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Selenium-Bridged Clusters. Synthesis and Characterization of Selenium-Bridged Fe−Mo Clusters $Cp_2Mo_2Fe_2Se_3(CO)_6$, $Cp_2Mo_2Fe_2Se_2(CO)_7$, and $Cp_2Mo_2FeSe(CO)_7$

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Reflux of a benzene solution containing $Fe_3(CO)_9Se_2$ and $Cp_2Mo_2(CO)_6$ yielded the known cluster $Cp_2Mo_2Fe_2Se_3(CO)_6$ (**1**) and the new clusters $Cp_2Mo_2Fe_2Se_2(CO)_7$ (**2**) and $Cp_2Mo_2FeSe(CO)_7$ (**3**). Compound **2** was also isolated from the room temperature reaction of $Fe_2(CO)_6Se_2$ with $Cp_2Mo_2(CO)_4$. In solution, **2** was found to slowly convert to **1**; on thermolysis, the conversion occurs rapidly. Both **2** and **3** have been characterized by spectroscopic and crystallographic methods. **2** crystallizes in the orthorhombic space group $Pna2_1$ with $a = 13.289(3)$ Å, $b = 12.059(2)$ Å, $c = 13.045(3)$ Å, $V = 2090.5(7)$ Å^3, and $Z = 4$. The structure refined to $R = 3.56\%$ and $R_w = 3.65\%$ for 2109 unique reflections ($F_o \geq 4\sigma(F_o)$). The structure of **2** consists of a Mo_2Fe_2 tetrahedron with the Fe−Fe edge bridged by a CO group. Triply bridging Se atoms cap the two Mo_2Fe faces, and there is a semitriply bridging CO group above one of the $MoFe_2$ faces. The remaining CO groups are terminally bonded. **3** crystallizes in the monoclinic space group $C2/c$ with $a = 30.756(7)$ Å, $b = 8.590(1)$ Å, $c = 15.115(3)$ Å, $\beta = 102.86(3)°$, $V = 3893.4(13)$ Å^3, and $Z = 8$. The structure refined to $R = 4.81\%$ and $R_w = 6.00\%$ for 3103 unique reflections ($F_o \geq 4\sigma(F_o)$). The structure of **3** consists of a Mo_2FeSe tetrahedron. Each Mo atom has one Cp and two terminally bonded CO groups, while the Fe atom has three CO groups bonded to it.

Introduction

Several synthetic approaches have been developed for the incorporation of chalcogen atoms in metal complexes.[2] Recent years have witnessed a marked increase in the interest in the use of selenium and tellurium as bridging and stabilizing ligands in numerous types of compounds. Oxidative decarbonylation of metal carbonyls by polychalcogenide ligands E_n^{2-} (E = S, Se, Te; $n = 2-6$) provides a convenient general route for introducing chalcogen atoms into metal clusters.[3] Some convenient synthetic methods for the incorporation of Se in metal complexes has made it possible to investigate the chemistry of Se-bridged complexes. The trialkylsilyl compounds $(R_3Si)_2Se$ have been extensively used to prepare a large variety of metal selenide clusters.[4] The reaction of $[WCl_2(PPh_2Me)_4]$ with $SiMe_3(SePh)$ produces $[W_2Se_2(PPh_2Me)_2(SePh)_4]$. The cationic cluster Se_4^{2+} has been shown to react with a mixture of $Fe(CO)_5$ and $W(CO)_6$ to form the mixed-metal species $[WFe(CO)_8(Se_2)]^{2+}$.[5] Recently, insertion of selenium into the Mo=Mo double bond in $(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)Mo_2Cp_2(CO)_2$ to form $[\mu\text{-}Se)(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)Mo_2Cp_2(CO)_2]$ has been reported.[6] The reduction of Na_2SeO_3 with $[HFe(CO)_4]^-$ provides a convenient route for obtaining $Fe_3(CO)_9(\mu\text{-}Se)_2$ which can be converted into $Fe_2(CO)_6(\mu\text{-}Se_2)$ on treatment with NaOMe followed by acidification.[7] Both compounds have been shown to be good starting materials for obtaining selenium-bridged clusters.[8] For instance, the octahedral clusters $Fe_3Ru(CO)_{11}Se_2$ and $Fe_4(CO)_{11}Se_2$ can be obtained by the room temperature reactions of $Fe_3(CO)_9(\mu\text{-}Se)_2$ with $Ru(CO)_4(C_2H_4)$ and $Fe(CO)_5$, respectively,[9] while $Fe_2Ru_2(CO)_{11}Se_2$ can be obtained by the room temperature reaction of $Ru(CO)_4(C_2H_4)$ with $Fe_2(CO)_6(\mu\text{-}Se_2)$.[10] Of the two starting materials, $Fe_3(CO)_9(\mu\text{-}Se)_2$ is more robust and can withstand mild heating, whereas $Fe_2(CO)_6(\mu\text{-}Se_2)$ is a much more reactive compound and it readily

