4.45 (d, *J* = 8 Hz, FeC*H*), 1.00–2.75 (m, $C_6\mathit{H}_9O$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.12, 215.75 (Fe*C*O), 213.49 (*C*═O), 143.36 (ipso), 128.54, 127.81, 124.97 ($S\mathit{C}_6H_5$), 86.92 (C_5H_5), 65.52 (FeCH*C*H), 41.97 (C(═O)*C*H_2), 34.51, 28.18, 24.19, 23.42 (cyclohexyl $(\mathit{C}H_2)_3$ and Fe*C*H). **A + B**: IR (FT, CH_2Cl_2) 2018, 1958 (FeCO), 1700 (CC(═O)C) cm^{-1}; MS (EI) *m/e* 396 (M^+), 340 (M – 2 CO), 230 (CpFeSPh); exact mass for $FeSC_{18}H_{20}O$ (M – 2 CO) calcd 340.0584, found 340.0576.

General Procedure for Reactions of Dialkylcuprates with 2c,d. (η^5-Cyclopentadienyl)dicarbonyl[1-methyl-1-(alkylthio)alkyl]iron (3e–g). A suspension of cuprous iodide (0.714 g, 3.75 mmol) in ether (20 mL) was cooled to –15 °C (for lithium dimethylcuprate) or to –50 °C (for lithium di-*n*-butylcuprate) under nitrogen. The alkyllithium (7.5 mmol) was added dropwise with stirring to the gray suspension. (The flask was brought to –30 °C for 10 min in the case of the di-*n*-butylcuprate.) The flask was then cooled to –78 °C, and **2c** or **2d** (1.0 g, 2.5 mmol) in methylene chloride (10 mL) was slowly added via a double-ended needle. The mixture was allowed to warm to 25 °C, and the solvent was removed in vacuo. The residue was extracted with methylene chloride (3 × 10 mL), and the combined extracts were concentrated under vacuum to afford a brown oil. Radial chromatography (4-mm alumina, 4:1 pentane/methylene chloride) yielded the adducts **3e–g**.

3e: obtained as yellow crystals in 63% yield from **2c** and lithium dimethylcuprate: ^1H NMR (300 MHz, $CDCl_3$) δ 4.84 (s, $C_5\mathit{H}_5$), 1.98 (s, $SC\mathit{H}_3$), 1.67 (s, $FeC(C\mathit{H}_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217.2 (Fe*C*O), 87.1 (C_5H_5), 67.9, 39.1, 12.5; IR (Nujol) 2018, 1952 (FeCO) cm^{-1}; MS (EI), *m/e* 238 (M – CO), 210 (M – 2 CO), 121 (FeCp), 89 ($C(SPh)(CH_3)_2$); exact mass for $C_{10}H_{14}FeOS$ (M – CO) calcd 238.0114, found: 238.0114.

3f: obtained as an impure brown oil, containing an unidentified contaminant having strong aliphatic absorptions in the ^1H NMR spectrum, in 51% yield from **2c** and lithium di-*n*-butylcuprate: ^1H NMR (300 MHz, acetone-d_6) δ 4.96 (s, $C_5\mathit{H}_5$), 1.90 (s, $SC\mathit{H}_3$), 1.71 (s, $FeCC\mathit{H}_3$), 1.25–1.82 (m, 10 H, $FeC(C\mathit{H}_2)_3CH_3$ and impurity), 0.96 (t, *J* = 7.3 Hz, 4 H, impurity), 0.90 (t, *J* = 6.9 Hz, $(CH_2)_3C\mathit{H}_3$); ^{13}C NMR (75 MHz, acetone-d_6) δ 218.7, 218.2 (Fe*C*O), 88.1 (C_5H_5), 49.5, 44.1, 36.9, 31.9, 24.0, 14.6, 12.5; MS (EI), *m/e* 280 (M – CO), 252 (M – 2 CO), 131 ($C(SCH_3)(CH_3)(C_4H_9)$, 121 (CpFe); exact mass for $C_{13}H_{20}FeOS$ (M – CO) calcd 280.0583, found 280.0564.

3g: obtained as a yellow brown oil in 60% yield from **2d** and lithium dimethylcuprate: ^1H NMR (300 MHz, $CDCl_3$) δ 7.14–7.42 (m, $SC_6\mathit{H}_5$), 4.87 (s, $C_5\mathit{H}_5$), 1.49 (s, $FeC(C\mathit{H}_3)_2$); IR (Nujol) 2038, 1952 (FeCO) cm^{-1}; MS, *m/e* 300 (M – CO), 272 (M – 2 CO), 230 (CpFeSPh), 218 (M – PhSH), 151 ($C(SPh)(CH_3)_2$), 121 (CpFe); exact mass for $C_{15}H_{16}FeOS$ (M – CO) calcd 300.0271, found: 300.0265.

Acknowledgment. We wish to thank Professor Robert C. Kerber (SUNY at Stony Brook) for very valuable discussions, Drs. Edward J. O'Connor and Ramnath S. Iyer for assistance in the initial phases of this work, and Dr. Thomas R. Sharp (University of Utah) for obtaining some of the mass spectrometric data. We are also pleased to acknowledge the award of a Lubrizol Fellowship to C.K. (1985–1986), the National Science Foundation (CHE 8120466), the donors of the Petroleum Research Fund, administred by the American Chemical Society, and the University of Notre Dame for providing generous support for this work, the National Science Foundation for providing matching funds for the purchase of the 300-MHz NMR spectrometer, and Professor Björn Åkermark and the Royal Institute of Technology (Stockholm, Sweden) for providing a visiting scientist position for P.H. (1986). Structures and schemes were drawn by using the ChemDraw program developed by Stewart Rubenstein.

Supplementary Material Available: Tables of thermal parameters, group parameters, and derived crystallographic coordinates for group atoms for complexes **2b** and **2c** and hydrogen atom coordinates and short interionic contacts for **2b** (7 pages); listings of structure factors for **2b** and **2c** (16 pages). Ordering information is given on any current masthead page.

Syntheses and Characterization of Organometallic Molybdenum–Iron–Sulfur and Molybdenum–Cobalt–Sulfur Clusters

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The photochemical reaction of $[MeCpMoS(SH)]_2$ (Cp = C_5H_5: MeCp = $CH_3C_5H_4$) with $Fe(CO)_5$ has resulted in the formation of $[MeCpMoS_2Fe(CO)_3]_2$ (I) in >50% yield. A second minor product, $(MeCp)_2Mo_2S_3Fe_2(CO)_6$ (II), has also been isolated from this reaction. Complex II has been prepared in better yield from the reduction of I with potassium graphite. X-ray diffraction studies of each of these complexes have been completed. I crystallizes in space group $P\bar{1}$ with a = 6.598 (2) Å, b = 10.168 (3) Å, c = 10.203 (3) Å, α = 99.81 (2)°, β = 107.55 (2)°, γ = 108.99 (2)°, V = 589.1 Å^3, and Z = 1. Complex II crystallizes in space group $P\bar{1}$ with a = 12.542 (2) Å, b = 10.724 (2) Å, c = 10.296 (1) Å, α = 121.35 (9)°, β = 93.90 (1)°, γ = 106.07 (1)°, V = 1088.5 (3) Å^3, and Z = 2. The structure of I contains a rather unusual planar array of metal ions, while II involves a butterfly arrangement of metal ions bridged by one μ_4- and two μ_3-sulfur ligands. The structures of these complexes are described and compared with those of related clusters. The reactions of $[MeCpMoS(SH)]_2$ with $CpFe(CO)_2I$ and $CpCo(CO)I_2$ have resulted in the formation of $[(MeCp)_2Mo_2S_4FeCp][I]$ (III) and $[(MeCp)_2Mo_2S_4CoCp][(I)_2]$ (IV), respectively. Complex III crystallizes in space group Cc with a = 19.348 (10) Å, b = 6.673 (3) Å, c = 17.524 (9) Å, β = 112.68 (4)°, V = 2087.3 (2) Å^3, and Z = 4. The metal ions of III lie in a plane that is perpendicular to the plane of sulfur atoms. The structure contains two μ_3-sulfur ligands and a η^2-S_2 ligand that bridges the two molybdenum ions. Spectral and electrochemical properties of the new clusters are discussed. Their reactions with unsaturated molecules and with electrophilic and nucleophilic reagents are compared to those of the related dinuclear molybdenum–sulfur complexes.

Introduction

The sulfido ligands in tetrasulfur-bridged cyclopentadienyl molybdenum dimers have been found to react with hydrogen and with unsaturated molecules, and a number of hydrogenation and hydrogenolysis reactions have been catalyzed.[1-3] It is interesting to consider the

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Table I. Selected Interatomic Distances and Angles for $[MeCpMoS_2Fe(CO)_3]_2$ (I)

Interatomic Distances (Å)			
Mo(1)–Mo(1a)	2.624 (2)	Fe(1)–C(7)	1.801 (4)
Mo(1)–S(1)	2.456 (3)	Fe(1)–C(8)	1.806 (4)
Mo(1)–S(2)	2.458 (2)	Fe(1)–C(9)	1.784 (5)
Mo(1)–S(1a)	2.395 (3)	Mo(1)–Fe(1a)	2.853 (3)
Mo(1)–S(2a)	2.393 (2)	Mo(1)···Fe(1)	3.612 (3)
Fe(1)–S(2)	2.232 (3)	S(1)···S(2a)	2.808 (3)
Fe(1)–S(1)	2.237 (2)	S(1)···S(2)	2.961 (3)
Angles (deg)			
S(1)–Mo(1)–S(2)	74.11 (6)	Fe(1)–S(1)–Mo(1a)	75.94 (7)
S(1)–Mo(1)–S(2a)	70.75 (8)	Fe(1)–S(2)–Mo(1a)	76.07 (9)
Fe(1)–S(1)–Mo(1)	100.55 (7)	S(1)–Fe(1)–S(2)	82.99 (7)
Fe(1)–S(2)–Mo(1)	100.64 (7)		

possible relevance of this sulfur-based reactivity to the catalytic molybdenum–sulfur sites in industrial and reductive enzyme systems. A characteristic common to the composition of these systems is the presence of one or more first-row group 8–10 metal ions. For example, Co or Ni ions incorporated onto the surface of the heterogeneous hydrodesulfurization catalysts have been found to promote the catalytic reactivity of the molybdenum sulfide sites.[4] The mechanism of this promotional effect is not well-understood. In the molybdenum-containing enzyme nitrogenase, the cofactor has been isolated and characterized as an iron–molybdenum–sulfur cluster with the approximate core composition $MoFe_{6-8}S_{8-10}$.[5] The structure and the nature of the reactive sites within the cofactor have not yet been determined.

