Synthesis of the Novel Thiolato-Bridged and Oxo-Capped Trimetallic Clusters $(\eta^5\text{-R}'C_5H_4)(CO)_2MFe_2(\mu_3\text{-O})(\mu\text{-RS})(CO)_6$ via Reactions of $[Et_3NH][(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]$ with Triply Bonded Dimers $[(\eta^5\text{-R}'C_5H_4)(CO)_2M]_2$ (M = Mo, W) and Subsequent Treatment with Air. Crystal Structures of $(\eta^5\text{-MeO}_2CC_5H_4)(CO)_2MoFe_2(\mu_3\text{-O})(\mu\text{-}t\text{-BuS})(CO)_6$ and $(\eta^5\text{-EtO}_2CC_5H_4)(CO)_2WFe_2(\mu_3\text{-O})(\mu\text{-EtS})(CO)_6$

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The complex salts $[Et_3NH][(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]$ (**1**: R = Et, *t*-Bu, Ph), prepared from $Fe_3(CO)_{12}$, RSH, and Et_3N, react in situ with the triply bonded dimers $[(\eta^5\text{-R}'C_5H_4)(CO)_2M]_2$ (**2**: M = Mo, W; R′ = H, MeCO, MeO_2C, EtO_2C) followed by treatment with air to give the series of novel clusters $(\eta^5\text{-R}'C_5H_4)(CO)_2MoFe_2(\mu_3\text{-O})(\mu\text{-RS})(CO)_6$ (compound, R, R′: **3a**, Et, H; **3b**, *t*-Bu, H; **3c**, Et, MeCO; **3d**, *t*-Bu, MeO_2C; **3e**, Ph, MeO_2C; **3f**, Et, EtO_2C; **3g**, *t*-Bu, EtO_2C; **3h**, Ph, EtO_2C) in 26−37% yields and $(\eta^5\text{-R}'C_5H_4)(CO)_2WFe_2(\mu_3\text{-O})(\mu\text{-RS})(CO)_6$ (compound, R, R′: **3i**, Et, MeO_2C; **3j**, *t*-Bu, MeO_2C; **3k**, Et, EtO_2C) in 12−17% yields. Single-crystal X-ray diffraction analyses of **3d** and **3k** confirmed that (i) these clusters consist of the M−S (M = Mo, W) edge-opened square-pyramidal cluster skeleton MFe_2SO with the M atom occupying its apical position and the Fe_2OS atoms constructing its pyramid base and (ii) clusters **3d** and **3k** are single isomers in which the *t*-Bu and Et groups are bonded to the bridged S atoms by an equatorial type of bond.

Introduction

In recent years the chemical reactions of diiron complex salts $[Et_3NH][(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]$ (**1**) have been intensively studied and widely utilized in the synthesis of organometallic compounds and particularly organometallic clusters.[1−9] Among the reactions studied were those with electrophiles that have no leaving group such as acetylenes and elemental sulfur.[3,4] As part of our project concerning the chemistry of the anions $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-$ (E = S, Se, Te),[8−10] we recently carried out an investigation on the reactions of **1** with the inorganic acetylene analogues $[(\eta^5\text{-R}'C_5H_4)(CO)_2M]_2$ (**2**, M = Mo, W) followed by treatment with air. Consequently, these reactions afforded a series of novel thiolato-bridged, oxo-capped trimetallic clusters $(\eta^5\text{-R}'C_5H_4)(CO)_2MFe_2(\mu_3\text{-O})(\mu\text{-RS})(CO)_6$ (**3a**−**k**), as described below.

Results and Discussion

Synthesis of $(\eta^5\text{-R}'C_5H_4)(CO)_2MFe_2(\mu_3\text{-O})(\mu\text{-RS})(CO)_6$ (3a−k). When salts of the type $[Et_3NH][(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]$ (**1**: R = Et, t-Bu, Ph) (prepared from $Fe_3(CO)_{12}$, RSH, and Et_3N) reacted with the triply bonded dimers $[(\eta^5\text{-R}'C_5H_4)(CO)_2M]_2$ (**2**: M = Mo, W; R′ = H, MeCO, MeO_2C, EtO_2C) followed by bubbling air into the reaction mixture in THF at room temperature, and after open-air TLC separation, the clusters $(\eta^5\text{-R}'C_5H_4)MFe_2(\mu_3\text{-O})(\mu\text{-RS})(CO)_6$ (**3a**−**k**) were isolated, in addition to the two minor byproducts $(\mu\text{-RS})_2Fe_2(CO)_6$ and $[(\eta^5\text{-R}'C_5H_4)(CO)_3M]_2$ (Scheme 1).

The former byproducts $(\mu\text{-RS})_2Fe_2(CO)_6$ are commonly obtained in the reactions involving **1**. The latter byproducts, singly bonded dimers, usually were obtained in the reactions of **2** and probably were derived by addition of CO evolved from **1** and/or **2** to the triple bond

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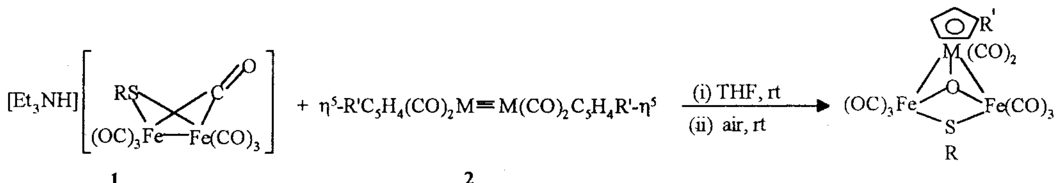
Scheme 1



