Notes

An Extraordinary Example of Metalloselectivity. Extraction of Copper from the Mixed-Metal Cluster $Cu_2Ru_6(CO)_{16}(\mu_6\text{-}C)(NCMe)_2$ by 1,5,9-Trithiacyclododecane

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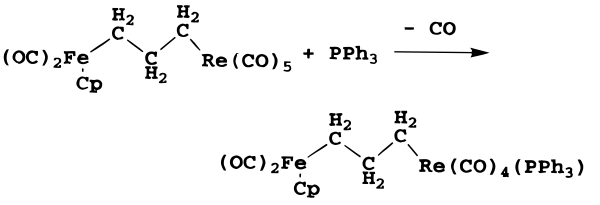
*Summary: The reaction of $Cu_2Ru_6(CO)_{16}(\mu_6\text{-}C)(NCMe)_2$, **1**, with the thiacrown ether 1,5,9-trithiacyclododecane (12S3) resulted in the extraction of both copper atoms from the ruthenium cluster complex by the thiacrown and formation of the salt $[Cu(\eta^3\text{-}12S3)(\eta^1\text{-}12S3)]_2[Ru_6(CO)_{16}(\mu_6\text{-}C)]$, **2**, in 56% yield. Compound **2** was characterized by a single-crystal X-ray diffraction analysis. The structures of the ions are similar to those found in previously reported salts.*

Introduction

Metalloselectivity is a term that is used to describe coordination preferences of a ligand for one type of metal relative to that of another when two or more types of metals are present in a polynuclear metal complex.[1] For example, the product obtained from the reaction of $Cp(CO)_2Fe(CH_2)_3Re(CO)_5$ with PPh_3 has the phosphine ligand substituted exclusively at the rhenium atom.[1a]



1)

We have recently discovered new routes to the formation of certain polythioether macrocycles (thiacrown ethers).[2] Thiacrown ethers are of interest because of there ability to bind effectively to heavy transition metal ions.[3] We and others have shown that they also bind effectively to ruthenium carbonyl cluster complexes.[4] In further studies of these reactions, we have investigated the reaction of the mixed-metal cluster complex $Cu_2Ru_6(CO)_{16}(\mu_6\text{-}C)(NCMe)_2$, **1**, with the thiacrown ether 1,5,9-trithiacyclododecane (12S3). The product $[Cu(\eta^3\text{-}12S3)(\eta^1\text{-}12S3)]_2[Ru_6(CO)_{16}(\mu_6\text{-}C)]$, **2**, was formed by a selective attack of the thioether at the copper atoms in a process that resulted in the complete extraction of both copper atoms from the original ruthenium cluster. These results are reported here.

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. All reactions were performed under a nitrogen atmosphere. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM-300 FT-NMR spectrometer. $Cu_2Ru_6(CO)_{16}(\mu_6\text{-}C)(NCMe)_2$, **1**, was prepared by the published procedure.[5] 1,5,9-Trithiacyclododecane, 12S3, was prepared by our recently reported procedure for the catalytic cyclooligomerization of thietane.[2c] Elemental analysis was performed by Oneida Research Services, Whitesboro, NY.

Preparation of $[Cu(\eta^3\text{-}12S3)(\eta^1\text{-}12S3)]_2[Ru_6(CO)_{16}(\mu_6\text{-}C)]$, 2. A 25-mg amount of **1** (0.020 mmol) was dissolved in 25 mL of CH_2Cl_2, and a 22-mg amount of 12S3 in 15 mL of CH_2Cl_2 was added. The color of the solution immediately changed from orange to a dark red. After the solution was stirred at 25 °C for 20 min, the solvent volume was reduced to approximately 15 mL and 30 mL of hexanes was added. A red precipitate formed and was filtered under nitrogen. The precipitate was washed with 30 mL of hexanes. The product can be recrystallized by dissolving in CH_2Cl_2 and precipating by the addition of hexane. This yielded 23.0 mg of $[Cu(\eta^3\text{-}12S3)(\eta^1\text{-}12S3)]_2[Ru_6(CO)_{16}(\mu_6\text{-}C)]$, **2**, in 56% yield. Analytical and spectral data for **2** are as follows. IR (ν_{CO} (cm^{-1}) in CH_2Cl_2): 2052 (w), 2005 (s), 1996 (s, sh), 1978 (m, sh), 1924 (w, br), 1810 (w, br). ^1H NMR (δ in CD_2Cl_2 at 25 °C): 2.81 (s, br, 48H), 1.99 (s, br, 24H). ^1H NMR (δ in CD_2Cl_2 at −78 °C): 2.94 (t, br, 8H), 2.85 (t, br, 8H), 2.7 (m, 8H), 2.61 (s, br, 24H), 2.23 (m, 1H), 1.98 (m, 1H), 1.82 (m, 8H), 1.77 (t, 24H). Anal. Calcd (found): C, 30.55 (30.94); H, 3.48 (3.44).