Although the cyclopentadienyl molybdenum systems do not closely approximate the compositions or structures of the catalyst systems discussed above, they have permitted the identification of fundamentally new reactivity patterns of bridging sulfido ligands that may have applicability in other metal–sulfur systems. As part of a general program to investigate the electronic and steric factors that influence this reactivity, we have attempted to study the effects of group 8–10 metal ions on the properties of these molybdenum dimers. Our approach has been to react an equivalent of an iron or cobalt complex or fragment with the sulfido ligands in a well-characterized molybdenum dimer. It was hoped that the resulting trinuclear cluster would retain the $Mo(\mu\text{-}S)_2Mo$ unit as a reactive site with hydrogen and unsaturated molecules and thereby function as a metallodithiolate analogue of the highly reactive methanedithiolate-bridged dimer.[1-3]

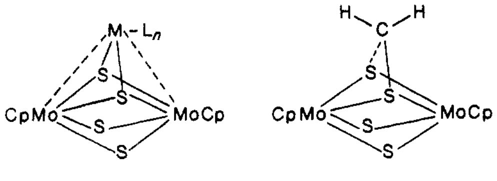

Table II. Positional and Thermal Parameters for the Atoms of $[MeCpMoS_2Fe(CO)_3]_2$ (I)

atom	x	y	z	U_{eq}, Å^2
Mo(1)	0.06372 (5)	0.05670 (3)	−0.09477 (3)	0.0264 (1)
Fe(1)	0.20799 (9)	0.23474 (6)	0.27877 (5)	0.0314 (3)
S(1)	0.3310 (1)	0.0997 (1)	0.15061 (9)	0.0305 (4)
S(2)	−0.0848 (2)	0.1682 (1)	0.06735 (9)	0.0328 (4)
C(1)	0.0011 (4)	−0.1452 (3)	0.2999 (3)	0.042 (2)
C(2)	−0.1423 (4)	−0.0675 (3)	0.3028 (3)	0.050 (2)
C(3)	−0.3527 (4)	−0.1425 (3)	0.1799 (3)	0.052 (2)
C(4)	−0.3394 (4)	−0.2667 (3)	0.1011 (3)	0.043 (2)
C(5)	−0.1207 (4)	−0.2683 (3)	0.1753 (3)	0.044 (2)
C(6)	−0.042 (1)	−0.3862 (6)	0.1393 (8)	0.076 (4)
C(7)	0.3897 (7)	0.2136 (5)	0.4384 (4)	0.041 (2)
C(8)	0.0401 (8)	0.2933 (5)	0.3679 (5)	0.047 (2)
C(9)	0.3978 (8)	0.4087 (5)	0.2842 (5)	0.048 (2)
O(1)	0.5026 (7)	0.1950 (5)	0.5344 (4)	0.070 (2)
O(2)	0.5231 (8)	0.5171 (4)	0.2863 (5)	0.077 (3)
O(3)	−0.0675 (8)	0.3300 (5)	0.4219 (5)	0.083 (3)

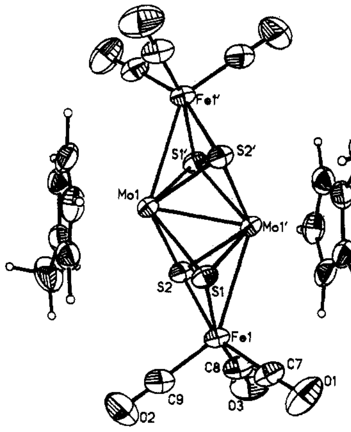

Figure 1. Perspective drawing and numbering scheme for $[MeCpMoS_2Fe(CO)_3]_2$ (I). Thermal ellipsoids for this and the following structures are shown at the 50% probability level.

We report here the synthesis and characterization of several new heteronuclear clusters resulting from these efforts. During the course of this work, the utility of $Cp_2Mo_2S_4$ complexes in cluster syntheses has been established by other workers as well, and their results are compared with ours in the following discussion.

Results and Discussion

Synthesis of $[MeCpMoS_2Fe(CO)_3]_2$ (I). The reaction of $[MeCpMo(S)SH]_2$ or of $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ with 1 equiv of iron pentacarbonyl in the presence of anhydrous trimethylamine *N*-oxide results in the formation of a green air stable molybdenum–iron–sulfur complex of the formulation $[MeCpMoS_2Fe(CO)_3]_2$ in low yield. No trinuclear complex is detected as a product in this reaction. The yield was increased slightly to 25% by using an excess of iron pentacarbonyl. However, the generally low yield appeared to be a result of a competing oxidation of the starting molybdenum dimer by the amine oxide. Photolysis of $[MeCpMo(S)SH]_2$ with an excess of iron pentacarbonyl provided a more efficient synthesis of complex I in greater than 50% yield.

The results of an X-ray diffraction study of I (Figure 1) have been reported in a preliminary communication[6] and will not be discussed here in detail. The centrosymmetric complex contains a planar array of metal atoms bridged by four μ_3-sulfido ligands. The sulfur atoms also lie in a plane that is perpendicular to the plane of metal

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atoms. The molybdenum–sulfur core is very similar to those of previously characterized dithiolate-bridged molybdenum dimers.[7] Each iron carbonyl fragment is displaced from the plane of sulfur atoms and is bonded to only one molybdenum ion.

Several molybdenum–iron complexes that are related to I have been characterized recently. The reaction of $[CpMo(CO)_2]_2$ with $Fe_2S_2(CO)_6$ has resulted in the formation of two complexes with the formulation of $Cp_2Mo_2Fe_2(\mu\text{-}S)_2(\mu\text{-}CO)_2(CO)_6$.[8,9] One of these is a planar isomer that is formally converted to complex I by substitution of the two μ-CO ligands with μ_3-S bridges. This substitution results in the formal oxidation of the metal centers, in the disruption of two metal–metal bonds, and in an increase of the cluster valence electron count[10] from 62 electrons in the carbonyl-bridged cluster to 66 electrons in complex I. The molybdenum–iron distances in both isomers of the carbonyl-bridged derivatives are only about 0.04–0.08 Å shorter than in I. The molybdenum–molybdenum distances, on the other hand, are more than 0.20 Å longer than in I. The decrease in this distance in I reflects the constraints of the bridging sulfur ligands.

The pentamethylcyclopentadienyl (Cp′) molybdenum dimer $(Cp')_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ reacts with iron pentacarbonyl under the same conditions as those reported here to form different products $[Cp'MoS_2Fe(CO)_2]_2$, $Cp'_2Mo_2S_4Fe(CO)_2$, and $Cp'_2Mo_2(S_2CO)S_2Fe(CO)_2$.[11] The metal core of the tetranuclear complex possesses the butterfly geometry normally associated with 62-electron clusters[10] while the trinuclear complexes possess the trigonal-bipyramidal M_3S_2 core. These systems illustrate how the steric and/or electronic properties of the cyclopentadienyl ligands play a determining role in the structure of the polynuclear products. Closely related reactions of $Ni(CO)_4$ and $Co_2(CO)_8$ with cyclopentadienyl and pentamethylcyclopentadienyl molybdenum dimers have resulted in tetranuclear clusters $Cp_2Mo_2S_4Ni_2(CO)_4$ and $Cp'_2Mo_2S_4Co_2(CO)_2$, respectively, for which butterfly geometries have been proposed (Co)[12] or verified by X-ray diffraction (Ni).[13]

Reactivity of I. Although complex I retains the structural core of the $Cp_2Mo_2S_4$ dimers, the iron carbonyl fragments effectively block reactivity at the sulfur ligands. For example, although the sulfido ligands in dinuclear molybdenum complexes react readily with alkynes,[2,14] the iron carbonyl fragment in I is not replaced by acetylene under thermal or photolytic conditions. The cluster is also resistant to Mo–Fe and Fe–S bond cleavage by electrophiles and nucleophiles. In attempted reactions of I with methyl fluorosulfonate or methyl iodide, the starting complex was recovered in each case in high yield. The stepwise addition of triethylborohydride and methyl iodide also resulted in recovery of the starting cluster.

Cyclic voltammetric studies reveal that compound I is redox active. The cluster undergoes two one-electron reductions, one reversible and one quasireversible, at −1.08 and −1.36 V vs. SCE at a platinum wire electrode. Completely irreversible oxidations are observed at +0.54 and 0.80 V. Nevertheless complex I was found to be quite inert to chemical oxidizing and reducing agents. For example, when the compound was stirred with silver tetrafluoroborate in THF, the starting cluster was recovered in nearly quantitative yield. Oxidation of I with trimethylamine *N*-oxide (0.5 equiv) under an atmosphere of acetylene resulted in the formation of a small amount of the bis(alkenedithiolate)-bridged product $[MeCpMo(SC_2H_2S)]_2$, <20%.[14] Approximately 80% of the starting material was recovered. The oxidation and loss of a carbonyl ligand from the iron tricarbonyl unit appears to facilitate replacement of the iron fragment. However, we were unable to use this method to replace only a single metal unit and form a trinuclear cluster of the type $(MeCpMo)_2(S_2Fe(CO)_3)(SCHCHS)$. Attempts to prepare this type of trinuclear derivative by the competitive reaction of iron carbonyl and an alkyne with $[MeCpMo(S)SH]_2$ were also unsuccessful. Only the bis(iron carbonyl) (I) and bis(alkyne) adducts[14] were isolated from these reactions.[15] The reaction of I with reducing agents is discussed below.

