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Insertion of Cyclopentadienylmetal Groups into the S−S Bond of $Mn_2(CO)_7(\mu\text{-}S_2)$

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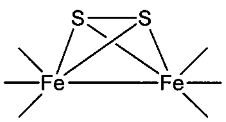
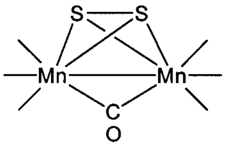
The reaction of $Mn_2(CO)_7(\mu\text{-}S_2)$, **2**, with $CpCo(CO)_2$ and $Cp^*Rh(CO)_2$ ($Cp^* = C_5Me_5$) yielded the new complexes $CpCoMn_2(CO)_6(\mu_3\text{-}S)_2$, **3**, and $Cp^*RhMn_2(CO)_6(\mu_3\text{-}S)_2$, **4**, in 79% and 38% yields, respectively. The reaction of **2** with $CpCo(CO)(PPh_3)$ yielded **3**, $CpCoMn_2(CO)_5(PPh_3)(\mu_3\text{-}S)_2$, **5** (a phosphine derivative of **3**), and $Mn_2(CO)_6(PPh_3)(\mu\text{-}S_2)$, **6** (a phosphine derivative of **2**). Compound **5** was also obtained in 88% yield from the reaction of **3** with PPh_3. All new products were characterized crystallographically. Compounds **3**−**5** are structurally similar and consist of a triangular Mn_2M cluster with triply bridging sulfido ligands on each side of the Mn_2M plane. Compound **6** contains an asymmetrical semibridging carbonyl ligand that is most strongly associated with the phosphine-substituted manganese atom.

Introduction

The simplest disulfide of iron carbonyl, $Fe_2(CO)_6(\mu\text{-}S_2)$, **1**, was first reported by Hieber in 1958[1] and has been extensively investigated over the years.[2−4] The chemistry of **1** is dominated by reactions at the sulfur atoms.[2−4] Reactions of **1** with metal complexes often proceeds by insertion of the metal atom into the sulfur−sulfur bond.[4] We have recently prepared the new simple disulfide of manganese carbonyl, $Mn_2(CO)_7(\mu\text{-}S_2)$, **2**, from the reaction of $Mn_2(CO)_9(NCMe)$ with thiirane.[5]

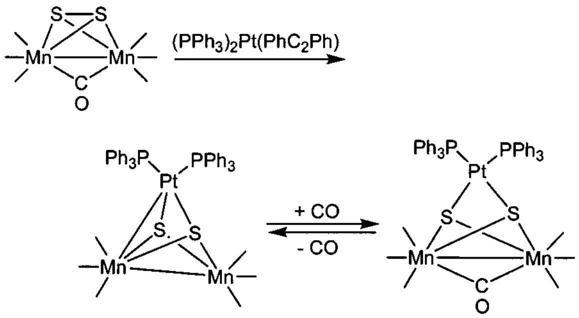


1



2

Compound **2** reacts with the platinum complex $Pt(PPh_3)_2(PhC_2Ph)$ by elimination of the PhC_2Ph ligand and insertion of the $Pt(PPh_3)_2$ fragment into the S−S bond to yield the complex $PtMn_2(CO)_6(PPh_3)_2(\mu_3\text{-}S)_2$.[6] Interestingly, $PtMn_2(CO)_6(PPh_3)_2(\mu_3\text{-}S)_2$ reversibly adds CO at 25 °C and 1 atm of pressure by an opening and closing of the Pt−Mn bond, eq 1.[6]



1)

In a continuation of our studies of the chemistry of **2**, we have now investigated its reactions with the complexes $CpCo(CO)_2$, $CpCo(CO)(PPh_3)$, and $Cp^*Rh(CO)_2$. All of these reactions proceed by loss of CO and facile insertion of the Cp-metal fragment into the S−S bond. All of the products have been characterized crystallographically. The results of these studies are reported here.

