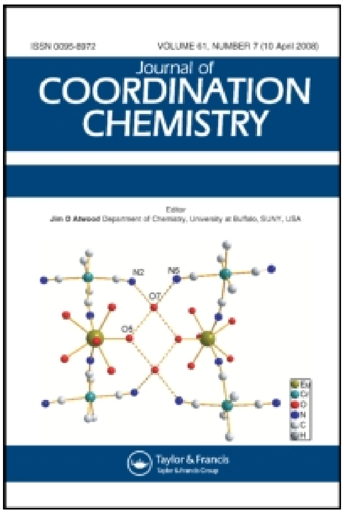

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SYNTHESIS OF SINGLE AND DOUBLE μ3-Se-CONTAINING TETRAHEDRAL MCoFe(μ_3-Se) AND MNiFe(μ_3-Se) (M = Mo, W) CLUSTERS *VIA* ISOLOBAL AND FUNCTIONAL REACTIONS. CRYSTAL AND MOLECULAR STRUCTURE OF η^5-MeO$_2$CC$_5$H$_4$(CO)$_2$WCoFe(μ_3-Se)(CO)$_6$

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SYNTHESIS OF SINGLE AND DOUBLE μ_3-Se-CONTAINING TETRAHEDRAL MCoFe(μ_3-Se) AND MNiFe(μ_3-Se) (M = Mo, W) CLUSTERS *VIA* ISOLOBAL AND FUNCTIONAL REACTIONS. CRYSTAL AND MOLECULAR STRUCTURE OF η^5-$MeO_2CC_5H_4(CO)_2WCoFe(\mu_3\text{-}Se)(CO)_6$

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The single isolobal displacement reaction of $(\mu_3\text{-}Se)FeCo_2(CO)_9$ with $\eta^5\text{-}RC_5H_4M(CO)_3Na$ can occur in refluxing THF to give single clusters $\eta^5\text{-}RC_5H_4(CO)_2MCoFe(\mu_3\text{-}Se)(CO)_6$ (**1a** M = Mo, R = EtO_2C; **1b** M = W, R = MeCO; **1c** M = W, R = MeO_2C), whereas the functional transformation reaction of **1b** with 2,4-dinitrophenylhydrazine affords its phenylhydrazone derivative $\eta^5\text{-}2,4\text{-}(NO_2)_2C_6H_3NHNC(Me)C_5H_4(CO)_2WCoFe(\mu_3\text{-}Se)(CO)_6$ (**2**). More interestingly, the double isolobal displacement reaction of two molecules of $(\mu_3\text{-}Se)FeCo_2(CO)_9$ with $[\eta^5\text{-}C_5H_4C(O)CH_2M(CO)_3Na]_2$ takes place in THF at reflux, giving double clusters $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[(CO)_2MCoFe(\mu_3\text{-}Se)(CO)_6]_2$ (**3a** M = Mo; **3b** M = W), whereas **3a** reacts with Cp_2Ni in refluxing THF to afford both single and double isolobal displacement products $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[(CO)_2MoNiFe(\mu_3\text{-}Se)(CO)_3Cp][(CO)_2MoCoFe(\mu_3\text{-}Se)(CO)_6]$ (**4**) and $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[(CO)_2MoNiFe(\mu_3\text{-}Se)(CO)_3Cp]_2$ (**5**). All products were characterized by analysis and spectroscopy, as well as for **1c** by an X-ray diffraction analysis.

Keywords: Isolobal displacement; functional transformation; μ_3-Se ligand; transition metal clusters; X-ray structure

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INTRODUCTION

In previous papers we reported a very useful isolobal displacement method to synthesize single and double μ_3-S-containing tetrahedral MCoFe(μ_3-S)[1] and MNiFe(μ_3-S) (M = Mo, W)[2,3] clusters. Further, we also reported some interesting transformation reactions of functional groups in those cluster complexes under the action of various reagents.[1,3] Since selenium-containing, and particularly the μ_3-Se-containing transition metal clusters are of great interest,[4–8] one might ask if the corresponding single and double μ_3-Se-containing transition metal clusters could be made by similar procedures and if they would have similar structures and properties. In this paper, we answer some of these questions by describing the synthesis and characterization of a series of μ_3-Se-containing tetrahedral MCoFe(μ_3-Se) and MNiFe(μ_3-Se) (M = Mo, W) cluster complexes.

