Selenium-Bridged Clusters. Synthesis and Structural Characterization of $Cp_2Mo_2Fe_2(\mu_4\text{-}Se)(\mu_3\text{-}Se)_2(CO)_6$

Pradeep Mathur,*,[1a] Md. Munkir Hossain,[1a] and Arnold L. Rheingold*,[1b]

Departments of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India, and University of Delaware, Newark, Delaware 19716

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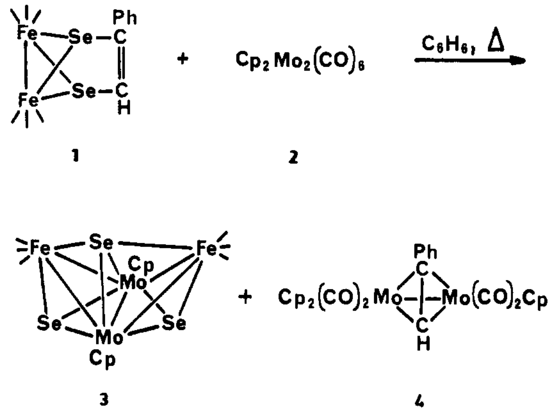
Summary: Thermolysis of $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(H)Se\}$ (1) and $Cp_2Mo_2(CO)_6$ (2) yields the new cluster $Cp_2Mo_2Fe_2(\mu_4\text{-}Se)(\mu_3\text{-}Se)_2(CO)_6$ (3) and $Cp_2Mo_2(CO)_4(PhCCH)$ (4). Structural characterization of 3 shows an unusual μ_4-Se ligand bridging the two wing-tip Fe atoms and the two hinge Mo atoms of the Mo_2Fe_2 butterfly-tetrahedron core.

In contrast to the use of the sulfido ligand for the purpose of cluster growth and stabilization,[2] the use of selenium and tellurium as potential bridging ligands in cluster synthesis has been much less investigated. The convenient synthesis of new reagents has however, in recent years, provided opportunities to explore the synthesis and characterization of transition metal cluster compounds containing the heavier chalcogenides.[3] One reason for interest in the cluster compounds containing tellurium is that the large chalcogenide ligand with its diffused orbitals may give rise to clusters with unusual structures and reactivity features. Recently, selenium-bridged transition metal complexes also attracted considerable interest.[4] The addition of phenylacetylene across the Se–Se bond of $Fe_2(CO)_6(\mu\text{-}Se_2)$ is known to form $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(H)Se\}$ (1).[5] Room temperature additions of $Pt(PPh_3)_2$ and of $Fe_2(CO)_6Se_2$ across the C=C bond in 1 yield products in which the acetylenic bond is reduced.[6] Here, we report on the reaction of 1 with $Cp_2Mo_2(CO)_6$ (2) to yield the new mixed-metal cluster $Cp_2Mo_2Fe_2(\mu_4\text{-}Se)(\mu_3\text{-}Se)_2(CO)_6$ (3) and the previously reported $Cp_2Mo_2(CO)_4(PhCCH)$ (4)[7] (eq 1).



(1)

Results and Discussion

When a benzene solution containing 1 and 2 is refluxed, the mixed-metal cluster 3 is obtained, along with the previously reported compound 4. Compound 3 has been structurally characterized by X-ray diffraction methods. An ORTEP diagram of its molecular structure is shown in Figure 1. The molecule consists of two $FeMo_2$ triangular arrays with a common Mo_2 edge and with an angle of 142.1° between the two $FeMo_2$ planes; each plane has a μ_3-bonded Se atom above it, and there is a further unique μ_4-Se atom which is bonded to all four metal atoms. The geometry of the μ_4-Se ligand observed here can be compared with that of μ_4-S found in $Cp_2Mo_2(\mu_4\text{-}S)(\mu_3\text{-}S)_2Co_2(CO)_4$,[8] $Cp_4Cr_2Ni_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)$,[9] $Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6^{2+}$,[10] and $Mo_4(NO)_4(\mu\text{-}S_2)_5(\mu_4\text{-}S)^{4-}$.[11] The large clusters $Co_9Se_{11}(PPh_3)_6$, $Ni_8Se_6(PPr_3)_4$, and $Ni_{34}Se_{22}(PPh_3)_{10}$ contain similar μ_4-Se ligands.[12] Thermolysis of $Cp_2Mo_2FeTe_2(CO)_7$ is reported to form $Cp_2Mo_2Fe_2Te_3(CO)_6$ with a structure analogous to that of $Cp_2Mo_2Co_2S_3(CO)_4$ and 3, although not confirmed crystallographically.[3g]

The Mo–Mo bond distance (2.743(2) Å) in 3 is longer than the Mo–Mo bond distance of 2.624(2) Å observed in $(CH_3C_5H_4)_2Mo_2(\mu_3\text{-}S)_4Fe_2(CO)_6$[13] but shorter than the Mo–Mo bond distance of 2.821(1) Å in $Cp'_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6(\mu\text{-}CO)_2$ and the Mo–Mo bond distance of 2.846(5) Å in

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(1) (a) Indian Institute of Technology. (b) University of Delaware.