Table III. Interconversions of $[MeCpMoS_2Fe(CO)_3]_2$ (I) and $(MeCp)_2Mo_2S_3Fe_2(CO)_6$ (II)

reducing agent	% product, II	% recovered reactant, I
lithium triethylborohydride		
1 equiv	2	45
5–10 equiv		decomp
sodium amalgam (4 equiv)	9	<1
zinc amalgam (16 equiv)	2	95
potassium graphite (5 equiv)	17	75

sulfur transfer agent	% product, I	% recovered reactant, II
elemental sulfur (2 equiv)	4	90
lithium disulfide (1 equiv)	8	20
ethylene sulfide (1 equiv)	<1	90

Synthesis of $(MeCpMo)_2S_3Fe_2(CO)_6$ (II). During the chromatographic isolation of I, a minor brown fraction was also isolated in very low yield (~1%) and formulated as $(MeCpMo)_2S_3Fe_2(CO)_6$ (II) on the basis of mass spectral data. Complex II was not detected until after a significant amount of I had formed in the photolytic reaction. This suggests that II results from the desulfurization of I. We have attempted to synthesize II in better yield by alternate synthetic routes. We found that photolysis of pure solutions of I did not produce II. Its presence as a byproduct in the photochemical synthesis of I may require an iron carbonyl species to act as a sulfur acceptor. However, complex I was not observed to react with other potential sulfur acceptors. For example, neither the photolysis of I with triphenylphosphine or the room temperature reaction of I with tri-*n*-butylphoshine resulted in the formation of II. Small amounts of decomposition products were observed, but most of starting complex I was recovered in each case.

While complex I was found to be rather inert to reducing agents, the reduction of I still proved to be the best method for the synthesis of II. The isolated yield of II and the amount of I recovered depended on the amount and type of reducing agent used (Table III). In the reduction with potassium graphite two dinuclear molybdenum products, $(MeCpMo)_2S_3O$ and $(MeCpMo)_2S_2O_2$,[16] were also isolated from the workup in low yield. This suggests that the reduced form of I removes excessive electron density by

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[15] In the ^1H NMR spectrum of the crude product resonances consistent with a trinuclear product were observed.[6] However, we were unable to isolate this complex.

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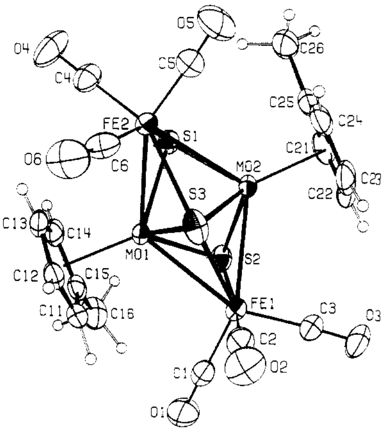

Figure 2. Perspective drawing and numbering scheme for $(MeCpMo)_2S_3Fe_2(CO)_6$ (II).

Table IV. Selected Interatomic Distances and Angles for $(MeCp)_2Mo_2S_3Fe_2(CO)_6$ (II)

Interatomic Distances (Å)			
Mo(1)-Mo(2)	2.673 (1)	Mo(2)-Fe(1)	2.810 (1)
Mo(1)-Fe(1)	2.797 (1)	Mo(2)-Fe(2)	2.852 (1)
Mo(1)-Fe(2)	2.755 (1)	Mo(2)-S(1)	2.355 (1)
Mo(1)-S(1)	2.388 (1)	Mo(2)-S(2)	2.375 (1)
Mo(1)-S(2)	2.382 (1)	Mo(2)-S(3)	2.300 (1)
Mo(1)-S(3)	2.316 (1)	S(1)···S(2)	3.029 (1)
Fe(1)-S(2)	2.229 (1)	Fe(2)-S(1)	2.222 (1)
Fe(1)-S(3)	2.511 (1)	Fe(2)-S(3)	2.595 (1)
Fe(1)-C(1)	1.782 (4)	Fe(2)-C(4)	1.788 (4)
Fe(1)-C(2)	1.813 (4)	Fe(2)-C(5)	1.777 (4)
Fe(1)-C(3)	1.795 (4)	Fe(2)-C(6)	1.780 (4)
Fe(1)···Fe(2)	4.644 (1)		
Angles (deg)			
Mo(1)-Fe(1)-Mo(2)	57.0 (1)	Fe(1)-Mo(1)-Fe(2)	113.6 (1)
Mo(1)-Fe(2)-Mo(2)	56.9 (1)	Fe(1)-Mo(2)-Fe(2)	110.2 (1)
Mo(1)-S(1)-Mo(2)	68.6 (1)	Fe(1)-S(3)-Fe(2)	130.9 (1)
Mo(1)-S(2)-Mo(2)	68.4 (1)	S(1)-Fe(2)-S(3)	92.6 (1)
Mo(1)-S(3)-Mo(2)	70.8 (1)	S(2)-Fe(1)-S(3)	93.7 (1)

extrusion of one sulfur atom to form II or by loss of the iron carbonyl fragments.[17] Although the conversion of I to II is initiated by a reducing agent, the process actually involves a net loss of cluster valence electrons in a transformation from a 66- to a 64-electron cluster.

The sulfur elimination that converts complex I to complex II can be partially reversed by the reaction of II with a sulfur source, such as elemental sulfur or lithium disulfide. As shown in Table III, these reactions result in the low-yield formation of complex I. In the system with lithium disulfide, most of complex II has reacted in some way, but no other tetranuclear products have been identified.

X-ray Diffraction Study of II. Single crystals of II were grown by slow evaporation of a concentrated dichloromethane solution. The cluster crystallizes in the centrosymmetric space group $P\bar{1}$. A perspective view of the complex is shown in Figure 2, and selected bond distances and angles are listed in Table IV. The core of the structure contains a butterfly arrangement of metal atoms with one μ_4- and two μ_3-sulfido ligands. All of the iron and sulfur atoms lie in a plane which is perpendicular to the molybdenum–molybdenum axis.

Several distortions in the molybdenum–iron–sulfur core of this complex are observed relative to that of I. The molybdenum–molybdenum distance in II is 0.05 Å longer than in I and is 0.07–0.10 Å longer than in the related tetrasulfur-bridged molybdenum dimers.[7] The molybdenum–iron distances are slightly shorter than in I but are equivalent to the distances between these metals in other sulfur-bridged clusters discussed above.[9,11] Although the Fe_1 atom symmetrically bridges the molybdenum atoms, the Fe_2 atom is approximately 0.10 Å closer to Mo_1 than Mo_2. The reason for this unsymmetrical interaction is not clear.

Table V. Positional and Thermal Parameters for the Atoms of $(MeCp)_2Mo_2S_3Fe_2(CO)_6$ (II)

atom	x	y	z	U_{eq}, Å^2
Mo(1)	0.27071 (2)	0.08131 (3)	-0.06295 (3)	0.02169 (8)
Mo(2)	0.26294 (2)	0.11102 (3)	-0.30526 (3)	0.02520 (9)
Fe(1)	0.23803 (4)	0.34531 (5)	-0.02156 (5)	0.0327 (2)
Fe(2)	0.15646 (4)	-0.19218 (5)	-0.35927 (5)	0.0288 (1)
S(1)	0.34547 (7)	-0.04974 (9)	-0.28188 (9)	0.0293 (2)
S(2)	0.39986 (7)	0.3003 (1)	-0.0542 (1)	0.0328 (2)
S(3)	0.10813 (7)	0.0582 (1)	-0.2085 (1)	0.0396 (3)
O(1)	0.3306 (3)	0.5508 (3)	0.3215 (3)	0.065 (1)
O(2)	0.0016 (3)	0.3379 (4)	-0.0147 (4)	0.066 (1)
O(3)	0.2942 (3)	0.5972 (4)	-0.0750 (4)	0.066 (1)
O(4)	0.2146 (3)	-0.4510 (3)	-0.3948 (4)	0.069 (1)
O(5)	0.0392 (4)	-0.3578 (4)	-0.6922 (4)	0.090 (1)
O(6)	-0.0509 (3)	-0.2941 (4)	-0.2684 (4)	0.072 (1)
C(1)	0.2934 (3)	0.4692 (4)	0.1881 (4)	0.042 (1)
C(2)	0.0915 (4)	0.3359 (4)	-0.0195 (4)	0.045 (1)
C(3)	0.2721 (3)	0.4968 (4)	-0.0585 (4)	0.043 (1)
C(4)	0.1929 (3)	-0.3496 (4)	-0.3799 (4)	0.041 (1)
C(5)	0.0894 (4)	-0.2891 (5)	-0.5627 (4)	0.049 (1)
C(6)	0.0281 (3)	-0.2507 (4)	-0.3060 (4)	0.044 (1)
C(11)	0.2660 (3)	0.1736 (4)	0.1994 (4)	0.033 (1)
C(12)	0.1797 (3)	0.0193 (4)	0.0966 (4)	0.034 (1)
C(13)	0.2356 (3)	-0.0858 (4)	0.0229 (4)	0.034 (1)
C(14)	0.3565 (3)	0.0051 (4)	0.0779 (4)	0.035 (1)
C(15)	0.3764 (3)	0.1649 (4)	0.1873 (4)	0.032 (1)
C(16)	0.4924 (3)	0.3007 (5)	0.2822 (5)	0.050 (1)
C(21)	0.3726 (4)	0.1765 (5)	-0.4526 (5)	0.050 (1)
C(22)	0.3118 (5)	0.2755 (5)	-0.3921 (5)	0.058 (2)
C(23)	0.1930 (4)	0.1818 (6)	-0.4634 (5)	0.057 (2)
C(24)	0.1807 (4)	0.0257 (5)	-0.5653 (4)	0.046 (1)
C(25)	0.2925 (3)	0.0206 (5)	-0.5606 (4)	0.041 (1)
C(26)	0.3211 (5)	-0.1222 (6)	-0.6607 (5)	0.067 (2)

The metal–(μ_3-sulfur) distances in II are significantly shorter than those in $[MeCpMoS_2Fe(CO)_3]_2$ (I) or than the μ_2-sulfur distances in other Mo(III) dimers. Compared to other sulfur-bridged complexes, these Mo–S (2.37 Å) and Fe–S (2.22 Å) distances are typical for a trivalent sulfur atom bridging these metals.[8,9,11] The molybdenum–(μ_4-sulfur) distances (ca. 2.30 Å) are 0.05–0.09 Å shorter than the corresponding distances to the μ_3-sulfur ligands, while the iron–(μ_4-sulfur) distances (ca. 2.55 Å) are more than 0.30 Å longer than the corresponding distances to the μ_3-sulfur ligands.

The distance between sulfur atoms of the μ_3-sulfur ligands (3.029 (1) Å) is similar to the sulfur–sulfur distances in the dinuclear complexes with $Cp_2Mo_2S_4$ cores.[7] The distances are much less than twice the van der Waals radius of sulfur (3.70 Å). While the sulfur–sulfur separations do not indicate a formal bond, they do suggest that there may be significant interactions between sulfur atoms.