EXPERIMENTAL

General Comments

All reactions were carried out under highly purified tank nitrogen using standard Schlenk or vacuum-line techniques. TLC was performed using silica gel G (10–40 μm). THF and diglyme were distilled from Na/benzophenone ketyl. The compounds (μ_3-Se)FeCo$_2$(CO)$_9$,[9] Cp$_2$Ni,[10] RC$_5$H$_4$Na (R = MeO$_2$C, EtO$_2$C, MeCO)[11] and Na$_2$[η^5-C$_5$H$_4$C(O)CH$_2$]$_2$[12] were prepared according to literature methods. Other solvents and reagents were of commercial origin and used without further purification. IR spectra were recorded on a Nicolet FT-IR 5DX infrared spectrophotometer. ^{1}H NMR spectra were recorded on Jeol FX 90Q and Bruker AC-P 200 spectrometers. C/H analyses and MS determinations were performed on a Perkin-Elmer 240C analyzer and an HP 5988A spectrometer, respectively. Melting points are uncorrected.

η^5-EtO$_2$CC$_5$H$_4$(CO)$_2$MoCoFe(μ_3-Se)(CO)$_6$ (1a)

A 100 cm^3 three-necked flask fitted with a magnetic stir-bar, a rubber septum, and a reflux condenser topped with a nitrogen inlet tube, was charged with 0.784 g (4.90 mmol) of EtO$_2$CC$_5$H$_4$Na, 1.250 g (4.75 mmol) of Mo(CO)$_6$ and 20 cm^3 of THF. The mixture was stirred at reflux for 1.5 h and upon cooling to room temperature, 1.200 g (2.38 mmol) of (μ_3-Se)Fe-Co$_2$(CO)$_9$ was added in one portion. The mixture was refluxed for an additional 0.5 h. Solvent was removed under vacuum and the residue was extracted with CH_2Cl_2. The extracts were subjected to TLC separation using 1 : 1 (v/v) CH_2Cl_2/petroleum ether as eluent. From the main red-brown band was obtained 1.010 g (65%) of **1a** as a red-brown solid, m.p. 78–79°C. *Anal.* Calcd. for $C_{16}H_9CoFeMoO_{10}Se$(%): C, 29.52; H, 1.39; Found: C, 29.59; H, 1.94. IR (KBr, disk): $\nu_{(C\equiv O)}$ 2072(vs), 2011(s), 1996(s), 1968(vs), 1908(vs), 1875(vs); $\nu_{(C=O)}$ 1730(s) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, δ): 1.32 (t, 3H, $J = 7.2$ Hz, CH_3), 4.27 (q, 2H, $J = 7.2$ Hz, CH_2), 5.32, 5.48 (q, q, 2H, H^3, H^4), 5.80 (t, 2H, H^2, H^5) ppm. MS (EI), *m/z* (^{98}Mo, ^{80}Se): 598 ($M^+ - 2CO$, 11.7%), 542 ($M^+ - 4CO$, 14.3), 514 ($M^+ - 5CO$, 14.3), 486 ($M^+ - 6CO$, 46.2), 458 ($M^+ - 7CO$, 26.5), 430 ($M^+ - 8CO$, 24.1), 293 (MoFe $CoSe^+$, 15.6).

η^5-$MeCOC_5H_4(CO)_2WCoFe(\mu_3\text{-}Se)(CO)_6$ (1b)

