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Cluster Synthesis. 18. Metal–Metal Exchange Reactions. The Synthesis and Structural Characterizations of $Ru_3Mo_2(CO)_{10}(\mu\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ and $RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)$

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The compound $RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)$ (3) was prepared in 49% yield by a double metal–metal exchange reaction involving $Ru_3(CO)_9(\mu_3\text{-}S)$ (1) and $[CpMo(CO)_2]_2$ at 80 °C. The compound $Ru_3Mo_2(CO)_{10}(\mu\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (2) was also isolated in 2% yield. Compounds 1–3 were characterized by X-ray crystallographic methods. For 1: space group $P2_1$, $a = 9.302$ (3) Å, $b = 19.973$ (6) Å, $c = 13.103$ (3) Å, $\beta = 91.00$ (2)°, $V = 2434$ (1) Å^3, and $Z = 6$. The structure was solved by direct methods and was refined (4124 reflections) to the final values of the residuals $R = 0.022$ and $R_{wF} = 0.024$. The molecule consists of a triangular cluster of three ruthenium atoms with a triply bridging sulfido ligand on one side of the cluster and a triply bridging carbonyl ligand on the other side. For 2: space group $P\bar{1}$, $a = 15.906$ (3) Å, $b = 16.462$ (3) Å, $c = 11.668$ (2) Å, $\alpha = 93.52$ (2)°, $\beta = 109.60$ (2)°, $\gamma = 75.42$ (1)°, $V = 2645$ (1) Å^3, and $Z = 4$. The structure was solved by the heavy-atom method and was refined (6078 reflections) to the final values of the residuals $R = 0.038$ and $R_{wF} = 0.040$. The molecule consists of a square-pyramidal cluster of three ruthenium and two molybdenum atoms. The two molybdenum atoms lie in basal positions. A quadruply bridging sulfido ligand bridges the base of the cluster. For 3: space group $P2_1/c$, $a = 12.429$ (4) Å, $b = 15.700$ (4) Å, $c = 10.049$ (2) Å, $\beta = 90.28$ (3)°, $V = 1961$ (1) Å^3, and $Z = 4$. The structure was solved by direct methods and was refined (2566 reflections) to the final values of the residuals $R = 0.028$ and $R_{wF} = 0.028$. The molecule consists of a triangular cluster of two molybdenum and one ruthenium atoms supported by a triply bridging sulfido ligand. 3 was formed from 1 by the replacement of two ruthenium carbonyl groups for two cyclopentadienyl molybdenum carbonyl groups. Compound 2 was converted into 3 (57% yield) under similar reaction conditions and is believed to be an intermediate in its formation.

Introduction

The synthesis of mixed-metal carbonyl cluster compounds by the process of metal–metal exchange is a method that is receiving increasing attention.[1-6] In a metal–metal exchange reaction the number of metal atoms in the product will be the same as in the starting material. Mechanistically, however, these reactions usually proceed through a sequence of metal-addition and -elimination steps and traverse an intermediate of higher nuclearity, eq 1, which is frequently unobserved. Bridging ligands are

$$M_xL_a + M'_yL'_b \rightarrow M_xM'_yL_aL_b \rightarrow M_{x-y}M'_yL_{a-m}L'_b + M_yL_m \quad (1)$$

known to stabilize higher nuclearity clusters,[1,2,7,8] and in metal–metal exchange reactions involving clusters that have bridging ligands, the higher nuclearity intermediates can often be isolated and characterized.[2]

Vahrenkamp has recently reported the preparation of the compound $RuMo_2(CO)_7(\mu_3\text{-}S)Cp_2$ (3) from $RuCo_2(CO)_9(\mu_3\text{-}S)$ by a series of exchange reactions that sequentially substitute molybdenum-containing moieties for the cobalt carbonyl groupings.[4] We have now discovered a new route to 3 through a one-step reaction of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) with $[CpMo(CO)_2]_2$. The pentanuclear compound $Ru_3Mo_2(CO)_{10}(\mu\text{-}CO)_2(\mu_4\text{-}S)Cp_2$ (2) was isolated and shown to be an intermediate in the formation of 3.

Experimental Section

General Data. Although the reaction products are air-stable, all reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were stored over 4-Å molecular sieves. $Ru_3(CO)_{12}$ and $[CpMo(CO)_3]_2$ were purchased from Strem Chemical Co. and were used without further purification. $[CpMo(CO)_2]_2$ was prepared from $[CpMo(CO)_3]_2$ by the published procedure.[9] $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) and $Ru(CO)_5$ were prepared by the previously reported procedures.[10,11] All chromatographic separations were carried out in air. TLC separations were performed on plates (0.25 mm Kieselgel 60 F_{254}, E. Merck, W. Germany) purchased from Bodman Chemicals. IR spectra were recorded on a Nicolet 5 DXB FT IR spectrophotometer. ^1H NMR spectra were run on a Brüker AM-300 spectrometer operating at 300 MHz. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

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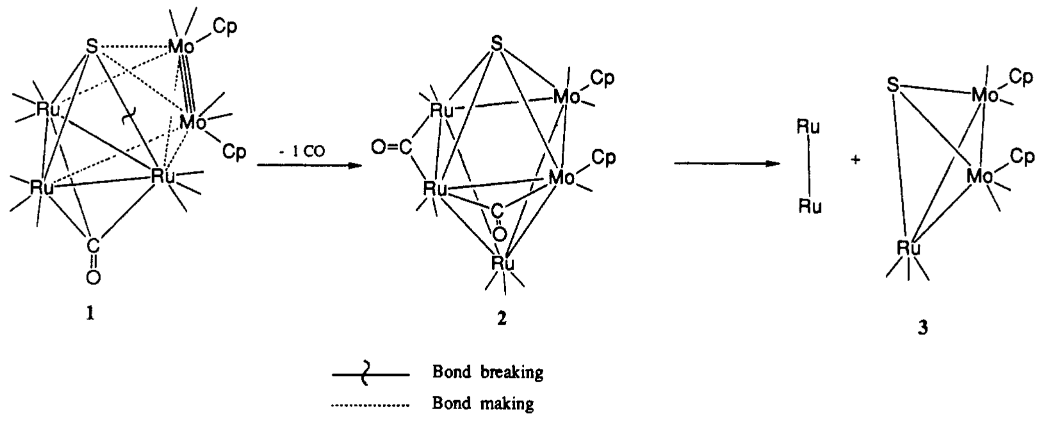
Table I. Crystallographic Data for the Structural Analyses for Compounds 1–3

	1	2	3
formula	$Ru_3SO_{10}C_{10}$	$Ru_3Mo_2SO_{12}C_{22}H_{10}$	$RuMo_2SO_7C_{17}H_{10}$
temp, ±3 °C	24	23	23
space group	$P2_1$, No. 4	$P\bar{1}$, No. 2	$P2_1/c$, No. 14
a (Å)	9.302 (3)	15.906 (3)	12.429 (4)
b (Å)	19.973 (6)	16.462 (3)	15.700 (4)
c (Å)	13.103 (3)	11.668 (2)	10.049 (2)
α (deg)	90.0	93.52 (2)	90.0
β (deg)	91.00 (2)	109.60 (2)	90.28 (2)
γ (deg)	90.0	75.42 (1)	90.0
V (Å^3)	2434 (1)	2645 (1)	1961 (1)
M_r	615.4	993.5	651.3
Z	6	4	4
ρ_{calcd}, g/cm^3	2.52	2.49	2.21
	(A) Measurement of Intensity Data		
radiatn	Mo Kα (0.71069Å)	Mo Kα (0.71069 Å)	Mo Kα (0.710 69 Å)
monochromator	graphite	graphite	graphite
detector aperture (mm)			
horizontal	4.0	4.0	4.0
vertical	4.0	4.0	4.0
cryst faces	011, $0\bar{1}\bar{1}$, $0\bar{1}2$ $01\bar{2}$, $10\bar{1}$, $\bar{1}01$	100, $\bar{1}00$, $0\bar{1}2$ $01\bar{2}$, $1\bar{1}\bar{1}$, 120	
cryst size (mm)	0.14 × 0.13 × 0.61	0.14 × 0.20 × 0.20	
cryst orientatn			
lattice directn	[100]	[121]	[101]
deg from ϕ axis	4.4	10.4	7.7
reflctns measd	$h,k,\pm l$	$h,\pm k,\pm l$	$h,k,\pm l$
max 2θ, deg	50.0	48.0	50.0
scan type	moving crystal–stationary counter	moving crystal–stationary counter	moving crystal–stationary counter
ω-scan width (A + 0.347 tan θ)°, A =	1.10	1.00	1.10
background (time at each end of scan)	$^1/_4$ scan time	$^1/_4$ scan time	$^1/_4$ scan time
ω-scan rate (deg/min)[a]	4.0	4.0	4.0
no. of reflctns measd	4771	8698	3844
data used ($F^2 \geq 3.0\sigma(F^2)$)	4124	6078	2566
	(B) Treatment of Data		
absorptn correctn	analytical	empirical	empirical
coeff (cm^{-1})	28.6	26.7	21.2
transmissn coeff			
max	0.77	1.00	1.00
min	0.67	0.89	0.87
P factor	0.02	0.02	0.02
final residuals			
R_F	0.022	0.038	0.028
R_{wF}	0.024	0.040	0.028
goodness of fit	1.35	1.75	1.27
largest shift/error value of final cycle	0.01	0.07	0.01
largest peak in final diff Fourier (e/Å^3)	0.60	2.72	0.42
no. of variables	648	721	253

[a] Rigaku software uses a multiple-scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results are added to the first scan etc. A maximum of three scans was permitted per reflection.