Two complexes have been isolated previously which are structurally similar to $[(MeCp)_2Mo_2S_3Fe_2(CO)_6]$ (II). $[Cp_2Mo_2S_3Co_2(CO)_4]$ was prepared from $[CpMoS(SH)]_2$ and $Co_2(CO)_8$,[13] and $[Cp_2Cr_2S_3Ni_2(Cp)_2]$ was prepared from $[Cp_2Cr_2(SC(CH_3)_3)_2(S)]$ and $[CpNi(CO)]_2$.[18] Both of these products, which have been characterized by X-ray crys-

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(17) The oxygen-containing complexes were not detected in the crude product; it appears that exchange of oxygen for sulfur ligands occurs during the chromatographic workup on alumina. Spectral characterizations of these products are included in the Experimental Section.

(18) Pasynskii, A. A.; Eremenko, I. L.; Ellert, O. G.; Novatortsev, V. M.; Rakitin, Y. V.; Kalinnekov, V. T.; Shklover, V. G.; Struchkoo, Y. T. *J. Organomet. Chem.* **1982**, *234*, 315.

tallography, also contain a "butterfly" arrangement of metal atoms with two μ_3-sulfur ligands and one μ_4-sulfur atom. Compared to the $Fe(CO)_3$ fragment, each CpNi or $Co(CO)_2$ fragment has either one more or one less valence electron, respectively, which is available for cluster bonding. Therefore, the cobalt and nickel clusters contain 62 and 66 valence electrons, respectively. This variation in valence electron counts appears to correlate with the number of metal–metal bonds in each of the clusters. $Cp_2Mo_2S_3Co_2(CO)_4$ contains five metal–metal bonds as expected for a 62-electron cluster, while the 64-electron complex II is tentatively assigned only four M–M bonds. The molybdenum–molybdenum distance in II is significantly longer than this distance in related molybdenum dimers. A localized electron counting scheme, which assumes that the neutral μ_4- and μ_3-sulfur ligands contribute six and four valence electrons, respectively, shows that each molybdenum atom achieves an 18-electron configuration without the assignment of a formal molybdenum–molybdenum bond. The Mo–Mo distance in II is primarily a result of the steric constraints imposed by the five bridging atoms in this geometry and does not accurately reflect the extent of metal–metal interaction. The 66-electron chromium–nickel complex contains three metal–metal bonds. Two of the Cr–Ni distances on opposite wing edges of this butterfly cluster are nonbonding distances of 2.86 Å. No correlation between the dihedral angle between the two butterfly wings of the metal core and the number of valence electrons in this series of complexes is apparent.[19,20]

Formal oxidation states can be assigned to the metal atoms in these clusters assuming the normal oxidation states for each ligand, i.e. S^{2-}, Cp^-. Complex I has been described formally as a Mo(III)/Mo(III) complex coordinated by two Fe(II) centers.[6] The application of the same electron counting formalisms to complex II results in its description as a Mo(II)/Mo(II) dimer with two Fe(II) units. A comparison of the spectroscopic characteristics of complexes I and II are consistent with the proposal that a reduction occurs at the molybdenum centers of II. In the infrared spectra of the two complexes the frequencies of the carbonyl stretches are nearly identical. This suggests that the electronic character of the iron centers has not changed. One less carbonyl stretch is observed in the spectrum of complex II; this reflects the symmetrical coordination of the iron tricarbonyl fragment in this complex relative to I. In the ^1H NMR spectrum of II the chemical shifts of the cyclopentadienyl protons at 5.19 and 5.10 ppm are shifted by more than 1 ppm to higher field strength than the Cp protons in I. In characterizations of related dinuclear molybdenum complexes in this series we have observed that the cyclopentadienyl resonances shift upfield as the formal molybdenum ion oxidation state is decreased.[2]

Cyclic voltammetric studies on acetonitrile solutions of $[(MeCp)_2Mo_2S_3Fe_2(CO)_6]$ (II) show two quasi-reversible reductions at −0.96 and −1.55 V vs. SCE (Figure 3) and two irreversible oxidations at +0.57 and +0.99 V vs. SCE. The current amplitude of the first reduction wave is roughly twice that of the second reduction and of each oxidation and is tentatively assigned as a two-electron process. Specific redox couples are not assigned to these waves due to the number and interaction of redox active sites in the clusters.

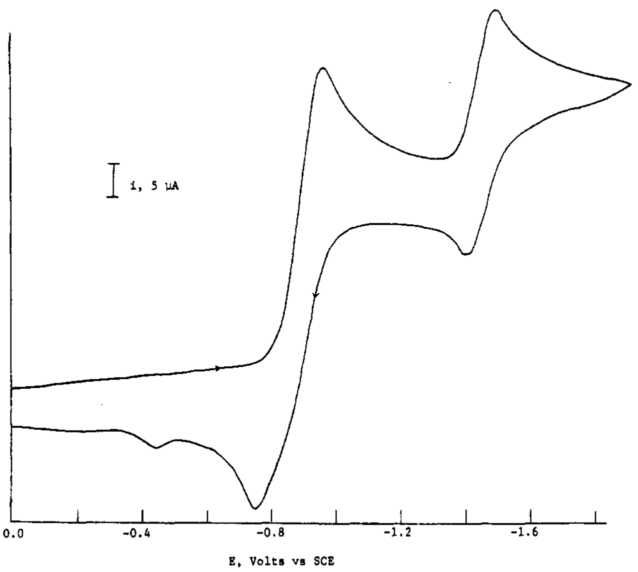

Figure 3. Cyclic voltammogram of $(MeCpMo)_2S_3Fe_2(CO)_6$ (II) ($\sim 2 \times 10^{-3}$ M) recorded in 0.1 M $(n\text{-}Bu)_4NBF_4/CH_3CN$ at a scan rate of 100 mV/s.

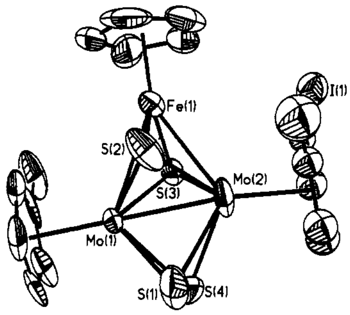

Figure 4. Perspective drawing and numbering scheme for $[(MeCp)_2Mo_2(S_2)(S)_2FeCp][I]$ (III).

Synthesis and Characterization of $[(MeCp)_2Mo_2S_4FeCp][I]$ (III). The reaction of the hydrosulfido complex $[MeCpMo(S)(SH)]_2$ with 1 equiv of $CpFe(CO)_2I$ in refluxing toluene for 16 h led to the formation of a red molybdenum–iron product that was formulated as $[(MeCp)_2Mo_2S_4FeCp][I]$ (III). The air-stable salt was purified by column chromatography and was isolated in approximately 44% yield. The composition of III is supported by spectral data. The ^1H NMR spectrum shows two multiplets at 5.35 and 5.19 ppm (total relative intensity 8) and a singlet at 4.81 ppm (relative intensity 5), which are assigned to the Mo–CpMe and Fe–Cp groups, respectively. The mass spectrum shows a parent fragment at *m*/*e* 599 that is consistent with the proposed formulation of the cation. Conductivity data measured in acetonitrile solution were found to be in the range expected for a 1:1 electrolyte.[21]

An X-ray diffraction study of III was carried out in order to verify the mode of coordination of the Cp–Fe fragment to the dinuclear molybdenum complex and to establish the bonding modes of the sulfido ligands in the cluster. Single crystals of III were grown by slow evaporation of a concentrated acetonitrile solution. The complex crystallizes in the acentric space group *Cc*. The cation contains a triangular array of metal ions with three metal–metal bonds and two μ_3-sulfido ligands. The molybdenum ions are also bridged by an μ_2-η^2-disulfido ligand. The iodide

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(19) Dihedral angles are 125° (Co_2Mo_2 cluster), 141° (Fe_2Mo_2 cluster), and 127° (Ni_2Cr_2 cluster).

(20) A relationship between the number of valence electrons and the dihedral angle has been observed in a series of ruthenium clusters with butterfly geometries: Carty, A. J.; MacLaughlin, S. A.; Van Wagner, J.; Taylor, N. J. *Organometallics* **1982**, *1*, 1013.

(21) (a) Dutta, R. L.; Meek, D. W.; Busch, D. H. *Inorg. Chem.* **1970**, *9*, 1215. (b) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table VI. Selected Interatomic Distances and Angles for $[(MeCp)_2Mo_2(S_2)(S)_2FeCp][I]$ (III)

Interatomic Distances (Å)			
Mo(1)–Mo(2)	2.598 (2)	Mo(1)–Fe(1)	2.804 (2)
Mo(1)–S(1)	2.436 (5)	Mo(1)–S(2)	2.362 (3)
Mo(1)–S(3)	2.391 (3)	Mo(1)–S(4)	2.435 (6)
Mo(2)–Fe(1)	2.755 (3)	Mo(2)–S(1)	2.458 (3)
Mo(2)–S(2)	2.369 (4)	Mo(2)–S(3)	2.385 (4)
Mo(2)–S(4)	2.464 (6)	Fe(1)–S(2)	2.140 (4)
Fe(1)–S(3)	2.120 (3)	S(1)–S(4)	2.046 (10)
Angles (deg)			
S(1)–Mo(1)–S(2)	77.4 (2)	S(2)–Fe(1)–S(3)	101.6 (1)
S(2)–Mo(1)–S(3)	88.0 (1)	Mo(1)–S(1)–Mo(2)	64.1 (1)
S(1)–Mo(1)–S(4)	49.7 (2)	Mo(1)–S(2)–Mo(2)	66.6 (1)
Mo(1)–Mo(2)–Fe(1)	63.1 (1)	Mo(1)–S(2)–Fe(1)	76.8 (1)
Mo(1)–Fe(1)–Mo(2)	55.7 (1)		