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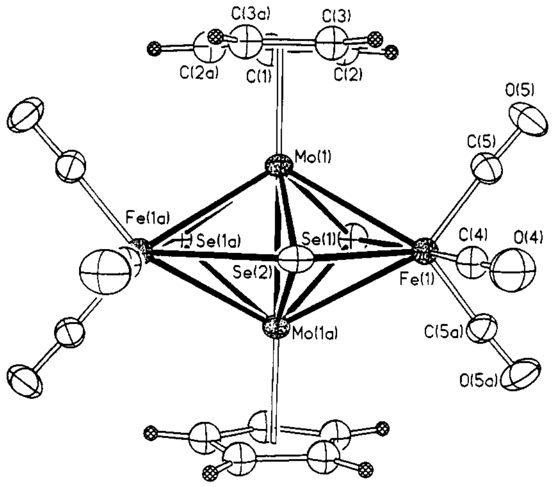

Figure 1. ORTEP diagram of $Cp_2Mo_2Fe_2(\mu_4\text{-}Se)(\mu_3\text{-}Se)_2(CO)_6$ (**3**) with the atom-numbering scheme. Selected distances (Å) and angles (deg), with esd's in parentheses: Mo(1)–Se(1), 2.498(1); Mo(1)–Se(2), 2.411(2); Mo(1)–Mo(1a), 2.743(2); Mo(1)–Fe(1a), 2.849(2); Mo(1)–Fe(1), 2.849(2); Se(1)–Fe(1), 2.336(2); Se(2)–Fe(1), 2.636(2); Mo(1)–Se(1)–Mo(1a), 66.6(1); Mo(1)–Se(1)–Fe(1), 72.1(1); Fe(1)–Se(2)–Fe(1a), 127.2(1); Mo(1)–Fe(1)–Mo(1a), 57.6(1); Mo(1)–Se(2)–Mo(1a), 69.3(1).

$Cp_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6(\mu\text{-}CO)_2$.[14] All of these compounds feature the Mo_2Fe_2 butterfly core structure. The bonds between the iron atoms and μ_4-Se (Fe–Se = 2.636 Å) are longer than the bonds between the iron atoms and μ_3-Se (Fe–Se = 2.336 Å). However, the bonds between the molybdenum atoms and the two types of Se ligands show the reverse trend; the bonds from the Mo atoms to the triply bridging Se atoms (Mo–Se = 2.498 Å) are longer than those to μ_4-Se (Mo–Se = 2.411 Å). The Fe and Se atoms reside on a crystallographically defined mirror plane. Assuming that each Se acts as a 4-electron donor, compound **3** is a 62-electron cluster, and the formal application of the 18-electron rule would predict five metal-metal bonds, as observed. According to the PSEP theory, the presence of six skeletal electron pairs in **3** correctly predicts the bicapped-trigonal-bipyramidal structure.

The formation of **3** was not observed when $Fe_2(CO)_6(\mu\text{-}Se_2)$ was stirred at room temperature with the triple-bonded complex $Cp_2Mo_2(CO)_4$ in benzene solvent. The presence of the coordinated phenylacetylene influences the reactivity of **1** in two ways. The rapid decomposition of $Fe_2(CO)_6(\mu\text{-}Se_2)$ on heating prevents the use of thermolytic conditions in its reactions. The phenylacetylene imparts some stability to **1**, and this facilitates the use of thermolytic conditions. Secondly, with the reactive sites of Se blocked in **1**, addition across the Fe–Fe bond becomes possible, as is observed in the formation of **3**. Under the reaction conditions, some decomposition of **1** takes place, leading to the release of phenylacetylene, which reacts with **2** to yield **4**. The decomposition of **1** would also account for the one extra Se ligand in **3**.

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 hexane solutions in 0.1 mm path length NaCl cells. NMR spectra were obtained on a Varian XL-300 spectrometer at 25 °C.