Scheme I



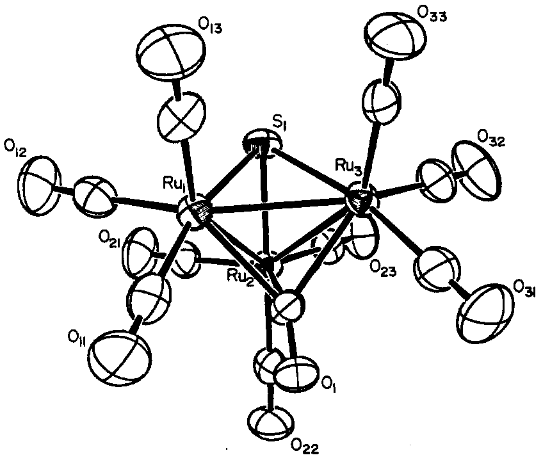


Figure 1. An ORTEP diagram of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) (molecule A) showing 50% probability thermal ellipsoids.

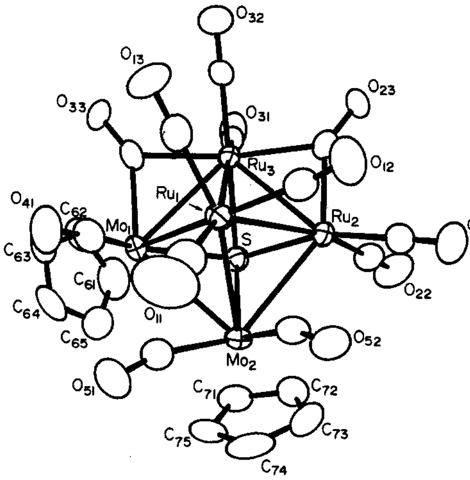


Figure 2. An ORTEP diagram of $Ru_3Mo_2(CO)_{10}(\mu\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (2) (molecule A) showing 50% probability thermal ellipsoids.

Table II. Intramolecular Distances (Å) for $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1)[a]

atom	atom	dist	atom	atom	dist
Ru1A	C13A	1.91 (1)	Ru2B	C1B	2.188 (9)
Ru1A	C11A	1.92 (1)	Ru2B	S1B	2.354 (2)
Ru1A	C12A	1.93 (1)	Ru2B	Ru3B	2.788 (1)
Ru1A	C1A	2.213 (8)	Ru2C	C21C	1.89 (1)
Ru1A	S1A	2.341 (2)	Ru2C	C22C	1.91 (1)
Ru1A	Ru3A	2.790 (1)	Ru2C	C23C	1.935 (9)
Ru1A	Ru2A	2.802 (1)	Ru2C	C1C	2.180 (9)
Ru1B	C11B	1.90 (1)	Ru2C	S1C	2.361 (2)
Ru1B	C12B	1.91 (1)	Ru2C	Ru3C	2.806 (2)
Ru1B	C13B	1.93 (1)	Ru3A	C33A	1.91 (1)
Ru1B	C1B	2.174 (9)	Ru3A	C32A	1.91 (1)
Ru1B	S1B	2.349 (3)	Ru3A	C31A	1.93 (1)
Ru1B	Ru2B	2.800 (1)	Ru3A	C1A	2.193 (8)
Ru1B	Ru3B	2.806 (1)	Ru3A	S1A	2.340 (2)
Ru1C	C13C	1.93 (1)	Ru3B	C31B	1.90 (1)
Ru1C	C12C	1.93 (1)	Ru3B	C32B	1.93 (1)
Ru1C	C11C	1.93 (1)	Ru3B	C33B	1.94 (1)
Ru1C	C1C	2.203 (8)	Ru3B	C1B	2.165 (9)
Ru1C	S1C	2.354 (2)	Ru3B	S1B	2.354 (2)
Ru1C	Ru3C	2.786 (1)	Ru3C	C31C	1.91 (1)
Ru1C	Ru2C	2.795 (1)	Ru3C	C33C	1.91 (1)
Ru2A	C21A	1.92 (1)	Ru3C	C32C	1.92 (1)
Ru2A	C23A	1.93 (1)	Ru3C	C1C	2.168 (9)
Ru2A	C22A	1.93 (1)	Ru3C	S1C	2.349 (2)
Ru2A	C1A	2.163 (9)	O1A	C1A	1.17 (1)
Ru2A	S1A	2.334 (2)	O1B	C1B	1.17 (1)
Ru2A	Ru3A	2.812 (1)	O1C	C1C	1.17 (1)
Ru2B	C22B	1.91 (1)	C(A)	$O(A)_{t\text{-}av}$	1.13 (1)
Ru2B	C23B	1.92 (1)	C(B)	$O(B)_{t\text{-}av}$	1.13 (1)
Ru2B	C21B	1.94 (1)	C(C)	$O(C_{t\text{-}av}$	1.13 (1)

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

Reaction of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) with $[CpMo(CO)_2]_2$. $[CpMo(CO)_2]_2$ (65 mg, 0.150 mmol), dissolved in 70 mL of benzene, was heated to reflux, and a solution of 1 (61 mg, 0.100 mmol), dissolved in 15 mL of benzene, was added via a syringe. The reaction solution was refluxed for 3 h under a continuous purge with nitrogen. The solvent was then removed in vacuo. The residue was dissolved in a CH_2Cl_2/hexane (25/75) solvent mixture and chromatographed on a Florisil column with the same solvent. A brown band containing 4.0 mg (9%) of $Ru_7(CO)_{20}(\mu_4\text{-}S)_2$[12] was eluted first. A pink band containing 24 mg of $[CpMo(CO)_3]_2$ was eluted with a hexane/CH_2Cl_2 (1/1) solvent mixture. A small green band was eluted with pure CH_2Cl_2. A red band was eluted with a CH_2Cl_2/THF (8/2) solvent mixture. The green band contains a mixture of the compounds $Ru_4Mo_2(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CO)Cp_2(\mu_4\text{-}S)$ (4; 9%) and $Ru_5Mo_2(CO)_{14}(\mu_4\text{-}\eta^2\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (5; 3%) which contain quadruply bridging carbonyl ligands.[13] These compounds will be described in detail in a forthcoming report.[14] The red band was further purified by TLC on silica gel using a hexane/CH_2Cl_2 (7/3) solvent mixture to yield 32 mg of red $RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)$ (3;[4] 49%) and 2.1 mg of brown $Ru_3Mo_2(CO)_{10}(\mu\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (2; 2%). For 2: IR [ν(CO), cm^{-1}, in CH_2Cl_2) 2065 (s), 2034 (vs), 2019 (vs), 2004 (m, sh), 1979 (m), 1960 (w, sh), 1906 (vw), 1856 (vw, sh), 1830 (w), 1784 (w); ^1H NMR (δ in $CDCl_3$) 5.44 (s, C_5H_5). Anal. Calcd C, 26.59; H, 1.01. Found: C, 26.37; H, 0.94.

Thermolysis of $Ru_3Mo_2(CO)_{10}(\mu_4\text{-}S)$ (2). 2 (11.0 mg, 0.0111 mmol) was refluxed in 25 mL of cyclohexane solvent for 3 h under a continuous purge with nitrogen. The solvent was then removed in vacuo. The residue was dissolved in a minimum amount of CH_2Cl_2 and was chromatographed by TLC on silica gel by using a hexane/CH_2Cl_2 (7/3) solvent mixture. This yielded the following compounds in order of elution: 1.2 mg of 5 (8%), 2.7 mg of 4 (21%), and 4.1 mg of 3 (57%).

