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Synthesis, Structure, and Reactivity of Mixed-Metal Clusters Bearing η^1 -Acetylide Groups, $(\eta^5\text{-C}_5\text{H}_5)\text{MFe}_2(\mu_3\text{-E})_2(\text{CO})_6(\eta^1\text{-CCPh})$ (M = Mo or W and E = Se or Te)

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Reaction of $\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2$ (E = Se, Te) with $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})$ (M = Mo, W), in the presence of trimethylamine-*N*-oxide (TMNO), in acetonitrile solvent at 60 °C yields the novel mixed-metal clusters $(\eta^5\text{-C}_5\text{H}_5)\text{MFe}_2(\mu_3\text{-E})_2(\text{CO})_6(\eta^1\text{-CCPh})$ (**1**, E = Se, M = Mo; **2**, E = Se, M = W; **3**, E = Te, M = Mo; **4**, E = Te, M = W) bearing η^1 -acetylide groups. The reaction of **1** or **3** with dicobalt octacarbonyl at room temperature gives the mixed-metal clusters $(\eta^5\text{-C}_5\text{H}_5)\text{MoFe}_2\text{Co}_2(\mu_3\text{-E})_2(\text{CO})_9(\mu\text{-CCPh})$ (**5**, **6**). Structures of **1** and **6** have been established crystallographically.

Introduction

Metal acetylide complexes evince interest from several perspectives: as useful precursors for preparation of organometallic polymers,^{1–6} as components in NLO materials,^{7,8} and as new liquid crystals.^{9,10} Formation of the cluster-bound polycarbon units occurs as a result of coupling of acetylide units from two different mononuclear acetylide molecules^{11–15} or coupling of two acetylide units with CO to form a pentanone ligand.^{16,17} Acetylide coupling is found to be sensitive to reaction conditions used as well as the nature of cluster frame-

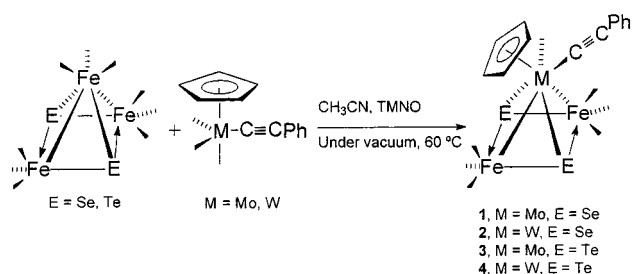
work atoms. Under aerobic conditions some clusters bearing both the oxo and the acetylide units are obtainable.^{18–20} Formation of chalcogen-bridged and acetylide-bearing mixed-metal clusters from the thermolytic reactions of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2]$ (E = chalcogen atom) and $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{C}\equiv\text{CPh})]$ (M = Mo or W) may be thought to occur by a mechanism involving an initial decarbonylation at the iron center followed by attachment of the electron-deficient iron atom at the triple bond of the coordinated acetylide group of the mononuclear acetylide complex, or by loss of one or more carbonyls from the metal acetylide compound and complexation by lone pairs of the triply bridging chalcogen atoms of the tri-iron cluster. Formation of new metal–metal bonds, acetylide coupling, and rearrangements to give the most stable cluster framework would follow to yield the final products. The nature of the acetylide coupling on the newly formed mixed-metal cluster would be a consequence of the relative orientations of the adding metal acetylide units as well as the nature of the chalcogens. Importantly, since decarbonylation is a necessary step in the overall mechanism, the nature of the reaction conditions is also expected to play an important role.

Our previous attempts at preparation of mixed Fe/Mo or Fe/W clusters bearing uncoupled, η^1 -acetylide moieties have been unsuccessful; under anaerobic conditions, either dimerization of the mononuclear acetylide complexes takes place or clusters bearing coupled acetylide units are formed.²¹ Under aerobic and mild

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Scheme 1



thermolytic reaction conditions, oxo-bridged mixed-metal complexes are obtained in which the acetylide units remain uncoupled, but are π -bonded, and hence the acetylide triple bond is unutilizable for further reactions.^{18–20} We report here on the first example of a mixed-metal cluster bearing a η^1 -bound acetylide group in which the C=C triple bond remains intact and, hence, susceptible to attack by electrophiles.

