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Article

New Disulfido Molybdenum–Manganese Complexes Exhibit Facile Addition of Small Molecules to the Sulfur Atoms

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The reaction of $Mn_2(CO)_7(\mu\text{-}S_2)$ (**1**) with $[CpMo(CO)_3]_2$ ($Cp = C_5H_5$) and $[Cp^*Mo(CO)_3]_2$ ($Cp^* = C_5(CH_3)_5$) yielded the new mixed-metal disulfide complexes $CpMoMn(CO)_5(\mu\text{-}S_2)$ (**2**) and $Cp^*MoMn(CO)_5(\mu\text{-}S_2)$ (**3**) by a metal–metal exchange reaction. Compounds **2** and **3** both contain a bridging disulfido ligand lying perpendicular to the Mo–Mn bond. The bond distances are Mo–Mn = 2.8421(10) and 2.8914(5) Å and S–S = 2.042(2) and 1.9973(10) Å for **2** and **3**, respectively. A tetranuclear metal side product $CpMoMn_3(CO)_{13}(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**4**) was also isolated from the reaction of **1** with $[CpMo(CO)_3]_2$. Compounds **2** and **3** react with CO to yield the dithiocarbonato complexes $CpMoMn(CO)_5[\mu\text{-}SC({=}O)S]$ (**5**) and $Cp^*MoMn(CO)_5[\mu\text{-}SC({=}O)S]$ (**6**) by insertion of CO into the S–S bond. Similarly, *tert*-butylisocyanide was inserted into the S–S bond of **2** and **3** to yield the complexes $CpMoMn(CO)_5[\mu\text{-}S(C{=}NBu^t)S]$ (**7**) and $Cp^*MoMn(CO)_5[\mu\text{-}S(C{=}NBu^t)S]$ (**8**), respectively. Ethylene and dimethylacetylene dicarboxylate also inserted into the S–S bond of **2** and **3** at room temperature to yield the ethanedithiolato ligand bridged complexes $CpMoMn(CO)_5(\mu\text{-}SCH_2CH_2S)$ (**9**), $Cp^*MoMn(CO)_5(\mu\text{-}SCH_2CH_2S)$ (**10**), $CpMoMn(CO)_5[\mu\text{-}SC(CO_2Me){=}C(CO_2Me)S]$ (**11**), and $Cp^*MoMn(CO)_5[\mu\text{-}SC(CO_2Me){=}C(CO_2Me)S]$ (**12**). Allene was found to insert into the S–S bond of **2** by using one of its two double bonds to yield the complex $CpMoMn(CO)_5[\mu\text{-}SCH_2C({=}CH_2)S]$ (**13**). The molecular structures of the new complexes **2**–**7** and **9**–**13** were established by single-crystal X-ray diffraction analyses.

Introduction

Metal disulfides are of interest because of their value as catalysts for the removal of organosulfur compounds from the feedstocks[1] and as solid state lubricants.[2] Sulfido ligands are valuable agents for the synthesis and stabilization of metal cluster complexes.[3] Transition metal complexes containing the disulfido ligand exhibit a range of interesting reactivity at the sulfur atoms.[4] Metal-containing groups can be inserted into the sulfur−sulfur bond to yield mixed-metal clusters containing two sulfido ligands,[5] and small unsaturated organic molecules can be inserted into the sulfur−sulfur bond to yield complexes containing dithiolato ligands.[6] The disulfido ligand can exhibit a variety of bridging coordination geometries in polynuclear metal complexes.[7]

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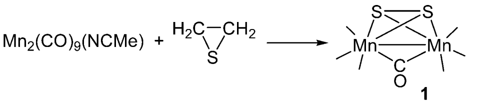
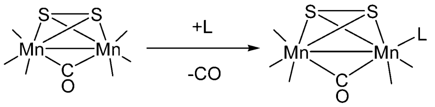
Recently, we have prepared the new disulfidodimanganese carbonyl complex $Mn_2(CO)_7(\mu\text{-}S_2)$, **1**, from the reaction of $Mn_2(CO)_9(NCMe)$ with thiirane, eq 1.[8,9] Compound **1** engages in a wide variety of reactions including simple CO ligand substitution[9] (eq 2), insertion of thioethers into the manganese−manganese bond[10] (eq 3), and insertions of metal groupings into the sulfur−sulfur bond (eq 4).[11,12]



(1)

1



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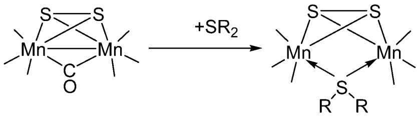

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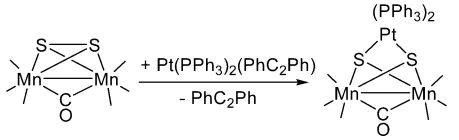
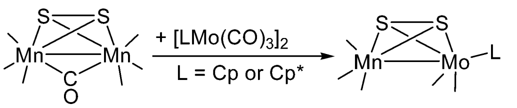


(4)

We have now found that **1** reacts with $[CpMo(CO)_3]_2$ and $[Cp^*Mo(CO)_3]_2$, Cp = C_5H_5 and Cp* = $C_5(CH_3)_5$, by an unexpected metal−metal exchange process to yield the new heterodinuclear metal complexes $CpMoMn(CO)_5(\mu\text{-}S_2)$ **(2)** and $Cp^*MoMn(CO)_5(\mu\text{-}S_2)$ **(3)**, which contain a bridging disulfido ligand. Compounds **2** and **3** both show high reactivity toward the insertion of a range of unsaturated small organic molecules into the S−S bond. The results of these studies are reported here.

Results and Discussion

The new heterodinuclear compounds $CpMoMn(CO)_5(\mu\text{-}S_2)$ **(2)** and $Cp^*MoMn(CO)_5(\mu\text{-}S_2)$ **(3)** were obtained from the reaction of $Mn_2(CO)_7(\mu\text{-}S_2)$ **(1)** with $[CpMo(CO)_3]_2$ and $[Cp^*Mo(CO)_3]_2$ at 25 °C in 26% yields, eq 5. When the preparation of **2** was conducted under identical conditions in the absence of room light, the yield was less than 2%. When the reaction was conducted by irradiation with a 60 W halogen lamp placed 6 in. from the reaction vessel, the yield was only 7% compared to the 23% with room light. It was subsequently shown that product **2** is light sensitive and degrades considerably during exposure to the 60 W halogen lamp.



(5)

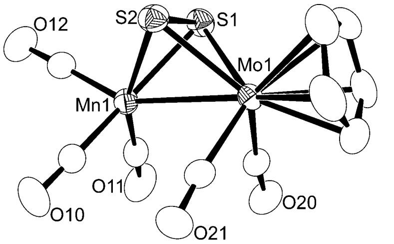


Figure 1. An ORTEP diagram of the molecular structure of $CpMoMn(CO)_5(\mu\text{-}S_2)$ (**2**) showing 50% probability thermal ellipsoids.

Compound **3** was also obtained from the reaction of **1** with $[Cp^*Mo(CO)_2]_2$ (which is commercially available), but the yield is better when the reaction is carried out under an atmosphere of CO. Since $[Cp^*Mo(CO)_2]_2$ reacts readily with CO to yield $[Cp^*Mo(CO)_3]_2$,[13] it is almost certain that it is $[Cp^*Mo(CO)_3]_2$ not the $[Cp^*Mo(CO)_2]_2$ that is reacting with the **1** to give the product **3** in this reaction too. The infrared spectra of **2** and **3** indicate that all of the carbonyl ligands are of a terminal type. The ^1H NMR spectra of **2** and **3** exhibit singlets at $\delta = 5.6$ ppm for the C_5H_5 ligand in **2** and $\delta = 1.99$ ppm for the five methyl groups on the Cp* ligand in **3**. The ^{13}C NMR spectrum of **3** at −40 °C exhibits resonances at 234.7 ppm (2 CO), 225 ppm (2 CO, br), and 223 ppm (1 CO, br) due to the carbonyl ligands. The latter two are broad and are probably bonded to the manganese atom. This broadness is probably due to spin-relaxation induced by the large quadrupole moment of the manganese atom.