Crystallographic Analyses

Yellow rod-like crystals of 1 were grown from solutions in a hexane/benzene (9/1) solvent mixture by cooling to 0 °C. Brown crystals of 2 were grown from solutions in a benzene/acetone (3/1) solvent mixture by slow evaporation at 10 °C. Red crystals of 3 were grown from solutions in a hexane/CH_2Cl_2 solvent mixture by slow evaporation at 25 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic four-circle diffractometer. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the diffractometer automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., College Station, TX. Neutral atom scattering factors were calculated by the standard procedures.[15a]

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

Table III. Selected Intramolecular Bond Angles (deg) for $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1)[a]

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C13A	Ru1A	S1A	96.2 (3)	C23B	Ru2B	C21B	97.3 (5)	C33C	Ru3C	Ru2C	119.5 (3)
C13A	Ru1A	Ru3A	94.5 (3)	C23B	Ru2B	S1B	95.1 (3)	C32C	Ru3C	S1C	95.3 (3)
C13A	Ru1A	Ru2A	147.6 (3)	C23B	Ru2B	Ru3B	147.2 (3)	C32C	Ru3C	Ru1C	97.2 (3)
C11A	Ru1A	S1A	166.8 (3)	C23B	Ru2B	Ru1B	94.3 (3)	C32C	Ru3C	Ru2C	148.0 (3)
C11A	Ru1A	Ru3A	116.4 (3)	C21B	Ru2B	C1B	132.1 (4)	C1C	Ru3C	S1C	89.6 (2)
C11A	Ru1A	Ru2A	115.9 (3)	C21B	Ru2B	S1B	94.7 (3)	C1C	Ru3C	Ru1C	51.0 (2)
C12A	Ru1A	S1A	94.5 (3)	C21B	Ru2B	Ru3B	95.5 (3)	C1C	Ru3C	Ru2C	50.0 (2)
C12A	Ru1A	Ru3A	146.9 (3)	C21B	Ru2B	Ru1B	147.0 (3)	S1C	Ru3C	Ru1C	53.77 (6)
C12A	Ru1A	Ru2A	95.7 (3)	C1B	Ru2B	S1B	88.3 (2)	S1C	Ru3C	Ru2C	53.62 (6)
C1A	Ru1A	S1A	88.0 (2)	C1B	Ru2B	Ru3B	49.8 (2)	Ru1C	Ru3C	Ru2C	59.96 (3)
C1A	Ru1A	Ru3A	50.4 (2)	C1B	Ru2B	Ru1B	49.8 (2)	Ru2A	S1A	Ru3A	73.97 (7)
C1A	Ru1A	Ru2A	49.4 (2)	S1B	Ru2B	Ru3B	53.67 (6)	Ru2A	S1A	Ru1A	73.63 (7)
S1A	Ru1A	Ru3A	53.40 (6)	S1B	Ru2B	Ru1B	53.38 (6)	Ru3A	S1A	Ru1A	73.15 (7)
S1A	Ru1A	Ru2A	53.06 (6)	Ru3B	Ru2B	Ru1B	60.29 (3)	Ru1B	S1B	Ru2B	73.09 (7)
Ru3A	Ru1A	Ru2A	60.38 (3)	C21C	Ru2C	S1C	169.5 (3)	Ru1B	S1B	Ru3B	73.28 (7)
C11B	Ru1B	S1B	94.9 (3)	C21C	Ru2C	Ru1C	118.9 (3)	Ru2B	S1B	Ru3B	72.65 (7)
C11B	Ru1B	Ru2B	146.0 (3)	C21C	Ru2C	Ru3C	117.5 (3)	Ru3C	S1C	Ru1C	72.65 (6)
C11B	Ru1B	Ru3B	92.7 (3)	C22C	Ru2C	S1C	98.3 (3)	Ru3C	S1C	Ru2C	73.15 (7)
C12B	Ru1B	C13B	92.6 (4)	C22C	Ru2C	Ru1C	93.0 (3)	Ru1C	S1C	Ru2C	72.70 (6)
C12B	Ru1B	S1B	169.3 (3)	C22C	Ru2C	Ru3C	148.1 (3)	O1A	C1A	Ru2A	132.8 (7)
C12B	Ru1B	Ru2B	116.7 (3)	C23C	Ru2C	S1C	93.3 (3)	O1A	C1A	Ru3A	132.4 (6)
C12B	Ru1B	Ru3B	119.4 (3)	C23C	Ru2C	Ru1C	146.2 (3)	O1A	C1A	Ru1A	131.9 (7)
C13B	Ru1B	S1B	93.0 (3)	C23C	Ru2C	Ru3C	97.1 (3)	Ru2A	C1A	Ru3A	80.4 (3)
C13B	Ru1B	Ru2B	95.9 (3)	C1C	Ru2C	S1C	89.0 (2)	Ru2A	C1A	Ru1A	79.6 (3)
C13B	Ru1B	Ru3B	145.5 (3)	C1C	Ru2C	Ru1C	50.8 (2)	Ru3A	C1A	Ru1A	78.6 (3)
C1B	Ru1B	S1B	88.8 (2)	C1C	Ru2C	Ru3C	49.6 (2)	O1B	C1B	Ru3B	133.1 (7)
C1B	Ru1B	Ru2B	50.3 (2)	S1C	Ru2C	Ru1C	53.54 (6)	O1B	C1B	Ru1B	131.8 (7)
C1B	Ru1B	Ru3B	49.6 (2)	S1C	Ru2C	Ru3C	53.23 (6)	O1B	C1B	Ru2B	131.2 (7)
S1B	Ru1B	Ru2B	53.53 (6)	Ru1C	Ru2C	Ru3C	59.65 (3)	Ru3B	C1B	Ru1B	80.6 (3)
S1B	Ru1B	Ru3B	53.43 (6)	C33A	Ru3A	S1A	94.5 (3)	Ru3B	C1B	Ru2B	79.7 (3)
Ru2B	Ru1B	Ru3B	59.65 (3)	C33A	Ru3A	Ru1A	94.8 (3)	Ru1B	C1B	Ru2B	79.9 (3)
C13C	Ru1C	S1C	95.7 (3)	C33A	Ru3A	Ru2A	146.1 (3)	O1C	C1C	Ru3C	133.4 (7)
C13C	Ru1C	Ru3C	93.3 (3)	C32A	Ru3A	S1A	96.3 (3)	O1C	C1C	Ru2C	132.5 (7)
C13C	Ru1C	Ru2C	147.3 (3)	C32A	Ru3A	Ru1A	147.6 (3)	O1C	C1C	Ru1C	131.1 (7)
C12C	Ru1C	S1C	167.9 (3)	C32A	Ru3A	Ru2A	93.8 (3)	Ru3C	C1C	Ru2C	80.4 (3)
C12C	Ru1C	Ru3C	116.4 (3)	C31A	Ru3A	S1A	167.9 (3)	Ru3C	C1C	Ru1C	79.2 (3)
C12C	Ru1C	Ru2C	116.7 (3)	C31A	Ru3A	Ru1A	115.4 (3)	Ru2C	C1C	Ru1C	79.2 (3)
C11C	Ru1C	S1C	94.5 (3)	C31A	Ru3A	Ru2A	119.3 (3)	O11A	C11A	Ru1A	179 (1)
C11C	Ru1C	Ru3C	147.2 (3)	C1A	Ru3A	S1A	88.5 (2)	O11B	C11B	Ru1B	179 (1)
C11C	Ru1C	Ru2C	96.6 (3)	C1A	Ru3A	Ru1A	51.0 (2)	O11C	C11C	Ru1C	177 (1)
C1C	Ru1C	S1C	88.6 (2)	C1A	Ru3A	Ru2A	49.3 (2)	O12A	C12A	Ru1A	177 (1)
C1C	Ru1C	Ru3C	49.8 (2)	S1A	Ru3A	Ru1A	53.45 (6)	O12B	C12B	Ru1B	177 (1)
C1C	Ru1C	Ru2C	50.0 (2)	S1A	Ru3A	Ru2A	52.91 (6)	O12C	C12C	Ru1C	177.0 (9)
S1C	Ru1C	Ru3C	53.58 (6)	Ru1A	Ru3A	Ru2A	60.02 (3)	O13A	C13A	Ru1A	178 (1)
S1C	Ru1C	Ru2C	53.76 (6)	C31B	Ru3B	S1B	169.9 (3)	O13B	C13B	Ru1B	177 (1)
Ru3C	Ru1C	Ru2C	60.38 (4)	C31B	Ru3B	Ru2B	119.2 (3)	O13C	C13C	Ru1C	177.0 (9)
C21A	Ru2A	S1A	95.3 (3)	C31B	Ru3B	Ru1B	117.9 (3)	O21A	C21A	Ru2A	177 (1)
C21A	Ru2A	Ru1A	94.5 (3)	C32B	Ru3B	S1B	99.3 (3)	O21B	C21B	Ru2B	176 (1)
C21A	Ru2A	Ru3A	146.7 (3)	C32B	Ru3B	Ru2B	93.6 (3)	O21C	C21C	Ru2C	178.8 (8)
C23A	Ru2A	S1A	94.7 (3)	C32B	Ru3B	Ru1B	149.3 (3)	O22A	C22A	Ru2A	178.3 (9)
C23A	Ru2A	Ru1A	146.8 (3)	C33B	Ru3B	S1B	93.2 (3)	O22B	C22B	Ru2B	178 (1)
C23A	Ru2A	Ru3A	95.8 (3)	C33B	Ru3B	Ru2B	146.5 (3)	O22C	C22C	Ru2C	177.8 (9)
C22A	Ru2A	S1A	170.0 (3)	C33B	Ru3B	Ru1B	98.2 (3)	O23A	C23A	Ru2A	178 (1)
C22A	Ru2A	Ru1A	118.1 (2)	C1B	Ru3B	S1B	88.9 (2)	O23B	C23B	Ru2B	178 (1)
C22A	Ru2A	Ru3A	119.5 (3)	C1B	Ru3B	Ru2B	50.5 (2)	O23C	C23C	Ru2C	177.7 (9)
C1A	Ru2A	S1A	89.4 (2)	C1B	Ru3B	Ru1B	49.8 (2)	O31A	C31A	Ru3A	178 (1)
C1A	Ru2A	Ru1A	51.0 (2)	S1B	Ru3B	Ru2B	53.67 (6)	O31B	C31B	Ru3B	177.1 (9)
C1A	Ru2A	Ru3A	50.3 (2)	S1B	Ru3B	Ru1B	53.28 (7)	O31C	C31C	Ru3C	178.0 (9)
S1A	Ru2A	Ru1A	53.31 (6)	Ru2B	Ru3B	Ru1B	60.06 (3)	O32A	C32A	Ru3A	179 (1)
S1A	Ru2A	Ru3A	53.12 (5)	C31C	Ru3C	S1C	96.9 (3)	O32B	C32B	Ru3B	177.3 (8)
Ru1A	Ru2A	Ru3A	59.60 (3)	C31C	Ru3C	Ru1C	148.1 (3)	O32C	C32C	Ru3C	180 (1)
C22B	Ru2B	S1B	169.1 (3)	C31C	Ru3C	Ru2C	93.9 (3)	O33A	C33A	Ru3A	179.0 (9)
C22B	Ru2B	Ru3B	116.8 (3)	C33C	Ru3C	S1C	168.7 (3)	O33B	C33B	Ru3B	175 (1)
C22B	Ru2B	Ru1B	118.6 (3)	C33C	Ru3C	Ru1C	115.6 (3)	O33C	C33C	Ru3C	179 (1)

