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Article

Disulfides of Manganese Carbonyl. Synthesis of $Mn_2(CO)_7(\mu\text{-}S_2)$ and Its Reactions with Tertiary Phosphines and Arsines

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The reaction of $Mn_2(CO)_9(NCMe)$ with thiirane yielded the sulfidomanganese carbonyl compounds $Mn_2(CO)_7(\mu\text{-}S_2)$, **2**, $Mn_4(CO)_{15}(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **3**, and $Mn_4(CO)_{14}(NCMe)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **4**, by transfer of sulfur from the thiirane to the manganese complex. Compound **3** was obtained in better yield from the reaction of **2** with CO, and compound **4** is obtained from the reaction of **2** with NCMe. The reaction of **2** with PMe_2Ph yielded the tetramanganese disulfide $Mn_4(CO)_{15}(PMe_2Ph)_2(\mu_3\text{-}S)_2$, **5**, and $S{=}PMe_2Ph$. The reaction of **5** with PMe_2Ph yielded $Mn_4(CO)_{14}(PMe_2Ph)_3(\mu_3\text{-}S)_2$, **6**, by ligand substitution. The reaction of **2** with $AsMe_2Ph$ yielded the new complexes $Mn_4(CO)_{14}(AsMe_2Ph)_2(\mu_3\text{-}S_2)_2$, **7**, $Mn_4(CO)_{14}(AsMe_2Ph)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **8**, $Mn_6(CO)_{20}(AsMe_2Ph)_2(\mu_4\text{-}S_2)_3$, **9**, and $Mn_2(CO)_6(AsMe_2Ph)(\mu\text{-}S_2)$, **10**. Reaction of **2** with $AsPh_3$ yielded the monosubstitution derivative $Mn_2(CO)_6(AsPh_3)(\mu\text{-}S_2)$, **11**. Reaction of **7** with PMe_2Ph yielded $Mn_4(CO)_{15}(AsMe_2Ph)_2(\mu_3\text{-}S)_2$, **12**. The phosphine analogue of **7**, $Mn_4(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S_2)_2$, **13**, was prepared from the reaction of $Mn_2(CO)_9(PMe_2Ph)$ with Me_3NO and thiirane. Compounds **2**–**9** and **11**–**13** were characterized by single-crystal X-ray diffraction. Compound **2** contains a disulfido ligand that bridges two $Mn(CO)_3$ groups that are joined by a Mn–Mn single bond, 2.6745(5) Å in length. A carbonyl ligand bridges the Mn–Mn bond. Compounds **3** and **4** contain four manganese atoms with one triply bridging and one quadruply bridging disulfido ligand. Compounds **5** and **6** contain four manganese atoms with two triply bridging sulfido ligands. Compound **9** contains three quadruply bridging disulfido ligands imbedded in a cluster of six manganese atoms.

Introduction

The synthesis of high-nuclearity transition metal carbonyl cluster compounds has continued to grow in importance over the years.[1] Larger and larger metal cluster complexes are being synthesized.[2] Metal cluster complexes are also used as precursors to nanoparticles on supports for use in catalysis.[3] The synthesis of metal cluster complexes is often facilitated by using bridging ligands derived from the main group elements,[4] and the sulfido ligand has been shown to

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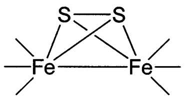
be one of the most useful of all.[4−6] Disulfides are also good ligands for transition elements,[7] and certain metal disulfides have been shown to be important as catalysts for hydrodesulfurization.[8]

The simplest disulfide of iron carbonyl, $Fe_2(CO)_6(\mu\text{-}S_2)$, **1**, was first reported by Hieber in 1958[9] and has been extensively investigated over the years.[10] Curiously, there are very few examples of transition-metal carbonyl disulfides analogous to **1**. Most reactions of **1** with metal complexes occur at the sulfur atoms. For example, heterometallic clusters can be prepared by the insertion of unsaturated metal fragments into the S−S bond (eq 1).[11]



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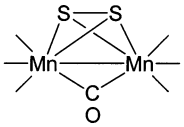

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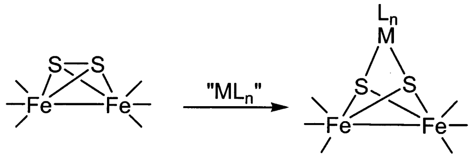

(1)

Thiiranes have been shown to be good reagents for the synthesis of sulfido metal carbonyl complexes by transfer of the sulfur atom to the metal atoms of metal carbonyl complexes.[12] By using this approach, we have now prepared the new *disulfide* of manganese carbonyl $Mn_2(CO)_7(\mu\text{-}S_2)$, **2**. We have also investigated the reactions of **2** with tertiary phosphines and tertiary arsines. These results are reported here. A preliminary report of this work has been published.[13]

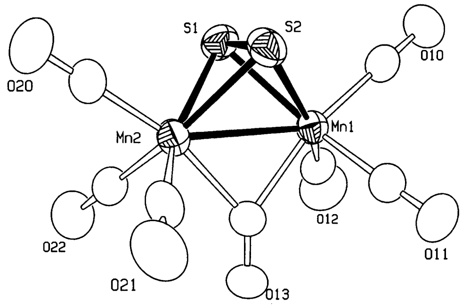

Figure 1. ORTEP diagram of the molecular structure of $Mn_2(CO)_7(\mu\text{-}S_2)$, **2**, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−Mn(2) = 2.6745(5), Mn(1)−S(1) = 2.2890(8), Mn(1)−S(2) = 2.2877(7), Mn(2)−S(1) = 2.2855(8), Mn(2)−S(2) = 2.2842(8), S(1)−S(2) = 2.0474(11), Mn(1)−C(13) = 2.033(3), and Mn(2)−C(13) = 2.084(3).

Results

The reaction of $Mn_2(CO)_9(NCMe)$ with thiirane in hexane solvent at 25 °C yielded the new compound $Mn_2(CO)_7(\mu\text{-}S_2)$, **2**, in 36% yield and two minor products: $Mn_4(CO)_{15}(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **3**, in 4% yield and $Mn_4(CO)_{14}(NCMe)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **4**, in 6% yield. The infrared spectrum of **2** in the carbonyl region exhibits a low-energy absorption band at 1894 cm^{-1} that is attributed to a bridging carbonyl ligand. The ^{13}C NMR spectrum at−25 °C shows three resonances: two at 212.5 and 213.5 ppm (assigned to the terminal carbonyl ligands) and one at 236.5 ppm (assigned to a bridging carbonyl ligand). These resonances are very broad at room temperature, presumably due to relaxation caused by the quadrupole moment of the manganese nucleus. Variable-temperature measurements indicate that the broadening was due to a ligand exchange process. The molecular structure of **2** was established by a single-crystal X-ray diffraction analysis.

An ORTEP of the molecular structure of **2** is shown in Figure 1. Compound **1** has a structure similar to that of $Fe_2(CO)_6(\mu\text{-}S_2)$ except for the presence of a bridging carbonyl ligand between the two manganese atoms. There are two $Mn(CO)_3$ groups containing terminal CO ligands that are joined by a metal−metal single bond, 2.6745(5) Å. The Mn−Mn distance is considerably shorter than that observed in $Mn_2(CO)_{10}$, 2.8950(6)[14] and 2.9038(6) Å,[15] but slightly longer than found in $Mn_2(CO)_4(PMe_3)_2(\mu\text{-}CO)(\mu\text{-}SMe)_2$, 2.581(1)

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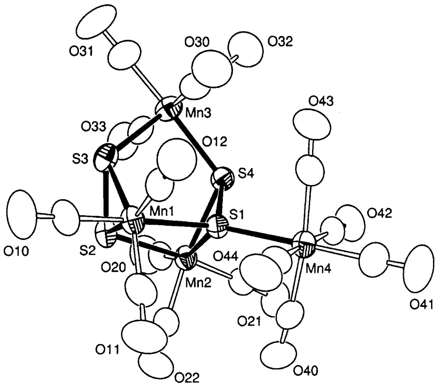

Figure 2. Side view of the molecular structure of $Mn_2(CO)_{15}(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **3**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−S(1) = 2.3817(9), Mn(1)−S(2) = 2.3590(10), Mn(1)−S(3) = 2.3098(10), Mn(2)−S(1) = 2.3397(9), Mn(2)−S(2) = 2.3784(9), Mn(2)−S(4) = 2.3518(10), Mn(3)−S(3) = 2.3464(11), Mn(3)−S(4) = 2.3445(9), Mn(4)−S(1) = 2.3859(9), S(1)−S(4) = 2.0924(12), and S(2)−S(3) = 2.0771(13).

