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Article

Syntheses and Reactivity of the Diselenido Molybdenum–Manganese Complex CpMoMn(CO)$_5$(μ-Se$_2$)

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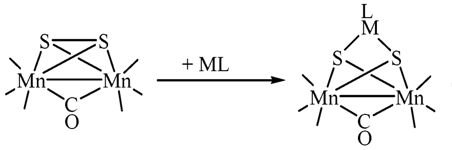
Reaction of CpMoMn(CO)$_8$ with elemental selenium and Me$_3$NO in the absence of light yielded the diselenido complex CpMoMn(CO)$_5$(μ-Se$_2$), **2**. Compound **2** contains a bridging diselenido ligand lying perpendicular to the Mo–Mn bond, Mo–Mn = 2.8421(10) Å. In the presence of room light, the reaction yielded the tetranuclear metal complex Cp$_2$Mo$_2$Mn$_2$(CO)$_7$(μ_3-Se)$_4$, **3** (36% yield), and **2** (7% yield). Compound **2** reacted with ethylene to yield the ethanediselenato complex CpMoMn(CO)$_5$(μ-SeCH$_2$CH$_2$Se), **4**, by insertion of ethylene into the Se–Se bond. Compound **2** also reacted with (PPh$_3$)$_2$Pt(PhC$_2$Ph) and CpCo(CO)$_2$ to yield the complexes CpMoMnPt(PPh$_3$)$_2$(CO)$_5$(μ_3-Se)$_2$, **5**, and Cp$_2$CoMoMn(CO)$_5$(μ_3-Se)$_2$, **6**, respectively, by insertion of the metal groupings CpCo and Pt(PPh$_3$)$_2$ into the Se–Se bond of **2**. The oxo compound Cp$_2$CoMo(O)Mn(CO)$_5$(μ_3-Se)$_2$, **7**, was obtained from **6** by decarbonylation at molybdenum by using Me$_3$NO. The molecular structures of the complexes **2**–**7** were established by single-crystal X-ray diffraction analyses.

Introduction

Transition-metal carbonyl complexes containing the disulfido ligand are of interest because they exhibit interesting reactivity at the sulfur atoms.[1] Oxidative addition of low-valent metal complexes to complexes containing disulfido ligands is often used as a method for preparing heteronuclear metal complexes with sulfido ligands by insertion of a metal group into the sulfur−sulfur bond. Sulfur-containing metal complexes are often used as models for biologically active metal sites.[2] Sulfido ligands have been shown to be of great value for the synthesis and stabilization of polynuclear metal complexes.[3] Selenido ligands should also be of great value for this purpose; however, the chemistry of metal selenide complexes has been much less studied.[4]

Recently, we have prepared the new disulfido complexes Mn$_2$(CO)$_7$(μ-S$_2$)[5,6] and CpMoMn(CO)$_5$(μ-S$_2$).[7] These complexes exhibit a range of reactivity about the disulfido ligand including insertions of metal complexes into the S−S bond,[8,9] eq 1, and ligands into the metal−metal bond,[10] eq 2.



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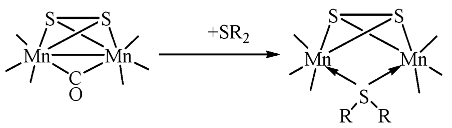

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10.1021/ic030077z CCC: $25.00

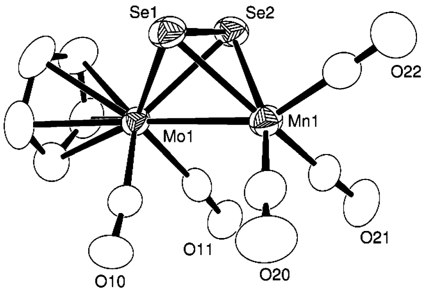


Figure 1. An ORTEP diagram of the molecular structure of **2** showing 50% thermal ellipsoid probability.

Table 1. Selected Intramolecular Bond Distances and Angles for **2**[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Mo(1)	Mn(1)	2.8772(8)	Mn(1)	Se(1)	2.4367(8)
Mo(1)	Se(1)	2.5740(6)	Mn(1)	Se(2)	2.4218(7)
Mo(1)	Se(2)	2.5702(5)	Se(1)	Se(2)	2.3144(6)

(b) Angles

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Mn(1)	Se(1)	Mo(1)	70.03(2)	Se(1)	Mn(1)	Se(2)	56.90(2)
Mn(1)	Se(2)	Mo(1)	70.32(2)	Se(1)	Mo(1)	Se(2)	53.476(15)
Mn(1)	Mo(1)	Se(1)	52.747(18)	Se(1)	Se(2)	Mn(1)	61.88(2)
Mn(1)	Mo(1)	Se(2)	52.424(17)	Se(1)	Se(2)	Mo(1)	63.346(17)
Mo(1)	Mn(1)	Se(1)	57.227(19)	Se(2)	Se(1)	Mn(1)	61.23(2)
Mo(1)	Mn(1)	Se(2)	57.259(19)	Se(2)	Se(1)	Mo(1)	63.179(16)

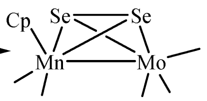
[a] Estimated standard deviations in the least significant figure are given in parentheses.

We have now found that $\mathrm{CpMoMn(CO)_8}$, **1**, reacts with elemental selenium in the presence of $\mathrm{Me_3NO}$ to yield the complex $\mathrm{CpMoMn(CO)_5(\mu\text{-}Se_2)}$, **2**, the selenium homologue of $\mathrm{CpMoMn(CO)_5(\mu\text{-}S_2)}$. We have investigated the reactivity of compound **2** toward ethylene and some selected metal complexes and determined the structures of all of these products. The results of these studies are reported here.

Results and Discussion

The new heterodinuclear compound **2** was obtained in 30% yield from the reaction of **1** with elemental selenium in the presence of $\mathrm{Me_3NO}$ at 40 °C, eq 3, in the absence of light.

$$\mathrm{CpMoMn(CO)_8} \xrightarrow[{}^{1}\!/_{4}\mathrm{Se_8}]{\mathrm{Me_3NO}}$$



(3)

The infrared spectrum of **2** indicates that all of the carbonyl ligands are of a terminal type. The ^{1}H NMR spectrum exhibits a single resonance for the Cp ligand at 5.51 ppm.