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

Anomalous dispersion corrections were applied to all non-hydrogen atoms.[15b] Full-matrix least-squares refinements minimized the function: $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compound 1 crystallized in the monoclinic crystal system. The systematic absences, 0*k*0, $k = 2n + 1$, in the data were consistent with either of the space groups $P2_1$ or $P2_1/m$. The data were corrected for absorption by the analytical method. Attempts to solve the structure by direct methods (MITHRIL) in both space groups were successful only for the space group $P2_1$. The $P2_1$ choice was further supported by the successful refinement. With $Z = 6$, the crystal of 1 contains three independent formula equivalents of 1 in the asymmetric unit. All atoms were refined with anisotropic thermal parameters. After the final least-squares

Table IV. Positional Parameters and *B*(eq) for $Ru_3Mo_2(CO)_{10}(\mu\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (2)

atom	*x*	*y*	*z*	*B*(eq), Å^2	atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru1A	−0.33205 (5)	0.08088 (4)	0.08734 (7)	2.22 (3)	C13A	−0.3121 (7)	−0.0227 (7)	0.1616 (9)	3.4 (5)
Ru1B	0.16195 (6)	0.41241 (5)	0.41667 (8)	2.84 (4)	C13B	0.086 (1)	0.5086 (8)	0.330 (1)	5.4 (7)
Ru2A	−0.20994 (5)	0.11951 (4)	−0.03412 (7)	2.22 (3)	C21A	−0.2757 (7)	0.1091 (6)	−0.200 (1)	3.1 (5)
Ru2B	0.36866 (6)	0.37620 (5)	0.53881 (7)	2.69 (4)	C21B	0.3790 (8)	0.3913 (6)	0.702 (1)	3.7 (5)
Ru3A	−0.12582 (5)	0.02494 (4)	0.18052 (7)	2.18 (3)	C22A	−0.1297 (8)	0.1664 (6)	−0.088 (1)	3.5 (5)
Ru3B	0.28899 (6)	0.46548 (5)	0.32091 (8)	2.98 (4)	C22B	0.5027 (8)	0.3310 (6)	0.5928 (9)	3.3 (5)
Mo1A	−0.22247 (6)	0.15138 (5)	0.,31481 (7)	2.27 (4)	C23A	−0.1256 (7)	0.0019 (6)	−0.0034 (9)	3.0 (5)
Mo1B	0.19259 (6)	0.33779 (5)	0.19260 (8)	3.04 (4)	C23B	0.3723 (8)	0.4919 (6)	0.502 (1)	4.0 (5)
Mo2A	−0.31413 (6)	0.25635 (5)	0.07736 (7)	2.20 (4)	C31A	0.0097 (8)	0.0115 (6)	0.2485 (9)	2.9 (5)
Mo2B	0.28460 (6)	0.23609 (5)	0.43768 (8)	2.50 (4)	C31B	0.3800 (8)	0.4743 (6)	0.247 (1)	4.1 (6)
S1A	−0.1494 (2)	0.1757 (1)	0.1653 (2)	2.3 (1)	C32A	−0.1088 (8)	−0.0918 (6)	0.1955 (9)	3.1 (5)
S1B	0.3558 (2)	0.3149 (1)	0.3414 (2)	2.6 (1)	C32B	0.2336 (9)	0.5828 (7)	0.304 (1)	4.4 (6)
O11A	−0.5485 (6)	0.1237 (6)	0.048 (1)	7.2 (6)	C33A	−0.1498 (7)	0.0254 (6)	0.3539 (8)	2.7 (5)
O11B	−0.0035 (7)	0.3665 (6)	0.469 (1)	8.1 (7)	C33B	0.1704 (8)	0.4630 (7)	0.149 (1)	3.8 (6)
O12A	−0.3791 (7)	−0.0038 (5)	−0.1529 (7)	5.8 (5)	C41A	−0.3372 (8)	0.1140 (6)	0.316 (1)	3.4 (5)
O12B	0.1920 (7)	0.5131 (6)	0.6435 (8)	7.7 (6)	C41B	0.058 (1)	0.3675 (7)	0.197 (1)	5.0 (7)
O13A	−0.3089 (6)	−0.0862 (5)	0.2022 (7)	5.3 (5)	C51A	−0.4041 (8)	0.2598 (6)	0.171 (1)	3.5 (5)
O13B	0.0248 (7)	0.5700 (6)	0.2836 (8)	7.0 (5)	C51B	0.1510 (8)	0.2274 (6)	0.354 (1)	3.8 (5)
O21A	−0.3141 (6)	0.1044 (5)	−0.3008 (7)	4.8 (4)	C52A	−0.4025 (7)	0.2145 (6)	−0.068 (1)	3.0 (5)
O21B	0.3864 (6)	0.3995 (6)	0.8025 (7)	6.2 (5)	C52B	0.2500 (8)	0.2804 (7)	0.581 (1)	4.0 (6)
O22A	−0.0812 (6)	0.1952 (5)	−0.1184 (8)	5.4 (5)	C61A	−0.116 (1)	0.225 (1)	0.443 (1)	5.2 (8)
O22B	0.5846 (5)	0.3045 (5)	0.6265 (7)	5.5 (5)	C61B	0.269 (1)	0.269 (1)	0.058 (1)	7 (1)
O23A	−0.0918 (6)	−0.0555 (4)	−0.0508 (6)	4.3 (4)	C62A	−0.1098 (9)	0.1569 (8)	0.503 (1)	4.6 (6)
O23B	0.3985 (7)	0.5508 (5)	0.5470 (8)	6.2 (5)	C62B	0.197 (2)	0.335 (1)	−0.003 (1)	7 (1)
O31A	0.0907 (5)	0.0050 (5)	0.2910 (6)	4.4 (4)	C63A	−0.198 (1)	0.1587 (7)	0.516 (1)	4.4 (7)
O31B	0.4366 (6)	0.4736 (5)	0.2019 (9)	6.5 (5)	C63B	0.110 (1)	0.323 (1)	−0.005 (1)	6.3 (8)
O32A	−0.0968 (6)	−0.1622 (5)	0.2066 (7)	5.2 (5)	C64A	−0.2617 (9)	0.2337 (8)	0.464 (1)	4.7 (6)
O32B	0.2028 (7)	0.6524 (5)	0.2931 (8)	6.6 (5)	C64B	0.129 (1)	0.248 (1)	0.055 (1)	6.2 (8)
O33A	−0.1227 (5)	−0.0281 (4)	0.4291 (6)	3.9 (4)	C65A	−0.211 (1)	0.2749 (7)	0.417 (1)	5.5 (8)
O33B	0.1268 (6)	0.5172 (5)	0.0767 (7)	5.5 (5)	C65B	0.226 (1)	0.2144 (8)	0.092 (1)	6.5 (8)
O41A	−0.3977 (6)	0.0975 (5)	0.3423 (7)	5.1 (5)	C71A	−0.2480 (8)	0.3744 (6)	0.128 (1)	3.5 (5)
O41B	−0.0245 (6)	0.3790 (6)	0.1739 (8)	6.4 (5)	C71B	0.4365 (8)	0.1404 (6)	0.509 (1)	3.9 (5)
O51A	−0.4670 (6)	0.2779 (5)	0.2085 (7)	5.0 (4)	C72A	−0.2528 (9)	0.3550 (6)	0.011 (1)	3.9 (6)
O51B	0.0768 (6)	0.2086 (5)	0.3144 (9)	5.9 (5)	C72B	0.3918 (8)	0.1175 (6)	0.392 (1)	3.9 (6)
O52A	−0.4632 (5)	0.2118 (4)	−0.1578 (6)	3.8 (4)	C73A	−0.350 (1)	0.3631 (7)	−0.061 (1)	5.0 (7)
O52B	0.2344 (6)	0.2856 (5)	0.6733 (7)	5.4 (5)	C73B	0.3059 (8)	0.0956 (6)	0.389 (1)	4.4 (6)
C11A	−0.4670 (8)	0.1124 (7)	0.066 (1)	3.9 (6)	C74A	−0.4061 (9)	0.3885 (6)	0.015 (1)	4.8 (6)
C11B	0.0598 (8)	0.3793 (7)	0.447 (1)	4.4 (6)	C74B	0.3025 (9)	0.1050 (6)	0.509 (1)	4.4 (6)
C12A	−0.3547 (8)	0.0311 (6)	−0.065 (1)	3.7 (6)	C75A	−0.3417 (8)	0.3960 (6)	0.130 (1)	3.8 (5)
C12B	0.1904 (8)	0.4705 (7)	0.563 (1)	4.5 (6)	C75B	0.383 (1)	0.1322 (7)	0.580 (1)	4.8 (6)