Å.[16] The shortness of the Mn−Mn bond in **2** can be attributed to the presence of the two bridging ligands, one disulfido ligand and one carbonyl ligand. The S−S bond of bridging disulfido ligand in **2** is oriented perpendicular to the Mn−Mn bond, and both sulfur atoms are bonded to each manganese atom. The S−S bond distance, 2.0474(11) Å, is slightly longer than that found in $Fe_2(CO)_6(\mu\text{-}S_2)$, 2.021(3)[17a] and 2.007(5) Å.[17b] The Mn−S bond distances, 2.2842(8)−2.2890(8) Å, are typical of Mn−S single bonds. Assuming the disulfido ligand in **2** serves as a six-electron donor, each manganese atom achieves an 18-electron configuration in the presence of a Mn−Mn single bond. The bridging carbonyl ligand exhibits a slightly asymmetrical bonding to the metal atoms, Mn(1)−C(13) = 2.033(3) and Mn(2)−C(13) = 2.084(3) Å. There is no electronic reason for this asymmetry, and thus, it is probably due to crystal packing effects. Küllmer et al. reported the compound $Mn_2(CO)_5(PMe_3)_2(\mu\text{-}S_2)$, a bis(trimethylphosphine) derivative of **2** formed by the oxidative cleavage of $SnMe_3$ groups from $Mn_2(CO)_5(PMe_3)_2(\mu\text{-}SSnMe_3)_2$.[18a] The compound is probably structurally similar to **2**. Its IR spectrum indicated the presence of a bridging CO ligand, but further details of the structure are not available because it was not characterized crystallographically.

The molecular structure of **3** is shown in Figure 2. Compound **3** contains 4 manganese atoms, 4 sulfur atoms, and a total of 15 terminal carbonyl ligands distributed as shown in the figure. The Mn(1)···Mn(2) distance of 3.5419(7) Å is believed to be nonbonding. All manganese atoms are linked through the disulfido ligand bridges, and there are no Mn−Mn bonds. There are two bridging disulfido ligands. Ligand S(2)−S(3) is a triply bridging ligand that serves as a six-electron donor. Ligand S(1)−S(4) is a quadruply bridging ligand that serves as an eight-electron donor. The Mn−S bond distances span a wide range, 2.3098(10)−2.5859(9) Å, but all can be regarded as Mn−S single bonds. Compound **3** was obtained some years ago by Küllmer et al. as a product of the oxidative cleavage of the $SnMe_3$ groups from $Mn_2(CO)_8(\mu\text{-}SSnMe_3)_2$.[18]

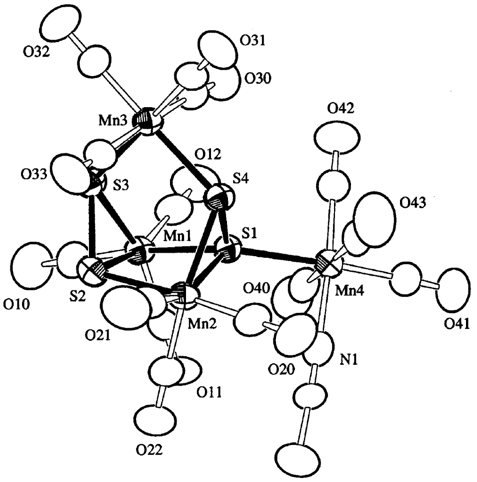

Figure 3. Side view of the molecular structure of $Mn_2(CO)_{15}(NCMe)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **4**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−S(1) = 2.374(2), Mn(1)−S(2) = 2.366(2), Mn(1)−S(3) = 2.322(2), Mn(2)−S(1) = 2.356(2), Mn(2)−S(2) = 2.399(2), Mn(2)−S(4) = 2.332(2), Mn(3)−S(3) = 2.355(2), Mn(3)−S(4) = 2.351(2), Mn(4)−S(1) = 2.425(2), Mn(4)−N(1) = 2.017(6), S(1)−S(4) = 2.097(2), and S(2)−S(3) = 2.087(2).

An ORTEP of the molecular structure of **4** is shown in Figure 3. Compound **4** is a simple NCMe derivative of **3**. The NCMe ligand is coordinated to the manganese atom Mn(4). The Mn(4)−S(1) bond distance has increased in length from 2.3859(9) Å in **3** to 2.425(2) Å in **4**. The ^1H NMR spectrum of **4** shows a single resonance at 2.58 ppm due to the methyl group of the NCMe ligand.

Compound **3** was also obtained in a very good yield (90% yield) from the reaction of **2** with CO at 25 °C. Interestingly, **4** was also obtained from **2** by reaction with NCMe, but the yield was low in this case, 9%. A mechanism for the formation of these compounds will be described below.

When **2** was allowed to react with PMe_2Ph at 25 °C, the unexpected product $Mn_4(CO)_{15}(PMe_2Ph)_2(\mu_3\text{-}S)_2$, **5**, was obtained in 37% yield. The molecular structure of compound **5** was established crystallographically and is shown in Figure 4. Like **3** and **4,** compound **5** contains four manganese atoms, but it has only two sulfur atoms in the form of sulfido ligands and these serve as triply bridging ligands. The molecule contains C_2 symmetry in the solid state. Two of the manganese atoms Mn(1) and Mn(1′) are joined by a Mn−Mn single bond, 2.6356(16) Å. Each manganese atom in the central group has three terminal carbonyl ligands. The S(1)···S(1*) distance 2.829(2) Å is too long to permit any direct S−S bonding. An $Mn(CO)_4(PMe_2Ph)$ group is attached to each sulfur atom. The presence of four manganese atoms in **5** indicates that it was formed by a condensation of 2 equiv of **2**. The loss of two sulfur atoms can be explained by the formation of $S{=}PMe_2Ph$ that also occurs in this reaction.

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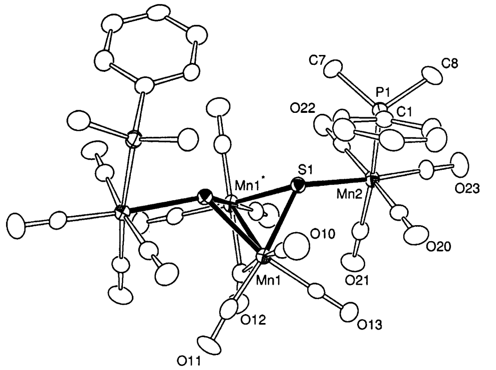


Figure 4. ORTEP diagram of the molecular structure of $Mn_4(CO)_{15}(PMe_2Ph)_2(\mu_3\text{-}S)_2$, **5**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−Mn(1*) = 2.6356(16), Mn(1)−S(1) = 2.3458(15), Mn(1*)−S(1) = 2.3449(15), Mn(2)−S(1) = 2.3992(14), and Mn(1)−C(12) = 2.058(6).