1 **2** **3a-k**

	3a	3b	3c	3d	3e	3f	3g	3h	3i	3j	3k
M	Mo	Mo	Mo	Mo	Mo	Mo	Mo	Mo	W	W	W
R	Et	t-Bu	Et	t-Bu	Ph	Et	t-Bu	Ph	Et	t-Bu	Et
R′	H	H	MeCO	MeO_2C	MeO_2C	EtO_2C	EtO_2C	EtO_2C	MeO_2C	MeO_2C	EtO_2C

Table 1. Yields (%) of 3a−k Obtained by Two Procedures

	3a	3b	3c	3d	3e	3f	3g	3h	3i	3j	3k
from first proc	32	33	26	35	37	37	27	35	17	13	12
From second proc	17	19	16	26	21	16	16	19	4	5	6

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 3d

Mo(1)−Fe(1)	2.735(2)	Mo(1)−Fe(2)	2.7405(9)
Mo(1)−O(11)	1.975(3)	Mo(1)−C(1)	1.960(6)
Mo(1)−C(2)	1.970(6)	Mo(1)−C(9)	2.350(5)
C(13)−C(14)	1.467(8)	C(14)−O(10)	1.196(7)
C(14)−O(9)	1.329(7)	Fe(1)−S(1)	2.316(2)
S(1)−C(16)	1.890(6)	Fe(1)−C(3)	1.797(6)
Fe(2)−C(6)	1.783(6)	Fe(1)−O(11)	1.936(3)
Fe(2)−O(11)	1.936(3)	Fe(2)−S(1)	2.332(2)
Fe(1)−Mo(1)−Fe(2)	69.40(2)	Fe(1)−Mo(1)−O(11)	45.03(10)
Fe(1)−Mo(1)−C(1)	65.7(2)	Fe(2)−Mo(1)−C(2)	65.2(2)
Mo(1)−Fe(1)−O(11)	46.22(10)	Mo(1)−Fe(2)−O(11)	46.11(10)
Mo(1)−Fe(1)−S(1)	83.48(5)	Mo(1)−Fe(2)−S(1)	83.08(4)
Fe(1)−S(1)−Fe(2)	84.23(5)	Fe(1)−S(1)−C(16)	118.0(2)
Fe(2)−S(1)−C(16)	119.3(2)	C(13)−C(14)−O(10)	124.1(6)
O(9)−C(14)−O(10)	123.0(6)	Mo(1)−C(1)−O(1)	166.6(5)
Mo(1)−C(2)−O(2)	167.5(5)	Fe(1)−O(11)−Fe(2)	107.3(2)
Mo(1)−O(11)−Fe(1)	88.7(1)	Mo(1)−O(11)−Fe(2)	88.9(1)

of **2**.[11−13] While $(\mu\text{-RS})_2Fe_2(CO)_6$ and $[(\eta^5\text{-R}'C_5H_4)(CO)_3M]_2$ produced in this study are known, the products **3a−k** are new; they are deeply colored, air-stable solids and have been fully characterized by elemental analysis, spectroscopy, and X-ray crystallography.

At present, we do not know clearly about the mechanism for production of **3a−k**. However, it is apparent that for formation of **3a−k** from this procedure the structural units $R'C_5H_4(CO)_2M$ and $RSFe_2(CO)_6$ were derived from **1** and **2**, respectively, and the μ_3-O atom coordinated to the three metals MFe_2 originated most likely from the oxygen of bubbling air. In addition, we found that **3a−k** could also be prepared by another procedure, which includes reactions of **1** with **2** without subsequently bubbling air but is followed directly by an open-air TLC separation. In this procedure the μ_3-O atoms in **3a−k** most likely originated from the oxygen present in air during the course of open-air TLC separation. For comparison, Table 1 lists the yields of **3a−k** prepared by two such procedures. As can be seen, the yields of **3a−k** from the first procedure (with bubbling air plus open-air TLC) are much higher than those from the second procedure (without bubbling air but with only open-air TLC).

It is worth pointing out that in the first procedure the 0.5 h of air-bubbling time is optimal for preparation of **3a−k** and extending the air-bubbling time generally leads to a decrease in their yields. For example, for **3d** the yield is 35% for 0.5 h of air bubbling, whereas yields of **3d** are respectively 30% and 27% for 1 and 2 h of air bubbling, possibly due to the composition of **3d** to a certain degree in the prolonged presence of air. In addition, we found that, in contrast to the second procedure, separation of the products by TLC in an anaerobic drybox, instead of open-air TLC separation, gave only a trace of **3a−k**, which further supports the source of μ_3-O in **3a−k** being from the oxygen of air. In fact, in the presence of air the reactions involving transition metal complexes usually yield products containing oxygen atoms such as $Cp_2Mo_2O_2(\mu\text{-Te})(\mu\text{-NPh})$,[14] $Cp_2Mo_2O_2(\mu\text{-O})(\mu\text{-E})(E = S, Te)$,[15] and $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe_2(CO)_7(\mu_3\text{-O})$,[16] in which the oxygen atoms are bonded to transition metals in terminal, bridged, and capped coordination manners.

Molecular Structures of 3d and 3k. To confirm the structures of compounds **3a−k**, the single-crystal diffraction analyses of two representative compounds **3d** and **3k** were undertaken. Significant bond lengths and angles for each structure are listed in Tables 2 and 3, respectively. ORTEP plots of each are shown in Figures 1 and 2, respectively.

