

Disulfido Metal Carbonyl Complexes Containing Manganese

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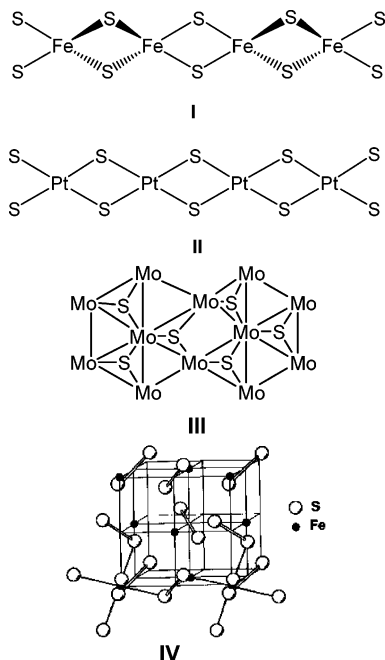
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ABSTRACT

An Account of recent studies of the chemistry of new disulfido metal carbonyl complexes containing manganese is presented. The coordination of the disulfido ligands, the nature of reactions at the manganese atom(s) and the nature of insertion reactions at the disulfido ligands are discussed.

Introduction

Metal disulfides are known to exist in a variety of extended structures, including one-dimensional chains such as KFeS_2 , **I**, and K_2PtS_2 , **II**,¹ two-dimensional sheets, such as MoS_2 , **III**, one of today's most effective hydrodesulfurization catalysts,² and three-dimensional structures, such as iron pyrite, **IV**, which has recently been found to be a



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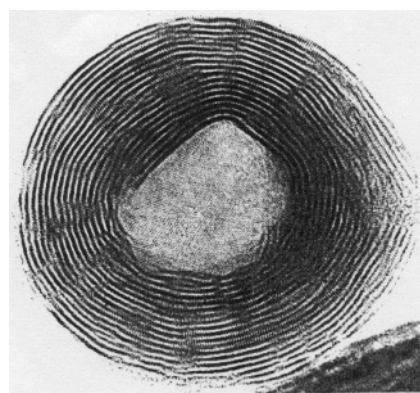


FIGURE 1. An inorganic fullerene structure composed of WS_2 .^{4a}

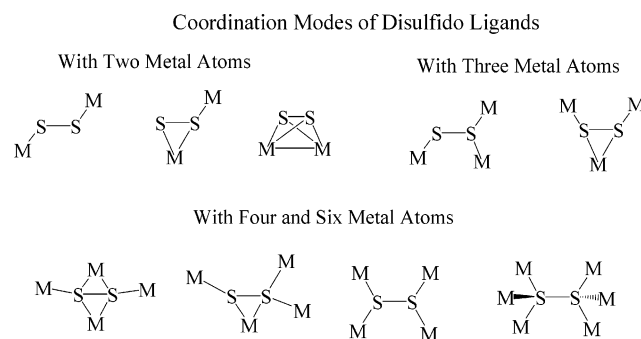


FIGURE 2. Representations of the various confirmed coordination modes of the disulfido ligand.

valuable material for use in photoelectrochemical solar cells due to its very high light absorption coefficient.³

Recent studies have shown that metal disulfides can also exhibit a variety of important nanostructures.⁴ For example, WS_2 can be convoluted into fullerene-like nested nanospheres, Figure 1, and one-dimensional nanotubes.⁴ Metal sulfide nanoparticles have recently been observed to serve as catalysts with unusually high reactivities.^{2e,5}

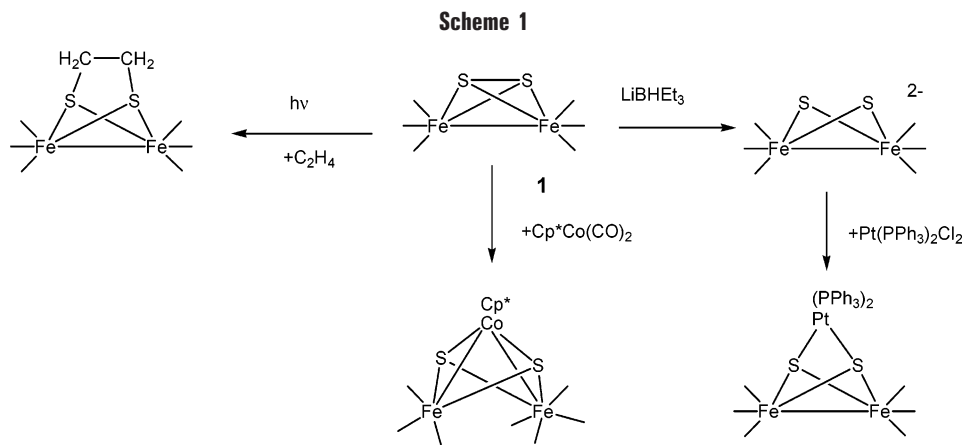
The disulfido ligand is a special disulfide because it contains a S–S bond. The S–S bond can be cleaved to yield two sulfido ligands. The disulfido ligand has been shown to exhibit a variety of bridging coordination modes that contain from two to six metal atoms, see Figure 2.⁶

The simplest disulfido complex of iron carbonyl is the compound $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$, **1**, that was reported over 40 years ago.⁷ The reactivity of **1** is dominated by the addition of small molecules and metal-containing groups at the sulfur atoms.⁸ These reactions generally involve cleavage of the sulfur–sulfur bond, see Scheme 1.