The molecular structures of **2** and **3** were both established by single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **2** is shown in Figure 1. Compound **3** is structurally similar with the exception of the additional methyl groups on the Cp ligand. Selected bond distances and angles for **2** and **3** are listed in Table 2. Both compounds contain one molybdenum and one manganese atom joined by a Mo−Mn single bond, 2.8421(10) Å in **2**, and 2.8914(5) Å in **3**, that is bridged by a disulfido ligand. Both Mo−Mn distances are considerably shorter than that found in $CpMoMn(CO)_8$, 3.083(8) Å, which contains no bridging ligands.[14] The shortness of the molybdenum−manganese bond in **2** and **3** can be attributed to the bridging disulfido ligand.[8,9] Interestingly, the Mo−Mn distance in **3** is significantly longer than that in **2**. One might want to attribute this to steric repulsions caused by the larger Cp* ligand in **3**. In support of this, the Mo−Mo bond distance in $[Cp^*Mo(CO)_3]_2$ is longer than that observed in $[CpMo(CO)_3]_2$, 3.284(1) Å[15] versus 3.235(1) Å.[16] However, as shown below in the comparison of the metal−metal bond

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Table 1. Crystallographic Data for Compounds **2**−**7** and **9**−**13**

	2	**3**	**4**	**5**	**6**	**7**
empirical formula	$MnMoO_5S_2C_{10}H_5$	$MoMnS_2O_5C_{15}H_{15}$	$Mn_3MoO_{13}S_2C_{18}H_5$	$MnMoO_6S_2C_{11}H_5$	$MoMnS_2O_6C_{16}H_{15}$	$MnMoNO_5S_2C_{15}H_{14}$
fw	420.14	490.27	754.10	448.15	518.28	503.27
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
lattice params						
a (Å)	11.0575(11)	11.8571(6)	9.4646(5)	8.9976(4)	11.0142(4)	9.4347(5)
b (Å)	8.2471(8)	12.3756(7)	15.8502(9)	16.3390(8)	12.9423(5)	19.519(1)
c (Å)	14.5820(15)	12.2448(7)	16.9337(9)	19.9004(9)	13.9602(5)	10.6607(5)
α (deg)	90	90	90	90	90	90
β (deg)	98.005(3)	91.929(1)	103.576(1)	98.984(1)	90	105.042(1)
γ (deg)	90	90	90	90	90	90
V (Å^3)	1316.8(2)	1759.77(17)	2469.3(2)	2889.7(2)	1990.01(13)	1895.99(17)
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$Pnma$	$P2_1/n$
Z value	4	4	4	8	4	4
ρ_{calc} (g/cm^3)	2.119	1.813	2.028	2.060	1.730	1.763
μ (Mo Kα) (mm^{-1})	2.237	1.655	2.228	2.051	1.502	1.571
temp (K)	293	173	173	296	296	296
no. obsd ($I > 2\sigma(I)$)	1721	3101	4180	3987	2311	3854
no. of params	172	222	334	379	132	229
GOF	1.021	1.038	1.087	1.059	1.062	1.013
max shift in final cycle	0.000	0.001	0.001	0.001	0.001	0.001
residuals: R1; wR2^a	0.0403; 0.0699	0.0275; 0.0590	0.0346; 0.0723	0.0423; 0.0728	0.0282; 0.0765	0.0298; 0.0694
transm coeff, max/min	1.0/0.878	1.0/0.890	1.0/0.832	1.000/0.917	1.0/0.863	1.0/0.862
largest peak in final diff. Fourier (e$^-$/Å^3)	0.481	0.405	0.618	0.461	0.413	0.493

	9	**10**	**11**	**12**	**13**
empirical formula	$MnMoO_5S_2C_{12}H_9$	$MoMnS_2O_5C_{17}H_{19}$	$MnMoO_9S_2C_{16}H_{11}$	$MoMnS_2O_9C_{21}H_{21}$	$MnMoO_5S_2C_{13}H_9$
fw	448.19	518.32	562.25	632.38	460.20
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic
lattice params					
a (Å)	8.9625(15)	8.9107(4)	9.3598(12)	10.2318(7)	8.6479(7)
b (Å)	9.1008(14)	9.6230(4)	9.7534(12)	11.8012(8)	9.1002(7)
c (Å)	18.700(3)	12.7682(6)	11.7759(15)	12.0211(8)	22.7655(17)
α (deg)	80.702(17)	80.407(1)	84.218(2)	67.714(1)	91.428(2)
β (deg)	88.72(2)	80.923(1)	72.867(2)	66.092(1)	99.149(2)
γ (deg)	85.34(2)	68.804(1)	80.131(2)	74.876(1)	116.848(1)
V (Å^3)	1500.2(4)	1000.82(8)	1010.7(2)	1218.05(14)	1568.6(2)
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z value	4	2	2	2	4
ρ_{calc} (g/cm^3)	1.984	1.720	1.848	1.724	1.949
μ (Mo Kα) (mm^{-1})	1.970	1.490	1.497	1.253	1.887
temp (K)	293	296	296	294	293
no. obsd ($I > 2\sigma(I)$)	6257	4542	3191	4275	6742
no. of params	379	311	264	314	397
GOF	1.035	1.042	1.041	1.031	1.039
max shift in final cycle	0.001	0.002	0.001	0.001	0.001
residuals: R1; wR2^a	0.0417; 0.0921	0.0220; 0.0572	0.0582; 0.2561	0.0258; 0.0650	0.0455; 0.1104
transm coeff, max/min	1.0/0.833	1.0/0.911	1.0/0.883	1.0/0.918	1.0/0.911
largest peak in final diff. Fourier (e$^-$/Å^3)	1.180	0.331	1.572	0.331	0.913

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/\sigma^2(F_o^2)$. $GOF = [\Sigma_{hkl}(w(|F_o^2| - |F_c^2|))^2/(n_{data} - n_{vari})]^{1/2}$.

distances for compounds **5** and **6**, and **9** and **10**, it is the Cp* compound that contains the shortest metal−metal bond, so other factors must also be affecting the length and strength of the metal−metal bond. As found in many other dinuclear disulfido complexes,[4,8,17−19] the S−S bond of the disulfido ligand is oriented perpendicular to the metal−metal bond and both sulfur atoms are bonded to both metal atoms. The Mn−S bond distances, Mn(1)−S(1) = 2.2968(16) [2.2782(8)] Å and Mn(1)−S(2) = 2.2981(16) [2.3030(8)] Å (the values in brackets are for compound **3**), are similar to those in **1**: Mn(1)−S(1) = 2.2890(8) Å, Mn(1)−S(2) = 2.2877(7) Å, Mn(2)−S(1) = 2.2855(8) Å, Mn(2)−S(2) = 2.2842(8) Å. The Mo−S distances, Mo(1)−S(1) = 2.4372(16) [2.4548(7)] Å, Mo(1)−S(2) = 2.4492(16) [2.5064(7)] Å, are similar to those found for the bridging disulfido ligand in the related compound $Cp^*Mo(\mu\text{-}S_2)(\mu\text{-}S)_2Cp^*$, Mo−S = 2.446(4), 2.449(5), 2.448(5), and 2.443(4) Å.[17] The S−S bond distances in **2** and **3** are 2.042(2) and 1.9973(10) Å respectively. These values are similar to those found in **1** (2.0474(11) Å) and in $Fe_2(CO)_6(\mu\text{-}S_2)$, 2.021(3)[18] and 2.007(5) Å,[19] but it is notable that the S−S distance in **3** is significantly shorter than that in **2**. Recall that the opposite was true for the metal−metal bond distances

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Table 2. Selected Intramolecular Distances and Angles for $CpMoMn(CO)_5(\mu\text{-}S_2)$ (**2**) and $Cp^*MoMn(CO)_5(\mu\text{-}S_2)$ (**3**)[a]

(a) Distances

2			3		
atom	atom	distance (Å)	atom	atom	distance (Å)
Mn(1)	Mo(1)	2.8421(10)	Mn(1)	Mo(1)	2.8914(5)
Mn(1)	S(1)	2.2968(16)	Mn(1)	S(1)	2.2782(8)
Mn(1)	S(2)	2.2981(16)	Mn(1)	S(2)	2.3030(8)
Mo(1)	S(1)	2.4372(16)	Mo(1)	S(1)	2.4548(7)
Mo(1)	S(2)	2.4492(16)	Mo(1)	S(2)	2.5064(7)
S(1)	S(2)	2.042(2)	S(1)	S(2)	1.9973(10)

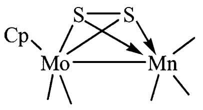
(b) Angles

2				3			
atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Mn(1)	S(1)	Mo(1)	73.73(5)	Mn(1)	S(1)	Mo(1)	75.21(2)
Mn(1)	S(2)	Mo(1)	73.47(5)	Mn(1)	S(2)	Mo(1)	73.78(2)
Mn(1)	Mo(1)	S(1)	50.87(4)	Mn(1)	Mo(1)	S(1)	49.623(19)
Mn(1)	Mo(1)	S(2)	50.82(4)	Mn(1)	Mo(1)	S(2)	49.885(19)
Mo(1)	Mn(1)	S(1)	55.40(4)	Mo(1)	Mn(1)	S(1)	55.17(2)
Mo(1)	Mn(1)	S(2)	55.71(4)	Mo(1)	Mn(1)	S(2)	56.338(19)
S(1)	Mn(1)	S(2)	52.77(6)	S(1)	Mn(1)	S(2)	51.69(3)
S(1)	Mo(1)	S(2)	49.40(5)	S(1)	Mo(1)	S(2)	47.47(2)
S(1)	S(2)	Mn(1)	63.58(6)	S(1)	S(2)	Mn(1)	63.51(3)
S(1)	S(2)	Mo(1)	64.99(6)	S(1)	S(2)	Mo(1)	64.91(3)
S(2)	S(1)	Mn(1)	63.65(6)	S(2)	S(1)	Mn(1)	64.79(3)
S(2)	S(1)	Mo(1)	65.61(6)	S(2)	S(1)	Mo(1)	67.62(3)

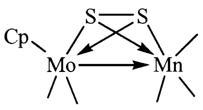
[a] Estimated standard deviations in the least significant figure are given in parentheses.

of the two compounds, see above. It is possible that the weakening of the metal−metal bond in **3** results in a stronger S−S bond. Both molecular orbitals would have the same symmetry and there should affect one another through orbital mixing.