As can be seen from Figures 1 and 2, the molecules of **3d** and **3k** contain an M−S edge-opened square-pyramidal skeleton MFe_2OS (M = Mo, W) with the M atom as its top and a planar Fe_2OS as its base. The MFe_2OS skeleton, wherein the oxygen atom is μ_3-coordinated to MFe_2 atoms, has one substituted cyclopentadienyl ligand and two CO ligands coordinated to the M atom, two sets of three CO ligands coordinated to two Fe atoms, and one *t*-Bu or Et group bound to the S atom bridged between two Fe atoms. **3d** and **3k** are typical examples of 50-electron clusters which, according to the 18-electron rule, should possess two Mo−Fe or two W−Fe metal−metal single bonds. This is consistent

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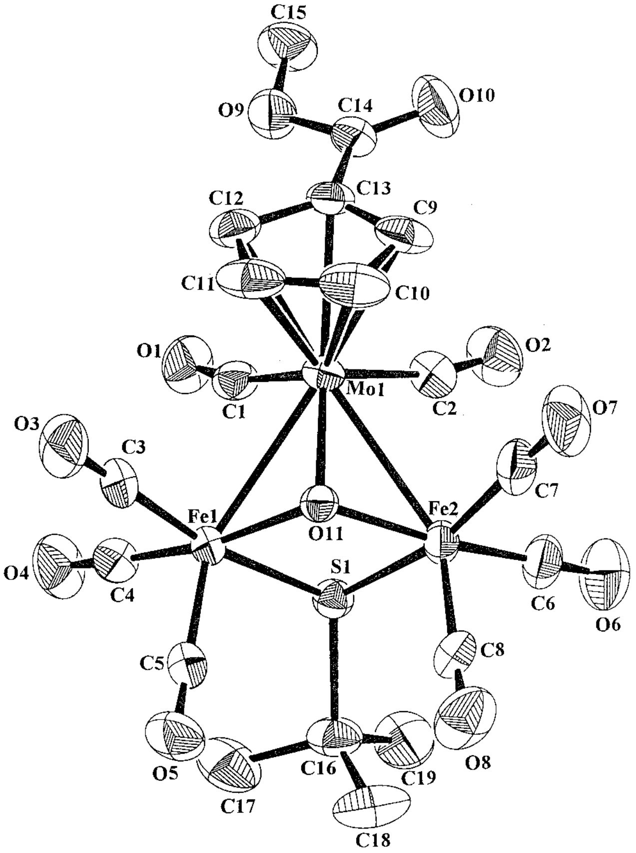

Figure 1. ORTEP view of **3d** with atom-labeling scheme.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 3k

Fe(1)−W	2.7447(7)	Fe(2)−W	2.7404(6)
W−O(1)	1.942(3)	W−C(1)	1.959(4)
W−C(2)	1.965(5)	Fe(1)−S	2.312(1)
Fe(2)−S	2.302(1)	Fe(1)−O(1)	1.949(3)
Fe(2)−O(1)	1.952(3)	Fe(1)−C(3)	1.801(6)
Fe(2)−C(6)	1.801(6)	S−C(17)	1.818(5)
C(13)−C(14)	1.492(7)	C(14)−O(10)	1.194(6)
C(14)−O(11)	1.317(6)	W−C(9)	2.338(4)
Fe(1)−W−Fe(2)	69.25(2)	Fe(1)−W−O(1)	45.23(8)
Fe(1)−W−C(1)	65.0(1)	C(9)−W−C(1)	83.9(2)
Fe(2)−W−O(1)	45.42(8)	W−Fe(1)−O(1)	45.02(8)
W−Fe(1)−S	82.72(3)	W−Fe(1)−C(3)	88.9(2)
W−Fe(2)−S	83.01(3)	W−Fe(2)−O(1)	45.11(8)
W−Fe(2)−C(7)	120.7(2)	Fe(1)−S−Fe(2)	84.98(4)
Fe(1)−S−C(17)	113.5(2)	Fe(2)−S−C(17)	110.7(2)
W−C(1)−O(2)	167.3(4)	W−C(2)−O(3)	168.2(4)
O(10)−C(14)−O(11)	126.2(5)	O(10)−C(14)−C(13)	123.1(5)
W−O(1)−Fe(1)	89.7(1)	Fe(1)−O(1)−Fe(2)	106.1(1)

with the bond lengths of Mo−Fe(2.735(2), 2.7405(9) Å) in **3d** and W−Fe (2.7447(7), 2.7404(6) Å) in **3k**, which are comparable to Mo−Fe and W−Fe single-bond lengths in similar Mo/Fe- and W/Fe-containing compounds.[16,17] The nonbonding distances between two Fe atoms in **3d** and **3k** are 3.118 and 3.116 Å, respectively, which fall well out of the range for normal single Fe−Fe bond lengths.[18] For the planar pyramid base Fe_2OS, the bond lengths of Fe−O (average), Fe−S (average), and Mo−O in **3d** are 1.936(3), 2.324(2), and 1.975(3) Å, whereas those of Fe−O (average), Fe−S (average), and W−O in **3k** are 1.950(3), 2.307(1), and 1.942(3) Å, respectively. The dihedral angles between two planes of the Fe_2OS base and the Cp ring are 56.23 and 56.04° in **3d** and **3k**, respectively. To our knowledge, such an open-pyramid MFe_2OS skeleton has never been found in transition-metal/main-group-element clusters, so far. Among the eight carbonyl ligands attached to metals of the skeleton, two carbonyls bound to the Mo or W atom are semibridging and the others attached to Fe atoms are terminal. For semibridging carbonyls Curtis's definition[19] is $0.1 \leq d = (d_2 - d_1)/d_1 \leq 0.6$. For C(1)O(1) of **3d**, since d_2 = Fe(1)···C(1) = 2.629(6) Å and d_1 = Mo(1)−C(1) = 1.960(6) Å, $\alpha_{C(1)O(1)} = 0.34$. For C(2)O(2) of **3d**, since d_2 = Fe(2)···C(2) = 2.618(6) Å and d_1 = Mo(1)−C(2) = 1.970(6) Å, $\alpha_{C(2)O(2)} = 0.33$. They both fall into the α range for semibridging carbonyls. In addition, since the angles Fe(1)Mo(1)C(1) = 65.7(2)° and Fe(2)Mo(1)C(2) = 65.2(2)°, C(1)O(1) and C(2)O(2) are bridges across the Mo(1)Fe(1) and Mo(1)Fe(2) bonds, respectively. Similarly, for **3k** the α values for semibridging carbonyls C(1)O(2) and C(2)O(3) can be calculated as 0.33 and 0.35. The two carbonyls are bridges across the WFe(1) and WFe(2) bonds, since the angles Fe(1)-WC(1) and Fe(2)WC(2) are 65.0(1) and 66.2(1)°, respectively. For the substituted cyclopentadienyl ligands the distance Mo···Cp ring centroid = 2.034 Å in **3d** is almost the same as the distance W···Cp ring centroid = 2.023 Å in **3k**. The bond lengths C(13)C(14) (1.467(8) and 1.492(7) Å) in **3d** and **3k** are much shorter than a normal C−C single bond; thus, the π-systems of the substituents should be quite well conjugated with the Cp ring π-systems of **3d** and **3k**. To see clearly the orientations of *t*-Bu and Et groups, condensed ORTEP drawings of **3d** and **3k** in which their eight CO carbo-