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$\text{Mn}_2(\text{CO})_7(\mu\text{-S}_2)$ and Its Derivatives

We have recently discovered that $\text{Mn}_2(\text{CO})_9(\text{NCMe})$, an activated form of $\text{Mn}_2(\text{CO})_{10}$, reacts with thiirane to yield the new disulfido complex $\text{Mn}_2(\text{CO})_7(\mu\text{-S}_2)$, **2**.⁹ The structure of **2** is very similar to that of **1**, except that it contains an additional carbonyl ligand serving as a bridge between the two manganese atoms, see Figure 3. The sulfur–sulfur

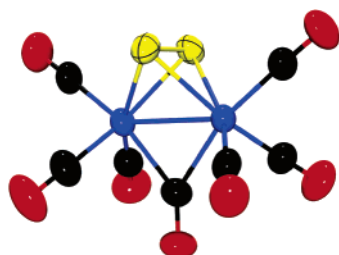


FIGURE 3. An ORTEP diagram of the molecular structure of **2**, Mn = blue, S = yellow.

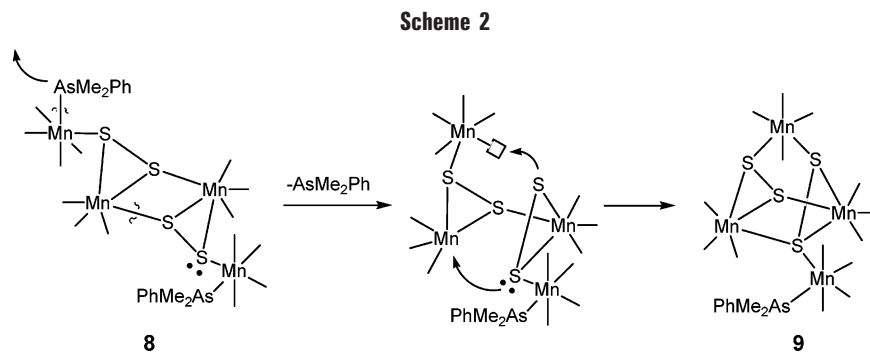
bond of the disulfido ligand is oriented perpendicular to the manganese–manganese bond and is only slightly longer, 2.0474(11) Å, than the S–S bond in **1**, 2.021(3)^{10a} and 2.007(5) Å.^{10b} The presence of the additional CO ligand relative to **1** is required to increase the electron count on the manganese atoms to 18, since manganese has one less electron than iron. Although the manganese–manganese bond in **2** is single, the Mn–Mn bond distance, 2.6745(5) Å, is considerably shorter than that in $\text{Mn}_2(\text{CO})_{12}$, 2.8950(6)¹¹ and 2.9038(6) Å,¹² because of the presence of the bridging ligands. Unlike most bridging carbonyl ligands that exhibit relatively low-energy stretching frequencies, 1700–1850 cm^{-1} , the stretching frequency of the

bridging CO ligand in **2** is 1894 cm^{-1} , indicating that there is relatively little π -back-bonding to this ligand.

Two higher nuclearity disulfido-containing complexes, $\text{Mn}_4(\text{CO})_{15}(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)$, **3**, and $\text{Mn}_4(\text{CO})_{14}(\text{NCMe})(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)$, **4**, were also formed in the reaction that gave **2**.⁹ These compounds can be obtained from **2** by the addition of CO and NCMe, respectively. Compound **3** was first reported by Vahrenkamp as a product of the cleavage the SnMe_3 groups from $\text{Mn}_2(\text{CO})_8(\mu\text{-SSnMe}_3)_2$ by iodine.¹³ Compounds **3** and **4** are structurally similar, and each contains four manganese atoms with two bridging disulfido ligands. One of the disulfido ligands bridges three manganese atoms, while the other is bonded to all four manganese atoms.

Surprisingly, the reaction of **2** with tertiary phosphines does not lead to phosphine-substituted derivatives but instead leads to (bis-sulfido)tetramanganese compounds, such as $\text{Mn}_4(\text{CO})_{15}(\text{PMe}_2\text{Ph})_2(\mu_3\text{-S})_2$, **5**, and $\text{S}=\text{PMe}_2\text{Ph}$ that were obtained from the reaction of **2** with PMe_2Ph .¹⁴ The formation of the latter product suggests reactivity between the phosphine and the disulfido ligand. A related sulfur abstraction is described below. Compound **5** contains two triply bridging sulfido ligands.