The disulfido ligand can be viewed as a neutral six-electron donor to the metal atoms. In homodinuclear disulfido complexes, such as **1** and $Fe_2(CO)_6(\mu\text{-}S_2)$, each metal grouping contains 14 electrons and the electrons are donated symmetrically by the disulfido ligand, three to each metal atom. In **2** the two metal groupings contain unequal numbers of electrons, that is, the $CpMo(CO)_2$ group contains 15 electrons and $Mn(CO)_3$ group has only 13 electrons. In order to achieve an 18-electron configuration on each metal atom, the disulfido ligand in **2** donates four electrons to manganese metal atom and two electrons to molybdenum metal atom, see structure **A**. Alternatively, one could imagine an equal distribution of the disulfido electrons with formation of a heteropolar metal−metal bond, see structure **B**.



A



B

It is well-known that heterodinuclear metal complexes containing unsupported metal−metal bonds can be readily prepared by thermal and photochemical homolysis of the metal−metal bonds in mixtures of two homodinuclear metal complexes.[20] 17-Electron intermediates are presumably involved in some of these reactions. The fact that the yield of **2** is increased in the presence of room light suggests that photoactivated species are involved in this reaction too. This could imply that 17-electron intermediates or photodecarbonylated species are involved. We think that the latter is less likely because the yield of **3** was lower when $[Cp^*Mo(CO)_2]_2$ was used in the preparation in place of $[Cp^*Mo(CO)_3]_2$.

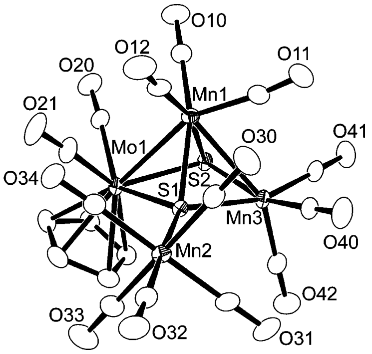


Figure 2. An ORTEP diagram of the molecular structure of $CpMoMn_3(CO)_{13}(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**4**) showing 50% probability thermal ellipsoids.

Table 3. Selected Intramolecular Bond Distances and Angles for $CpMoMn_3(CO)_{13}(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**4**)[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Mo(1)	Mn(1)	2.8280(6)	Mn(1)	S(2)	2.3195(9)
Mn(1)	Mn(3)	2.7379(7)	Mn(2)	S(1)	2.4132(9)
Mo(1)	S(1)	2.4836(8)	Mn(3)	S(1)	2.2936(9)
Mo(1)	S(2)	2.4569(9)	Mn(3)	S(2)	2.2675(10)
Mn(1)	S(1)	2.3054(9)	C	O	1.139(4) (av)

(b) Angles

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
S(1)	Mn(1)	S(2)	77.12(3)	S(1)	Mn(3)	Mn(1)	53.66(2)
S(1)	Mn(1)	Mn(3)	53.27(2)	S(2)	Mo(1)	S(1)	71.40(3)
S(2)	Mn(1)	Mn(3)	52.49(3)	S(2)	Mo(1)	Mn(1)	51.48(2)
S(1)	Mn(1)	Mo(1)	56.78(2)	S(1)	Mo(1)	Mn(1)	50.94(2)
S(2)	Mn(1)	Mo(1)	55.97(2)	Mn(3)	S(1)	Mn(1)	73.07(3)
Mn(3)	Mn(1)	Mo(1)	84.385(18)	Mn(3)	S(1)	Mn(2)	126.83(4)
S(2)	Mn(3)	S(1)	78.40(3)	Mn(1)	S(1)	Mn(2)	128.13(4)
S(2)	Mn(3)	Mn(1)	54.23(3)	Mn(3)	S(1)	Mo(1)	102.93(3)
Mn(1)	S(1)	Mo(1)	72.28(3)	Mn(2)	S(1)	Mo(1)	128.97(4)
Mn(3)	S(2)	Mn(1)	73.28(3)	Mn(3)	S(2)	Mo(1)	104.56(3)
Mn(1)	S(2)	Mo(1)	72.55(3)				

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

A second product, $CpMoMn_3(CO)_{13}(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**4**), was obtained (10% yield) from the reaction of **1** with $[CpMo(CO)_3]_2$. The reaction of **1** with $[Cp^*Mo(CO)_3]_2$ did not give the analogous compound but gave instead the known compound $Mn_4S_4(CO)_{15}$.[8,21] Compound **4** was characterized crystallographically. An ORTEP diagram of this molecule is shown in Figure 2, and selected bond distances and angles are listed in Table 3. This molecule contains four metal atoms: one molybdenum and three manganese. Three of the metal atoms, the one molybdenum and two of the manganese

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(20) (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. Eds.; Pergamon: Oxford, 1982; Chapter 40, p 778. (b) Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 2675. (c) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246.

(21) (a) Küllmer, V.; Rottinger, E.; Vahrenkamp, H. *Z. Naturforsch., B* **1979**, *34*, 224. (b) Küllmer, V.; Rottinger, E.; Vahrenkamp, H. *J. Chem. Soc., Chem. Commun.* **1977**, 782.

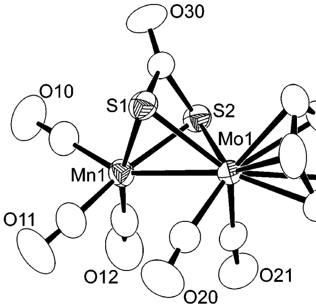
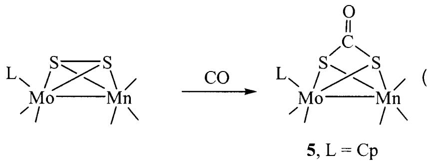


Figure 3. An ORTEP diagram of the molecular structure of CpMoMn(CO)$_5$[μ-SC(=O)S] (**5**) showing 50% probability thermal ellipsoids.

atoms, are assembled in a cluster that is bridged by two sulfido ligands. Sulfur S(2) is a triply bridging sulfido ligand. S(1) similarly bridges the three metal atoms of the cluster, but it is also bonded to a pendant Mn(CO)$_5$ group. This structural arrangement is not unusual. A number of years ago, Seyferth et al. reported the structurally similar iron−manganese compound Fe$_2$Mn$_2$(CO)$_{14}$(μ_3-S)(μ_4-S), which contains a sulfido ligand with a pendant Mn(CO)$_5$ group.[22]

The reactions of **2** and **3** with CO yielded the CO adducts Cp*MoMn(CO)$_5$(μ-SC(=O)S) (**5**) and Cp*MoMn(CO)$_5$(μ-SC(=O)S) (**6**) in 51% and 59% yields, respectively, at room temperature/1 atm of CO. Compounds **5** and **6** were characterized by a combination of IR, ^{1}H NMR, and ^{13}C NMR and by single-crystal X-ray diffraction analyses. The infrared spectra of **5** and **6** in the terminal CO ligand region are similar to those of **2** and **3**, but they also exhibit a low-energy absorption band at 1741 and 1735 cm^{-1}, which can be attributed to the CO group in the dithiocarbonato ligand. An ORTEP diagram of the molecular structure of **5** is shown in Figure 3. Compound **6** is structurally similar. Selected bond distances and angles for both compounds are listed in Table 4. Compound **5** contains two independent molecules in the asymmetric crystal unit. In the solid state, the molecular structure of **6** contains a crystallographically imposed reflection plane passing through the molybdenum and manganese atoms and the CO group of the dithiocarbonato ligand. The structures of **5** and **6** are similar to those of **2** and **3** except for the presence of a CO group between the two sulfur atoms. The S$_2$CO group is a dithiocarbonato ligand formed formally by the insertion of CO into the S−S bond, eq 6. The C−O distance in the dithiocarbonato ligand is short, 1.184(6) [1.173(6)] Å for **5** and 1.181(5) Å for **6**, and indicative of CO multiple bonding. The manganese and molybdenum metal atoms are mutually bonded, Mo−Mn = 2.7419(9) [2.7485(9)] Å for **5** and 2.7248(5) Å for **6**, and both distances are significantly shorter than those in **2** and **3**, 2.8421(10) and 2.8914(5) Å. The two sulfur atoms are not mutually bonded (S···S = 2.795(4) and 2.801(4) Å for **5** and 2.7999(12) Å for **6**). This again suggests a correlation, as noted and explained above for the differences between **2** and **3**, that longer sulfur−sulfur distances correlate with shorter metal−metal distances. A similar effect was observed for the two related iron compounds, Fe$_2$(CO)$_6$(μ-S$_2$), Fe−Fe = 2.552(2)[15] and 2.555(1) Å,[16] and Fe$_2$(CO)$_6$(μ-SC(O)S), Fe−Fe = 2.4875(9) Å.[17] The latter also contains a dithiocarbonato ligand. Both sulfur atoms of the dithiocarbonato ligand in **5** and **6** are bonded to both metal atoms, and the Mn−S distances, 2.3343(15), 2.3466(15), 2.3278(15), and 2.3467(15) Å, are significantly shorter than the Mo−S distances, 2.4580(13), 2.4696(16), 2.4702(15), and 2.4703(14) Å for **5**, and Mo(1)−S(1) = 2.4693(6) Å and Mn(1)−S(1) = 2.3429(7) Å for **6**.