The molecular structure of **2** was established by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 1. Selected bond distances and angles for **2** are listed in Table 1. Compound **2** is structurally similar to its sulfur homologue $\mathrm{CpMoMn(CO)_5(\mu\text{-}S_2)}$.[7] The molecule contains one molybdenum atom and one manganese atom joined by a Mo−Mn single bond that is bridged by a diselenido ligand. The Mo−Mn distance 2.8772(8) Å is slightly longer than that found for the disulfido complex $\mathrm{CpMoMn(CO)_5(\mu\text{-}S_2)}$, 2.8421(10) Å, but shorter than that of the Cp* complex $\mathrm{Cp^*MoMn(CO)_5(\mu\text{-}S_2)}$, 2.8914(5) Å.[7] The Mo−Mn distance is much shorter than that found in the compound $\mathrm{CpMoMn(CO)_8}$, 3.083(8) Å, which contains no bridging ligands.[11] The shortness of the molybdenum−manganese bond in **2** can thus be attributed to the presence of the bridging diselenido ligand.[5,6] The Mn−Se distances, 2.4367(8) and 2.4218(7) Å, are significantly shorter than the Mo−Se distances, 2.5740(6) and 2.5702(5) Å, as expected for the smaller manganese atom. The Mn−Se bond distances in **2** are slightly shorter than those found in the diselenido complex $\mathrm{[Mn_2(Se_2)_2(CO)_6]^{2-}}$, 2.474(4)−2.525(2) Å,[12] but are similar to those found for the bridging selenido complex $\mathrm{[CH_3C_5H_4Cr(\mu\text{-}SPh)]_2(\mu_4\text{-}Se)Mn_2(CO)_8}$, 2.413(2) and 2.415(3) Å.[13] The Mo−Se distances are similar to those found for the bridging diselenido ligand in the related compound $\mathrm{(EtO_2C)CpMo(\mu\text{-}Se_2)(\mu\text{-}SPh)_2MoCp(CO_2Et)}$, Mo−Se = 2.558(1)−2.572(1) Å.[14] As found in many binuclear metal disulfido and diselenido complexes,[14−20] the Se−Se bond of the diselenido ligand is oriented perpendicular to the metal−metal bond, and both selenium atoms are bonded to both metal atoms. The Se−Se bond distance in **2**, 2.3144(6) Å, is slightly longer than those found for the diselenido complexes $\mathrm{Fe_2(CO)_6(\mu\text{-}Se_2)}$, 2.293(2) Å,[19] and $\mathrm{Fe_2(CO)_{6-n}(\mu\text{-}Se_2)(PPh_3)_n}$ [n = 1, 2.297(2) Å; n = 2, 2.296(1) Å],[20] but slightly shorter than those found for $\mathrm{[Mn_2(Se_2)_2(CO)_6]^{2-}}$, 2.327(2) Å,[12] and $\mathrm{(EtO_2C)CpMo(\mu\text{-}Se_2)(\mu\text{-}SPh)_2MoCp(CO_2Et)}$, Se−Se = 2.319(1).[14]

Viewed without charge, the diselenido ligand in **2** serves as a six-electron donor to the metal atoms. In the absence of the diselenido ligand, the metal groupings in **2** contain unequal numbers of electrons (i.e., the $\mathrm{CpMo(CO)_2}$ group contains 15 electrons, and the $\mathrm{Mn(CO)_3}$ group has only 13 electrons). If the Mo−Mn bond is viewed as an equal sharing of the two electrons, then the diselenido ligand in **2** must donate four electrons to the manganese metal atom and two electrons to the molybdenum metal atom for 18-electron configurations to be achieved at both metal atoms (**A**)

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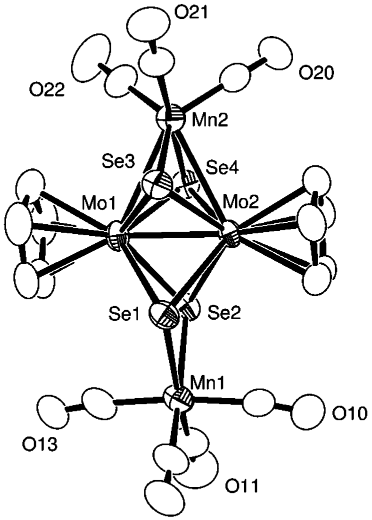
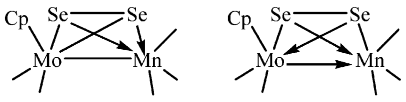


Figure 2. An ORTEP diagram of the molecular structure of **3** showing 50% thermal ellipsoid probability.

However, if the Mo−Mn bond is viewed as a heteropolar metal−metal bond (**B**), then the electrons of the diselenido ligand would be divided equally between the metal atoms. The true picture is probably some combination of these two representations.



A **B**

Compound **2** was also obtained when the reaction of **1** with selenium was performed in the presence of room light, but it was then only a minor product (7% yield). Under these conditions the major product was the new tetranuclear *tetra*selenido complex Cp$_2$Mo$_2$Mn$_2$(CO)$_7$(μ_3-Se)$_4$, **3** (36% yield). Details of the molecular structure of **3** were established by single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 2. Selected bond distances and angles are listed in Table 2. The structure of **3** contains four metal atoms: two of molybdenum and two of manganese. The two molybdenum atoms are mutually bonded, Mo(1)−Mo(2) = 2.6259(9) Å. This Mo−Mo distance is considerably shorter than that found in [CpMo(CO)$_3$]$_2$, 3.235(1) Å,[21] but electron counting suggests that the Mo−Mo bond in **3** is still no more than a metal−metal single bond, and the shortness of the bond can be attributed to the presence of the four bridging selenido ligands. A manganese tricarbonyl group is bonded to both molybdenum atoms, forming a triangular cluster of three metal atoms, Mo(1)−Mn(2) = 2.9733(14) Å and Mo(2)−Mn(2) = 2.9716(14) Å, that contains two of the selenido ligands as triple bridges on each side of the triangle. The second manganese atom has four terminal carbonyl ligands and is linked to the cluster solely by the other two selenido ligands.