Results and Discussion

Clusters **1–4** were obtained in yields of 23–43% by reacting $\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2$ (E = Se, Te) with $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})$ (M = Mo, W) in the presence of trimethylamine-*N*-oxide (TMNO) in acetonitrile solvent at 60 °C in an evacuated sealed tube (Scheme 1). There was some decomposition, but no observation in the reaction mixture of the known dimers $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]_2\{\mu\text{-1,2-PhC-CC}\equiv\text{CPh}\}$ ²² and $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]_2\{\mu\text{-1,2-PhC-C(CO)C}\equiv\text{CPh}\}$.¹⁶ Apart from **1–4**, the only other compounds to be observed and isolated from the reaction were trace amounts of the starting materials. The new compounds are air stable in solid but decompose in solution over a period of 2–3 days. Infrared spectra of **1–4** show a similar four-band pattern in the terminal carbonyl region, and ¹H NMR spectra confirm the presence of $(\eta^5\text{-C}_5\text{H}_5)$ and phenyl groups.

The X-ray crystal analysis of **1** (Figure 1) shows a distorted square pyramidal core for Fe_2MoSe_2 in which the Mo atom sits at the apical site, as in the previously reported cluster $\text{Fe}_2\text{MoSe}_2(\text{CO})_{10}$.²³ The Mo atom of **1** differs in having a single carbonyl group, a $(\eta^5\text{-C}_5\text{H}_5)$ ligand, and a $\eta^1\text{-C}\equiv\text{CPh}$ group. The acetylide C–C bond distance in **1** is longer (1.221(12) Å) than the acetylide triple bond distances seen in $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{C}\equiv\text{CPh})$ (1.196(9) Å), $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]_2\{\mu\text{-1,2-PhC-CC}\equiv\text{CPh}\}$ ²² (1.208(5) Å), and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]_2\{\mu\text{-1,2-PhC-C(CO)C}\equiv\text{CPh}\}$ ¹⁶ (1.197(5) Å) but still within the acetylenic triple-bond range. Formal replacement of three carbonyls on the Mo atom of $\text{Fe}_2\text{MoSe}_2(\text{CO})_{10}$ by one $(\eta^5\text{-C}_5\text{H}_5)$ ligand and a $\eta^1\text{-C}\equiv\text{CPh}$ group in **1** lead to a marginal increase in the Mo–Fe bond lengths (Mo–Fe in $\text{Fe}_2\text{MoSe}_2(\text{CO})_{10}$, 2.823(4) and 2.794(4) Å; in **1**, 2.9085(15) and 2.8228(15) Å). All other bond distances are similar in the two compounds.

Formation of **1–4** involves a formal conversion of the Fe_3E_2 unit to an Fe_2E_2 unit and addition of a $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})(\text{C}\equiv\text{CPh})$ group to it. Although the exact

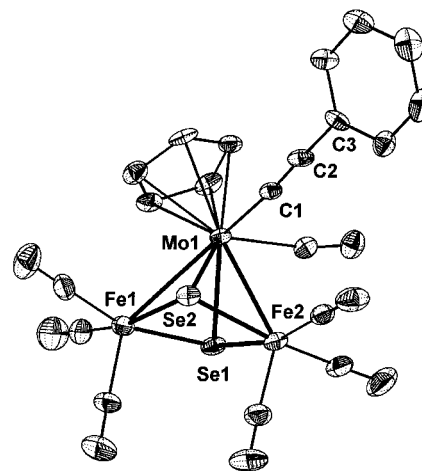


Figure 1. ORTEP diagram of **1** with 30% probability ellipsoids. Selected bond distances (Å) and bond angles (deg): C(1)–C(2) = 1.221(12), Mo(1)–Fe(1) = 2.9085(15), Mo(1)–Fe(2) = 2.8228(15), Mo(1)–Se(2) = 2.5277(12), Mo(1)–Se(1) = 2.5557(11), Fe(1)–Se(2) = 2.3625(17), Fe(2)–Se(1) = 2.3866(17), C(1)–C(2)–C(3) = 178.2(10), Fe(1)–Mo(1)–Fe(2) = 74.65(4), Mo(1)–Se(1)–Fe(1) = 72.58(5), Mo(1)–Se(2)–Fe(2) = 70.03(4).