Results and Discussion

The reaction of $Mn_2(CO)_7(\mu\text{-}S_2)$, **2**, with $CpCo(CO)_2$ and $Cp^*Rh(CO)_2$ ($Cp^* = C_5Me_5$) yielded the new complexes $CpCoMn_2(CO)_6(\mu_3\text{-}S)_2$, **3**, and $Cp^*RhMn_2(CO)_6(\mu_3\text{-}S)_2$, **4**, in 79% and 38% yields, respectively. The infrared spectra of compounds **3** and **4** show absorptions consistent with terminal carbonyl ligands only. The ^1H NMR spectrum of **3** exhibits a single resonance at $\delta = 4.70$ ppm that can be assigned to the cyclopentadienyl group. The ^1H NMR spectrum of **4** exhibits a single resonance at $\delta = 1.80$ ppm for the methyl groups on the Cp* ring.

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10.1021/om020028e CCC: $22.00

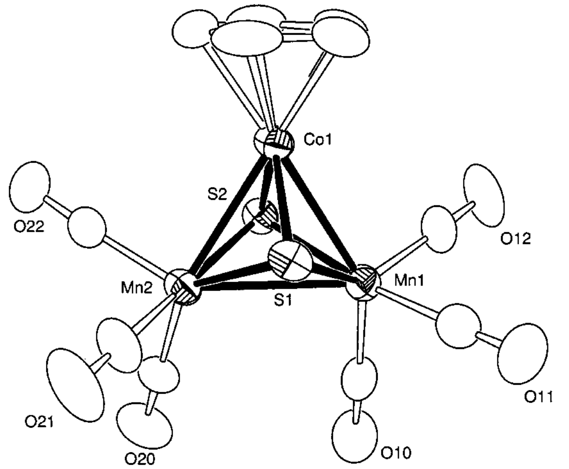

Figure 1. ORTEP diagram of $CpCoMn_2(CO)_6(\mu_3\text{-}S)_2$, **3**, showing 50% probability thermal ellipsoids. Selected bond distances (Å): Mn(1)−Mn(2) = 2.7714(7), Mn(1)−S(1) = 2.2013(10), Mn(1)−S(2) = 2.2386(9), Mn(2)−S(1) = 2.2114(9), Mn(2)−S(2) = 2.2547(9), Mn(1)−Co(1) = 2.6163(6), Mn(2)−Co(1) = 2.5966(6).

The molecular structure of **3** is shown in Figure 1. Selected bond distances are listed in Table 1. The crystal of **3** contains two independent molecules in the asymmetric crystal unit. The compound contains a triangular cluster of two manganese and one cobalt atom with a triply bridging sulfido ligand on each side of the Mn_2-Co plane. There are three metal−metal bonds. Because of the larger size of manganese, the Mn−Mn bond, Mn(1)−Mn(2) = 2.7714(7) Å [Mn(3)−Mn(4) = 2.7724(7) Å], is slightly longer than the Mn−Co bonds: Mn(1)−Co(1) = 2.6163(6) Å, Mn(2)−Co(1) = 2.5966(6) Å [Mn(3)−Co(2) = 2.6001(6) Å, Mn(4)−Co(2) = 2.5951(6) Å]. The Mn−Mn distance in **3** is also significantly longer than that observed in **2**, 2.6745(5) Å,[5] and in $Mn_2(CO)_7(\mu_3\text{-}S)_2Pt(PPh_3)_2$, 2.638(2) Å,[6] but is slightly shorter than that in $Mn_2(CO)_6(\mu_3\text{-}S)_2Pt(PPh_3)_2$, 2.8154(14) Å. It is significantly shorter than the Mn−Mn bond distance observed in $Mn_2(CO)_{10}$, 2.895(1)[7] and 2.9038(6) Å,[8] which contains no bridging carbonyl ligands. The Mn−S distances, 2.2013(10)−2.2547(9) Å, are slightly shorter than those in $Mn_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2$, but are not unusual when compared with other Mn_2S_2 analogues.[5] The Co−S bond distances in **3** [2.1401(9)−2.1628(9) Å] are similar to those found in $Cp^*CoFe_2S_2(CO)_6$ [2.158(2) and 2.165(2) Å].[4a]

An ORTEP diagram of the molecular structure of $Cp^*RhMn_2(CO)_6(\mu_3\text{-}S)_2$, **4**, is shown in Figure 2. Selected bond distances are listed in Table 1. The structure is very similar to that of **3** and also contains two independent molecules in the crystal. The Mn−Mn distance in **4**, 2.7794(9) Å [2.7886(9) Å], is very similar to that in **3**. As expected, the Mn−Rh bond distances [range 2.7308(7)−2.7858(7) Å] are significantly longer than the Mn−Co distances found in **3**, but are typical of those found in complexes containing Mn−Rh bonds.[9]