On the other hand, tertiary arsines, which are less reactive toward sulfur than phosphines, react with **2** by the expected ligand substitution route.¹⁴ For example, the reaction of **2** with AsPh_3 yields the monosubstitution derivative $\text{Mn}_2(\text{CO})_6(\text{AsPh}_3)(\mu\text{-S}_2)$, **6**. The arsine ligand is positioned trans to the bridging CO ligand. The reaction of **1** with AsMe_2Ph proceeds similarly to yield the substitution product $\text{Mn}_2(\text{CO})_6(\text{AsMe}_2\text{Ph})(\mu\text{-S}_2)$, **7**, but also yields the new complexes $\text{Mn}_4(\text{CO})_{14}(\text{AsMe}_2\text{Ph})_2(\mu_3\text{-S}_2)_2$, **8**,



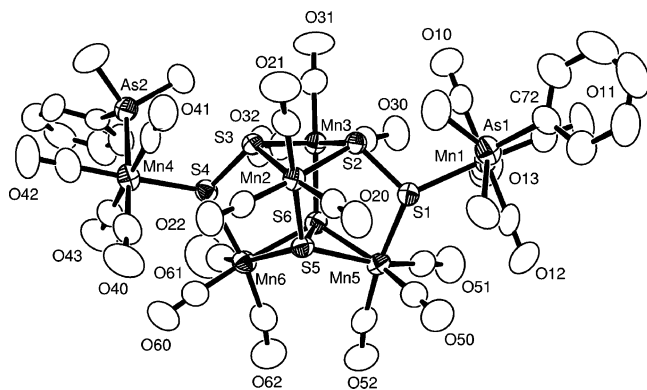


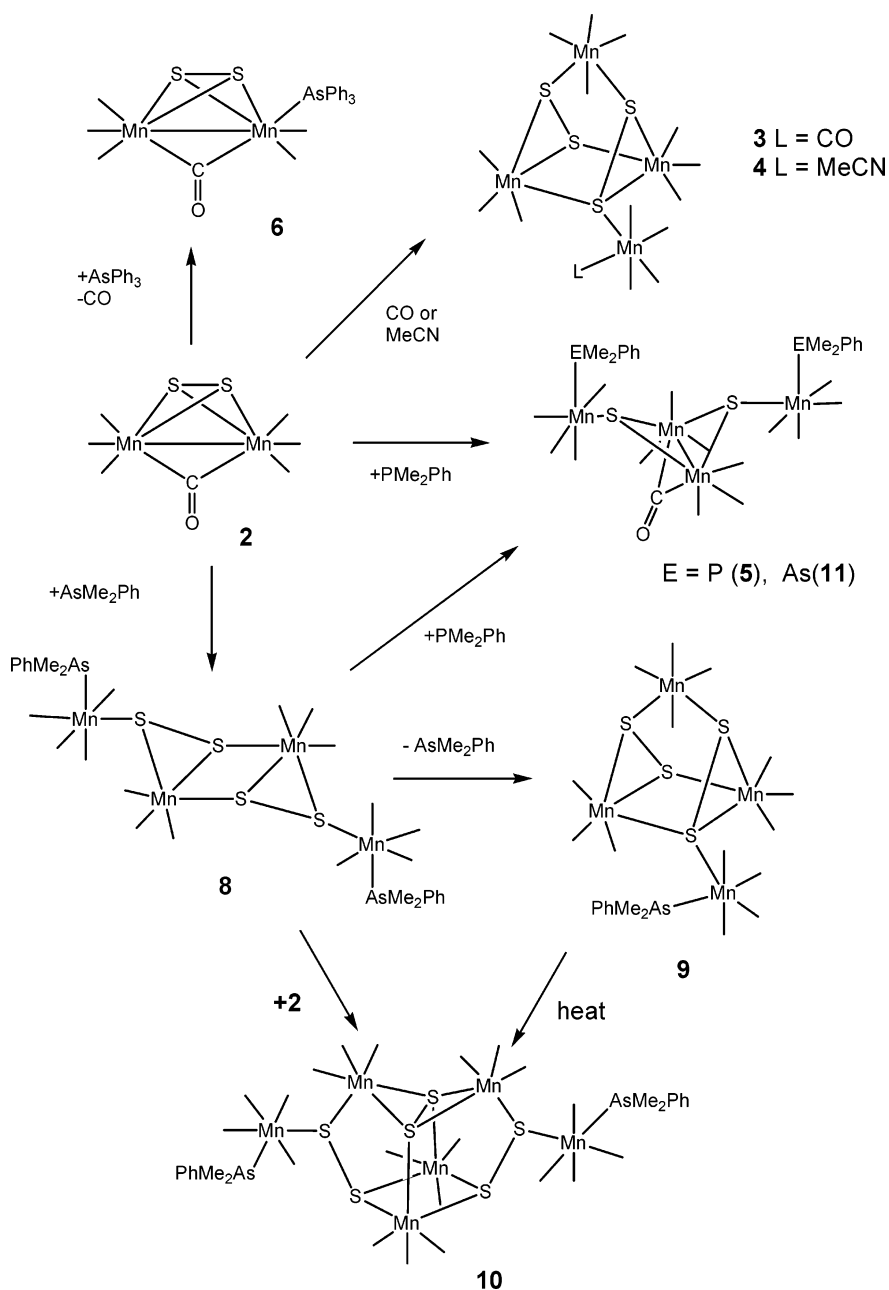
FIGURE 4. An ORTEP diagram of the structure of **10**.