mechanistic details are not known, certain observations lead us to suggest possible steps likely to be involved in the formation of **1–4**. In the presence of TMNO, $\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2$ is known to convert to $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ in about 30% yield. We investigated the direct reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ with $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})$ (room temperature stirring, in the presence of and without TMNO), but did not observe formation of compounds **1–4**. Also, the fact that we do not observe any formation of the known dimers $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]_2\{\mu\text{-1,2-PhC-CC}\equiv\text{CPh}\}$ ²² and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]_2\{\mu\text{-1,2-PhC-C(CO)C}\equiv\text{CPh}\}$ ¹⁶ leads us to believe that, in the presence of TMNO/NCMe, $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})$ forms $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})(\text{NCMe})_2(\text{C}\equiv\text{CPh})$ (**A**) as a possible intermediate (formation of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NCMe})(\text{C}\equiv\text{CPh})$ would have yielded the dimers). Intermediate **A** can now react in one of two ways: Pathway 1 shows its reaction with the in-situ formed $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ (E = Se, Te), which involves loss of the two acetonitrile ligands and addition of the coordinatively unsaturated $(\text{C}_5\text{H}_5)\text{M}(\text{CO})(\text{C}\equiv\text{CPh})$ unit across the E–E bond of $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ to form intermediate **B** in much the same way as has been observed in the formation of $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_6(\mu_3\text{-Se})_2$ from the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ with $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$.²⁴ Intermediate **B** rearranges to **1–4** by a process involving cleavage of the Fe–Fe bond and formation of new Fe–M bonds. An alternate option available for **A** is its reaction with the starting iron cluster $\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2$. Pathway 2 shows that upon loss of the two acetonitrile ligands, the unsaturated $(\text{C}_5\text{H}_5)\text{M}(\text{CO})(\text{C}\equiv\text{CPh})$ unit can add to the triply bridging Se atoms to form intermediate **C**, as for instance in the formation of $\text{Fe}_4(\text{CO})_{11}(\mu_4\text{-Se})_2$ and $\text{Fe}_3\text{Ru}(\text{CO})_{11}(\mu_4\text{-Se})_2$ from reactions of $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Se})_2$ with $\text{Fe}(\text{CO})_5$ and $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$, respectively.²⁵ Formation of new Fe–M bonds and simultaneous loss of one $\text{Fe}(\text{CO})_3$ unit would result in **1–4**.

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Chart 1. Pathway 1

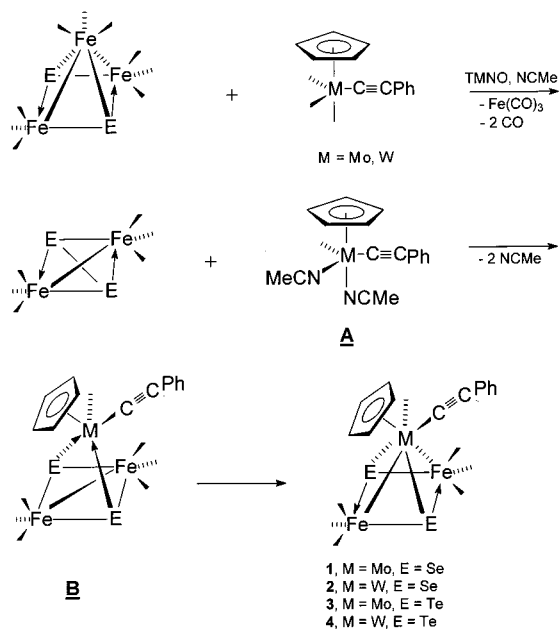
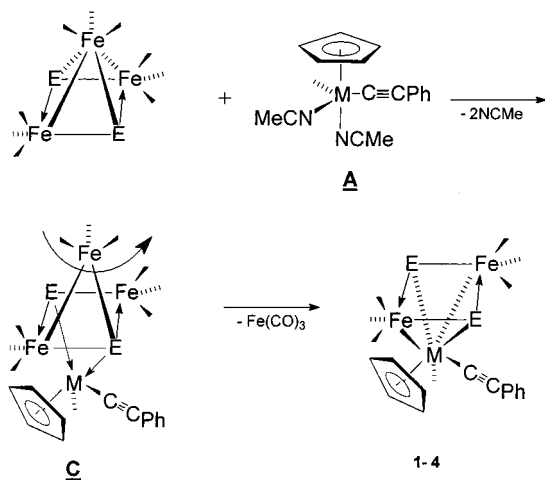
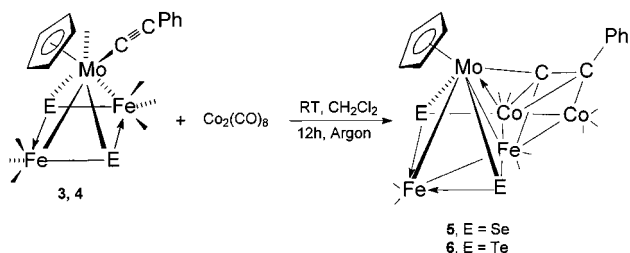