Table VII. Positional and Thermal Parameters for the Atoms of $[(MeCp)_2Mo_2(S_2)(S)_2FeCp][I]$ (III)

atom	x	y	z	U_{eq}, Å^2
Mo(1)	0.0049 (1)	−0.1530 (1)	0.0108 (1)	0.0036 (1)
Mo(2)	−0.1287 (1)	−0.2341 (3)	0.0040 (1)	0.0071 (1)
Fe(1)	−0.1016 (1)	−0.3056 (2)	−0.1368 (1)	0.0038 (1)
I(1)	−0.3603 (1)	0.1238 (2)	−0.2522 (1)	0.0078 (1)
S(1)	−0.0173 (2)	−0.2463 (12)	0.1338 (2)	0.0109 (2)
S(2)	−0.0511 (2)	−0.4724 (5)	−0.0246 (2)	0.0065 (1)
S(3)	−0.1063 (2)	−0.0139 (4)	−0.0912 (2)	0.0042 (1)
S(4)	−0.0512 (2)	0.0369 (10)	0.0909 (2)	0.0106 (2)
C(11)	0.0985 (5)	−0.2149 (11)	−0.0386 (5)	0.0050 (5)
C(12)	0.1257 (5)	−0.2572 (11)	0.0474 (5)	0.0063 (6)
C(13)	0.1279 (5)	−0.0746 (11)	0.0898 (5)	0.0069 (6)
C(14)	0.1020 (5)	0.0806 (11)	0.0300 (5)	0.0087 (8)
C(15)	0.0838 (5)	−0.0061 (11)	−0.0493 (5)	0.0056 (5)
C(16)	0.0589 (8)	0.1124 (30)	−0.1311 (12)	0.0095 (8)
C(21)	−0.2064 (11)	−0.3089 (23)	0.0739 (7)	0.0058 (6)
C(22)	−0.2260 (11)	−0.1061 (23)	0.0512 (7)	0.0064 (7)
C(23)	−0.2537 (11)	−0.0932 (23)	−0.0364 (7)	0.0055 (6)
C(24)	−0.2512 (11)	−0.2879 (23)	−0.0678 (7)	0.0038 (5)
C(25)	−0.2220 (11)	−0.4212 (23)	0.0003 (7)	0.0047 (5)
C(26)	−0.2109 (25)	−0.6493 (56)	−0.0126 (25)	0.0093 (10)
C(21a)	−0.2036 (12)	−0.4637 (25)	0.0502 (9)	0.0066 (7)
C(22a)	−0.2204 (12)	−0.5302 (25)	−0.0320 (9)	0.0066 (7)
C(23a)	−0.2508 (12)	−0.3658 (25)	−0.0860 (9)	0.0071 (8)
C(24a)	−0.2529 (12)	−0.1977 (25)	−0.0372 (9)	0.0055 (6)
C(25a)	−0.2236 (12)	−0.2583 (25)	0.0470 (9)	0.0050 (6)
C(26a)	−0.2279 (15)	−0.1432 (36)	0.1171 (16)	0.0054 (6)
C(31)	−0.1067 (7)	−0.5455 (16)	−0.2162 (7)	0.0121 (10)
C(32)	−0.1799 (7)	−0.4802 (16)	−0.2275 (7)	0.0073 (6)
C(33)	−0.1867 (7)	−0.2758 (16)	−0.2519 (7)	0.0066 (6)
C(34)	−0.1178 (7)	−0.2148 (16)	−0.2556 (7)	0.0086 (8)
C(35)	−0.0683	−0.3814 (16)	−0.2335 (7)	0.0094 (8)

counterion is located roughly 5 Å from the Fe–Mo(2)–S(3) face. A perspective view of the salt is shown in Figure 4, and selected bond distances and angles and the atomic parameters are listed in Tables VI and VII, respectively. The molybdenum sulfur core in III is very similar to those of other tetrasulfur-bridged molybdenum dimers and is nearly identical with that of $[Cp'_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)]$.[22] The bond distances and angles in the core of III are also very similar to those observed for the neutral trinuclear complexes $[Cp'_2Mo_2S_4Fe(CO)_2]$ and $Cp'_2Mo_2S_2(S_2CO)Fe(CO)_2]$ that were discussed above.[11]

The cyclopentadienyl ligand on the Mo(2) atom in III is disordered and was treated isotropically in the final refinement of the structure. The cyclopentadiene ring shown in Figure 4 is approximately parallel to the ring on Mo(1). The disordered Cp ring is shifted back toward the iodide counterion by about 5° and is rotated with its methyl group positioned between the sulfur atoms of the disulfur bridge. The relatively unusual disorder occurs in approximately 50% of the molecules in the crystal. Review of the collected data and refinement gave no clear explanation as to the cause of the disorder.

Reactivity of III. The gross structure of III is consistent with our goal of incorporating an iron fragment into the dinuclear molybdenum complex while retaining two μ_2-sulfur atoms as potentially reactive sites. However, the electronic characteristics of III appear to be significantly different from the methanedithiolate-bridged molybdenum complex discussed in the Introduction because of the iron–molybdenum bond formation within the cluster. The insertion of an activated alkyne into a disulfido ligand has been observed previously in a photochemical reaction.[23] Complex III appeared to react rapidly with hexafluoro-2-butyne even under room light, but we were unable to identify the resulting brown precipitate, which was insoluble in common solvents. No evidence was observed for reaction between III and unactivated acetylene.

Several examples of the reactions of coordinated disulfide ligands with nucleophiles have been reported previously.[24] However, when complex III was stirred with an equivalent of methyllithium or ethylmagnesium bromide in THF at −78 °C and at room temperature, approximately 95% of the starting complex was recovered. The inert character of complex III under these conditions was particularly surprising in view of the cationic nature of the complex.

The reaction of III with the strong reducing agent potassium graphite (~2 equiv) results in a color change from red to brown. When the potassium graphite reduction was monitored by NMR, we observed the formation of a new diamagnetic product with resonances at 4.42, 6.46, and 6.54 ppm that can be assigned to the single C_5H_5 and two C_5H_4 groups, respectively. The C_5H_5 resonance is shifted upfield by 0.4 ppm compared to that in III while the C_5H_4 resonances are shifted downfield by more than 1.0 ppm. The electrochemical reduction of III at a platinum electrode is an irreversible process (E_p = −0.84 V vs. SCE); the potassium graphite reduction described here may be accompanied by bond cleavage or rearrangement, but the trinuclear cluster appears to remain intact. The addition of methyl iodide (1–2 equiv) to the filtered solution of reduced III yields a new cationic dimethylated complex that was isolated in low yield. One possible formulation is $[(MeCpMo)_2(SMe)_2S_2FeCp]I$. The proposed identity of the product cation is consistent with FAB mass spectral data. In the ^1H NMR spectrum, in addition to a singlet at 2.11 ppm (relative intensity 6) assigned to the methyl groups of the MeCp ligands, two additional singlets (each of relative intensity 3) are observed at 2.67 and 1.59 ppm. Although the sulfur ligands seem to be the most likely sites of methylation, the large chemical shift difference for the two methyl groups is difficult to explain in the absence of structural data.

When the potassium graphite reduction is carried out in the presence of ethylene or acetylene and monitored by NMR, the resonances of the reduced derivative are observed initially but are slowly replaced by the spectrum of the bis(alkene) or -(alkyne) adduct $[MeCpMoSC_nH_{2n}S]_2$.[13] The tendency for a reduced heteronuclear cluster to eliminate the iron ligand fragment from the dinuclear molybdenum core was observed for

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(23) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1979**, *182*, C39.

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related iron–molybdenum clusters discussed above and may be a fairly general characteristic of these systems.

Synthesis of a Cobalt–Molybdenum Cluster. The reaction of the hydrosulfido-bridged molybdenum dimer $[MeCpMo(S)(SH)]_2$ with 1 equiv of $CpCo(CO)I_2$ has resulted in the formation of a black molybdenum–cobalt product $(MeCpMo)_2S_4CoCpI_2$ (**IV**). The reaction proceeds at room temperature in dichloromethane and is apparently complete in an hour. These conditions are relatively mild compared to the preparation of the analogous iron complex III. Thin-layer chromatography indicated that the molybdenum–cobalt product decomposed on alumina or silica and could not be purified by chromatography. The complex was therefore recrystallized several times from dichloromethane and was obtained in approximately 30% yield. In the ^1H NMR spectrum, resonances for inequivalent MeCp–Mo and for the Cp–Co protons are observed at 5.92, 5.85, and 5.78 ppm, respectively. The infrared spectrum confirms that the carbon monoxide ligand of the starting cobalt complex has been displaced. Elemental analysis supports the formulation of the product and confirms that it is isolated in pure form.

Cyclic voltammetric studies of complex IV show two reversible and one quasi-reversible reductions at −0.08, −0.52, and −0.76 V vs. SCE, respectively. Two quasi-reversible oxidations are observed at +0.25 and +0.65 V. The oxidation behavior of IV is similar to that observed for III, and the waves are assigned to the oxidation of the iodide anion.[25] The reduction behavior of complex IV is much more extensive than that of III; these differences appear to reflect the different redox properties of cobalt(III) and iron(II). Cobalt(III) complexes that contain π-accepting ligands are generally stable upon reduction, and redox couples corresponding to the lower oxidation states (II, I, 0) are often detected electrochemically. This behavior is not so frequently observed for the reduction of iron(II) complexes.[26]

The structure of complex IV has not been determined crystallographically. A 48-electron dication is isoelectronic with $[(MeCpMo)_2S_4FeCp]^+$ and is expected to be isostructural with this cluster. However, the FAB mass spectrum of complex IV contains a parent molecular ion (m/e 602) and fragmentation pattern for the monovalent cation $[(MeCpMo)_2S_4CoCp]^+$. Envelopes corresponding to the divalent cation $[(MeCpMo)_2S_4CoCp]^{2+}$ or an iodide-containing species $[(MeCpMo)_2S_4CoCpI]^+$ were not observed. The monovalent cation may be formed from the divalent species by the loss of a proton upon ionization or by reduction from the matrix. It may also be formed from an iodide derivative by the loss of HI upon ionization. Conductivity studies of IV could only be carried out over a limited concentration range because of poor solubility characteristics. However the data observed lie within the normal range for a 1:1 electrolyte in acetonitrile.[21] The results imply a significant interaction between one of the iodide ions and the molybdenum–cobalt core. Attempts to obtain crystals of this complex suitable for X-ray diffraction as well as to prepare $(MeCpMo)_2S_4CoCp$ derivatives involving different anions for comparative purposes are in progress.