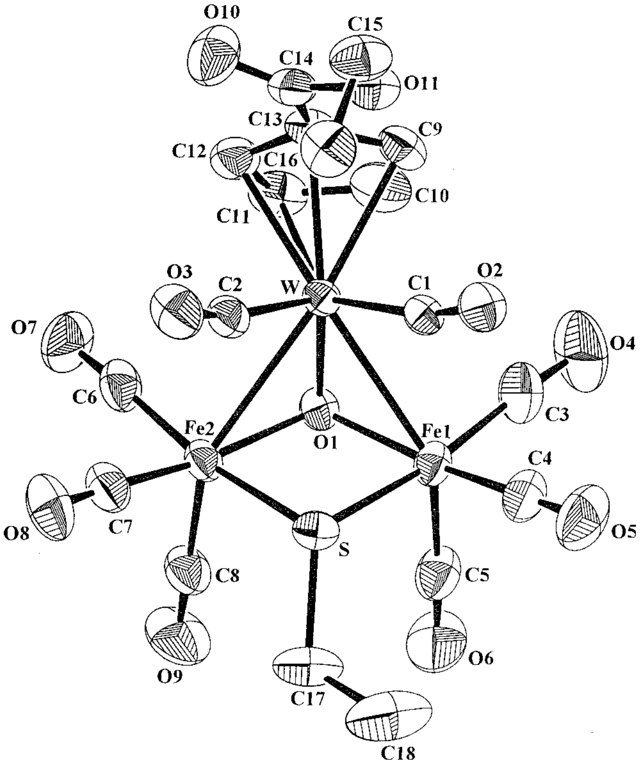

Figure 2. ORTEP view of **3k** with atom-labeling scheme.

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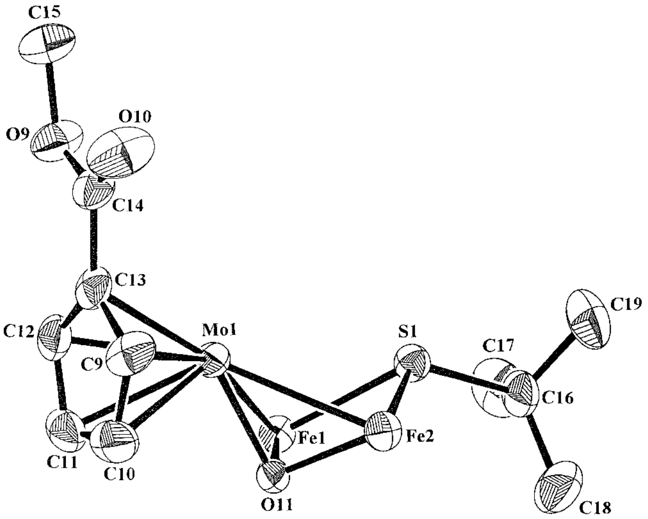

Figure 3. Condensed ORTEP drawing of **3d**.

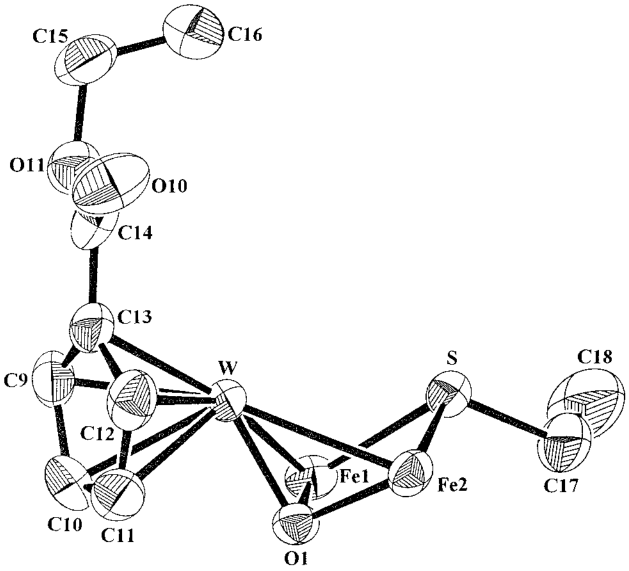

Figure 4. Condensed ORTEP drawing of **3k**.

nyls are omitted are shown in Figures 3 and 4. As easily seen from Figures 3 and 4, the *t*-Bu group of **3d** and the Et group of **3k** lie in an equatorial, not axial, position[20] relative to the oxo-capped MFe_2S butterfly skeleton.