Chart 2. Pathway 2



Scheme 2



To test the reactivity of the η^1 -acetylide group of **1–4**, we investigated the reaction of compounds **1** and **3** with $\text{Co}_2(\text{CO})_8$ and observe the formation of $(\eta^5\text{-C}_5\text{H}_5)\text{MoFe}_2\text{-Co}_2(\mu_3\text{-E})_2(\text{CO})_9(\mu\text{-CCPh})$ (E = Se, **5**; E = Te, **6**) in yields of 66% and 63%, respectively (Scheme 2). IR and NMR spectroscopy indicate **5** and **6** to be isostructural. The structure of **5**, determined crystallographically and shown in Figure 2, shows the expected addition of the Co_2 unit across the $\text{C}\equiv\text{C}$ triple bond of **3**. Decarbonylation at the metal centers leads to formation of Fe–Fe, two Fe–Co, and one Co–Mo bond, as well as one new E–Co bond (Pathway 3). All the metal centers are

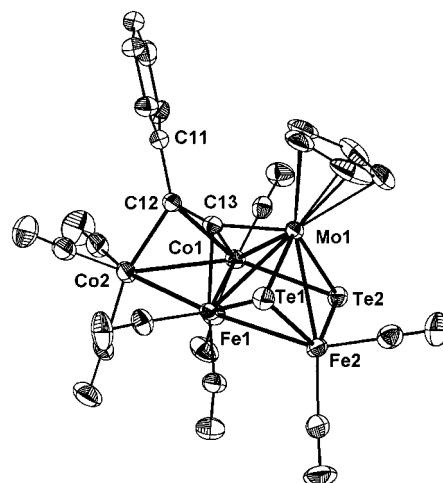
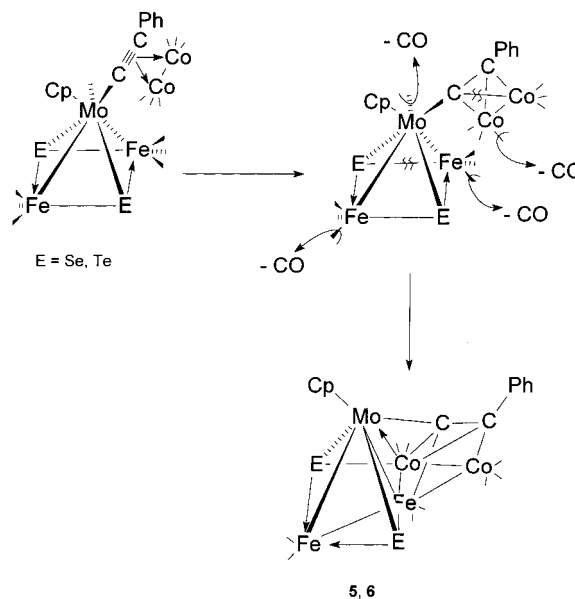


Figure 2. ORTEP diagram of **6** with 30% probability ellipsoids. Selected bond distances (Å) and bond angles (deg): C(12)–C(13) = 1.368(9), Mo(1)–Fe(1) = 2.6918(10), Mo(1)–Fe(2) = 2.7328(11), Co(1)–Co(2) = 2.5387(13), Co(1)–Te(2) = 2.5267(10), Mo(1)–Te(1) = 2.6614(7), C(11)–C(12)–C(13) = 126.1(6), Fe(1)–Mo(1)–Fe(2) = 58.05(3), Co(2)–Co(1)–Mo(1) = 110.76(4), Mo(1)–Te(1)–Fe(2) = 64.42(3), Fe(1)–Co(1)–Te(2) = 85.89(4).

Chart 3. Pathway 3



electron precise, if it is assumed that the Co–Mo bond is a donor acceptor bond.