The reaction of **2** with $CpCo(CO)(PPh_3)$ at 25 °C for 24 h yielded three compounds. The major product was **3**. The two minor products were identified as $CpCoMn_2(CO)_5(PPh_3)(\mu_3\text{-}S)_2$, **5**, 5% yield, and $Mn_2(CO)_6(PPh_3)(\mu\text{-}S_2)$, **6**, 12% yield. Compound **5** was not obtained when the reaction was performed at 0 °C, but was obtained independently in very good yield (88%) from the reaction of **3** with PPh_3 at 25 °C. Compounds **5** and **6** were both characterized by a combination of IR, ^1H NMR, ^{31}P NMR, and single-crystal X-ray diffraction analysis. Compound **5** is a simple phosphine-substituted derivative of **3**. An ORTEP diagram of the molecular structure of **5** is shown in Figure 3. Selected bond distances for **5** are listed in Table 1. The manganese−manganese and manganese−cobalt distances in **5** are not significantly different from those in **3**: Mn(1)−Mn(2) = 2.7792(6) Å; Mn(1)−Co(1) = 2.6010(6) Å, Mn(2)−Co(1) = 2.6319(6) Å. Interestingly, the PPh_3 ligand is coordinated to one of the manganese atoms, Mn(1)−P(1) = 2.2892(8) Å, and not the cobalt atom to which it was originally coordinated.

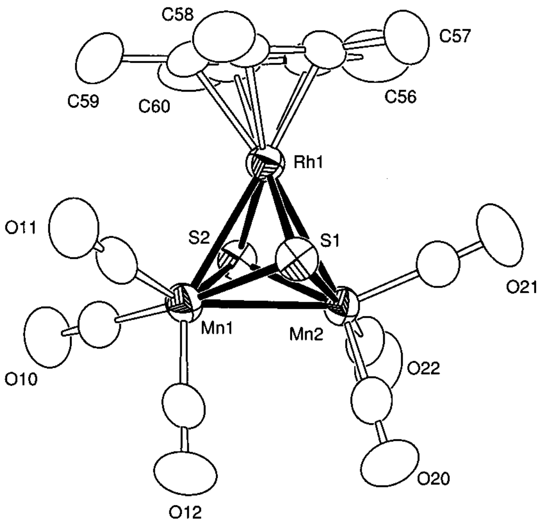

Figure 2. ORTEP diagram of the molecular structure of $Cp^*RhMn_2(CO)_6(\mu_3\text{-}S)_2$, **4**, showing 50% probability thermal ellipsoids. Selected bond distances for two independent molecules (Å): Mn(1)−Mn(2) = 2.7886(9), Mn(3)−Mn(4) = 2.7794(9), Mn(1)−S(1) = 2.2696(12), Mn(1)−S(2) = 2.2159(12), Mn(2)−S(1) = 2.2571(12), Mn(2)−S(2) = 2.2222(12), Mn(3)−S(3) = 2.2259(13), Mn(3)−S(4) = 2.2627(12), Mn(4)−S(3) = 2.2239(12), Mn(4)−S(4) = 2.2646(13), Mn(1)−Rh(1) = 2.7308(7), Mn(2)−Rh(1) = 2.7761(7), Mn(3)−Rh(2) = 2.7858(7), Mn(4)−Rh(2) = 2.7473(7).

An ORTEP diagram of compound **6** is shown in Figure 4. Selected bond distances are listed in Table 1. Compound **6** is structurally similar to that of the parent complex **2** with the exception of the presence of the phosphine ligand. It contains a bridging disulfide ligand, S−S = 2.0410(8) Å, which is similar to that found in **2**, where S−S = 2.0474(11) Å.[5] The Mn−Mn bond distance, 2.6747(5) Å, is not significantly different from that found in **2**, 2.6745(5) Å. Compound **6** contains a strong semibridging carbonyl ligand, C(12)−O(12). This ligand

