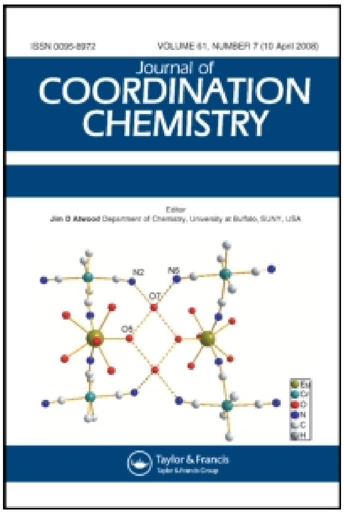

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REACTIONS OF [η^5-RC$_5$H$_4$ (CO)$_2$Mo]$_2$ (Mo≡Mo) WITH (μ-PhSe)$_2$Fe$_2$ (CO)$_6$. SYNTHESIS AND CHARACTERIZATION OF SELENOLATO-BRIDGED TRANSITION METAL COMPLEXES [η^5-RC$_5$H$_4$Mo (CO) (μ-SePh)]$_2$ (R = MeCO, MeO$_2$C) AND η^5-RC$_5$H$_4$MoFe$_2$ (CO)$_4$ (μ_3-Se) [μ,η^1: η^2-C(0)Ph] (μ-SePh)$_2$ (R = H, MeCO, EtO$_2$C)

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REACTIONS OF [η^5-RC$_5$H$_4$ (CO)$_2$Mo]$_2$ (Mo$\equiv$Mo) WITH (μ-PhSe)$_2$Fe$_2$ (CO)$_6$. SYNTHESIS AND CHARACTERIZATION OF SELENOLATO-BRIDGED TRANSITION METAL COMPLEXES [η^5-RC$_5$H$_4$Mo (CO) (μ-SePh)]$_2$ (R = MeCO, MeO$_2$C) AND η^5-RC$_5$H$_4$MoFe$_2$ (CO)$_4$ (μ_3-Se) [μ, η^1: η^2-C(O)Ph] (μ-SePh)$_2$ (R = H, MeCO, EtO$_2$C)

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Mo$\equiv$Mo triply bonded dimers [η^5-RC$_5$H$_4$ (CO)$_2$Mo]$_2$ react with (μ-PhSe)$_2$Fe$_2$ (CO)$_6$ in boiling xylene to give selenolato-bridged bimetallic complexes [η^5-RC$_5$H$_4$Mo(CO) (μ-SePh)]$_2$ (R = MeCO, MeO$_2$C). However, irradiation of a benzene solution of [η^5-RC$_5$H$_4$(CO)$_2$Mo]$_2$ (R = H, MeCO, EtO$_2$C) and (μ-PhSe)$_2$Fe$_2$ (CO)$_6$ with a 400W high pressure mercury lamp gave rise to selenolato-bridged trimetallic clusters η^5-RC$_5$H$_4$MoFe$_2$(CO)$_2$ (μ_3-Se) [μ,η^1:η^2-C (O) Ph] (μ-SePh)$_2$ (R = H, MeCO, EtO$_2$C). All products were characterized by elemental analysis and spectroscopic methods, as well as by an X-ray diffraction analysis of the product η^5-MeCOC$_5$H$_4$MoFe$_2$(CO)$_4$ (μ_3-Se)[μ, η^1:η^2-C(O)Ph](μ-SePh)$_2$.

Keywords: Mo$\equiv$Mo triple bond; selenolato-bridged complexes; thermal and photochemical reactions; X-ray structure

INTRODUCTION

The group 6 metal-metal triply bonded dimers [η^5-RC$_5$H$_4$(CO)$_2$M]$_2$(η^5-RC$_5$H$_4$ = parent and substituted cyclopentadienyl; M = Cr, Mo, W) have been shown to be very useful in the synthesis of group 6 metal and group 16 element-containing

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clusters.[1–3] In order to prepare novel selenolato ligand and molybdenum-containing clusters, we recently started to investigate new reactions of Mo≡Mo triply bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ with $(\mu\text{-PhSe})_2\text{Fe}_2(\text{CO})_6$ under thermolysis and photolysis conditions. Herein we report the synthesis and characterization of some new cluster compounds from the reactions studied and describe the crystal structure of a novel cluster $\eta^5\text{-MeCO C}_5\text{H}_4\text{MoFe}_2(\text{CO})_4(\mu_3\text{-Se})\ [\mu,\eta^1{:}\eta^2\text{-C(O)Ph}](\mu\text{-SePh})_2$.

EXPERIMENTAL

General Comments

All reactions were performed under prepurified tank nitrogen using vacuum-line techniques. The ultraviolet irradiation was carried out in a Fuji HB-400 photolysis apparatus with a 400W high pressure mercury lamp. Xylene and benzene were distilled from sodium/benzophenone ketyl prior to use. Preparative TLC was carried out on a glass plate (26 × 19 cm) coated with silica gel G (10–40 μm). The compounds $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ (R = H, MeCO, MeO_2C, EtO_2C)[4–5] and $(\mu\text{-PhSe})_2\text{Fe}_2(\text{CO})_6$[6] were prepared according to literature methods. IR and ^{1}H NMR spectra were recorded on a Nicolet FT-5DX infrared spectrophotometer and a Bruker AC-P200 NMR spectrometer, respectively. C/H analyses and MS determinations were performed by a Perkin-Elmer 240C analyzer and an HP 5988A or M-80 LC/MS spectrometer, respectively. Melting points were determined on a Yanaco MP-500 apparatus and were not corrected.