Spectroscopic Characterization of 3a−k. In addition to the X-ray single-crystal structures of **3d** and **3k**, the IR and ^1H NMR spectra of **3a**−**k** were also determined. The IR spectra of **3a**−**k** show five to six strong absorption bands in the range 2090−1815 cm^{-1}, characteristic of the terminal and semibridging carbonyls attached to Fe and Mo/W atoms, respectively. This is consistent with the results of single-crystal diffraction analyses for **3d** and **3k**. In addition, the IR spectrum of **3c** shows one strong absorption band at 1688 cm^{-1} for its ketonic carbonyl, whereas those of **3d**−**k** exhibit one strong band at 1704−1737 cm^{-1} for their ester carbonyls. The ^1H NMR spectra of **3a**−**k** indicate the presence of their respective R and R′ organic groups. For example, for **3a**,**b**, the ^1H NMR spectrum of **3a** shows one singlet at δ 5.80 for its parent Cp ring and one triplet at δ 1.10 and one quartet at δ 2.40 for Et, whereas that of **3b** exhibits two singlets at δ 5.28 and 5.47 for its Cp ring and two singlets at δ 1.30 and 1.40 for its *t*-Bu group. This implies that **3a** consists of an single isomer but **3b** is a mixture of two isomers.[21,22] For **3a** the isomer should have an equatorial Et ($\delta(CH_2)$ 2.40, $\delta(CH_3)$ 1.10),[21] whereas for **3b** one isomer should have an equatorial *t*-Bu (δ 1.40) and the other should have an axial *t*-Bu (δ 1.30).[23] For the other products **3c**−**k** the four protons on substituted Cp rings show two sets of signals at about δ 6.7 and 5.5. The set of signals at higher field is assigned to H^3 and H^4 protons remote from the substituent, whereas the set of signals at lower field is ascribed to H^2 and H^5 protons close to the substituent, since the substituents are electron-withdrawing groups.[24] In addition, the ^1H NMR spectra of organic groups R attached to the bridged sulfur atoms show one singlet at about δ 7.3 for Ph and at about δ 1.3 for *t*-Bu and one triplet at about δ 1.1 and one quartet at about δ 2.4 for Et. This implies that products **3c**−**k** consist of an single isomer, which should have the R groups attached to the bridged S atoms by an equatorial type of bond.[20−22] Such isomer assignments, similar to those for **3a**,**b**, were primarily made on the basis of the ^1H NMR data of R groups attached to the bridged sulfur atom and the structure similarity between $(\mu\text{-RS})_2Fe_2(CO)_6$ and **3a**,**k**, both of which have a butterfly skeleton of Fe_2S_2 or MFe_2S (see the single-crystal structures described above).[22,23]

Experimental Section

All reactions were carried out under prepurified tank nitrogen using standard Schlenk or vaccum-line techniques. Tetrahydrofuran (THF) was distilled from sodium−benzophenone ketyl, while triethylamine was distilled from potassium hydroxide under nitrogen. Mercaptans RSH (R = Et, *t*-Bu, Ph) were of commercial origin and used without further purification. Triiron dodecacarbonyl,[25] $[(\eta^5\text{-R}'C_5H_4)(CO)_2Mo]_2$ (R′ = H, MeCO, MeO_2C, EtO_2C),[13,26] and $[(\eta^5\text{-R}'C_5H_4)W(CO)_2]_2$ (R′ = MeO_2C, EtO_2C)[12] were prepared according to literature procedures. Products **3a**−**k** were purified by open-air chromatography (silica gel G 10−40 μm); the second band separated with ease from the first band of the least polar byproducts $(\mu\text{-RS})_2Fe_2(CO)_6$ but with diffculty (particular for the tungsten homologues **3i**−**k**) from the third band of byproducts $[(\eta^5\text{-RC}_5H_4)(CO)_3M]_2$ due to their very close polarity. The products for analyses were further purified by recrystallization from petroleum ether/CH_2Cl_2. IR and ^1H NMR spectra were recorded on a Nicolet FT-IR 5DX infrared spectrophotometer and a Jeol FX-90Q NMR spectrometer, respectively. C/H analyses were performed on a Perkin-Elmer Model 240C analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Preparations of 3a−k by the First Procedure. Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2MoFe_2(\mu_3\text{-O})(\mu\text{-EtS})(CO)_6$ (3a). A 100 mL three-necked flask equipped with a magnetic stirbar, a rubber septum, and a nitrogen inlet tube was charged with

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1.00 g (1.98 mmol) of $Fe_3(CO)_{12}$ and 30 mL of THF. To the resulting green solution were added 0.16 mL (2 mmol) of EtSH and 0.28 mL (2 mmol) of Et_3N, and the mixture was stirred at room temperature for about 0.5 h to give a brown solution of $[Et_3NH][(\mu\text{-}EtS)(\mu\text{-}CO)Fe_2(CO)_6]$. To this solution was added 0.43 g (1.0 mmol) of $[(\eta^5\text{-}C_5H_5)(CO)_2Mo]_2$, and the mixture was stirred at room temperature for 0.5 h under a bubbling stream of N_2. The N_2 stream was then changed to an air stream, which was bubbled into the reaction mixture at room temperature for 0.5 h. Solvent was removed at reduced pressure. The residue was subjected to open-air TLC separation using 10:1 (v/v) petroleum ether/acetone as eluent. The first and third bands were identified as the known compounds $(\mu\text{-}EtS)_2Fe_2(CO)_6$ and $[\eta^5\text{-}C_5H_5(CO)_3Mo]_2$, in small quantities. From the second band was obtained 184 mg (32%) of **3a** as a yellow-green solid. **3a**: mp 105 °C dec. Anal. Calcd for $C_{15}H_{10}Fe_2MoO_9S$: C, 31.39; H, 1.76. Found: C, 31.00; H, 1.42. IR (KBr, disk): $\nu_{C\equiv O}$ 2073 (s), 2049 (vs), 1991 (vs), 1868 (s), 1819 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.10 (t, $J = 7.2$ Hz, 3H, CH_3), 2.40 (q, $J = 7.2$ Hz, 2H, CH_2), 5.80 (s, 5H, C_5H_5) ppm.

Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2MoFe_2(\mu_3\text{-}O)(\mu\text{-}t\text{-}BuS)(CO)_6$ (3b). The same procedure was used as that for preparation of **3a**. To a solution of $[Et_3NH][(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ prepared from 0.28 mL (2 mmol) of *t*-BuSH was added 0.44 g (1.0 mmol) of $[(\eta^5\text{-}C_5H_5)(CO)_2Mo]_2$. After removal of small amounts of the known compounds $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$ and $[(\eta^5\text{-}C_5H_5)(CO)_3Mo]_2$, 200 mg (33%) of **3b** was obtained as a deep green solid. **3b**: mp 121−122 °C. Anal. Calcd for $C_{17}H_{14}Fe_2MoO_9S$: C, 33.91; H, 2.34. Found: C, 33.73; H, 2.28. IR (KBr, disk): $\nu_{C\equiv O}$ 2051 (s), 2021 (vs), 1980 (vs), 1926 (s), 1835 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30,1.40 (s, s, 9H, *t*-C_4H_9), 5.28, 5.47 (s, s, 5H, C_5H_5) ppm.

Preparation of $(\eta^5\text{-}MeCOC_5H_4)(CO)_2MoFe_2(\mu_3\text{-}O)(\mu\text{-}EtS)(CO)_6$ (3c). To a solution of $[Et_3NH][(\mu\text{-}EtS)(\mu\text{-}CO)Fe_2(CO)_6]$ was added 0.55 g(1.0 mmol) of $[(\eta^5\text{-}MeCOC_5H_4)(CO)_2Mo]_2$. After removal of small amounts of the known compounds $(\mu\text{-}EtS)_2Fe_2(CO)_6$ and $[(\eta^5\text{-}MeCOC_5H_4)(CO)_3Mo]_2$, 160 mg (26%) of **3c** was obtained as a deep green solid. **3c**: mp 143 °C dec. Anal. Calcd for $C_{17}H_{12}Fe_2MoO_{10}S$: C, 33.14; H, 1.96. Found: C, 33.26; H, 1.89. IR (KBr, disk): $\nu_{C\equiv O}$ 2080 (s), 2057 (s), 2023 (vs), 2004 (vs), 1981 (s), 1869 (s); $\nu_{C=O}$ 1688 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.11 (t, $J = 7.2$ Hz, 3H, CH_3), 2.34 (q, $J = 7.2$ Hz, 2H, CH_2), 2.52 (s, 3H, CH_3CO), 5.39 (br s, 2H, H^3, H^4), 6.66 (br s, 2H, H^2, H^5) ppm.

Preparation of $(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2MoFe_2(\mu_3\text{-}O)(\mu\text{-}t\text{-}BuS)(CO)_6$ (3d). To a solution of $[Et_3NH][(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ was added 0.55 g (1.0 mmol) of $[(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2Mo]_2$. After removal of small amounts of known compounds $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$ and $[\eta^5\text{-}MeO_2CC_5H_4(CO)_3Mo]_2$, 230 mg (35%) of **3d** was obtained as a deep green solid. If air was bubbled for 1 h or for 2 h, 200 mg (30%) or 180 mg (27%) of **3d** was obtained, respectively. **3d**: mp 110 °C dec. Anal. Calcd for $C_{19}H_{16}Fe_2MoO_{11}S$: C, 34.58; H, 2.44. Found: C, 34.39; H, 2.38. IR (KBr, disk): $\nu_{C\equiv O}$ 2073 (s), 2049 (vs), 1983 (vs), 1877 (vs), 1836 (s); $\nu_{C=O}$ 1721 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.32 (s, 9H, *t*-C_4H_9), 3.96 (s, 3H, OCH_3), 5.46 (t, 2H, H^3, H^4), 6.66 (t, 2H, H^2, H^5) ppm.

Preparation of $(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2MoFe_2(\mu_3\text{-}O)(\mu\text{-}PhS)(CO)_6$ (3e). To a solution of $[Et_3NH][(\mu\text{-}PhS)(\mu\text{-}CO)Fe_2(CO)_6]$ prepared from 0.2 mL (2 mmol) of PhSH was added 0.55 g(1.0 mmol) of $[(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2Mo]_2$. After removal of amounts of the known compounds $(\mu\text{-}PhS)_2Fe_2(CO)_6$ and $[(\eta^5\text{-}MeO_2CC_5H_4)(CO)_3Mo]_2$, 248 mg (37%) of **3e** was obtained as a deep green solid. **3e**: mp 119−121 °C. Anal. Calcd for $C_{21}H_{12}Fe_2MoO_{11}S$: C, 37.09; H, 1.78. Found: C, 37.02; H, 1.40. IR (KBr, disk): $\nu_{C\equiv O}$ 2082 (s), 2049 (s), 2000 (vs), 1975 (s), 1877 (s), 1827 (m); $\nu_{C=O}$ 1721 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.92 (s, 3H, OCH_3), 5.56 (t, 2H, H^3, H^4), 6.64 (t, 2H, H^2, H^5), 7.28 (s, 5H, C_6H_5) ppm.

