Synthesis and Characterization of Transition-Metal Hydrido/Chalcogenido/Carbonyl Clusters $(\eta^5\text{-}RC_5H_4)(CO)_2MFe_2H(\mu_3\text{-}E)(CO)_6$ (M = Mo, W; E = S, Se) and Their Derivatives $(\eta^5\text{-}2,4\text{-}(NO_2)_2C_6H_3NHNC(Me)C_5H_4)(CO)_2WFe_2H(\mu_3\text{-}S)(CO)_6$ and $(\eta^5\text{-}RC_5H_4)(CO)_2MFeCo(\mu_3\text{-}S)(CO)_5(PPh_3)$ Generated from Isolobal and Functional Transformation Reactions. Crystal Structures of $(\eta^5\text{-}MeCOC_5H_4)(CO)_2WFe_2H(\mu_3\text{-}E)(CO)_6$ (E = S, Se) and $(\eta^5\text{-}MeCOC_5H_4)(CO)_2MFeCo(\mu_3\text{-}S)(CO)_5(PPh_3)$ (M = Mo, W)[†]

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The tetrahedral hydrido/chalcogenido/carbonyl clusters $(\eta^5\text{-}RC_5H_4)(CO)_2MFe_2H(\mu_3\text{-}E)(CO)_6$ (**1**−**10**; R = H, MeCO, MeO_2C; M = Mo, W; E = S, Se) were synthesized by the isolobal displacement reaction of $(\eta^5\text{-}RC_5H_4)(CO)_2MCoFe(\mu_3\text{-}E)(CO)_6$ with $NaHFe(CO)_4$/40% H_3PO_4 in 15−44% yields. A further transformation reaction of the acetyl functionality of **5** (M = W, E = S, R = MeCO) with $2,4\text{-}(NO_2)_2C_6H_3NHNH_2$ gave its phenyl hydrazone derivative $(\eta^5\text{-}2,4\text{-}(NO_2)_2C_6H_3NHNC(Me)C_5H_4)(CO)_2WFe_2H(\mu_3\text{-}S)(CO)_6$ (**11**) in 40% yield, whereas further isolobal reaction of **1**−**6** (M = Mo, W; E = S; R = H, MeCO, MeO_2C) with $(PPh_3)_3CoCl$ afforded the isolobal displacement products $(\eta^5\text{-}RC_5H_4)(CO)_2MFeCo(\mu_3\text{-}S)(CO)_5(PPh_3)$ (**12**−**17**; M = Mo, W; R = H, MeCO, MeO_2C) in 15−41% yields. All the products were characterized by elemental analysis and IR and ^1H NMR (some by additional MS and ^{77}Se NMR) spectroscopy; also, products **5** (R = MeCO, M = W, E = S), **9** (R = MeCO, M = W, E = Se), **13** (M = Mo, R = MeCO), and **16** (M = W, R = MeCO) were characterized by single-crystal X-ray diffraction analyses. In addition, the mechanisms for the isolobal reactions, which yielded products **1**−**10** and **12**−**17**, have been briefly discussed.

Introduction

Over the last two decades transition-metal hydrido/carbonyl clusters have been attracting considerable attention, largely due to their important role in understanding some relevant catalytic processes,[1] the interesting structures exhibited by various coordination modes (such as terminal, edge, face-bridging, or interstitial) of the hydrido ligands,[2] and the useful reactivity related to the hydrido ligands in the synthesis of numerous organometallic cluster complexes.[3] However, up to now, very little attention has been paid to transition-metal hydrido/carbonyl clusters which contain chalcogenido ligands. Such clusters are more of interest, since incorporation of chalcogen elements, particularly sulfur and selenium, would greatly increase the stability and considerably improve the properties of the transition-metal hydrido/carbonyl clusters.[4−7] In

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[†] Dedicated to Professor Dietmar Seyferth, on the occasion of his 70th birthday and in recognition of his outstanding contributions to organometallic chemistry.

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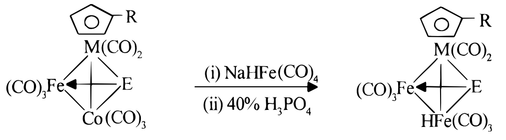
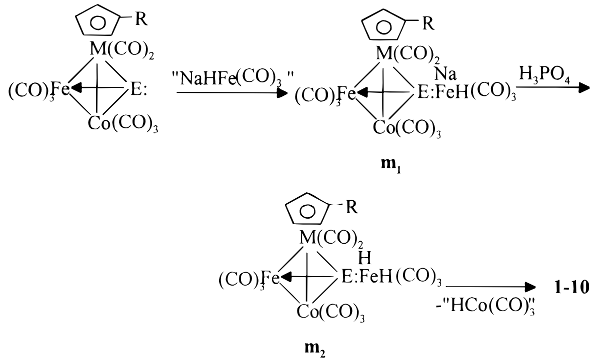
Scheme 1



1-10

Clusters	1	2	3	4	5	6	7	8	9	10
M	Mo	Mo	Mo	W	W	W	Mo	Mo	W	W
E	S	S	S	S	S	S	Se	Se	Se	Se
R	H	MeCO	MeO$_2$C	H	MeCO	MeO$_2$C	MeCO	MeO$_2$C	MeCO	MeO$_2$C

Scheme 2



this article, we describe the synthesis and characterization of such hydrido/chalcogenido/carbonyl cluster complexes and their derivatives prepared through new types of isolobal and functional transformation reactions, as well as the molecular structures of four representative clusters determined by single-crystal X-ray diffraction.

Results and Discussion

Synthesis and Characterization of $(\eta^5$-RC$_5$H$_4)$(CO)$_2$MFe$_2$H$(\mu_3$-E)(CO)$_6$ (1−10; M = Mo, W; E = S, Se). The thermal reaction of tetrahedral MCoFe$(\mu_3$-E) clusters $(\eta^5$-RC$_5$H$_4)$(CO)$_2$MCoFe$(\mu_3$-E)(CO)$_6$ with an excess amount of NaHFe(CO)$_4$ in THF at reflux followed by treatment of the residue with a 40% aqueous H$_3$PO$_4$ solution at room temperature afforded the corresponding tetrahedral MFe$_2(\mu_3$-E) clusters $(\eta^5$-RC$_5$H$_4)$(CO)$_2$MFe$_2$H$(\mu_3$-S)(CO)$_6$ (**1**−**6**) in 25−44% yields and $(\eta^5$-RC$_5$H$_4)$(CO)$_2$MFe$_2$H$(\mu_3$-Se)(CO)$_6$ (**7**−**10**) in 15−17% yields, as shown in Scheme 1.

For production of **1**−**10** we suggest a possible reaction pathway, shown in Scheme 2; that is, the reaction would involve an initial coordination of the lone pair of electrons on a μ_3-E atom of the starting clusters with the 16e species NaHFe(CO)$_3$ (generated from NaHFe(CO)$_4$ by loss of one CO ligand) to form the intermediate **m$_1$**, which could be then acidolyzed by aqueous H$_3$PO$_4$ to give another intermediate, **m$_2$**. Finally, an intramolecular rearrangement of HFe(CO)$_3$ from the outside of the tetrahedral cluster core of **m$_2$**, followed by elimination of one molecule of HCo(CO)$_3$, would afford products **1**−**10**. This mechanism seems to be plausible, because of the following facts. (i) During the course of the reaction gas (CO) evolution was observed and iron carbonyls easily lose a CO to form a 16e species.[8] (ii) The coordination of μ_3-E with a 16e species is a well-known process in similar systems.[9] (iii) After the reagent NaHFe(CO)$_4$ was added, some precipitate formed, which was possibly the intermediate **m**$_1$. (iv) It is believed that the aqueous H$_3$PO$_4$ is necessary for converting the intermediate **m$_1$** to **m$_2$** and finally to the products, since TLC showed no **1**−**10** generated before adding it.

Apparently, according to the principle of isolobal analogy,[10] products **1**−**10** can be simply regarded as derived from an isolobal displacement reaction of the Co(CO)$_3$ (d^9 ML$_3$) structural unit in starting clusters by the isolobal fragment HFe(CO)$_3$ (d^7 ML$_4$) generated in situ from the reagent NaHFe(CO)$_4$. It is noteworthy that although the isolobal displacement reactions are often used in the synthesis of transition-metal clusters,[11−15] this is the first example carried out between such a starting cluster and the isolobal reagent NaHFe(CO)$_4$.

