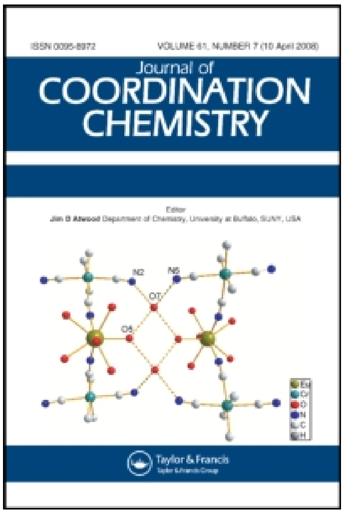

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PREPARATION AND CHARACTERIZATION OF CLUSTERS CONTAINING THE MNiRuS (M = Mo OR W) CORE

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Three chiral derivatives (μ_3-S)NiRuM(CO)$_5$(η^5-C$_5$H$_5$)[η^5-C$_5$H$_4$C(O)H] (**1**, M = Mo; **2**, M = W) and {(μ_3-S)RuNiMo(CO)$_5$(η^5-C$_5$H$_5$)[η^5-C$_5$H$_4$C(O)]}$_2$-1,4-C$_6$H$_4$ (**3**) were synthesized by the thermal reactions of (μ_3-S)CoRuM(CO)$_8$[η^5-C$_5$H$_4$C(O)H] (M = Mo; W), {(μ_3-S)RuCoMo(CO)$_8$[η^5-C$_5$H$_4$C(O)]}$_2$-1,4-C$_6$H$_4$ with NiCp$_2$ in THF at reflux. Further reactions of clusters **1** and **2** with 2,4-dinitrophenylhydrazine catalyzed by 98% H$_2$SO$_4$ gave two novel clusters **4** and **5**. The results show that the metal fragment Co(CO)$_3$ in (μ_3-S)CoRuM(CO)$_8$[η^5-C$_5$H$_4$C(O)H] could be exchanged by NiCp. These complexes were characterized by elemental analysis, IR and ^{1}H NMR spectra. The molecular structure of compound **1** was determined by single-crystal X-ray diffraction. The crystals of cluster **1** are triclinic with space group $P\bar{1}$, $a = 7.641(3)$, $b = 8.819(4)$, $c = 15.097(7)$ Å, empirical formula C$_{16}$H$_{10}$MoNiO$_6$RuS, $M_r = 586.02$ g mol^{-1}, $Z = 2$, $D_c = 2.123$ g cm^{-3}, $\mu = 2.646$ mm^{-1}, final $R = 0.0275$, $R_w = 0.0693$.

Keywords: Synthesis; Metal exchange; Chiral cluster; Crystal structure

INTRODUCTION

In recent years routes to hetero-metal transition metal clusters have advanced from the age of serendipity into the era of logical, controlled syntheses with some degree of mechanistic understanding [1–4]. A large number of hetero-metal clusters have been synthesized; furthermore, the chemistry of chiral tetrahedral hetero-metal clusters is of growing interest [5]. A motivation for preparing skeleton chiral clusters was to provide unambiguous evidence for cluster catalysis through asymmetric induction [6]. The pioneering work of Vahrenkamp, provided proof of the concept [7].

In our research group considerable efforts have been directed to the synthesis of chiral tetrahedral clusters containing four different atoms or groups at the vertices of the tetrahedron. Recently we have described the synthesis and structure of some

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chiral clusters containing the core MoRuCoS [5f,8]. In this article we report novel chiral clusters containing the SRuNiMo core.

EXPERIMENTAL

General Procedure and Material

All reactions were carried out under nitrogen of high purity using standard Schlenk vacuum techniques. All solvents were dried according to standard procedure before use. Chromatographic separations and purifications were performed on 160–200 mesh silica gel. (μ_3-S)CoRuM$(CO)_8$[η^5-$C_5H_4C(O)H$] (M = Mo, W) [5f] and $NiCp_2$ [9] were prepared according to published methods.

IR spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer, and ^{1}H NMR spectra on a Bruker-AM 400 MHz spectrometer; C/H determinations were performed using a Carlo-Erba 1160 instrument.