Thermolysis of $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ *with* $(\mu\text{-PhSe})_2\text{Fe}_2(\text{CO})_6$

(A) PREPARATION OF $[\eta^5\text{-MeCOC}_5\text{H}_4\text{Mo(CO)}\ (\mu\text{-SePh})]_2$ (1)

A 100 cm^3 two-necked flask fitted with a magnetic stir-bar, a rubber septum, and a reflux condenser topped with a nitrogen inlet tube, was charged with 1.000 g (1.930 mmol) of $[\eta^5\text{-MeCOC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$, 1.142 g (1.930 mmol) of $(\mu\text{-PhSe})_2\text{Fe}_2(\text{CO})_6$ and 30 cm^3 of xylene. The mixture was refluxed for 10 h. Solvent was removed *in vacuo* and the residue was extracted with CH_2Cl_2. The extracts were subjected to TLC separation with 6:1 benzene/ether as eluent to give a greenish yellow to dark-brown band from which 0.048g (3%) of **1** was obtained as a mixture of **1a** (*trans/anti*) and **1b** (*trans/syn*) isomers, m.p. 220–221°C. *Anal.* Calcd for $\text{C}_{28}\text{H}_{24}\text{Mo}_2\text{O}_4\text{Se}_2$(%): C, 43.4; H, 3.1. Found: C, 43.1; H, 3.1. IR(KBr, disk): $\nu(C\equiv O)$, 1934m, 1901s, 1844vs; $\nu(C\equiv O)$, 1672vs cm^{-1}. ^1H NMR ($CDCl_3$, TMS, δ): 1.92(s, 3H, CH_3 of **1b**), 2.06(s, 6H, $2CH_3$ of **1a**), 2.24 (s, 3H, CH_3 of **1b**), 5.40–6.08(m, 16H, $4C_5H_4$), 7.28(br. s, 20H, $4C_6H_5$)ppm. MS (EI), *m/z*(^{98}Mo, ^{80}Se): 647[1.4%, $(M\text{-}2CO\text{-}Ph)^+$], 638[2.8, $(M\text{-}2CO\text{-}2MeCO)^+$], 510[1.4, $Mo_2(SePh)_2{}^+$], 410[3.4, $(MeCOC_5H_4)_2MO_2{}^+$, 324[1.8, $(C_5H_4)_2MO_2{}^+$, 234 (2.1, Ph_2Se^+), 178(2.3, $MoSe^+$), 157 (2.3, $PhSe^+$), 154(17.5, $Ph_2{}^+$), 98 (1.4, Mo^+), 77(56.1, Ph^+).

(B) PREPARATION OF $[\eta^5\text{-}MeO_2CC_5H_4Mo(CO)\ (\mu\text{-}SePh)]_2$ (2)

A flask as described above was charged with 1.000 g(1.818 mmol) of $[\eta^5\text{-}MeO_2CC_5H_4(CO)_2Mo]_2$, 1.076 g(1.818 mmol) of $(\mu\text{-}PhSe)_2Fe_2(CO)_6$ and 30 cm^3 of xylene and the mixture was refluxed for 10 h. Similar work-up as above was followed to give 0.127g (9%) of **2** as a mixture of **2a** (*trans/anti*) and **2b** (*trans/syn*) isomers, m. p. 185–187°C. *Anal.* Calcd for $C_{28}H_{24}Mo_2O_6Se_2$(%): C, 41.7; H, 3.0. Found: C, 41.5; H, 3.0. IR(KBr, disk): $\nu(C\equiv O)$, 1926s, 1877s, 1852vs; $\nu(C{=}O)$, 1721s cm^{-1}. ^1H NMR ($CDCl_3$, TMS, δ): 3.48(s, 3H, CH_3 of **2b**), 3.60(s, 6H, $2CH_3$ of **2a**), 3.72(s, 3H, CH_3 of **2b**), 5.40–6.00(m, 16H, $4C_5H_4$), 7.30(br. s, 20H, $4C_6H_5$)ppm. MS(EI), *m/z*(^{98}Mo, ^{80}Se): 314[7.4%, $(Phse)_2{}^+$, 234 (3.8, Ph_2Se^+), 178(0.6, $MoSe^+$), 157(29.2, $PhSe^+$), 154(15.8, $Ph_2{}^+$), 98(1.2, Mo^+), 92[17.4, $C_5H_4(CO)^+$], 80(5.7, Se^+), 77(74.6, Ph^+).

Photolysis of $[\eta^5\text{-}RC_5H_4(CO)_2Mo]_2$ **with** $(\mu\text{-}PhSe)_2Fe_2(CO)_6$

(A) PREPARATION OF $\eta^5\text{-}C_5H_5MoFe_2\,(CO)_4\,(\mu_3\text{-}Se)\ [\mu\text{-}\eta^1{:}\eta^2\text{-}C(O)Ph]\ (\mu\text{-}SePh)_2$ (3)

