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Synthesis and Structure Studies of Sulfido/Molybdenum/Late-Transition-Metal Clusters with a General Formula $Cp_2Mo_2M'_{2-3}S_{2-4}(CO)_n$

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Several new bimetallic sulfur clusters, $Cp_2Mo_2Co_3S_2(CO)_7$ (**3**), $Cp_2Mo_2Co_2S_3(CO)_4$ (**4**), $Cp_2Mo_2Co_2S_2(CO)_6$ (**5**), and $Cp_2Mo_2Fe_2S_4(CO)_6$ (**6**), were synthesized from the reaction of late-transition-metal carbonyls and a Mo/S dimer, $Cp_2Mo_2(SMe)_2(CO)_2$ (**1**). Overall yields from the reaction are better than those of reported methods. Compound **3** has an unprecedented framework stoichiometry $Mo_2Co_3S_2$, and **4** contains a μ_4-S ligand. The bonding interactions and 4e donor property of the μ_4-S ligand are illustrated with EHMO studies. Both **3** and **4** can be viewed as capped butterfly clusters with a $Co(CO)_3$ group or a sulfur atom as the capping group. The geometrical similarity and interconversion among clusters with four, five, and seven framework members are discussed in terms of skeleton electron counting theories. Compound **6** is geometrically an edge-shared bisquare pyramid. This shape gives a less compact structure than those of similar M_4S_4 cubane clusters. X-ray crystallography data are as follows. **3**: monoclinic space group $P2_1/c$; $a = 8.174(4)$, $b = 18.473$ (7), $c = 14.436$ (11) Å; $\beta = 97.92$ (5)°; $Z = 4$; $R = 0.053$. **4**: monoclinic space group $C2/c$; $a = 15.374$ (5), $b = 11.888$ (7), $c = 10.346$ (4) Å; $\beta = 103.83$ (3)°; $Z = 4$; $R = 0.031$. **6**: space group $P2_1/c$; $a = 6.588$ (2), $b = 16.666$ (4), $c = 19.834$ (5) Å; $\beta = 92.26$ (2)°; $Z = 4$; $R = 0.034$.

Introduction

The study of heteronuclear early-transition-metal/late-transition-metal/sulfido clusters, M/M'/S, has been stimulated by discoveries that some important biological systems may contain M/M'/S cores, e.g. a Mo/Fe/S core in nitrogenase,[1] by ideas of modeling solid and heterogeneous catalytic processes with these clusters[2] or using these clusters as supported catalysts or their precursors,[3] and by the potential applications of these clusters in catalytic hydrodesulfurization (HDS) and CO hydrogenation reactions.[4]

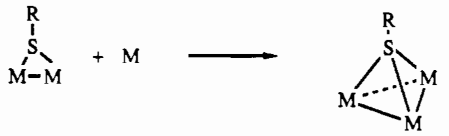
Synthetic methods for heteronuclear clusters have been well reviewed.[5] As poor yields and lack of systematic methods are general problems in cluster syntheses, there have been efforts to develop rational syntheses or stepwise syntheses of clusters in recent years. Two general strategies have been adopted in the rational preparation of bimetallic sulfur clusters. One is transmetalation,[6] in which a homonuclear cluster is synthesized first and then converted to a heteronuclear one by metal group displacement. The other is "heterometallic condensation", to form a bimetallic cluster directly from two different metal complexes.[7]

The second approach is most successful when several coupling sites that facilitate the nuclearity increase are present in the reactants. Some factors that are important in successful condensation reactions are listed below.

1. Easily Displaceable Ligands. The increase of metal nuclearity usually requires the elimination of ligands such as CO or H_2.

2. Expansion of the Coordination Number of the Ligands (μ_n-L). The increase of metal nuclearity is often also accompanied by an increase of ligand coordination number, *n*. Thio or sulfido ligands are especially amenable to coordination number expansion (eqs 1-4).[8]


(1)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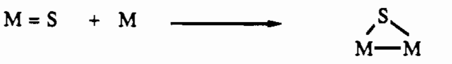
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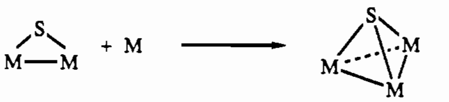
(4)

3. S–S Bond. The S–S bond of disulfido ligands is also useful in forming new M–S bonds via metal oxidative insertion.[9] This

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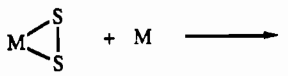
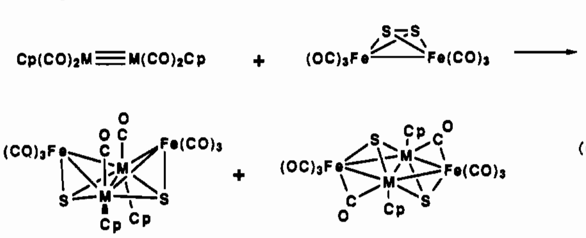
bond reorganization is functionally equivalent to expansion of the sulfur coordination number (eq 5).



(5)

4. Metal–Metal Multiple Bonds. Metal–metal multiple bonds have been intensively studied, and their reactivity has been well documented.[10] They may show high reactivities toward both electrophiles and nucleophiles. Several bimetallic clusters were successfully synthesized by combining the reactivities of metal–metal triple bonds and S–S bonds (eq 6).[11-13]



(6)

M= Cr, Mo (7a)

M= Mo (7b)

Another challenging topic in cluster chemistry is understanding the relationship among bonding, reactivity, and structure, especially in clusters that contain atoms or groups with unusual bonding geometries. Several systems of electron counting for transition-metal clusters have been developed since the early extension of the borane cluster theory to transition-metal clusters.[14] These methods try to relate the geometrical shapes of a cluster to its electronic structure, as deduced from the number and types of metal atoms and ligands present.

This paper reports the syntheses and structural results for several new bimetallic sulfur clusters with the general formula $Cp_2Mo_2M'_{2-3}S_{2-4}(CO)_x$. A new synthetic reaction that gave overall yields better than those of previous methods was developed. The principal bonding interactions of a μ_4-S ligand with the cluster core were determined by EHMO calculations. Bonding and geometrical shapes for M_4, M_5, M_4S, M_4S_3, and M_5S_2 cores were also explored with the aid of EHMO modeling and the results compared to skeleton electron counting theories.