General Procedure for Preparing Complexes 1, 2 and 3

The cluster (μ_3-S)CoRuMo$(CO)_8$[η^5-$C_5H_4C(O)H$] (100 mg, 0.17 mmol) and $NiCp_2$ (50 mg, 0.26 mmol) were dissolved in THF (25 cm^3). The mixture was refluxed for 12 h, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (5 cm^3). Then the extracts were subjected to column chromatographic separation using 1 : 2 CH_2Cl_2/petroleum ether as eluent. Several small bands with one major one were developed. From the main black band 70 mg (72.2%) of (μ_3-S)NiRuMo$(CO)_5$(η^5-C_5H_5)[η^5-$C_5H_4C(O)H$] (**1**) was obtained as a black solid. Anal. Calcd. for $C_{16}H_{10}O_6MoNiRuS$(%): C, 32.79; H, 1.72. Found: C, 32.86; H, 1.78. IR (νCO): 2056vs, 1979vs, 1924s, 1822s, (C=O) 1681 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.61 (s, 1H, COH), 6.05–5.62 (m, 4H, C_5H_4), 5.38 (s, 5H, C_5H_5).

2: Yield 26.3%. Anal. Calcd. for $C_{16}H_{10}O_6WNiRuS$(%): C, 28.51; H, 1.50. Found: C, 28.48; H, 1.52. IR (KBr): (νCO) 2054vs, 1977vs, 1923s, 1815s, (C=O) 1678s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.61 (s, 1H, COH), 6.02–5.69 (m, 4H, C_5H_4), 5.44 (s, 5H, C_5H_5).

3: Yield 34.8%. Anal. Calcd. for $C_{38}H_{22}O_{12}Mo_2Ni_2Ru_2S_2$(%): C, 36.62; H, 1.78. Found: C, 36.74; H, 1.72. IR (KBr): IR (νCO) 2083w, 2058vs, 1977vs, 1934w, 1890s, (C=O) 1646m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.87 (s, 4H, C_6H_4), 6.13–5.62 (q, 8H, $2C_5H_4$), 5.32 (s, 10H, $2C_5H_5$).

General Procedure for Preparing Complexes 4 and 5

2,4-Dinitrophenylhydrazine solution (1.0 cm^3), prepared by dissolving 2,4-dinitrophenylhydrazine (500 mg) in 98% H_2SO_4 (2.5 cm^3), H_2O (5 cm^3) and ethanol (17.5 cm^3), was added to an ethanol solution (15 cm^3) in which cluster **1** (30 mg, 0.05 mmol) was dissolved. The mixture was treated at room temperature for 1 h, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (5 cm^3). Then the extracts were subjected to silica-gel column chromatography using 1 : 1 CH_2Cl_2/petroleum ether as eluent. Several small bands with a major brown one were developed. From the main brown band was obtained 25 mg, (65.8%) of cluster **4** as a brown solid. Anal. Calcd. for $C_{22}H_{14}O_9N_4MoNiRuS$(%): C, 34.49; H, 1.84; N, 7.31. Found: C, 34.54; H, 1.88; N, 7.25. IR (KBr): 2058vs, 1972vs, 1981vs, 1850m, 1614s (C=N) and 1584s (NO_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.24 (s, 1H, N–H), 9.15 (s, 1H, H^3 of benzene ring), 8.38–8.36 (d, 1H, H^5 of benzene ring, $J = 8.24$ Hz), 7.96–7.93 (d, 1H, H^6 of benzene ring, $J = 9.36$), 7.81 (s, 1H, H–C=N), 6.02–5.58 (q, 4H, C_5H_4), 5.36 (s, 5H, C_5H_5).

5: Yield 81.4%. Anal. Calcd. for $C_{22}H_{14}O_9N_4WNiRuS$(%): C, 30.94; H, 1.65; N, 6.56. Found: C, 30.88; H, 1.68; N, 6.60. IR (KBr): 2056vs, 1985vs, 1968m, 1939m, 1846m, 1615s (C=N) and 1586m (NO_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.27 (s, 1H, N–H), 9.15 (s, 1H, H^3 of benzene ring), 8.37 (d, 1H, H^5 of benzene ring), 7.95–7.92 (d, 1H, H^6 of benzene ring), 7.80 (s, 1H, H–C=N), 6.03–5.63 (q, 4H, C_5H_4), 5.43 (s, 5H, C_5H_5).