$\text{Mn}_4(\text{CO})_{14}(\text{AsMe}_2\text{Ph})(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)$, **9**, and $\text{Mn}_6(\text{CO})_{20}(\text{AsMe}_2\text{-Ph})_2(\mu_4\text{-S}_2)_3$, **10**. Compound **8** has a novel structure

containing two triply bridging sulfido ligands. It could be viewed as a dimer of an AsMe_2Ph adduct of **2**. When heated, **8** loses one AsMe_2Ph ligand and the cluster closes to yield **9**. See Scheme 2 for the proposed transformation. This transformation may be general and could account for the formation of compounds **3** and **4**, too. Reaction of **8** with PMe_2Ph yielded $\text{Mn}_4(\text{CO})_{15}(\text{AsMe}_2\text{Ph})_2(\mu_3\text{-S})_2$, **11** (an arsine analogue of **5**), by the phosphine-assisted removal of two sulfur atoms, presumably one from each disulfido ligand.

Compound **10** contains a novel structure with three quadruply bridging disulfido with six manganese atoms. One of these, S(5)–S(6), which is imbedded in the cluster, has a long S–S bond, 2.098(2) Å, see Figure 4. We have been able to prepare **10** independently by the combina-

Scheme 3



tion of **8** with **2**. These reactions of **2** are summarized in Scheme 3.

Thioethers react with **2** in yet another manner. Thioethers displace the bridging CO ligand and insert a sulfur atom into the Mn–Mn bond.¹⁵ For example, the reaction of **2** with SMe_2 yielded $\text{Mn}_2(\text{CO})_6(\mu\text{-S}_2)(\mu\text{-SMe}_2)$, **12**, see Figure 5.

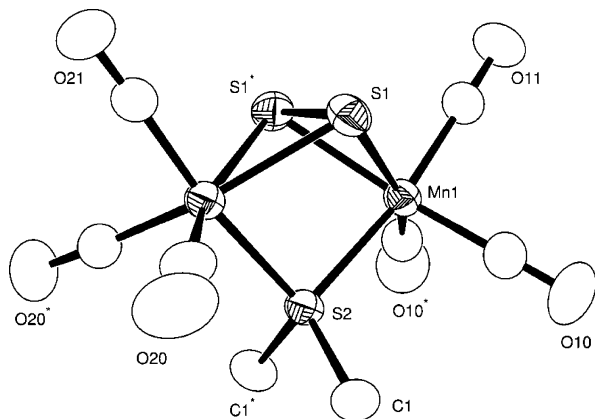
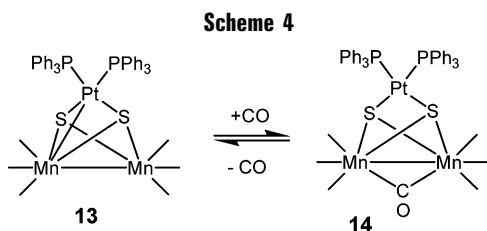


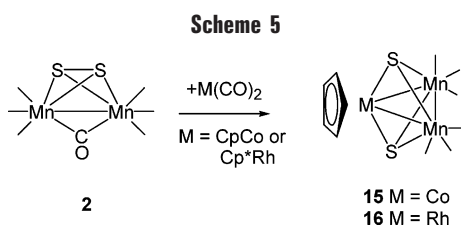
FIGURE 5. An ORTEP diagram of the structure of **12**.