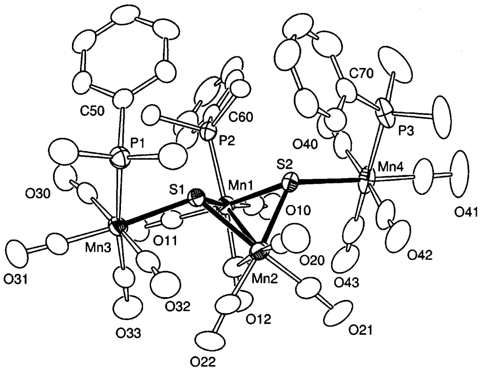


Figure 5. ORTEP diagram of the molecular structure of $Mn_4(CO)_{14}(PMe_2Ph)_3(\mu_3\text{-}S)_2$, **6**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−Mn(2) = 2.6695(9), Mn(1)−S(1) = 2.3907(12), Mn(1)−S(2) = 2.3664(12), Mn(2)−S(1) = 2.3424(12), Mn(2)−S(2) = 2.3152(12), Mn(1)−C(12) = 1.854(9), and Mn(2)−C(12) = 2.340(4).

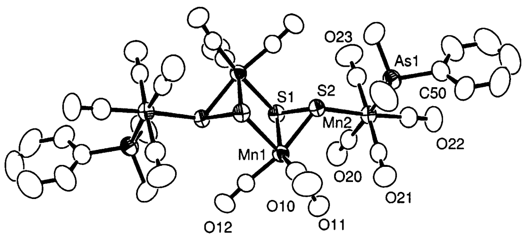
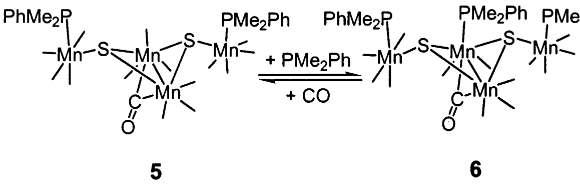


Figure 6. ORTEP diagram of the molecular structure of $Mn_4(CO)_{14}(AsMe_2Ph)_2(\mu_3\text{-}S_2)_2$, **7**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−S(1) = 2.4100(13), Mn(1)−S(1*) = 2.3801(12), Mn(1)−S(2) = 2.3309(12), Mn(2)−S(2) = 2.3816(13), Mn(2)−As(1) = 2.4299(8), and S(1)−S(2*) = 2.0701(15).

When **5** was treated with PMe_2Ph at 25 °C, its phosphine derivative $Mn_4(CO)_{14}(PMe_2Ph)_3(\mu_3\text{-}S)_2$, **6**, was formed in 43% yield. An ORTEP of the molecular structure of compound **6** is shown in Figure 5. Compound **6** is structurally very similar to that of the parent complex **5**. The phosphine ligand was introduced by a CO ligand substitution at one of the central manganese atoms Mn(1). The Mn−S and Mn−Mn distances to the phosphine substituted manganese atom are all longer than those in **5** and are also longer than those to the unsubstituted manganese atom. This may simply be a consequence of the increased steric interactions around Mn(1) produced by the bulky phosphine ligand. The bridging carbonyl ligand C(12)−O(12) in **6** has developed an asymmetrical bridging coordination and is more strongly coordinated to Mn(1) than Mn(2), Mn(1)−C(12) = 1.854(9) and Mn(2)−C(12) = 2.340(4) Å. This can be explained in the following way. When the terminal CO ligand is replaced on a metal atom by a better σ-donor and poorer π-acceptor ligand, then the bridging CO ligand becomes more strongly bonded to that metal atom to remove some of the increase in electron density that has occurred on that metal atom as a result of the substitution.[19] Interestingly, when solutions of **6** are purged with CO at 25 °C, it converted back to **5** by the replacement of the phosphine ligand with the CO ligand (eq 2).



(2)

The reaction of $Mn_2(CO)_7(\mu\text{-}S_2)$, **2**, with $AsMe_2Ph$ in hexane yielded four isolable products. The two principal products have been identified as new higher nuclearity compounds $Mn_4(CO)_{14}(AsMe_2Ph)_2(\mu_3\text{-}S_2)_2$, **7**, in 61% yield and $Mn_4(CO)_{14}(AsMe_2Ph)(\mu_3\text{-}S_2)_2$, **8**, in 16% yield. Only one of the two minor products, $Mn_6(CO)_{20}(AsMe_2Ph)_2(\mu_4\text{-}S_2)_3$, **9** (1% yield), has been characterized crystallographically, because it was not possible to obtain crystals of the second minor product.

Details of structure of **7** were established by a single-crystal X-ray diffraction analysis, and its molecular structure is shown in Figure 6. Complex **7** consists of an open tetranuclear cluster containing four manganese atoms and four triply bridging sulfido ligands. It contains an inversion center in the Mn_2S_2 plane. Two manganese atoms, Mn(1) and Mn(1*), and two sulfur atoms, S(1) and S(1*), form a square plane, and two Mn−S edges of the plane are bridged by $Mn(CO)_4(AsMe_2Ph)S$ substituents. All Mn−S bond distances, 2.3309(12)− 2.4100(13) Å, are similar to those found for other sulfido carbonyl complexes. The Mn−S bond distances bridged by the sulfido ligand, Mn(1)−S(1*) and Mn(1*)−S(1) = 2.3801(12) Å, are slightly shorter than others, Mn(1)−S(1) and Mn(1*)−S(1*) = 2.4100(13) Å. Assuming each sulfido ligand serves as four-electron donor, each manganese atom in the cluster then achieves an 18-electron configuration. All manganese atoms are octahedrally coordinated. Two manganese atoms, Mn(1) and Mn(1′), are surrounded by three sulfur atoms and three carbonyl ligands. The ^1H NMR spectrum of **7** exhibits a multiplet of resonances at $\delta = 7.6-7.3$ ppm that can be assigned to the phenyl group of $AsMe_2Ph$ ligand and two singlets at $\delta = 2.05$ and 2.04 ppm for the inequivalent methyl groups on the $AsMe_2Ph$ ligands. Compound **7** appears to be a dimer of an unobserved intermediate "$Mn_2(CO)_7(AsMe_2Ph)(\mu_3\text{-}S_2)$" formed by simple addition of $AsMe_2Ph$ to **2**.

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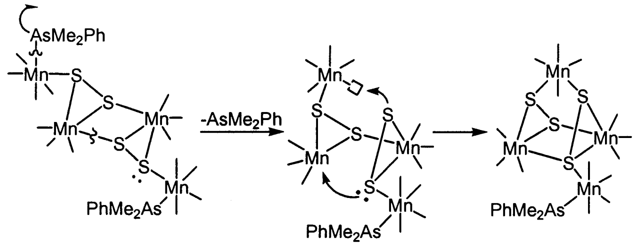
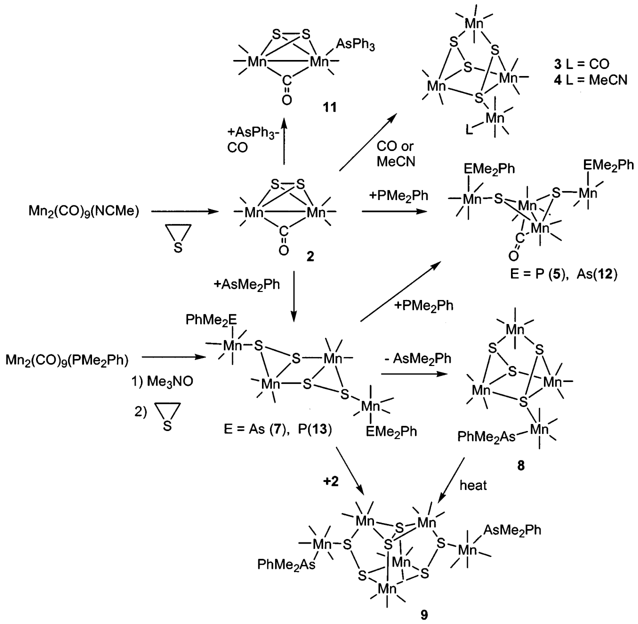
(19) Adams, R. D.; Kwon, O. S.; Smith, M. D. *Organometallics* **2001**, *21*, 1960.