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decomposes on heating. It adds organic and inorganic moieties readily at room temperature. Although the reactions of the Mo≡Mo triple-bonded compound $Cp_2Mo_2(CO)_4$ with PhSeMgBr or PhSeLi to give $[Cp(CO)_2Mo(\mu\text{-}SePh)]_2$ and with $Fe_2(CO)_6(\mu\text{-}S_2)$ to form $Cp_2Mo_2Fe_2S_2(CO)_8$ have been reported,[11] there is no report on its reactivity with $Fe_2(CO)_6(\mu\text{-}Se_2)$. Here we report the thermolysis of $Fe_3(CO)_9(\mu\text{-}Se)_2$ with $Cp_2Mo_2(CO)_6$ and the room temperature reaction of $Fe_2(CO)_6(\mu\text{-}Se_2)$ with the Mo≡Mo triple-bonded compound $Cp_2Mo_2(CO)_4$.

Experimental Section

General Procedures. Reactions and manipulations were carried out under an inert atmosphere of argon by means of standard Schlenk techniques. Solvents were deoxygenated immediately prior to use. Infrared spectra were recorded on a Nicolet 5DXB FT spectrometer as dichloromethane solutions in 0.1-mm path length NaCl cells. NMR spectra were obtained on a Varian XL-300 spectrometer at 25 °C. The starting materials $Fe_2(CO)_6Se_2$, $Fe_3(CO)_9Se_2$,[7] $Cp_2Mo_2(CO)_6$, and $Cp_2Mo_2(CO)_4$[12] were prepared as reported in the literature.

Thermolytic Reaction of $Fe_3(CO)_9Se_2$ and $Cp_2Mo_2(CO)_6$. A mixture of $Fe_3(CO)_9Se_2$ (0.15 g, 0.26 mmol) and $Cp_2Mo_2(CO)_6$ (0.098 g, 0.16 mmol) in 75 mL of benzene was refluxed for 24 h. The solution was filtered through Celite to remove insoluble material. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with 1/1 (v/v) hexane/dichloromethane mixture afforded the following compounds, in order of elution: the known brown $Cp_2Mo_2Fe_2(CO)_6Se_3$ (**1**) (5 mg, 3%), dark brown (almost black) $Cp_2Mo_2Fe_2(CO)_7Se_2$ (**2**) (49 mg, 31%), and brown $Cp_2Mo_2Fe(CO)_7Se$ (**3**) (26 mg, 25%). **2**: IR (ν(CO), cm^{-1}) 2018 (s), 1989 (vs), 1973 (s), 1957 (s), 1828 (br, m), 1732 (br, m); ^{1}H NMR ($CDCl_3$) δ 5.49, 5.18; mp 121 °C dec. Anal. Calcd for **2**: C, 25.9; H, 1.27. Found: C, 26.0; H, 1.42. **3**: IR (ν(CO), cm^{-1}) 2036 (vs), 2023 (s), 1982 (vs), 1955 (br, s), 1888 (br, m), 1840 (br, m); ^{1}H NMR ($CDCl_3$) δ 5.28; mp 97 °C dec. Anal. Calcd for **3**: C, 31.3; H, 1.53. Found: C, 31.3; H, 1.62.

Reaction of $Fe_2(CO)_6Se_2$ and $Cp_2Mo_2(CO)_4$. A mixture of freshly prepared $Cp_2Mo_2(CO)_4$ (0.075 g, 0.13 mmol) and $Fe_2(CO)_6Se_2$ (0.098 g, 0.2 mmol) in 30 mL of CH_2Cl_2 was stirred at room temperature for 24 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel TLC plates. Using 1/1 (v/v) hexane/dichloromethane mixture as eluent, the following bands were obtained in order of elution: a trace amount of **1** followed by the dark brown band of **2** (69 mg, 52%). When longer reaction times were employed, the yield of **1** increased at the expense of **2**. Stirring of a CH_2Cl_2 solution containing pure **2** for 24 h and chromatographic workup as before yielded equal quantities of **1** and **2**.