Heterometallic Complexes

Metal-containing groups readily insert into the S–S bond of **2** to yield complexes having two triply bridging sulfido ligands. For example, the reaction of **2** with $\text{Pt}(\text{PPh}_3)_2(\text{PhC}_2\text{Ph})$ yielded the new complex $\text{Mn}_2(\text{CO})_6\text{Pt}(\text{PPh}_3)_2(\mu_3\text{-S})_2$, **13**, by loss of CO from **2** and PhC_2Ph from the $\text{Pt}(\text{PPh}_3)_2(\text{PhC}_2\text{Ph})$ and then insertion of the $\text{Pt}(\text{PPh}_3)_2$ group into the S–S bond of **2**.¹⁶ Complex **13** contains an open Mn_2Pt cluster with one Mn–Mn bond, 2.8154(14) Å, and one Mn–Pt bond, 2.9109(10) Å. Interestingly, **13** reacts with CO to form the adduct $\text{Mn}_2(\text{CO})_6(\mu\text{-CO})\text{Pt}(\text{PPh}_3)_2(\mu_3\text{-S})_2$, **14**, by cleavage of the Pt–Mn bond. The CO addition is readily reversible, and simple purge of solutions of **14** with nitrogen converts it back to **13** quantitatively, Scheme 4.

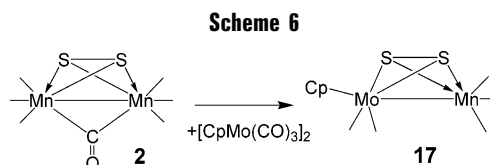


The reactions of **2** with $\text{CpCo}(\text{CO})_2$ or $\text{Cp}^*\text{Rh}(\text{CO})_2$ yield the complexes $\text{CpCoMn}_2(\text{CO})_6(\mu_3\text{-S})_2$, **15**, and $\text{Cp}^*\text{RhMn}_2(\text{CO})_6(\mu_3\text{-S})_2$, **16**, by insertion of the cobalt and rhodium atoms into the S–S bond and the formation of two new

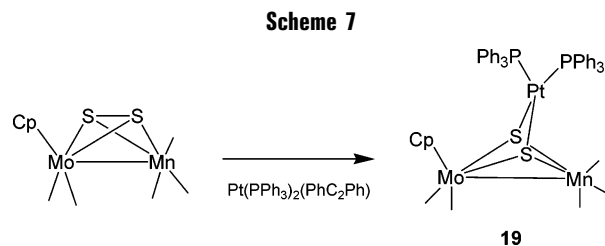


metal–metal bonds, Scheme 5. The sulfur atoms become triply bridging sulfido ligands on each side of the Mn_2M plane.¹⁷

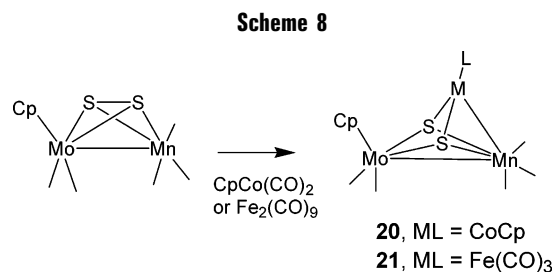
Compound **2** reacts with $[\text{CpMo}(\text{CO})_3]_2$ and $[\text{Cp}^*\text{Mo}(\text{CO})_3]_2$ by a metal–metal exchange process to yield the new dinuclear mixed metal complexes $\text{CpMoMn}(\text{CO})_5(\mu\text{-S}_2)$, **17**, and $\text{Cp}^*\text{MoMn}(\text{CO})_5(\mu\text{-S}_2)$, **18**, in good yield.¹⁸ The disulfido ligand in these compounds bridges the Mo–Mn bond similarly to that in **2**, but it donates its electrons unsymmetrically by formally giving four electrons to the Mn atom and only two electrons to the Mo atom, Scheme 6.



Compounds **17** and **18** also add metal-containing groups by insertion into the S–S bond. For example, the reaction of **17** with $\text{Pt}(\text{PPh}_3)_2(\text{PhC}_2\text{Ph})$ yielded the new bis-sulfido mixed metal complex $\text{CpMoMn}(\text{CO})_5\text{Pt}(\text{PPh}_3)_2(\mu_3\text{-S})_2$, **19**, by loss of the PhC_2Ph ligand and insertion of the $\text{Pt}(\text{PPh}_3)_2$ fragment into the S–S bond, see Scheme 7, but unlike the reaction of $\text{Pt}(\text{PPh}_3)_2(\text{PhC}_2\text{Ph})$ with **2**, no new metal–metal bonds were made in this reaction.¹⁹



The reaction of **17** with $\text{CpCo}(\text{CO})_2$ yields $\text{Cp}_2\text{MoMnCo}(\text{CO})_5(\mu_3\text{-S})_2$, **20**, by insertion of a CpCo group into the S–S bond. In this reaction, two CO ligands were lost from the $\text{CpCo}(\text{CO})_2$ and only one metal–metal bond was formed, a Co–Mn bond, see Scheme 8.²⁰ The reaction of **2** with $\text{Fe}_2(\text{CO})_9$ proceeds similarly to yield the compound $\text{CpMoMnFe}(\text{CO})_8(\mu_3\text{-S})_2$, **21**, with formation of an Fe–Mn bond.²⁰