Table 2. Selected Intramolecular Bond Distances and Angles for **3**[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Mo(1)	Mo(2)	2.6259(9)	Mo(2)	Se(4)	2.5160(10)
Mo(1)	Se(1)	2.6415(11)	Mo(1)	Mn(2)	2.9733(14)
Mo(1)	Se(2)	2.6277(11)	Mo(2)	Mn(2)	2.9716(14)
Mo(1)	Se(3)	2.4807(10)	Mn(1)	Se(1)	2.5087(16)
Mo(1)	Se(4)	2.5074(10)	Mn(1)	Se(2)	2.4817(15)
Mo(2)	Se(1)	2.6234(10)	Mn(2)	Se(3)	2.3259(14)
Mo(2)	Se(2)	2.6190(10)	Mn(2)	Se(4)	2.3528(15)
Mo(2)	Se(3)	2.4918(10)			

(b) Angles

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Se(2)	Mn(1)	Se(1)	71.78(4)	Se(3)	Mo(2)	Se(1)	69.38(3)
Se(3)	Mn(2)	Se(4)	99.48(5)	Se(4)	Mo(2)	Se(1)	116.61(3)
Se(3)	Mn(2)	Mo(2)	54.48(3)	Se(2)	Mo(2)	Se(1)	67.85(3)
Se(4)	Mn(2)	Mo(2)	54.92(3)	Se(3)	Mo(2)	Mo(1)	57.92(3)
Se(3)	Mn(2)	Mo(1)	54.17(3)	Se(4)	Mo(2)	Mo(1)	58.32(3)
Se(4)	Mn(2)	Mo(1)	54.68(3)	Se(2)	Mo(2)	Mo(1)	60.13(3)
Se(2)	Mn(2)	Mo(1)	52.43(3)	Se(1)	Mo(2)	Mo(1)	60.43(3)
Se(3)	Mo(1)	Se(4)	91.41(3)	Se(3)	Mo(2)	Mn(2)	49.44(3)
Se(3)	Mo(1)	Mo(2)	58.33(3)	Se(4)	Mo(2)	Mn(2)	49.93(3)
Se(4)	Mo(1)	Mo(2)	58.65(3)	Se(2)	Mo(2)	Mn(2)	112.22(4)
Se(3)	Mo(1)	Se(2)	116.06(4)	Se(1)	Mo(2)	Mn(2)	112.25(4)
Se(4)	Mo(1)	Se(2)	69.29(3)	Mo(1)	Mo(2)	Mn(2)	63.82(3)
Mo(2)	Mo(1)	Se(2)	59.80(3)	Mn(1)	Se(1)	Mo(2)	101.63(4)
Se(3)	Mo(1)	Se(1)	69.25(3)	Mn(1)	Se(1)	Mo(1)	101.77(5)
Se(4)	Mo(1)	Se(1)	116.26(4)	Mo(2)	Se(1)	Mo(1)	59.83(3)
Mo(2)	Mo(1)	Se(1)	59.74(3)	Mn(1)	Se(2)	Mo(2)	102.49(5)
Se(2)	Mo(1)	Se(1)	67.46(3)	Mn(1)	Se(2)	Mo(1)	102.90(5)
Se(3)	Mo(1)	Mn(2)	49.48(3)	Mo(2)	Se(2)	Mo(1)	60.07(3)
Se(4)	Mo(1)	Mn(2)	49.96(3)	Mn(2)	Se(3)	Mo(1)	76.35(4)
Mo(2)	Mo(1)	Mn(2)	63.75(3)	Mn(2)	Se(3)	Mo(2)	76.08(4)
Se(2)	Mo(1)	Mn(2)	111.91(4)	Mo(1)	Se(3)	Mo(2)	63.75(3)
Se(1)	Mo(1)	Mn(2)	111.66(4)	Mn(2)	Se(4)	Mo(1)	75.36(4)
Se(3)	Mo(2)	Se(4)	90.95(3)	Mn(2)	Se(4)	Mo(2)	75.14(4)
Se(3)	Mo(2)	Se(2)	115.97(3)	Mo(1)	Se(4)	Mo(2)	63.03(3)
Se(4)	Mo(2)	Se(2)	69.30(3)				

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

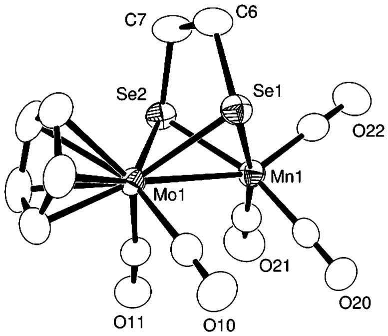


Figure 3. An ORTEP diagram of the molecular structure of **4** showing 50% thermal ellipsoid probability.

Reaction of **2** with ethylene (1 atm, 25 °C) in the absence of light yielded the ethylene adduct CpMoMn(CO)$_5$(μ-SeCH$_2$CH$_2$Se), **4**, in 34% yield. The yield of **4** was increased to 56% when the reaction was performed under similar conditions in the presence of room light. Compound **4** was characterized by a combination of IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. Details of the structure of **4** were established by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of the molecular structure of **4** is shown in Figure 3. Selected bond distances and angles are listed in Table 3. The structure of **4** is similar to that of **2** except for the presence of an ethylene group attached to

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Table 3. Selected Intramolecular Bond Distances and Angles for **4**[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Mo(1)	Mn(1)	2.8139(4)	Mn(1)	Se(1)	2.4221(4)
Mo(1)	Se(1)	2.5859(3)	Mn(1)	Se(2)	2.4107(5)
Mo(1)	Se(2)	2.5738(3)	C(6)	C(7)	1.492(5)

(b) Angles

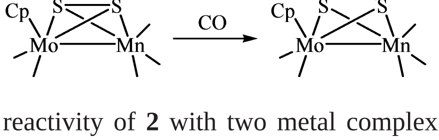
atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Mn(1)	Se(1)	Mo(1)	68.281(12)	Se(1)	Mn(1)	Se(2)	81.561(15)
Mn(1)	Se(2)	Mo(1)	68.650(12)	Se(1)	Mo(1)	Se(2)	75.435(11)
Mn(1)	Mo(1)	Se(1)	53.096(10)	C(6)	Se(1)	Mn(1)	101.86(10)
Mn(1)	Mo(1)	Se(2)	52.932(11)	C(6)	Se(1)	Mo(1)	102.95(10)
Mo(1)	Mn(1)	Se(1)	58.622(11)	C(7)	Se(2)	Mn(1)	103.98(11)
Mo(1)	Mn(1)	Se(2)	58.418(11)	C(7)	Se(2)	Mo(1)	100.63(11)