Table I. Spectroscopic Data

compd	NMR,^{a} ppm	IR,^{b} cm^{-1}	MS^c
trans-$Cp_2Mo_2(SMe)_2(CO)_2$ (**1a**)	5.44 (5 H, Cp)	1833 (vs)	P (472)
	5.29 (5 H, Cp)	1799 (m)	P − CO
	2.36 (6 H, Me)		P − 2CO
			P − 2CO − 2Me
	91.10 (10 C, Cp)		etc.
	32.58 (2 C, Me)		
cis-$Cp_2Mo_2(SMe)_2(CO)_2$ (**1b**)	5.39 (5 H, Cp)	1830	same as above
	2.29 (3 H, Me)		
	90.97 (C, Cp)		
	34.24 (C, Me)		
$Cp_2Co_3Mo_2S_2(CO)_7$ (**3**)	paramag	1977 (s)	P − CO (732)
		1855 (s)	P − 2CO (705)
		1816 (m)	etc.
$Cp_2Co_2Mo_2S_3(CO)_4$ (**4**)	5.73 (5 H, Cp)	1984 (s)	P (648)
		1950 (s)	P − CO
			P − 2CO
			P − 3CO
			P − 4CO
			etc.
$Cp_2Co_2Mo_2S_2(CO)_7$ (**5**)	5.54 (5 H, Cp)	2041 (s)	P − CO (672)
		2004 (vs)	P − 2CO
		1808 (ms)	etc.
$Cp_2Fe_2Mo_2S_4(CO)_6$ (**6**)	6.29 (5 H, Cp)	2035	n.o.^{d}
		1969	

[a] All NMR data are from $CDCl_3$ unless further indicated. ^1H and ^{13}C spectra are indicated by H and C, respectively. [b] All IR data are referred to CO stretch frequency in KBr unless further indicated. [c] All mass spectra are obtained by electron impact unless further indicated. P stands for parent ion. Parentheses contain *m/e* values. [d] Not observed.

Experimental Section

All manipulations and reactions were carried out under purified nitrogen gas with standard Schlenk techniques or in an inert-atmosphere box unless indicated otherwise. KBr samples for IR spectra were usually prepared in air. Reagent grade solvents were dried and distilled prior to use. Toluene, tetrahydrofuran (THF), and diethyl ether were distilled from Na/benzophenone. Hexane was distilled from CaH_2. Dichloromethane was either predried over CaH_2 and then distilled from P_2O_5 or directly distilled from CaH_2. NMR data were collected on a Bruker AM-300 or a Bruker WM-360 spectrometer. IR data were obtained on Nicolet 60-SX, Nicolet 5-DX, and Nicolet 5DXB machines. Mass spectra were collected on either a VG-70-250-S high-resolution mass spectrometer or a Finnigan 4021 quadrupole mass spectrometer. Elemental analyses were carried out by Galbraith Laboratories Inc.

Preparation of $Cp_2Mo_2(SMe)_2(CO)_2$ (1a,b). A 250-mL 3-neck flask with a condenser and a gas inlet was charged with 20 g (41 mmol) of $Cp_2Mo_2(CO)_6$ and 120 mL of toluene. This solution was refluxed under a slow nitrogen sweep to form the Mo triply bonded compound $Cp_2Mo_2(CO)_4$, which is indicated by the color change from purple red to brick red or by IR spectra of the solution.[15] Me_2S_2 (4 mL, 44 mmol) was then added to the solution (after it cooled to room temperature) dropwise with a syringe. The solution was then heated to about 80 °C for 3 h until the color of the solution turned to greenish brown and gas evolution has ceased. The temperature was increased and the solution refluxed for an additional 5 h. The completeness of the reaction was checked by monitoring the IR spectra. The solution was filtered, concentrated under vacuum, and then kept at 0 °C. The brown crystalline product was obtained in about 85% yield. This is a mixture of trans **1a** and cis **1b** in the molar ratio of 4:1 and is pure enough to be used as starting material for subsequent syntheses. The two isomers can be separated by either column chromatography or extraction and recrystallization. The latter is more convenient. The more soluble brown trans **1a** was extracted with 3:1 toluene and hexane and then recrystallized from the extraction. The green cis **1b** was recrystallized from 3:1 CH_2Cl_2

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and toluene. Alternatively, **1a** could be washed down from a neutral alumina column with toluene and **1b** could be collected in an eluate of 2:1 CH_2Cl_2 and THF. Spectra are described in Table I. Anal. Found (calcd for $C_{14}H_{16}Mo_2S_2$): C, 35.25 (35.60); H, 3.44 (3.42); S, 13.6 (13.58).

Preparation of $Cp_2Mo_2S_2(SMe)_2$ (2). A 200-mL 3-neck flask was charged with 1.0 g (31 mmol) of sulfur. A solution of compound **1** (7.0 g, 14.8 mmol) in 120 mL of THF was transferred slowly to the above flask. After 5 min at room temperature, gas evolution was noted. The solution was stirred for an additional 12 h and then filtered. Compound **2** was crystallized from the filtrate in about 50% yield. This compound showed the same spectral properties as described previously.[17d]

Synthesis of $Cp_2Mo_2Co_3S_2(CO)_7$ (3). A 3-neck flask equipped with a condenser and a gas inlet was charged with 2.8 g (5.9 mmol) of **1** and 20 mL of THF. Another 20 mL of THF solution of 2.6 g (7.6 mmol) of $Co_2(CO)_8$ was transferred to the above flask with a cannula at room temperature. The mixture was heated to reflux for 20 h or until the reaction was complete, as indicated by the IR spectrum of the solution. The black brown solution was then filtered. After concentration, the filtrate was subjected to column chromatography through a 55 × 3.5 cm column filled with degassed, neutral, active alumina. The column was eluted sequentially with hexane, a 1:1 mixture of hexane and toluene, toluene, a mixture of toluene and CH_2Cl_2 (ca. 2:1), and pure CH_2Cl_2. A purple brown band, a red brown band, and a black brown band were then obtained in that order. The first eluate, which was mainly composed of **3**, was again chromatographed through a new column. Pure **3** was collected with a 2:1 toluene and hexane eluate as the first purple red band in about 25–30% yield. Needlelike single crystals for X-ray structural determination were obtained by slow evaporation of the toluene solvent. See Table I for the spectral data.