Except for product **1**, which was previously reported,[16] all the other products are new and have been characterized by elemental analysis and spectroscopy. The IR spectra of **1**−**10** showed several absorption bands in the range 1819−2090 cm^{-1} for their hydrido and carbonyl ligands attached to metal atoms, and those of **2, 3, 5, 6**, and **7**−**10** displayed one additional absorption band in the range 1683−1737 cm^{-1} for their ketonic or ester carbonyls. The ^{1}H NMR spectra of **1** and **4** exhibited one singlet at ca. 5.4 ppm for their parent Cp ring, whereas those of **2, 3, 5, 6**, and **7**−**10** showed two singlets for their substituted Cp rings at ca. 5.4 and ca. 5.8 ppm, assigned to H^3 and H^4 protons remote from the electron-withdrawing substituent, and H^2 and H^5 protons close to the substituent,[15,17−20] respectively. Interestingly, we found that in the ^{1}H NMR spectra of **1**−**3, 7**, and **8**, the hydrido ligand showed one sharp singlet in the range −22.12 to −23.54 ppm, whereas in those of **4**−**6, 9**, and **10** the hydrido ligand showed one sharp singlet in the range −20.24 to −21.43 ppm along with clearly visible satellite peaks due to coupling with the isotopic W atom ($J_{\text{W−H}}$ = 26.45−36.62 Hz). This observation of W−H coupling is obviously due to the facile hydride migration in hydrido cluster complexes[21−23]

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Chart 1

(**A**) edged H (**B**) facial H

and may suggest that the hydrido ligand present in clusters **1**−**10** would be best described as bridged along an Fe−M bond or over an Fe$_2$M triangular face, but not terminally bonded to one of the iron atoms,[2] as shown in Chart 1. It is worth noting that the δ_{W-H} and J_{W-H} values may vary greatly in different cluster systems. For example, in contrast to our tetrahedral clusters **4**−**6**, **9**, and **10** mentioned above, the δ_{W-H} and J_{W-H} values of the trigonal-bipyramidal cluster CpWRu$_4$(CO)$_{14}$(μ_3-H) are respectively equal to 14.83 ppm and 66 Hz at 270 K (slightly changed with temperature).[23] In addition, the chemical shift values of the hydride in clusters **1**−**10** vary in a regular manner. For example, for the clusters with the same μ_3-E atom, the chemical shifts of the Mo clusters are greater than those of the W clusters, whereas for the clusters with Mo or W atom the chemical shifts of the μ_3-S clusters are greater than those of the μ_3-Se clusters. ^{77}Se NMR spectroscopy has become an important tool for the characterization of Se-containing transition-metal clusters.[24] To observe the influence of an adjacent metal unit toward ^{77}Se NMR of the μ_3-Se atom in starting clusters and their products, we determined the ^{77}Se NMR spectra of **7** and its starting cluster. It is surprising that the change of an adjacent metal unit from Co(CO)$_3$ in the starting cluster (δ_{μ_3-Se} 467.62 ppm) to FeH(CO)$_3$ in product **7** (δ_{μ_3-Se} 610.31 ppm) can cause a shift of ^{77}Se NMR signal of the μ_3-Se atom up to 142 ppm. Finally, it should be noted that the EIMS of **1**−**10** usually displayed molecular ion peaks and corresponding fragment peaks indicative of successive loss of one hydrido ligand and one to eight CO ligands from their parent ions.

Single-Crystal Molecular Structures of 5 and 9. To further confirm the structures of **1**−**10**, we carried out X-ray crystallographic studies on clusters **5** and **9**. Molecular structures of **5** and **9** are presented in Figures 1 and 2, respectively. Selected bond lengths and angles are listed in Table 1.

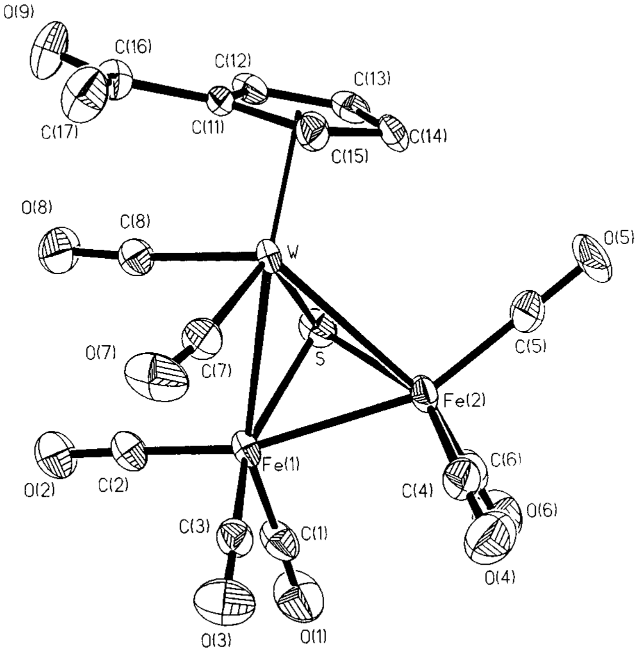

Figure 1. Molecular structure of **5** with atom-labeling scheme.

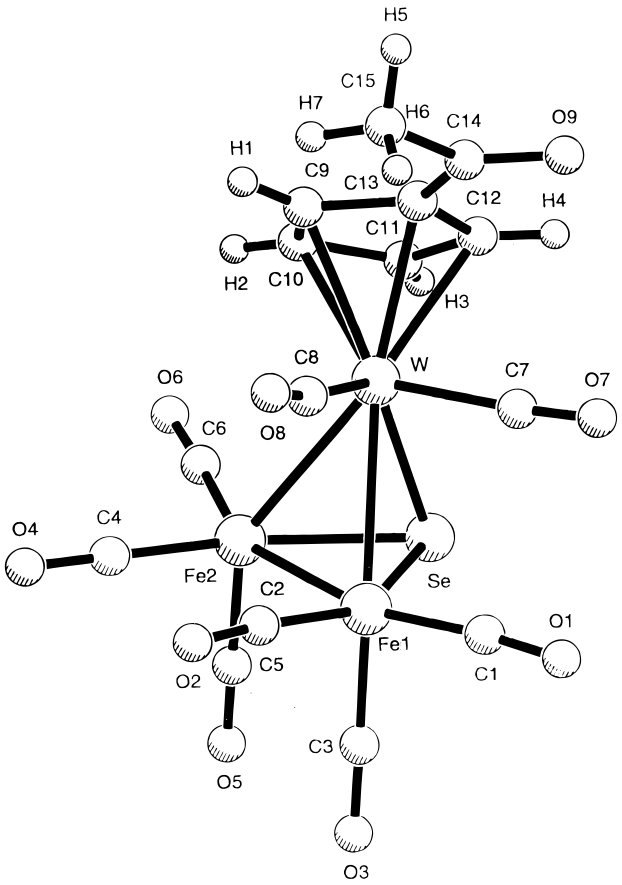

Figure 2. Molecular structure of **9** with atom-labeling scheme.

As seen in Figures 1 and 2, the molecules are actually isostructural. For example, while **5** consists of a distorted-tetrahedral WFe$_2$(μ_3-S) cluster core, **9** contains a distorted-tetrahedral WFe$_2$(μ_3-Se) cluster skeleton. Both **5** and **9** have one acetyl-substituted cyclopentadienyl ligand and two CO ligands coordinated to the W atom and six CO ligands attached to two Fe atoms. In fact, the corresponding geometric parameters of **5** and **9** are very close to each other and sometimes even identical, some of which are shown in Table 2. In addition, the corresponding geometric parameters, for example, the bond lengths involved in the cluster cores, namely Fe−Fe,[25] Fe−W,[15,26,27] Fe−S,[25] and W−S,[15,26,27] are comparable with those reported in corresponding clusters.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5 and 9