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

the two selenium atoms. The selenium atoms are not mutually bonded, and the nonbonding Se(1)···Se(2) distance of 3.1566(4) Å is even longer than that found in $Fe_2(CO)_6(\mu\text{-}SeCH_2CH_2Se)$, Se(1)···Se(2) = 3.105 Å.[22] The C−C distance, C(6)−C(7) = 1.492(5) Å, indicative of a carbon−carbon single bond, is similar to that found in $Fe_2(CO)_6(\mu\text{-}SeCH_2CH_2Se)$, C−C = 1.47(1) Å.[23] The two metal-containing groups $CpMo(CO)_2$ and $Mn(CO)_3$ are joined by a Mo−Mn single bond (2.8139(4) Å) which is considerably shorter than that found in **1**, 3.083(8) Å,[11] which contains no bridging ligand, and only slightly shorter than that found in **2**, 2.8772(8) Å. The $SeCH_2CH_2Se$ group is formed formally by the insertion of ethylene into the Se−Se bond. The ^1H NMR spectrum of **4** shows two multiplets due to the inequivalent hydrogen atoms on the methylene groups.

Direct insertion of acetylenes into the Se−Se bond of $Fe_2(CO)_6(\mu\text{-}Se_2)$ has been investigated by Mathur et al.[23] According to their investigation, the nature of the R group in RC≡CH has an important effect on the insertion of acetylene into the Se−Se bond. For example, phenylacetylene readily inserts into the Se−Se bond of $Fe_2(CO)_6(\mu\text{-}Se_2)$ in methanolic solution, but insertion of HC≡CH occurs only in the presence of sodium acetate.

In previous work, we observed that CO will insert into the S−S bond of $CpMoMn(CO)_5(\mu\text{-}S_2)$ to yield the dithiocarbonato complex $CpMoMn(CO)_5[\mu\text{-}SC(=O)S]$, eq 4.[7] Interestingly, compound **2** was unreactive toward insertion of CO into the Se−Se bond at 25 °C and 1 atm.



(4)

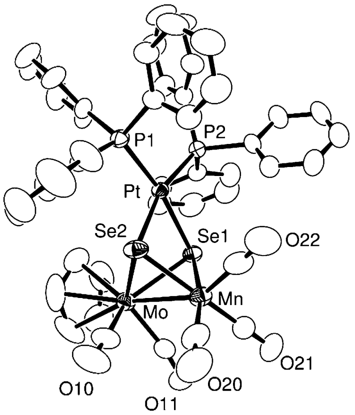


Figure 4. An ORTEP diagram of the molecular structure of **5** showing 50% thermal ellipsoid probability.

Table 4. Selected Intramolecular Bond Distances and Angles for **5**[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Mo	Mn	2.8026(10)	Mn	Se(1)	2.4568(11)
Mo	Se(1)	2.6255(8)	Mn	Se(2)	2.4655(12)
Mo	Se(2)	2.6215(8)	Pt	Se(1)	2.4635(6)
Pt	P(1)	2.2893(15)	Pt	Se(2)	2.4477(6)
Pt	P(2)	2.3016(15)			

(b) Angles

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
P(1)	Pt	P(2)	100.89(5)	Mn	Se(1)	Pt	95.14(3)
P(1)	Pt	Se(2)	92.16(4)	Mn	Se(1)	Mo	66.84(3)
P(2)	Pt	Se(2)	164.76(4)	Pt	Se(1)	Mo	92.28(2)
P(1)	Pt	Se(1)	168.90(4)	Pt	Se(2)	Mn	95.33(3)
P(2)	Pt	Se(1)	89.97(4)	Pt	Se(2)	Mo	92.74(2)
Se(2)	Pt	Se(1)	77.43(2)	Mn	Se(2)	Mo	68.78(3)
Se(2)	Mo	Se(1)	71.67(2)	Se(1)	Mn	Se(2)	77.23(3)
Se(2)	Mo	Mn	53.94(3)	Se(1)	Mn	Mo	59.46(3)
Se(1)	Mo	Mn	53.70(2)	Se(2)	Mn	Mo	59.27(3)

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

The reactivity of **2** with two metal complexes was also investigated. The reaction of **2** with $Pt(PPh_3)_2(PhC_2Ph)$ at 25 °C yielded the new compound $CpMoMnPt(PPh_3)_2(CO)_5(\mu_3\text{-}S)_2$, **5**, in 57% yield. The IR spectrum of compound **5** shows four absorptions in the CO region. The ^1H NMR spectrum of **5** exhibits multiplets in the region 7.4−7.1 ppm that can be assigned to the phenyl groups of the phosphine ligands and a single resonance at 5.25 ppm for the Cp ligand. The $^{31}P\{^1H\}$ NMR spectrum of **5** exhibits a single resonance at 19.46 ppm with ^{195}Pt satellites (J_{Pt-P} = 2762 Hz) for the two equivalent phosphine ligands. An ORTEP diagram of the molecular structure of **5** is shown in Figure 4. Selected bond distances and angles are listed in Table 4. This molecule contains three metal atoms but only one metal−metal bond, and that is between the molybdenum and manganese atoms. The Mo−Mn distance of 2.8026(10)Å is similar to those in **2** and **4**. The platinum atom has a planar coordination geometry, and this plane is nearly perpendicular to the Mo−Mn vector.

The reaction of **2** with $CpCo(CO)_2$ yielded the new compound $Cp_2CoMoMn(CO)_5(\mu_3\text{-}Se)_2$, **6**, in 27% yield. The infrared spectrum of **5** shows four absorptions in the carbonyl region that can be attributed to the terminal CO ligands. The

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(22) Mathur, P.; Manimaran, B.; Trivedi, R.; Hossain, M. M.; Arabatti, M. *J. Organomet. Chem.* **1996**, *515*, 155.