A reaction vessel, equipped with a quartz immersion well and a 400W high pressure mercury lamp, was charged with 0.500 g(1.152 mmol) of $[\eta^5\text{-}C_5H_5(CO)_2Mo]_2$, 0.682g(1.152 mmol) of $(\mu\text{-}PhSe)_2Fe_2\,(CO)_6$ and 220 cm^3 of benzene. The mixture was irradiated for 12 h with nitrogen bubbling. Solvent was removed *in vacuo* and the residue was subjected to TLC separation using 2:1 petroleum ether/CH_2Cl_2 as eluent to give a dark-brown band from which 0.090g, (9% based on Fe) of **3** was isolated, m. p. 179°C(dec.). *Anal.* Calcd for $C_{28}H_{20}Fe_2MoO_5Se_3$(%): C, 38.2; H, 2.3. Found: C, 38.0; H, 2.2. IR(KBr, disk): $\nu(C\equiv O)$, 2008s, 1975vs, 1959vs, 1926s; $\nu(C{=}O)$, 1573w cm^{-1}. ^1H NMR ($CDCl_3$, TMS, δ): 5.38 (s, 5H, C_5H_5), 7.09(s, 5H, C_6H_5), 7.36(s, 5H, C_6H_5), 7.67(s, 5H, C_6H_5)ppm.

(B) PREPARATION OF η^5-$MeCOC_5H_4MoFe_2(CO)_4$ (μ_3-Se) [μ-η^1:η^2-C(O) Ph] (μ-SePh)$_2$ (4)

The same photolysis vessel as above was charged with 1.000 g (1.930 mmol) of [η^5-$MeCOC_5H_4(CO)_2Mo]_2$, 1.142 g (1.929 mmol) of (μ-PhSe)$_2$Fe$_2$ (CO)$_6$ and 220 cm^3 of benzene, and the mixture was irradiated for 12 h. Similar work-up was followed (except for using 3:1 petroleum ether/acetone as eluent) to give 0.288g (16%) of dark-brown solid **4**, m. p. 165°C(dec.). *Anal.* Calcd for $C_{30}H_{22}Fe_2MoO_6Se_3$(%): C, 39.0; H, 2.4. Found: C, 38.7; H, 2.7. IR(KBr, disk): ν(C≡O), 2016s, 1983vs, 1959vs, 1918s; ν(C=O), 1680s, 1573w cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS, δ): 2.19(s, 3H, CH$_3$), 5.34[d, 2H, (H^3, H^4)], 5.78[d, 2H, (H^2, H^5)], 7.10(s, 5H, C$_6$H$_5$), 7.35(s, 5H, C$_6$H$_5$), 7.65(s, 5H, C$_6$H$_5$) ppm. MS(FD), *m/z*(^{98}Mo, ^{56}Fe, ^{80}Se): 928(M$^+$, 23%).

(C) PREPARATION OF η^5-$EtO_2CC_5H_4MoFe_2(CO)_4$(μ_3-Se) [μ-η^1:η^2-C(O)Ph] (μ-SePh)$_2$ (5)

The same photolysis vessel was charged with 0.500 g (0.865 mmol) of [η^5-EtO$_2$ CC$_5$H$_4$ (CO)$_2$Mo]$_2$, 0.512 g (0.865 mmol) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$ and 220 cm^3 of benzene, and the mixture was irradiated for 12 h. Similar work-up was followed (except for using 1:1 petroleum ether/acetone as eluent) to give 0.123g (15%) of dark-brown solid **5**, m. p. 152–154°C. *Anal.* Calcd for $C_{31}H_{24}Fe_2MoO_7Se_3$(%): C, 39.1; H, 2.5. Found: C, 39.1; H, 2.6. IR(KBr, disk): ν(C≡O), 2016s, 1983vs, 1959vs, 1926s, 1918s; ν(C=O), 1721s, 1573w cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS, δ): 1.26(t, J = 6.0Hz, 3H, CH$_3$), 4.17 (q, J = 6.0Hz, 2H, CH$_2$), 5.44[d, 2H, (H^3, H^4)], 5.77[d, 2H, (H^2, H^5)], 7.00–7.21 (m, 5H, C$_6$H$_5$), 7.21–7.50(m, 5H, C$_6$H$_5$), 7.50–7.79(m, 5H, C$_6$H$_5$)ppm.

Crystal structure determination of 4

Suitable crystals of **4** for X-ray diffraction analysis were obtained by slow evaporation of a CH$_2$Cl$_2$/hexane solution at room temperature. Details of crystal parameters, data collections and structure refinements are given in Table I. A black crystal measuring 0.20 × 0.20 × 0.30 mm was glued on a glass fibre with epoxy resin and mounted on a Rigaku AFC7R diffractometer equipped with a graphite monochromator. A total of 7683 independent reflections were collected at room temperature, with MoKα radiation (λ = 0.71069 Å) by the ω-2θ scan mode to a maximum 2θ of 45.0°. Of the total reflections, 5678 were considered to be observed with $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was also applied. The structure was solved by direct methods (SAPI 91) and Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in final calculations but not refined. All calculations were performed using the TEXSAN program package.