Crystallographic Analyses. Crystals of **2** suitable for diffraction analysis were grown by slow evaporation of solvent

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Table 1. Crystallographic Data for Compound 2

empirical formula	$Ru_6Cu_2S_{12}O_{16}C_{53}H_{72}$
fw	2083.37
cryst system	monoclinic
lattice params	
a (Å)	16.437(3)
b (Å)	21.947(5)
c (Å)	20.690(3)
α (deg)	90.0
β (deg)	94.30(1)
γ (deg)	90.0
V (Å^3)	7443(2)
space group	$P2_1/c$ (No. 14)
Z value	4
D_{calc} (g/cm^3)	1.86
μ(Mo Kα) cm^{-1}	21.4
temp (°C)	20
$2\theta_{max}$ (deg)	45.0
no. observns. used ($I > 3\sigma(I)$)	6182
no. variables	802
residuals: *R*; R_w[a]	0.034; 0.032
goodness of fit indicator[a]	1.55
max shift/error on final cycle	0.12
largest peak in final diff map (e/Å^3)	0.55
abs cor; max/min	empirical; 1.00/0.81

[a] $R = \sum_{hkl}(||F_o| - |F_c||)/\sum_{hkl}|F_o|$; $R_w = [\sum_{hkl}w(|F_o| - |F_c|^2)/\sum_{hkl}wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$; GOF $= [\sum_{hkl}[w(|F_o| - |F_c|)]^2/(n_{data} - n_{vari})]^{1/2}$.

from a solution in a CH_2Cl_2/hexane (2/1) solvent mixture at 25 °C. The crystal used for data collection was mounted in thin-walled glass capillary. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. The unit cell was determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed on a Digital Equipment Corp. Vaxstation 3520 computer with use of the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz–polarization (*Lp*) and absorption corrections were applied. Neutral atom scattering factors were calculated by the standard procedures.[6a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[6b] Full matrix least-squares refinements minimized the following function: $\sum_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}Lp$.

Compound **2** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely on the basis of the patterns of systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were calculated using idealized geometries with C–H = 0.95 Å. The scattering contributions of the hydrogen atoms were included in the structure factor calculations, but their positions were not refined. The thermal parameters on the carbon atoms of one of the four 12S3 ligands, C(99)–C(105), exhibited slightly larger than normal values. This might be due to some minor disorder for these atoms in that ring.

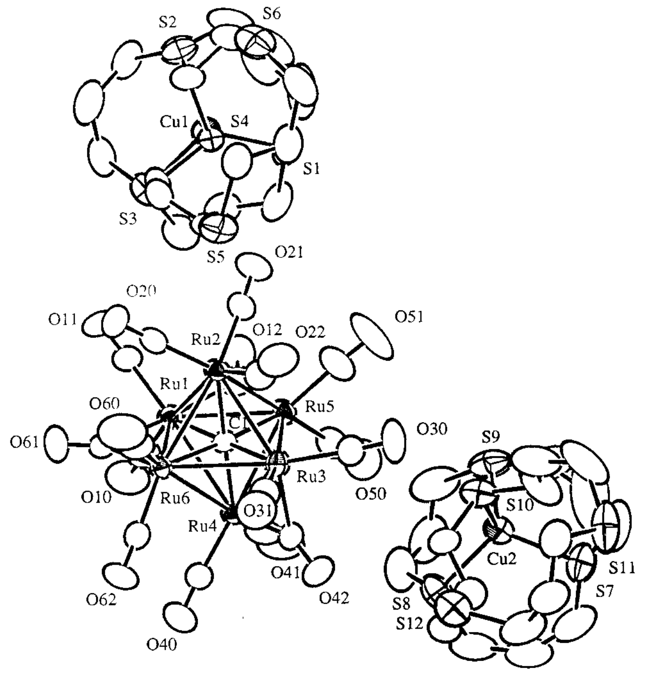


Figure 1. ORTEP diagram of $[Cu(\eta^3\text{-12S3})(\eta^1\text{-12S3})]_2[Ru_6(CO)_{16}(\mu_6\text{-C})]$, **2**, showing 40% probability thermal ellipsoids.

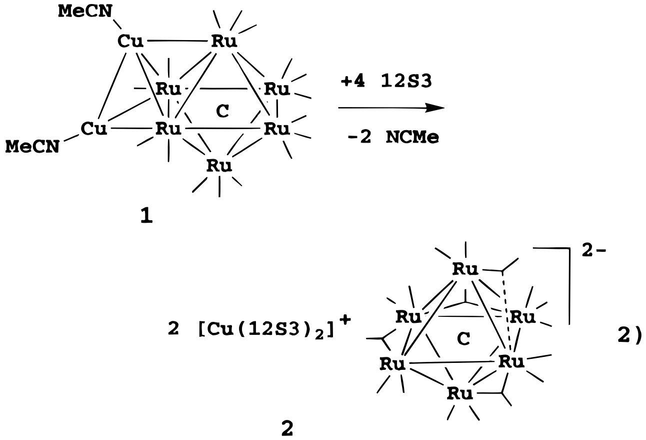
Table 2. Intramolecular Distances for 2[a]