Scheme 1



7 **8**

Scheme 2



The reaction of **2** with PMe_2Ph did not produce the phosphine analogue of **7** but yielded **5** instead, a tetramanganese species with two fewer sulfur atoms than **7**; see above. The phosphine analogue of **7** was, however, obtained from the reaction of an activated form of $Mn_2(CO)_9(PMe_2Ph)$ with thiirane. When $Mn_2(CO)_9(PMe_2Ph)$ was treated sequentially with Me_3NO and thiirane, $Mn_4(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S_2)_2$, **13**, the phosphine analogue of **7**, was obtained in 31% yield (Scheme 2). The crystal structure of **13** is shown in Figure 7. It is structurally similar to **7** but has PMe_2Ph ligands in place of the $AsMe_2Ph$ ligands.

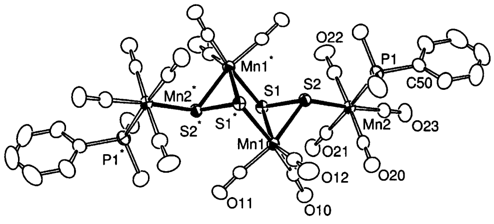


Figure 7. Side view of the molecular structure of $Mn_4(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S_2)_2$, **13**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−S(1) = 2.3805(7), Mn(1)−S(2) = 2.3330(7), Mn(1)−S(1*) = 2.4142(7), Mn(2)−S(2) = 2.3826(7), and S(1)−S(2) = 2.0732(8).

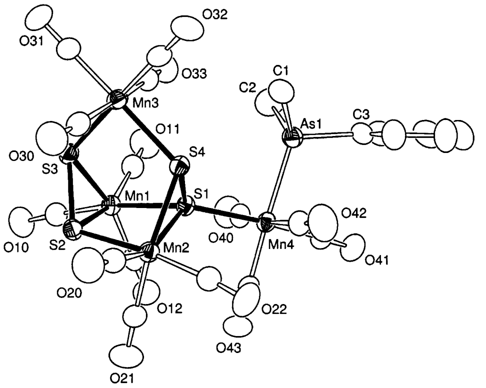


Figure 8. ORTEP diagram of the molecular structure of $Mn_4(CO)_{14}(AsMe_2Ph)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **8**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−S(1) = 2.3795(7), Mn(1)−S(2) = 2.3466(7), Mn(1)−S(3) = 2.3336(7), Mn(2)−S(1) = 2.4198(7), Mn(2)−S(2) = 2.3428(7), Mn(2)−S(4) = 2.3208(7), Mn(3)−S(3) = 2.3625(7), Mn(3)−S(4) = 2.3468(7), Mn(4)−S(1) = 2.4065(6), and Mn(4)−As(1) = 2.4454(5).

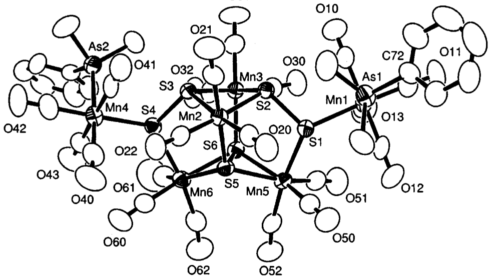


Figure 9. ORTEP diagram of the molecular structure of $Mn_6(CO)_{20}(AsMe_2Ph)_2(\mu_4\text{-}S_2)_3$, **9**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−S(1) = 2.4214(18), Mn(2)−S(2) = 2.3613(17), Mn(2)−S(3) = 2.3453(16), Mn(2)−S(5) = 2.3489(18), Mn(3)−S(2) = 2.3479(16), Mn(3)−S(3) = 2.3579(18), Mn(3)−S(6) = 2.3432(18), Mn(4)−S(4) = 2.4238(19), Mn(5)−S(1) = 2.3704(18), Mn(5)−S(5) = 2.4144(19), Mn(5)−S(6) = 2.4045(17), Mn(6)−S(4) = 2.3765(19), Mn(6)−S(5) = 2.4057(18), Mn(6)−S(6) = 2.4326(17), S(1)−S(2) = 2.079(2), S(3)−S(4) = 2.082(2), and S(5)−S(6) = 2.098(2).

An ORTEP diagram of the molecular structure of **8** is shown in Figure 8. Like compound **4**, compound **8** is a simple derivative of **3** and contains an $AsMe_2Ph$ on the manganese atom Mn(4) cis to the manganese−sulfur bond Mn(4)−S(1). All Mn−S bond distances in **8**, 2.3208(7)−2.4198(7) Å, are similar to those of **3** and **4**. Compound **8** can be obtained directly from **7** by thermal elimination of one $AsMe_2Ph$ ligand. The formation of **8** by loss of $AsMe_2Ph$ from **7** is achieved very simply. The manganese atom from which the $AsMe_2Ph$ ligand was lost forms a new bond to the second disulfido group, and after a slight rearrangement the structure of **8** is obtained; see Scheme 1. Likewise, compounds **3** and **4** are probably formed from similar open precursors analogous to **7**.

An ORTEP diagram of the structure **9** is shown in Figure 9. Compound **9** contains six manganese atoms and three μ_4-disulfido ligands. There are no metal−metal bonds, but all the metal atoms are linked through the bridging disulfido ligands. The S−S bond distances range from 2.079(2) to 2.098(2) Å and are slightly longer than that found in **2**, 2.0474(11) Å, but are similar to that found in **7**, 2.0701(15) Å. Each manganese atom in the central cluster core contains three terminal carbonyl ligands, but two of them, C(62)−O(62) and C(52)−O(52), are slightly nonlinear [Mn(6)−C(62)−O(62) = 169.1(7)° and Mn(5)−C(52)−O(52) =

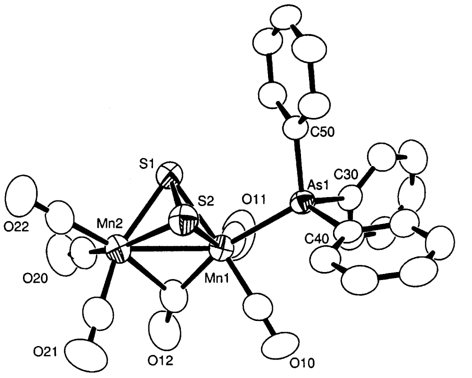


Figure 10. ORTEP diagram of the molecular structure of $Mn_2(CO)_6(AsPh_3)(\mu\text{-}S_2)$, **11**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−Mn(2) = 2.6740(7), Mn(1)−S(1) = 2.3016(1), Mn(1)−S(2) = 2.3013(10), Mn(2)−S(1) = 2.2813(12), Mn(2)−S(2) = 2.2839(11), S(1)−S(2) = 2.0390(14), Mn(1)−C(12) = 1.876(5), Mn(2)−C(12) = 2.238(4), and Mn(1)−As(1) = 2.4331(6).