The flask described above was charged with 0.660 g (5.08 mmol) of $MeCOC_5H_4Na$, 1.670 g (4.75 mmol) of $W(CO)_6$ and 20 cm^3 of diglyme. The mixture was stirred at reflux for 6 h. After the solvent was removed under vacuum, 20 cm^3 of THF and 1.200 g (2.38 mmol) of (μ_3-Se)$FeCo_2(CO)_9$ were added and the mixture was refluxed for an additional 0.5 h. After the same workup as for **1a**, 1.060 g (63%) of **1b** was obtained as a red-brown solid, m.p. 104–105°C. *Anal.* Calcd. for $C_{15}H_7CoFeO_9SeW$(%): C, 25.42; H, 1.00; Found: C, 25.49; H, 0.75. IR (KBr, disk): $\nu_{(C\equiv O)}$ 2073(vs), 2032(vs), 2016(vs), 1991(vs), 1967(vs), 1901(s), 1868(s); $\nu_{(C=O)}$ 1688(s) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, δ): 2.44 (s, 3H, CH_3), 5.54, 5.72 (q, q, 2H, H^3, H^4), 5.80–6.04 (m, 2H, H^2, H^5) ppm. MS (EI), *m/z* (^{184}W, ^{80}Se): 710 (M^+, 0.1%), 682 ($M^+ - CO$, 0.1), 654 ($M^+ - 2CO$, 0.3), 626 ($M^+ - 3CO$, 0.3), 598 ($M^+ - 4CO$, 0.4), 570 ($M^+ - 5CO$, 1.3), 542 ($M^+ - 6CO$, 1.9), 514 ($M^+ - 7CO$, 1.3), 486 ($M^+ - 8CO$, 2.3), 379 ($WFeSeCo^+$, 0.2).

η^5-$MeO_2CC_5H_4(CO)_2WCoFe(\mu_3\text{-}Se)(CO)_6$ (1c)

The same procedure as for **1b** was followed, except using 0.720 g (4.90 mmol) of $MeO_2CC_5H_4Na$ instead of $MeCOC_5H_4Na$; 1.250 g (73%) of **1c** was obtained as a red-brown solid, m.p. 85–86°C. *Anal.* Calcd. for $C_{15}H_7CoFeO_{10}SeW$(%): C, 24.86; H, 0.97; Found: C, 24.93; H, 0.95. IR (KBr, disk): $\nu_{(C\equiv O)}$ 2065(vs), 2024(vs), 2008(vs), 1967(vs), 1918(s); $\nu_{(C=O)}$ 1729 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, δ): 3.94 (s, 3H, CH_3), 5.54, 5.72 (q, q, 2H, H^3, H^4), 5.96 (t, 2H, H^2, H^5). MS (EI), *m/z* (^{184}W, ^{80}Se): 726 (M^+, 0.1%), 698 ($M^+ - CO$, 0.1), 670 ($M^+ - 2CO$, 0.5) 642 ($M^+ - 3CO$, 0.4) 614 ($M^+ - 4CO$, 0.7), 586 ($M^+ - 5CO$, 1.9), 558 ($M^+ - 6CO$, 2.8), 530 ($M^+ - 7CO$, 1.8), 502 ($M^+ - 8CO$, 1.8), 379 ($WFeSeCo^+$, 0.3).

η^5-2,4-$(NO_2)_2C_6H_3NHNC(Me)C_5H_4(CO)_2WCoFe(\mu_3\text{-}Se)(CO)_6$ (**2**)

A solution of 2,4-dinitrophenylhydrazine (2.000 g, 10 mmol) in 10 cm^3 of 98% H_2SO_4 was added dropwise to a stirred solution prepared from 14 cm^3 of H_2O and 46 cm^3 of 95% EtOH. The resulting red-orange solution of 2,4-dinitrophenylhydrazine was filtered out and kept under nitrogen for use. The flask described above was charged with 0.280 g (0.39 mmol) of **1b**, 3 cm^3 of 2,4-dinitrophenylhydrazine solution and 20 cm^3 of EtOH. The mixture was stirred for 7 h at room temperature, filtered and washed with EtOH (10 cm^3 × 2). The solid was redissolved in methylene chloride and purified by TLC using 2 : 1 (v/v) CH_2Cl_2/petroleum ether as eluent. The main yellow-orange band was collected to afford 0.200 g (58%) of **2** as a brown solid, m.p. 150°C (dec). *Anal.* Calcd. for $C_{21}H_{11}CoFeN_4O_{12}SeW$(%): C, 28.38; H, 1.25; N, 6.30; Found: C, 27.99; H, 1.18; N, 6.14. IR (KBr, disk): $\nu_{(C\equiv O)}$ 2065(s), 2016(vs), 1991(vs), 1920(s), 1852(m); $\nu_{(C=N)}$ 1614(s) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, δ): 2.24 (s, 3H, CH_3), 5.52, 5.64 (q, q, 2H, H^3, H^4), 5.88 (q, 2H, H^2, H^5), 7.96 (d, 1H, $J = 6.4$ Hz, H^6 of benzene ring), 8.40 (d, 1H, $J = 6.4$ Hz, H^5 of benzene ring), 9.16 (s, 1H, H^3 of benzene ring), 11.36 (s, 1H, NH) ppm.