Synthesis of $Cp_2Mo_2Co_2S_3(CO)_4$ (4) and $Cp_2Mo_2Co_2S_2(CO)_7$ (5). Method 1. A 3-neck flask equipped with a condenser and a gas inlet was charged with 1.38 g (2.9 mmol) of **1** and 15 mL of THF. A 10-mL THF solution of $Co_2(CO)_8$ (1.0 g, 2.9 mmol) was transferred dropwise to the above flask with a cannula at room temperature. The mixture was refluxed for 17 h until the reaction was complete, as indicated by the IR spectrum of the solution. After it was concentrated, the black filtrate was transferred to the top of a 40 × 2.5 cm chromatographic column filled with predried, neutral, active alumina. The column was washed sequentially with hexane, toluene, diethyl ether, and CH_2Cl_2. Compound of **4** was collected in toluene as the second dark brown band, and **5** was contained in the mixture of toluene and diethyl ether as the third, dark purple brown band. Single crystals of **4** were obtained by slow diffusion of hexane into a toluene solution of **4**. Compound **5** crystallized from toluene as square, rod-shaped crystals. Attempts to grow single crystals for X-ray analysis failed. Melting point of **5**: 238–239 °C. See Table I for spectral data.

Method 2. Compound **4** was also prepared from the reaction of **2** and $Co_2(CO)_8$. For procedures of this method, refer to the previously reported synthesis of the methylcyclopentadienyl derivative, $(MeCp)_2Mo_2Co_2S_3(CO)_4$.[13]

Synthesis of $Cp_2Mo_2Fe_2S_4(CO)_6$ (6). Method 1. $Fe_2(CO)_9$ (0.8 g, 2.1 mmol) and **1** (1.0 g, 2.1 mmol) were dissolved in 25 mL of THF in a 3-neck flask equipped with a condenser and a gas inlet at room temperature. The mixture was heated to reflux for 15 h. The extent of reaction was monitored by IR spectroscopy. The mixture was filtered and then concentrated; the filtrate was transferred to a 40 × 2.5 cm chromatography column of degassed, neutral, active alumina. The first band, which washed down with a 1:1 mixture of hexane and toluene, contained the remaining reactants. Compound **6** was collected in a mixture of 1:3 hexane and toluene in the second band. The other two major products, planar and butterfly $Cp_2Mo_2Fe_2S_2(CO)_8$, were then eluted in a mixture of 2:1 ethyl ether and toluene and pure CH_2Cl_2, respectively. Single crystals of **6** for X-ray analysis were obtained by slow evaporation of solvent of the toluene solution.

Table II. Crystallographic Data for $Cp_2Mo_2Co_3S_2(CO)_7$

chem formula	$C_{17}H_{10}Co_3Mo_2O_7S_2$
mol wt	759.1
space group	$P2_1/c$
a–c, Å	8.174 (4), 18.473 (7), 14.436 (11)
β, deg	97.92 (5)
V, Å^3	2159
Z	4
D_{calc}, g/cm^3	2.335
cryst dimens, mm	0.221 × 0.345 × 1.760
abs coeff (Mo Kα), cm^{-1}	35.5
scan range	Mo Kα_1 − 0.8 to Mo Kα_2 + 0.9
bkgd:time ratio	0.8
2θ, deg	45
no. of rflcns collcd	2785
no. of rflcns > 3σ	2605
R, R_w	0.053, 0.053
residual, e/Å^3	0.95

Table III. Fractional Atomic Coordinates and Isothermal Parameters for $Cp_2Mo_2Co_3S_2(CO)_7$

atom	x	y	z	U, Å^2
Mo1	0.2560 (01)	0.3932 (00)	0.6972 (00)	0.0303
Mo2	0.2555 (01)	0.2611 (00)	0.7711 (00)	0.0336
Co1	0.0804 (02)	0.3720 (01)	0.8381 (01)	0.0402
Co2	0.3945 (02)	0.3735 (01)	0.8726 (01)	0.0390
Co3	−0.0298 (01)	0.3207 (01)	0.6848 (01)	0.0401
S1	0.4910 (03)	0.3262 (01)	0.7531 (01)	0.0396
S2	0.1772 (03)	0.2873 (01)	0.6136 (01)	0.0408
C1	−0.0902 (12)	0.4078 (05)	0.7489 (07)	0.0526
O1	−0.1806 (09)	0.4555 (04)	0.7373 (06)	0.0710
C2	−0.0424 (14)	0.3392 (06)	0.9209 (08)	0.0661
O2	−0.1228 (13)	0.3196 (06)	0.9736 (07)	0.1261
C3	0.1356 (16)	0.4563 (06)	0.8899 (07)	0.0710
O3	0.1470 (12)	0.5139 (05)	0.9189 (07)	0.0983
C4	0.4915 (14)	0.4586 (05)	0.8863 (06)	0.0558
O4	0.5597 (12)	0.5125 (04)	0.8966 (05)	0.0865
C5	0.4866 (13)	0.3357 (06)	0.9809 (07)	0.0551
O5	0.5442 (11)	0.3100 (05)	1.0501 (05)	0.0852
C6	−0.1383 (12)	0.2454 (05)	0.7237 (08)	0.0568
O6	−0.2131 (10)	0.1988 (04)	0.7458 (07)	0.0865
C7	−0.1689 (14)	0.3450 (05)	0.5844 (08)	0.0594
O7	−0.2576 (12)	0.3603 (05)	0.5198 (06)	0.1002
C11	0.3608 (15)	0.4581 (05)	0.5792 (07)	0.0566
C12	0.4171 (12)	0.4923 (05)	0.6627 (07)	0.0521
C13	0.2830 (16)	0.5223 (04)	0.6984 (07)	0.0618
C14	0.1382 (12)	0.5032 (05)	0.6360 (07)	0.0562
C15	0.1909 (15)	0.4638 (05)	0.5620 (06)	0.0547
C21	0.3191 (15)	0.1765 (05)	0.8938 (07)	0.0595
C22	0.1602 (14)	0.1627 (05)	0.8510 (08)	0.0616
C23	0.1627 (15)	0.1401 (05)	0.7590 (08)	0.0658
C24	0.3358 (17)	0.1425 (05)	0.7447 (07)	0.0676
C25	0.4269 (13)	0.1647 (05)	0.8284 (08)	0.0598

Method 2. Compound **6** also can be prepared from $Cp_2Mo_2S_2(SH)_2$ and $Fe_2(CO)_9$[13] or $Fe(CO)_5$ in the presence of Me_3NO.[16]

X-ray Crystal Structure Determinations. Crystals were mounted in 0.2–0.4 mm i.d. capillaries under N_2 atmosphere. The cell constants were determined from 15 centered reflections collected on a Syntex $P2_1$ diffractometer. SHELX-86 and SHELX-76 computing programs were used in the solution and refinement. Direct methods were used to locate the heavy atoms in solving the structure. Carbon and oxygen atoms were located from difference maps after a least-squares refinement of heavy-atom positions. Absorption corrections were performed on all compounds except **4**. Anisotropic full-matrix refinement was applied to all non-hydrogen atoms. Hydrogen atoms of the Cp rings were placed at the calculated positions with d_{C-H} = 1.07 Å and refined with isotropic temperature factors equal to 0.050 Å^2. Weighted refinements were applied at later stages, and the agreement indices R and R_w were used in evaluating refinement results throughout.[6] The summary of the crystallographic data and the fractional atomic coordinates for **3** are given in Tables II and III.