TABLE I Details of crystal parameters, data collections and structure refinements for **4**

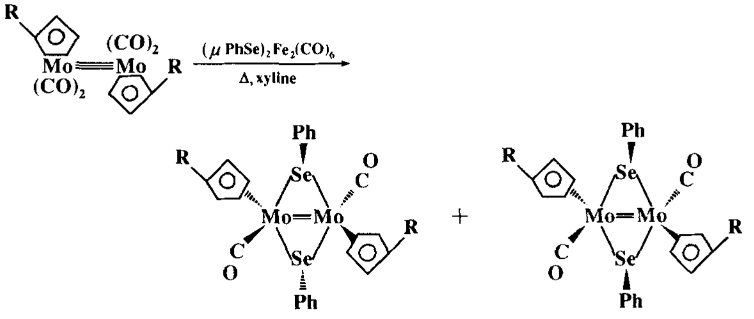
Formula	$C_{30}H_{22}Fe_2MoO_6Se_3$
M	923.01
Colour, habit	black, prismatic
Crystal size/mm	0.20 × 0.20 × 0.30
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	14.704(3)
b/Å	19.031(5)
c/Å	12.708(3)
α/°	104.22(2)
β/°	112.98(2)
γ/°	95.86(2)
V/Å^3	3094(1)
Z	4
Dc/g cm^{-3}	1.981
$F(000)$	1784
μ(Mo-Kα)/cm^{-1}	48.93
T/K	293
Diffractometer	Rigaku AFC7R
$2\theta_{max}$/°	45.0
Scan speed(in ω)/°min^{-1}	16.0
Scan width/°	1.00 + 0.30 tanθ
Transmission factors	0.3120–1.0000
Reflections collected	8061
Unique reflections	7683
Observed reflections [I>3.00$\sigma(I)$]	5678
R	0.050
$R_w{}^r$	0.059
Max. residuals/e Å^{-3}	3.27(close to heavy atoms)

RESULTS AND DISCUSSION

Thermolysis of [η^5-$RC_5H_4(CO)_2Mo]_2$(R = MeCO, MeO_2C) and (μ-PhSe)$_2Fe_2$(CO)$_6$; Synthesis and Characterization of [η^5-$RC_5H_4Mo(CO)(\mu$-SePh)]$_2$ (1, R = MeCO; 2, R = MeO_2C)

An equimolar amount of [η^5-$RC_5H_4(CO)_2Mo]_2$ (R = MeCO, MeO_2C) and (μ-PhSe)$_2Fe_2(CO)_6$ reacted in xylene at reflux for about 10 h, after removal of the solvent and the residue subjected to TLC separation, to give bimetallic complexes [η^5-$RC_5H_4Mo(CO)(\mu$-SePh)]$_2$(**1**, R = MeCO; **2**, R = MeO_2C). Both were isolated as a mixture of two isomers; *i.e.*, *trans/anti* isomer **1a** and *trans/*

syn isomer **1b**, and *trans/anti* isomer **2a** and *trans/syn* isomer **2b**, which have RC_5H_4 and CO ligands in *trans* positions with respect to the Mo_2Se_2 ring, as shown in (1).



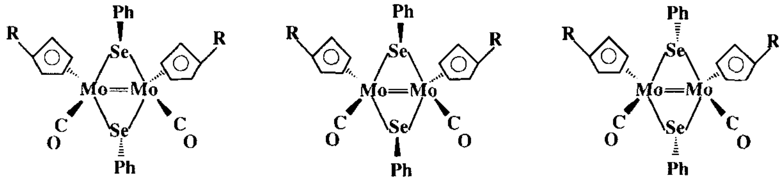
(*trans/anti*) **(*trans/syn*)**

1a, R = COMe
2a, R = CO₂Me

1b, R = COMe
2b, R = CO₂Me

(1)

In principle, for complexes of the type $[\eta^5\text{-}RC_5H_4Mo(CO)(\mu\text{-}SePh)]_2$, five isomers are possible, based on *trans* or *cis* arrangement of RC_5H_4 and carbonyl ligands, and *anti* or *syn* orientation of the phenyl groups on the Se atoms with respect to the Mo_2Se_2 ring. Besides two *trans/anti* and *trans/syn* isomers, three other possible isomers which all have the RC_5H_4 and carbonyl ligands in *cis* positions are shown in Scheme 1.



(*cis/anti*) **(*cis/syn*)** **(*cis/syn*)**

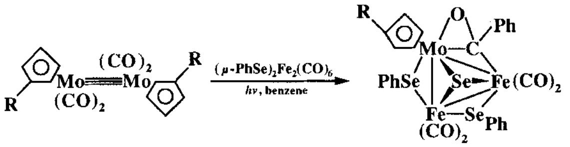
Scheme 1

However, for complexes **1** and **2**, we propose that only the *trans/anti* and *trans/syn* isomers mentioned above exist, in view of the following facts. Their sulfur analogue $[\eta^5\text{-}MeCOC_5H_4Mo(CO)\ (\mu\text{-}SPh)]_2$ prepared through a similar reaction of $[\eta^5\text{-}MeCOC_5H_4(CO)_2Mo]_2$ with $(\mu\text{-}PhS)_2Fe_2(CO)_6$ exists only as *trans/anti* and *trans/syn* isomers, and which were characterized by X-ray crystallography.[7] All complexes of the type $[\eta^5\text{-}RC_5H_4Mo(CO)\ (\mu\text{-}ER')]_2$ ($E{=}S^{8-12}$, Se^{13}) prepared so far have not been isolated as *cis* isomers. These facts suggest that the *cis* isomers are probably unstable and convert into *trans* isomers easily under reaction conditions.