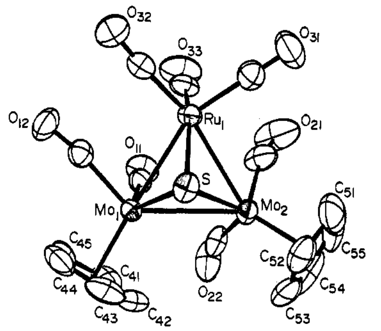

Figure 3. An ORTEP diagram of $RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)$ (3) showing 50% probability thermal ellipsoids.

refinement cycle, a test of the enantiomorphic form was made by inverting all the atomic coordinates and refining again. No significant difference were observed between the *R* values of the two refinements; thus, the atomic coordinates for the first enantiomorphic form were retained and are reported here.

Compound 2 crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the strcture. The data were corrected for absorption by the empirical method. The structure was solved by a combination of Patterson and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries of the C_5H_5 rings. Their contributions were added to the structure factor (SF) calculations, but their positions were not refined.

Compound 3 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely from the systematic absences observed in the data. The data were corrected for absorption by the empirical method. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries for the C_5H_5 rings. Their contributions were added to the SF calculations, but their positions were not refined.

Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement. Tables of observed and calculated SF amplitudes, values of the anisotropic thermal parameters, and final positional parameters for three independent molecules of 1 are available (see supplementary material).

Results

The principal product obtained from the reaction of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) with $[CpMo(CO)_2]_2$ was $RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)$ (3; 49% yield). A number of minor products, 4 (9%),[13] 5 (3%),[13] and $Ru_3Mo_2(CO)_{10}(\mu\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (2; 2%), were also obtained. The metal nuclearity of 2 suggested that it was a direct product of the reaction and possibly an intermediate in the formation of 3. This was confirmed by an independent experiment in which 2 was converted into 3 in 57% yield. Compounds 2 and 3 were characterized by single-crystal X-ray diffraction analyses. For comparative purposes a crystallographic analysis of 1 was also performed and these results are included with this report.

Table V. Intramolecular Distances (Å) for $Ru_3Mo_2(CO)_{10}(\mu\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (2)[a]

atom	atom	dist	atom	atom	dist
Ru1A	C13A	1.87 (1)	Mo1A	C33A	2.09 (1)
Ru1A	C12A	1.88 (1)	Mo1A	C63A	2.25 (1)
Ru1A	C11A	1.90 (1)	Mo1A	C64A	2.28 (1)
Ru1A	Ru3A	2.852 (1)	Mo1A	C62A	2.30 (1)
Ru1A	Ru2A	2.876 (1)	Mo1A	C65A	2.31 (1)
Ru1A	Mo1A	2.963 (1)	Mo1A	C61A	2.34 (1)
Ru1A	Mo2A	2.981 (1)	Mo1A	S1A	2.455 (2)
Ru1B	C13B	1.83 (1)	Mo1A	Mo2A	3.066 (1)
Ru1B	C12B	1.88 (1)	Mo1B	C41B	1.98 (1)
Ru1B	C11B	1.90 (1)	Mo1B	C33B	2.07 (1)
Ru1B	Ru3B	2.845 (1)	Mo1B	C64B	2.26 (1)
Ru1B	Ru2B	2.883 (1)	Mo1B	C63B	2.26 (1)
Ru1B	Mo1B	2.950 (1)	Mo1B	C62B	2.31 (1)
Ru1B	Mo2B	2.998 (1)	Mo1B	C65B	2.31 (1)
Ru2A	C22A	1.87 (1)	Mo1B	C61B	2.32 (1)
Ru2A	C21A	1.87 (1)	Mo1B	S1B	2.444 (3)
Ru2A	C23A	2.01 (1)	Mo1B	Mo2B	3.110 (1)
Ru2A	S1A	2.418 (2)	Mo2A	C52A	1.98 (1)
Ru2A	Ru3A	2.769 (1)	Mo2A	C51A	2.00 (1)
Ru2A	Mo2A	2.911 (1)	Mo2A	C74A	2.28 (1)
Ru2B	C22B	1.87 (1)	Mo2A	C73A	2.30 (1)
Ru2B	C21B	1.87 (1)	Mo2A	C75A	2.31 (1)
Ru2B	C23B	2.00 (1)	Mo2A	C72A	2.34 (1)
Ru2B	S1B	2.425 (3)	Mo2A	C71A	2.36 (1)
Ru2B	Ru3B	2.756 (1)	Mo2A	S1A	2.407 (3)
Ru2B	Mo2B	2.908 (1)	Mo2B	C51B	1.96 (1)
Ru3A	C32A	1.89 (1)	Mo2B	C52B	1.97 (1)
Ru3A	C31A	1.89 (1)	Mo2B	C74B	2.28 (1)
Ru3A	C23A	2.16 (1)	Mo2B	C75B	2.30 (1)
Ru3A	C33A	2.172 (9)	Mo2B	C73B	2.31 (1)
Ru3A	S1A	2.425 (2)	Mo2B	C71B	2.34 (1)
Ru3A	Mo1A	2.920 (1)	Mo2B	C72B	2.36 (1)
Ru3B	C31B	1.89 (1)	Mo2B	S1B	2.407 (2)
Ru3B	C32B	1.90 (1)	C(A)	$O(A)_{av}$	1.15 (1)
Ru3B	C23B	2.15 (1)	C(B)	$O(B)_{av}$	1.15 (1)
Ru3B	C33B	2.21 (1)	Ru2A	C52A	2.84 (1)
Ru3B	S1B	2.422 (3)	Ru2B	C52B	2.84 (1)
Ru3B	Mo1B	2.911 (1)	Mo1A	C51A	2.89 (1)
Mo1A	C41A	1.98 (1)	Mo1B	C51B	3.01 (1)

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

Description of the Structures. (a) $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1). Compound 1 crystallized in the monoclinic space group $P2_1$ with three independent molecules in the asymmetric crystal unit. All three molecules are structurally similar, and an ORTEP diagram of molecule A is shown in Figure 1. Intramolecular distances and selected intramolecular angles are listed in Tables II and III. The molecule consists of a triangular cluster of three ruthenium atoms connected by three metal–metal bonds. Over all three molecules the Ru–Ru distances lie in the narrow range of 2.786 (1)–2.812 (1) Å; the average equals 2.798 (3) Å. Each molecule contains a triply bridging sulfido ligand on one side of the cluster and a triply bridging carbonyl ligand on the other side. The Ru–S distances range from 2.334 (2) to 2.361 (2) Å. The Ru–C distances to the triply bridging carbonyl ligands exhibit a wider range, 2.163 (9)–2.213 (8) Å. Each metal atom contains three linear terminal carbonyl ligands. All these Ru–C distances lie in the range of 1.89 (1)–1.94 (1) Å. Compound 1 is structurally very similar to that of the iron[16] and osmium[17] homologues that have been reported previously.