Anticipating formation of a disulfido iron–manganese complex, we examined the reaction of $\text{CpFeMn}(\text{CO})_7$ with thirane in the presence of the decarbonylation reagent Me_3NO , but instead of a dimetal disulfido complex, we obtained the diironmanganese complex $[\text{CpFeMn}(\text{CO})_5(\mu_3\text{-S}_2)]_2$, **22**, analogous to **8**, see Figure 6.²¹ Curiously,

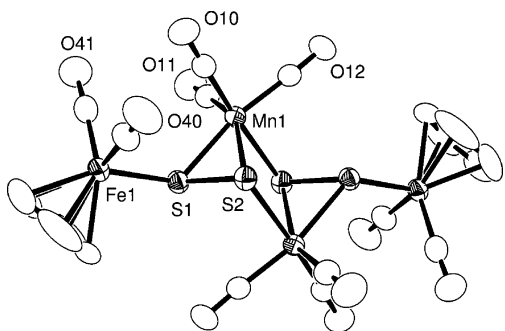


FIGURE 6. An ORTEP diagram of $[\text{CpFeMn}(\text{CO})_5](\mu_3\text{-S}_2)_2$, **22**.

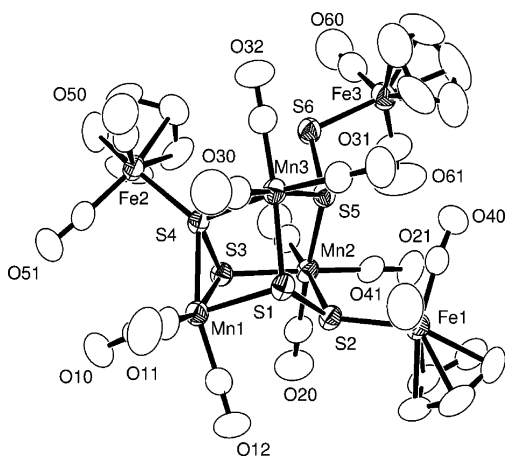


FIGURE 7. An ORTEP diagram of $[\text{CpFeMn}(\text{CO})_5]_3(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)_2$, **23**.

compound **22** spontaneously condenses without loss of any ligands to form a trimer $[\text{CpFeMn}(\text{CO})_5]_3(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)_2$, **23**, by expanding the coordination of the manganese atoms and the sulfur atoms of the disulfido ligands, see Figure 7.²¹

The reaction of **2** with $[\text{CpNi}(\text{CO})_2]$ yielded the new trinuclear metal complex $\text{Cp}_2\text{Ni}_2\text{Mn}(\text{CO})_3(\mu_3\text{-S})_2$, **24**, and a minor hexanuclear metal complex $\text{Cp}_2\text{Ni}_2\text{Mn}_4(\text{CO})_{14}(\mu_6\text{-S}_2)(\mu_3\text{-S})_2$, **25**, see Scheme 9.²² Formally, a $\text{Mn}(\text{CO})_4$ was displaced from **2**, but unlike the reaction of **2** with $[\text{CpMo}(\text{CO})_3]_2$, both CpNi groups were added in the formation of **24** and the S–S bond of the disulfido ligand was cleaved to form two triply bridging sulfido ligands. Compound **24** contains an odd number of valence electrons. Electron paramagnetic resonance (EPR) and magnetic susceptibility measurements revealed the presence of one unpaired electron. The EPR measurement indicates that the unpaired electron has 14% population on manganese. This is consistent with molecular calculations that show the unpaired electron occupies a delocalized antibonding orbital that is shown in Figure 8.

Compound **25** is unusual because it contains a μ_6 -disulfido ligand shown by atoms S(1) and S(3), see Figure

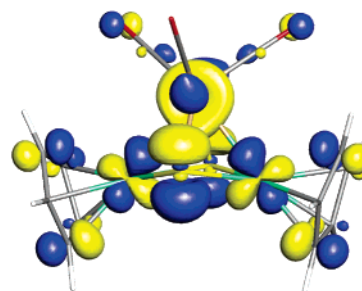


FIGURE 8. A representation of the singly occupied antibonding molecular orbital in compound **24**.

9. The S(1)–S(3) bond distance is very long, 2.2573(12) Å. It is even longer than the S–S distance, 2.153(6) Å, of μ_6 -disulfido ligand in iron pyrite **IV**, which contains six iron atoms coordinated to the disulfido ligand.