(23) (a) Mathur, P.; Dash, A. K.; Hossain, M. M.; Satyanarayana, C. V. V. *J. Organomet. Chem.* **1995**, *493*, 257. (b) Mathur, P.; Hossain, M. M.; Das, K.; Sinha, U. C. *J. Chem. Soc., Chem. Commun.* **1993**, 46. (c) Mathur, P.; Hossain, M. M. *Organometallics* **1993**, *12*, 2398.

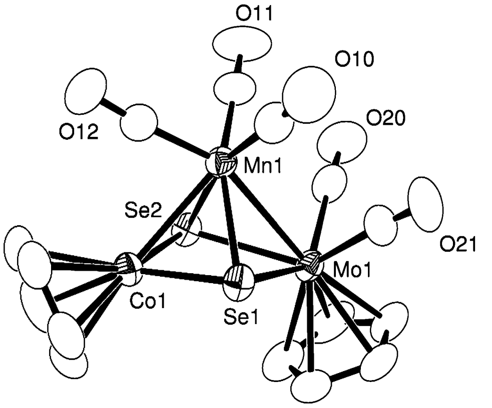


Figure 5. An ORTEP diagram of the molecular structure of **6** showing 50% thermal ellipsoid probability.

Table 5. Selected Intramolecular Bond Distances and Angles for **6**[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Mo(1)	Mn(1)	2.9023(5)	Mn(1)	Se(1)	2.4041(5)
Co(1)	Mn(1)	2.6481(6)	Mn(1)	Se(2)	2.4068(5)
Mo(1)	Se(1)	2.5765(4)	Co(1)	Se(1)	2.2629(5)
Mo(1)	Se(2)	2.5922(4)	Co(1)	Se(2)	2.2771(5)

(b) Angles

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Se(1)	Co(1)	Se(2)	87.248(17)	Se(1)	Mo(1)	Se(2)	74.602(11)
Se(1)	Co(1)	Mn(1)	57.987(15)	Se(1)	Mo(1)	Mn(1)	51.637(12)
Se(2)	Co(1)	Mn(1)	57.922(14)	Se(2)	Mo(1)	Mn(1)	51.581(12)
Se(1)	Mn(1)	Se(2)	81.245(16)	Co(1)	Se(1)	Mn(1)	69.063(16)
Se(1)	Mn(1)	Co(1)	52.950(14)	Co(1)	Se(1)	Mo(1)	98.191(15)
Se(2)	Mn(1)	Co(1)	53.289(13)	Mn(1)	Se(1)	Mo(1)	71.189(13)
Se(1)	Mn(1)	Mo(1)	57.174(12)	Co(1)	Se(2)	Mn(1)	68.789(16)
Se(2)	Mn(1)	Mo(1)	57.547(13)	Co(1)	Se(2)	Mo(1)	97.376(15)
Se(1)	Mn(1)	Mo(1)	82.465(15)	Mn(1)	Se(2)	Mo(1)	70.872(14)

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

^{1}H NMR spectrum of **6** exhibits two single resonances at 5.09 and 4.76 ppm that can be assigned to the Cp rings on the metal atoms. An ORTEP diagram of the molecular structure of **6** is shown in Figure 5. Selected bond distances and angles are listed in Table 5. The molecule contains three metal atoms with two metal−metal bonds, Mo(1)−Mn(1) = 2.9023(5) Å and Mn(1)−Co(1) = 2.6481(6) Å. Because of the larger size of molybdenum, the Mo−Mn bond is significantly longer than the Mn−Co bond. The Mo−Mn distance in **6** is slightly shorter than that in **1** (3.083(8) Å), but slightly longer than those found in **2** (2.8772(8) Å) and **4** (2.8139(4) Å). The Mn−Co distance in **6** is slightly longer than that in CpCoMn$_2$(CO)$_6$(μ_3-S)$_2$, 2.5966(6) Å,[9] and considerably shorter than those found in MnCo(CO)$_8$(2,6-xylyl-NC), 2.870(1) Å, and MnCo(CO)$_7$(2,6-xylyl-NC)$_2$, 2.9035(7) Å, which have no bridging ligands.[24] The cobalt atom in **6** can achieve an 18-electron configuration by deriving three electrons from the two bridging selenido ligands and one electron from the Mn−Co bond (**C**) or in an alternative view by deriving two electrons from two bridging selenido ligands and two electrons from the Mn atom via formation of a heteropolar metal to metal (**D**).

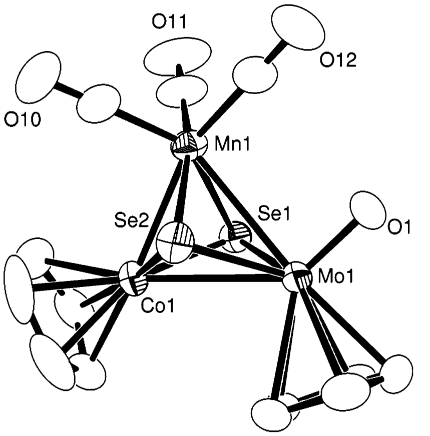
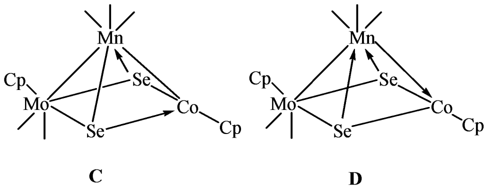


Figure 6. An ORTEP diagram of the molecular structure of **7** showing 50% thermal ellipsoid probability.