Table I. Crystallographic Data for 3

formula	$C_{16}H_{10}Mo_2Fe_2O_6Se_3$
fw	838.71
cryst syst	orthorhombic
space group	*Cmcm*
a, Å	10.459(3)
b, Å	12.789(4)
c, Å	15.540(5)
Z	4
D_{calcd} g cm^{-3}	1.340
μ(Mo Kα), cm^{-1}	36.42
V, Å^3	2078.6(10)
F(000)	784
$2\theta_{max}$, deg	55.0
scan type	Wyckoff
scan speed, deg/min	variable; 6.00–20.00 in ω
scan range (ω), deg	1.00°
hkl ranges	$h = 0–13$, $k = 0–16$, $l = 0–20$
no. of reflns collected	1309
no. of obsd reflns	920 ($F > 5.0\ \sigma(F)$)
abs corr	semiempirical
solution	direct methods
refinement	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
extinction corr	$\chi = 0.00015(4)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
no. of params refined	77
final *F* indices, %	$R = 5.00$, $R_w = 5.98$
GOF	1.37

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)
Mo(1)	1312(1)	1108(1)	2500	28(1)[a]
Se(1)	0	25(1)	3506(1)	38(1)[a]
Se(2)	0	2659(1)	2500	33(1)[a]
Fe(1)	0	1742(1)	4020(1)	30(1)[a]
C(1)	3193(23)	154(22)	2500	48(8)
C(1′)	3230(33)	2057(28)	2500	37(11)
C(2)	3209(16)	764(14)	3228(13)	44(6)
C(2′)	3264(25)	1315(19)	3223(18)	37(9)
C(3)	3275(15)	1791(13)	2949(13)	45(6)
C(3′)	3208(24)	300(22)	2981(20)	40(9)
C(4)	0	3130(10)	4236(9)	41(4)[a]
C(5)	1305(9)	1482(7)	4732(6)	42(3)[a]
O(4)	0	3960(8)	4450(9)	66(4)[a]
O(5)	2096(7)	1347(6)	5213(5)	61(3)[a]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Preparation of 3 and 4. A mixture of **1** (108 mg, 0.2 mmol) and **2** (74 mg, 0.15 mmol) in 75 mL of dry benzene was refluxed for 24 h. The solvent was removed in vacuo, and the products were isolated by TLC using a 1/1 (v/v) hexane/dichloromethane mixture as eluent. **3**: yield 9 mg (7%); IR(ν(CO), cm^{-1}) 2019 (m), 2000 (vs), 1955 (s); ^{1}H NMR (δ; in $CDCl_3$) 5.01; mp 120–122 °C. Anal. Calcd for **3**: C, 22.8; H, 1.18. Found: C, 22.5; H, 2.05. **4**: yield 18 mg (23%); IR (ν(CO), cm^{-1}) 1995 (s), 1930 (vs), 1850 (s); ^{1}H NMR (δ; in $CDCl_3$) 5.3 (s, C_5H_5, 10H), 5.45 (s, C*H*, 1H), 7.20–7.34 (m, *Ph*, 5H); mp 134–136 °C. Anal. Calcd for **4**: C, 49.4; H, 2.98. Found: C, 49.3; H, 3.12. Compound **4** was also prepared by refluxing a benzene solution containing equimolar amounts of **2** and phenylacetylene (45% yield) and by stirring at room temperature a benzene solution of equimolar amounts of $Cp_2Mo_2(CO)_4$ and phenylacetylene (almost quantitative yield).

Crystal Structure Determination of 3. Purple-maroon crystals of **3** were grown from a hexane/dichloromethane solution by slow evaporation of solvent at 10 °C. A crystal of approximate dimensions 0.10 × 0.30 × 0.50 mm^3 was selected for the X-ray diffraction study. The data were collected on a Siemens P4 diffractometer generating Mo Kα radiation at room temperature. The crystal data and data collection solution, and refinement parameters are summarized in Table I. Final positional and

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[14] Williams, P. D.; Curtis; Dubby, D. N.; Butler, W. M. *Organometallics* **1983**, *2*, 165.

displacement parameters are listed in Table II. The centrosymmetric space group was chosen on the initial basis of E values and retained on the basis of the refinement statistics and the symmetry of the molecule. A semiempirical absorption correction based on 180 data (5 reflections, 10° increments) was applied, $T(\max)/T(\min) = 3.17$. The cyclopentadienyl carbon atoms were each found in two positions with roughly equal occupations; these atoms were refined isotropically. All other non-hydrogen atoms were refined anisotropically with the hydrogen atoms treated as idealized isotropic contributions.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and hydrogen atom parameters (7 pages). Ordering information is given on any current masthead page.

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