Mr = 600.05) was grown from a C_6H_{14}-CH_2Cl_2 solution. The space group was P-1. The cell parameters were determined on a Rigaku AFC 7R diffractometer with graphite-monochromated Mo-Kα radiation: $a = 7.9606(8)$, $b = 8.5604(9)$, $c = 14.7793(16)$ Å, $\beta = 105.057(2)°$, $Z = 2$, $V = 945.51(17)A^{-3}$, $D_c = 2.108 gcm^{-3}$, $\mu = 2.568 mm^{-1}$, $2\theta = 56.48°$ and $F(000) = 584$. Of the 5809 reflections collected, 5194 were unique ($R_{int} = 0.0498$). The intensities of three representative reflections were measured every 200. The final cycle of full-matrix least-squares refined was based on 4192 observed reflections [$I > 2.00\sigma(I)$] and 292 variable parameters and converged at final $R = 0.0380$, $Rw = 0.0674$. Minimum and maximum final electron densities were –0.542 and $0.874 eÅ^{-3}$. The calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

We are grateful to the National Natural Science Foundation of China for financial support.

Received 23 July 2001; accepted 6 November 2001
Paper 01/993

References

1 H. Vahrenkamp, *Adv. Organomet. Chem.*, 1983, **22**, 169.
2 F.G.A. Stone, *Angew. Chem. Int. Engl.,* 1984, **23**, 89.
3 M.L. Ziegler and H.P. Neumann, *Chem. Ber.*, 1989, **112**, 115.
4 T. Albiez, H. Bantel, H. Vahrenkamp, *Chem. Ber.*, 1990, **123**, 1805.
5 R.C. Lin, Y. Chi, S.M. Peng and G.H. Li, *Inorg. Chem.*, 1992, **31**, 3818.
6 E.R. Ding, S.L.Wu, C.G. Xia and Y.Q. Yin, *J. Organomet. Chem.,* 1998, **568**, 157.
7 E.R. Ding, Q.S.Li, Y.Q.Yin and J. Sun, *J. Chem. Res.*, 1998, 624.