Preparation of $(\eta^5\text{-}EtO_2CC_5H_4)(CO)_2MoFe_2(\mu_3\text{-}O)(\mu\text{-}EtS)(CO)_6$ (3f). To a solution of $[Et_3NH][(\mu\text{-}EtS)(\mu\text{-}CO)Fe_2(CO)_6]$ was added 0.58 g (1.0 mmol) of $[(\eta^5\text{-}EtO_2CC_5H_4)(CO)_2Mo]_2$. After removal of small amounts of $(\mu\text{-}EtS)_2Fe_2(CO)_6$ and $[(\eta^5\text{-}EtO_2CC_5H_4)(CO)_3Mo]_2$, 240 mg (37%) of **3f** was obtained as a deep green solid. **3f**: mp 138 °C dec. Anal. Calcd for $C_{18}H_{14}Fe_2MoO_{11}S$: C, 33.47; H, 2.18. Found: C, 33.40; H, 1.97. IR (KBr, disk): $\nu_{C\equiv O}$ 2070 (s), 2054 (s), 1999 (vs), 1971 (vs), 1889 (s), 1839 (s); $\nu_{C=O}$ 1723 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.04 (t, $J = 7.2$ Hz, 3H, $SCH_2C\mathbf{H}_3$), 1.40 (t, $J = 7.2$ Hz, 3H, $OCH_2C\mathbf{H}_3$), 2.32 (q, $J = 7.2$ Hz, 2H, SCH_2), 4.39 (q, $J = 7.2$ Hz, 2H, OCH_2), 5.46 (t, 2H, H^3, H^4), 6.60 (t, 2H, H^2, H^5) ppm.

Preparation of $(\eta^5\text{-}EtO_2CC_5H_4)(CO)_2MoFe_2(\mu_3\text{-}O)(\mu\text{-}t\text{-}BuS)(CO)_6$ (3g). To a solution of $[Et_3NH][(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ was added 0.58 g (1.0 mmol) of $[\eta^5\text{-}EtO_2CC_5H_4(CO)_2Mo]_2$. After removal of small amounts of the known compounds $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$ and $[(\eta^5\text{-}EtO_2CC_5H_4)(CO)_3Mo]_2$, 184 mg (27%) of **3g** was obtained as a deep green solid. **3g**: mp 135 °C dec. Anal. Calcd for $C_{20}H_{18}Fe_2MoO_{11}S$: C, 35.64; H, 2.69. Found: C, 35.64; H, 2.88. IR (KBr, disk): $\nu_{C\equiv O}$ 2072 (s), 2049 (vs), 1983 (vs), 1885 (s), 1844 (s); $\nu_{C=O}$ 1721 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ1.32 (s, 9H, *t*-C_4H_9), 1.47 (t, $J = 7.2$ Hz, 3H, CH_3), 4.45 (q, $J = 7.2$ Hz, 2H, CH_2), 5.48 (t, 2H, H^3, H^4), 6.70 (t, 2H, H^2, H^5) ppm.

Preparation of $(\eta^5\text{-}EtO_2CC_5H_4)(CO)_2MoFe_2(\mu_3\text{-}O)(\mu\text{-}PhS)(CO)_6$ (3h). To a solution of $[Et_3NH][(\mu\text{-}PhS)(\mu\text{-}CO)Fe_2(CO)_6]$ was added 0.58 g (1.0 mmol) of $[(\eta^5\text{-}EtO_2CC_5H_4(CO)_2Mo]_2$. After removal of small amounts of the known compounds $(\mu\text{-}PhS)_2Fe_2(CO)_6$ and $[(\eta^5\text{-}EtO_2CC_5H_4(CO)_3Mo]_2$, 240 mg (35%) of **3h** was obtained as a deep-brown solid. **3h**: mp 124 °C dec. Anal. Calcd for $C_{22}H_{14}Fe_2MoO_{11}S$: C, 38.07; H, 2.03. Found: C, 37.82; H, 2.09. IR (KBr, disk): $\nu_{C\equiv O}$ 2090 (s), 2057 (vs), 2000 (vs), 1868 (s), 1827 (s); $\nu_{C=O}$ 1704 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.44 (t, $J = 7.2$ Hz, 3H, CH_3), 4.46 (t, $J = 7.2$ Hz, 2H, CH_2), 5.58 (t, 2H, H^3, H^4), 6.70 (t, 2H, H^2, H^5), 7.30 (s, 5H, C_6H_5) ppm.

Preparation of $(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2WFe_2(\mu_3\text{-}O)(\mu\text{-}EtS)(CO)_6$ (3i). To a solution of $[Et_3NH][(\mu\text{-}EtS)(\mu\text{-}CO)Fe_2(CO)_6]$ was added 0.73 g (1.0 mmol) of $[(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2W]_2$. After removal of small amounts of the known compounds $(\mu\text{-}EtS)_2Fe_2(CO)_6$ and $[(\eta^5\text{-}MeO_2CC_5H_4)(CO)_3W]_2$, 120 mg (17%) of **3i** was obtained as a deep green solid. **3i**: mp 127−128 °C. Anal. Calcd for $C_{17}H_{12}Fe_2O_{11}SW$: C, 28.36; H, 1.68. Found: C, 28.37; H, 1.67. IR (KBr, disk): $\nu_{C\equiv O}$ 2079 (s), 2053 (vs), 1991 (vs), 1972 (vs), 1869 (s), 1815 (s); $\nu_{C=O}$ 1729 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.16 (t, $J = 7.2$ Hz, 3H, CH_3), 2.38 (q, $J = 7.2$ Hz, 2H, CH_2), 3.94 (s, 3H, OCH_3), 5.65 (t, 2H, H^3, H^4), 6.72 (t, 2H, H^2, H^5) ppm.