Complexes **1** and **2** containing both selenolate and functionally substituted cyclopentadienyl ligands were synthesized through a new type of reaction as mentioned above, and can be formally viewed as adducts of Mo≡Mo triply bonded dimers with two PhSe ligands generated *in situ* from thermolysis of $(\mu\text{-PhSe})_2Fe_2(CO)_6$·C/H analysis data for **1** and **2** are in good agreement with the formulations. IR spectra for **1** and **2** show three bands at frequencies between 1844 and 1934 cm^{-1}, characteristic of terminal carbonyls. In addition, for **1** the IR spectrum exhibits one ketonic carbonyl band at 1672 cm^{-1}, and for **2** one ester band at 1721 cm^{-1}. ^1H NMR spectra demonstrate the existence of both phenyl groups and substituted cyclopentadienyl ligands. It is worth pointing out that in the ^1H NMR spectra of **1** and **2** the methyl groups give rise to three singlets. This clearly indicates that they both consist of two isomers **1a-b** and **2a-b**, respectively. Isomers **1a** and **2a** are centrosymmetric and have two $\eta^5\text{-RC}_5H_4$ ligands in same environment, so that the two methyl groups of $\eta^5\text{-RC}_5H_4$ ligands give one singlet at δ 2.06 ppm for **1a** and δ 3.60 ppm for **2a**. However, since **1b** and **2b** are non-symmetric and the two $\eta^5\text{-RC}_5H_4$ groups are in different environments, the two methyl groups give two singlets of equal intensity; for **1b** one is found at δ 1.92 ppm and the other at δ 2.24 ppm while for **2b** one is at δ 3.48 ppm and the other at δ 3.72 ppm. All ^1H NMR data for Me groups of **1a** and **1b** correspond closely to those of Me groups in *trans/anti* and *trans/syn* isomers of the corresponding sulfur analogue $[\eta^5\text{-MeCOC}_5H_4Mo(CO)\ (\mu\text{-SPh})]_2$.[7] From the integrated values for the singlets of **1a** and **1b** (or **2a** and **2b**) the isomer ratios **1a**:**1b** and **2a**:**2b** were calculated to be about 1:2. Although the mass spectra did not exhibit molecular ion peaks, corresponding fragment ion peaks are in accordance with the structures.

Photolysis of $[\eta^5\text{-RC}_5H_4(CO)_2Mo]_2$ (R=H, MeCO, EtO$_2$C) and $(\mu\text{-PhSe})_2Fe_2(CO)_6$; Synthesis and characterization of $\eta^5\text{-RC}_5H_4MoFe_2(CO)_4\ (\mu_3\text{-Se})\ [\mu,\eta^1 : \eta^2\text{-C(O)Ph}]\ (\mu\text{-SePh})_2$ (3, R = H; 4, R = MeCO; 5, R = EtO$_2$C)

Apart from the thermolysis reaction described above, a benzene solution of $[\eta^5\text{-RC}_5H_4(CO)_2Mo]_2$(R=H, MeCO, EtO$_2$C) and $(\mu\text{-PhSe})_2Fe_2(CO)_6$ (equimolar) was irradiated for 12 h in a vessel equipped with a quartz immersion well and a high pressure mercury lamp; after removal of the solvent and the residue being subjected to TLC separation, trimetallic clusters $\eta^5\text{-RC}_5H_4MoFe_2(CO)_4\ (\mu_3\text{-Se})\ [\mu,\eta^1 : \eta^2\text{-C(O)Ph}]\ (\mu\text{-SePh})_2$ (**3**, R = H; **4**, R = MeCO; **5**, R = EtO$_2$C) were obtained, as shown in (2). Cluster complexes **3–5** were unexpectedly prepared through the photolysis reaction mentioned above and have been characterized by C/H analysis, IR and ^1H NMR spectroscopies. IR spectra of **3–5** show four to five absorption bands between 1918 and 2016 cm^{-1}, characteristic of terminal



3, R=H
4, R=MeCO
5, R=EtO$_2$C

(2)

carbonyls attached to iron atoms, and one band at 1573 cm^{-1}, attributed to a ketonic carbonyl in a benzoyl group $\mu,\eta^1:\eta^2$-PhCO. In addition, the IR spectrum of **4** also exhibits one band at 1680 cm^{-1} for its acyl carbonyl, whereas that of **5** shows one band at 1721cm^{-1} for its ester carbonyl. ^{1}H NMR spectra of **3–5** show three sets of peaks from δ 7–8 ppm, assigned to three phenyl groups. Furthermore, the ^{1}H NMR spectrum of **3** shows a singlet at δ 5.38 ppm for five protons of cyclopentadienyl, whereas the ^{1}H NMR spectra of **4** and **5** exhibit two doublets between δ 5.24–5.85 ppm for four protons of the substituted cyclopentadienyl. The doublet at low field has been assigned to two protons of H^2 and H^5 close to the substituent, whereas the doublet at high field bas been attributed to H^3 and H^4 remote from the substituent, since the substituents are all electron-withdrawing groups. The FD mass spectrum of **4** displays its molecular ion peak at *m/z* 928. It is worth pointing out that the yields of all the complexes are fairly low from both thermolysis and photolysis reactions. This is probably due to the severe decomposition of the starting materials during the course of the reactions, leading to many inseparable bands and intractable residues.