Thermolysis of 2. A benzene solution (10 mL) of pure **2** (10 mg) was refluxed for 2 h. The solution was filtered through Celite to remove insoluble material, and the solvent was removed in vacuo. The residue was subjected to chromatographic workup on silica gel TLC plates. Using 1/1 (v/v) hexane/dichloromethane mixture as eluent, a single brown band was isolated and identified as compound **1** (3 mg).

Table 1. Crystallographic Data for $Cp_2Mo_2FeSe(CO)_7$ and $Cp_2Mo_2Fe_2Se_2(CO)_7$

	(a) Crystal Parameters	
formula	$C_{17}H_{10}Fe_2Mo_2O_7Se_2$ (**2**)	$C_{17}H_{10}FeMo_2O_7Se$ (**3**)
fw	787.8	652.9
cryst system	orthorhombic	monoclinic
space group	*Pna*2$_1$	*C*2/*c*
a, Å	13.289(3)	30.756(7)
b, Å	12.059(2)	8.590(1)
c, Å	13.045(3)	15.115(3)
β, deg		102.86(3)
V, Å^3	2090.5(7)	3893.4(13)
Z	4	8
cryst dimens, mm	0.24 × 0.36 × 0.40	0.40 × 0.40 × 0.42
cryst color	dark red	cherry red
D(calc), g cm^3	2.503	2.228
μ(Mo Kα), cm^{-1}	60.52	39.10
temp, K	293	296
T(max)/*T*(min)	0.695/0.396	0.709/0.634
	(b) Data Collection	
diffractometer	Siemens P3	
monochromator	graphite	
radiation (λ, Å)	Mo Kα (0.710 73)	
2θ scan range, deg	4−55	4−55
data collected (*h*,*k*,*l*)	−17,−15,+16	±39,+11,+19
no. of rflns collcd	2711	4646
no. of indpt rflns	2504	4470
no. of indpt obsvd rflns $F_o \geq 4\sigma(F_o)$	2109	3103
std rflns	3 std/197 rflns	3 std/197 rflns
var in stds, %	<1	<1
	(c) Refinement	
R(*F*), %	3.56	4.81
R($_w$*F*), %	3.65	6.00
Δ/σ(max)	0.003	0.05
$\Delta(\varrho)$, e Å^{-3}	0.88	0.78
N_o/N_v	7.8	11.5
GOF	1.02	1.12

X-ray Crystallographic Structure Determination. Crystallographic data are collected in Table 1. Crystals were mounted on glass fibers with epoxy cement. Preliminary photographic evidence revealed *mmm* and 2/*m* Laue symmetry for **2** and **3**, respectively.[13] For **2**, either the space groups *Pnma* or *Pna*2$_1$ were indicated by systematic absences in the diffraction data; similarly, for **3**, either the space groups *C*2/*c* or *Cc* were indicated. For **2**, all evidence pointed to the noncentrosymmetric alternative, and for **3**, the centrosymmetric alternative produced superior results. For **2** a Roger's test, performed on the reported hand, yielded η = 0.91(7). Semi-empirical corrections for absorption were applied to both data sets.

The structures were solved by direct methods. All non-hydrogen atoms were anisotropically refined (except as noted below), and hydrogen atoms were included in computations as idealized contributions. Four peaks in the final difference map for **3**, ranging from 2.4 to 3.0 e Å^3, formed a tetrahedron inversionally and dimensionally related to the heavy-atom core of the structure. The atoms of the second core structure were refined with weighted, composite scattering terms representing the average of the core's composition. This was required because no core substituents could be located to conform to individual atom identities. The minority core (given as primed atoms in the supplementary material) has an approximate occupancy of 5%. Inclusion of the disorder model reduced the *R* factor from 6.9 to 4.8% and eliminated all difference map peaks above 0.78 e Å^3. The crystallographic computations used various PC and VAX versions of the SHELXTL software libraries (G. Sheldrick, distributed by Siemens XRD, Madison, WI). Selected bond distances and angles for **2** and **3** are given in Tables 2 and 3, respectively.