Preparation of $(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2WFe_2(\mu_3\text{-}O)(\mu\text{-}t\text{-}BuS)(CO)_6$ (3j). To a solution of $[Et_3NH][(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ was added 0.73 g (1.0 mmol) of $[(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2W]_2$. After removal of small amounts of the known compounds $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$ and $[(\eta^5\text{-}MeO_2CC_5H_4)(CO)_3W]_2$, 96 mg (13%) of **3j** was obtained as a deep green solid. **3j**: mp 130−132 °C. Anal. Calcd for $C_{19}H_{16}Fe_2O_{11}SW$: C, 30.51; H, 2.16. Found: C, 30.34; H, 2.26. IR (KBr, disk): $\nu_{C\equiv O}$ 2071 (s), 2044 (vs), 1991 (vs), 1881 (s), 1825 (s); $\nu_{C=O}$ 1737 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30 (s, 9H, *t*-C_4H_9), 3.92 (s, 3H, OCH_3), 5.48 (t, 2H, H^3, H^4), 6.76 (t, 2H, H^2, H^5) ppm.

Preparation of $(\eta^5\text{-}EtO_2CC_5H_4)(CO)_2WFe_2(\mu_3\text{-}O)(\mu\text{-}EtS)(CO)_6$ (3k). To a solution of $[Et_3NH][(\mu\text{-}EtS)(\mu\text{-}CO)Fe_2(CO)_6]$ was added 0.75 g(1.0 mmol) of $[(\eta^5\text{-}EtO_2CC_5H_4(CO)_2W]_2$. After removal of small amounts of the known compounds $(\mu\text{-}EtS)_2Fe_2(CO)_6$ and $[(\eta^5\text{-}EtO_2CC_5H_4(CO)_3W]_2$, 88 mg (12%) of **3k** was obtained as a deep green solid. **3k**: mp 120−122 °C. Anal. Calcd for $C_{18}H_{14}Fe_2O_{11}SW$: C, 29.46; H, 1.92. Found: C, 29.20; H, 2.10. IR (KBr, disk): $\nu_{C\equiv O}$ 2070 (s), 2052 (vs), 1988 (vs), 1970 (s), 1882 (s), 1829 (s); $\nu_{C=O}$ 1725 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.08 (t, $J = 7.2$ Hz, 3H, $SCH_2C\mathbf{H}_3$), 1.41 (t, $J = 7.2$ Hz, 3H, $OCH_2C\mathbf{H}_3$), 2.38 (q, $J = 7.2$ Hz, 2H, SCH_2), 4.40 (q, $J = 7.2$ Hz, 2H, OCH_2), 5.64 (t, 2H, H^3, H^4), 6.76 (t, 2H, H^2, H^5) ppm.

Table 4. Crystal Data Collection and Refinement for 3d and 3k

	3d	**3k**
mol formula	$C_{19}H_{16}Fe_2MoO_{11}S$	$C_{18}H_{14}Fe_2O_{11}SW$
mol wt	660.02	733.91
cryst syst	orthorhombic	triclinic
space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
a, Å	9.684(7)	8.9875(8)
b, Å	27.84(2)	18.179(4)
c, Å	8.815(1)	7.3216(8)
α, deg		94.45(1)
β, deg		101.345(8)
γ, deg		98.35(1)
V, Å^3	2376(2)	1154.6(3)
Z	4	2
density (calcd), g cm^{-3}	1.844	2.111
F(000)	1312	704
μ(Mo Kα), cm^{-1}	18.66	63.59
diffractometer	Rigaku AFC7R	Rigaku AFC7R
temp, °C	20	20
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å)	Mo Kα ($\lambda = 0.710\ 69$ Å)
scan type	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{max}$, deg	55	50.0
no. of observns, *n*	2586	3817
no. of variables, *p*	307	299
R	0.028	0.021
R_w	0.033	0.031
largest peak in final diff map, e Å^{-3}	0.36	0.60

Preparations of 3a−k by the Second Procedure. Products **3a−k** were also prepared (using the same amounts of corresponding starting materials) by a second procedure, which is almost the same as the first procedure described above, except without the air-bubbling step before the open-air TLC separatron. The quantities and yields of **3a−k** obtained by the second procedure are as follows: **3a**, 100 mg (17%); **3b**, 115 mg (19%); **3c**, 50 mg (8%); **3d**, 170 mg (26%); **3e**, 142 mg (21); **3f**, 100 mg (16%); **3g**, 110 mg (16%); **3h**, 130 mg (19%); **3i**, 30 mg (4%); **3j**, 40 mg (5%); **3k**, 40 mg (6%).

Crystal Structure Determinations of 3d and 3k. Single-crystals of **3d** and **3k** suitable for X-ray diffraction were grown by slow evaporation of their CH_2Cl_2/petroleum ether solutions in a refrigerator. A single crystal of **3d** or **3k** measuring approximately 0.20 × 0.20 × 0.30 mm was mounted on a glass fiber and placed in a Rigaku AFC7R diffractometer with graphite-monochromated Mo−Kα radiation and a 12 kW rotating anode generator. All reflections (3095 reflections for **3d** and 4047 for **3k**) were collected at 20 °C by the $\omega-2\theta$ scan mode, the independent reflections of which with $I \geq 3\sigma(I)$ were considered to be observed and used in subsequent refinements. Data were corrected for Lp and absorption factors.

The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Final refinement by the full-matrix least-squares method for non-hydrogen atoms converged to weighted and unweighted agreement factors. All calculations were performed on a Micro-Vax II computer using the TEXSAN program package. Details of crystal parameters, data collection, and structure refinement for **3d** and **3k** are given in Table 4.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **3d** and **3k** (18 pages). Ordering information is given on any current masthead page.

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