Results

Synthesis. $Cp_2Mo_2(SMe)_2(CO)_2$ (1) and $Cp_2Mo_2S_2(SMe)_2$ (2). Trans **1a** and cis **1b** were obtained in 4:1 molar ratio in a total

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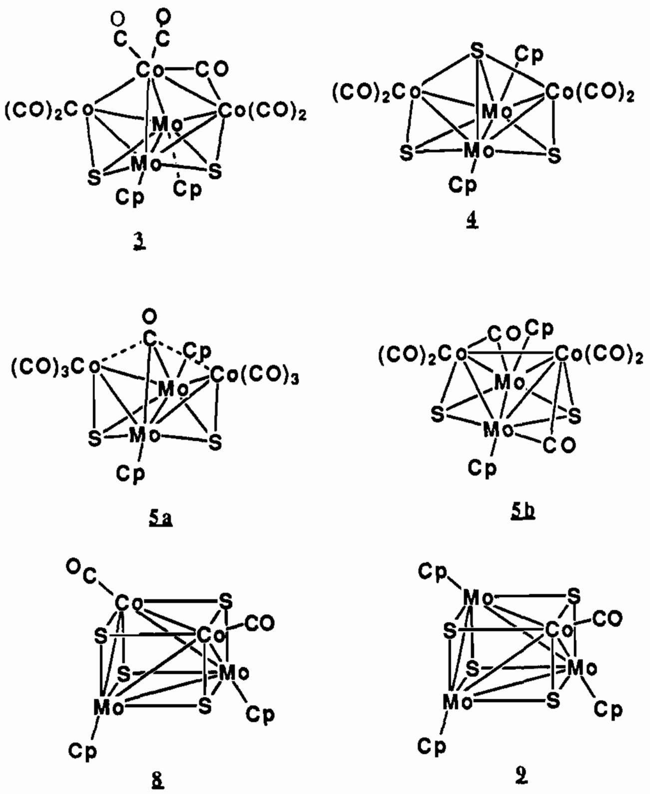
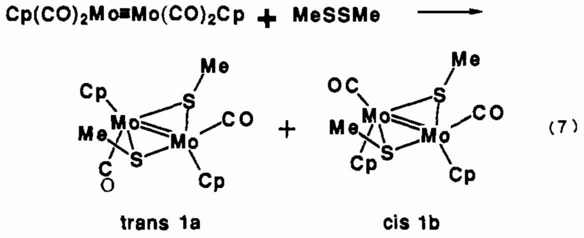
Chart I



yield of 80–90% from the reaction of $Cp_2Mo_2(CO)_4$ and Me_2S_2 (eq 7). Trans and cis isomers were identified by NMR and IR



(7)

spectra. In the ^1H NMR spectra, trans **1a** and cis **1b** showed two and one Cp peaks, respectively. Two ν_{CO} absorption bands appeared in the IR spectra of **1a**, accounting for its low symmetry; one ν_{CO} peak was observed in **1b**. The crystal structure of the SBu analogue of trans **1a** has been reported before.[17i]

Reactivity of **1b** toward metal carbonyls is significantly lower than that of **1a**. The reactions usually needed longer time and higher temperature for completion with **1b**.

Mo/Co Clusters. $Cp_2Mo_2Co_3S_2(CO)_7$ (3). Cluster **3** (Chart I) was isolated, together with **4** and **5**, from route 3 starting with **1** and $Co_2(CO)_8$ in 1:1.3 molar ratio. No significant amount **3** could be isolated from the corresponding reaction with a 1:1 molar ratio carried out in a refluxing toluene solution. Cluster **3** has an unprecedented framework stoichiometry $Co_3Mo_2S_2$, which was identified by X-ray structural analysis. The parent ion peak did not appear in the mass spectrum obtained by electron impact ionization. The highest peak observed was *m/e* 732, corresponding to the ion $[P-CO]^+$. The paramagnetism of **3** was evident in that the complex did not exhibit a ^1H NMR spectrum; however, accurate susceptibility data were not obtained due to an insufficient amount of sample and the low sensitivity of the magnetometer used. The IR spectrum showed a weak ν_{CO} of the bridge CO at 1816 cm^{-1}.

Table IV. Selected Bond Distances (Å) for $Cp_2Mo_2Co_3S_2(CO)_7$

	Framework		
Mo1–Mo2	2.663 (01)	Co1–Co3	2.462 (02)
Mo1–Co1	2.674 (02)	Mo1–S1	2.333 (02)
Mo1–Co2	2.652 (01)	Mo1–S2	2.342 (03)
Mo1–Co3	2.678 (01)	Mo2–S1	2.315 (02)
Mo2–Co1	2.750 (01)	Mo2–S2	2.327 (02)
Mo2–Co2	2.701 (01)	Co2–S1	2.177 (02)
Mo2–Co3	2.720 (01)	Co3–S2	2.186 (03)
Co1–Co2	2.547 (02)		
	Ligands		
Mo1–C11	2.341 (08)	Co2–C4	1.759 (10)
Mo1–C12	2.348 (09)	Co2–C5	1.781 (10)
Mo1–C13	2.396 (08)	Co3–C1	1.954 (10)
Mo1–C14	2.368 (08)	Co3–C6	1.781 (10)
Mo1–C15	2.347 (08)	Co3–C7	1.772 (11)
Mo2–C21	2.365 (08)	C1–O1	1.147 (11)
Mo2–C22	2.342 (08)	C2–O2	1.131 (12)
Mo2–C23	2.359 (09)	C3–O3	1.143 (13)
Mo2–C24	2.333 (09)	C4–O4	1.141 (11)
Mo2–C25	2.345 (09)	C5–O5	1.147 (11)
Co1–C1	1.883 (10)	C6–O6	1.128 (11)
Co1–C2	1.770 (10)	C7–O7	1.135 (12)
Co1–C3	1.758 (11)		

$Cp_2Mo_2Co_2S_3(CO)_4$ (4), $Cp_2Mo_2Co_2S_2(CO)_6$ (5), $Cp_2Mo_2Co_2S_4(CO)_2$ (8), and $Cp_2Mo_3CoS_4(CO)$ (9). Compound **4** was separated as the major product from the reaction of **2** and $Co_2(CO)_8$ together with **5**, **8**, and trace amount of **9**. The disulfide cluster **5** was the dominant product (40–45% yield) in the reaction of **1** with $Co_2(CO)_8$. Compound **3** did not appear or appeared in small, variable amounts from either of these two routes when they were carried out in a refluxing toluene solution with a 1:1 molar ratio of reactants.