(b) $Ru_3Mo_2(CO)_{10}(\mu\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (2). Compound 2 crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric crystal unit. Both molecules are structurally similar. An ORTEP diagram of molecule A is shown in Figure 2. Final positional parameters are listed in Table IV. Intramolecular bond distances and selected bond angles are listed in Tables V and VI, respectively. The molecule consists of a square-pyramidal cluster of three ruthenium and two molybdenum atoms. The two molybdenum atoms occupy basal positions of the pyramid. A quadruply bridging sulfido ligand spans the square base. Carbonyl ligands bridge two of the basal edges of the cluster, C(33)–O(33) across Mo(1)–Ru(3) and C(23)–O(23) across Ru(2)–Ru(3). The Mo(1)–Mo(2) bond length is 3.066 (1) Å [3.110 (1) Å]. The quantity in brackets corresponds to the distance in molecule B. These distances are shorter than the Mo–Mo single bond length, 3.235 (1) Å, observed in sterically crowded molecule $[CpMo(CO)_3]_2$.[18] Interestingly, there is no significant difference between the CO-bridged Mo(1)–Ru(3) distance, 2.920 (1) Å [2.911 (1) Å], and the unbridged distance Mo(2)–Ru(2), 2.911 (1) Å [2.908 (1) Å]. The Ru(2)–Ru(3) metal–metal bond is the shortest in the molecule, 2.756 (1) Å [2.796 (1) Å]. Similar Ru–Ru bond distances were observed for the CO-bridged bonds in the structurally similar cluster $Ru_5(CO)_{11}(\mu\text{-}CO)_4(\mu_4\text{-}S)$ (4).[19] The Ru–Mo and Ru–Ru bonds to the apical atom Ru(1) are significantly longer than the corresponding bonds in the base of the pyramid, Ru(1)–Mo(1) = 2.963 (1) Å [2.950 (1) Å] and Ru(1)–Mo(2) = 2.981 (1) Å [2.998 (1) Å]; Ru(1)–Ru(2) = 2.876 (1) Å [2.883 (1) Å] and Ru(1)–Ru(3) = 2.852 (1) Å [2.845 (1) Å]. A similar effect was observed in compound 4.[19] Compound 2 contains two bridging carbonyl ligands, ν = 1830 and 1784 cm^{-1}. There are two carbonyl ligands on Mo(2) that are weakly semibridging. The remaining carbonyl ligands, distributed as shown in Figure 2, are all of a terminal type. The ^1H NMR spectrum shows only one cyclopentadienyl resonance, δ 5.44. However, in the solid-state structure the rings are inequivalent. The implied solution equivalence could be the result of a dynamic averaging process involving very simple bridge–terminal CO ligand shifts. For example, the semibridging ligand, C(52)–O(52), shifts to a full bridge across the Mo(2)–Ru(2) bond, and the full bridge, C(33)–O(33), shifts into a semibridging mode on Mo(1). Compound 2 contains a total of 76 valence electrons. It obeys both the polyhedral skeletal electron pair theory and the effective atomic number rule, although within the framework of the latter theory the Mo(2)–Ru(2) bond would be regarded as donor–acceptor bond from Mo(2) to Ru(2).[20]

(c) $RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)$ (3). An ORTEP drawing of the molecular structure of 3 is shown in Figure 3. Positional parameters are listed in Table VII. Intramolecular bond distances and angles are listed in Tables VIII and IX, respectively. The molecule consists of a triangular cluster of two molybdenum and one ruthenium atom

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Table VI. Selected Intramolecular Angles (deg) for $Ru_3Mo_2(CO)_{10}(\mu\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (2)[a]