Crystal structure determination of 4

In order to further confirm the novel structures of **3–5**, an X-ray diffraction study of **4** was undertaken. Table II lists final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms. Although there are two crystallographically independent molecules (*i.e.*, **4a** and **4b**) in the asymmetric unit (see Figure 1), only selected bond lengths and angles for **4a** are listed in Table III. This is because the structural features of the two independent molecules **4a** and **4b** are essentially the same. As seen from Figure 1, the molecule contains a tetrahedral cluster core MoFe$_2$(μ_3-Se), an acetylcyclopentadienyl ligand coordinated to a Mo atom and two pairs of terminal carbonyls bonded to two iron atoms, respectively. In addition, two metal-metal bonds of the molecule, Mo(1)-Fe(2) and Fe(1)-Fe(2), are all bridged by a benzeneselenolato ligand, whereas the metal-metal bond Mo(1)-Fe (1) is bridged by a $\mu,\eta^1:\eta^2$-benzoyl ligand. The Se(1)-Fe(1) bond length (2.391(2) Å) is somewhat longer than Se(1)-Fe(2) (2.350(2) Å); the three Fe-Se(Ph) bond lengths are quite close (avg. 2.380 Å). It is noteworthy that the Mo(1)-Fe(1) bond length of 2.634(2) Å is much shorter than the Mo(1)-Fe(2) bond length of 2.843 (2) Å due to the different bridging ligands. In this molecule each metal atom obeys the EAN rule; it is a 48-electron cluster with the benzoyl ligand being a three-electron donor. The benzoyl ligand was possibly formed by attack of a phenyl radical generated from $(\mu\text{-PhSe})_2Fe_2(CO)_6$ at the carbon atom of the carbonyl attached to the Mo atom. This benzoyl ligand belongs to a $\mu,\eta^1 : \eta^2$-coordination mode with the carbonyl carbon atom bonded to Mo(1) and Fe(1) atoms and the oxygen atom bonded to Mo(1).

TABLE II Atomic coordinates and equivalent isotropic temperature factors for **4**

atom	*x/a*	*y/b*	*z/c*	B_{eq}
Mo(1)	0.56569(6)	-0.18559(4)	0.25509(7)	2.71(2)
Mo(2)	0.06583(6)	-0.25414(4)	0.69504(7)	2.78(2)
Se(1)	0.41546(8)	-0.23457(6)	0.27599(10)	3.66(3)
Se(2)	0.48581(8)	-0.29955(6)	0.47811(10)	3.77(3)
Se(3)	0.54606(8)	-0.31761(5)	0.13314(9)	3.45(2)
Se(4)	-0.08760(8)	-0.31404(6)	0.69942(9)	3.67(3)
Se(5)	-0.02039(8)	-0.35136(6)	0.93077(9)	3.76(3)
Se(6)	0.04602(8)	-0.13742(6)	0.82292(9)	3.81(3)
Fe(1)	0.5663(1)	-0.19095(7)	0.4605(1)	3.07(3)
Fe(2)	0.5225(1)	-0.31850(7)	0.3077(1)	3.01(3)
Fe(3)	0.0202(1)	-0.23731(8)	0.8968(1)	3.18(3)
Fe(4)	0.0604(1)	-0.35649(7)	0.8005(1)	2.80(3)
O(1)	0.7189(4)	-0.1835(3)	0.3660(5)	3.2(2)
O(2)	0.6967(9)	-0.1673(6)	0.032(1)	8.8(4)
O(3)	0.7600(6)	-0.1858(4)	0.6547(7)	5.1(2)
O(4)	0.4985(7)	-0.0732(5)	0.5864(8)	6.9(3)
O(5)	0.7225(6)	-0.3484(4)	0.4266(6)	4.6(2)
O(6)	0.3886(8)	-0.4662(5)	0.1753(9)	8.0(3)
O(7)	0.2178(4)	-0.2389(3)	0.8237(5)	3.0(2)
O(8)	0.2322(8)	-0.0956(5)	0.6378(9)	8.1(3)
O(9)	0.2204(6)	-0.1814(4)	1.1002(7)	4.7(2)
O(10)	-0.1017(8)	-0.1610(6)	1.003(1)	9.8(4)
O(11)	0.2520(6)	-0.3615(4)	0.9889(6)	4.7(2)
O(12)	-0.0059(7)	-0.5129(4)	0.6539(8)	6.7(2)
C(1)	0.6023(9)	-0.0689(5)	0.2415(9)	4.0(3)
C(2)	0.498(1)	-0.0878(7)	0.216(1)	5.1(4)
C(3)	0.4493(9)	-0.1465(7)	0.104(1)	4.9(3)
C(4)	0.5187(8)	-0.1684(7)	0.058(1)	5.0(3)
C(5)	0.6107(8)	-0.1189(5)	0.1438(9)	3.5(3)
C(6)	0.705(1)	-0.1252(7)	0.123(1)	6.0(4)
C(7)	0.803(1)	-0.0792(8)	0.220(2)	7.5(5)
C(8)	0.6810(7)	-0.1379(5)	0.4253(8)	3.1(2)
C(9)	0.7467(8)	-0.0642(5)	0.5078(9)	3.8(3)
C(10)	0.8492(10)	-0.0553(7)	0.549(1)	8.3(4)
C(11)	0.913(1)	0.0094(10)	0.630(2)	13.8(6)
C(12)	0.875(2)	0.0692(9)	0.667(2)	11.7(6)
C(13)	0.773(1)	0.0625(7)	0.625(1)	7.4(4)
C(14)	0.7090(9)	-0.0051(6)	0.548(1)	5.2(3)
C(15)	0.6190(9)	-0.2873(6)	0.723(1)	4.8(3)
C(16)	0.6757(9)	-0.3164(7)	0.8122(9)	5.0(3)
C(17)	0.6924(9)	-0.3850(7)	0.784(1)	5.1(3)
C(18)	0.652(1)	-0.4294(6)	0.667(1)	5.4(3)