(6)

5, L = Cp
6, L = Cp*

Table 4. Selected Intramolecular Distances and Angles for CpMoMn(CO)$_5$[μ-Sc(=O)S] (**5**) and Cp*MoMn(CO)$_5$[μ-Sc(=O)S] (**6**)[a]

(a) Distances

5			**6**		
atom	atom	distance (Å)	atom	atom	distance (Å)
Mn(1)	Mo(1)	2.7419(9)	Mn(1)	Mo(1)	2.7248(5)
Mn(2)	Mo(2)	2.7485(9)	Mn(1)	S(1)	2.3429(7)
Mn(1)	S(1)	2.3343(15)	Mo(1)	S(1)	2.4693(6)
Mn(1)	S(2)	2.3466(15)	S(1)	C(30)	1.791(2)
Mn(2)	S(3)	2.3278(15)	C(30)	O(30)	1.181(5)
Mn(2)	S(4)	2.3467(15)	S(1)	S(1*)	2.7999(12)
Mo(1)	S(1)	2.4580(13)			
Mo(1)	S(2)	2.4696(16)			
Mo(2)	S(4)	2.4702(15)			
Mo(2)	S(3)	2.4703(14)			
S(1)	C(30)	1.798(6)			
S(2)	C(30)	1.799(5)			
S(3)	C(60)	1.808(6)			
S(4)	C(60)	1.788(6)			
C(30)	O(30)	1.184(6)			
C(60)	O(60)	1.173(6)			
S(1)	S(2)	2.795(4)			
S(3)	S(4)	2.801(4)			

(b) Angles

5				**6**			
atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Mn(1)	S(1)	Mo(1)	69.75(4)	Mn(1)	S(1)	Mo(1)	68.918(18)
Mn(1)	S(2)	Mo(1)	69.35(4)	Mn(1)	Mo(1)	S(1)	53.350(16)
Mn(1)	Mo(1)	S(1)	53.01(4)	Mo(1)	Mn(1)	S(1)	57.732(18)
Mn(1)	Mo(1)	S(2)	53.21(4)	S(1)	Mn(1)	S(1*)	73.38(3)
Mo(1)	Mn(1)	S(1)	57.25(4)	S(1)	Mo(1)	S(1*)	69.08(3)
Mo(1)	Mn(1)	S(2)	57.44(4)	S(1)	C(12)	S(1*)	102.83(17)
S(1)	Mn(1)	S(2)	73.32(5)				
S(1)	Mo(1)	S(2)	69.10(5)				
S(1)	C(30)	S(2)	101.9(3)				
Mn(2)	S(3)	Mo(2)	69.83(4)				
Mn(2)	S(4)	Mo(2)	69.53(4)				
Mn(2)	Mo(2)	S(3)	52.65(4)				
Mn(2)	Mo(2)	S(4)	53.12(4)				
Mo(2)	Mn(2)	S(3)	57.52(4)				
Mo(2)	Mn(2)	S(4)	57.35(4)				
S(3)	Mn(2)	S(4)	73.62(5)				
S(3)	Mo(2)	S(4)	69.07(5)				
S(3)	C(60)	S(4)	102.3(3)				

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

In order to obtain some information about the mechanism of insertion of the CO into the S−S bond, we performed the reactions of **2** and **3** with ^{13}CO. This yielded the compound

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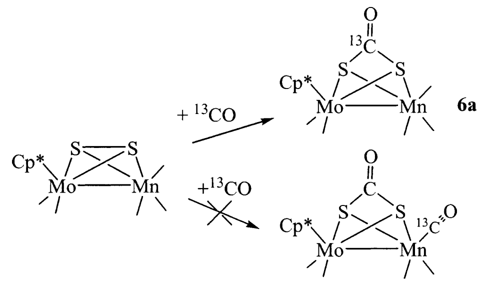
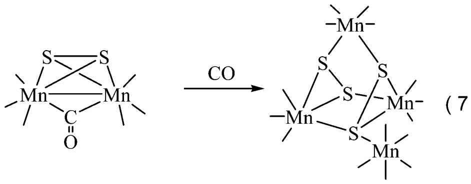
(22) Seyferth, D.; Henderson, R. S.; Fackler, J. P., Jr.; Mazany, A. M. *J. Organomet. Chem.* **1981**, *213*, C21.

Scheme 1



CpMoMn(CO)$_5$(μ-S^{13}C(═O)S) (**5a**) and Cp*MoMn(CO)$_5$(μ-S^{13}C(═O)S) (**6a**) with apparently 100% incorporation of ^{13}CO into the dithiocarbonato ligand. In support of this, the IR frequency of the dithiocarbonato carbonyl band was reduced from 1741 to 1686 cm^{-1} and from 1735 to 1694 cm^{-1} as expected for such an isotopic substitution. The low-temperature ^{13}C NMR spectra of **5a** and **6a** show intense resonances at 176.7 and 177.3 ppm, which can be assigned to ^{13}C-labeled CO in the dithiocarbonato ligand. There was no significant enhancement of the intensities of the CO ligands, suggesting no significant incorporation of ^{13}CO in these positions. On the basis of this data, we can safely conclude that the formation of **5** and **6** is a result of insertion of an unbound molecule of CO directly into the S−S bond of **2** and **3** without prior coordination to a metal atom, see Scheme 1. Interestingly, the reaction of **1** with CO does not give CO insertion into the S−S bond, but yields instead the bis(disulfido)tetramanganese complex Mn$_4$(CO)$_{15}$(μ_3-S$_2$)(μ_4-S$_2$) by an aggregation process involving cleavage of the manganese−manganese bonds, eq 7.[8,9]



(7)

Similarly, we found that like CO, compounds **2** and **3** also react readily with *tert*-butylisocyanide at room temperature by insertion of the isocyanide into the S−S bond to yield the new compounds CpMoMn(CO)$_5$[μ-S(CN═Bu^t)S] (**7**) and Cp*MoMn(CO)$_5$[μ-S(C═NBu^t)S] (**8**) in 33% and 36% yields, respectively. Both compounds show a low-energy absorption at 1684 and 1675 cm^{-1}, respectively, that we attribute to the C═N stretching vibration of the C═N function in the S(C═NBu^t)S ligand. Compound **7** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 4. Selected bond distances and angles are listed in Table 5. There is nothing unusual about the structure of this molecule. The Mo−Mn bond distance 2.7566(5) Å is very similar to that in **5**, and the C(6)−N(1) bond distance of 1.234(3) Å is typical of a C−N double bond and the nitrogen atom is nonlinear, C(6)−N(1)−C(50) = 124.34(19)°.

The facile insertions of CO and CNBu^t into the S−S bond of **2** and **3** prompted us to investigate their reactions with ethylene and dimethylacetylene dicarboxylate (DMAD).

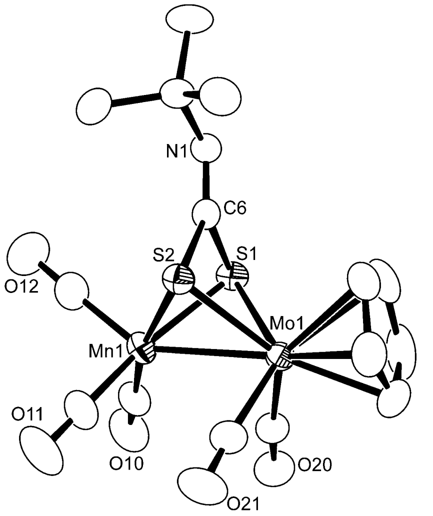


Figure 4. An ORTEP diagram of the molecular structure of CpMoMn(CO)$_5$[μ-S(N═Bu^t)S] (**7**) showing 40% probability thermal ellipsoids.