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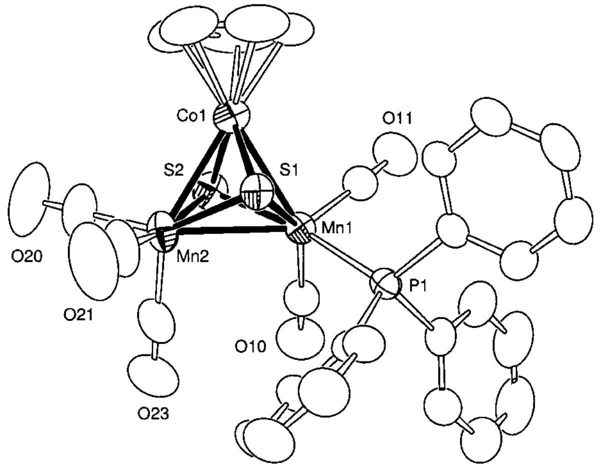


Figure 3. ORTEP diagram of $CpCoMn_2(CO)_5(PPh_3)(\mu_3\text{-}S)_2$, **5**, showing 50% probability thermal ellipsoids. Selected bond distances (Å): Mn(1)−Mn(2) = 2.7792(6), Mn(1)−S(1) = 2.2019(8), Mn(1)−S(2) = 2.2254(8), Mn(2)−S(1) = 2.2281(8), Mn(2)−S(2) = 2.2564(9), Mn(1)−Co(1) = 2.6010(6), Mn(2)−Co(1) = 2.6319(6).

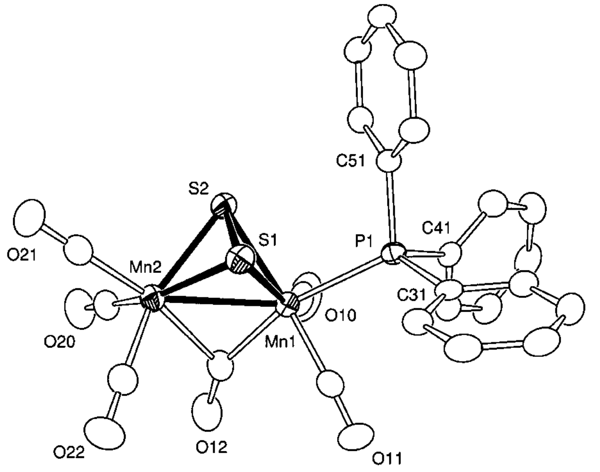
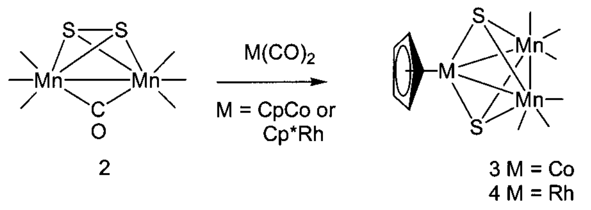


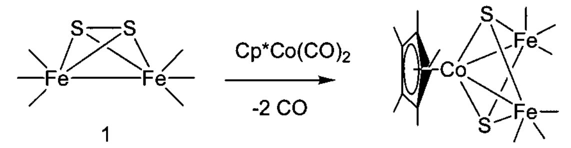
Figure 4. ORTEP diagram of $Mn_2(CO)_6(PPh_3)(\mu\text{-}S_2)$, **6**, showing 50% probability thermal ellipsoids. Selected bond distances (Å): Mn(1)−Mn(2) = 2.6747(5), Mn(1)−S(1) = 2.3036(6), Mn(1)−S(2) = 2.3097(6), Mn(2)−S(1) = 2.2924(7), Mn(2)−S(2) = 2.2870(7), S(1)−S(2) = 2.0410(8), Mn(1)−C(12) = 1.900(2), Mn(2)−C(12) = 2.204(2).