$[\eta^5\text{-}C_5H_4C(O)CH_2]_2[(CO)_2MoCoFe(\mu_3\text{-}Se)(CO)_6]_2$ (**3a**)

The flask described above was charged with 0.387 g (1.50 mmol) of $Na_2[\eta^5\text{-}C_5H_4C(O)CH_2]_2$, 0.792 g (3.00 mmol) of $Mo(CO)_6$ and 20 cm^3 of THF. The mixture was stirred at reflux for 15 h to give an intermediate $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[(CO)_3MoNa]_2$. Upon cooling to room temperature, 1.514 g (3.00 mmol) of $(\mu_3\text{-}Se)FeCo_2(CO)_9$ was added in one portion and the mixture was refluxed for an additional 0.5 h. Solvent was removed under vacuum and the residue was extracted with methylene chloride. The extracts were subjected to TLC separation using 3 : 2 (v/v) CH_2Cl_2/petroleum ether as eluent. From the main red-brown band was obtained 1.200 g (65%) of **3a** as a brown solid, m.p. 144°C (dec). *Anal.* Calcd. for $C_{30}H_{12}Co_2Fe_2Mo_2O_{18}Se_2$(%): C, 29.06; H, 0.97; Found: C, 29.25; H, 0.91. IR (KBr, disk): $\nu_{(C\equiv O)}$ 2073(vs), 2016(vs), 1959(vs), 1885(s); $\nu_{(C=O)}$ 1688(s) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, δ): 3.14 (s, 4H, CH_2CH_2), 5.48, 5.60 (q, q, 4H, H^3, $H^{3\prime}$, H^4, $H^{4\prime}$), 5.92 (t, 4H, H^2, $H^{2\prime}$, H^5, $H^{5\prime}$) ppm.

$[\eta^5\text{-}C_5H_4C(O)CH_2]_2[(CO)_2WCoFe(\mu_3\text{-}Se)(CO)_6]_2$ (3b)

The flask described above was charged with 0.387 g (1.50 mmol) of $Na_2[\eta^5\text{-}C_5H_4C(O)CH_2]_2$, 1.056 g (3.00 mmol) of $W(CO)_6$ and 20 cm^3 of diglyme. The mixture was stirred at reflux for 6 h to give an intermediate $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[(CO)_3WNa]_2$. After removal of the solvent under vacuum, 20 cm^3 of THF and 1.514 g (3.00 mmol) of $(\mu_3\text{-}Se)FeCo_2(CO)_9$ were added and the mixture was refluxed for an additional 0.5 h. The same workup as **3a** gave 0.318 g (15%) of **3b** as a brown solid, m.p. 154–155°C. *Anal.* Calcd. for $C_{30}H_{12}Co_2Fe_2O_{18}Se_2W_2$(%): C, 25.45; H, 0.85; Found: C, 25.43; H, 0.85. IR (KBr, disk): $\nu_{(C\equiv O)}$ 2073(vs), 2008(vs), 1967(vs), 1877(s); $\nu_{(C=O)}$ 1680(s) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, δ), 3.14 (s, 4H, CH_2CH_2), 5.54, 5.71 (q, q, 4H, H^3, $H^{3\prime}$, H^4, $H^{4\prime}$), 5.80–6.00 (m, 4H, H^2, $H^{2\prime}$, H^5, $H^{5\prime}$) ppm.