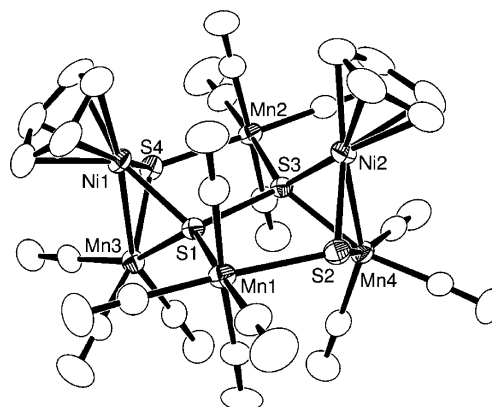


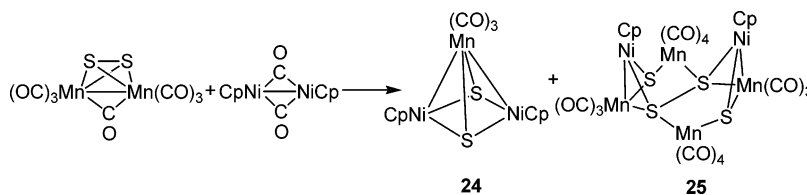
FIGURE 9. An ORTEP diagram of the molecular structure of $\text{Cp}_2\text{Ni}_2\text{Mn}_4(\text{CO})_{14}(\mu_6\text{-S}_2)(\mu_3\text{-S})_2$, **25**.

Insertion of Small Organic Molecules into the S–S Bond

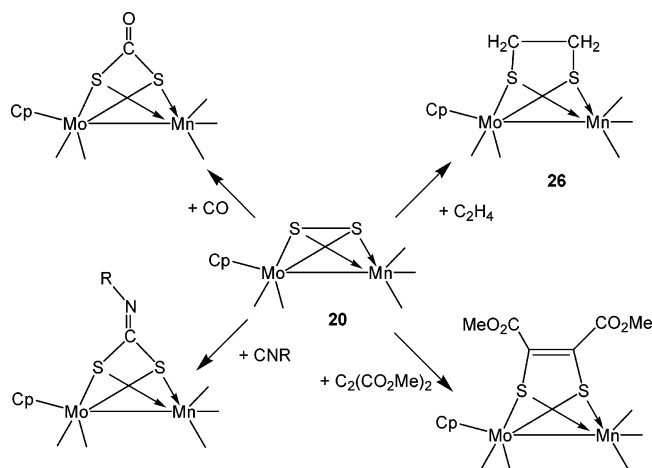
It has been shown that molecules containing a C–C double bond can be inserted into the S–S bond of **1** under photolytic conditions.²³ This has not yet been achieved with **2**; however, compounds **17** and **18** do readily engage in this interesting photoreaction at the disulfido ligand.¹⁸ For example, the reaction of **17** and **18** with ethylene leads to the ethanedithiolate complexes $\text{CpMoMn}(\text{CO})_5[\mu\text{-S}(\text{CH}_2)_2\text{S}]$, **26**, and $\text{Cp}^*\text{MoMn}(\text{CO})_5[\mu\text{-S}(\text{CH}_2)_2\text{S}]$, **27**. Carboxylate-substituted alkynes, CO, and even *tert*-butylisocyanide can also be inserted into the S–S bond of these compounds, see Scheme 10. It was shown by an isotopic labeling study that the inserted CO molecule was not derived from one of the CO ligands in the complex.

According to the rules of conservation of orbital symmetry, these insertion reactions are thermally forbidden,²³ and our studies have shown that they are, in fact, all

Scheme 9



Scheme 10



promoted by room light and do not proceed at all in the dark.²⁴ We have even been able to add C₆₀ across the S–S bond at one of its 6,6 ring junctions in the presence of room light to yield the complex CpMoMn(CO)₅(μ-S₂C₆₀), **28**, see Figure 10.²⁴ Rauchfuss has shown that C₆₀ can also be added across the S–S bond of **1**.²⁵

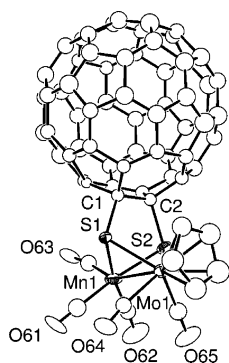
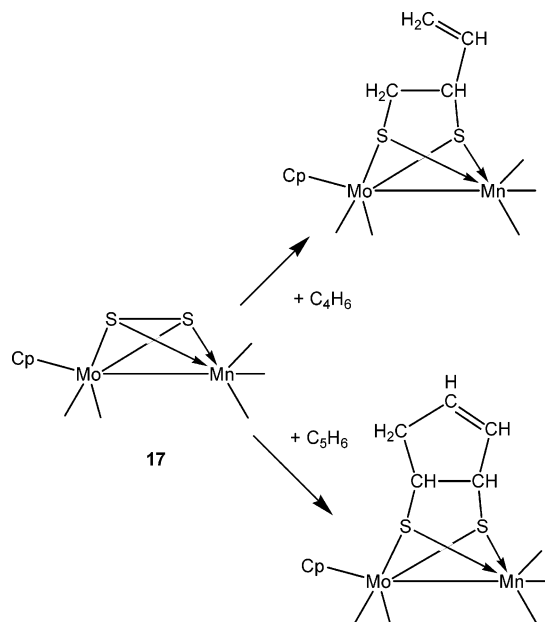


FIGURE 10. An ORTEP diagram of the molecular structure of **28**.