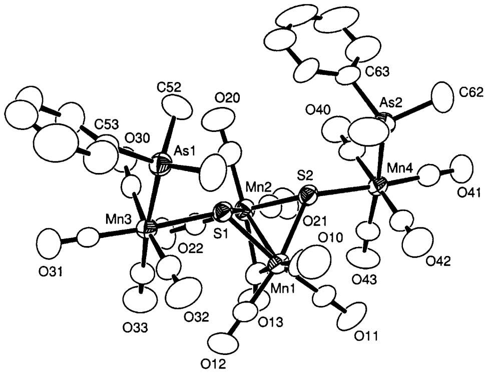
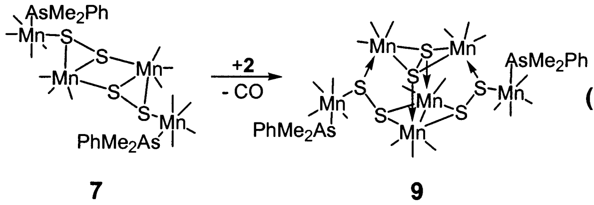


Figure 11. Side view of the molecular structure of $Mn_2(CO)_{15}(AsMe_2Ph)_2(\mu_3\text{-}S)_2$, **12**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−Mn(2) = 2.6354(18), Mn(1)−S(1) = 2.328(2), Mn(1)−S(2) = 2.343(3), Mn(2)−S(1) = 2.343(3), Mn(2)−S(2) = 2.347(3), Mn(3)−S(2) = 2.396(2), Mn(4)−S(2) = 2.400(3), S(1)−S(2) = 2.8284(30), Mn(1)−C(13) = 2.0074(11), and Mn(2)−C(13) = 2.052(10).

170.1(7)°]. This bending is probably due to the steric crowding in this region of the cluster. The disulfido ligands S(1)−S(2) and S(3)−S(4) serve as six-electron donors to the metal atoms. Ligand S(5)−S(6) serves as 10-electron donor, and all of the manganese atoms have 18-electron configurations. Compound **9** was also obtained from the reaction of **7** with **2** in 20% yield. It is easy to imagine the formation of **9** from **7** by addition of an $Mn_2(CO)_6(\mu\text{-}S_2)$ grouping with Mn−S bond rearrangements (eq 3). Thermal treatment of **8** at 40 °C also yields compound **9** in 20% yield.



(3)

The second minor product **10** could not be characterized crystallographically due to our inability to obtain single crystals of it, but its spectroscopic data indicate that it is probably the compound $Mn_2(CO)_6(AsMe_2Ph)(\mu\text{-}S_2)$, **10**, a simple $AsMe_2Ph$ derivative of **2**. It is analogous to the $AsPh_3$ derivative that we have also prepared and characterized; see below. The infrared spectrum of **10** in the CO region is similar to that of $Mn_2(CO)_6(PPh_3)(\mu\text{-}S_2)$[19] and exhibits a low-energy absorption band at 1877 cm^{-1} which is attributed to the bridging carbonyl ligand. The ^1H NMR spectrum of **10** exhibits multiple resonances at $\delta = 7.6-7.4$ ppm that can be assigned to the phenyl group of $AsMe_2Ph$ ligand and a single resonance at $\delta = 1.88$ ppm for the methyl groups on the $AsMe_2Ph$ ligand.

The simple arsine-substituted derivative of **2**, $Mn_2(CO)_6(AsPh_3)(\mu\text{-}S_2)$, **11**, was obtained and isolated from the reaction of **2** with an $AsPh_3$ (see Figure 10). The molecular structure of **11** is similar to that of $Mn_2(CO)_6(PPh_3)(\mu\text{-}S_2)$, which we obtained previously from the reaction of **2** with $CpCo(CO)(PPh_3)$.[19] The S−S distance in **11**, 2.0390(14) Å, is slightly shorter than that found in **2**, 2.0474(11) Å, and similar to that found in $Mn_2(CO)_6(PPh_3)(\mu\text{-}S_2)$, 2.0410(8) Å. The Mn−Mn bond distance, 2.6740(7) Å, is not significantly different from that found in **2**, 2.6745(5) Å, and in $Mn_2(CO)_6(PPh_3)(\mu\text{-}S_2)$, 2.6747(5) Å. Compound **11** also contains a semibridging carbonyl ligand with the strongest Mn−C bond to the arsine-substituted manganese atom, Mn(1)−C(12) = 1.876(5) Å and Mn(2)−C(12) = 2.238(4) Å. This can be explained similarly to that found in **6**; see above.

When **7** was allowed to react PMe_2Ph in methylene chloride solvent at room temperature, the new complex $Mn_4(CO)_{15}(AsMe_2Ph)_2(\mu_3\text{-}S)_2$, **12**, was obtained in 19% yield by abstraction of two of the sulfur atoms. Complex **12** was characterized by IR, ^1H NMR, elemental, and single-crystal X-ray diffraction analysis. The molecular structure of **12** is shown in Figure 11. Compound **12** has a structure analogous to that of **5**. The Mn−Mn bond distance, 2.6354(18) Å, is not significantly different from that of **5**, 2.6356(16) Å. The sulfur atoms are also not mutually bonded, S···S = 2.8284(30) Å. The bridging carbonyl ligand, C(13)−O(13), is very slightly asymmetrically coordinated, Mn(1)−C(13) = 2.074(11) Å and Mn(2)−C(13) = 2.052(10) Å. This is probably due to simple crystal packing effects. Compound **12** has 15 carbonyl ligands, one more carbonyl ligand than compound **7**, which must have been acquired at the expense of other molecules of **7**. This can help to explain the low yield of **12** in this reaction.

Discussion

The results of this study are summarized in Scheme 2. $Mn_2(CO)_9(NCMe)$ reacts with 2 equiv of thiirane to produce the disulfido complex **2** that is similar to the disulfido iron compound **1** except that **2** contains an additional carbonyl ligand that bridges the two metal atoms. The additional carbonyl ligand is required for the two manganese atoms to achieve 18-electron configurations. We found no evidence for a mono(sulfido)dimanganese complex although it seems reasonable to assume that such a species might have been traversed en route to **2**. Two bis(disulfido)tetramanganese minor products **3** and **4** were also formed. We showed independently that these are formed by reactions of **2** with CO and NCMe, respectively and it is likely that they were formed in this way in the original reaction of $Mn_2(CO)_9$-

(NCMe) with thiirane. The mechanism of aggregation will be discussed below. Interestingly, the reaction of **2** with PMe_2Ph did not yield a bis(*di*sulfido)tetramanganese products but yielded instead the bis(*mono*sulfido)tetramanganese product **5** and was accompanied by the formation of $PhMe_2P{=}S$. The formation of **5** involves a condensation of 2 equiv of **2** accompanied by the loss of two sulfur atoms which is explained by the formation of the $PhMe_2P{=}S$.