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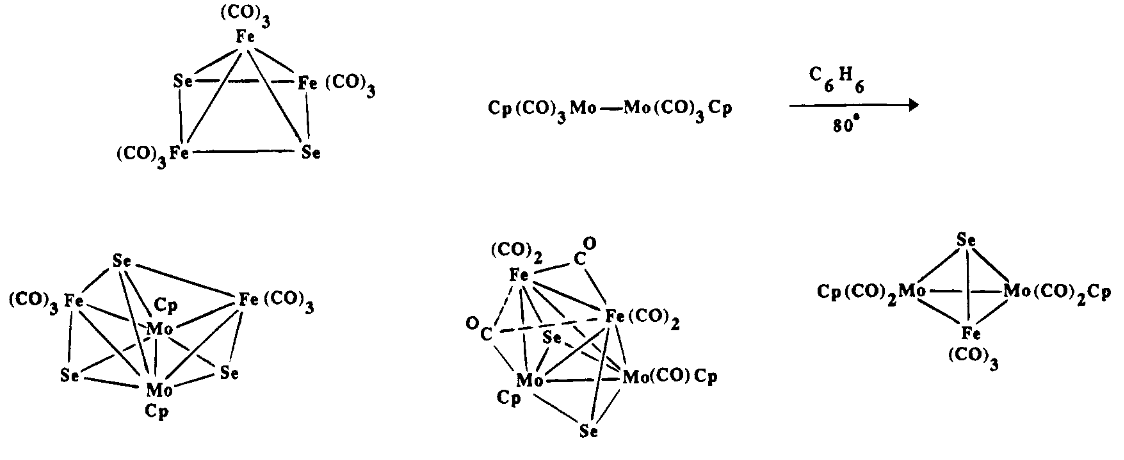
(13) A second polymorph of $Cp_2Mo_2FeSe(CO)_7$ (**3′**) was obtained after crystallization from a hexane/dichloromethane mixture at −10 °C. The structures of the two symmetry-independent molecules of the second polymorph and that of the first are chemically identical. *Crystal data for **3′***: deep red, monoclinic, *P*2$_1$/*c*, *a* = 20.322(9) Å, *b* = 12.728(5) Å, *c* = 16.295(7) Å, β = 113.33°, *V* = 3870(3) Å^3, *Z* = 8, *R*(*F*) = 9.22%.

Scheme 1



1 2 3

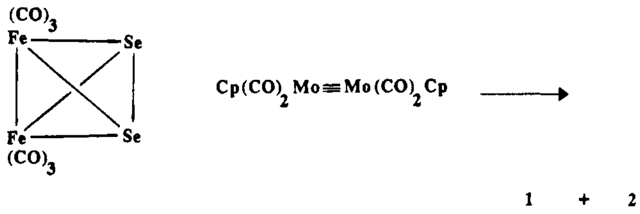
Table 2. Selected Bond Distances and Angles for $\mathrm{Cp_2Mo_2Fe_2Se_2(CO)_7}$

(a) Bond Distances (Å)			
Mo(1)—Mo(2)	2.820(1)	Mo(2)—C(11)	2.002(12)
Mo(1)—CNT(1)	2.015(7)	Fe(1)—Se(2)	2.442(2)
Mo(2)—CNT(2)	2.020(7)	Fe(1)—Se(1)	2.313(2)
Mo(1)—Se(1)	2.505(2)	Fe(1)—C(12)	1.768(12)
Mo(1)—Se(2)	2.504(2)	Fe(1)—C(13)	1.812(13)
Mo(1)—Fe(1)	2.811(2)	Fe(1)—C(14)	1.945(14)
Mo(1)—Fe(2)	2.810(2)	Fe(1)—C(15)	2.466(11)
Mo(1)—C(15)	1.976(11)	Fe(2)—C(14)	1.974(13)
Mo(2)—Se(1)	2.498(2)	Fe(2)—C(15)	2.463(11)
Mo(2)—Se(2)	2.500(2)	Fe(2)—C(16)	1.757(12)
Mo(2)—Fe(1)	2.826(2)	Fe(2)—C(17)	1.797(13)
Mo(2)—Fe(2)	2.816(2)		
(b) Bond Angles (deg)			
CNT(1)—Mo(1)—Mo(2)	140.7(3)	Mo(1)—Se(1)—Mo(2)	68.6(1)
CNT(1)—Mo(1)—Se(1)	115.1(3)	Mo(1)—Se(2)—Mo(2)	68.6(1)
CNT(1)—Mo(1)—Se(2)	115.4(3)	Mo(1)—Fe(1)—Mo(2)	60.0(1)
CNT(1)—Mo(1)—Fe(1)	149.1(3)	Mo(1)—Fe(2)—Mo(2)	60.2(1)
CNT(1)—Mo(1)—Fe(2)	149.7(3)	Mo(1)—C(15)—O(15)	158.1(9)
CNT(2)—Mo(2)—Mo(1)	178.2(3)	Se(1)—Mo(1)—Se(2)	111.2(1)
CNT(2)—Mo(2)—Se(1)	124.6(3)	Se(1)—Mo(2)—Se(2)	111.6(1)
CNT(2)—Mo(2)—Se(2)	123.9(3)	Fe(1)—Mo(1)—Fe(2)	51.5(1)
CNT(2)—Mo(2)—Fe(1)	118.9(3)	Fe(1)—Mo(2)—Fe(2)	51.3(1)
CNT(2)—Mo(2)—Fe(2)	118.5(3)		