Product **5**			
W−Fe(1)	2.805(1)	W−Fe(2)	2.875(1)
W−S	2.38(12)	Fe(1)−Fe(2)	2.582(2)
Fe(1)−S	2.204(3)	Fe(2)−S	2.212(3)
W−C(11)	2.273(9)	W−C(7)	1.991(8)
Fe(1)−C(1)	1.76(2)	Fe(2)−C(4)	1.79(1)
Fe(1)−W−Fe(2)	54.06(4)	Fe(1)−W−S	49.48(6)
Fe(2)−W-S	48.66(7)	Fe(2)−Fe(1)−S	54.35(9)
W−Fe(1)−Fe(2)	64.35(4)	W−Fe(2)−Fe(1)	61.59(4)
W−S−Fe(1)	75.32(7)	W−S−Fe(2)	77.40(7)
Fe(1)−S-Fe(2)	71.56(9)	W−Fe(1)−S	55.21(7)
Product **9**			
W−Se	2.5087(9)	W−Fe(1)	2.837(1)
W−Fe(2)	2.912(1)	Se−Fe(1)	2.329(1)
Fe(1)−Fe(2)	2.607(1)	Se−Fe(2)	2.337(1)
W−C(9)	2.300(7)	W−C(7)	2.024(8)
Fe(1)−C(1)	1.793(9)	Fe(2)−C(4)	1.799(10)
Se−W−Fe(1)	51.19(3)	Se−W−Fe(2)	50.39(3)
Fe(1)−W−Fe(2)	53.92(3)	W−Se−Fe(1)	71.71(4)
W−Se−Fe(2)	73.80(4)	Fe(2)−Se-Fe(1)	67.96(4)
W−Fe(1)−Se	57.09(3)	Se−Fe(1)−Fe(2)	56.17(4)
W−Fe(2)−Se	55.81(3)	W−Fe(2)−Fe(1)	61.57(3)

However, it should be noted that the W−Fe(2) bond lengths in **5** (2.875(1) Å) and **9** (2.912(1) Å) are much longer than the W−Fe(1) bond lengths in **5** (2.805(1) Å) and **9** (2.837(1) Å). Apparently, such metal−metal bond lengthening is due to the presence of the edged hydride and/or the facial hydride (see Chart 1), which is more strongly associated with the W−Fe(2) bond.

The following should also be noted. (i) The cyclopentadienyl ring of **5** or **9** is tilted with respect to the triangular base Fe(1)−Fe(2)−S or Fe(1)−Fe(2)−Se and gives dihedral angles of 42.85 and 40.63°, respectively. (ii) The π-system of the substituent acetyl group MeC═O in **5** and **9** is conjugated to a certain degree with the cyclopentadienyl π-system, since the dihedral angle between the Cp ring and the plane C(16)−O(9)−C(17) in **5** or the plane C(14)−O(9)−C(15) in **9** is quite small (4.78 and 3.87°, respectively) and the bond lengths of C(11)−C(16) in **5** and C(13)−C(14) in **9** (1.49(1) Å) are obviously shorter than that of a normal C−C single bond.

Reaction of 5 with $2,4\text{-}(NO_2)_2C_6H_3NHNH_2$. Synthesis and Characterization of $(\eta^5\text{-}2,4\text{-}(NO_2)_2C_6H_3NHNC(Me)C_5H_4)(CO)_2WFe_2H(\mu_3\text{-}S)(CO)_6$ (11). To examine the reactivity of the acetyl functionality on the Cp ring of the acetyl-containing tetrahedral $MFe_2(\mu_3\text{-}E)$ clusters, we carried out the reaction of **5** with a $H_2SO_4/EtOH/H_2O$ solution of (2,4-dinitrophenyl)hydrazine in EtOH at room temperature. As a result, the reaction afforded the corresponding tetrahedral $WFe_2(\mu_3\text{-}S)$ phenyl hydrazone derivative $(\eta^5\text{-}2,4\text{-}(NO_2)_2C_6H_3NHNC(Me)\text{-}C_5H_4)(CO)_2WFe_2H(\mu_3\text{-}S)(CO)_6$ (**11**) in 40% yield, as shown in Scheme 3.

The combustion analysis of **11** is consistent with its formulation. The IR spectrum of **11** showed four absorption bands for terminal carbonyls and the hydrido ligand in the range 2074−1888 cm^{-1} and one absorption band at 1615 cm^{-1} for the C═N double bond. The EIMS of **11** did not display a molecular ion peak but did show the corresponding ion peaks. With regard to the ^1H NMR spectrum, it is worth noting that while the four protons of the Cp ring of cluster **11** exhibited two singlets for H^3, H^4 and one doublet for H^2, H^5, that of starting cluster **5** showed two singlets for H^3, H^4 and H^2, H^5, respectively. In fact, this is not unusual, since the ^1H NMR spectra of a monosubstituted cyclopentadienyl ring in transition-metal complexes vary greatly in complexity, such as a single resonance, an A_2B_2 or A_2BB' pattern, or even a multiplet pattern, depending on the nature of the substituent and the chirality of the cluster cores.[15,17−20] In addition, it should be pointed out that although **5** showed the ^1H NMR signal for its hydrido ligand at −21.43 ppm, we did not observe the hydride signal of product **11** at high field up to −50 ppm. However, it is known that the absence of a high-field NMR signal should never be considered as evidence against the presence of an M−H group.[28] For product **11** the presence of an H−Fe group is necessary for achieving a 18-electron configuration of the iron atom. The fact that no hydride signal is observed for **11** is possibly due to the stronger delocalizing behavior of the hydride over the triangular Fe_2W plane as a facial μ_3-H.

The production of cluster **11** is apparently via a conventional functional transformation reaction of the acetyl-substituted Cp ring in cluster **5**. There are three basic strategies for synthesis of Cp-functionalized metal clusters, the first being introduction of prefunctionalized metal Cp precursors such as $(\eta^5\text{-}MeCOC_5H_4)(CO)_2M$ (M = Mo, W) into starting cluster cores by an isolobal displacement reaction.[13−15,20] A second strategy is direct functionalization of the parent Cp ring in cluster complexes,[29] which often leads to the collape of cluster cores.[15,20] The third involves transformation of the preattached functionality in clusters,[15,26] and the preparation of **11** further proves that the third strategy is successful, particularly for synthesis of those species that could not be prepared through the first and second strategies.

Reaction of 1−6 with $(PPh_3)_3CoCl$. Synthesis and Characterization of $(\eta^5\text{-}RC_5H_4)(CO)_2MFeCo(\mu_3\text{-}S)(CO)_5(PPh_3)$ (12−17). To investigate the chemical reactivity of the hydrido ligand in clusters **1−6**, we explored the reaction of **1−6** with an equimolar amount of $(PPh_3)_3CoCl$ in THF at room temperature. Interestingly, we found that this reaction afforded the series of unexpected products $(\eta^5\text{-}RC_5H_4)(CO)_2MFeCo(\mu_3\text{-}S)(CO)_5\text{-}(PPh_3)$ (**12−17**) (Scheme 4), along with a certain amount of byproducts, whose molecular formulas and structures have not been established as yet.

Products **12−17** are all new and have been characterized by elemental analysis and IR and ^1H NMR spectroscopy; in addtion, **13** and **16** have been characterized by X-ray diffraction analyses. The IR spectra of **12−17** showed four to six absorption bands in the range 2046−1852 cm^{-1}, characteristic of carbonyls attached to transition metals, and those of **13**, **14**, **16**, and **17** exhibited one absorption band in the range 1676−1729

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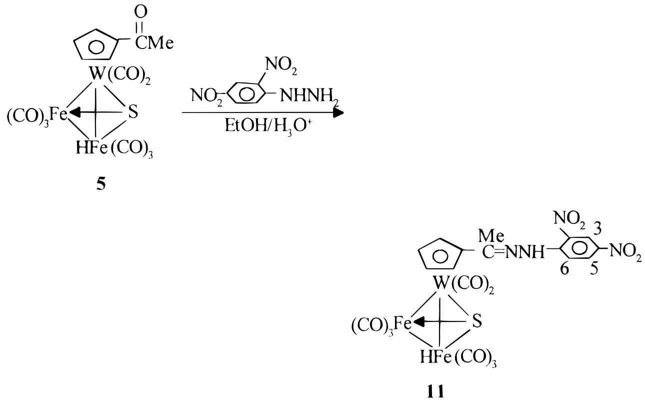
Table 2. Comparison of Geometric Parameters for 5 and 9

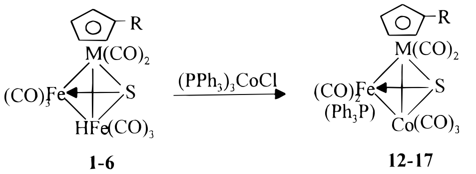
clusters	W−Fe (mean) (Å)	Fe−Fe (Å)	Fe−W−Fe (°)	W−Fe(1)−Fe(2) (°)	Cp*−W (Å)[a]
5	2.840(1)	2.582(2)	54.06(4)	64.35(4)	1.980
9	2.874(1)	2.607(1)	53.92(3)	64.52(3)	1.980

[a] Cp* = ring centroid.