To test the orbital symmetry principle further, we have investigated the reactions of **17** with some dienes, butadiene and cyclopentadiene. Although the 4 + 2 addition of a diene to **2** is thermally allowed, these reactions do not proceed in that fashion. Instead, these additions also proceed by the light-promoted 2 + 2 mechanism to give 1,2-dithiolato ligands, see Scheme 11.²⁴ Fe₂(CO)₆(μ-S₂) reacts similarly with dienes in the presence of UV irradiation.^{23a} We have recently made the diselenido homologue of **17**, CpMoMn(CO)₅(μ-Se₂), and it has a similar structure and reactivity to that of **17**.²⁶

Quinones are important in biological processes and quinone complexes have recently attracted attention because of their ability to form supramolecular networks in the solid state.²⁷ We have found that *para*-quinone reacts with **17** at the disulfido ligand by substitution of two hydrogen atoms on one of the C=C double bonds to yield the complex CpMoMn(CO)₅(μ-S₂C₆H₂O₂), **29**, a dithio-substituted quinone that contains the CpMoMn(CO)₅ grouping, see Figure 11.²⁸ It was proposed that this reaction proceeds via a 2 + 2 cycloaddition step, as described above for olefins, that is followed by a reaction

Scheme 11



with a second equivalent of *para*-quinone that oxidatively removes the two proximate hydrogen atoms from the first quinone ring. The quinone ring in **29** is reduced to a

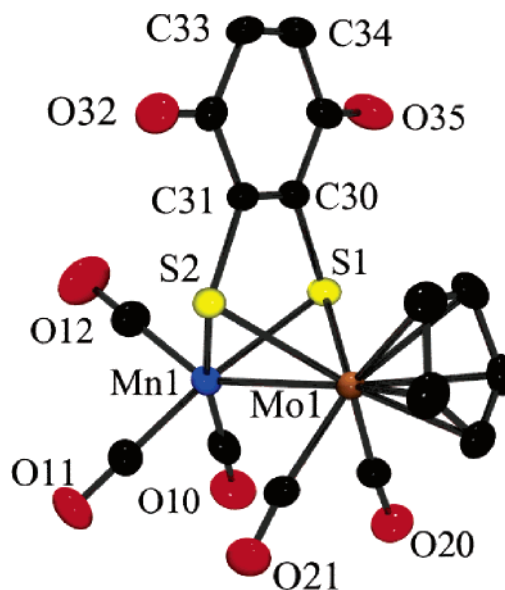


FIGURE 11. An ORTEP diagram of the molecular structure of **29**.

hydroquinone ring by reaction with hydrogen to yield the complex CpMoMn(CO)₅(μ-S₂C₆H₂(OH)₂), **30**, see Figure 12. The hydroquinone ring in **30** can be reoxidized to regenerate **29** by treatment with ferrocenium ion.

Conclusions

Our recent studies show that there are still a variety of dinuclear metal complexes containing disulfido ligands that can be readily prepared and are stable. They also have a more extensive and rich reaction chemistry than previously recognized. It is certain that more examples of these complexes will be forthcoming and they will continue to

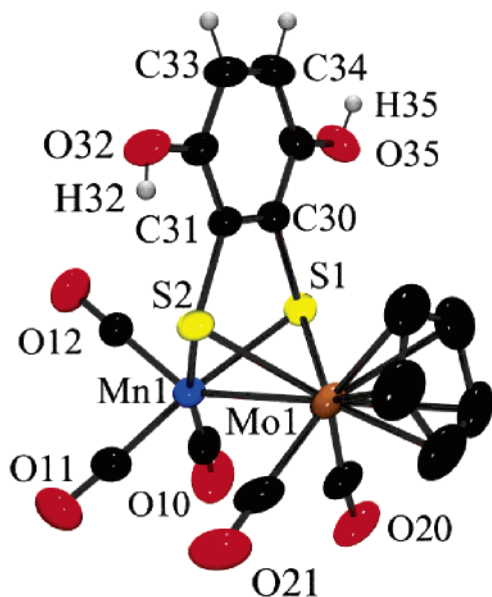


FIGURE 12. An ORTEP diagram of the molecular structure of **30**.

show a wide range of reactivity with small molecules and other metal complexes. They may even serve as useful reagents for the synthesis of new sulfide-containing nanomaterials.²⁹

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