Table 3. Selected Bond Distances and Angles for $\mathrm{Cp_2Mo_2FeSe(CO)_7}$

(a) Bond Distances (Å)			
CNT(1)—Mo(1)	2.001(8)	Mo(2)—Fe	2.843(1)
CNT(2)—Mo(2)	1.983(8)	Mo(2)—C(13)	1.996(11)
Mo(1)—Mo(2)	3.096(1)	Mo(2)—C(14)	1.986(14)
Mo(1)—Se	2.498(1)	Fe—Se	2.320(2)
Mo(1)—Fe	2.827(2)	Fe—C(15)	1.779(9)
Mo(1)—C(11)	1.954(7)	Fe—C(16)	1.762(17)
Mo(1)—C(12)	1.994(8)	Fe—C(17)	1.762(10)
Mo(2)—Se	2.520(1)		
(b) Bond Angles (deg)			
CNT(1)—Mo(1)—Mo(7)	158.1(3)	Se—Mo(2)—Fe	50.8(1)
CNT(1)—Mo(1)—Se	114.7(3)	Fe—Mo(2)—Mo(1)	56.7(1)
CNT(1)—Mo(1)—Fe	132.1(3)	Mo(1)—Se—Mo(2)	76.2(1)
CNT(1)—Mo(1)—C(11)	110.9(3)	Mo(1)—Se—Fe	71.7(1)
CNT(1)—Mo(1)—C(12)	111.9(3)	Mo(2)—Se—Fe	71.8(1)
Se—Mo(1)—Fe	51.2(1)	Mo(1)—Fe—Mo(2)	66.2(1)
Se—Mo(1)—Mo(2)	52.2(1)	Mo(1)—Fe—Se	57.1(1)
Fe—Mo(1)—Mo(2)	57.2(1)	Mo(2)—Fe—Se	57.3(1)
CNT(2)—Mo(2)—Mo(1)	128.4(3)	Mo(1)—C(11)—O(1)	166.0(6)
CNT(2)—Mo(2)—Se	119.0(3)	Mo(1)—C(12)—O(2)	169.6(7)
CNT(2)—Mo(2)—Fe	165.3(3)	Mo(2)—C(13)—O(3)	173.4(8)
Se—Mo(2)—Mo(1)	51.6(1)	Mo(2)—C(14)—O(4)	168.0(9)