Table 5. Selected Intramolecular Bond Distances and Angles for CpMoMn(CO)$_5$[μ-S(C═NBu^t)S] (**7**)[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Mn(1)	S(1)	2.3270(7)	S(1)	C(6)	1.808(2)
Mn(1)	S(2)	2.3308(7)	S(2)	C(6)	1.826(2)
Mn(1)	Mo(1)	2.7566(5)	N(1)	C(6)	1.234(3)
Mo(1)	S(1)	2.4613(6)	N(1)	C(50)	1.487(3)
Mo(1)	S(2)	2.4708(6)	C	O	1.138(3) (av)

(b) Angles

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
S(1)	Mn(1)	S(2)	72.91(2)	C(6)	S(1)	Mn(1)	85.57(7)
S(1)	Mn(1)	Mo(1)	57.167(17)	C(6)	S(1)	Mo(1)	87.67(7)
S(2)	Mn(1)	Mo(1)	57.383(17)	C(6)	S(2)	Mn(1)	85.06(7)
S(1)	Mo(1)	S(2)	68.274(19)	C(6)	S(2)	Mo(1)	86.99(7)
S(1)	Mo(1)	Mn(1)	52.600(17)	Mn(1)	S(2)	Mo(1)	70.003(19)
S(2)	Mo(1)	Mn(1)	52.614(16)	C(6)	N(1)	C(50)	124.34(19)
Mn(1)	S(1)	Mo(1)	70.233(19)	N(1)	C(50)	C(51)	108.7(2)
N(1)	C(6)	S(1)	125.23(17)	N(1)	C(50)	C(52)	105.74(19)
N(1)	C(6)	S(2)	135.51(18)	N(1)	C(50)	C(53)	110.8(2)
S(1)	C(6)	S(2)	99.20(11)				

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

When solutions of **2** and **3** were exposed to ethylene at 25 °C for 24 h, the ethylene adducts CpMoMn(CO)$_5$(μ-SCH$_2$CH$_2$S) (**9**) and Cp*MoMn(CO)$_5$(μ-SCH$_2$CH$_2$S) (**10**) were obtained in 16% and 52% yields, respectively. Both compounds were characterized by a combination of IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. The ^{1}H NMR spectra of **9** and **10** show two multiplets due to the inequivalent hydrogen atoms on the methylene groups. An ORTEP diagram of the molecular structure of **9** is shown in Figure 5. Compound **10** is structurally similar. Selected bond distances and angles for both compounds are listed in Table 6. Compound **9** contains two crystallographically independent molecules in the asymmetric crystal unit, and both molecules are structurally similar. Compounds **9** and **10** are both structurally similar to compounds **5** and **6** with the exception that they contain an ethylene group between the two sulfur atoms instead of a CO group. The Mo−Mn distances 2.7613(9) [2.7655(9)] Å for **9** and 2.7406(3) Å for **10** are similar

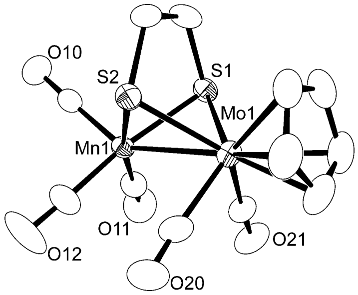


Figure 5. An ORTEP diagram of the molecular structure of CpMoMn(CO)$_5$(μ-SCH$_2$CH$_2$S) (**9**) showing 50% probability thermal ellipsoids.

Table 6. Selected Intramolecular Distances and Angles for CpMoMn(CO)$_5$(μ-SCH$_2$CH$_2$S) (**9**) and Cp*MoMn(CO)$_5$(μ-SCH$_2$CH$_2$S) (**10**)[a]

(a) Distances

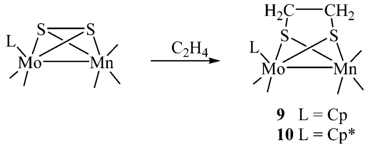
9			10		
atom	atom	distance (Å)	atom	atom	distance (Å)
Mn(1)	Mo(1)	2.7613(9)	Mn(1)	Mo(1)	2.7496(3)
Mn(2)	Mo(2)	2.7655(9)	Mn(1)	S(1)	2.3194(5)
Mn(1)	S(1)	2.2905(11)	Mn(1)	S(2)	2.3210(5)
Mn(1)	S(2)	2.3007(11)	Mo(1)	S(1)	2.4687(4)
Mn(2)	S(3)	2.3003(11)	Mo(1)	S(2)	2.4663(4)
Mn(2)	S(4)	2.3030(13)	C(6)	C(7)	1.494(3)
Mo(1)	S(1)	2.4568(11)	S(1)	S(2)	2.9539(6)
Mo(1)	S(2)	2.4573(11)			
Mo(2)	S(3)	2.4580(11)			
Mo(2)	S(4)	2.4564(12)			
C(6)	C(7)	1.503(6)			
C(55)	C(56)	1.512(6)			
S(1)	S(2)	2.959(4)			
S(3)	S(4)	2.922(4)			

(b) Angles

9				10			
atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Mn(1)	S(1)	Mo(1)	71.04(4)	Mn(1)	S(1)	Mo(1)	70.015(13)
Mn(1)	S(2)	Mo(1)	70.86(3)	Mn(1)	S(2)	Mo(1)	70.033(14)
Mn(1)	Mo(1)	S(1)	51.67(3)	Mn(1)	Mo(1)	S(1)	52.444(12)
Mn(1)	Mo(1)	S(2)	51.92(3)	Mn(1)	Mo(1)	S(2)	52.503(12)
Mo(1)	Mn(1)	S(1)	57.29(3)	Mo(1)	Mn(1)	S(1)	57.541(12)
Mo(1)	Mn(1)	S(2)	57.22(3)	Mo(1)	Mn(1)	S(2)	57.464(12)
S(1)	Mn(1)	S(2)	79.94(4))	S(1)	Mn(1)	S(2)	79.070(17)
S(1)	Mo(1)	S(2)	73.76(4)	S(1)	Mo(1)	S(2)	73.533(14)
C(6)	S(1)	Mn(1)	103.13(15)	C(6)	S(1)	Mn(1)	102.39(8)
C(6)	S(1)	Mo(1)	104.54(16)	C(6)	S(1)	Mo(1)	106.41(8)
C(7)	S(2)	Mn(1)	103.02(13)	C(7)	S(2)	Mn(1)	103.23(7)
C(7)	S(2)	Mo(1)	104.18(15)	C(7)	S(2)	Mo(1)	105.13(7)
Mn(2)	S(3)	Mo(2)	70.98(3)				
Mn(2)	S(4)	Mo(2)	70.97(4)				
Mn(2)	Mo(2)	S(3)	51.85(3)				
Mn(2)	Mo(2)	S(4)	51.93(3)				
Mo(2)	Mn(2)	S(3)	57.17(3)				
Mo(2)	Mn(2)	S(4)	57.10(4)				
S(3)	Mn(2)	S(4)	73.67(4)				
C(55)	S(3)	Mn(2)	103.85(15)				
C(55)	S(3)	Mo(2)	104.36(16)				
C(56)	S(4)	Mn(2)	103.78(16)				
C(56)	S(4)	Mo(2)	103.76(16)				

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

to those found in **5**−**7**, but significantly shorter than those found in **2** and **3**. The sulfur atoms are not mutually bonded, S(1)···S(2) = 2.959(4) Å, S(3)···S(4) = 2.922(4) Å for **9** and S(1)···S(2) = 2.9539(6) Å for **10**. These distances are only slightly shorter than the S···S distance found for the ethanedithiolato ligand in Mn$_2$(CO)$_7$(μ-SCH$_2$CH$_2$S), S···S = 2.9673(11) Å.[23]



Metal complexes containing ethanedithiolato ligands are conveniently obtained from reactions involving ethanedithiol[24] and 1,2,5,6-tetrathiacyclooctane.[23,25,26] Rakowski-Dubois has also shown that alkanedithiolato complexes can be obtained from the reaction of alkenes to sulfido ligands in certain dimolybdenum complexes,[27] and ethylene can be inserted into the S−S bond of Fe$_2$(CO)$_6$(μ-S$_2$) in the presence of UV−vis irradiation to yield Fe$_2$(CO)$_6$(μ-SCH$_2$CH$_2$S).[6c] Interestingly, compound **1** does not react with ethylene even under forcing conditions. The ethanedithiolato ligand bridged dimanganese complex is, however, stable and was obtained from the reaction of **1** with 1,2,5,6-tetrathiacyclooctane.[23]