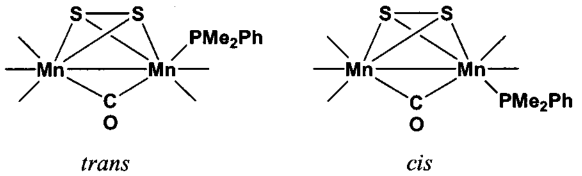
exhibits a low-energy absorption in the infrared at 1868 cm^{-1}. The ligand is most strongly associated to Mn(1) [Mn(1)−C(12) = 1.900(2) Å versus Mn(2)−C(12) = 2.204(2) Å], the same metal atom that contains the phosphine ligand, Mn(1)−P(1) = 2.3465(6) Å. The shift of the bridging CO ligand toward this metal atom can be explained as a compensation effect for the replacement of one of the terminal CO ligands on Mn(1) by the less efficient π-accepting phosphine ligand. We have observed similar effects on the bridging CO ligand in phosphine derivatives of the dimanganese dithiolate complex $Mn_2(SCH_2CH_2S)(CO)_7$.[10] Interestingly, the ^{31}P NMR spectrum shows two resonances, δ = 60.34 and 44.11 ppm. We believe that this can be explained by the existence of two slowly interconverting isomers of **6**; one with the structure shown in Figure 4 and another with the phosphine ligand in a site cis to the bridging CO ligand; see line structures below.

Scheme 1

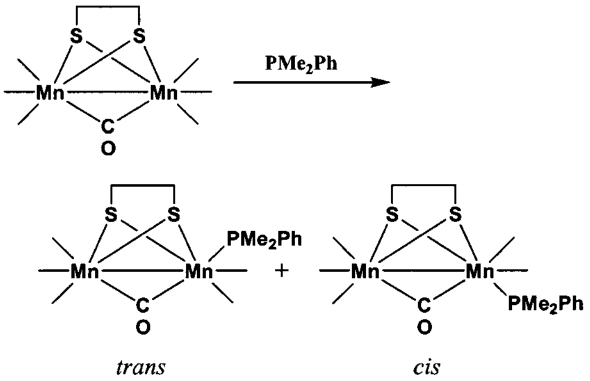


Scheme 2





Similar isomerism was observed for the related compound $Mn_2(\mu\text{-}SCH_2CH_2S)(CO)_6(PMe_2Ph)$, eq 2.[10]



(2)

The formation of compounds **3** and **4** can be imagined simply as the loss of the two CO ligands from the cobalt and rhodium atoms of $CpCo(CO)_2$ and $Cp^*Rh(CO)_2$, the loss of one CO ligand from the manganese complex **2**, insertion of the Cp-metal fragment into the sulfur−sulfur bond of the disulfide ligand, and formation of two new metal−metal bonds; see Scheme 1.

For comparison, the reaction of $Cp^*Co(CO)_2$ with **1** proceeds by loss of the two CO ligands from the cobalt complex and insertion of the cobalt atom into the S−S bond of the disulfide ligand; however in this case no ligands are eliminated from the iron atoms and the formation of the two Fe−Co bonds induces cleavage of the iron−iron bond; see Scheme 2.[4a] The cleavage of the Fe−Fe bond is required in order to preserve the 18-electron configurations at the two iron atoms.

By contrast, in these reactions of **2** there is also a loss of one CO ligand from the manganese atoms, and as a result, cleavage of the manganese−manganese bond is not required upon formation of the two manganese−cobalt bonds in **3**; indeed the manganese−manganese

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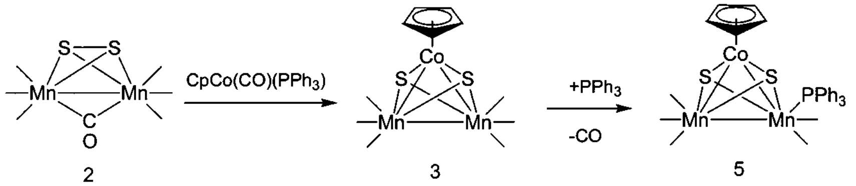
[10] Adams, R. D.; Kwon, O. S.; Smith, M. D. *Isr. J. Chem.*, submitted.