We believe that the key to understanding this unexpected condensation reaction is found in the reaction of **2** with $AsMe_2Ph$ that resulted in the formation of the bis(disulfido)-tetramanganese compound **7**, which possesses one more ligand and a more open structure than **3** and **4**; see Scheme 2. This became clearer when it was found that **7** was converted to the compound **8**, which also exhibits the same structure of the clusters of **3** and **4** by thermal elimination of one of its $AsMe_2Ph$ ligands. Accordingly, we propose that the compounds **3** and **4** are formed via unobserved intermediates analogous to **7** formed by the addition of one ligand to each of 2 equiv of **2**, dimerization, and then a ligand elimination to yield the final products. Indeed, we believe that the compound **5** is formed by a similar phosphine-substituted species analogous to **7**, and this was confirmed by the independent synthesis, isolation, and structural characterization of this intermediate **13**, which was obtained from the reaction of an activated form of the monophosphine derivative of $Mn_2(CO)_{10}$ with thiirane. Compound **13** was then transformed into **5** by abstraction of two sulfur atoms by treatment with free PMe_2Ph. In the reaction of **2** with PMe_2Ph there is always some free PMe_2Ph present and that would react with the intermediate **13** to transform it directly to **5**. The compound **13** can be isolated in the reaction of $Mn_2(CO)_9(PMe_2Ph)$ with thiirane only because the PMe_2Ph is coordinated to a manganese atom and apparently cannot react with the sulfido ligands as they are added to the manganese atoms. Interestingly, we found that **7** can also be converted into **12**, the bis(sulfido) analogue of **5** by sulfur abstraction with PMe_2Ph. Compound **12** was not obtained from the reaction of **2** with $AsMe_2Ph$. Apparently, $AsMe_2Ph$ is unable to abstract sulfur from **7**. The reason for this is very simple. As−S bonds are not as strong as P−S bonds,[20] so the sulfur abstraction reaction of **2** by $AsMe_2Ph$ does not proceed under the same conditions as those for PMe_2Ph. Because of this lower affinity for arsenic for sulfur, we were able to obtain compound **11**, the $AsPh_3$ substitution product of **2**. The reaction of **2** with PPh_3 does not yield the PPh_3 derivative of **2** although we have obtained this by other methods.[19]

The interesting tris(disulfido)hexamanganese compound **9** was obtained in low yield when **8** was heated. It appeared to us that **9** could be formed simply by a combination of **7** with **2** and loss of a single CO ligand. This was subsequently confirmed and, indeed, provided the best yield of **9**.

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere by using the standard Schlenk techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet 5DXBO FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 300 MHz. ^{31}P NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 161.9 MHz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). $Mn_2(CO)_{10}$ was purchased from Strem Chemical Co. Thiirane was purchased from Aldrich and vacuum distilled prior to use. $PPhMe_2$ and $AsPh_3$ were purchased from Aldrich and used as received. $Mn_2(CO)_9(NCMe)$,[21] $Mn_2(CO)_9(PMe_2Ph)$,[22] and $AsMe_2Ph$[23] were prepared according to the published procedures. Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

Synthesis of $Mn_2(CO)_7(\mu\text{-}S_2)$, 2. A sample of $Mn_2(CO)_9(NCMe)$ (98 mg, 0.243 mmol) was dissolved in 100 mL of hexane in a 100 mL three-neck round-bottom flask. To this solution, 30 μL (2 equiv) of vacuum-distilled pure thiirane was added via syringe and allowed to stir at room temperature for 24 h. The volatiles were removed in vacuo, and the products were separated by column chromatography over silica gel by using hexane/CH_2Cl_2 (3/1, v/v) solvent mixture as eluant. A 32.6 mg amount (36% yield) of a red product $Mn_2(CO)_7(\mu\text{-}S_2)$, **2**, 3.9 mg (4%) of an orange-brown product $Mn_4(CO)_{15}(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **3**, and 5.6 mg (6%) of an orange-brown product $Mn_4(CO)_{14}(NCMe)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **4**, were obtained in order of elution. Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane) 2079 (w), 2044 (vs), 2007 (m), 1982 (vs), 1946 (vw), 1894 (w); ^{13}C NMR (−25 °C, toluene-d_8) 212.5, 213.5, and 236.5. Anal. Calcd: C, 22.71. Found: C, 23.29. Spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane) 2140 (w), 2091 (m), 2065 (vs), 2031 (m), 2024 (vs), 2014 (s), 2008 (s), 1983 (m), 1958 (m), 1949 (w), 1934 (m), 1919 (w). Anal. Calcd: C, 23.45. Found: C, 23.54. Spectral data for **4**: IR ν_{CO} (cm^{-1} in hexane) 2116 (w), 2091 (m), 2047 (vs), 2036 (vs), 2021 (vs), 2010 (vs), 1997 (vs), 1979 (s), 1948 (s), 1939 (m), 1922 (m), 1907 (w); ^{1}H NMR ($CDCl_3$) 2.58 (bs, 3H). Anal. Calcd: C, 24.60; H, 0.38. Found: C, 24.46; H, 0.35.

Reaction of 2 with CO. A sample of **2** (79 mg, 0.2135 mmol) was dissolved in 15 mL of distilled hexane in a 25 mL three-neck round-bottom flask. CO gas was then slowly purged through this solution for 20 min, and it was then allowed to stir at room temperature for 24 h under CO atmosphere. After the solution was stirred, the solvent was removed in vacuo and the residue was separated on a silica gel column by using a hexane/CH_2Cl_2 (2/1, v/v) solvent mixture. This yielded 74 mg (90%) of **3**.

Reaction of 2 with MeCN. A sample of **2** (13.4 mg, 0.036 mmol) was dissolved in 15 mL of distilled MeCN in a 25 mL three-neck round-bottom flask. The red solution was allowed to stir at room temperature for 3 h. After the solution was stirred, the solvent was removed in vacuo and the residue was separated by TLC by using hexane/CH_2Cl_2 (3/2, v/v) solvent mixture to yield 1.3 mg (9%) of **4** and 3.6 mg of an unstable red product that could not be fully characterized. IR spectral data for the red product: ν_{CO} (cm^{-1} in CH_2Cl_2) 2091 (m), 2056 (s), 2018 (vs), 2003 (vs), 1970 (s), 1930 (s).

Reaction of 2 with PMe_2Ph. A sample of **2** (84.5 mg, 0.2285 mmol) was dissolved in 30 mL of hexane in a 50 mL three-neck round-bottom flask equipped with a stir bar, gas inlet, gas outlet, and a rubber septum. To this solution was added 32.5 μL (0.2285 mmol) of PMe_2Ph via syringe. An immediate color change from red to red-brown was observed. The solution was allowed to stir at

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(21) Koelle, U. J. *Organomet. Chem.* **1978**, *155*, 53.

(22) Reimann, R. H.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1976**, 2109.

(23) Burrows, G. J.; Turner, E. E. *J. Chem. Soc.* **1920**, *117*, 1373.

room temperature for 2 h. The precipitate was then collected by filtration, was washed with cold hexane (3 × 10 mL), and then was dried in vacuo. This yielded 45.3 mg (37%) of red-brown product $Mn_4S_2(CO)_{15}(PMe_2Ph)_2(\mu_3\text{-}S)_2$, **5**. Spectral data for **5**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2081 (m), 2069 (s), 2016 (vs), 1960 (m), 1934 (s); ^{1}H NMR (CD_2Cl_2) δ 7.48−7.69 (m, 10H), 2.07 (d, $^3J_{P-H}$ = 9 Hz, 12H); ^{31}P NMR ($CDCl_3$) δ 15.0 (s). Anal. Calcd for **5**·CH_2Cl_2: C, 36.08; H, 2.27. Found: C, 36.69; H, 2.12.

Reaction of 5 with PMe$_2$Ph. A sample of **5** (11.0 mg, 0.011 mmol) was dissolved in 5 mL of CH_2Cl_2 in a 25 mL three-neck round-bottomed flask. To this solution was added via syringe 1.65 μL of PMe_2Ph, and the mixture was then allowed to stir for 30 min. The volatiles were removed in vacuo, and the residue was separated by TLC by using hexane/methylene chloride (2/1, v/v) solvent mixture as eluant. **A** 5.3 mg (43% yield) amount of red-brown product $Mn_4(CO)_{14}(PMe_2Ph)_3(\mu_3\text{-}S_2)_2$, **6**, was obtained. Spectral data for **6**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2074 (m), 2065 (m), 2009 (sh), 1998 (vs), 1988 (s), 1951(m), 1909 (s); ^{1}H NMR (CD_2Cl_2) δ 7.7−7.3 (m, 15H), 2.037 (d, $^3J_{P-H}$ = 9 Hz, 16H), 1.966 (d, $^3J_{P-H}$ = 9 Hz, 16H), 1.346 (d, $^3J_{P-H}$ = 9 Hz, 16H); ^{31}P NMR ($CDCl_3$) δ 33.7, 20.5. Anal. Calcd C, 41.85; H, 3.05. Found: C, 41.53; H, 3.34.