Scheme 2



Results and Discussion

When a benzene solution containing $\mathrm{Fe_3Se_2(CO)_9}$ and $\mathrm{Cp_2Mo_2(CO)_6}$ was refluxed for 24 h, the following three compounds were isolated: $\mathrm{Cp_2Mo_2Fe_2Se_3(CO)_6}$, **1** (3%), $\mathrm{Cp_2Mo_2Fe_2Se_2(CO)_7}$, **2** (31%), and $\mathrm{Cp_2Mo_2FeSe(CO)_7}$, **3** (25%) (Scheme 1). In solid form all three compounds are air stable; in dichloromethane solution, **2** was found to convert to **1** slowly. When a benzene solution containing **2** was refluxed for 2 h, **1** was obtained in 48% yield. Compound **2** was also obtained in 51% yield from the room temperature reaction of $\mathrm{Fe_2Se_2(CO)_6}$ and $\mathrm{Cp_2Mo_2(CO)_4}$ (Scheme 2). Compound **1** was identified on the basis of comparison of its IR and ^{1}H NMR data with that reported earlier.[14] It has previously been prepared from the thermolysis of benzene solution containing $\mathrm{(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(Ph)Se\}}$ and $\mathrm{Cp_2Mo_2(CO)_6}$, and its structure has been established by X-ray diffraction methods. Compounds **2** and **3** were characterized by IR and ^{1}H NMR spectroscopy. The IR spectrum of **2** in solution displayed ν(CO) at 1732 and 1828 cm^{-1} and an envelope of absorptions at 2018–1957 cm^{-1}. The ^{1}H NMR spectrum of **2** indicated nonequivalent Cp groups. The solution IR spectrum of **3** indicated the presence of only terminally bonded carbonyl groups, and its ^{1}H NMR spectrum showed a single peak for the Cp groups.

Dark red crystals of **2** were obtained from hexane solution at −10 °C, and an X-ray analysis was undertaken. The molecular structure of **2** is shown in Figure 1. The basic cluster geometry consists of a $\mathrm{Mo_2Fe_2}$ tetrahedron with each $\mathrm{Mo_2Fe}$ face capped by a μ_3-Se atom. Overall, the structure of **2** is similar to $\mathrm{Cp_2Mo_2Fe_2Te_2(CO)_7}$.[15] One of the Mo atoms possesses a semitriply bridging CO ligand (Mo(1)—C(15)—O(15) = 158.1-

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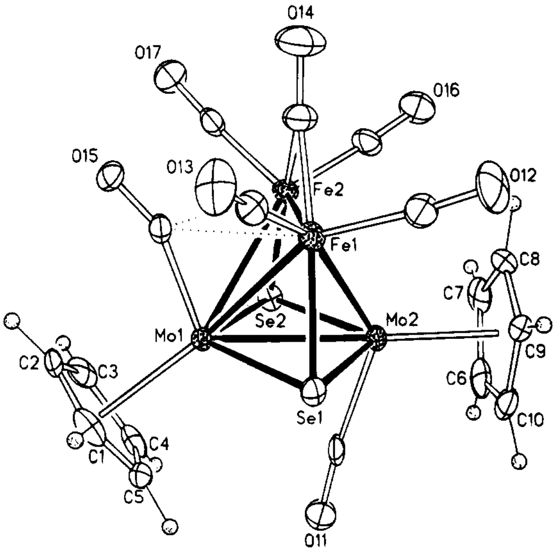


Figure 1. Molecular geometry and atom-labeling scheme for $Cp_2Mo_2Fe_2Se_2(CO)_7$ (**2**).

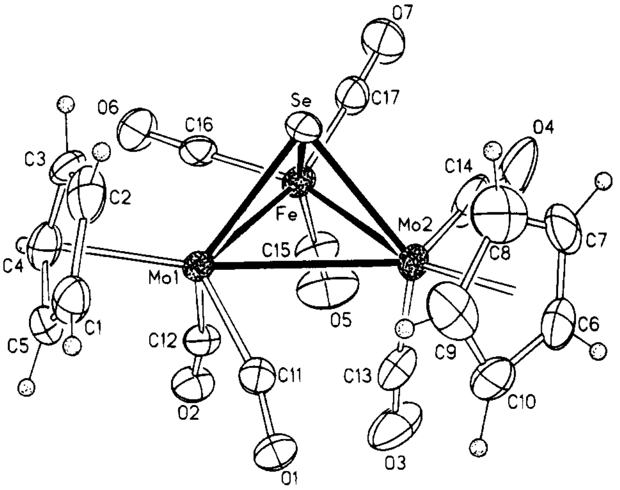
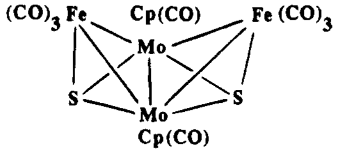


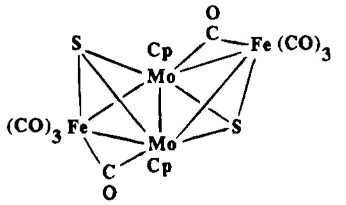
Figure 2. Molecular geometry and atom-labeling scheme for $Cp_2Mo_2FeSe(CO)_7$ (**3**).