Cluster **4** was identified by single-crystal X-ray diffraction analysis and IR and NMR spectroscopies. The structure of **5** was based on NMR, IR, and MS spectra, as single crystals suitable for diffraction analysis were not obtained. The mass spectrum of **5** gave the highest peak at *m/e* 672, which corresponds to the formula of $Cp_2Mo_2Co_2S_2(CO)_6$. The IR spectrum of **5** indicates a typical μ_2-CO stretching frequency at 1808 cm^{-1} (1816 cm^{-1} for bridge CO in **3**). A reasonable structure for this 60-VSE compound will be a bicapped tetrahedron, as drawn in **5b** (Chart I). However, our MO modeling shows that a bicapped tetrahedron may be less stable than the corresponding 62-VSE butterfly cluster. Alternatively, $Cp_2Mo_2Co_2S_2(CO)_7$, a 62-VSE butterfly cluster with one more carbonyl group may be proposed, as drawn in **5a**. In fact, an isoelectronic cluster, $Cp_4Mo_2Ni_2S_2(CO)$, in which the CpNi fragments occupy the positions of the $Co(CO)_3$ groups in structure **5a**, has been characterized,[18] but the IR spectrum of the nickel complex shows a very low frequency band (1650 cm^{-1}) for the μ_4-CO. Hence, structure **5b** is favored, but an X-ray structure determination is needed for unambiguous identification of **5**.

The 60-VSE cubane cluster **8** was characterized previously.[19] Compound **9** was observed in mass spectra with very small abundance, and crystals obtained by another route have been characterized by X-ray crystallography.[20]

Mo/Fe Clusters. $Cp_2Mo_2Fe_2S_4(CO)_6$ (6) and $Cp_2Mo_2Fe_2S_2(CO)_8$ (7a,b). Three synthetic routes have been used to search for new Mo/Fe/S clusters. The reaction of triply bonded $Cp_2Mo_2(CO)_4$ with $Fe_2S_2(CO)_6$ remains as the best single step reaction of preparing disulfido clusters cis **7a** and trans **7b**. The reaction of **1** with $Fe_2(CO)_9$ gave predominantly **7** and about a 15% yield of **6**. Although the single-step yield of the latter route for preparing disulfido clusters **7** is not as high as that in the former, the overall yield, including the preparation of starting materials, is better. For the tetrasulfido cluster **6** (the core structure is shown in Figure 3), the reaction of **2** with $Fe_2(CO)_9$ gave the best result. A photolysis reaction for preparing an analogue of **6** has been published.[21] Cluster **6** was identified by

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Table V. Selected Bond Angles (deg) for $Cp_2Mo_2Co_3S_2(CO)_7$

Mo2–Mo1–Co1	62.0 (0)	Mo1–Co1–Mo2	58.8 (0)
Mo2–Mo1–Co2	61.1 (0)	Mo1–Co1–Co2	61.0 (0)
Co1–Mo1–Co2	57.1 (0)	Mo2–Co1–Co2	61.2 (0)
Mo2–Mo1–Co3	61.2 (0)	Mo1–Co1–Co3	62.7 (0)
Co1–Mo1–Co3	54.8 (0)	Mo2–Co1–Co3	62.6 (0)
Co2–Mo1–Co3	104.4 (0)	Co2–Co1–Co3	114.5 (1)
Mo2–Mo1–S1	54.7 (1)	Mo1–Co2–Mo2	59.7 (0)
Co1–Mo1–S1	99.3 (1)	Mo1–Co2–Co1	61.9 (0)
Co2–Mo1–S1	51.3 (1)	Mo2–Co2–Co1	63.1 (0)
Co3–Mo1–S1	115.3 (1)	Mo1–Co2–S1	56.7 (1)
Mo2–Mo1–S2	54.9 (1)	Mo2–Co2–S1	55.4 (1)
Co1–Mo1–S2	97.6 (1)	Co1–Co2–S1	107.8 (1)
Co2–Mo1–S2	115.4 (1)	Mo1–Co3–Mo2	59.1 (0)
Co3–Mo1–S2	51.1 (1)	Mo1–Co3–Co1	62.5 (0)
S1–Mo1–S2	83.7 (1)	Mo2–Co3–Co1	63.9 (0)
Mo1–Mo2–Co1	59.2 (0)	Mo1–Co3–S2	56.5 (1)
Mo1–Mo2–Co2	59.3 (0)	Mo2–Co3–S2	55.3 (1)
Co1–Mo2–Co2	55.7 (0)	Co1–Co3–S2	108.7 (1)
Mo1–Mo2–Co3	59.6 (0)	Mo1–S1–Mo2	69.9 (1)
Co1–Mo2–Co3	53.5 (0)	Mo1–S1–Co2	71.9 (1)
Co2–Mo2–Co3	102.0 (0)	Mo2–S1–Co2	73.9 (1)
Mo1–Mo2–S1	55.4 (1)	Mo1–S2–Mo2	69.6 (1)
Co1–Mo2–S1	97.7 (1)	Mo1–S2–Co3	72.4 (1)
Co2–Mo2–S1	50.7 (1)	Mo2–S2–Co3	74.1 (1)
Co3–Mo2–S1	114.3 (1)	Co1–C1–Co3	79.8 (4)
Mo1–Mo2–S2	55.5 (1)	Co1–C1–O1	140.5 (9)
Co1–Mo2–S2	95.9 (1)	Co3–C1–O1	139.7 (9)
Co2–Mo2–S2	114.1 (1)		
Co3–Mo2–S2	50.6 (1)		
S1–Mo2–S2	84.4 (1)		