Summary and Conclusions. The reaction of organometallic iron and cobalt compounds with terasulfur-bridged molybdenum dimers have led to the characterization of new tetranuclear and trinuclear clusters. In general, the metal–metal bond formation in the new clusters results in a loss of the steric and/or electronic factors that permit exceptional reactivity at the sulfido ligands. The trinuclear clusters of the type $Cp_2Mo_2S_4MCp$ (M = Fe, Co) are perhaps the most interesting products of this study because they provide the further opportunity to examine the possible interconversion and reactivity of μ-S_2 and (μ-S)$_2$ ligands as a function of the redox state of the complex.

Experimental Section

Methods and Materials. Reactions carried out under nitrogen were performed by using standard Schlenk techniques or in a Vacuum Atmospheres drybox. Reactions carried out under vacuum or under gaseous reagents were performed in a pressure flask fitted with a Kontes Teflon high-vacuum stopcock. Product manipulations were performed in air unless noted. Air- and moisture-sensitive compounds were stored under ultra-high purity (UHP) grade nitrogen in a glovebox.

The complexes $[MeCpMo(S)SH]_2$,[27] $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$,[1] and $CpCo(CO)I_2$[28] were prepared as reported previously. $Fe(CO)_5$, $CpFe(CO)_2I$, and potassium graphite (29% K) were purchased from Alfa. Acetonitrile used for electrochemical and conductivity studies was first distilled from P_2O_5 and then from CaH_2. THF was distilled from CaH_2. Trimethylamine *N*-oxide dihydrate was dried by sublimation and stored under nitrogen.

Instrumentation. Routine ^1H NMR spectra were obtained at 90 MHz on either a Varian EM-390 or a JEOL FX-90Q spectrometer. High-field ^1H NMR were obtained at 250 MHz on a Bruker WM-250 spectrometer. Proton chemical shifts are reported to 0.01 ppm relative to internal tetramethylsilane. Infrared spectra were obtained on either a Perkin-Elmer 337 or a Beckman IR4250 spectrophotometer. Spectra were calibrated by use of a standard polystyrene reference film. Samples were analyzed as Nujol mulls between potassium bromide plates. Electron-impact (EI) mass spectra were obtained at an ionizing voltage of 70 eV on either a Varian MAT CH-5 or a VG Analytical 7070 EQ-HF mass spectrometer. Fast atom bombardment (FAB) mass spectra were obtained on the VG Analytical spectrometer using gycerol, thioglycerol, or 2,2′-thiodiethanethiol as the matrix. Conductivity was measured with a Serfass conductivity bridge, Model RC M15, and a Yellow Springs Instruments platinized conductivity cell, Model 3403. Conductivities were measured at sample concentrations of 1×10^{-4} and 5×10^{-4} M in distilled acetonitrile. A 1×10^{-4} M potassium iodide solution was measured as a standard 1:1 electrolyte. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI.

Cyclic voltammograms were obtained with a Princeton Applied Research 174 A polarographic analyzer using platinum wire working and counter electrodes and a saturated calomel reference electrode. Sample concentrations were approximately 10^{-4} M in distilled acetonitrile that contained 10^{-1} M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Samples were analyzed under nitrogen at scan rates of 50 and 200 mV/s. Ferrocene ($E_{1/2}$ = 0.42 V) was run as a standard prior to sample analysis.

X-ray Crystallography. Data for the structures (Table VIII) were collected at 25 °C on a Nicolet P$\bar{1}$ or Syntex P$\bar{1}$ autodiffractometer using Mo Kα radiation monochromatized by a graphite crystal. The procedures, which were similar for all three structures, are summarized in Table VIII. The measured data were corrected for Lorentz and polarization effects.[27] Salient features of the solutions and refinements of the structures are also given in Table VIII.

Synthesis of $[MeCpMoS_2Fe(CO)_3]_2$ (I). (a) Reaction of $[MeCpMoS(SH)]_2$ with Iron Pentacarbonyl and Trimethylamine *N*-Oxide. $[MeCpMoS(SH)]_2$ (1.1 g, 2.3 mmol) and $Fe(CO)_5$ (0.80 ml, 6.1 mmol) were added to ca. 150 mL of distilled dichloromethane in a 250-mL Schlenk flask. Trimethylamine

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Table VIII. Crystallographic Data

	Crystal Data		
formula	$[((CH_3)C_5H_4)MoS_2Fe(CO)_3]_2$	$[((CH_3)C_5H_4)_2Mo_2S_3Fe_2(CO)_6]$	$[((CH_3)C_5H_4)_2Mo_2S_4Fe(C_5H_5)][I]$
M_r	758.14	726.08	726.24
space group	$P\bar{1}$	$P\bar{1}$	Cc
cryst system	triclinic	triclinic	monoclinic
a, Å	6.598 (2)[a]	12.542 (2)[b]	19.348 (10)[c]
b, Å	10.168 (3)	10.724 (2)	6.673 (3)
c, Å	10.203 (3)	10.296 (1)	17.524 (9)
α, deg	99.81 (2)	121.35 (9)	90.00
β, deg	107.55 (2)	93.90 (1)	112.68 (4)
γ, deg	108.99 (2)	106.07 (1)	90.00
V, Å^3	589.1 (4)	1088.5 (3)	2087.3 (2)
D(obsd), g/cm^3	2.0[d]	not measured	2.26[e]
z	1	2	4
D(calcd), g/cm^3	2.14	2.21	2.31
F(000)	370	740	1392
μ, cm^{-1}	26.0	28.13	36.93
	Data Collection and Reduction		
diffractometer	Nicolet P1	Nicolet P1	Nicolet P3F
radiatn, Å	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
takeoff angle for graphite monochromator, deg	4.0	4.0	4.0
temp, K	294–296	294–296	294–296
cryst dimens, mm	0.4 × 0.3 × 0.3	0.6 × 0.4 × 0.2	0.1 × 0.2 × 0.2
scan technique	θ–2θ	θ–2θ	θ–2θ
$2\theta_{min}$, $2\theta_{max}$, deg	3, 60	3, 50	3.0, 45.0
hkl values scanned	$\pm h,\pm k,\pm l$	$\pm h,\pm k,\pm l$	$\pm h,\pm k,\pm l$
scan speed, deg/min	4.0	3.0–24.0	4.0–60
scan range, deg below Kα_1 and above Kα_2	0.8, 0.8	0.7, 0.9	0.9, 0.9
bkgd counter	stationary crystal–stationary background time = $^1/_2$ scan time	stationary crystal–stationary background time = $^1/_2$ scan time	stationary crystal–stationary background time = $^1/_2$ scan time
check reflctns	(020); (1,1,-4)	(601); (031); (-4,5,0); (5,-2,4)	(800); (008); (020); (1,-1,-3)
frequency	every 50 measurements	every 100 measurements	every 96 measurements
variation	random, net 0% decay	random, net 0% decay	random, net 0% decay
no. of reflctns measured	6887	7724	6608
no. of unique reflctns	3444	3861	2737
agreement factor during averaging	0.015	0.016	0.0112
no. of obsd reflctns	3069	3485	2541
σ criterion	F 6 × $\sigma(F)$	F 6 × $\sigma(F)$	F 6 × $\sigma(F)$
abs correctn	none applied	empirical	empirical
R(merge), (before, after)		0.080, 0.032	0.073, 0.035
transmissn factors	none available	0.99, 0.79	0.657, 0.437
	Structure Determination and Refinement		
method of phase determination	Patterson and DIRDIF	Patterson and DIRDIF	Patterson
programs	SHELX, PLATO, PLUTO, and others	SHELX, PLATO, PLUTO, and others	SHELXTL
scattering factors	neutral atoms	neutral atoms	neutral atoms
R and R_w	0.041, 0.049	0.025, 0.034	0.038, 0.061
weight	$1.00/(\sigma^2(F) + 0.0001F^2)$	$7.88/(\sigma^2(F) + 0.0003F^2)$	$1.00/(\sigma^2(F) + 0.002F^2)$
no. of parameters	146	291	184
ratio of observns to parameters	21:1	12:1	14:1
max shift/error (non-hydrogen)	0.140	0.074	0.01 for U_{33} of C_{33}
max shift/error (hydrogen)	-1.0 for C6 methyl rotational parameter	0.671 for C16 methyl rotational parameter	
av shift/error	0.075	0.05	0.002
residual electron density, e/A^3	2.0 (0.8 Å from Mo(1))	0.80 (0.9 Å from Mo(2))	1.25 (0.6 Å from Mo(2))

[a] Cell dimensions were determined by least-squares fit of the setting angles of 15 reflections with 2θ in the range 6.8–18.7°. [b] Cell dimensions were determined by least-squares fit of the setting angles of 29 reflections with 2θ in the range of 35–47°. [c] Cell dimensions were determined by least-squares fit of the setting angles of 15 reflections with 2θ in the range of 8–21°. [d] By flotation methods in 1,3-dibromopropane/methyl iodide. [e] By flotation methods in methyl iodide.

N-oxide (0.35 g, 4.7 mmol) was added under nitrogen, and the solution was stirred at room temperature for 1 h. The solution was then filtered, and the solvent was removed under vacuum. The green product $[MeCpMoS_2Fe(CO)_3]_2$ (I) was isolated in approximately 25% yield by column chromatography on alumina with 25% dichloromethane in hexane as the eluent. This yield is based on the molybdenum starting material. Use of $[(MeCp)_2Mo_2S_2(S_2)]$ as the molybdenum starting material gives similar results.