X-ray Crystallography of Cluster 1

The black crystals used for X-ray determination were obtained from a hexane/CH_2Cl_2 solution at −20°C. Preliminary examination and data collection were performed with Mo Kα ($\lambda = 0.71073$ Å) radiation on a CCD area detector equipped with a graphite monochromator. Data were collected by the ω/ϕ scan technique. The structures were solved by the direct method using the SHELXS-97 program and refined by the full-matrix least-squares method on F^2 using the SHELXS-97 program [10]. The non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated by geometrical methods. Crystal data and experimental details are collected in Table I.

TABLE I Crystallographic data and structure refinement for Cluster **1**

Cluster	***1***
Empirical formula	$C_{16}H_{10}MoNiO_6RuS$
Formula weight	586.02
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.641(3)
b (Å)	8.819(4)
c (Å)	15.097(7)
α (°)	97.706(7)
β (°)	93.969(6)
γ (°)	113.401(6)
Volume (Å^3)	916.8(7)
Z	2
Calculated density (Mg/m^3)	2.123
Absorption coefficient (mm^{-1})	2.646
F(000)	568
θ range for data collection (°)	2.56 to 25.02
Limiting indices	$-9 \leq h \leq 9$, $-10 \leq k \leq 5$, $-17 \leq l \leq 17$
Reflections collected	3830
Independent reflections	3216 ($R_{int} = 0.0156$)
Completeness to θ (°)	99.4% ($\theta = 25.02$)
Data/restraints/parameters	3216/0/235
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R1=0.0275$, $wR2 = 0.0693$
Largest diff. Peak and hole (e Å^{-3})	0.913 and −0.466

RESULTS AND DISCUSSION

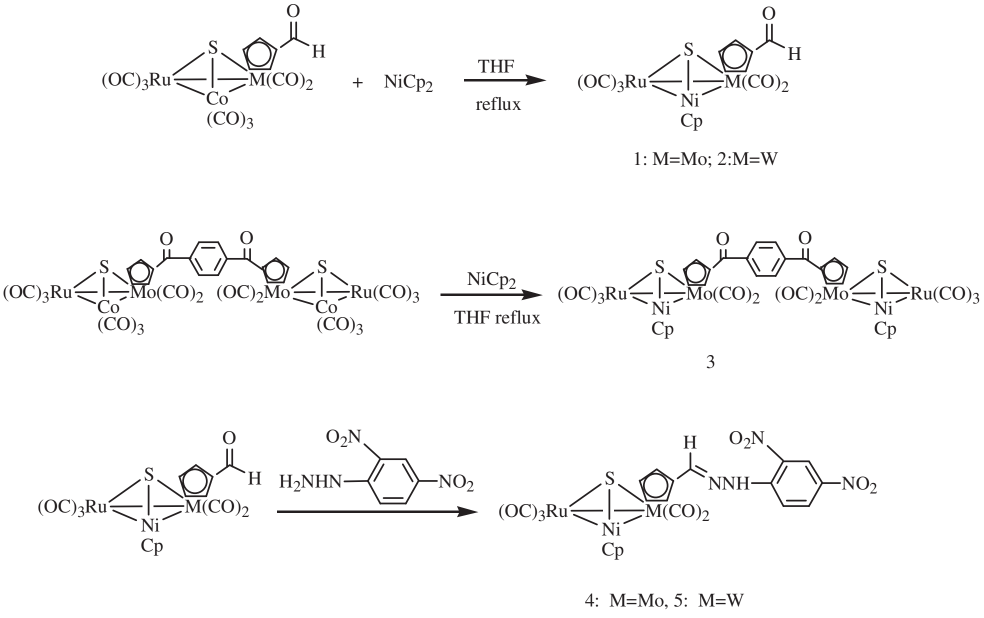
Preparation

The reactions described in this work are summarized in Scheme 1. When $NiCp_2$ was treated with $(\mu_3\text{-}S)CoRuM(CO)_8[\eta^5\text{-}C_5H_4C(O)H]$ (M = Mo, W) and $\{(\mu_3\text{-}S)RuCoMo\text{-}(CO)_8[\eta^5\text{-}C_5H_4C(O)]\}_2\text{-}1,4\text{-}C_6H_4$ in THF refluxing for 10–15 h, the expected Clusters **1**–**3** were obtained in yields of 26–72%. Further reactions of **1** and **2** with 2,4-dinitrophenylhydrazine in ethanol at room temperature catalyzed by 98% H_2SO_4 gave two novel clusters, **4** and **5**, in yields of 65–82%.