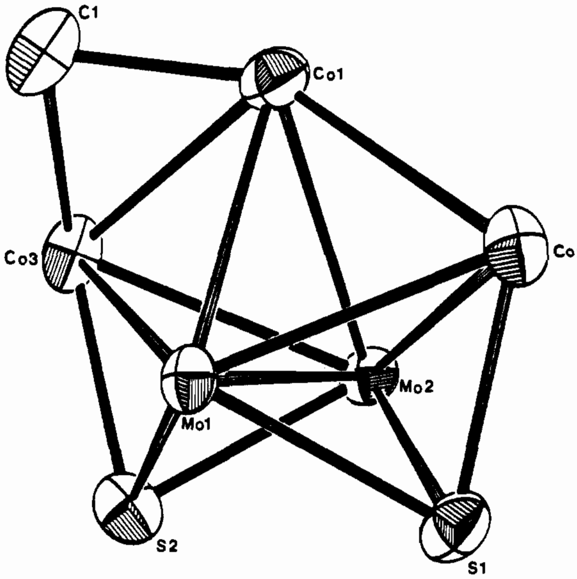

Figure 1. ORTEP plot (50% probability thermal ellipsoids) for the core structure of $Cp_2Mo_2Co_3S_2(CO)_7$.

a single-crystal X-ray structure determination and by spectroscopic methods. Compounds **7a** and **7b** have been reported.[12,13]

Structures. $Cp_2Mo_2Co_3S_2(CO)_7$ (3). Crystallographic data, fractional atomic coordinates, selected bond distances, and bond angles are listed in Tables II–V. ORTEP plots for the framework and the molecule are given in Figures 1 and 2, respectively. The structure of **3** is formed from a Mo_2Co_2 butterfly core by capping its M_4 cavity with a $Co(CO)_3$ fragment. The existence of the unsymmetric bridge CO causes the tilt of the capping Co atom, resulting in a larger Co1–Co2 distance as compared to the Co1–Co3 distance, the dihedral angle *D*1 > *D*2 (refer to Table VI for definition of *D*1 and *D*2), and other unevenness of Mo–Co bond lengths. The Mo–Mo distance, 2.668 Å, is normal in comparison with those of other similar butterfly clusters. The total 71 valence shell electrons (VSE) is 1 electron short of a normal M_5, trigonal-bipyramidal metal cluster.

$Cp_2Mo_2Co_2S_3(CO)_4$ (4). The methylcyclopentadienyl derivative was reported previously.[13] The structure found by X-ray analysis of the Cp analogue prepared here is identical with that of the previous reported MeCp cluster within experimental error. More "hypercoordinate" atoms[22] have been discovered since the first recognized in the carbide cluster $Fe_5C(CO)_{15}$.[23] Additional examples of μ_4-S ligands are found in Mo_4,[24] Ni_4,[25] Cr_2Ni_2,[26] and Mo_2Fe_2[27] clusters. The dihedral angles in **3** and **4** are compared in Table VI.

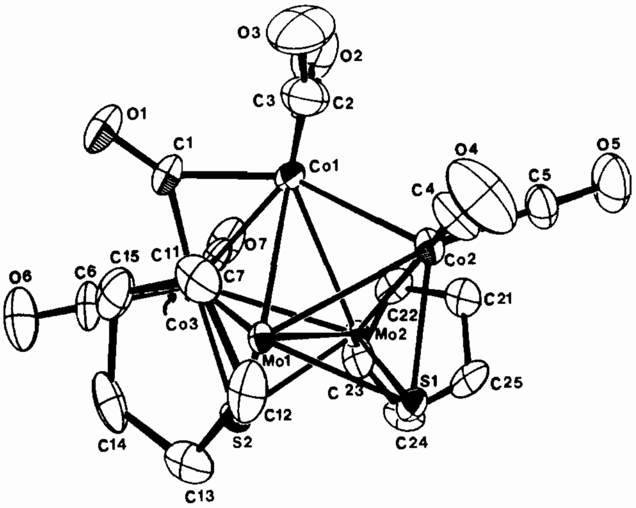

Figure 2. ORTEP plot (35% probability thermal ellipsoids) for the molecular structure of $Cp_2Mo_2Co_3S_2(CO)_7$.

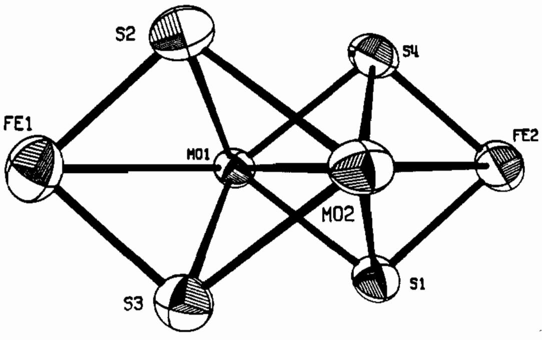

Figure 3. ORTEP plot (50% probability thermal ellipsoids) for the molecular structure of $Cp_2Mo_2Fe_2S_4(CO)_6$.

Table VI. Comparison of Dihedral Angles[a] (deg) in $Cp_2Mo_2Co_3S_2(CO)_7$ (3) and $Cp_2Mo_2Co_2S_3(CO)_4$ (4)

	*D*1	*D*2	*D*3	*D*4	*D*5
3	66.1	62.8	60.9	60.8	109.4
4	62.4	62.4	61.9	61.9	111.4

[a] Key:

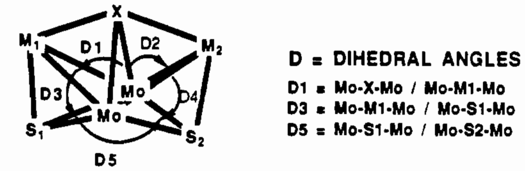

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Table VII. Equations of Planes for $Cp_2Mo_2Fe_2S_4(CO)_6$

	Plane Mo1–S1–Fe2–S4			
variables[a]	$L = 0.3847$	$M = 0.9228$	$N = 0.0186$	$D = 7.445$
atoms	Mo1	Fe2	S1	S4
deviations, Å	0.0867	−0.0939	0.1023	−0.0951
	Plane Mo2–S2–Fe1–S3			
variables[a]	$L = 0.3866$	$M = 0.9222$	$N = -0.0112$	$D = 5.622$
atoms	Mo2	Fe1	S2	S3
deviation, Å	−0.1011	0.1099	−0.1186	0.1898

[a] Where $Lx + My + Nz + D = 0$.