(b) Photolysis of $[MeCpMoS(SH)]_2$ with Iron Pentacarbonyl. $[MeCpMoS(SH)]_2$ (0.58 g, 1.2 mmol) and $Fe(CO)_5$ (3.0 mL, 23 mmol) were added to ca. 75 mL of toluene in a Pyrex pressure tube. The solution was freeze–thaw–degassed two times, and the flask was sealed under vacuum at −196 °C. The solution was stirred and photolyzed for 1 h, approximately 3 in. from a 450-W Hanovia mercury arc lamp. The solution was then filtered in air, and the solvent was removed under vacuum. The resulting solid was chromatographed on an alumina column with 10% dichloromethane in hexane. $[(MeCp)_2Mo_2S_3Fe_2(CO)_6]$ (II) was eluted from the column first in 1.3% yield. Characterization data for this product are given in a following section. $[MeCpMoS_2Fe(CO)_3]_2$ was then eluted as the second fraction in 54% yield based on the molybdenum starting material: ^1H NMR ($CDCl_3$) δ 6.31 (apparent triplet from an AA′XX′ pattern, 4, C_5H_4, J_{HH} = 2.4 Hz), 6.02 (apparent triplet from an AA′XX′ pattern, 4, C_5H_4, J_{HH} = 2.4 Hz), 2.34 (s, 6, CH_3); IR (cm^{-1}, Nujol) 3080 (w), 2030 (s), 1980 (s), 1960 (s, br), 1490 (m), 1260 (m), 1100 (w), 1030 (w), 875 (m), 815 (s), 600 (m), 585 (m), 556 (m), 490 (w); mass spectrum, m/e 758 (M^+), 730 ($M^+ - CO$), 702 ($M^+ - 2CO$), 646 ($M^+ - 4CO$), 618 ($M^+ - 5CO$), 590 ($M^+ - 6CO$), 511 ($M^+ - 6CO - (CH_3)C_5H_4$), 432 ($M^+ - 6CO - 2(CH_3)C_5H_4$), 295 ($((CH_3)C_5H_4)_2Mo_2S_4Fe_2^{2+}$). $E_{1/2}$, V vs. SCE: -1.08, $\Delta E = 75$ mV, $i_{pc}/i_{pa} = 0.7$; -1.36, $\Delta E = 270$ mV, $i_{pc}/i_{pa} = 0.9$; $+0.54$, $\Delta E = 200$ mV, $i_{pc}/i_{pa} = 0.9$; $E_p = +0.80$, irreversible.

Reaction of I with Lithium Triethylborohydride and Methyl Iodide. $[MeCpMoS_2Fe(CO)_3]_2$ (0.14 g, 0.19 mmol) was dissolved in ca. 50 mL of distilled THF under nitrogen. $LiBH(C_2H_5)_3$ (0.06 mL, 0.11 mmol) was added, and the solution was stirred at room temperature for 4 h. Methyl iodide (0.04 mL, 0.64 mmol) was then added, and the solution was stirred for 2 days. The solvent was removed under reduced pressure followed by column chromatography on alumina with 25% dichloromethane in hexane. Approximately 90% of the starting material was recovered as the first fraction. This fraction also contained a small amount, less than 1%, of $[(MeCp)_2Mo_2S_3Fe_2(CO)_6]$. This was followed by two molybdenum dimers, $[(MeCp)_2Mo_2S_3O]$ and $[(MeCp)_2Mo_2S_2O_2]$, each in less than 1% yield and characterized by their ^1H NMR spectra. (a) $[(MeCp)_2Mo_2S_3O]$: ^1H NMR ($CDCl_3$) δ 6.25, 5.36 (2d, 4, C_5H_4, $J = 2.4$ Hz), 5.75, 5.56 (2d, 4, C_5H_4, $J = 2.2$ Hz), 2.25 (s, 3, CH_3), 2.18 (s, 3, CH_3); IR (cm^{-1}, Nujol) 1030 (w), 900 (m), 875 (w), 840 (m), 820 (m), 488 (m), 452 (w); mass spectrum, *m/e* 462 (M^+), 446 ($M^+ - O$), 430 ($M^+ - S$), 382 ($M^+ - OS_2$), 366 ($M^+ - 3S$), 350 ($(MeCp)_2Mo_2$). (b) $[(MeCp)_2Mo_2S_2O_2]$: ^1H NMR ($CDCl_3$) δ 6.19 (m, 4, C_5H_4, $J = 2.4$ Hz), 5.48 (m, 4, C_5H_4, $J = 2.4$ Hz), 2.17 (s, 6, CH_3); mass spectrum, *m/e* 446 (M^+), 430 ($M^+ - O$), 350 ($MeCpMo_2$).

Reaction of I with Sodium Amalgam and Methyl Iodide. $[MeCpMoS_2Fe(CO)_3]_2$ (0.14 g, 0.19 mmol) was dissolved in ca. 40 mL of distilled THF under nitrogen. The solution was transferred over sodium amalgam (0.0074 g, 0.32 mmol of Na in 2 mL of Hg) and stirred rapidly for ca. 15 min. When the color of the solution changed from green to brown, the solution was filtered under nitrogen into a Schlenk flask. Methyl iodide (0.040 mL, 0.64 mmol) was then added, and the solution was stirred at room temperature for 15 min. The solvent was removed under vacuum followed by column chromatography on alumina with 25% dichloromethane in hexane. Again, approximately 90% of the starting material was recovered that contained a small amount of $[(MeCp)_2Mo_2S_3Fe_2(CO)_6]$. $[(MeCp)_2Mo_2S_3O]$ and $[(MeCp)_2Mo_2S_2O_2]$ were detected in less than 1% yield.

Synthesis of $[(MeCp)_2Mo_2S_3Fe_2(CO)_6]$ (II). (a) $[(MeCp_2Mo_2S_3Fe_2(CO)_6]$ was first prepared and isolated in 1% yield by the photolysis of $[MeCpMoS(SH)]_2$ with iron pentacarbonyl, vide supra. **(b) Reaction of $[MeCpMoS_2Fe(CO)_3]_2$ with Potassium Graphite.** $[MeCpMoS_2Fe(CO)_3]_2$ (0.20 g, 0.27 mmol) was dissolved in ca. 25 mL of distilled THF and transferred to a pressure flask. The solution was freeze–thaw–degassed three times and sealed under vacuum at −196 °C. Potassium graphite (0.20 g, 1.5 mmol) was added under nitrogen in a glovebox. The flask was sealed under nitrogen, and the solution was stirred for 17 h at room temperature. The solution was then filtered in air, and the solvent was removed by rotoevaporation. Products were separated by column chromatography on alumina with 10% dichloromethane in hexane. $[(MeCp)_2Mo_2S_3Fe_2(CO)_6]$ was isolated in 16.6% yield. Approximately 75% of the starting material was recovered and less than 1% of $[(MeCp)_2Mo_2S_3O]$ and $[(MeCp)_2Mo_2S_2O_2]$ were isolated: ^1H NMR ($CDCl_3$) δ 5.19 (apparent triplet from an AA′XX′ pattern, 4, C_5H_4, $J_{HH} = 1.9$ Hz), 5.10 (apparent triplet from an AA′XX′ pattern, 4, C_5H_4, $J_{HH} = 1.9$ Hz), 2.06 (s, 6, CH_3); IR (cm^{-1}, Nujol), 2030 (s), 1960 (s, br), 1030 (w), 870 (w), 820 (m), 600 (m), 580 (m), 555 (w), 485 (w); mass spectrum, *m/e* 726 (M^+), 698 ($M^+ - CO$), 670 ($M^+ - 2CO$), 642 ($M^+ - 3CO$), 614 ($M^+ - 4CO$), 586 ($M^+ - 5CO$), 558 ($M^+ - 6CO$), 479 ($M^+ - 6CO - MeCp$), 279 ($(MeCp)_2Mo_2S_4Fe_2^{2+}$). Anal. Calcd for $C_{18}H_{14}O_6S_3Mo_2Fe_2$: C, 29.77; H, 1.95; S, 13.25. Found: C, 29.86; H, 2.04; S, 13.34. $E_{1/2}$, V vs. SCE: -0.96, $\Delta E = 215$ mV, $i_{pc}/i_{pa} = 1.0$; -1.55, $\Delta E = 100$ mV, $i_{pc}/i_{pa} = 1.0$; $E_p = +0.57$, irreversible; $E_p = +0.99$, irreversible.

Thermal Reaction of $[MeCpMoS_2Fe(CO)_3]_2$ with Triphenylphosphine. $[MeCpMoS_2Fe(CO)_3]_2$ (0.055 g, 0.072 mmol) and triphenylphosphine (0.13 g, 0.49 mmol) was dissolved in ca. 10 mL of toluene under nitrogen. Approximately 40 mL of decane was added, and the solution was heated to reflux for 30 min. A brown precipitate formed that was completely insoluble in all common solvents and could not be characterized by conventional techniques such as NMR, IR, or mass spectroscopy.

Photolysis of $[MeCpMoS_2Fe(CO)_3]_2$ with Triphenylphosphine. $[MeCpMoS_2Fe(CO)_3]_2$ (0.049 g, 0.065 mmol) and triphenylphosphine (0.10 g, 0.39 mmol) were dissolved in ca. 100 mL of toluene in a quartz pressure flask. The solution was twice freeze–thaw–degassed and sealed under vacuum. The solution was then photolyzed ca. 4 in. from a 450-W Hanovia mercury arc lamp for approximately 1 h. Solvent was removed under vacuum, and the products were separated by chromatography on alumina with 30% toluene in hexane. Triphenylphosphine and triphenylphosphine sulfide were identified by ^1H NMR and mass spectral data.[29] The only molybdenum-containing product that could be characterized was $[(MeCp)_2Mo_2S_2O_2]$.

Reaction of $[MeCpMoS_2Fe(CO)_3]_2$ with Tri-*n*-butylphosphine. $[MeCpMoS_2Fe(CO)_3]_2$ (0.20 g, 0.26 mmol) was dissolved in ca. 40 mL of distilled THF under nitrogen. Tri-*n*-butylphosphine (0.15 mL, 0.60 mmol) was added, and the solution was stirred at room temperature for 72 h. The solvent was removed under vacuum, and the products were separated by chromatography on alumina. Approximately 95% of the starting material was recovered that was followed by a small amount (less than 1%) of $[(MeCp)_2Mo_2S_3O]$ and $[(MeCp)_2Mo_2S_2O_2]$.

Reaction of $[(MeCp)_2Mo_2S_3Fe_2(CO)_6]$ with Lithium Disulfide. A THF solution of Li_2S_2 was prepared as described by Gladysz.[30] $[(MeCp)_2Mo_2S_3Fe_2(CO)_6]$ (0.026 g, 0.036 mmol) was dissolved in ca. 30 mL of distilled THF under nitrogen. The THF solution of Li_2S_2 (1.0 mL, 0.041 mmol) was added, and the solution was then stirred at room temperature for 48 h. The solution was filtered in air, the solvent was removed under vacuum, and the products were separated by chromatography on alumina with 10% chloroform in hexane. $[MeCpMoS_2Fe(CO)_3]_2$ was isolated in 8.2% yield; however, only about 20% of the starting material was recovered. $[(MeCp)_2Mo_2S_3O]$ and $[(MeCp)_2Mo_2S_2O_2]$ (less than 1% each) were also isolated and characterized by ^1H NMR.