Scheme 3

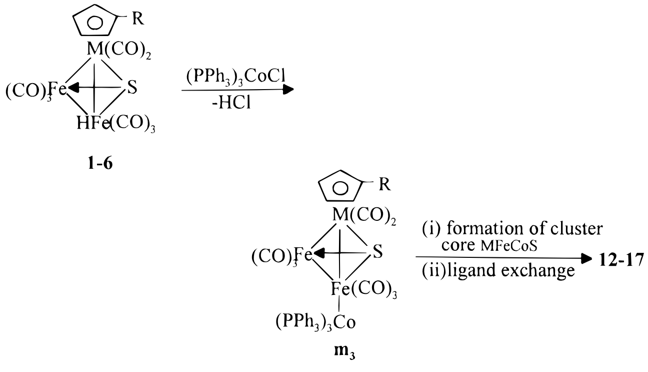


Scheme 4



Clusters	12	13	14	15	16	17
M	Mo	Mo	Mo	W	W	W
R	H	MeCO	MeO$_2$C	H	MeCO	MeO$_2$C

Scheme 5



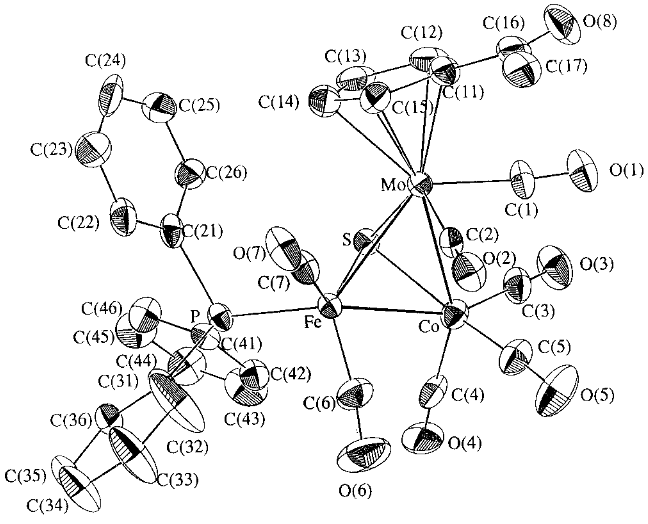


Figure 3. Molecular structure of **13** with atom-labeling scheme.

cm^{-1}, characteristic of their respective acetyl and ester groups. The ^{1}H NMR spectra of **12**−**17** indicated the presence of their corresponding organic groups: Ph$_3$P, Cp, and substituted Cp. For instance, the ^{1}H NMR spectra of the parent Cp ring in clusters **12** and **15** showed a singlet at 5.30 and 5.25 ppm, respectively; those of the substituted Cp ring in **13**, **14**, **16**, and **17** displayed two multiplets at 5.16−5.92 and 5.84−6.24 ppm, respectively, assigned to H^3, H^4 and H^2, H^5 protons of the substituted Cp ring. Such ^{1}H NMR spectral patterns for monosubstituted Cp rings in **13**, **14**, **16**, and **17** also depend primarily on the nature of the substituent on Cp rings and the chirality of the whole molecule.[15,17−20]

From the viewpoint of isolobal reactions,[10,11] it is easy to understand the formation of **12**−**17.** That is, products **12**−**17** can be simply regarded as derived from an isolobal displacement reaction of a HFe(CO)$_3$ (d^7 ML$_4$) structural unit in **1**−**6** by its isolobal fragment (PPh$_3$)$_3$-Co (d^9 ML$_3$) generated from (PPh$_3$)$_3$CoCl, followed by simple CO/PPh$_3$ ligand exchange. These isolobal reactions seem to be initiated by the first electrophilic attack of (PPh$_3$)$_3$CoCl at the Fe atom attached to a hydrido ligand to eliminate one molecule of HCl and concurrently to generate the intermediate **m$_3$**. Then, if the (PPh$_3$)$_3$Co unit in **m$_3$** replaces its neighboring Fe(CO)$_3$ followed by CO/PPh$_3$ ligand exchange, **12**−**17** will be produced (Scheme 5).

The proposed intermediate **m$_3$** has not been isolated yet, but its presence could be detected by TLC at low temperature. For example, when the reaction of **1** with (PPh$_3$)$_3$CoCl was carried out at −10 °C for 2 h, TLC showed the reaction mixture contained a substance as a brown spot appearing on the TLC plate. After the reaction mixture was warmed to room temperature and was stirred for 1 h at this temperature, TLC showed the reaction mixture did not have that substance and two new spots appeared on the TLC plate, which correspond to cluster **12** and an unidentified byproduct. In addition, the formation of **m$_3$** is not unusual, since it is well-known that transition-metal hydrides easily lose their hydrido ligands using electrophilic metal chlorides to give the corresponding metal−metal complexes.[28] However, at present we are not very clear about the mechanism and more work remains to be done in the future.

Single-Crystal Molecular Structures of 13 and 16. To unequivocally confirm the structures of **12**−**17**, X-ray single-crystal diffraction analyses for **13** and **16** were undertaken. ORTEP plots of **13** and **16** are depicted in Figures 3 and 4, respectively. Selected bond lengths and angles are listed in Table 3. As seen in Figures 3 and 4, these molecules are also isostructural.

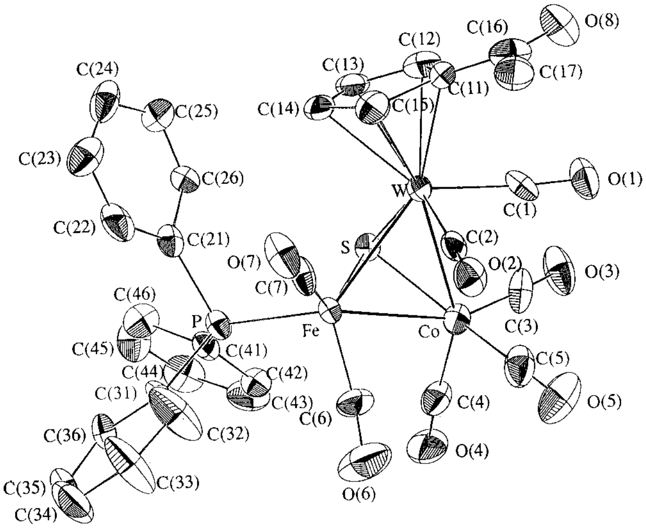


Figure 4. Molecular structure of **16** with atom-labeling scheme.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 13 and 16

	Product **13**		
Mo−Fe	2.762(2)	Mo−Co	2.829(2)
Co−Fe	2.607(2)	Mo−S	2.371(3)
Co−S	2.198(3)	Fe−S	2.188(3)
Fe−P	2.208(3)	Mo−C(1)	1.97(1)
Mo−C(11)	2.27(1)	Co−C(1)	2.90(2)
Fe−Mo−Co	55.57(5)	Co−Fe−Mo	63.51(5)
Fe−Co−Mo	60.92(5)	S−Fe−P	95.3(1)
Fe−S−Co	72.9(1)	Co−S−Mo	76.38(9)
S−Mo−Fe	49.76(7)	S−Mo−Co	49.05(7)
S−Co−Fe	53.37(8)	S−Co−Mo	54.56(7)
	Product **16**		
W−Fe	2.733(2)	W−Co	2.800(3)
Co−Fe	2.617(3)	W−S	2.358(4)
Co−S	2.187(4)	Fe−S	2.184(4)
Fe−P	2.219(4)	Co−C(1)	2.81(2)
W−C(1)	1.99(2)	W−C(11)	2.27(2)
Fe−W−Co	56.45(7)	Fe−Co−W	60.48(7)
Co−Fe−W	63.07(7)	S−Fe−P	96.1(2)
Fe−S−Co	73.6(1)	Fe−S−W	73.9(1)
Co−S−W	76.0(1)	S−W−Fe	50.1(1)
S−W−Co	49.3(1)	S−Co−Fe	53.2(1)

For instance, while **13** contains a distorted-tetrahedral MoFeCo(μ_3-S) cluster core, **16** contains a distorted-tetrahedral WFeCo(μ_3-S) cluster skeleton. Additionally, in these two molecules there exist one η^5-acetylcyclopentadienyl and two CO ligands coordinated to the Mo or W atom, three CO ligands coordinated to the Co atom, and one PPh_3 ligand (located opposite to the $Co(CO)_3$ structural unit) and two CO ligands coordinated to the Fe atom.