$[\eta^5\text{-}C_5H_4C(O)CH_2]_2[(CO)_2MoNiFe(\mu_3\text{-}Se)(CO)_3Cp]$-$[(CO)_2MoCoFe(\mu_3\text{-}Se)(CO)_6]$ (4) and $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[(CO)_2MoNiFe(\mu_3\text{-}Se)(CO)_3Cp]_2$ (5)

The flask described above was charged with 1.265 g (1.02 mmol) of **3a**, 0.578 g (3.06 mmol) of Cp_2Ni and 30 cm^3 of THF. The mixture was stirred at reflux for 12 h. Solvent was removed under vacuum and the residue was extracted with methylene chloride. The extracts were subjected to TLC separation using 4 : 1 (v/v) CH_2Cl_2/petroleum ether as eluent. From the first brown-green band was obtained 0.115 g (9%) of **4** as a brown-green solid, m.p. 151°C (dec). *Anal.* Calcd. for $C_{32}H_{17}CoFe_2Mo_2NiO_{15}Se_2$(%): C, 31.49; H, 1.40. Found: C, 31.91; H, 1.53. IR (KBr, disk): $\nu_{(C\equiv O)}$ 2073(vs), 2024(vs), 1999(vs), 1967(vs), 1951(vs), 1877(s); $\nu_{(C=O)}$ 1680(s) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, δ): 3.08 (s, 4H, CH_2CH_2), 5.32 (s, 5H, C_5H_5), 5.40–5.54; 5.58–5.74 (m, m, 4H, H^3, $H^{3\prime}$, H^4, $H^{4\prime}$), 5.84–6.12 (m, 4H, H^2, $H^{2\prime}$, H^5, $H^{5\prime}$) ppm. From the second deep-green band was obtained 0.225 g (18%) of **5** as a black-green solid, m.p. 202°C (dec). *Anal.* Calcd. for $C_{34}H_{22}Fe_2Mo_2Ni_2O_{12}Se_2$(%): C, 33.99; H, 1.85; Found: C, 33.73; H, 1.91. IR (KBr, disk). $\nu_{(C\equiv O)}$ 2073(w), 2032(vs), 1983(vs), 1950(vs), 1877(vs); $\nu_{(C=O)}$ 1680(s) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, δ): 3.04 (s, 4H, CH_2CH_2), 5.30 (s, 10H, $2C_5H_5$), 5.40–5.52, 5.58–5.70 (m, m, 4H, H^3, $H^{3\prime}$, H^4, $H^{4\prime}$), 5.96–6.12 (m, 4H, H^2, $H^{2\prime}$, H^5, $H^{5\prime}$) ppm.

Crystal Structure Determination of 1c

Suitable crystals of **1c** for X-ray diffraction analysis were grown by slow evaporation of a CH_2Cl_2/hexane solution at −20°C. Details of crystal

TABLE I Details of crystal parameters, data collection and structure refinement for **1c**

Formula	$C_{15}H_7CoFeO_{10}SeW$
M	724.80
Crystal size (mm)	0.85 × 0.55 × 0.35
Crystal system	Monoclinic
Space group	$P2/n$
a (Å)	17.606(6)
b (Å)	11.844(6)
c (Å)	19.033(6)
β (°)	95.85(3)
V (Å^3)	3948(5)
Z	8
Dc (g cm^{-3})	2.44
F(000)	2704
μ(Mo-Kα) (cm^{-1})	93.69
T (K)	296
Diffractometer	Enraf-nonius CAD4
$2\theta_{max}$ (°)	49.9
Scan width (°)	$0.60 + 0.35\tan\theta$
Transmission factors	0.9531-1.000
Reflections collected	7527
Unique reflections	7298
Observed reflections [$I > 3.00\sigma(I)$]	4815
R	0.049
R_w	0.059
Max., residuals (eÅ^3)	1.54

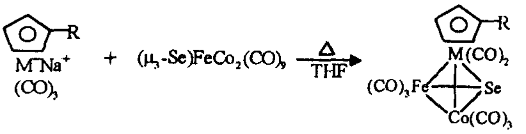
parameters, data collections and structure refinements are given in Table I. A brown crystal measuring 0.85 × 0.55 × 0.35 mm was mounted on a glass fibre and placed on an Enraf-Nonius CAD4 diffractometer with a graphite monochromator. A total of 7298 independent reflections were collected at 23°C with MoKα radiation ($\lambda = 0.71069$ Å) by a $\omega/2\theta$ scan mode. Of the total reflections, 4815 were considered to be observed with $I > 3\sigma(I)$ and used in subsequent refinement. Data were corrected for Lp factors.

The structure was solved by direct methods and Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in final calculations but not refined. All calculations were performed on a micro-VAX II computer using the TEXSAN program system.