When compound **6** was treated with Me$_3$NO, the compound Cp$_2$CoMo(O)Mn(CO)$_3$(μ_3-Se)$_2$, **7**, was obtained in 44% yield. Compound **7** was also characterized crystallographically. The crystal structure of **7** contains two independent formula equivalents in the asymmetric unit. Both molecules are structurally similar, and an ORTEP diagram representing the molecular structure of one of these is shown in Figure 6. Selected intramolecular bond distances and angles are listed in Table 6. Compound **7** is structurally similar to **6** in that it contains a triangular arrangement of three metal atoms with two triply bridging sulfido ligands. However, unlike **6**, compound **7** contains three metal−metal bonds including one between cobalt and molybdenum, Co−Mo = 2.9787(5) Å [2.9964(5) Å]. In this way all three metal atoms achieve 18-electron configurations. There is a terminal oxo ligand on the molybdenum atom. The Mo−O bond is short, 1.696(2) Å [1.698(2) Å]. This is similar to Mo−O bond distances in related molecules such as Cp$_2$Mo$_2$(O)$_2$[μ-(MeO$_2$C)C$_2$(CO$_2$Me)], Mo−O = 1.688(2) and 1.706(2) Å,[25a] [Cp$_2$MoWFe$_2$(O)$_2$(μ_3-S)$_2$(CO)$_9$(CCPh)$_2$], Mo−O = 1.687(2) Å,[25b] and [Cp$_2$Mo$_2$(O)$_2$(μ-S)$_2$], Mo−O = 1.705(4) Å.[25c] The Mo−O bond is formulated as a double bond and exhibits its stretching vibration in the infrared at 891 cm^{-1}. In the reaction of **6** with Me$_3$NO, both of the CO ligands on the molybdenum atom were removed and an oxo ligand was added.

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(24) Beck, K.; Alexander, J. J.; Bauer, J. A. K.; Nauss, J. L. *Inorg. Chim. Acta* **1999**, *288*, 159.

(25) (a) Stichbury, J. C.; Mays, M. J.; Raithby, P. R.; Rennie, M.-A.; Fullalove, M. R. *J. Chem. Soc., Chem. Commun.* **1995**, 1269. (b) Mathur, P.; Mukhopadhyay, S.; Ahmed, M. O.; Lahiri, G. K.; Chakraborty, S.; Walawalkar, M. G. *Organometallics* **2000**, *19*, 5787. (c) Gorzellik, M.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1991**, *412*, 95.

Scheme 1

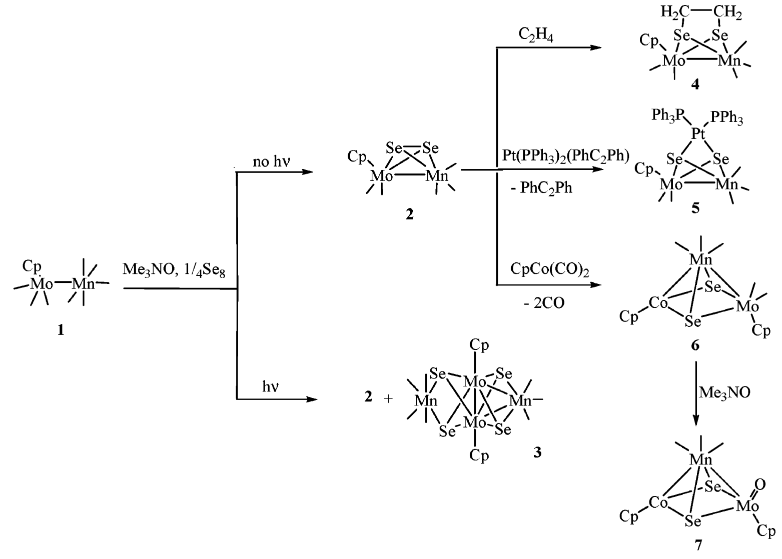


Table 6. Selected Intramolecular Bond Distances and Angles for **7**[a]

(a) Distances

atom	atom	distance (Å)	atom	atom	distance (Å)
Mo(1)	Mn(1)	2.9946(5)	Mo(2)	Mn(2)	2.9975(5)
Mn(1)	Co(1)	2.5574(6)	Mn(2)	Co(2)	2.5784(6)
Mo(1)	Co(1)	2.9787(5)	Mo(2)	Co(2)	2.9964(5)
Mn(1)	Se(1)	2.3885(5)	Mn(2)	Se(3)	2.3887(5)
Mn(1)	Se(2)	2.4163(5)	Mn(2)	Se(4)	2.4056(5)
Mo(1)	Se(1)	2.4459(4)	Mo(2)	Se(3)	2.4478(4)
Mo(1)	Se(2)	2.4492(4)	Mo(2)	Se(4)	2.4560(4)
Co(1)	Se(1)	2.3080(5)	Co(2)	Se(3)	2.2988(5)
Co(1)	Se(2)	2.3076(5)	Co(2)	Se(4)	2.3014(5)
Mo(1)	O(1)	1.696(2)	Mo(2)	O(2)	1.698(2)

(b) Angles

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Se(1)	Mn(1)	Se(2)	91.796(18)	Se(3)	Mn(2)	Se(4)	91.288(17)
Se(1)	Mo(1)	Se(2)	89.640(13)	Se(3)	Mo(2)	Se(4)	88.702(12)
Se(1)	Co(1)	Se(2)	96.760(17)	Se(3)	Co(2)	Se(4)	96.349(17)
Co(1)	Mo(1)	Mn(1)	50.697(13)	Co(2)	Mo(2)	Mn(2)	50.956(12)
Mn(1)	Co(1)	Mo(1)	64.974(14)	Mn(2)	Co(2)	Mo(2)	64.545(13)
Mo(1)	Mn(1)	Co(1)	64.329(14)	Mo(2)	Mn(2)	Co(2)	64.499(13)

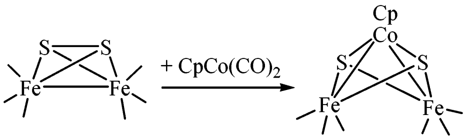
[a] Estimated standard deviations in the least significant figure are given in parentheses.

A summary of the reactions and products described in this study is shown in Scheme 1. The reaction of mixed-metal carbonyl complex with elemental selenium in the presence of Me_3NO yields new mixed-metal diselenide compound **2** when the reaction is performed in the absence of light. In the presence of room light, compound **2** is a minor product and the new compound **3** is formed. Interestingly, compound **3** is not formed in the absence of light, and we have also not been able to obtain **3** from **2** by irradiation with room light or UV irradiation. We conclude that **2** and **3** must be formed by independent reaction pathways. Like its sulfur-containing homologue, compound **2** readily added ethylene by insertion into the Se−Se bond to form compound **4**, but unlike its sulfur homologue, it does not insert CO into the Se−Se bond.