In addition, the two cyclopentadienyl rings of **13** and **16** are tilted with respect to the triangular base FeCoS respectively at dihedral angles of 48.03 and 47.91°, and the π-system of the acetyl group is well-conjugated with the cyclopentadienyl π-system, since the dihedral angles between the Cp ring and the plane C(16)O(8)C(17) are almost coplanar and the C(11)−C(16) bond lengths equal 1.47 Å (**13**) and 1.44 Å (**16**), which lie between the bond lengths of normal carbon−carbon single and double bonds.

Finally, it is worth pointing out that **13** and **16** contain the same cluster cores MoFeCo(μ_3-S) and WFeCo(μ_3-S) as the reported clusters CpMoFeCo(μ_3-S)$(CO)_7$(MePrPhP) and CpWFeCo(μ_3-S)$(CO)_7$(MePrPhP),[30] respectively. However, different from the two reported clusters in which there are a parent Cp ligand and a MePrPhP ligand bound to the Co atom, clusters **13** and **16** have a functionally substituted Cp ligand and a PPh_3 ligand axially bonded to the Fe atom. It is due to such differences that the corresponding bond lengths and angles involved in those cluster cores are slightly varied.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) was distilled from Na/benzophenone under nitrogen. Ethanol and 40% H_3PO_4 were deoxygenated by bubbling N_2 for about 15 min prior to use. 2,4-Dinitrophenylhydrazine was of commercial origin and was used without further purification. (η^5-RC_5H_4)$(CO)_2$MFeCo(μ_3-S)$(CO)_6$ (R = H, MeCO, MeO_2C; M = Mo, W),[15,31] (η^5-RC_5H_4)$(CO)_2$MFeCo(μ_3-Se)$(CO)_6$ (R = MeCO, MeO_2C; M = Mo, W),[32] $(PPh_3)_3CoCl$,[33] and a THF solution of $NaHFe(CO)_4$[34] were prepared according to literature methods. Preparative TLC was carried out on glass plates (26 × 20 cm) coated with silica gel (10−40 μm). IR spectra were recorded on a Nicolet FT-5DX infrared spectophotometer. ^{1}H and ^{77}Se NMR spectra were recorded on a Bruker AC-P 200 spectrometer. C/H analyses and MS determinations were performed on a Perkin-Elmer 240C analyzer and an HP 5988A spectrometer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Preparation of (η^5-C_5H_5)$(CO)_2$MoFe$_2$H(μ_3-S)$(CO)_6$ (1). A 100 mL three-necked flask equipped with a magnetic stir bar, a rubber septum, and a reflux condenser topped with a nitrogen inlet tube was charged with 0.456 g (0.86 mmol) of (η^5-C_5H_5)$(CO)_2$MoFeCo(μ_3-S)$(CO)_6$, 10 mL of THF solution containing ca. 3.00 mmol of $NaHFe(CO)_4$, and 20 mL of THF. The mixture was stirred at reflux for 3 h, and then the solvent was removed at reduced pressure to give a brown-black residue, to which was added 20 mL of a 40% aqueous H_3PO_4 solution. The mixture was stirred at room temperature for 10 min and was extracted with a given amount of ether several times until the aqueous phase became colorless. The combined ether phases were dried over anhydrous $CaCl_2$. After removal of $CaCl_2$, the solvent was evaporated to give a residue, which was subjected to TLC separation with 1/3 (v/v) CH_2Cl_2/petroleum ether as eluent. From the brown-yellow band was obtained 0.160 g (35%) of **1** as a brown solid, mp 127−128 °C. Anal. Calcd for $C_{13}H_6Fe_2MoO_8S$: C, 29.47; H, 1.14. Found: C, 29.58; H, 1.45. IR (KBr disk): $\nu_{C\equiv O}$ 2057 (s), 1983 (vs), 1860 (s), 1819 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −22.62 (s, 1H, $MoFe_2H$), 5.31 (s, 5H, C_5H_5) ppm. MS (EI, ^{98}Mo): *m/z* (relative intensity) 532 (M^+, 9.6), 531 (M^+ − H, 5.2), 504 (M^+− CO, 12.3), 476 (M^+− 2CO, 10.3), 448 (M^+− 3CO, 15.1), 420 (M^+− 4CO, 15.3), 392 (M^+− 5CO, 42.8), 364 (M^+− 6CO, 74.7), 336

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(34) The THF solution of $NaHFe(CO)_4$ was prepared by the following improved method according to the literature (King, R. B. Transition-Metal Compounds. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, p 95): 5.0 g (125 mmol) of NaOH was dissolved in 10 mL of H_2O and 20 mL of MeOH, through which nitrogen was bubbled for 0.5 h. To this solution was added 4.2 mL (30 mmol) of $Fe(CO)_5$, and then this mixture was stirred at room temperature for 0.5 h. After removal of all the volatiles at reduced pressure, the residue was extracted with THF to give 100 mL of a THF solution containing ca. 30 mmol of $NaHFe(CO)_4$.

(M$^+$− 7CO, 43.5), 308 (M$^+$− 8CO, 88.1), 243 (MoFe$_2$HS$^+$, 4.0), 242 (MoFe$_2$S$^+$, 5.3).

Preparation of (η^5-MeCOC$_5$H$_4$)(CO)$_2$MoFe$_2$H(μ_3-S)(CO)$_6$ (2). The same procedure as that for **1** was followed, but using 0.667 g (1.18 mmol) of (η^5-MeCOC$_5$H$_4$)(CO)$_2$MoFeCo(μ_3-S)(CO)$_6$ instead of (η^5-C$_5$H$_5$)(CO)$_2$MoFeCo(μ_3-S)(CO)$_6$ to give 0.300 g (44%) of **2** as a brown solid, mp 101 °C dec. Anal. Calcd for C$_{15}$H$_8$Fe$_2$MoO$_9$S: C, 31.50; H, 1.41. Found: C, 31.58; H, 1.19. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2090 (s), 2065 (s), 2007 (vs), 1994 (vs), 1862 (s), 1824 (s) cm^{-1}; $\nu_{\text{C=O}}$ 1683 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −23.51 (s, 1H, MoFe$_2$H), 2.35 (s, 3H, CH$_3$), 5.43 (s, 2H, H^3, H^4), 5.90 (s, 2H, H^2, H^5) ppm. MS (EI, ^{98}Mo): *m/z* (relative intensity) 574 (M$^+$, 0.6), 573 (M$^+$− H, 0.8), 518 (M$^+$− 2CO, 1.5), 490 (M$^+$− 3CO, 2.6), 462 (M$^+$− 4CO, 1.5), 434 (M$^+$− 5CO, 2.1), 406 (M$^+$− 6CO, 11.5), 378 (M$^+$− 7CO, 10.6), 350 (M$^+$− 8CO, 10.3), 243 (MoFe$_2$HS$^+$, 1.4), 242 (MoFe$_2$S$^+$, 6.2).

Preparation of (η^5-MeO$_2$CC$_5$H$_4$)(CO)$_2$MoFe$_2$H(μ_3-S)(CO)$_6$ (3). The same procedure as that for **1** was followed, but using 0.649 g (1.10 mmol) of (η^5-MeO$_2$CC$_5$H$_5$)(CO)$_2$MoFeCo(μ_3-S)(CO)$_6$ instead of (η^5-C$_5$H$_5$)(CO)$_2$MoFeCo(μ_3-S)(CO)$_6$ to give 0.225 g (35%) of **3** as a brown solid, mp 95 °C dec. Anal. Calcd for C$_{15}$H$_8$Fe$_2$MoO$_{10}$S: C, 30.65; H, 1.37. Found: C, 30.20; H, 1.60. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2082 (s), 2057 (s), 2008 (vs), 1983 (vs), 1885 (vs), 1844 (s) cm^{-1}; $\nu_{\text{C=O}}$ 1721 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −23.54 (s, 1H, MoFe$_2$H), 3.77 (s, 3H, CH$_3$), 5.41 (s, 2H, H^3, H^4), 5.96 (s, 2H, H^2, H^5) ppm. MS (EI, ^{98}Mo): *m/z* (relative intensity) 590 (M$^+$, 7.8), 589 (M$^+$− H, 4.3), 534 (M$^+$− 2CO, 8.2), 506 (M$^+$− 3CO, 15.5), 478 (M$^+$− 4CO, 13.0), 450 (M$^+$− 5CO, 16.4), 422 (M$^+$− 6CO, 66.4), 394 (M$^+$− 7CO, 59.1), 366 (M$^+$− 8CO, 53.6), 243 (MoFe$_2$HS$^+$, 5.3), 242 (MoFeS$^+$, 9.8).