RESULTS AND DISCUSSION

Synthesis and Characterization of Single and Double Clusters 1a–c, 2, 3a, b, 4 and 5

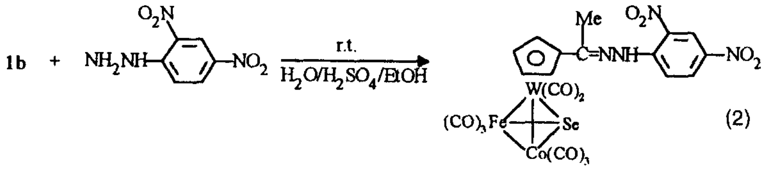
Analogous to the preparation of single MCoFe(μ_3-S) (M = Mo, W) cluster complexes,[1] we found that the mononuclear transition metal isolobal reagents η^5-$RC_5H_4(CO)_3MNa$ (M = Mo, W; R = MeCO, MeO_2C, EtO_2C) reacted with (μ_3-Se)$FeCo_2(CO)_9$ in THF at reflux, *via* a single isolobal displacement reaction,[1,3] to afford three new single MCoFe(μ_3-Se) clusters **1a–c**, as red-brown solids in 63–73% yields (*1*). We also found that cluster complex **1b** could undergo a functional transformation reaction with an aqueous H_2SO_4/EtOH solution of 2,4-dinitrophenylhydrazine to give its phenyl hydrazone derivative **2**, a new single WCoFe(μ_3-Se) cluster, as a deep-brown solid in 58% yield (*2*).



(1)

1a-c

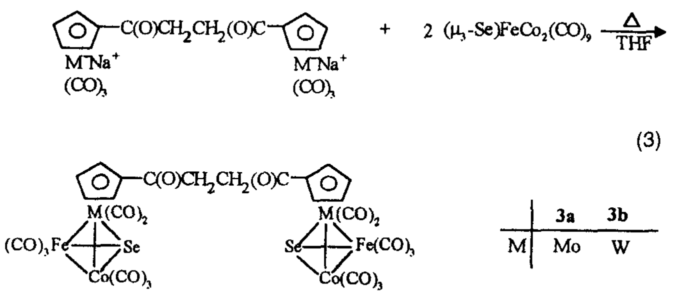
	1a	1b	1c
M	Mo	W	W
R	EtO_2C	MeCO	MeO_2C



(2)

2

On the basis of preparation of single MCoFe(μ_3-Se) clusters mentioned above, we further found that the dinuclear transition metal isolobal reagents $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[(CO)_3MNa]_2$ (M = Mo, W) reacted with two molecules of (μ_3-Se)$FeCO_2(CO)_9$ in THF at reflux, *via* a double isolobal displacement reaction,[1,13] to produce two new double MCoFe(μ_3-Se) clusters **3a,b** in 68% and 15% yields, respectively (*3*).

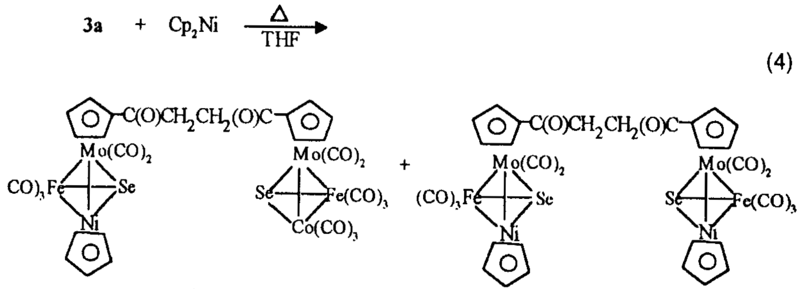


(3)