It is well known that the d^9 ML_3 metal fragment $Co(CO)_3$ can be displaced by isolobal fragments $Cp^*(CO)_2M$ (Cp^* = Cp or functionally substituted Cp; M = Mo, W) and NiCp in isolobal displacement reactions [5,11]. However, no products derived from isolobal displacement of the fragment $Cp(CO)_2M$ by $\eta^5\text{-}C_5H_5Ni$ were found under such conditions. This result suggests that the isolobal fragment $Co(CO)_3$ is a much better leaving group than $\eta^5\text{-}C_5H_4M(CO)_2$ in such reaction conditions.

Characterization

These clusters are air-stable black or brown solids. The elemental analyses, IR and ^1H NMR spectra are consistent with their expected structures. In the IR spectra, all showed terminal carbonyl absorption bands in the range 2090–1920 cm^{-1} and bridging or semi-bridging carbonyl bands between 1900 and 1800 cm^{-1}. The IR spectra of **1**–**3** showed a ketone carbonyl absorption band between 1640 and 1681 cm^{-1}, and those of **4** and **5** showed an absorption band around 1614 cm^{-1} for C=N stretching. The absorption bands around 1585 cm^{-1} in the spectra of **4** and **5** are characteristic for nitro groups bound to the benzene ring.



1: M=Mo; 2:M=W

3

4: M=Mo, 5: M=W

SCHEME 1.

The ^{1}H NMR spectra of all clusters showed the presence of hydrogen atoms in their corresponding organic group. For the substituted cyclopentadienyl, the ^{1}H NMR spectra of all clusters exhibit two doublets in the range δ 6.13–5.58, with the upfield doublet assigned to the two protons at the 3,4-positions of the substituted cyclopentadienyl rings and the other assigned to the 2,5-protons, resulting from the different deshielding effects of the electron-withdrawing groups C=O and C=N on these nuclei. In ^{1}H NMR spectra of **1** and **2**, the singlet at δ 9.61 arises from the proton resonance of CHO. The ^{1}H NMR spectrum of **3** shows a singlet at δ 7.87 assigned to the protons in the C_6H_4 unit. For the hydrazone cluster complexes **4** and **5**, the singlet around δ 7.81 was assigned to the proton in the N=CH unit, and a quartet in the range δ 9.15–7.92 was assigned to the protons in the C_6H_3 unit, and the singlet around δ 11.20 at the downfield side is the proton signal of the N–NH unit, which is in agreement with the literature value [12].

X-ray Crystal Structure Analysis

The final atomic coordinates and thermal parameters of the non-hydrogen atoms for Cluster **1** are given in Table II. Selected bond lengths and angles are listed in Table III. The molecular structure of Cluster **1** is presented in Fig. 1. As can be seen from Fig. 1, the structure of Cluster **1** contains a slightly distorted tetrahedral core NiMoRuS, which carries two carbonyl groups on Mo, three carbonyl groups on Ru, one cyclopentadienyl ligand attached to the Ni atom, and one substituted cyclopentadienyl ligand coordinated to the Mo atom. The bond lengths and angles involving the cluster core

TABLE II Atomic coordinates and equivalent isotropic displacement parameters for Cluster **1**

Atom	*x*	*y*	*x*	*U*(*eq*)
Mo(1)	2246(1)	7541(1)	8273(1)	36(1)
Ni(1)	3022(1)	6814(1)	6616(1)	37(1)
Ru(1)	2187(1)	9369(1)	6851(1)	40(1)
S(1)	219(1)	6596(1)	6873(1)	38(1)
C(1)	4711(7)	11 206(6)	7021(3)	57(1)
O(1)	6205(6)	12 219(5)	7084(3)	96(1)
C(2)	1788(7)	9239(6)	5585(3)	59(1)
O(2)	1556(7)	9128(6)	4825(2)	91(1)
C(3)	783(7)	10 726(6)	7115(3)	53(1)
O(3)	−30(6)	11 535(5)	7262(3)	82(1)
C(4)	2432(7)	9829(6)	8641(3)	54(1)
O(4)	2556(7)	11 097(5)	9031(2)	82(1)
C(5)	5082(7)	8632(6)	8244(3)	50(1)
O(5)	6714(5)	9287(5)	8330(2)	72(1)
C(6)	−1744(9)	6536(9)	9184(4)	74(2)
O(6)	−3264(6)	5553(7)	8767(3)	98(2)
C(7)	30(6)	6284(6)	9200(3)	47(1)
C(8)	1824(8)	7305(7)	9761(3)	66(1)
C(9)	3148(7)	6625(7)	9552(3)	63(1)
C(10)	2230(7)	5215(6)	8887(3)	56(1)
C(11)	342(6)	4989(5)	8668(3)	46(1)
C(12)	3240(11)	4622(7)	6048(6)	90(2)
C(13)	4960(12)	5714(12)	6594(4)	94(2)
C(14)	5661(8)	7165(9)	6224(5)	87(2)
C(15)	4461(12)	6956(11)	5479(5)	90(2)
C(16)	2990(10)	5438(11)	5379(4)	90(2)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Selected bond distances (Å) and angles (°) for Cluster **1**