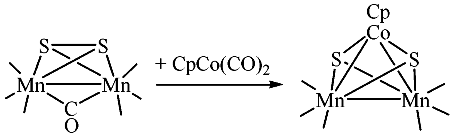
The insertion of the $Pt(PPh_3)_2$ group into the Se−Se bond of **2** proceeds without formation of a metal−metal bond to platinum. The insertion of the $Pt(PPh_3)_2$ group into the S−S bond of $Fe_2(CO)_6(\mu\text{-}S_2)$ proceeds similarly,[26] but the insertion of the $Pt(PPh_3)_2$ group into the S−S bond of $Mn_2(CO)_7(\mu\text{-}S_2)$ involves the formation of a Pt−Mn bond with the loss of one CO ligand.[8]

Compound **2** readily inserts the CpCo group into the Se−Se bond of diselenido ligand to yield the trimetallic compound **6**, which contains only one metal−metal bond to cobalt, and that is to manganese. By contrast previous studies have shown that $CpCo(CO)_2$ inserts into the S−S bonds of $Fe_2(CO)_6(\mu\text{-}S_2)$[27] and $Mn_2(CO)_7(\mu\text{-}S_2)$[9] to yield trinuclear metal complexes with the formation of two metal−metal bonds to cobalt, eqs 5 and 6.

It is anticipated that compound **2** will react with a variety of metal complexes to yield new metal selenide cluster complexes.



(5)



(6)

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere using Schlenk techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo-Nicolet Avatar FTIR spectrophotometer. ^1H NMR spectra were recorded on a

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(26) Day, V. W.; Lesch, D. A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 1290.

(27) Cowie, M.; DeKock, R. L.; Wagenmaker, T. R.; Seyferth, D.; Henderson, R. S.; Gallagher, M. K. *Organometallics* **1989**, *8*, 119.

Varian Inova 300 spectrometer operating at 300 MHz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). $Mn_2(CO)_{10}$, $[CpMo(CO)_3]_2$, and selenium powder (gray) were purchased from Strem Co. $Me_3NO{\cdot}2H_2O$ was purchased from Aldrich and used without further purification. $CpMoMn(CO)_8$[28] was prepared according to the published procedures. Product separations were performed by TLC in air on Analtech 0.25, 0.5, and 1.0 mm silica gel 60 Å F_{254} glass plates.

Reaction of CpMoMn(CO)$_8$ with Me$_3$NO and Se in the Absence of Light. A 50 mg (0.114 mmol) amount of $CpMoMn(CO)_8$ was dissolved in 20 mL of CH_2Cl_2 in a 50 mL three-neck round-bottom flask equipped with a stir bar, gas inlet, and gas outlet. To this solution were added 22 mg (0.20 mmol) of $Me_3NO{\cdot}2H_2O$ and 20 mg (0.25 mmol) of Se. The flask was wrapped in aluminum foil to avoid light. The solution was then heated to reflux for 20 h. The volatiles were removed in vacuo, and the residue was separated by column chromatography over silica gel by using a hexane/CH_2Cl_2 (5:1, v/v) solvent mixture as eluant. Two bands eluted to yield 17.2 mg of unreacted **1** and 11.5 mg of **2** (30% yield based on the amount of **1** consumed). Spectral data for **2**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2021(vs), 1975(m), 1932(m), 1911(sh); ^{1}H NMR (δ in $CDCl_3$) 5.51 (s, 5H, Cp). Anal. Calcd: C, 23.18; H, 1.17. Found: C, 23.37; H, 0.98.

Reaction of CpMoMn(CO)$_8$ with Me$_3$NO and Se in Room Light. A 50 mg (0.114 mmol) amount of $CpMoMn(CO)_8$ was dissolved in 20 mL of CH_2Cl_2 in a 50 mL three-neck round-bottom flask equipped with a stir bar, gas inlet, and gas outlet. To this solution were added 22 mg (0.20 mmol) of $Me_3NO{\cdot}2H_2O$ and 20 mg (0.25 mmol) of selenium. The resulting solution was heated to reflux for 20 h in the presence of room light. The volatiles were removed in vacuo, and the residue was separated by column chromatography over silica gel by using a hexane/CH_2Cl_2 (5:1, v/v) solvent mixture as eluant. A 19.2 mg (36%) amount of **3** and 4.3 mg of **2** (7%) were obtained in order of elution. Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2048(m), 2001(vs), 1974(w), 1952(s, br); (in hexane) 2048(m), 2003(vs), 1976(w), 1953(vs), 1937(w); ^{1}H NMR (δ in $CDCl_3$) 5.81(s, 10H). Anal. Calcd: C, 21.63; H, 1.07. Found: C, 21.43; H, 1.06.

Reaction of 2 with Ethylene. A solution of **2** (6.0 mg, 0.031 mmol) in benzene (20 mL) was stirred under an atmosphere of ethylene at room temperature for 20 h. The solvent was then removed in vacuo, and the residue was separated by TLC on silica gel using a 1:1 hexane/CH_2Cl_2 solvent mixture to yield 5.7 mg (34%) of **4**. Spectral data for **4**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2018(vs), 1974(m), 1942(s), 1914(w); ^{1}H NMR (δ in $CDCl_3$) 5.41(s, 5H), 2.60(m, 2H), 2.10(m, 2H). Anal. Calcd for $C_{12}H_9MnMoO_5Se_2$: C, 26.59; H, 1.67. Found: C, 26.91; H, 1.79. When the reaction was performed under similar conditions in the presence of room light, the yield of **4** was increased to 56%.