Preparation of (η^5-C$_5$H$_5$)(CO)$_2$WFe$_2$H(μ_3-S)(CO)$_6$ (4). The same procedure as that for **1** was followed, but using 0.719 g (1.16 mmol) of (η^5-C$_5$H$_5$)(CO)$_2$WFeCo(μ_3-S)(CO)$_6$ instead of (η^5-C$_5$H$_5$)(CO)$_2$MoFeCo(μ_3-S)(CO)$_6$ to give 0.180 g (25%) of **4** as a brown solid, mp 139−140 °C. Anal. Calcd for C$_{13}$H$_6$Fe$_2$MoO$_8$SW: C, 25.28; H, 0.98. Found: C, 25.10; H, 0.91. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2065 (s), 2016 (vs), 1983 (vs), 1967 (vs), 1950 (s), 1918 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −20.24 (s, 1H, $J_{\text{W-H}}$ = 36.62 Hz, WFe$_2$H), 5.46 (s, 5H, C$_5$H$_5$) ppm. MS (EI, ^{184}W): *m/z* (relative intensity) 618 (M$^+$, 0.6), 617 (M$^+$− H, 0.31), 590 (M$^+$− CO, 0.7), 562 (M$^+$− 2CO, 0.4), 534 (M$^+$− 3CO, 0.9), 506 (M$^+$− 4CO, 0.8), 478 (M$^+$− 5CO, 2.2), 450 (M$^+$− 6CO, 4.1), 422 (M$^+$− 7CO, 2.7), 394 (M$^+$− 8CO, 6.2), 328 (WFe$_2$S, 0.13).

Preparation of (η^5-MeCOC$_5$H$_4$)(CO)$_2$WFe$_2$H(μ_3-S)(CO)$_6$ (5). The same procedure as that for **1** was followed, but using 1.450 g (2.20 mmol) of (η^5-MeCOC$_5$H$_4$)(CO)$_2$WFeCo(μ_3-S)(CO)$_6$ instead of (η^5-C$_5$H$_5$)(CO)$_2$MoFeCo(μ_3-S)(CO)$_6$ to give 0.402 g (28%) of **5** as a brown solid, mp 126−127 °C. Anal. Calcd for C$_{15}$H$_8$Fe$_2$O$_9$SW: C, 27.31; H, 1.22. Found: C, 27.25; H, 1.35. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2065 (vs), 2016 (vs), 1991 (vs), 1967 (vs), 1942 (vs) cm^{-1}; $\nu_{\text{C=O}}$ 1688 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −21.43 (s, $J_{\text{W-H}}$ = 26.45 Hz, 1H, WFe$_2$H), 2.41 (s, 3H, CH$_3$), 5.51 (s, 2H, H^3, H^4), 5.79 (s, 2H, H^2, H^5) ppm. MS (EI, ^{184}W): *m/z* (relative intensity) 660 (M$^+$, 3.4), 659 (M$^+$− H, 1.7), 632 (M$^+$− CO, 1.6), 604 (M$^+$− 2CO, 7.0), 576 (M$^+$− 3CO, 13.4), 548 (M$^+$− 4CO, 9.9), 520 (M$^+$− 5CO, 11.5), 492 (M$^+$− 6CO, 52.9), 464 (M$^+$− 7CO, 59.6), 436 (M$^+$− 8CO, 65.5), 329 (WFe$_2$HS$^+$, 3.3), 328 (WFe$_2$S$^+$, 4.9).

Preparation of (η^5-MeO$_2$CC$_5$H$_4$)(CO)$_2$WFe$_2$H(μ_3-S)(CO)$_6$ (6). The same procedure as that for **1** was followed, but using 0.997 g (1.48 mmol) of (η^5-MeO$_2$CC$_5$H$_4$)(CO)$_2$WFeCo(μ_3-S)(CO)$_6$ instead of (η^5-C$_5$H$_5$)(CO)$_2$MoFeCo(μ_3-S)(CO)$_6$ to give 0.270 g (27%) of **6** as a brown solid, mp 110−110 °C. Anal. Calcd for C$_{15}$H$_8$Fe$_2$O$_{10}$SW: C, 26.66; H, 1.19. Found: C, 26.58; H, 1.28. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2065 (vs), 2024 (vs), 1991 (vs), 1959 (vs) cm^{-1}; $\nu_{\text{C=O}}$ 1737 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −21.11 (s, $J_{\text{W-H}}$ = 29.12 Hz, 1H, WFe$_2$H), 3.77 (s, 3H, CH$_3$), 5.37 (s, 2H, H^3, H^4), 5.81 (s, 2H, H^2, H^5) ppm. MS (EI, ^{184}W): *m/z* (relative intensity) 676 (M$^+$, 1.8), 620 (M$^+$− 2CO, 2.4), 592 (M$^+$− 3CO, 3.9), 564 (M$^+$− 4CO, 5.4), 536 (M$^+$− 5CO, 5.3), 508 (M$^+$− 6CO, 23.3), 477 (M$^+$− 7CO, 2.0), 452 (M$^+$− 8CO, 19.8), 329 (WFe$_2$HS$^+$, 1.0), 328 (WFe$_2$S$^+$, 1.7).

Preparation of (η^5-MeCOC$_5$H$_4$)(CO)$_2$MoFe$_2$H(μ_3-Se)(CO)$_6$ (7). A flask equipped the same as that for **1** was charged with 0.497 g (0.80 mmol) of (η^5-MeCOC$_5$H$_4$)(CO)$_2$MoFeCo(μ_3-Se)(CO)$_6$, 10 mL (ca. 3.00 mmol) of NaHFe(CO)$_4$, and 20 mL of THF. The mixture was refluxed for 2 h, and then a workup identical with that for **1** using 1/1 (v/v) CH$_2$Cl$_2$/petroleum ether as eluent gave 0.075 g (15%) of **7** as a brown solid, mp 69−70 °C. Anal. Calcd for C$_{15}$H$_8$Fe$_2$MoO$_9$Se: C, 29.11; H, 1.30. Found: C, 29.19; H, 1.05. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2082 (s), 2057 (s), 2008 (vs), 1983 (vs), 1852 (s), 1819 (m) cm^{-1}; $\nu_{\text{C=O}}$ 1688 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −22.50 (s, 1H, MoFe$_2$H), 2.36 (s, 3H, CH$_3$), 5.37 (s, 2H, H^3, H^4), 5.79 (s, 2H, H^2, H^5) ppm. ^{77}Se NMR (CDCl$_3$, Me$_2$Se): δ 610.31 (s) ppm. MS (EI, ^{98}Mo): *m/z* (relative intensity) 622 (M$^+$, 1.0), 621 (M$^+$− H, 0.6), 566 (M$^+$− 2CO, 0.9), 538 (M$^+$− 3CO, 3.0), 582 (M$^+$− 6CO, 1.6), 454 (M$^+$− 7CO, 7.1), 426 (M$^+$− 8CO, 7.0), 291 (MoFe$_2$HS$^+$, 0.9), 290 (MoFe$_2$S$^+$, 2.0).