Synthesis of $[(MeCp)_2Mo_2S_4FeCp)][I]$ (III). $[MeCpMoS(SH)]_2$ (0.56 g, 1.2 mmol) and $[CpFe(CO)_2(I)]$ (0.39 g, 1.3 mmol) were dissolved in ca. 150 mL of toluene. The solution was refluxed under nitrogen for 16 h, cooled to room temperature, and filtered in air. The solvent was removed by rotoevaporation, and the products were separated by chromatography on alumina with acetonitrile. A red, unidentified product was isolated first, in less than ca. 5% yield, and provided the following spectra data: ^1H NMR ($CDCl_3$) δ 5.35 (s, 4, C_5H_4), 5.31 (s, 4, C_5H_4), 5.02 (s, 5, C_5H_5), 2.13 (s, 3, CH_3), 2.01 (s, 3, CH_3); IR (cm^{-1}, Nujol) 3050 (w), 2900 (w), 2190 (m), 1600 (w), 1480 (m), 1450 (m), 1040 (w), 1020 (w), 820 (m). The mass spectrum shows molybdenum envelopes at *m/e* 711, 665, 599, 567, 534, and 480. Immediately after this product was removed from the column, a second red product, $[(MeCp)_2Mo_2S_4FeCp][I]$ (III), was isolated in 44% yield and characterized by the following spectral data: ^1H NMR ($CDCl_3$) δ 5.35 (m, 4, C_5H_4), 5.19 (m, 4, C_5H_4), 4.81 (s, 5, C_5H_5), 2.10 (s, 6, CH_3), IR (cm^{-1}, Nujol) 1020 (w), 850 (w), 830 (w), 720 (w); mass spectrum, *m/e* 599 ($(MeCp)_2Mo_2S_4Fe(C_5H_5)^+$), 534 ($(MeCp)_2Mo_2S_4Fe^+$), 446 ($(MeCp)_2Mo_2S_3^+$). Anal. Calcd for $C_{17}H_{19}S_4Mo_2FeI$: C, 28.11; H, 2.64; S, 17.66. Found: C, 28.10; H, 2.66; S, 17.48. $E_{1/2}$, V vs. SCE: $E_p = -0.84$, irreversible; $+0.27$, $\Delta E = 300$ mV, $i_{pc}/i_{pa} = 0.6$; 0.68, $\Delta E = 185$ mV, $i_{pc}/i_{pa} = 1.0$. Molar conductivity in CH_3CN, Λ_M ($cm^2\ \Omega^{-1}\ mol^{-1}$): 148 ($1 \times 10^{-4}$ M); 134 (5×10^{-4} M).

Reaction of III with Potassium Graphite and Methyl Iodide. A suspension of $[(MeCp)_2Mo_2S_4FeCp][I]$ (III) (0.16 g, 0.22 mmol) was prepared in ca. 40 mL of distilled THF, transferred to a pressure tube, and twice freeze–thaw–degassed. Potassium graphite (0.077 g, 0.57 mmol) was added to the solution in a glovebox and stirred under nitrogen for 45 min. The solution was filtered, and methyl iodide (0.009 mL, 0.15 mmol) was added. The solution was then stirred for 12 h at room temperature, and the solvent was removed under vacuum. Very small amounts of $[(MeCp)_2Mo_2S_3O]$ and $[(MeCp)_2Mo_2S_2O_2]$ were isolated by column

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chromatography on alumina. An additional product was isolated in ca. 10% yield and tentatively characterized as $[(MeCp)_2Mo_2(SCH_3)_2S_2FeCp][I]$: ^1H NMR ($CDCl_3$) δ 5.44 (m, 2, C_5H_4), 5.29 (m, 4, C_5H_4), 5.07 (m, 2, C_5H_4), 5.01 (s, 5, C_5H_5), 2.67 (s, 3, CH_3), 2.11 (s, 6, CH_3), 1.59 (s, 3, CH_3); mass spectrum, *m/e* 629 (M^+), 614 ($M^+ - CH_3$), 599 ($M^+ - 2CH_3$), 582 ($M^+ - SCH_3$), 567 ($M^+ - S(CH_3)_2$), 535 ($M^+ - 2SCH_3$).

Reaction of III with Potassium Graphite and Acetylene or Ethylene. A suspension of $[(MeCp)_2Mo_2S_4FeCp][I]$ (III) (0.16 g, 0.22 mmol) was prepared in ca. 40 mL of distilled THF and twice freeze–thaw–degassed. Potassium graphite (0.036 g, 0.26 mmol) was added to the solution in a glovebox and stirred under nitrogen for 4 h. The solution was filtered and the solvent removed under vacuum. The brown solid was then dissolved in ca. 3 mL of deuteriochloroform and transferred to two NMR tubes. The solvent in each tube was freeze–thaw–degassed three times and sealed under 1 atm of either acetylene or ethylene. Initially, the ^1H NMR spectra show an intermediate product with the following resonances: δ 6.54 (m), 6.46 (m), 4.42 (s), 2.04 (s), 1.95 (s). This product slowly disappeared with the formation of $[MeCpMo(SC_2H_2S)]_2$[12] and $[MeCpMo(SC_2H_4S)]_2$,[12] respectively.

Synthesis of $[(MeCp)_2Mo_2S_4CoCp][(I)_2]$ (IV). $[MeCpMoS(SH)]_2$ (0.30 g, 0.62 mmol) and $[CpCo(CO)(I)_2]$ (0.25 g, 0.62 mmol) were dissolved in ca. 50 mL of dichloromethane under nitrogen. The solution was stirred at room temperature for ca. 1 h and the solvent removed under vacuum. The solid was redissolved in 20 mL of dichloromethane and filtered in air. A black solid, $[(MeCp)_2Mo_2S_4CoCp][(I)_2]$ (IV), was isolated in 28.6% yield and characterized by the following spectral data: ^1H NMR (CD_3CN) δ 5.92 (m, 4, C_5H_4), 5.85 (m, 4, C_5H_4), 5.78 (s, 5, C_5H_5), 2.25 (s, 6, CH_3); IR (cm^{-1}, Nujol) 1035 (w), 845 (m); mass spectrum, *m/e* 602 ($(MeCp)_2Mo_2S_4Co(C_5H_5)^+$), 570 ($M^+ - S$), 538 ($M^+ - 2S$), 505 ($M^+ - S - C_5H_5$), 473 ($M^+ - 2S - C_5H_5$). Anal. Calcd for $C_{17}H_{19}S_4Mo_2CoI_2$: C, 23.85; H, 2.24; S, 14.98. Found: C, 24.03; H, 2.37; S, 14.95. $E_{1/2}$, V vs. SCE: −0.08, ΔE = 90 mV, i_{pc}/i_{pa} = 1.0; −0.52, ΔE = 80 mV, i_{pc}/i_{pa} = 0.8; −0.76, ΔE = 100 mV, i_{pc}/i_{pa} = 0.4; +0.25, ΔE = 160 mV, i_{pc}/i_{pa} = 0.9; +0.65, ΔE = 135 mV, i_{pc}/i_{pa} = 0.9. Molar conductivity in CH_3CN, Λ_M ($cm^2\ \Omega^{-1}\ mol^{-1}$): 158 ($1 \times 10^{-4}$ M); 116 (5×10^{-4} M).

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Registry No. I, 85534-08-3; II, 107270-94-0; III, 107246-75-3; IV, 107246-76-4; $[MeCpMoS(SH)]_2$, 75675-65-9; $Fe(CO)_5$, 13463-40-6; $(MeCp)_2Mo_2S_3O$, 107246-77-5; $(MeCp)_2Mo_2S_2O_2$, 107246-78-6; Li_2S_2, 51148-09-5; $CpFe(CO)_2(I)$, 12078-28-3; $[(MeCp)_2Mo_2(SCH_3)_2S_2FeCp][I]$, 107246-79-7; $CpCo(CO)(I)_2$, 12012-77-0; trimethylamine *N*-oxide, 1184-78-7.

Supplementary Material Available: Tables of calculated and observed structure amplitudes for the structures of $[MeCpMoS_2Fe(CO)_3]_2$ (I), $(MeCpMo)_2S_3Fe_2(CO)_6$ (II), and $[(MeCpMo)_2(S_2)(S)_2FeCp][I]$ (III) (45 pages). Ordering information is given on any current masthead page.

Monomeric Bis(pentamethylcyclopentadienyl)titanium(III)[1] Complexes with Halide, Borohydride, Amide, Alkoxide, and Carboxylate Ligands. X-ray Structure of Bis(pentamethylcyclopentadienyl)titanium(III) Chloride

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The synthesis and characterization of monomeric Cp^*_2TiX complexes (X = Cl, Br, I, BH_4, $OCMe_3$, O_2CH) are reported. These 15-electron d^1 systems have one unpaired electron and form perfect Curie paramagnetic systems. They are NMR and ESR active. ^1H NMR spectra show broad lines (width 600–5000 Hz) for the Cp* hydrogens between 14.0 and 18.4 ppm. Observation of the protons of the non-Cp* ligands is possible if they are positioned at least β with respect to the metal. The ESR spectra are singlets (g = 1.939–1.978), with for some complexes the expected Ti isotope hyperfine splitting. Hyperfine splittings due to interaction with hydrogen or other nuclei of the ligands are not observed. The structure of Cp^*_2TiCl (1) was determined by X-ray diffraction. 1 crystallizes in the monoclinic space group $P2_1/n$, with a = 9.339 (2) Å, b = 13.632 (1) Å, c = 15.140 (3) Å, β = 99.55 (1)°, and Z = 4. The structure was refined to R = 0.045 and R_w = 0.050 for 290 parameters and 2909 observed reflections (with $F > 3\sigma(F)$). The molecule exhibits an approximate twofold noncrystallographic axis along the Ti–Cl bond. The chlorine ligand is coordinated in the equatorial plane of a bent-sandwich permethyltitanocene fragment (Ti–Cl = 2.363 (1) Å). The Cp* rings coordinate in a true η^5 way to the metal. Methyl–methyl contacts between the staggered Cp* ligands cause a deviation of one of the methyl groups out of the plane of the ring and away from the metal of 0.40 (1) Å.

Introduction

With the exciting chemistry of bis(pentamethylcyclopentadienyl) compounds of group 3[2,3] and the lanthanides,[4,5] Cp^*_2MR, developing rapidly the last few years, it is relevant to study the relations between these classes of

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(1) In this paper the following abbreviations are used: Cp = η^5-C_5H_5; Cp′ = η^5-C_5H_4Me; Cp* = η^5-C_5Me_5.

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