$Cp_2Mo_2Fe_2S_4(CO)_6$ (6). It has been recognized since the late 1960s or early 1970s that clusters containing either a homonuclear or a heteronuclear M_4S_4 core often adopt the so-called cubane structure.[28] These structures usually obey the noble gas rule, and clusters with 60 VSE (with six M–M bonds) to 72 VSE (no M–M bonds) are known. The core structure of **6**, which was synthesized independently by two groups,[13,16] has a quite different geometrical arrangement, an edge-sharing bisquare pyramid. As shown in Figure 3, Mo1 and Mo2 atoms each serve as an apex in one pyramid and member of the square base in the other pyramid; the Mo–Mo bond is the shared edge between the two pyramids. One square pyramid is formed by Mo2, the apex, and Mo1–S1–Fe2–S4, the square base. The other pyramid is composed of Mo1 and the Mo2–S2–Fe1–S3 plane. The equations of planes for the Mo1–S1–Fe2–S4 and Mo2–S2–Fe1–S3 bases, together with atomic deviations from these planes, are given in Table VII. Considering the differences of atomic radii among the three elements, these equations of planes support the assignment of the edge-shared bisquare-pyramidal structure.

Two groups of Mo–S bond lengths were observed, the apex Mo–S and the base Mo–S bonds. The first group includes Mo1–S2, Mo1–S3, Mo2–S1, and Mo2–S4; average $d_{Mo-S} = 2.390$ Å, and values range from 2.385 to 2.400 Å. The second group involves Mo1–S1, Mo1–S4, Mo2–S2, and Mo2–S3; average $d_{Mo-S} = 2.454$ Å, and values range between 2.448 and 2.460 Å. These differences arise from the fact that the S atoms in the basal Mo–S–Fe bridges span a nonbonded Mo···Fe pair ($d_{Mo-Fe} = 3.599$ Å) whereas the shorter set span a Mo–Mo bond. Bridge–metal distances usually contract when a metal–metal bond is present.[29]

Discussion

Synthetic Routes. Three routes have been used to prepare bimetallic clusters of the type $Cp_2Mo_2M'_xS_{2-4}(CO)_y$ (where M′ = Fe, Co, and Ni).

$$\text{route 1:}\quad [CpMo(CO)_2]_2 + Fe_2S_2(CO)_6 \rightarrow \text{products}$$

$$\text{route 2:}\quad \underset{\mathbf{2}}{[CpMoS(SMe)]_2} + M'_x(CO)_y \rightarrow \text{products}$$

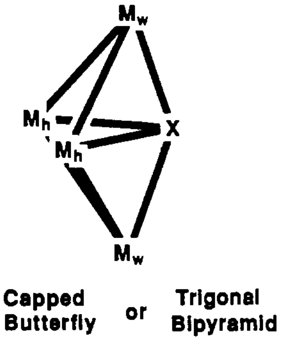
$$\text{route 3:}\quad \underset{\mathbf{1}}{[CpMo(SMe)(CO)]_2} + M'_x(CO)_y \rightarrow \text{products}$$

Route 1 has been used to prepare some Mo/Fe/S clusters (cf. eq 6), but this route is limited by the paucity of late-transition-metal disulfides. Some group 7 M_2S_2 complexes have been prepared in high yields recently,[30] but Co and Ni analogues are rare.[31]

On the other hand, a great number of Mo/S dimers with various bridge or terminal thio or sulfido ligands are well-known.[17] A kinetic study on cyclopentadienylmolybdenum dimers with tetrathiolato or sulfido ligands carried out by DuBois and co-workers showed that sulfido ligands μ_2-S in Mo dimers reacted with benzyl isocyanide via an associative mechanism, while thiolato ligands, μ_2-SR, reacted through a dissociative process.[32] Recent ^{95}Mo NMR and molecular orbital studies indicated that complexes with bridging dithio and disulfido ligands exhibit higher nucleophilicity of their sulfur atoms over other tetrasulfur Mo dimers.[33] This nucleophilicity is utilized in route 2.

Only a few cyclopentadienylmolybdenum thiolato dimers $[CpMo(SR)L]_2$ (used in route 3) and their applications in cluster building have been reported.[17j,k] These dimers contain a Mo=Mo double bond, which may aid the cluster-forming reaction by suppressing fragmentation of the Mo–Mo bond. Our results show that **1** in route 3 is less active than **2** in route 2 in reactions with late-transition-metal carbonyls. This lower reactivity may be explained by the lower basicity of a μ_2-SR ligand vs a μ_2-S ligand and by the fact that a S–Me bond must be cleaved to form the final clusters. In spite of its lower reactivity, higher overall yields are often achieved in route 3 due to the high-yield synthesis of **1**.

Bonding Considerations. It is interesting to compare the bonding in the cluster **3** (Mo_2Co_3 core) with that in cluster **4** (Mo_2Co_2S core). A bimetallic $M_2M'_3$ cluster may be regarded as a capped butterfly or as a distorted trigonal bipyramid. A "type 1" distortion results when all three M′ atoms occupy equatorial positions in the trigonal bipyramid or—in the butterfly notation—when M′ atoms are at the hinge (M_h) and capping positions (X).



The most likely type 1 distortion is an elongation or compression along the 3-fold axis caused by movement of the M atoms in the wing-tip positions (M_w).

The type 2 distortion, movement of the capping atom X toward or away from the M_4 cavity, is more probable when M′ atoms occupy the wing tips (M_w) and capping positions (X) and the M atoms are at the hinge positions (M_h).

Dahl and co-workers have synthesized and characterized a series of $M_2Ni_3(CO)_{16}{}^{2-}$ clusters (M = Cr, Mo, W) that have 76 valence shell electrons (VSE).[34] Lauher was shown that the bonding capacity of a trigonal bipyramid rises from 72 VSE to 76 VSE as the axial–equatorial M–M′ bonds are stretched.[35]

In Teo's topological approach, the VSE count for a metal cluster is given by $VSE = 2[8V - F + 2 + X]$, where V = number of (transition metal) vertices, F = number of faces, and $X = 0$ or 2 for a trigonal bipyramid. X represents the number of "missing" cluster antibonding orbitals or the number of electron pairs in excess of the EAN. Multiple values of X indicate "a perturbation in the polyhedral structure and/or variation in the cluster bonding capabilities."[14f] Thus, VSE = 72 or 76 for a trigonal bipyramid. Teo states[14g] that most trigonal-bipyramidal structures known to data have 76 VSE with an elongated, i.e., type 1, distortion.