Scheme 3



Scheme 4

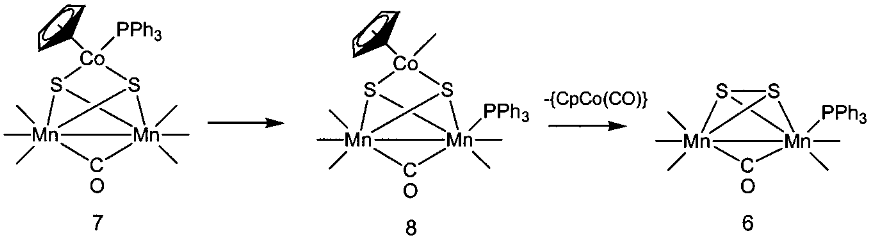


Table 1. Selected Bond Distances for Compounds 3, 4, 5, and 6

compound	Mn−Mn	Mn−S	Mn−M (M = Co or Rh)
3	Mn(1)−Mn(2) = 2.7714(7) Mn(3)−Mn(4) = 2.7724(6)	Mn(1)−S(1) = 2.2013(10) Mn(1)−S(2) = 2.2386(9) Mn(2)−S(1) = 2.2114(9) Mn(2)−S(2) = 2.2547(9) Mn(3)−S(3) = 2.2041(9) Mn(3)−S(4) = 2.2543(9) Mn(4)−S(3) = 2.1971(9) Mn(4)−S(4) = 2.2589(9)	Mn(1)−Co(1) = 2.6163(6) Mn(2)−Co(1) = 2.5966(6) Mn(3)−Co(2) = 2.6001(6) Mn(4)−Co(2) = 2.5951(6)
4	Mn(1)−Mn(2) = 2.7886(9) Mn(3)−Mn(4) = 2.7794(9)	Mn(1)−S(1) = 2.2696(12) Mn(1)−S(2) = 2.2159(12) Mn(2)−S(1) = 2.2571(12) Mn(2)−S(2) = 2.2222(12) Mn(3)−S(3) = 2.2259(13) Mn(3)−S(4) = 2.2627(12) Mn(4)−S(3) = 2.2239(12) Mn(4)−S(4) = 2.2646(13)	Mn(1)−Rh(1) = 2.7308(7) Mn(2)−Rh(1) = 2.7761(7) Mn(3)−Rh(2) = 2.7858(7) Mn(4)−Rh(2) = 2.7473(7)
5	Mn(1)−Mn(2) = 2.7792(6)	Mn(1)−S(1) = 2.2019(8) Mn(1)−S(2) = 2.2254(8) Mn(2)−S(1) = 2.2281(8) Mn(2)−S(2) = 2.2564(9)	Mn(1)−Co(1) = 2.6010(6) Mn(2)−Co(1) = 2.6319(6)
6	Mn(1)−Mn(2) = 2.6747(5)	Mn(1)−S(1) = 2.2924(7) Mn(1)−S(2) = 2.2870(7) Mn(2)−S(1) = 2.3036(6) Mn(2)−S(2) = 2.3097(6)	

bond must be preserved in order for the manganese atoms to maintain 18-electron configurations in the product.

The formation of **5** from **2** and CpCo(CO)(PPh$_3$) may be analogous to the formation of **3** with the addition of a phosphine/CO substitution step, Scheme 3. We showed independently that **3**, which is also formed in the initial reaction, will react with free phosphine to yield **5** in good yield (88%) under similar conditions.

Interestingly, compound **6**, a phosphine derivative of **2**, was also obtained in the reaction of **2** with CpCo(CO)(PPh$_3$). Curiously, we have found in previous work that **2** does not react with free phosphines including PPh$_3$ to yield phosphine derivatives of **2**.[5] This suggests that the formation of **6** may have occurred by an intramolecular phosphine exchange process of some sort that might have involved some unobserved intermediate species such as **7** and **8**; see Scheme 4. The intermediate **7** could also be a precursor to **3** and **5**.

Our studies reported here further demonstrate the viability of the new manganese disulfide compound **2** to serve as a reagent for the synthesis of new sulfidomanganese carbonyl compounds. With appropriate allowances for the smaller number of electrons that manganese possesses, the mixed metal products obtained from these reactions of **2** are similar in many respects to those obtained from the corresponding reactions of compound **1**.

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were dried by 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 400 MHz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). CpCo(CO)$_2$ (Cp = C$_5$H$_5$) and Cp*Rh(CO)$_2$ (Cp* = C$_5$Me$_5$) were purchased from Strem Co. and were used without further purification. CpCo(CO)(PPh$_3$)[11] was prepared according to the published procedures. Unless indicated otherwise, product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

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Table 2. Crystallographic Data for Compounds 3−6