(9)°), similar to the one seen in $Cp_2Mo_2Fe_2Te_2(CO)_7$ (Mo—C—O = 156.3(9)°) and in $Cp_2Mo_2Fe_2S_2(CO)_8$ (Mo—C—O = 159(3)°).[16] The Fe—Fe bond distance of 2.442(2) Å in **2** is somewhat short; it is 0.133 Å shorter than the Fe—Fe bond distance in $Fe_2Se_2(CO)_6$[17] and 0.208 Å shorter than the average Fe—Fe bond distance in $Fe_2Se_2(CO)_9$.[18] The C(14)—O(14) bond distance of 1.171(18) Å compares well with the average bridging carbonyl C—O distance of 1.176 Å in $Fe_2(CO)_9$[19] but is shorter than the μ-C—O distance of 1.191 Å observed in $Cp_2Mo_2Fe_2Te_2(CO)_7$. The C(15)—O(15) bond distance of 1.165(14) Å is similar to the semitriply bridging C—O bond distance of 1.167(13) Å in $Cp_2Mo_2Fe_2Te_2(CO)_7$.

Red crystals of **3** were grown by slow evaporation of its hexane/dichloromethane solution, and an X-ray analysis was undertaken. The molecular structure of **3** is depicted in Figure 2. The structure consists of a $FeMo_2Se$ tetrahedron; each Mo atom possesses one Cp and two CO groups, while the Fe atom has three CO groups bonded to it. A similar structure has been proposed for the Te compound $Cp_2Mo_2FeTe(CO)_7$, although not confirmed crystallographically. The Fe—C—O and Mo—C—O bonding parameters in **3** are unexceptional. The average Fe—Mo bond distance of 2.835 Å in **3** is similar to the corresponding distance of 2.847 Å in $Cp_2Mo_2Fe_2Se_3(CO)_6$ but shorter than the Fe—Mo bond distances of 2.905 Å in $H(Cp)MoCoFe(CO)_8(\mu_3\text{-}GeBu^t)$[20] and 2.95 Å in $(MeCp)_2Mo_2Fe_2S_4(CO)_6$.[21] The Mo—Mo bond distance of 3.096(1) Å in **3** is significantly longer than the Mo—Mo bond distances of 2.743(2) Å in $Cp_2Mo_2Fe_2Se_3(CO)_6$ and 2.624(2) Å in $(MeCp)_2Mo_2Fe_2S_4(CO)_6$ but comparable to the average Mo—Mo bond distance of 3.116 Å in $Cp_3Mo_3(CO)_6(\mu_3\text{-}As)$.[22] The Mo—Se and Fe—Se bond lengths in **3** are comparable to the corresponding bond lengths in $Cp_2Mo_2Fe_2Se_3(CO)_6$.



'Braunstein' isomer



'Curtis' isomer

Figure 3. The cis-"Braunstein" and the trans-"Curtis" isomers of $Cp_2Mo_2Fe_2S_2(CO)_8$.

The reaction of $Fe_2S_2(CO)_6$ with $Cp_2Mo_2(CO)_4$ is reported to form the cis-"Braunstein" and the trans-"Curtis" isomers of $Cp_2Mo_2Fe_2S_2(CO)_8$ (Figure 3).[16,23] Compound **1** differs from the Se analog of the Braunstein isomer in having two fewer CO groups but in having one more Se ligand. Compound **2** has one less CO group than the Braunstein analog but an additional metal—metal bond.

The Te analogs of the Braunstein and Curtis isomers, *cis*-$Cp_2Mo_2Fe_2Te_2(CO)_8$ and *trans*-$Cp_2Mo_2Fe_2Te_2(CO)_8$, are not known. In our reactions of $Fe_2Se_2(CO)_6$ with $Cp_2Mo_2(CO)_4$ or of $Fe_3Se_2(CO)_9$ with $Cp_2Mo_2(CO)_6$, $Cp_2Mo_2Fe_2Se_2(CO)_8$ was not observed. The formation of **2** from the room temperature reaction of $Fe_2Se_2(CO)_6$ with $Cp_2Mo_2(CO)_4$ can be thought to occur by the addition of the Mo_2 compound across the Se—Se bond of $Fe_2Se_2(CO)_6$ accompanied by the loss of three CO groups. Whether this addition is accompanied by the loss of one CO group first and scission of the Fe—Fe bond to form an unstable $Cp_2Mo_2Fe_2Se_2(CO)_8$, which immediately undergoes a further loss of two CO groups and re-formation of the Fe—Fe bond to yield **2** is not known. The formation of **1** from **2** formally involves the addition