Cluster 3, with an Mo_2Co_3 core, has 71 VSE, i.e., 1 electron short of the 72 VSE count required when $X = 0$. Open-shell Fenske–Hall calculations suggest the odd electron is delocalized

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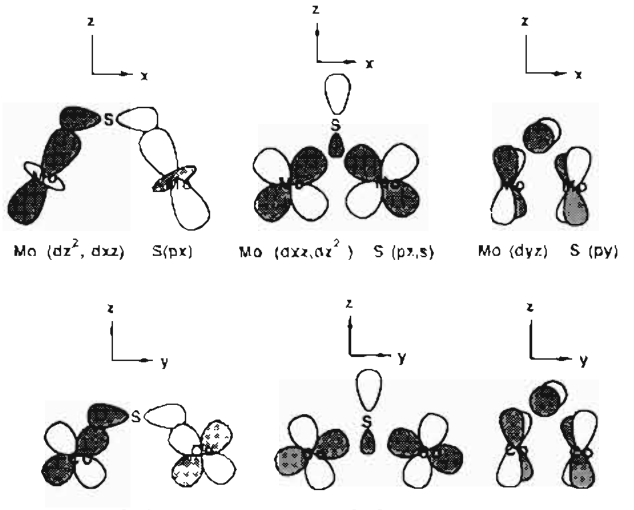

Figure 4. Principal orbital interactions of the μ_4-S atom in $Cp_2Mo_2Co_2S_3(CO)_4$. Diagrams are arranged in the order of descending overlap populations for each M/S interaction.

over the Mo2–Co1–Co2 face.[36]

Teo's equation can be modified for inclusion of main-group elements in the cluster framework as VSE = 2[8(TM) + 2(MG) – F + 2 + X], where TM = number of transition-metal vertices and MG = number of main-group vertices. The factor "2" is derived by ignoring exopolyhedral bonds to or lone pairs on the main-group vertex atoms.[37] Thus, the Mo_2Co_2S core in **4** requires 2[8(4) + 2(1) – 6 + 2 + X] = 60 + 2X VSE (X = 0 or 2). The observed 60-VSE count in **4** is consistent with a value of X = 0, and clusters **3** and **4** have comparable electronic structures. This might be anticipated by noting that the $Co(CO)_3$ fragment is isolobal with S (three orbitals used for constructing the cluster framework in each case), but the former fragment contributes 1 less electron (3) than the sulfur atom (4).

It is interesting to note that the $Mo_2Co_3S_2$ and $Mo_2Co_2S_3$ cores can be treated as bicapped trigonal bipyramids (i.e., counting the μ_3-sulfur atoms as part of the cluster framework), using Teo's equation as modified above. For the M_5S_2 core, VSE = 2[8(5) + 2(2) – 10 + 2 + X] = 72 + 2X, and for M_4S_3 core, VSE = 2[8(4) + 2(3) – 10 + 2 + X] = 60 + 2X. That the VSE requirements are identical with those based on a trigonal bipyramid with the μ_3-S ligands merely donating 4 electrons to the total electron count reflects the well-known fact that capping a triangular face of a cluster does not change the electron count.

The core of cluster **6**, $Mo_2Fe_2S_4$, is formed from two edge-shared square pyramids. Apparently, this structural feature has not been observed in all-metal, M_8 clusters and is extremely rare even for metal–heteroatom clusters. Teo's rule 6 states that X = number of shared edges; in this case X = 1, and VSE = 2[8(8) – 10 + 2 + X] = 112 + 2X = 114 for an all-metal cluster. For the M_4S_4 core, we have VSE = 2[8(4) + 2(4) – 10 + 2 + X] = 64 + 2X = 66 for X = 1. The observed electron count for **6** is 66.

These results suggest that μ_3- and μ_4-sulfido ligands can be considered to be an integral part of the cluster polyhedron and that there exists a very close relationship between the geometries and electronic structures of M_nS_x clusters and the corresponding M_{n+x} all-metal clusters.

In the treatment, both μ_3- and μ_4-sulfido ligands were considered to donate 4 electrons to the cluster VSE count. As part of our ongoing studies on the electronic structures of metal sulfido clusters, we had occasion to perform EHMO studies of cluster **4**.

Here, we briefly mention the main features of the bonding of μ_3- and μ_4-sulfido ligands: (1) mostly S atomic p orbitals are used, although a significant fraction of the overlap populations involve sulfur 3s orbitals; (2) in **4**, the overlap populations are fairly evenly divided between Co–S (40%) and Mo–S (60%) bonds; (3) the total M–S overlap population to the μ_4-S atom is 1.55 compared to 1.57 for the metal–μ_3-S bonds (this suggests both μ_3- and μ_4-S donate the same number of electrons). The fact that the same overlap population is spread over four M–S bonds in the μ_4 ligand rather than concentrated in three bonds in the μ_3 ligand provides the rationale for the longer μ_4-S to metal bonds. The principal orbital interactions are illustrated in Figure 4.

Conclusions. $Cp_2Mo_2(SR)_2(CO)_2$ derivatives have been shown to be useful precursors to new bimetallic sulfido clusters. A modification of Teo's topological equation to include main-group vertices shows the close similarity of geometries of sulfido clusters and all-metal cluster cores.

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Supplementary Material Available: Tables VIIIS–XIS (fractional atomic positions, bond distances, and bond angles for **4**), Tables XIIS–XVS (fractional atomic positions, bond distances, and bond angles for **6**), Tables XVIS–XVIIIS (thermal parameters for **3**, **4**, and **6**), and Figures 5S–7S (PLUTO plots for molecules and cores of **4** and **6**) (14 pages); Tables XIXS–XXIS (F_o vs F_c data for clusters **3**, **4**, and **6**) (25 pages). Ordering information is given on any current masthead page.

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Redox Chemistry of Diphenyl Diselenide and Its Chemistry in the Presence of Protons, Hydroxide, Water, and Hydrogen Peroxide

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In acetonitrile, diphenyl diselenide (PhSeSePh) undergoes a reversible one-electron reduction (–0.85 V vs SCE), which is similar to the electrochemical behavior of dioxygen. PhSeSePh facilitates the oxidation of water and hydroxide ion and the reduction of protons. In combination with HOOH, PhSeSePh is photocatalyzed and proton-catalyzed to form a 1:1 adduct, which reacts with two more HOOH molecules to form two PhSe(O)OH molecules. This adduct adds to olefins (RCH=CHR') to form RCH(OH)CH(SePh)R'.

The chemistry of organoselenium compounds has been extensively investigated because of their utility in organic synthesis.[1–3] Barton and co-workers[4] have demonstrated that the Gif system (iron catalyst, O_2, zinc dust, acetic acid, and pyridine) for the

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