TABLE II (*Continued*)

atom	*x/a*	*y/b*	*z/c*	B_{eq}
C(19)	0.5949(9)	−0.4022(6)	0.5762(10)	4.8(3)
C(20)	0.5778(8)	0.3323(5)	0.6046(9)	3.6(3)
C(21)	0.6726(9)	−0.3475(6)	0.1474(9)	4.2(3)
C(22)	0.672(1)	−0.4209(7)	0.126(1)	7.3(4)
C(23)	0.760(1)	−0.4444(8)	0.131(2)	8.9(5)
C(24)	0.846(1)	−0.395(1)	0.158(1)	7.4(5)
C(25)	0.845(1)	−0.3231(9)	0.177(1)	7.1(5)
C(26)	0.756(1)	−0.2991(7)	0.174(1)	5.4(4)
C(27)	0.6439(8)	−0.3381(5)	0.3796(9)	3.5(3)
C(28)	0.4396(10)	−0.4099(7)	0.227(1)	5.0(3)
C(29)	0.6847(9)	−0.1875(5)	0.5794(9)	3.9(3)
C(30)	0.5284(8)	−0.1182(6)	0.5401(9)	4.0(3)
C(31)	−0.0442(9)	−0.2462(7)	0.5060(9)	4.8(3)
C(32)	0.0319(8)	−0.1825(6)	0.5532(8)	3.8(3)
C(33)	0.1245(8)	−0.2113(6)	0.5679(8)	3.7(3)
C(34)	0.0990(9)	−0.2900(6)	0.5292(8)	3.8(3)
C(35)	−0.0064(9)	−0.3117(6)	0.4907(8)	4.2(3)
C(36)	0.225(1)	−0.1611(7)	0.618(1)	5.2(3)
C(37)	0.318(1)	−0.1923(9)	0.643(1)	7.1(4)
C(38)	0.1773(7)	−0.3102(5)	0.7646(8)	2.7(2)
C(39)	0.2417(8)	−0.3577(5)	0.7289(9)	3.4(3)
C(40)	0.2002(8)	−0.4221(6)	0.6325(9)	4.0(3)
C(41)	0.263(1)	−0.4656(6)	0.603(1)	5.6(4)
C(42)	0.364(1)	−0.4468(8)	0.672(1)	6.8(4)
C(43)	0.4057(10)	−0.3826(8)	0.769(1)	6.8(4)
C(44)	0.3449(8)	−0.3387(6)	0.797(1)	4.8(3)
C(45)	0.173(1)	−0.0679(6)	0.9395(9)	4.8(3)
C(46)	0.261(1)	−0.0648(6)	0.926(1)	5.2(3)
C(47)	0.346(1)	−0.0111(8)	1.008(1)	6.8(4)
C(48)	0.342(2)	0.0378(10)	1.101(2)	9.5(6)
C(49)	0.258(2)	0.0363(9)	1.118(1)	10.0(6)
C(50)	0.167(1)	−0.0178(8)	1.034(1)	7.5(4)
C(51)	0.1058(9)	−0.2953(6)	1.186(1)	5.0(3)
C(52)	0.167(1)	−0.3012(8)	1.298(1)	6.0(4)
C(53)	0.1967(1o)	−0.3669(9)	1.305(1)	6.3(4)
C(54)	0.1649(9)	−0.4262(8)	1.205(1)	5.5(4)
C(55)	0.1040(9)	−0.4206(6)	1.0937(10)	4.5(3)
C(56)	0.0733(8)	−0.3562(6)	1.0855(9)	3.7(3)
C(57)	0.1427(8)	−0.2037(5)	1.0206(10)	3.4(3)
C(58)	−0.057(1)	−0.1926(7)	0.960(1)	5.8(4)
C(59)	0.0214(8)	−0.4526(6)	0.7117(9)	3.6(3)
C(60)	0.1777(8)	−0.3604(5)	0.9155(9)	3.5(3)

TABLE III Selected bond lengths (Å) and angles (°) for **4a**

Mo(1)—Se(1)	2.445(1)	Mo(1)—Se(3)	2.527(1)
Mo(1)—Fe(1)	2.634(2)	Mo(1)—Fe(2)	2.843(2)
Mo(1)—O(1)	2.130(6)	Mo(1)—C(8)	2.057(9)
Se(1)—Fe(1)	2.391(2)	Se(1)—Fe(2)	2.350(2)
Se(2)—Fe(1)	2.378(2)	Se(2)—Fe(2)	2.383(2)
Se(2)—C(20)	1.941(10)	Se(3)—Fe(2)	2.379(2)
Se(3)—C(21)	1.95(1)	Fe(1)—Fe(2)	2.543(2)
Fe(1)—C(8)	2.13(1)	O(1)—C(8)	1.32(1)

TABLE III (*Continued*)