Mo(1)–S(1)	2.3681(13)	Mo(1)–C(4)	1.965(5)
Mo(1)–Ni(1)	2.6645(12)	Mo(1)–C(5)	1.998(5)
Mo(1)–Ru(1)	2.8607(10)	C(4)–O(4)	1.156(5)
Ni(1)–S(1)	2.1407(14)	C(5)–O(5)	1.136(5)
Ni(1)–Ru(1)	2.5624(11)	C(6)–O(6)	1.204(7)
Ru(1)–S(1)	2.3134(14)	C(6)–C(7)	1.458(7)
C(10)–C(11)	1.385(6)	C(9)–C(10)	1.386(7)
C(12)–C(16)	1.360(10)	Ru(1)–C(2)	1.895(5)
C(12)–C(13)	1.402(10)	Ru(1)–C(3)	1.922(5)
Ni(1)–Ru(1)–Mo(1)	58.55(2)	S(1)–Mo(1)–Ni(1)	49.92(4)
Ni(1)–S(1)–Ru(1)	70.12(4)	S(1)–Mo(1)–Ru(1)	51.47(3)
Ni(1)–S(1)–Mo(1)	72.25(4)	Ni(1)–Mo(1)–Ru(1)	55.12(3)
Ru(1)–S(1)–Mo(1)	75.32(3)	S(1)–Ni(1)–Ru(1)	58.11(3)
S(1)–Ru(1)–Mo(1)	53.20(3)	S(1)–Ni(1)–Mo(1)	57.83(3)
S(1)–Ru(1)–Ni(1)	51.78(4)	Ru(1)–Ni(1)–Mo(1)	66.331(17)
C(4)–Mo(1)–C(5)	85.8(2)	C(4)–Mo(1)–Ru(1)	63.81(13)

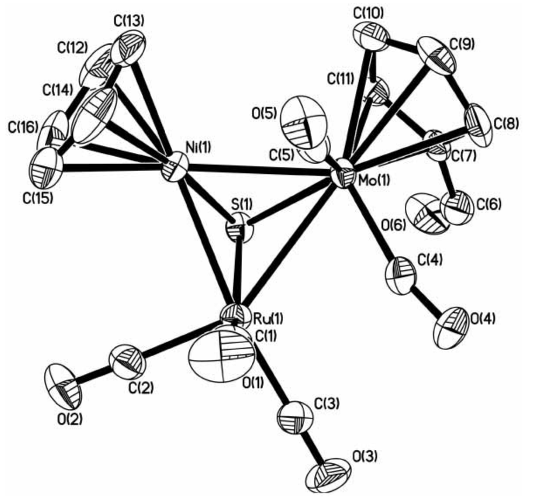


FIGURE 1 Crystal structure of Cluster **1**.

are very close to those in the analog [13]. The acute angles in the tetrahedral geometry of Cluster **1** about the basal atoms range from 49.92 to 58.55° and those about the sulfur atom average 72.56°, which deviates considerably from perfect tetrahedral geometry. Cluster **1** contains a total of 48 electrons and is electronically saturated. It should be pointed out that the carbonyl of C(4)–O(4) bound to the Mo atom is semi-bridging, owing to its asymmetric parameter $\alpha = (d_2 - d_1)/d_1 = 0.35$ [$d_2 =$ Ru···C(4) = 2.6613 Å, $d_1 =$ Mo–C(4) = 1.965 Å] falling in the range of α values defined for semi-bridging carbonyls by Curtis [14].

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