Preparation of (η^5-MeO$_2$CC$_5$H$_4$)(CO)$_2$MoFe$_2$H(μ_3-Se)(CO)$_6$ (8). The same procedure as that for **7** was followed, but using 0.758 g (1.19 mmol) of (η^5-MeO$_2$CC$_5$H$_4$)(CO)$_2$MoFeCo(μ_3-Se)(CO)$_6$ in place of (η^5-MeCOC$_5$H$_4$)(CO)$_2$MoFeCo(μ_3-Se)(CO)$_6$ to afford 0.120 g (16%) of **8** as a brown solid, mp 61−62 °C. Anal. Calcd for C$_{15}$H$_8$Fe$_2$MoO$_{10}$Se: C, 28.38; H, 1.27. Found: C, 28.23; H, 1.55. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2077 (s), 2055 (vs), 2033 (s), 2005 (vs), 1993 (vs), 1877 (m) cm^{-1}; $\nu_{\text{C=O}}$ 1721 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −22.12 (s, 1H, MoFe$_2$H), 3.87 (s, 3H, CH$_3$), 5.39 (s, 2H, H^3, H^4), 5.93 (s, 2H, H^2, H^5) ppm. MS (EI, ^{98}Mo): *m/z* (relative intensity) 554 (M$^+$− 3CO, 0.9), 524 (M$^+$− 4CO, 1.1), 496 (M$^+$− 5CO, 0.7), 442 (M$^+$− 7CO, 0.7), 414 (M$^+$− 8CO, 1.1), 356 (C$_5$H$_5$MoFeHSe$^+$, 1.9), 193 (Fe$_2$HSe$^+$, 0.6), 192 (Fe$_2$Se$^+$, 3.2).

Preparation of (η^5-MeCOC$_5$H$_4$)(CO)$_2$WFe$_2$H(μ_3-Se)(CO)$_6$ (9). The same procedure as that for **7** was followed, but using 1.999 g (2.82 mmol) of (η^5-MeCOC$_5$H$_4$)(CO)$_2$WFeCo(μ_3-Se)(CO)$_6$ in place of (η^5-MeCOC$_5$H$_4$)(CO)$_2$MoFeCo(μ_3-Se)(CO)$_6$ to afford 0.309 g (15%) of **9** as a brown-red solid, mp 120−121 °C. Anal. Calcd for C$_{15}$H$_8$Fe$_2$O$_9$SeW: C, 25.49; H, 1.14. Found: C, 25.27; H, 1.44. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2065 (vs), 2008 (vs), 1991 (vs), 1959 (vs), 1942 (vs) cm^{-1}; $\nu_{\text{C=O}}$ 1688 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −20.91 (s, $J_{\text{W-H}}$ = 32.55 Hz, 1H, WFe$_2$H), 2.32 (s, 3H, CH$_3$), 5.39 (s, 2H, H^3, H^4), 5.65 (s, 2H, H^2, H^5) ppm. MS (EI, ^{184}W): *m/z* (relative intensity) 708 (M$^+$, 4.8), 707 (M$^+$− H, 2.6), 652 (M$^+$− 2CO, 2.5), 624 (M$^+$− 3CO, 14.6), 596 (M$^+$− 4CO, 9.6), 568 (M$^+$− 5CO, 8.8), 540 (M$^+$− 6CO, 94.7), 512 (M$^+$− 7CO, 50.1), 484 (M$^+$− 8CO, 56.8), 377 (WFe$_2$HSe$^+$, 5.5), 376 (WFe$_2$Se$^+$, 12.2).

Preparation of (η^5-MeO$_2$CC$_5$H$_4$)(CO)$_2$WFe$_2$H(μ_3-Se)(CO)$_6$ (10). The same procedure as that for **7** was followed, but using 0.700 g (0.97 mmol) of (η^5-MeO$_2$CC$_5$H$_4$)(CO)$_2$WFeCo(μ_3-Se)(CO)$_6$ in place of (η^5-MeCOC$_5$H$_4$)(CO)$_2$MoFeCo(μ_3-Se)(CO)$_6$ to afford 0.120 g (17%) of **10** as a brown solid, mp 100−101 °C. Anal. Calcd for C$_{15}$H$_8$Fe$_2$O$_{10}$SeW: C, 24.93; H, 1.12. Found: C, 24.87; H, 1.13. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2057 (s), 2016 (vs), 1991 (vs), 1959 (vs), 1942 (s) cm^{-1}; $\nu_{\text{C=O}}$ 1729 s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −20.52 (s, $J_{\text{W-H}}$ = 34.59 Hz, 1H, WFe$_2$H), 3.89 (s, 3H, CH$_3$), 5.44 (s, 2H, H^3, H^4), 5.83 (s, 2H, H^2, H^5) ppm. MS (EI, ^{184}W): *m/z* (relative intensity) 724 (M$^+$, 3.4), 723 (M$^+$− H, 1.9), 696 (M$^+$− CO, 0.4), 668 (M$^+$− 2CO, 3.4), 640 (M$^+$− 3CO, 4.7), 612 (M$^+$− 4CO, 4.9), 584 (M$^+$− 5CO, 4.5), 556 (M$^+$− 6CO, 17.5), 528 (M$^+$− 7CO, 17.4), 500 (M$^+$− 8CO, 15.8), 377 (WFe$_2$HSe$^+$, 2.8), 376 (WFe$_2$Se$^+$, 3.4).

Preparation of (η^5-2,4-(NO$_2$)$_2$C$_6$H$_3$NHNC(Me)C$_5$H$_4$)(CO)$_2$WFe$_2$H(μ_3-S)(CO)$_6$ (11). A 100 mL three-necked flask equipped with a magnetic stir bar, a rubber septum, and a nitrogen inlet tube was charged with 0.32 g (0.48 mmol) of **5**, 50 mL of ethanol, and 4.4 mL of a (2,4-dinitrophenyl)hydrazine (ca. 0.60 mmol) solution prepared by dissolving 1.0 g of (2,4-dinitrophenyl)hydrazine in 5 mL of 98% concentrated sulfuric acid, 12 mL of water, and 22 mL of 95% ethanol. The mixture

Table 4. Crystal Data and Data Collection and Refinement Details for 5, 9, 13, and 16

	5	**9**	**13**	**16**
mol formula	$C_{15}H_8Fe_2O_9SW$	$C_{15}H_7Fe_2O_9SeW$	$C_{32}H_{22}CoFeMoO_8PS$	$C_{32}H_{22}CoFeO_8PSW$
mol wt	659.83	705.72	808.28	896.18
cryst syst	triclinic	triclinic	orthorhombic	orthorhombic
cryst size, mm	0.20 × 0.30 × 0.25	0.20 × 0.30 × 0.40	0.45 × 0.22 × 0.18	0.50 × 0.50 × 0.30
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$Pna2_1$ (No. 33)	$Pna2_1$ (No. 33)
a, Å	7.888(3)	10.657(3)	11.675(1)	11.753(7)
b, Å	10.587(2)	12.191(3)	16.375(2)	16.286(5)
c, Å	12.125(2)	7.848(2)	18.681(2)	18.553(5)
α, deg	104.04(1)	97.54(2)		
β, deg	97.87(2)	103.69(2)		
γ, deg	103.98(3)	103.21(2)		
V, Å^3	933(1)	945.8(4)	3571(1)	3551(3)
Z	2	2	4	4
D_{calcd}, g cm^{-3}	2.35	2.478	1.503	1.676
F(000)	624	658	1616	1744
μ(Mo Kα), cm^{-1}	79.75	95.56	13.40	43.10
temp, °C	26	20	23	23
radiation, Å	0.710 73	0.710 69	0.710 73	0.710 73
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{\mathrm{max}}$, deg	46	50	50	50
no. of observns, n	2566	2830	2963	2831
R	0.028	0.036	0.050	0.042
R_{w}	0.036	0.050	0.065	0.053
goodness of fit	2.27	2.12	1.79	1.45
largest diff peak, e Å^{-3}	0.97	1.38	0.94	0.83

was stirred at room temperature for 3 h and concentrated to ca. 15 mL to give a precipitate. The precipitate was filtered out, dissolved in CH_2Cl_2, and then subjected to TLC separation using 3/:2 (v/v) CH_2Cl_2/petroleum ether as eluent. From the brown-yellow band 0.164 g (40%) of **11** was obtained as a brown-yellow solid, mp 160 °C dec. Anal. Calcd for $C_{21}H_{12}Fe_2N_4O_{12}SW$: C, 30.30; H, 1.44; N, 6.67. Found: C, 29.90; H, 1.36; N, 6.34. IR (KBr disk): $\nu_{C\equiv O}$ 2074 (vs), 2016 (vs), 1970 (vs), 1888 (s) cm^{-1}; $\nu_{C=N}$ 1615 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 3H, CH_3), 5.53, 5.68 (s, s, 2H, H^3, H^4), 5.93 (d, 2H, H^2, H^5), 7.89 (d, 1H, H^6 of benzene ring), 8.33 (d, 1H, H^5 of benzene ring), 9.14 (s, 1H, H^3 of benzene ring), 11.28 (s, 1H, NH) ppm. MS (EI): m/z (relative intensity) 288 ($C_5H_4((Me)NNHC_6H_3(NO_2)_2{}^+$, 2.5), 284 ($Fe_2S(CO)_5{}^+$, 4.5), 144 ($Fe_2S^+$, 5.0), 141 ($Fe(CO)_3{}^+$, 2.2).