Se(1)—Mo(1)—Se(3)	85.59(4)	Se(1)—Mo(1)—Fe(1)	56.00(4)
Se(1)—Mo(1)—Fe(2)	52.12(4)	Se(1)—Mo(1)—O(1)	126.7(2)
Se(1)—Mo(1)—C(8)	107.6(3)	Se(3)—Mo(1)—Fe(2)	52.19(4)
Se(3)—Mo(1)—O(1)	89.5(2)	Se(3)—Mo(1)—C(8)	121.4(2)
Fe(1)—Mo(1)—Fe(2)	55.17(5)	Fe(1)—Mo(1)—O(1)	75.2(2)
Fe(1)—Mo(1)—C(8)	52.2(3)	Fe(2)—Mo(1)—O(1)	84.1(2)
Fe(2)—Mo(1)—C(8)	91.4(3)	O(1)—Mo(I)—C(8)	36.6(3)
Mo(1)—Se(1)—Fe(1)	66.01(5)	Mo(1)—Se(1)—Fe(2)	72.69(5)
Fe(1)—Se(1)—Fe(2)	64.88(5)	Fe(1)—Se(2)—Fe(2)	64.57(6)
Mo(1)—Se(3)—Fe(2)	70.75(5)	Mo(1)—Fe(1)—Se(1)	57.99(4)
Mo(1)—Fe(1)—Fe(2)	66.58(5)	Mo(1)—Fe(1)—C(8)	49.8(2)
Se(1)—Fe(1)—Se(2)	77.68(6)	Se(1)—Fe(1)—Fe(2)	56.80(5)
Se(1)—Fe(1)—C(8)	107.3(3)	Se(2)—Fe(1)—Fe(2)	57.80(5)
Mo(1)—Fe(2)—Se(1)	55.19(4)	Mo(1)—Fe(2)—Se(3)	57.06(4)
Mo(1)—Fe(2)—Fe(1)	58.24(5)	Se(1)—Fe(2)—Fe(1)	58.33(5)
Se(2)—Fe(2)—Fe(1)	57.63(5)	Mo(1)—O(1)—C(8)	68.7(5)
Mo(1)—C(8)—Fe(1)	78.0(3)	Mo(1)—C(8)—O(1)	74.7(5)
Mo(1)—C(8)—C(9)	140.4(7)	Fe(1)—C(8)—O(1)	114.8(6)
O(1)—C(8)—C(9)	118.1(9)		

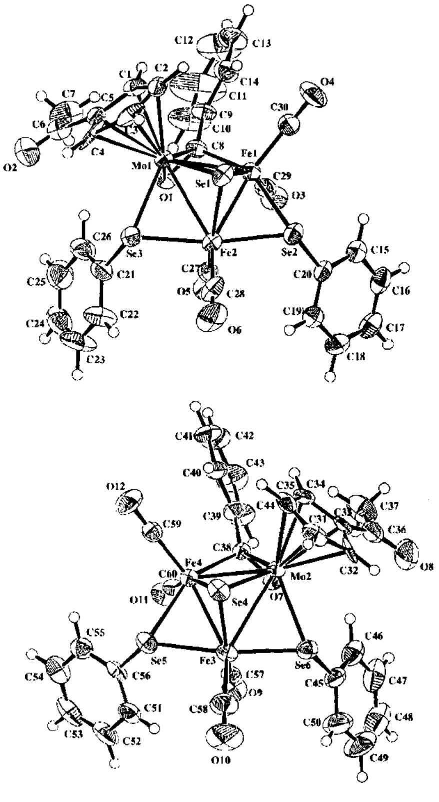
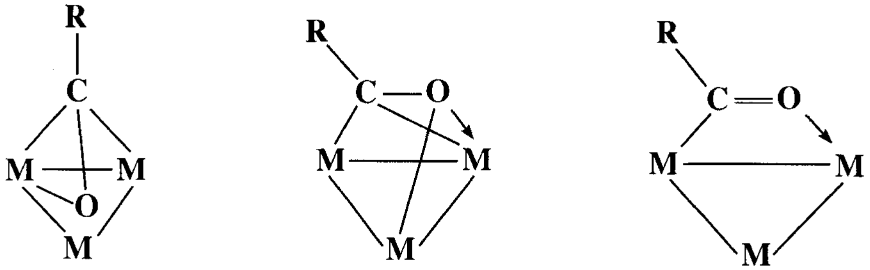


FIGURE 1 Molecular Structure of 4, Showing Atom Labeling Scheme.



I II III

Scheme 2

Such a ligated mode (mode I) is in good agreement with the low IR stretching frequency (1573 cm^{-1}) of the carbonyl in the benzoyl ligand and is not observed in other trimetallic clusters. For bonding modes of acyl groups as bridging ligand in trimetallic systems, II and III were previously found in the cases of $[Fe_3(CO)_9(COMe)]^-$ and $[Os_3(CO)_{10}(COMe)]^-$ respectively.[14–15] In $[Os_3(CO)_{10}(COMe)]^-$ two metal atoms are bridged (mode III) and the RC=O group retains most of its C=O double bond character.[15] However, in $[Fe_3(CO)_9(COMe)]^-$, three metals are bridged by the acyl group (mode II) and the C=O double bond of the RC=O group (1.32(2) Å) has been considerably lengthened.[14] In our molecule, one of the two iron atoms and the molybdenum atom are bridged by a benzoyl group (mode I) and the C=O bond length of the benzoyl group (1.32(1) Å) is essentially the same as that in $[Fe_3(CO)_9(COMe)]^-$. However, its oxygen atom, in contrast to that in $[Fe_3(CO)_9(COMe)]^-$, is not coordinated to the third metal atom. The coordination modes I–III are shown in Scheme 2.

SUPPLEMENTAL MATERIAL AVAILABLE

Tables of fractional atomic coordinates, thermal parameters, interatomic parameters, observed and calculated factors are available on request from the authors.

Acknowledgments

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