The reaction of dimethylacetylene dicarboxylate (DMAD) with **2** and **3** provided the new compounds CpMoMn(CO)$_5$[μ-SC(CO$_2$Me)=C(CO$_2$Me)S] (**11**) and Cp*MoMn(CO)$_5$[μ-SC(CO$_2$Me)=C(CO$_2$Me)S] (**12**) in 42% and 43% yields, respectively. The infrared spectra of **11** and **12** both exhibit a low-energy absorption band at 1715 and 1734 cm^{-1} that is attributed to carbonyl of the CO$_2$Me groups. The ^{1}H NMR spectra of **11** and **12** both show two singlets: 3.76 ppm for **11** and 3.70 ppm for **12** for the CO$_2$Me protons and 6.07 and 2.10 ppm for the Cp and Cp* ligands. Both compounds were characterized by single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **11** is shown in Figure 6. Compound **12** is structurally similar. Selected bond distances and angles for both compounds are listed in Table 7. Compounds **11** and **12** are structurally similar to **9** and **10** except that they contain a (MeO$_2$C)C=C(CO$_2$Me) group inserted between the sulfur atoms instead of a CH$_2$CH$_2$ group. The Mo−Mn distances in **11** and **12**, 2.7130(17) and 2.7003(4) Å, respectively, are slightly shorter than those in **9** and **10**. This may be due to the electron-withdrawing character of the (MeO$_2$C)C=C(CO$_2$Me) group. The distance between the carbon atoms C(43) and C(44), 1.315(14) and 1.321(3) Å for **11** and **12**, is typical of a carbon−carbon double bond.

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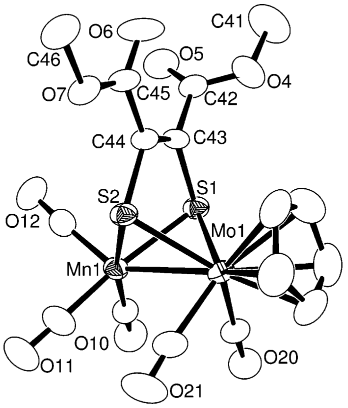

Figure 6. An ORTEP diagram of the molecular structure of $CpMoMn(CO)_5[\mu\text{-}SC(CO_2Me){=}C(CO_2Me)S]$ (**11**) showing 40% probability thermal ellipsoids.

Table 7. Selected Intramolecular Distances and Angles for $CpMoMn(CO)_5(\mu\text{-}SC(CO_2Me){\equiv}C(CO_2Me)S)$ (**11**) and for $Cp^*MoMn(CO)_5(\mu\text{-}SC(CO_2Me){\equiv}C(CO_2Me)S)$ (**12**)[a]

(a) Distances

11			**12**		
atom	atom	distance (Å)	atom	atom	distance (Å)
Mn(1)	Mo(1)	2.7130(17)	Mn(1)	Mo(1)	2.7003(4)
Mn(1)	S(1)	2.331(3)	Mn(1)	S(1)	2.3526(7)
Mn(1)	S(2)	2.324(3)	Mn(1)	S(2)	2.3757(7)
Mo(1)	S(1)	2.482(3)	Mo(1)	S(1)	2.4841(6)
Mo(1)	S(2)	2.468(2)	Mo(1)	S(2)	2.4978(6)
S(1)	C(43)	1.784(9)	S(1)	C(43)	1.798(2)
S(2)	C(44)	1.791(10)	S(2)	C(44)	1.784(2)
C(43)	C(44)	1.315(14)	C(43)	C(44)	1.321(3)

(b) Angles

11				**12**			
atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Mn(1)	S(1)	Mo(1)	68.54(8)	Mn(1)	S(1)	Mo(1)	67.813(17)
Mn(1)	S(2)	Mo(1)	68.88(7)	Mn(1)	S(2)	Mo(1)	67.239(18)
Mn(1)	Mo(1)	S(1)	53.08(7)	Mn(1)	Mo(1)	S(1)	53.777(16)
Mn(1)	Mo(1)	S(2)	53.06(6)	Mn(1)	Mo(1)	S(2)	54.222(16)
Mo(1)	Mn(1)	S(1)	58.38(7)	Mo(1)	Mn(1)	S(1)	58.410(17)
Mo(1)	Mn(1)	S(2)	58.06(7)	Mo(1)	Mn(1)	S(2)	58.539(16)
S(1)	Mn(1)	S(2)	79.80(9)	S(1)	Mn(1)	S(2)	79.06(2)
S(1)	Mo(1)	S(2)	74.20(8)	S(1)	Mo(1)	S(2)	74.324(19)
C(43)	S(1)	Mn(1)	101.2(3)	C(43)	S(1)	Mn(1)	100.56(7)
C(43)	S(1)	Mo(1)	100.1(3)	C(43)	S(1)	Mo(1)	102.65(7)
C(44)	S(2)	Mn(1)	101.7(3)	C(44)	S(2)	Mn(1)	99.99(8)
C(44)	S(2)	Mo(1)	100.1(3)	C(44)	S(2)	Mo(1)	101.94(7)

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

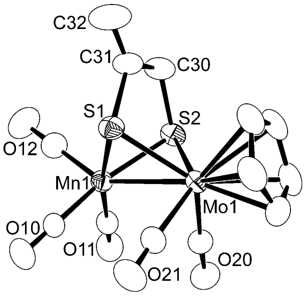

Figure 7. An ORTEP diagram of the molecular structure of $CpMoMn(CO)_5[\mu\text{-}SCH_2C({=}CH_2)S]$ (**13**) showing 40% probability thermal ellipsoids.

Table 8. Selected Intramolecular Bond Distances and Angles for $CpMoMn(CO)_5[\mu\text{-}SCH_2C({=}CH_2)S]$ (**13**)[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Mn(1)	S(1)	2.3120(12)	S(1)	C(31)	1.789(5)
Mn(1)	S(2)	2.3055(13)	S(2)	C(30)	1.821(5)
Mn(1)	Mo(1)	2.7539(7)	S(3)	C(71)	1.767(5)
Mn(2)	S(3)	2.3046(12)	S(4)	C(70)	1.816(5)
Mn(2)	S(4)	2.3057(13)	C(30)	C(31)	1.485(7)
Mn(2)	Mo(2)	2.7604(7)	C(31)	C(32)	1.289(7)
Mo(1)	S(1)	2.4685(12)	C(70)	C(71)	1.469(7)
Mo(1)	S(2)	2.4618(11)	C(71)	C(72)	1.312(7)
Mo(2)	S(3)	2.4600(11)	C	O	1.138(6) (av)
Mo(2)	S(4)	2.4633(12)			

(b) Angles

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
S(2)	Mn(1)	S(1)	80.03(4)	S(3)	Mo(2)	Mn(2)	52.01(3)
S(2)	Mn(1)	Mo(1)	57.42(3)	C(31)	S(1)	Mn(1)	102.71(16)
S(1)	Mn(1)	Mo(1)	57.53(3)	C(31)	S(1)	Mo(1)	102.88(18)
S(3)	Mn(2)	S(4)	79.53(4)	Mn(1)	S(1)	Mo(1)	70.26(3)
S(3)	Mn(2)	Mo(2)	57.27(3)	C(30)	S(2)	Mn(1)	103.78(18)
S(4)	Mn(2)	Mo(2)	57.34(3)	C(30)	S(2)	Mo(1)	102.72(17)
S(1)	Mo(1)	S(2)	74.06(4)	Mn(1)	S(2)	Mo(1)	70.48(3)
S(1)	Mo(1)	Mn(1)	52.20(3)	C(71)	S(3)	Mn(2)	101.10(17)
S(2)	Mo(1)	Mn(1)	52.10(3)	C(71)	S(3)	Mo(2)	104.56(16)
S(4)	Mo(2)	S(3)	73.60(4)	Mn(2)	S(3)	Mo(2)	70.73(3)
S(4)	Mo(2)	Mn(2)	52.01(3)	Mn(2)	S(4)	Mo(2)	70.65(3)
C(70)	S(4)	Mn(2)	103.31(18)	C(70)	S(4)	Mo(2)	103.33(18)
C(31)	C(30)	S(2)	112.7(3)	C(71)	C(70)	S(4)	111.8(3)
C(32)	C(31)	C(30)	124.7(5)	C(72)	C(71)	C(70)	122.3(5)
C(32)	C(31)	S(1)	119.5(5)	C(72)	C(71)	S(3)	120.6(5)
C(30)	C(31)	S(1)	115.8(3)	C(70)	C(71)	S(3)	116.8(3)