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C13A	Ru1A	Ru3A	77.1 (3)	C32A	Ru3A	Ru1A	101.3 (3)	Ru1B	Mo1B	Mo2B	59.24 (3)
C13A	Ru1A	Ru2A	124.9 (3)	C32A	Ru3A	Mo1A	124.9 (3)	C52A	Mo2A	Ru2A	68.0 (3)
C13A	Ru1A	Mo1A	93.4 (3)	C31A	Ru3A	Ru2A	113.8 (3)	C52A	Mo2A	Ru1A	62.0 (3)
C13A	Ru1A	Mo2A	155.5 (3)	C31A	Ru3A	Ru1A	168.2 (3)	C52A	Mo2A	Mo1A	120.1 (3)
C12A	Ru1A	Ru3A	99.4 (3)	C31A	Ru3A	Mo1A	109.2 (3)	C51A	Mo2A	Ru2A	132.2 (3)
C12A	Ru1A	Ru2A	69.6 (3)	C23A	Ru3A	Ru2A	46.1 (3)	C51A	Mo2A	Ru1A	73.8 (3)
C12A	Ru1A	Mo1A	157.6 (3)	C23A	Ru3A	Ru1A	88.8 (3)	C51A	Mo2A	Mo1A	65.7 (3)
C12A	Ru1A	Mo2A	112.0 (3)	C23A	Ru3A	Mo1A	139.1 (3)	S1A	Mo2A	Ru2A	53.06 (6)
C11A	Ru1A	Ru3A	165.5 (3)	C33A	Ru3A	Ru2A	136.8 (3)	S1A	Mo2A	Ru1A	75.86 (6)
C11A	Ru1A	Ru2A	135.7 (3)	C33A	Ru3A	Ru1A	83.4 (2)	S1A	Mo2A	Mo1A	51.60 (6)
C11A	Ru1A	Mo1A	109.9 (3)	C33A	Ru3A	Mo1A	45.5 (3)	Ru2A	Mo2A	Ru1A	58.42 (3)
C11A	Ru1A	Mo2A	94.8 (3)	S1A	Ru3A	Ru2A	55.00 (6)	Ru2A	Mo2A	Mo1A	87.58 (3)
Ru3A	Ru1A	Ru2A	57.82 (3)	S1A	Ru3A	Ru1A	78.16 (6)	Ru1A	Mo2A	Mo1A	58.66 (3)
Ru3A	Ru1A	Mo1A	60.25 (3)	S1A	Ru3A	Mo1A	53.71 (6)	C51B	Mo2B	Ru2B	133.0 (3)
Ru3A	Ru1A	Mo2A	89.46 (3)	Ru2A	Ru3A	Ru1A	61.53 (3)	C51B	Mo2B	Ru1B	74.7 (3)
Ru2A	Ru1A	Mo1A	90.23 (3)	Ru2A	Ru3A	Mo1A	93.28 (4)	C51B	Mo2B	Mo1B	68.5 (3)
Ru2A	Ru1A	Mo2A	59.57 (3)	Ru1A	Ru3A	Mo1A	61.77 (3)	C52B	Mo2B	Ru2B	68.1 (3)
Mo1A	Ru1A	Mo2A	62.10 (3)	C31B	Ru3B	Ru2B	114.3 (3)	C52B	Mo2B	Ru1B	63.1 (3)
C13B	Ru1B	Ru3B	76.7 (4)	C31B	Ru3B	Ru1B	166.6 (3)	C5iB	Mo2B	Mo1B	120.4 (3)
C13B	Ru1B	Ru2B	126.4 (4)	C31B	Ru3B	Mo1B	107.2 (4)	S1B	Mo2B	Ru2B	53.27 (6)
C13B	Ru1B	Mo1B	89.5 (4)	C32B	Ru3B	Ru2B	124.9 (3)	S1Bv	Mo2B	Ru1B	75.20 (6)
C13B	Ru1B	Mo2B	152.6 (4)	C32B	Ru3B	Ru1B	100.8 (4)	S1B	Mo2B	Mo1B	50.64 (6)
C12B	Ru1B	Ru3B	97.0 (4)	C32B	Ru3B	Mo1B	125.1 (3)	Ru2B	Mo2B	Ru1B	58.40 (3)
C12B	Ru1B	Ru2B	69.7 (3)	C23B	Ru3B	Ru2B	46.0 (3)	Ru2B	Mo2B	Mo1B	86.83 (4)
C12B	Ru1B	Mo1B	156.2 (4)	C23B	Ru3B	Ru1B	89.5 (3)	Ru1B	Mo2B	Mo1B	57.71 (3)
C12B	Ru1B	Mo2B	113.4 (3)	C23B	Ru3B	Mo1B	139.6 (3)	Mo2A	S1A	Ru2A	74.21 (7)
C11B	Ru1B	Ru3B	168.2 (4)	C3oB	Ru3B	Ru2B	136.4 (3)	Mo2A	S1A	Ru3A	116.3 (1)
C11B	Ru1B	Ru2B	133.3 (4)	C33B	Ru3B	Ru1B	81.7 (3)	Mo2A	S1A	Mo1A	78.18 (7)
C11B	Ru1B	Mo1B	111.1 (3)	C33B	Ru3B	Mo1B	45.2 (3)	Ru2A	S1A	Ru3A	69.74 (7)
C11B	Ru1B	Mo2B	93.4 (3)	S1B	Ru3B	Ru2B	55.39 (6)	Ru2A	S1A	Mo1A	116.2 (1)
Ru3B	Ru1B	Ru2B	57.53 (3)	S1B	Ru3B	Ru1B	78.00 (6)	Ru3A	S1A	Mo1A	73.50 (7)
Ru3B	Ru1B	Mo1B	60.27 (3)	S1B	Ru3B	Mo1B	53.60 (6)	Mo2B	S1B	Ru3B	116.9 (1)
Ru3B	Ru1B	Mo2B	89.52 (3)	Ru2B	Ru3B	Ru1B	61.92 (3)	Mo2B	S1B	Ru2B	74.01 (7)
Ru2B	Ru1B	Mo1B	90.41 (4)	Ru2B	Ru3B	Mo1B	93.80 (4)	Mo2B	S1B	Mo1B	79.75 (8)
Ru2B	Ru1B	Mo2B	59.24 (3)	Ru1B	Ru3B	Mo1B	61.65 (3)	Ru3B	S1B	Ru2B	69.31 (7)
Mo1B	Ru1B	Mo2B	63.05 (3)	C33A	Mo1A	Ru3A	47.9 (2)	Ru3B	S1B	Mo1B	73.47 (7)
C22A	Ru2A	Ru3A	117.5 (3)	C33A	Mo1A	Ru1A	82.1 (3)	Ru2B	S1B	Mo1B	116.5 (1)
C22A	Ru2A	Ru1A	166.2 (3)	C33A	Mo1A	Mo2A	132.7 (2)	O23A	C23A	Ru2A	143.0 (8)
C22A	Ru2A	Mo2A	105.3 (3)	C63A	Mo1A	Ru3A	129.5 (3)	O23A	C23A	Ru3A	133.8 (7)
C21A	Ru2A	Ru3A	140.6 (3)	C63A	Mo1A	Ru1A	143.1 (3)	Ru2A	C23A	Ru3A	83.2 (4)
C21A	Ru2A	Ru1A	104.5 (3)	C63A	Mo1A	Mo2A	142.7 (3)	O23B	C23B	Ru2B	143 (1)
C21A	Ru2A	Mo2A	113.1 (3)	C64A	Mo1A	Ru3A	164.2 (3)	O23B	C23B	Ru3B	134.1 (9)
C23A	Ru2A	Ru3A	50.7 (3)	C64A	Mo1A	Ru1A	135.5 (3)	Ru2B	C23B	Ru3B	83.3 (4)
C23A	Ru2A	Ru1A	91.1 (3)	C64A	Mo1A	Mo2A	107.4 (3)	Mo1A	C33A	Ru3A	86.6 (4)
C23A	Ru2A	Mo2A	143.0 (3)	C62A	Mo1A	Ru3A	106.5 (3)	O33B	C33B	Mo1B	146 (1)
S1A	Ru2A	Ru3A	55.25 (6)	C62A	Mo1A	Ru1A	159.7 (3)	O33B	C33B	Ru3B	128.3 (9)
S1A	Ru2A	Ru1A	77.79 (6)	C62A	Mo1A	Mo2A	137.6 (3)	Mo1B	C33B	Ru3B	85.7 (4)
S1A	Ru2A	Mo2A	52.73 (6)	C65A	Mo1A	Ru3A	142.3 (4)	C62A	C61A	C65A	108 (1)
Ru3A	Ru2A	Ru1A	60.65 (3)	C65A	Mo1A	Ru1A	143.2 (3)	C62B	C61B	C65B	108 (1)
Ru3A	Ru2A	Mo2A	92.55 (3)	C65A	Mo1A	Mo2A	87.7 (3)	C61A	C62A	C63A	110 (1)
Ru1A	Ru2A	Mo2A	62.01 (3)	C61A	Mo1A	Ru3A	111.7 (3)	C61B	C62B	C63B	108 (1)
C22B	Ru2B	Ru3B	117.1 (3)	C61A	Mo1A	Ru1A	159.0 (3)	C62A	C63A	C64A	108 (1)
C22B	Ru2B	Ru1B	166.2 (3)	C61A	Mo1A	Mo2A	104.3 (4)	C62B	C63B	C64B	108 (1)
C22B	Ru2B	Mo2B	105.2 (3)	S1A	Mo1A	Ru3A	52.79 (6)	C63A	C64A	C65A	106 (1)
C21B	Ru2B	Ru3B	139.7 (3)	S1A	Mo1A	Ru1A	75.55 (6)	C65B	C64B	C63B	108 (1)
C21B	Ru2B	Ru1B	103.0 (3)	Su1A	Mo1A	Mo2A	50.22 (6)	C64A	C65A	C61A	108 (1)
C21B	Ru2B	Mo2B	111.9 (3)	Ru3A	Mo1A	Ru1A	57.99 (3)	C64B	C65B	C61B	108 (1)
C23B	Ru2B	Ru3B	50.7 (3)	Ru3A	Mo1A	Mo2A	86.58 (3)	C72A	C71A	C75A	107 (1)
C23B	Ru2B	Ru1B	91.5 (3)	Ru1A	Mo1A	Mo2A	59.24 (3)	C75B	C71B	C72B	109 (1)
C23B	Ru2B	Mo2B	143.6 (3)	C33B	Mo1B	Ru3B	49.1 (3)	C71A	C72A	C73A	109 (1)
S1B	Ru2B	Ru3B	55.30 (6)	C33B	Mo1B	Ru1B	81.3 (3)	C71B	C72B	C73B	108 (1)
S1B	Ru2B	Ru1B	77.22 (6)	C33B	Mo1B	Mo2B	132.8 (3)	C72A	C73A	C74A	107 (1)
S1B	Ru2B	Mo2B	52.72 (6)	S1B	Mo1B	Ru3B	52.93 (6)	C74B	C73B	C72B	106 (1)
Ru3B	Ru2B	Ru1B	60.55 (3)	S1B	Mo1B	Ru1B	75.64 (6)	C75A	C74A	C73A	106 (1)
Ru3B	Ru2B	Mo2B	93.17 (4)	S1B	Mo1B	Mo2B	49.61 (6)	C75B	C74B	C73B	108 (1)
Ru1B	Ru2B	Mo2B	62.36 (3)	Ru3B	Mo1B	Ru1B	58.08 (3)	C71A	C75A	C74A	110 (1)
C32A	Ru3A	Ru2A	125.9 (3)	Ru3B	Mo1B	Mo2B	86.19 (4)	C71B	C75B	C74B	109 (1)

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

connected by three metal–metal bonds. The Mo–Ru distances, Mo(1)–Ru(1) = 2.9129 (8) Å and Mo(2)–Ru(1) = 2.8989 (9) Å, are very similar to those in the base of the square pyramid of 2. The Mo(1)–Mo(2) bond of 3.0282 (8) Å is slightly shorter than the Mo–Mo bond in 2. Compound 3 contains a triply bridging sulfido ligand. The Ru–S distance of 2.314 (2) Å is shorter than the two Mo–S distances, 2.385 (2) and 2.371 (2) Å. There are seven carbonyl ligands. The three CO ligands on Ru(1) are linear. Those on the molybdenum atoms are weakly semi-

Table VII. Positional Parameters and *B*(eq) for $RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)$ (3)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru1	0.67769 (4)	0.11364 (3)	0.34105 (4)	2.89 (2)
Mo1	0.72835 (4)	0.02149 (3)	0.09769 (4)	2.51 (2)
Mo2	0.77768 (4)	−0.05221 (3)	0.36970 (5)	2.77 (2)
S	0.6092 (1)	−0.0164 (1)	0.2733 (1)	3.11 (6)
O11	0.9262 (4)	0.1438 (3)	0.1219 (5)	5.3 (2)
O12	0.5983 (4)	0.1796 (3)	0.0057 (4)	5.0 (2)
O21	0.9012 (5)	0.0845 (3)	0.5260 (7)	9.4 (4)
O22	0.9794 (4)	−0.0628 (4)	0.1934 (5)	6.9 (3)
O31	0.6274 (4)	0.1239 (3)	0.6333 (5)	6.2 (3)
O32	0.4829 (4)	0.2212 (3)	0.2720 (5)	5.4 (3)
O33	0.8357 (5)	0.2616 (3)	0.3522 (6)	7.6 (3)
C11	0.8526 (5)	0.1007 (4)	0.1200 (5)	3.4 (3)
C12	0.6445 (5)	0.1236 (4)	0.0505 (5)	3.4 (3)
C21	0.8473 (6)	0.0421 (4)	0.4583 (7)	5.4 (4)
C22	0.8987 (5)	−0.0522 (4)	0.2488 (6)	4.5 (3)
C31	0.6458 (5)	0.1198 (4)	0.5231 (6)	4.1 (3)
C32	0.5579 (5)	0.1815 (4)	0.2927 (6)	3.8 (3)
C33	0.7772 (5)	0.2064 (4)	0.3502 (6)	4.2 (3)
C41	0.8291 (5)	−0.0473 (5)	−0.0613 (6)	4.6 (3)
C42	0.7736 (6)	−0.1118 (4)	0.0049 (7)	4.6 (3)
C43	0.6650 (6)	−0.0991 (5)	−0.0164 (7)	5.2 (4)
C44	0.6514 (6)	−0.0267 (5)	−0.0952 (7)	5.3 (4)
C45	0.7555 (6)	0.0062 (5)	−0.1247 (6)	4.9 (4)
C51	0.7215 (7)	−0.1235 (5)	0.5614 (7)	6.0 (4)
C52	0.6828 (6)	−0.1689 (4)	0.4550 (7)	4.7 (4)
C53	0.7679 (8)	−0.2001 (4)	0.3816 (7)	5.5 (4)
C54	0.8602 (7)	−0.1738 (6)	0.445 (1)	7.4 (5)
C55	0.8318 (9)	−0.1257 (6)	0.555 (1)	7.6 (6)

bridging ligands. The metal atoms in 3 contain 48 valence electrons. It is thus electron-precise.[20]