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Scheme 3

$$Fe_3Se_2(CO)_9 \xrightarrow{\Delta} Fe_2(CO)_6Se_2 + \text{'}Fe(CO)_x\text{'} + \text{'}Se\text{'}$$

$$\text{'}Fe(CO)_x\text{'} + \text{'}Se\text{'} + Cp_2Mo_2(CO)_6 \longrightarrow Cp_2Mo_2FeSe(CO)_7$$

of a Se atom across the Fe—Fe bond of **2** and the loss of one CO group. The source of the third Se atom in **1** is the substantial decomposition of **2** in solution. When thermolytic or photolytic conditions are used, $Fe_3Se_2(CO)_9$ is known to form $Fe_2Se_2(CO)_6$ as well as $Fe(CO)_x$ fragments. The formation of **2** from the thermolysis of $Fe_3Se_2(CO)_9$ and $Cp_2Mo_2(CO)_6$ therefore probably occurs via an initial formation of $Fe_2Se_2(CO)_6$ which then adds the Mo_2 unit. Formation of $Fe(CO)_x$ and Se under the thermolytic reaction conditions would account for the formation of compound **3**. Rauchfuss has obtained the arachno-cluster $Cp_2Mo_2FeTe_2(CO)_7$ from the high-temperature and CO high-pressure reaction of $Fe_3Te_2(CO)_9$ and $Cp_2Mo_2(CO)_6$. On thermolysis, $Cp_2Mo_2FeTe_2(CO)_7$ forms the clusters $Cp_2Mo_2Fe_2Te_3(CO)_6$, $Cp_2Mo_2Fe_2Te_2(CO)_7$, and $Cp_2Mo_2FeTe(CO)_7$. In our reactions we did not observe the formation of the arachno cluster $Cp_2Mo_2FeSe_2(CO)_7$. This is understandable on two counts: first, the reaction conditions employed by us were milder than those employed by Rauchfuss for the preparation of $Cp_2Mo_2FeTe_2(CO)_7$, and second, the Se analog of $Cp_2Mo_2FeTe_2(CO)_7$ would not be expected to be stable. For instance, whereas $Fe_3Te_2(CO)_9$ readily adds PPh_3 and forms the arachno cluster $Fe_3Te_2(CO)_9PPh_3$, the S and Se analogs do not undergo such ligand additions. Our observation that compound **3** is formed only under thermolytic conditions suggests the sequence of events depicted in Scheme 3.

Conclusion

In this paper we have described the synthesis of Se-bridged Fe–Mo mixed-metal clusters **1**–**3**. The use of two different starting materials, $Fe_3Se_2(CO)_9$ and $Fe_2(CO)_6Se_2$, in our syntheses gives some indication about the mechanism of formation of **1**–**3**. When thermolytic conditions are used on $Fe_3Se_2(CO)_9$, formation of $Fe_2(CO)_6Se_2$ and the fragments of $Fe(CO)_x$ and Se takes place. The initial step in the formation of **1** can be thought of as involving the addition of $Fe_2(CO)_6Se_2$ and Se to $Cp_2Mo_2(CO)_6$. The formation of **2** and **3** similarly can be considered to occur by the addition of $Fe_2(CO)_6Se_2$ and the addition of $Fe(CO)_x$ and Se to the Mo_2 compound, respectively. Although the precise mechanism for the formation of **1**–**3** is not established, the isolation of these new Se-bridged clusters demonstrates the utility of $Fe_3Se_2(CO)_9$ and $Fe_2(CO)_6Se_2$ for the synthesis of Se-bridged mixed-metal cluster compounds.

Acknowledgment. We are grateful to the Department of Atomic Energy, Government of India, for financial assistance (to P.M.).

Supplementary Material Available: For **2** and **3**, tables of crystal data, atomic coordinates, bond distances, bond angles, anisotropic temperature factors, and hydrogen atom parameters (18 pages). Ordering information is given on any current masthead page.

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