Reaction of 6 with CO. A sample of **6** (5.3 mg, 0.0049 mmol) was dissolved in 15 mL of CH_2Cl_2 in a 25 mL three-neck round-bottomed flask. The resulting solution was purged with CO for 1 h at room temperature. The volatiles were removed in vacuo, and the residue was separated by TLC using a hexane/methylene chloride (3/2, v/v) solvent mixture as eluant. A 2.1 mg (44%) amount of **5** and 1.8 mg (34%) of unreacted **6** were obtained in order of elution.

Reaction of 2 with AsMe$_2$Ph. A sample of **1** (90 mg, 0.243 mmol) was dissolved in 40 mL of hexane in a 100 mL three-neck round-bottomed flask. To this solution was added via syringe 25 μL of $AsMe_2Ph$. This solution was then stirred at room temperature for 3 h. A precipitate formed and was filtered off, washed with cold hexane, and dried in vacuo to yield 82 mg (61%) of yellow product $Mn_4(CO)_{14}(AsMe_2Ph)_2(\mu_3\text{-}S_2)_2$, **7**. The filtrates was concentrated and separated by TLC using hexane/methylene chloride (2/1, v/v) solvent mixture as eluant. A 1.6 mg (1%) amount of red-brown product $Mn_2(CO)_6(AsMe_2Ph)(\mu\text{-}S_2)$, **10**, 17.6 mg (16%) of red-brown product $Mn_4(CO)_{14}(AsMe_2Ph)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$, **8**, and 1.5 mg (1%) of dark red product $Mn_6(CO)_{20}(AsMe_2Ph)_2)(\mu_4\text{-}S_2)_3$, **9**, were obtained in order of elution. Spectral data for **7**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2083 (m), 2013 (vs), 1991 (w), 1972 (w), 1912 (s); ^{1}H NMR (δ in CD_2Cl_2) 7.6−7.3 (m, 10H), 2.05 (d, 6H), 2.04 (d, 6H). Anal. Calcd for **7**: C, 34.63; H, 2.13. Found: C, 34.42; H, 2.25. Spectral data for **8**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2099 (w), 2088 (m), 2026 (vs), 2008 (sh), 1978 (m), 1938 (m); ^{1}H NMR (δ in CD_2Cl_2) 7.52 (m, 5H), 2.21 (s, 3H), 2.15 (s, 3H). Anal. Calcd for **8**: C, 28.65; H, 1.20. Found: C, 28.66; H, 1.13. Spectral data for **9**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2087 (m), 2041 (m), 2018 (vs), 1979 (w), 1939 (m); ^{1}H NMR (δ in CD_2Cl_2) 7.62−7.50 (m, 5H), 2.04 (s, 6H). Anal. Calcd for **9**: C, 29.89; H, 1.53. Found: C, 30.06; H, 1.40. Spectral data for **10**: IR ν_{CO} (cm^{-1} in hexane) 2043 (s), 2004 (s), 1999 (s), 1953 (vs), 1937 (w), 1877 (w); ^{1}H NMR (δ in CD_2Cl_2) 7.6−7.4 (m, 5H), 1.88 (s, 6H).

Reaction of 7 with 2. A sample of **7** (7.0 mg, 0.0063 mmol) and **2** (3.5 mg, 0.0095 mmol) were dissolved in 5 mL of methylene chloride in a 25 mL three-neck round-bottomed flask. This solution was heated to reflux with stirring for 3 h. The volatiles were removed in vacuo, and the residue was separated by TLC by using hexane/methylene chloride (2/1, v/v) solvent mixture as eluant. This yielded 2.6 mg (45%) of **8** and 2.2 mg (24%) of **9** in order of elution.

Thermolysis of 7. A sample of **7** (30.5 mg, 0.0276 mmol) was dissolved in 15 mL of methylene chloride in a 25 mL three-neck round-bottomed flask. This solution was heated to reflux for 1.5 h. The volatiles were removed in vacuo, and the residue was separated by TLC by using hexane/methylene chloride (2/1, v/v) solvent mixture as eluant. A 1.1 mg (4% yield) amount of **10**, 2.5 mg (10%) of **8**, and 2.6 mg (13%) of **9** were obtained in order of elution.

Thermolysis of 8. A sample of **8** (17.0 mg, 0.0184 mmol) was dissolved in 15 mL of methylene chloride in a 25 mL three-neck round-bottomed flask. This solution was heated to reflux for 5 h. The volatiles were removed in vacuo, and the residue was separated by TLC by using a hexane/methylene chloride (2/1, v/v) solvent mixture. This yielded 2.2 mg of unreacted **8** and 2.4 mg of **9** (21% yield based on the consumption of **8**).

Reaction of 2 with AsPh$_3$. A sample of **2** (15.5 mg, 0.0419 mmol) was dissolved in 10 mL of hexane in a 25 mL three-neck round-bottomed flask. To this solution was added 12.6 mg of $AsPh_3$. This solution was then stirred at room temperature for 20 h. The volatiles were removed in vacuo, and the residue was separated by TLC by using a hexane/methylene chloride (2/1. v/v) solvent mixture. A 2.0 mg (7%) of orange $Mn_2(CO)_6(AsPh_3)(\mu\text{-}S_2)$, **11**, was obtained. Spectral data for **11**: IR ν_{CO} (cm^{-1} in hexane) 2043 (s), 2003 (s), 1953 (vs), 1942 (sh), 1871 (w); ^{1}H NMR (δ in CD_2Cl_2) 7.5−7.2 (m, 15H). Anal. Calcd for **11**: C, 44.46; H, 2.33. Found: C, 44.49; H, 2.59.

Reaction of 7 with PMe$_2$Ph. A sample of **7** (23.3 mg, 0.021 mmol) was dissolved in 10 mL of methylene chloride in a 25 mL three-neck round-bottomed flask. To this solution was added 3.1 μL (1.0 equiv) of PMe_2Ph via syringe. The resulting solution was stirred at room temperature for 20 min. The volatiles were removed in vacuo, and the residue was separated by TLC by using a hexane/methylene chloride (1/1, v/v) solvent mixture. This yielded 4.2 mg (19%) of red-brown product $Mn_4(CO)_{15}(AsMe_2Ph)_2(\mu_3\text{-}S)_2$, **12**. Spectral data for **12**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2081 (w), 2069 (m), 2018 (vs), 1960 (w), 1934 (m); ^{1}H NMR (δ in CD_2Cl_2) 7.6−7.4 (m, 10H), 1.93 (s, 12H). Anal. Calcd for **12**: C, 34.85; H, 2.08. Found: C, 34.78; H, 1.91.

Preparation of Mn$_4$(CO)$_{14}$(PMe$_2$Ph)$_2$(μ_3-S$_2$)$_2$, 13. A sample of $Mn_2(CO)_9(PMe_2Ph)$ (97.2 mg, 0.194 mmol) was dissolved in 15 mL of MeCN in a 25 mL three-neck round-bottomed flask. To this solution was added 17.5 mg (0.2333 mmol) of Me_3NO, and the mixture was allowed to stir for 1 h. The resulting solution was passed through a 10 cm silica gel fitted glass frit. The volatiles were removed in vacuo, and the residue was redissolved in a 50 mL of hexane/2 mL of CH_2Cl_2 solvent mixture. A 23.3 μL volume of thiirane was added via syringe and allowed to stir for 12 h. The volatiles were removed in vacuo, and the residue was separated by TLC using a hexane/methylene chloride (3/2, v/v) solvent mixture as eluant to yield 4.6 mg (5%) of unreacted $Mn_2(CO)_9(PMe_2Ph)$ and 29.1 mg (31%) of orange product $Mn_4(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S_2)_2$, **13**, in order of elution. Spectral data for **13**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2083 (m), 2009 (vs), 1988 (m), 1971 (m), 1911 (s); ^{1}H NMR (δ in CD_2Cl_2) 7.67−7.53 (m, 10H), 2.162 (d, J_{P-H} = 9 Hz, 6H), 2.155 (d, J_{P-H} = 9 Hz, 6H). Anal. Calcd for **13**: C, 35.45; H, 2.18. Found: C, 34.96; H, 2.03.