Ru(1)–Ru(2)	2.8755(8)	Ru(4)–Ru(5)	2.8994(9)
Ru(1)–Ru(4)	2.9891(8)	Ru(4)–Ru(6)	2.9064(9)
Ru(1)–Ru(5)	2.8480(8)	Ru(4)–C(1)	2.024(7)
Ru(1)–Ru(6)	2.8377(8)	Ru(5)–C(1)	2.037(7)
Ru(1)–C(1)	2.057(7)	Ru(6)–C(1)	2.040(7)
Ru(2)–Ru(3)	2.882(1)	Cu(1)–S(1)	2.267(3)
Ru(2)–Ru(5)	2.8836(9)	Cu(1)–S(2)	2.269(3)
Ru(2)–Ru(6)	2.8638(9)	Cu(1)–S(3)	2.266(3)
Ru(2)–C(1)	2.066(7)	Cu(1)–S(4)	2.333(2)
Ru(3)–Ru(4)	2.8359(9)	Cu(2)–S(7)	2.236(3)
Ru(3)–Ru(5)	2.9502(9)	Cu(2)–S(8)	2.262(3)
Ru(3)–Ru(6)	2.927(1)	Cu(2)–S(9)	2.265(3)
Ru(3)–C(1)	2.046(7)	Cu(2)–S(10)	2.315(3)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Results and Discussion

The reaction of $Cu_2Ru_6(CO)_{16}(\mu_6\text{-C})(NCMe)_2$, **1**, with the thiacrown ether 1,5,9-trithiacyclododecane (12S3) resulted in the complete extraction of both copper atoms from the mixed-metal cluster by the thiacrown and formation of the salt $[Cu(\eta^3\text{-12S3})(\eta^1\text{-12S3})]_2[Ru_6(CO)_{16}(\mu_6\text{-C})]$, **2**, in 56% yield, eq 2. The structure of the $[Ru_6(CO)_{16}(\mu_6\text{-C})]^{2-}$ anion and two of the proximate $[Cu(\eta^3\text{-12S3})(\eta^1\text{-12S3})]^+$ cations is shown in Figure 1. Selected interatomic distances are listed in Table 2. The anion is similar to that found in the solid-state structure of the salt $[AsPh_4]_2[Ru_6(CO)_{16}(\mu_6\text{-C})]$, **3**, except that in **3**



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(6) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, pp 99–101, Table 2.2B. (b) *Ibid.*, pp 149–150, Table 2.3.1.

the anion contains four bridging carbonyl ligands.[7] In the case of **2**, there are instead three bridging CO with the fourth C(12)−O(12) in a semibridging mode, Ru(2)−C(22) = 1.94(1) Å, Ru(3)···C(22) = 2.56(1) Å and Ru(2)−C(22)−O(22) = 155.8(9)°. There are two $[Cu(\eta^3\text{-}12S3)(\eta^1\text{-}12S3)]^+$ monocations in the structure of **2**. Both are structurally similar to that found for the cation in the complex $[Cu(\eta^3\text{-}9S3)(\eta^1\text{-}9S3)][PF_6]$.[8] Each copper ion is coordinated to four sulfur atoms from the two 12S3 ligands in an approximate tetrahedral geometry, but one 12S3 ligand is tridentate (η^3), and the other is monodentate (η^1). Interestingly, the ^{1}H NMR spectrum at room temperature shows only two singlets for the methylene groups indicative of a dynamic process that leads to an averaging of the ligands (i.e. $\eta^3 \rightleftharpoons \eta^1$). This was confirmed by recording a spectrum at −78 °C, which showed a series of multiplets indicating that the exchange process is then slow on the ^{1}H NMR time scale at that temperature.

The most important feature of this reaction is that the thiacrown ligands did not engage in coordination to the ruthenium atoms, as they are capable of doing,[4] but instead are bonded exclusively to the copper atoms. This may have been a result of the lability of the NCMe ligands which were coordinated to the copper atoms in **1**, but it is also known that the thiacrowns have a strong affinity for coordination to copper as well as the other coinage metals. The binding is so effective that the copper atoms have been completely removed from bonding to the ruthenium cluster by a process that even results in the formation of ions!

While the removal of metals from mixed-metal complexes is not a typical goal, the contamination of precious metal heterogenous catalysts by certain heavy metals is a major problem.[10] Perhaps, thiacrowns could be used as a treatment for the regeneration of some contaminated forms of heterogenous catalysts.

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Supporting Information Available: Tables of atomic positional and *B* parameters, bond distances, bond angles, and anisotropic thermal parameters for the structural analysis (20 pages). Ordering information is given on any current masthead page.

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