	3	4	5	6
empirical formula	$Mn_2CoS_2O_6C_{11}H_5$	$Mn_2RhS_2O_6C_{11}H_5$	$Mn_2CoS_2PO_5C_{28}H_{20}$	$Mn_2S_2PO_6C_{24}H_{15}$
fw	466.08	580.19	700.34	604.33
cryst syst	triclinic	triclinic	monoclinic	monoclinic
lattice params				
a (Å)	10.0593(5)	9.0984(5)	10.7639(7)	10.6883(10)
b (Å)	12.5617(7)	13.5527(7)	25.0939(16)	13.5221(12)
c (Å)	14.5614(8)	17.7743(9)	11.6339(8)	17.5040(16)
α (deg)	110.7110(10)	92.7230(10)	90	90
β (deg)	95.0770(10)	94.4110(10)	112.3810(10)	100.924(2)
γ (deg)	112.0260(10)	102.3520(10)	90	90
V (Å^3)	1542.73(14)	2130.03(19)	2905.6(3)	2484.0(4)
space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
Z value	4	4	4	4
ρ_{calc} (g/cm^3)	2.007	1.809	1.601	1.616
μ(Mo Kα) (mm^{-1})	2.966	2.156	1.655	1.287
temperature (K)	293	293	293	190
$2\theta_{max}$ (deg)	52.80	52.80	52.78	52.88
no. obsd ($I > 2\sigma(I)$)	4418	5906	4544	4286
no. variables	398	498	352	316
goodness of fit	0.989	0.930	1.000	0.996
max. shift in final cycle	0.001	0.001	0.001	0.001
residuals: R_1; wR_2	0.0325; 0.0550	0.0372; 0.0692	0.0373; 0.0840	0.0317; 0.0747
abs corr (max./min.)	SADABS	SADABS	SADABS	SADABS
transmn coeff, max./min.	0.745−0.494	0.862−0.648	0.894−0.736	0.831−0.621
largest peak in final diff Fourier (e$^-$/Å^3)	0.452	0.512	0.414	0.331

Preparation of $Mn_2(CO)_7(\mu\text{-}S_2)$, 2. $Mn_2(CO)_9(NCMe)$ (98 mg, 0.243 mmol) was dissolved in 100 mL of hexane in a 200 mL three-neck round-bottom flask equipped with a stir bar and gas inlet. To this solution was added 30 μL (2 equiv) of vacuum distilled thiirane via syringe. The solution was allowed to stir at 25 °C for 24 h. The reaction mixture was then concentrated, and the product was isolated by column chromatography over 20 cm silica gel using hexane solvent to elute. A red band was collected, and the solvent was removed in vacuo. The residue was redissolved in a minimal amount of hexane/methylene chloride (5:1, v/v), and the product was obtained in a pure form by crystallization at −80 °C over a period of 12 h. A total of 32.6 mg of red crystals of $Mn_2(CO)_7S_2$, **2** (36% yield), was obtained. 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.

Reaction of 2 with $CpCo(CO)_2$. Compound **2** (20.0 mg, 0.054 mmol) was dissolved in 5 mL of deoxygenated THF in a 25 mL three-neck round-bottomed flask equipped with a stir bar and a nitrogen inlet. To this solution was added 6.0 μL of $CpCo(CO)_2$ via syringe. This solution was stirred at 25 °C for 4 h. The volatiles were removed in vacuo, and the product was separated by TLC using hexane solvent as an eluant to yield 21.1 mg of $CpCoMn_2(CO)_6(\mu_3\text{-}S)_2$, **3**, 79% yield. Spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane) 2044 (s), 2007 (vs), 1978 (m), 1956 (sh); ^{1}H NMR (δ in $CDCl_3$) 4.70 (s, 5H). Anal. Calcd: C, 28.34; H, 1.08. Found: C, 28.54; H 1.24.

Synthesis of $Cp^*RhMn_2(CO)_6(\mu_3\text{-}S)_2$, 4. Compound **2** (8.1 mg, 0.022 mmol) and $Cp^*Rh(CO)_2$ (6.5 mg, 0.022 mmol) were dissolved in 10 mL of THF in a 25 mL three-neck round-bottomed flask equipped with a stir bar and a nitrogen inlet. This solution was stirred at 25 °C for 6 h. The volatiles were removed in vacuo. The product was separated by TLC by using hexane/methylene chloride (3:1, v/v) solvent mixture as an eluant. A total of 4.2 mg (38% yield) of $Cp^*RhMn_2(CO)_6(\mu_3\text{-}S)_2$, **4**, was obtained. Spectral data for **4**: IR ν_{CO} (cm^{-1} in hexane) 2034 (s), 1999 (vs), 1972 (sh), 1959 (w), 1948 (sh); ^{1}H NMR (δ in $CDCl_3$) 1.8 (s, 15H). Anal. Calcd: C, 33.12; H, 2.61. Found: C, 32.98; H, 2.59.