Preparation of (η^5-C_5H_5)(CO)$_2$MoFeCo(μ_3-S)(CO)$_5$(Ph_3P) (12). The same flask as for **1** was charged with 0.375 g (0.71 mmol) of (η^5-C_5H_5)(CO)$_2$MoFe$_2$H(μ_3-S)(CO)$_6$, 0.630 g (0.71 mmol) of (PPh_3)$_3$CoCl, and 20 mL of THF. The mixture was stirred at room temperature for 2 h, and then the solvent was removed at reduced pressure. The residue was subjected to TLC separation using 1/4 (v/v) acetone/petroleum ether as eluent. From the first brown band was obtained 0.098 g (18%) of **12** as a brown-black solid, mp 119−120 °C. Anal. Calcd for $C_{30}H_{20}CoFeMoO_7PS$: C, 47.03; H, 2.63. Found: C, 47.10; H, 2.59. IR (KBr disk): $\nu_{C\equiv O}$ 2040 (s), 2001 (vs), 1975 (vs), 1948 (vs), 1905 (s), 1861 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.30 (s, 5H, C_5H_5), 7.12−7.74 (m, 15H, 3C_6H_5) ppm. From the second brown band was obtained 0.110 g of byproduct as a black solid, which has not been fully characterized.

Preparation of (η^5-$MeCOC_5H_4$)(CO)$_2$MoFeCo(μ_3-S)(CO)$_5$(Ph_3P) (13). The same procedure as that for **12** was followed, but using 0.190 g (0.33 mmol) of (η^5-$MeCOC_5H_4$)(CO)$_2$MoFe$_2$H(μ_3-S)(CO)$_6$ instead of (η^5-C_5H_5)(CO)$_2$MoFe$_2$H(μ_3-S)(CO)$_6$. From the first brown band was obtained 0.093 g (35%) of **13** as a brown-black solid, mp 136−137 °C. Anal. Calcd for $C_{32}H_{22}CoFeMoO_8PS$: C, 47.55; H, 2.74. Found: C, 47.59; H, 3.09. IR (KBr disk): $\nu_{C\equiv O}$ 2044 (vs), 1986 (vs), 1923 (s), 1898 (s) cm^{-1}; $\nu_{C=O}$ 1676 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 3H, CH_3), 5.28−5.56 (m, 2H, H^3, H^4), 5.84−5.96 (m, 2H, H^2, H^5), 7.43−7.76 (m, 15H, 3C_6H_5) ppm. From the second brown band was obtained 0.077 g of byproduct as a black solid, which has not been fully characterized.

Preparation of (η^5-$MeO_2CC_5H_4$)(CO)$_2$MoFeCo(μ_3-S)(CO)$_5$(Ph_3P) (14). The same procedure as that for **12** was followed, but using 0.335 g (0.57 mmol) of (η^5-$MeO_2CC_5H_4$)(CO)$_2$MoFe$_2$H(μ_3-S)(CO)$_6$ instead of (η^5-C_5H_5)(CO)$_2$MoFe$_2$H(μ_3-S)(CO)$_6$. From the first brown band was obtained 0.191 g (41%) of **14** as a brown-black solid, mp 80−81 °C. Anal. Calcd for $C_{32}H_{22}CoFeMoO_9PS$: C, 46.63; H, 2.69. Found: C, 46.38; H, 2.29. IR (KBr disk): $\nu_{C\equiv O}$ 2046 (vs), 1986 (vs), 1934 (s), 1888 (s) cm^{-1}; $\nu_{C=O}$ 1724 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.85 (s, 3H, CH_3), 5.30−5.51 (m, 2H, H^3, H^4), 5.91−6.04 (m, 2H, H^2, H^5), 7.48−7.76 (m, 15H, 3C_6H_5) ppm. From the second brown band was obtained 0.082 g of byproduct as a black solid, which has not been fully characterized.

Preparation of (η^5-C_5H_5)(CO)$_2$WFeCo(μ_3-S)(CO)$_5$(Ph_3P) (15). The same procedure as that for **12** was followed, but using 0.358 g (0.58 mmol) of (η^5-C_5H_5)(CO)$_2$WFe$_2$H(μ_3-S)(CO)$_6$ instead of (η^5-C_5H_5)(CO)$_2$MoFe$_2$H(μ_3-S)(CO)$_6$. From the first brown band was obtained 0.120 g (24%) of **15** as a brown-black solid, mp 172 °C dec. Anal. Calcd for $C_{30}H_{20}CoFeO_7PSW$: C, 42.19; H, 2.36. Found: C, 42.11; H, 2.28. IR (KBr disk): $\nu_{C\equiv O}$ 2032 (vs), 1975 (vs), 1950 (vs), 1909 (vs), 1893 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.25 (s, 5H, C_5H_5), 7.30−7.70 (m, 15H, 3C_6H_5) ppm. From the second brown band was obtained 0.081 g of byproduct as a black solid, which has not been fully characterized.

Preparation of (η^5-$MeCOC_5H_4$)(CO)$_2$WFeCo(μ_3-S)(CO)$_5$(Ph_3P) (16). The same procedure as that for **12** was followed, but using 0.348 g (0.52 mmol) of (η^5-$MeCOC_5H_4$)(CO)$_2$WFe$_2$H(μ_3-S)(CO)$_6$ instead of (η^5-C_5H_5)(CO)$_2$MoFe$_2$H(μ_3-S)(CO)$_6$. From the first brown band was obtained 0.131 g (28%) of **16** as a brown-black solid, mp 173−174 °C. Anal. Calcd for $C_{32}H_{22}CoFeO_8PSW$: C, 42.84; H, 2.45. Found: C, 43.13; H, 2.46. IR (KBr disk): $\nu_{C\equiv O}$ 2041 (vs), 1983 (vs), 1918 (s), 1893 (s) cm^{-1}; $\nu_{C=O}$ 1680 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 3H, CH_3), 5.16−5.92 (m, 2H, H^3, H^4), 6.05−6.24 (m, 2H, H^2, H^5), 7.36−7.70 (m, 15H, 3C_6H_5) ppm. From the second brown band was obtained 0.080 g of byproduct as a black solid, which has not been fully characterized.

Preparation of (η^5-$MeO_2CC_5H_4$)(CO)$_2$WFeCo(μ_3-S)(CO)$_5$(Ph_3P) (17). The same procedure as that for **12** was followed, but using 0.373 g (0.55 mmol) of (η^5-$MeO_2CC_5H_4$)(CO)$_2$WFe$_2$H(μ_3-S)(CO)$_6$ instead of (η^5-C_5H_5)(CO)$_2$MoFe$_2$H(μ_3-S)(CO)$_6$. From the first brown band was obtained 0.075 g (15%) of **17** as a brown-black solid, mp 148−149 °C. Anal. Calcd for $C_{32}H_{22}CoFeO_9PSW$: C, 42.14; H, 2.43. Found: C, 42.38; H, 2.73. IR (KBr disk): $\nu_{C\equiv O}$ 2041 (vs), 1991 (vs), 1967 (vs), 1852 (s) cm^{-1}; $\nu_{C=O}$ 1729 (m) cm^{-1}. ^{1}H NMR (d_6-acetone): δ 3.78 (s, 3H, CH_3), 5.40−5.85 (m, 2H, H^3, H^4), 6.00−6.12 (m, 2H, H^2, H^5), 7.32−7.68 (m, 15H, $3C_6H_5$) ppm. From the second brown band was obtained 0.050 g of byproduct as a black solid, which has not been fully characterized.

Crystal Structure Determinations of 5, 9, 13, and 16. Suitable crystals of **5, 9, 13**, and **16** for X-ray diffraction analyses were obtained by slow evaporation of their CH_2Cl_2/hexane solutions at about −20 °C. Each crystal was mounted on a glass fiber and placed on an Enraf-Nonius CAD4 or a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å or 0.710 69 Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 4. The structures were solved by direct methods and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. The calculation for **5** was performed on a PDP 11/44 computer using the SDP-PLUS program system, whereas the calculations for **9**, **13**, and **16** were carried out on a Micro Vax II computer using the TEXSAN program system.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **5**, **9**, **13**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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