Discussion

The value of the unsaturated compound $[CpMo(CO)_2]_2$ as a reagent for cluster synthesis has been demonstrated.[21,22] Metal–metal exchange reactions are a commonly used method for obtaining new heteronuclear clusters.[1-6]

The reaction of 1 with $[CpMo(CO)_2]_2$ at 80 °C yielded 3 through a reaction in which the two molybdenum atoms were added in one step to yield the pentanuclear intermediate 2. The importance of molybdenum–sulfur interactions is indicated since both molybdenum atoms in 2 are bonded to the sulfido ligand. As shown schematically in Scheme I, the Mo–Mo triply bonded unit in $[CpMo(CO)_2]_2$ was inserted into one of the Ru–S bonds. Each molybdenum atom formed two Mo–Ru bonds, and square-pyramidal cluster resulted. The yield of 2 was low because under the reaction conditions 2 is converted into 3. Details of the expulsion of the two ruthenium atoms

Table VIII. Intramolecular Distances (Å) for $RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)$ (3)[a]

atom	atom	dist
Ru1	C31	1.876 (7)
Ru1	C32	1.891 (7)
Ru1	C33	1.912 (7)
Ru1	S	2.314 (2)
Ru1	Mo2	2.8989 (9)
Ru1	Mo1	2.9129 (8)
Mo1	C12	1.969 (6)
Mo1	C11	1.994 (6)
Mo1	C45	2.274 (6)
Mo1	C44	2.286 (6)
Mo1	C41	2.303 (6)
Mo1	C43	2.348 (6)
Mo1	C42	2.360 (6)
Mo1	S	2.385 (2)
Mo1	Mo2	3.0282 (8)
Mo2	C21	1.931 (7)
Mo2	C22	1.938 (7)
Mo2	C55	2.289 (7)
Mo2	C54	2.295 (7)
Mo2	C53	2.329 (6)
Mo2	C51	2.338 (7)
Mo2	C52	2.343 (6)
Mo2	S	2.371 (2)
O11	C11	1.138 (6)
O12	C12	1.142 (6)
O21	C21	1.162 (7)
O22	C22	1.162 (7)
O31	C31	1.135 (7)
O32	C32	1.141 (7)
O33	C33	1.132 (7)
C41	C45	1.393 (9)
C41	C42	1.396 (9)
C42	C43	1.380 (9)
C43	C44	1.40 (1)
C44	C45	1.43 (1)
C51	C52	1.37 (1)
C51	C55	1.37 (1)
C52	C53	1.38 (1)
C53	C54	1.37 (1)
C54	C55	1.39 (1)

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

Table IX. Intramolecular Bond Angles (deg) for $RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)$ (3)[a]

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C31	Ru1	C32	93.0 (2)	C11	Mo1	S	123.8 (2)	Mo2	S	Mo1	79.10 (5)
C31	Ru1	C33	93.1 (3)	C11	Mo1	Ru1	76.5 (2)	O11	C11	Mo1	174.0 (5)
C31	Ru1	S	104.7 (2)	C11	Mo1	Mo2	89.0 (2)	O12	C12	Mo1	170.7 (5)
C31	Ru1	Mo2	92.4 (2)	S	Mo1	Ru1	50.60 (4)	O21	C21	Mo2	164.9 (6)
C31	Ru1	Mo1	153.1 (2)	S	Mo1	Mo2	50.25 (4)	O22	C22	Mo2	167.1 (5)
C32	Ru1	C33	95.3 (3)	Ru1	Mo1	Mo2	58.37 (2)	O31	C31	Ru1	179.4 (6)
C32	Ru1	S	97.7 (2)	C21	Mo2	C22	86.6 (3)	O32	C32	Ru1	175.3 (5)
C32	Ru1	Mo2	150.2 (2)	C21	Mo2	S	113.6 (2)	O33	C33	Ru1	178.2 (6)
C32	Ru1	Mo1	103.7 (2)	C21	Mo2	Ru1	63.1 (2)	C42	C41	C45	109.3 (6)
C33	Ru1	S	157.4 (2)	C21	Mo2	Mo1	102.2 (2)	C41	C42	C43	107.9 (6)
C33	Ru1	Mo2	113.7 (2)	C22	Mo2	S	115.5 (2)	C42	C43	C44	108.7 (6)
C33	Ru1	Mo1	106.0 (2)	C22	Mo2	Ru1	105.7 (2)	C43	C44	C45	107.8 (6)
S	Ru1	Mo2	52.66 (4)	C22	Mo2	Mo1	65.7 (2)	C41	C45	C46	106.3 (6)
S	Ru1	Mo1	52.80 (4)	S	Mo2	Ru1	50.89 (4)	C52	C51	C55	107.3 (8)
Mo2	Ru1	Mo1	62.80 (2)	S	Mo2	Mo1	50.66 (4)	C51	C52	C53	109.5 (7)
C12	Mo1	S	93.0 (2)	Ru1	Mo2	Mo1	58.83 (2)	C52	C53	C54	106.6 (7)
C12	Mo1	Ru1	71.4 (2)	Ru1	S	Mo2	76.45 (5)	C53	C54	C55	108.6 (8)
C12	Mo1	Mo2	129.3 (2)	Ru	S	Mo1	76.60 (4)	C54	C55	C51	108.0 (8)

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

were not provided by this study. Since no Ru_2Mo_2 species were observed, it is believed that both ruthenium carbonyl groups were eliminated rapidly. Most of the ruthenium was isolated as $Ru_3(CO)_{12}$. This could have passed through $Ru(CO)_5$ since this is known to convert into $Ru_3(CO)_{12}$ under the reaction conditions. Small amounts of ruthenium were used in the formation of higher nuclearity products.[13]

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Registry No. 1, 105121-22-0; **2**, 111189-74-3; **3**, 92067-61-3; **4**, 109013-40-3; **5**, 109064-30-4; $Ru_7(CO)_{20}(\mu_4\text{-}S)_2$, 109466-69-5; $[CpMo(CO)_3]_2$, 12091-64-4; $[CpMo(CO)_2]_2$, 56200-27-2.

Supplementary Material Available: Tables of positional parameters for compound 1, positional parameters of the hydrogen atoms for compounds 2 and 3, C–C and C–O distances for 1 and 2, and anisotropic thermal parameters for 1–3 (14 pages); listings of observed and calculated structure factor amplitudes for 1–3 (86 pages). Ordering information is given on any current masthead page.

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Preparation and Reactivity of Sodium Organocuprates[1]

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Sodium organocuprates, R_2CuNa, can be prepared from organosodium reagents (RNa) and CuCN or $CuBr{\cdot}SMe_2$ at −50 °C in THF. The resulting reagents show typical cuprate reactivity; however, they are less reactive toward a typical α-enone than the corresponding Li cuprates. Organocuprate reactivity toward 2-iodoheptane appears to be controlled by the counterion (CN^- vs I^-) rather than by the metal ion (Na^+ vs Li^+). Both $Bu_2CuNa{\cdot}NaCN$ and $Bu_2CuLi{\cdot}LiCN$ are very stable and react quantitatively with PhCOCl. Whereas treatment of di-*tert*-butyl thioketone with BuNa or BuLi yields predominately reduction product, treatment with the corresponding cuprates yields a substantial proportion of thiophilic addition product. The effects of 15-crown-5 and 12-crown-4 on $Bu_2CuNa{\cdot}NaCN$ and $Bu_2CuLi{\cdot}LiCN$ are also described.

Organocuprates arguably are the most important of the transition-metal organometallic reagents, and they are among the most important of all the many reagents currently applied to organic synthesis.[2] While the counterion in the Cu(I) precursor (X in Scheme I) has been varied widely (e.g., halide,[3-5] cyanide,[6] acetylide,[7] methanide,[8] mesitylenide,[9] alkoxide,[10] mercaptide,[10] amide,[11] phosphide,[11,12] triflate[13]), the only metal ions that have been partners with Cu in previous cuprates have been Li, Mg, and, to a *very* limited extent, Zn,[14,15] Cd,[15] Zr,[16] B,[17] and Hg.[18] Other metals have been added to organocopper reagents in the form of Lewis acids.[19] We have been able to prepare sodium cuprates by the addition of organosodium reagents to CuCN or $CuBr{\cdot}SMe_2$. These new species possess typical organocuprate reactivity but have some significant differences from the corresponding lithium cuprates.

Scheme I

$$CuX + 2RM \rightarrow R_2CuM{\cdot}MX \text{ (or } R_2Cu(X)M_2)$$

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