Reaction of 13 with PMe$_2$Ph. A sample of **13** (10.0 mg, 0.01 mmol) was dissolved in 3 mL of CH_2Cl_2 in a 25 mL three-neck round-bottomed flask. To this solution was added via syringe 2 equiv of PMe_2Ph and allowed to stir for 5 min. The volatiles were removed in vacuo, and the residue was separated by TLC by using

Table 1. Crystallographic Data for Compounds **2**−**5**

	2	**3**	**4**	**5**
empirical formula	$Mn_2S_2(CO)_7$	$Mn_4S_4(CO)_{15}$	$Mn_4S_4(CO)_{14}(NCMe)$	$Mn_4S_2(CO)_{15}(PMe_2Ph)_2 \cdot CH_2Cl_2$
fw	370.07	768.15	781.19	1150.16
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
lattice params				
a (Å)	6.8528(6)	9.3161(7)	9.619(2)	27.827(2)
b (Å)	10.0584(9)	15.5165(11)	16.059(2)	33.959(3)
c (Å)	17.306(2)	18.1976(13)	18.349(3)	9.4488(7)
α (deg)	90	90	90	90
β (deg)	90	96.028(2)	101.00(1)	90
γ (deg)	90	90	90	90
V (Å^3)	1190(2)	2616.0(3)	2782.4(7)	8929(1)
space group	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$Fdd2$ (No. 43)
Z value	4	4	4	4
ρ_{calc} (g/cm^3)	2.061	1.950	1.87	1.711
μ(Mo Kα) (mm^{-1})	2.485	2.273	21.37	1.573
temp (K)	293	293	293	190
$2\theta_{max}$ (deg)	52.76	52.8	43	52.80
no. of obsvns ($I > 2\sigma(I)$)	2326	3822	2582 ($I > 3\sigma(I)$)	4027
no. of params	163	343	353	274
goodness of fit	1.002	0.908	1.257	1.045
residuals: R1; wR2	0.0257; 0.0601	0.0374;0.0745	0.0324;0.0538	0.0504; 0.1331

Table 2. Crystallographic Data for Compounds **6**−**9**

	6	**7**	**8**	**9**
empirical formula	$Mn_4(CO)_{14}S_2(PMe_2Ph)_2 \cdot CH_2Cl_2$	$Mn_4(CO)_{14}S_4(AsMe_2Ph)_2$	$Mn_4(CO)_{14}S_4(AsMe_2Ph)$	$Mn_6(CO)_{20}S_6(AsMe_2Ph)_2$
fw	1175.36	1104.32	923.23	1446.38
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
lattice params				
a (Å)	10.5722(13)	29.1471(13)	9.0561(4)	9.9165(5)
b (Å)	21.011(3)	10.1212(4)	25.9062(11)	12.1757(6)
c (Å)	21.996(3)	14.7477(6)	13.7679(6)	22.3393(11)
α (deg)	90	90	90	87.392(1)
β (deg)	99.457(3)	108.551(1)	91.449(1)	89.006(1)
γ (deg)	90	90	90	71.276(1)
V (Å^3)	4819.6(11)	4124.6(3)	3229.5(2)	2551.8(2)
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z value	4	4	4	2
ρ_{calc} (g/cm^3)	1.620	1.778	1.897	1.882
μ(Mo Kα) (mm^{-1})	1.382	3.051	2.866	3.043
temp (K)	173	296	296	296
$2\theta_{max}$ (deg)	50.14	48.82	56.62	48.82
no. of obsvns ($I > 2\sigma(I)$)	6372	2577	6440	5414
no. of params	602	246	408	635
goodness of fit	1.027	1.002	1.048	1.000
residuals: R1; wR2	0.0482; 0.1224	0.0386; 0.0802	0.0334; 0.0711	0.0488; 0.0861

a hexane/methylene chloride (3/2, v/v) solvent mixture as eluant. This yielded 1.0 mg (10%) of **5**.

Crystallographic Analyses. Red crystals of **2** were grown from a hexane solution of the complex by cooling to −80 °C. Red crystals of **3**−**6, 8**, **9**, and **12**, yellow crystals of **7**, and orange crystals of **11** and **13** were grown by slow evaporation of the solvent from solutions of the complexes in hexane/CH_2Cl_2 (1:1) mixtures at −17 °C. The crystals of **2**, **3**, **7**−**9**, and **11**−**13** used in data collections were each glued onto the end of a thin glass fiber. The crystals of **5** and **6** used for data collection were frozen in oil onto the end of a thin glass fiber. X-ray intensity data for each structural analysis were measured on a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation (λ = 0.710 73 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 Tables 1−3. The raw intensity data frames were integrated with the SAINT+ program[24] that also applied corrections for Lorentz and polarization effects. 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 using the program SADABS.[25] All of the structures were solved by a combination direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were calculated by assuming idealized geometries and refined using the riding model. Refinements was carried out on F^2 by the method of full-matrix least squares by using the SHELXTL program library with neutral atom scattering factors.[25]

The data crystal of **4** was mounted in a thin-walled glass capillary. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation at 20 °C. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing

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

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

Table 3. Crystallographic Data for Compounds **11**−**13**

	11	**12**	**13**
empirical formula	$Mn_2(CO)_6S_2(AsPh_3)$	$Mn_4(CO)_{15}S_2(AsMe_2Ph)_2$	$Mn_4(CO)_{14}S_4(PMe_2Ph)_2$
fw	648.28	1068.21	1016.42
cryst syst	monoclinic	monoclinic	monoclinic
lattice params			
a (Å)	10.9214(5)	9.5812(14)	29.1716(18)
b (Å)	13.5672(7)	25.939(4)	10.0622(6)
c (Å)	17.6707(8)	16.459(2)	14.5491(9)
α (deg)	90	90	90
β (deg)	100.991(1)	102.061(4)	108.695(1)
γ (deg)	90	90	90
V (Å^3)	2570.3(2)	4000.9(10)	4045.3(4)
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
Z value	4	4	4
ρ_{calc} (g/cm^3)	1.675	1.773	1.669
μ(Mo Kα) (mm^{-1})	2.460	3.044	1.566
temp (K)	293	296	293
$2\theta_{max}$ (deg)	52.86	48.82	52.80
no. of obsvns ($I > 2\sigma(I)$)	3757	3249	3227
no. of params	316	491	246
goodness of fit	0.941	1.000	0.923
residuals: R1; wR2	0.0420; 0.0827	0.0610; 0.0956	0.0309; 0.0735

was performed on a Silicon Graphic Indigo 2 computer by using the TEXSAN motif structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures.[26a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[26b] Lorentz/polarization (Lp) and absorption corrections were applied to the data for each structure. Full matrix least-squares refinements minimized the function $\Sigma_{hkl}w(|F_o| \angle |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.06)I_{net})^2]^{1/2}/Lp$.

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Supporting Information Available: CIF tables for the structural analyses of **2**−**9** and **11**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0203670

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(26) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, pp 99−101, Table 2.2B. (b) Ibid., pp 149−150, Table 2.3.1.