Reaction of 2 with $CpCo(CO)(PPh_3)$ at 0 °C. Compound **2** (10.0 mg, 0.027 mmol) and $CpCo(CO)(PPh_3)$ (12.0 mg, 0.027 mmol) were dissolved in 15 mL of oxygen-free hexane in a 25 mL three-neck round-bottomed flask equipped with a stir bar and a nitrogen inlet. This solution was stirred at 0 °C for 30 min. The volatiles were removed in vacuo, and the products were separated by TLC. Elution with hexane/methylene chloride (2:1) solvent mixture yielded two compounds: **3** and $Mn_2(CO)_6(PPh_3)(\mu\text{-}S_2)$, **6**, in 31% and 14% yields, respectively. Spectral data for **6** (two isomers): IR ν_{CO} (cm^{-1} in hexane) 2042 (s), 2001 (s), 1961 (m), 1953 (vs), 1939 (w), 1868 (w); ^{1}H NMR (δ in CD_2Cl_2) 7.6−7.4 (m, 15H); ^{31}P NMR (δ in CD_2Cl_2) 60.34, 44.11. Anal. Calcd: C, 47.70; H, 2.50. Found: C, 47.84; H, 2.33.

Reaction of 2 with $CpCo(CO)(PPh_3)$ at 25 °C. Compound **2** (10.0 mg, 0.027 mmol) and $CpCo(CO)(PPh_3)$ (11.0 mg, 0.027 mmol) were dissolved in 15 mL of oxygen-free hexane in a 25 mL three-neck round-bottomed flask equipped with a stir bar and a nitrogen inlet. This solution was stirred at 25 °C for 24 h. The volatiles were removed in vacuo, and the product was separated by TLC. Elution with hexane/methylene chloride (2:1, v/v) solvent mixture yielded three compounds: 4.1 mg (33%) of **3**, 1.9 mg (12%) of **6**, and 0.9 mg (5%) of $CpCoMn_2(CO)_5(PPh_3)(\mu_3\text{-}S)_2$, **5**, in order of elution. Spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane) 2015 (vs), 1968 (s), 1945 (sh), 1905 (w); ^{1}H NMR (δ in CD_2Cl_2) 7.4−7.5 (m, 15H), 4.3 (s, 5H); ^{31}P NMR (δ in CD_2Cl_2) 73.1. Anal. Calcd: C, 48.02; H, 2.88. Found: C, 48.11; H, 2.79.

Reaction of 3 with PPh_3. Compound **3** (10.0 mg, 0.021 mmol) and PPh_3 (5.6 mg, 0.021 mmol) were dissolved in 10 mL of THF in a 25 mL three-neck round-bottomed flask equipped with a stir bar and a nitrogen inlet. This solution was stirred at 25 °C for 6 h. The volatiles were then removed in vacuo, and the product was separated by TLC by using hexane/methylene chloride (4:1) solvent mixture as an eluant. A total of 12.9 mg of **5** (88% yield) was obtained.

Crystallographic Analyses. A brown crystal of **3** and red crystals of **4**, **5**, and **6** were grown by slow evaporation of the solvent from solutions of the compounds in hexane/CH_2Cl_2 solvent mixtures at −17 °C. The crystals used in 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 2. The raw intensity data frames were integrated with the SAINT+ program,[12] which

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[12] *SAINT+* Version 6.02a; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

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.[13]

Compounds **3** and **4** crystallized in the triclinic system. The space group $P\bar{1}$ was assumed and confirmed by successful solution and refinement of the structure in each case. Compounds **5** and **6** both crystallized in the monoclinic crystal system. Systematic absences in the intensity data indicated the space groups $P2_1/c$ and $P2_1/n$, respectively. These were further confirmed by successful solution and refinement of the structures. All of the structures were solved by a combination of 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 by 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.[13]

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Supporting Information Available: Tables of final atomic coordinates, bond distances and angles, and anisotropic thermal parameters are available for the structural analyses of compounds **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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