Conclusion

The new mixed-metal clusters **1–4** were prepared in reasonable yields and were shown to contain a η^1 -acetylide group, which should be attractive for cluster growth reaction as well as coupling with acetylide moieties in other complexes. Preliminary investigations of the reactivity of **1** and **3** have led to isolation of the mixed Fe/Mo/Co clusters **5** and **6**. We are presently exploring the utility of **1–4** for addition of various units to the η^1 -acetylide group as well as to the triply bridging chalcogens in the cluster core.

Experimental Section

General Considerations. Reactions and manipulations were carried out using standard Schlenk line techniques under

an atmosphere of prepurified argon. Solvents were purified, dried, and distilled under an argon or nitrogen atmosphere prior to use. Reactions were monitored by TLC as well as by FT-IR spectroscopy. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrophotometer, as hexane solutions of the sample in a 0.1 mm path length NaCl cell, and NMR (^1H) were recorded on a Varian VXR-300S spectrometer in CDCl_3 . Elemental analyses were performed using a Carlo Erba automatic analyzer. The compounds $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2]^{26,27}$ and $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{C}\equiv\text{CPh})]^{28}$ ($\text{M} = \text{Mo}, \text{W}$) were prepared by established procedures.

Tungsten hexacarbonyl and molybdenum hexacarbonyl were purchased from Strem Chemical Co., phenylacetylene and cyclopentadiene were purchased from Aldrich Chemical Co., and these were used without further purification.

General Procedure for the Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{-MFe}_2(\text{CO})_6(\mu_3\text{-E})_2(\eta^1\text{-C}\equiv\text{CPh})]$ ($\text{M} = \text{Mo}, \text{W}$ and $\text{E} = \text{Se}, \text{Te}$) (1**–**4**).** In a typical procedure 0.044 mmol of $[\text{CpM}(\text{CO})_3(\text{CCPh})]$ [$\text{M} = \text{Mo}, \text{W}$] and 0.138 mmol of $\text{Fe}_3\text{E}_2(\text{CO})_9$ [$\text{E} = \text{Se}$ and Te] were dissolved in 20 mL of acetonitrile. To this dark purple colored solution was added dropwise 5 mg of freshly sublimed trimethylamine oxide (TMNO) in acetonitrile over a period of 20 min. The reaction mixture was allowed to stir at room temperature for 10 min. At this point vacuum was applied and the reaction mixture was heated to 60 °C, yielding a purple residue. This was dissolved in CH_2Cl_2 and filtered through Celite. The clear purple filtrate was concentrated and subjected to column chromatography. Elution with hexane–acetone (97:3 v/v) gave the pure products (**1**–**4**).

1. Yield = 10 mg, 39%. Anal. Found for $\text{C}_{20}\text{H}_{10}\text{O}_7\text{Se}_2\text{Fe}_2\text{Mo}$: C, 33.25; H, 1.45. Calcd: C, 32.97; H, 1.37. IR (hexane) $\nu\text{ cm}^{-1}$ (terminal CO): 2072m, 2044s, 2010m, 1987m. ^1H NMR (CDCl_3): δ 5.48 (s, 5H, C_5H_5), 7.09–7.18 (m, 5H, C_6H_5). Mp (°C): 118–120 (dec).

2. Yield = 10 mg, 28%. Anal. Found for $\text{C}_{20}\text{H}_{10}\text{O}_7\text{Se}_2\text{Fe}_2\text{W}$: C, 29.62; H, 1.30. Calcd: C, 29.41; H, 1.22. IR (hexane) $\nu\text{ cm}^{-1}$ (terminal CO): 2070m, 2041s, 2008m, 1983m. ^1H NMR (CDCl_3): δ 5.56 (s, 5H, C_5H_5), 7.09–7.17 (m, 5H, C_6H_5). Mp (°C): 125–128 (dec).

3. Yield = 15.6 mg, 43%. Anal. Found for $\text{C}_{20}\text{H}_{10}\text{O}_7\text{Te}_2\text{Fe}_2\text{W}$: C, 28.78; H, 1.15. Calcd: C, 29.08; H, 1.21. IR (hexane) $\nu\text{ cm}^{-1}$ (terminal CO): 2059m, 2034s, 1999m, 1977m. ^1H NMR (CDCl_3): δ 5.36 (s, 5H, C_5H_5), 7.17–7.27 (m, 5H, C_6H_5). Mp (°C): 140–142 (dec).