Reaction of 2 with (PPh$_3$)$_2$Pt(PhC$_2$Ph). A 14.5 mg (0.028 mmol) amount of **2** was dissolved in 20 mL of hexane in a 50 mL three-neck round-bottom flask equipped with a stir bar, gas inlet, and gas outlet. To this solution was added a solution containing 25 mg (0.028 mmol) of $Pt(PPh_3)_2(PhC_2Ph)$ dissolved in 5 mL of CH_2Cl_2. The solution was allowed to stir at room temperature for 1 h. A precipitate formed that was collected by filtration, then washed with hexane (3 × 10 mL), and dried in vacuo. This provided 20.6 mg of **5**, 57% yield. Spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane) 1994(vs), 1947(w), 1906(m), 1878(w); ^{1}H NMR (δ in $CDCl_3$) 7.4−7.1 (m, 30H, Ph), 5.25 (s, 5H, Cp); ^{31}P NMR (δ in $CDCl_3$) 19.462-

Table 7. Crystallographic Data for Compounds **2**−**7**

	2	**3**	**4**	**5**	**6**	**7**
empirical formula	$MoMnSe_2C_{10}H_5O_5$	$Mo_2Mn_2Se_4C_{17}H_{10}O_7$	$MoMnSe_2C_{12}H_9O_5$	$MoMnPtSe_2P_2O_5C_{46}H_{35}{\cdot}{}^1/_4CH_2Cl_2$	$CoMnMoSe_2C_{15}H_{10}O_5$	$CoMnMoSe_2C_{13}H_{10}O_4$
fw	513.94	943.85	541.99	1254.30	637.96	597.94
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
lattice params						
a (Å)	9.2490(7)	6.9050(5)	9.1898(6)	10.2811(7)	10.2700(5)	8.1398(4)
b (Å)	9.9566(7)	14.6015(9)	14.3501(9)	11.4291(8)	13.9275(7)	13.5251(6)
c (Å)	14.9689(10)	23.5023(15)	11.6492(7)	19.7990(14)	12.8698(6)	15.6805(7)
α (deg)	90	90	90	104.047(1)	90	80.127(1)
β (deg)	99.780(2)	90	94.088(1)	96.285(2)	90.211(1)	75.742(1)
γ (deg)	90	90	90	97.390(2)	90	74.684(1)
V (Å^3)	1358.43(17)	2369.6(3)	1532.32(17)	2214.1(3)	1840.82(15)	1063.20(13)
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Z value	4	4	4	2	4	4
ρ_{calcd} (g/cm^3)	2.513	2.646	2.349	1.881	2.302	2.477
μ(Mo Kα) (mm^{-1})	7.220	8.256	6.408	5.503	6.213	7.120
temp (K)	296	296	296	296	296	296
no. of obsd reflns ($I > 2\sigma(I)$)	2076	5079	3286	8340	3847	6650
no. of params	172	289	226	541	226	307
GOF[a]	0.993	1.045	1.024	1.018	1.025	1.023
max shift in final cycle	0.001	0.001	0.001	0.002	0.001	0.001
residuals:[a] R1, wR2	0.0300, 0.0629	0.0452, 0.1027	0.0238, 0.0513	0.0418, 0.0838	0.0290, 0.0687	0.0252, 0.0588
transm coeff, max/min	1/0.703	1/0.582	1/0.779	1/0.830	1/0.596	1/0.797
largest peak in final diff Fourier transform (e$^-$/ Å^3)	0.590	2.717	0.434	1.624	0.567	0.396

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

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(28) Ginley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 4908.

(s, $J_{Pt-P} = 2762$ Hz). Anal. Calcd: C, 44.53; H, 2.99. Found: C, 44.79; H, 2.86.

Reaction of 2 with CpCo(CO)$_2$. A sample of **2** (11.1 mg, 0.0216 mmol) was dissolved in 30 mL of hexane in a 50 mL three-neck round-bottom flask equipped with a stir bar, gas inlet, and gas outlet. To this solution was added 10 μL of CpCo(CO)$_2$, and the resulting solution was allowed to stir at room temperature for 20 h. The volatiles were removed in vacuo, and the residue was separated by column chromatography over silica gel by using a hexane/CH$_2$Cl$_2$ (1:1, v/v) solvent mixture as eluant. A 3.7 mg (27%) amount of **6** was obtained. Spectral data for **6**: IR ν_{CO} (cm^{-1} in hexane) 2021(vs), 1972(m), 1965(m), 1912(w); ^{1}H NMR (δ in CDCl$_3$) 5.09 (s, 5H), 4.76 (s, 5H). Anal. Calcd: C, 28.23; H, 1.43. Found: C, 28.24; H, 1.58.

Synthesis of 7. A sample of **6** (5.3 mg, 0.008 mmol) was dissolved in 1 mL of THF in a 25 mL three-neck round-bottom flask equipped with a stir bar, gas inlet, and gas outlet. To this solution was added 10 mL of a CH$_2$Cl$_2$ solution of Me$_3$NO (12.4 mg, 20 equiv), and the resulting solution was allowed to stir at room temperature for 5 h. During this time the color changed from dark green to dark brown. After stirring, the volatiles were removed in vacuo and the residue was separated by TLC using a hexane/CH$_2$Cl$_2$ (2:1, v/v) solvent mixture. A 2.2 mg (44% yield) amount of **7** was obtained. Spectral data for **7**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$) 1996(vs), 1922(br, m); ^{1}H NMR (δ in CDCl$_3$) 5.692 (s, 5H), 4.645 (s, 5H); MS(FAB) *m/z* 600 (M + 2, 5), 544 (M − 2CO, 10), 516 (M − 3CO, 100).

Crystallographic Analyses. Single crystals of **2** (red), **3** (black), **4** (orange-red), **5** (orange), **6** (dark-green), and **7** (dark-brown) suitable for diffraction analysis were grown by slow evaporation of solvent from solutions of the pure compounds in hexane/methylene chloride solvent mixtures at −17 °C. All crystals used for the data collections were glued onto the end of thin glass fibers. X-ray intensity data for each structural analysis were collected 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 7. The raw intensity data frames were integrated with SAINT+, which also applied corrections for Lorentz and polarization effects.[29] Final unit cell parameters are based on the least-squares refinement of all reflections with $I > 5(\sigma)I$ from the data sets. For each analysis an empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using SADABS.[29] Compounds **2**, **4**, and **6** crystallized in the monoclinic system. The space group $P2_1/n$ was identified for each of these compounds by the pattern of systematic absences in the intensity data. Compound **3** crystallized in the orthorhombic crystal system. The space group $P2_12_12_1$ was identified uniquely by the systematic absences observed in the data. Compounds **5** and **7** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. All structures were solved by a combination of direct methods and difference Fourier syntheses, and were refined by full-matrix least-squares on F^2 by using the SHELXTL program library[30] and neutral atom scattering factors. For each structure, all non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries. These were included as riding atoms in the final cycles of refinement in each structural analysis.

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Supporting Information Available: CIF tables for the structural analyses of **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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

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