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

Finally, we investigated the reaction of allene, $CH_2{=}C{=}CH_2$, with **2**. This reaction yielded the new compound $CpMoMn(CO)_5[\mu\text{-}SCH_2C({=}CH_2)S]$ (**13**) in 12% yield. Compound **13** was also characterized by single-crystal X-ray diffraction analysis. The crystal contains two symmetry independent formula equivalents in the asymmetric unit. Both molecules are structurally similar, and an ORTEP diagram of the molecular structure of one of these molecules is shown in Figure 7. Selected bond distances and angles are listed in Table 8. The molecule contains a $CpMoMn(CO)_5S_2$ core that is analogous to that of the compounds **5**−**12**, but contains instead a $CH_2{=}C{=}CH_2$ group inserted between the two sulfur atoms. The Mo−Mn distance in **13** is similar to that found in **9** and **10**, 2.7539(7) [2.7604(7)] Å. The compound was formed by a 1,2-insertion of the allene into the sulfur−sulfur bond of **2**. The C−C distance between the two carbon atoms bonded to the sulfur atoms is approaching that of a single bond, 1.485(7) [1.469(7)] Å, while the C−C distance to the *exo*-methylene group, 1.289(7) [1.312(7)] Å, is typical of a double bond as expected. The values are similar to those observed for similar ligands in the compounds $Fe_2(CO)_6[\mu\text{-}SCMe_2C({=}CMe_2)S]$, 1.519(4) and 1.338(4) Å,[28] and $[(CpMo)_2(\mu\text{-}S_2CH_2)SC({=}CH_2)(CH_2SC(CH_3)({=}CH_2)](SO_3F)$, 1.464(39) and 1.371(47) Å.[29] The latter compound was formed by the addition of 2 equiv of allene to the compound $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)](SO_3F)$. All four protons on the bridging $SCH_2C({=}CH_2)S$ group in **13** are inequivalent, and the ^1H NMR spectrum shows four mul-

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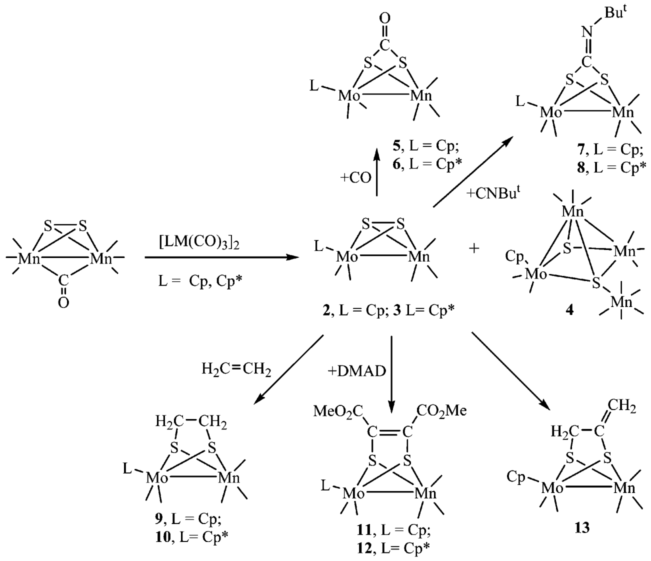
Scheme 2



tiplets at 3.06 (1H) ppm, 3.00 (1H) ppm, 2.10 (1H) ppm, and 2.64 (1H) ppm, in addition to the singlet at 5.47 (s, 5H) ppm due to the Cp ligand, which is consistent with this.

A summary of the reactions investigated in this study is shown in Scheme 2. The reactions of **1** with [CpMo(CO)$_3$]$_2$ and [Cp*Mo(CO)$_3$]$_2$ have yielded the new heterobinuclear disulfides **2** and **3**. The disulfido ligand in both of these compounds is very active toward the addition of unsaturated small molecules by insertion into the S−S bond at room temperature. It is anticipated that compounds **2** and **3** will both react with a variety of metal complexes to yield new heteronuclear cluster complexes. These studies are in progress and will be reported in the near future.

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere using Schlenk techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo-Nicolet Avatar FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 300 MHz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). [Cp*Mo(CO)$_2$]$_2$ (Cp* = C$_5$Me$_5$) and [CpMo(CO)$_3$]$_2$ were purchased from Strem. [Cp*Mo(CO)$_3$]$_2$[13] and Mn$_2$S$_2$(CO)$_6$(μ-S$_2$)[8,9] (**1**) were prepared according to the published procedures. Unless stated otherwise, all product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

Reaction of Mn$_2$(CO)$_7$(μ-S$_2$) with [CpMo(CO)$_3$]$_2$. A sample of [CpMo(CO)$_3$]$_2$ (79 mg, 0.161 mmol, 0.6 equiv) was dissolved in 30 mL of benzene in a 100 mL three-neck round-bottom flask equipped with a stir bar, gas inlet, and gas outlet. To this solution was added 100 mg (0.27 mmol) of **1**. The solution was stirred at room temperature for 24 h. The volatiles were removed in vacuo, and the residue was separated by column chromatography over silica gel by using a hexane/CH$_2$Cl$_2$ (2/1, v/v) solvent mixture as eluant. Orange CpMoMn(CO)$_5$(μ-S$_2$) **(2) (**30 mg; 26%, based on consumed **1**) and 21 mg of red CpMoMn$_3$(μ_3-S)(μ_4-S)(CO)$_{13}$ (**4**) (10% yield) were obtained in order of elution. Spectral data for **2**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$) 2026 (vs), 1981 (m), 1938 (s), 1915 (m); ^{1}H NMR (δ in CDCl$_3$) 5.60 (s, 5H); ^{13}C NMR (δ in CH$_2$Cl$_2$, −40 °C) 231 (MoCO), 224 (MnCO), 93 (Cp). Anal. Calcd: C, 28.59; H, 1.20. Found: C, 28.72; H, 1.05. Spectral data for **4**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$) 2134 (m), 2087 (vw), 2056 (s), 2047 (m), 2026 (s), 1997 (vs), 1973 (m), 1949 (m), 1923 (m); ^{1}H NMR (δ in CDCl$_3$) 5.62 (s, 5H). Anal. Calcd: C, 28.67; H, 0.67. Found: C, 28.93; H, 0.65. Compound **3** was obtained similarly in 26% yield (based on consumed **1**) from the reaction of **1** with [Cp*Mo(CO)$_3$]$_2$. This reaction also produced 23% yield of the known compound Mn$_4$S$_4$(CO)$_{15}$.[8,21] Spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane) 2026 (vs), 1974 (m), 1940 (s), 1925 (m); ^{1}H NMR (δ in CDCl$_3$) 1.97 (s, 15H); ^{13}C NMR (δ in CD$_2$Cl$_2$ at −40 °C) 234.7 (2 CO), 225 (2 CO, br), 223 (1 CO, br), 106.4 (Cp*), 11.1 (CH$_3$). Anal. Calcd: C, 37.02; H, 3.08. Found: C, 36.75; H, 2.91.

Reaction of 1 with [Cp*Mo(CO)$_2$]$_2$ under CO. A sample of [Cp*Mo(CO)$_2$]$_2$ (35 mg, 0.060 mmol) was dissolved in 20 mL of benzene in a 50 mL three-neck round-bottom flask equipped with a stir bar, gas inlet, and gas outlet. This solution was purged with CO for 1 min. **1** (15 mg, 0.040 mmol) was added to this solution, and the resulting solution was stirred at 30 °C for 20 h. The volatiles were removed in vacuo, and the residue was separated by column chromatography over silica gel by using a hexane/CH$_2$Cl$_2$ (2/1, v/v) solvent mixture as eluant. **3** (4.6 mg) was isolated in 23% yield (based on consumed **1**) as orange crystals.

Addition of CO to 2 and 3. A sample of **2** (9.4 mg, 0.0224 mmol) was dissolved in 20 mL of distilled benzene in a 50 mL three-neck round-bottom flask equipped with a stir bar, gas inlet, and gas outlet. CO gas was bubbled thorough this solution for 20 min, and it was then stirred at room temperature for 24 h under a CO atmosphere. After stirring, the solvent was removed in vacuo and the residue was separated by TLC using a hexane/CH$_2$Cl$_2$ (3/1, v/v) solvent mixture. Unreacted **2** (2.0 mg) and 5.1 mg of orange CpMoMn(CO)$_5$[μ-S(C═O)S] (**5**) (51% yield) were obtained in order of elution. Spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane) 2040 (vs), 1996 (m), 1968 (s), 1943 (m), 1741 (vs); ^{1}H NMR (δ in CDCl$_3$) 5.7 (s, 5H). Anal. Calcd: C, 29.48; H, 1.12. Found: C, 29.29; H, 0.96. When the reaction was performed using CO (enriched 99% with ^{13}CO), the product, CpMoMn(CO)$_5$[μ-S(^{13}C═O)S] (**5a),** was obtained in 47% yield. Spectral data for **5a**: IR νCO (cm^{-1} in CH$_2$Cl$_2$) 2037 (vs), 1993 (m), 1963 (s), 1931 (m), 1686 (w); ^{13}C NMR (δ in CH$_2$Cl$_2$, −40 °C) 232.2 (Mo−CO), 223.3 (Mn−CO), 221.7 (Mn−CO), 176.7 (S$_2$^{13}CO), 93.8 (Cp).