4. Yield = 9 mg, 23%. Anal. Found for $\text{C}_{20}\text{H}_{10}\text{O}_7\text{Te}_2\text{Fe}_2\text{W}$: C, 26.33; H, 1.00. Calcd: C, 26.28; H, 1.09. IR (hexane) $\nu\text{ cm}^{-1}$ (terminal CO): 2055m, 2029s, 1995m, 1970m. ^1H NMR (CDCl_3): δ 5.41 (s, 5H, C_5H_5), 7.10–7.25 (m, 5H, C_6H_5). Mp (°C): 147–150 (dec).

General Procedure for the Preparation of **5 and **6**.** In a typical procedure, to a dichloromethane solution of 0.067 mmol of **1** or **3** was added 3 equiv of $\text{Co}_2(\text{CO})_8$. The reaction mixture was allowed to stir at room temperature for 12 h. The reaction mixture was filtered through Celite to remove de-

composed materials, and the solvent was removed in vacuo. The residue was subjected to chromatographic workup on silica gel TLC plates using hexane–dichloromethane (50:50 v/v) to give the pure products (**5**, **6**).

5. Yield = 40 mg, 66%. Anal. Found for $\text{C}_{22}\text{H}_{10}\text{O}_9\text{Se}_2\text{Fe}_2\text{-MoCo}_2$: C, 29.60; H, 1.10. Calcd: C, 29.30; H, 1.11. IR (hexane) $\nu\text{ cm}^{-1}$ (terminal CO): 2090s, 2058s, 2034s, 2016w, 2005w. ^1H NMR (CDCl_3): δ 5.32 (s, 5H, C_5H_5), 7.34–7.70 (m, 5H, C_6H_5). Mp (°C): 148–150 (dec).

6. Yield = 42 mg, 63%. Anal. Found for $\text{C}_{22}\text{H}_{10}\text{O}_9\text{Te}_2\text{Fe}_2\text{-MoCo}_2$: C, 26.30; H, 0.97. Calcd: C, 26.42; H, 1.00. IR (hexane) $\nu\text{ cm}^{-1}$ (terminal CO): 2085s, 2053s, 2032s, 2016w, 2000w. ^1H NMR (CDCl_3): δ 5.30 (s, 5H, C_5H_5), 7.34–7.70 (m, 5H, C_6H_5). Mp (°C): 150–152 (dec).

Reaction of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2]$ with TMNO to Form $[\text{Fe}_2(\text{CO})_6(\mu\text{-E})_2]$. In a typical reaction, 250 mg of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2]$ was dissolved in acetonitrile (30 mL), and to this was added dropwise an acetonitrile solution of TMNO (10 mg in 10 mL) over a period of 30 min. The mixture was stirred for a further 15 min. The solvent was removed in vacuo, and the residue was subjected to column chromatography using silica gel. Elution with hexane yielded an orange band of $[\text{Fe}_2(\text{CO})_6(\mu\text{-E})_2]$ (yield: $\text{E} = \text{Se}$, 28%; $\text{E} = \text{Te}$, 33%).

X-ray Crystal Structure Determinations. Single crystals of **1** and **6** were grown from dichloromethane–hexane solvent mixtures at 0 °C. Data were collected on a Nonius MACH3 four-circle diffractometer (graphite-monochromatized Mo K α radiation) for the cell determination and intensity data collection. The unit cell parameters were derived and refined by using randomly selected reflections in the 2θ range 2–50°. The structure was solved by direct methods using the SHELXS97 program and refined by using SHELXL97 software.^{29,30} The non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms were geometrically fixed and refined using a riding model. Absorption correction was employed using ψ scans.³¹ The size of the crystals were 0.25 \times 0.20 \times 0.10 mm and 0.4 \times 0.25 \times 0.15 mm for **1** and **6**, respectively. Final R values: $I > 2\sigma(I)$, $R1 = 0.603$, $wR2 = 0.1477$; all data, $R1 = 0.0760$, $wR2 = 0.1643$ (**1**); $I > 2\sigma(I)$, $R1 = 0.0422$, $wR2 = 0.1088$; all data, $R1 = 0.0474$, $wR2 = 0.1137$ (**6**).

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Supporting Information Available: Details of the structure determination for **1** and **6**, including tables listing atomic coordinates, thermal parameters, and bond distances and angles and figures showing structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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