Compound **6** was obtained similarly in 59% yield from the reaction of **3** with CO at room temperature. Spectral data for **6**: IR ν_{CO} (cm^{-1} in hexane) 2033 (vs), 1983 (m), 1956 (s), 1937 (m), 1735 (m); ^{1}H NMR (δ in CDCl$_3$) 1.99 (s, 15H). Anal. Calcd: C, 37.08; H, 2.91. Found: C, 36.87; H, 2.88. When the reaction was performed using CO (enriched 99% with ^{13}CO), the orange product, Cp*MoMn(CO)$_5$[μ-S(^{13}C═O)S] (**6a),** was obtained in 49% yield. Spectral data for **6a**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$) 2037 (vs), 1993 (m), 1963 (s), 1931 (m), 1694 (w); ^{13}C NMR (δ in CD$_2$Cl$_2$ at −40 °C) 235.8 (2 CO), 224.3 (2 CO), 221.6 (1 CO), 177.3 (S$_2$^{13}CO), 106.8 (Cp*), 10.9 (CH$_3$).

Reactions of 2 and 3 with CN^{t}Bu. CN^{t}Bu (3.0 μL) was added to a solution of of **2** (10.0 mg, 0.0238 mmol) in 20 mL of CH$_2$Cl$_2$, and the solution was stirred for 24 h at room temperature. The solvent was then removed in vacuo, and the residue was separated by TLC on silica gel by using a 2/1 hexane/CH$_2$Cl$_2$ solvent mixture to yield 4.0 mg of unreacted **2** and 4.0 mg of orange of CpMoMn-(CO)$_5$[μ-S(CN═Bu^t)S] (**7**), 33% yield. Spectral data for **7**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$) 2029 (vs), 1986 (m), 1951 (s), 1922 (m), 1859 (vw), 1684 (vw, br); ^{1}H NMR (δ in CDCl$_3$) 5.78 (s, 5H), 1.33 (s, 9H). Anal. Calcd for C$_{15}$H$_{14}$MnMoNO$_5$S$_2$: C, 35.80; H, 2.80; N, 2.78. Found: C, 36.18; H, 3.08; N, 3.16.

The orange compound Cp*MoMn(CO)$_5$[μ-S(CNBu^t)S] (**8**) was prepared similarly in 36% yield from reaction of **3** with *tert*-butylisocyanide. Spectral data for **8**: IR ν_{CO} (cm^{-1} in hexane) 2027 (vs), 1976 (m), 1948 (s), 1928 (m), 1675 (vw, br); ^{1}H NMR (δ in CDCl$_3$) 2.05 (s, 15H), 1.34 (s, 9H). Anal. Calcd: C, 41.89; H, 4.22; N, 2.44. Found: C, 42.13; H, 4.23; N, 2.42.

Addition of Ethylene to 2 and 3. A solution of **2** (6.0 mg, 0.015 mmol) in benzene (20 mL) was stirred under ethylene atmosphere at room temperature for 24 h. The solvent was then removed in vacuo, and the residue was separated by TLC on silica gel using a 3/1 hexane/CH$_2$Cl$_2$ solvent mixture to yield 0.7 mg (12%) of unreacted CpMoMn(CO)$_5$(μ-S$_2$) and 1.0 mg (16%) of orange CpMoMn(CO)$_5$(μ-SCH$_2$CH$_2$S) (**9**). Spectral data for **9**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$) 2024 (vs), 1979 (m), 1946 (s), 1907 (m), 1712 (w); ^{1}H NMR (δ in CDCl$_3$) 5.47 (s, 5H), 2.48−2.44 (m, 2H), 2.07−2.03 (m, 2H). Anal. Calcd for $C_{12}H_9MnMoO_5S_2$: C, 32.16; H, 2.02. Found: C, 32.37; H, 1.96.

The orange compound **10** was prepared similarly in 52% yield from the reactions of **3** with ethylene. Spectral data for **10**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$) 2029 (vs), 1980 (m), 1948 (s), 1936 (m), 1734 (w); ^{1}H NMR (δ in CDCl$_3$) 2.29 (m, 2H), 2.02 (m, 2H), 1.96 (s, 15H). Anal. Calcd: C, 39.39; H, 3.70. Found: C, 39.61; H, 3.49.

Reaction of 2 and 3 with Dimethylacetylene Dicarboxylate (DMAD). To a solution of **2** (18.0 mg, 0.043 mmol) in CH$_2$Cl$_2$ (20 mL) was added 8.0 μL of dimethylacetylene dicarboxylate. The resulting solution was stirred at room temperature for 24 h. The solvent was then removed in vacuo, and the residue was separated by TLC on silica gel using a 2/1 hexane/CH$_2$Cl$_2$ solvent mixture to yield 2.6 mg of unreacted **2** and 10.2 mg of orange CpMoMn(CO)$_5$(μ-S(MeO$_2$C)CC(CO$_2$Me)S) (**11**) (42% yield). Spectral data for **11**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$) 2034 (vs), 1992 (s), 1958 (s), 1927 (m), 1715 (w); ^{1}H NMR (δ in CDCl$_3$) 6.07 (s, 5H), 3.76 (s, 6H). Anal. Calcd for $C_{16}H_{11}MnMoO_9S_2$: C, 34.18; H, 1.97.

The red compound CpMoMn(CO)$_5$[μ-S(MeO$_2$C)CC(CO$_2$Me)S] (**12**) was prepared similarly in 43% yield from 2.25 μL (0.018 mmol) of DMAD and **3** (6.0 mg, 0.0122 mmol) in benzene at room temperature in 18 h. Spectral data for **12**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$) 2029 (vs), 1980 (m), 1948 (s), 1936 (m), 1734 (w), 1717 (w); ^{1}H NMR (δ in CDCl$_3$) 3.70 (s, 6H), 2.10 (s, 15H). Anal. Calcd: C, 39.88; H, 3.35. Found: C, 39.76; H, 3.45.

Synthesis of CpMoMn(CO)$_5$[μ-SCH$_2$C(=CH$_2$)S] (13). A solution of **2** (30.0 mg, 0.0714 mmol) in 20 mL of CH$_2$Cl$_2$ was purged with allene gas for 5 min. The solution was then stirred at room temperature under an atmosphere of allene for 24 h. The solvent was then removed in vacuo, and the residue was separated by TLC on silica gel by using a 2/1 hexane/CH$_2$Cl$_2$ solvent mixture to yield 14.0 mg of unreactied **2** and 4.1 mg of CpMoMn(CO)$_5$[μ-SCH$_2$C(=CH$_2$)S] (**13**), 12% yield. Spectral data for **13**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$) 2025 (vs), 1981 (m), 1949 (m), 1910 (m); ^{1}H NMR (δ in CDCl$_3$) 5.47 (s, 5H), 3.0 (d, 2H), 2.6 (d, 2H). Anal. Calcd for $C_{13}H_9MnMoO_5S_2$: C, 33.93; H, 1.97. Found: C, 33.54; H, 2.01.

Crystallographic Analyses. Orange single crystals of **2**, **5**, **7**, **9** and **13** and dark-red single crystals of **4** and **12** suitable for diffraction analysis were grown by slow evaporation of solvent from solutions of the pure compounds in hexane/methylene chloride solvent mixtures at 4 °C. Orange single crystals of **3** and **11**, orange-red crystals of **6**, and red crystals of **10** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution of the pure compound in a hexane/CH$_2$Cl$_2$ solvent mixture at −17 °C. All crystals used for the data collections were glued onto the ends of thin glass fibers. X-ray intensity data for each structural analysis was measured on a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cells were determined on the basis of reflections obtained from sets of three orthogonal scans. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. The raw intensity data frames were integrated with SAINT+, which also applied corrections for Lorentz and polarization effects.[30] Final unit cell parameters are based on the least-squares refinement of all reflections with $I > 5\sigma(I)$ from the data sets. For each analysis an empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using SADABS.[31]

Compounds **2**−**5** and **7** crystallized in the monoclinic system. The space groups $P2_1/n$, $P2_1/c$, $P2_1/n$, $P2_1/c$, and $P2_1/n$, respectively, were identified uniquely by the patterns of systematic absences in the intensity data. Compound **6** crystallized in the orthorhombic crystal system. The systematic absences were consistent with the space groups *Pnma* and $Pna2_1$. The centric space group *Pnma* was assumed and confirmed by the successful solution and refinement of the structure. Compounds **9**−**13** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed in each case by the successful solution and refinement of the structure. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2, by using the SHELXTL program library[31] and neutral atom scattering factors. For each structure, all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were calculated by assuming idealized geometries and included as riding atoms in the final refinements.

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Supporting Information Available: ORTEP diagrams for compounds **3**, **6**, **10**, and **12** and crystallographic data in CIF format for the structural analyses of **2**−**7** and **9**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) *SAINT+*, version 6.02a; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(31) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.