	3a	3b
M	Mo	W

3a-b

More interestingly, it was found that the reaction of double cluster **3a** with an isolobal reagent Cp_2Ni in refluxing THF, *via* both single and double isolobal reactions,[2,13] afforded an unsymmetrical double cluster **4** and a symmetrical double cluster **5** in 9% and 18% yields, respectively (*4*). The former contains two different tetrahedral cluster cores MoNiFe(μ_3-Se) and MoCoFe(μ_3-Se), while the latter possesses two identical tetrahedral cluster cores of MoNiFe(μ_3-Se). It follows that the functional transformation reaction and the isolobal displacement reactions involving isolobal fragments[1,2,13] such as $Co(CO)_3(d^9ML_3)$, η^5-$RC_5H_4(CO)_2M$ (a single d^5ML_5 fragment generated *in situ* from η^5-$RC_5H_4(CO)_3MNa$), $[\eta^5$-$C_5H_4C(O)CH_2]_2[(CO)_2M]_2$ (a double d^5ML_5 fragment generated *in situ* from $[\eta^5$-$C_5H_4C(O)CH_2]_2[(CO)_3MNa]_2$) and $CpNi(d^9ML_3)$ generated from nickelocene have proved to be very effective in preparation of μ_3-Se containing tetrahedral transition metal clusters.



(4)

4

5

All the new single and double cluster complexes have been characterized by analysis and spectroscopy. For single clusters **1a–c** and **2**, the IR spectra showed terminal carbonyl bands in the range 1868–2073 cm^{-1}. The IR spectra of **1a–c** also showed ester and acetyl carbonyl bands at 1688–1730 cm^{-1}, while the IR spectrum of **2** exhibited an band for C=N at 1614 cm^{-1}. ^1H NMR spectra of the monosubstituted cyclopentadienyl ligands in single clusters **1a–c** and **2** showed corresponding proton resonance signals. For instance, the four protons on the substituted cyclopentadienyl ring, similar to those of corresponding μ_3-S cluster complexes,[1] belong to an AA′BB′ pattern and usually exhibited, due to overlap, two quartets at higher field assigned to H^3 and H^4, and one triplet (one multiplet for **1b**) at lower field assigned to H^2 and H^5 of the cyclopentadienyl ring. Although the mass spectrum of **1a** displayed only the corresponding fragment ion peaks, the mass spectra of **1b** and **1c** showed their molecular ion peaks. It is worth pointing out that the peak of fragment ion $[MFeCoSe]^+$ existed in all mass spectra of **1a–c**, which indicated that the tetrahedral cluster core MCoFe(μ_3-Se) is quite stable.

For double clusters **3a,b**, **4** and **5**, the IR spectra contained four to six absorption bands in the range 1877–2073 cm^{-1} for terminal carbonyls, besides one absorption band at around 1680 cm^{-1} for ketonic carbonyls. ^{1}H NMR spectra showed one singlet at about 3.1 ppm for the bridged ethylene group, whereas double clusters **4** and **5** exhibited another singlet at about 5.3 ppm for the parent Cp ring coordinated to the Ni atom. In addition, the four protons for each substituted cyclopentadienyl ring in **3a,b**, **4** and **5** are also in an AA′BB′ pattern and showed three sets of resonance signals due to overlap, namely, the upfield two sets of signals, usually two multiplets, were assigned to H^3 and H^4 remote from the succinoyl bridge and the downfield signal was attributed to H^2 and H^5 close to the bridge. It is worth noting that for **3a,b** and **5** there must be a pair of enantiomers and *meso* form and for **4** two pairs of enantiomers, due to the presence of tetrahedral cluster cores of chirality. However, they could not be separated into single optical isomers by TLC and might exist as a mixture of several optical isomers. This is consistent with the four protons for each substituted cyclopentadienyl ring of **3a,b**, **4** and **5** having such complicated ^{1}H NMR spectra.

Single-Crystal Structure of 1c

In order to further confirm the structures of the tetrahedral MCoFe(μ_3-Se) cluster complexes, an X-ray diffraction analysis of **1c** was undertaken. Final atomic coordinates with equivalent isotropic thermal factors are listed in Table II. Although there are two crystallographically independent molecules (*i.e.*, A and B) in the asymmetric unit (see Figure 1), only selected bond lengths and bond angles of A are listed in Table III. This is because the structural features of two independent molecules A and B are essentially the same. As seen from Figure 1, the molecule contains a chiral tetrahedral cluster core WCoFeSe, eight carbonyls and a MeO_2C-substituted cyclopentadienyl ring. The Se atom is coordinated to the W, Fe and Co atoms in a μ_3-type of arrangement. The substituted cyclopentadienyl ring is coordinated to the W atom and the distance of the W atom to cyclopentadienyl ring centroid is 1.99(1) Å. All eight carbonyls attached to W, Fe and Co atoms in the molecule are terminal, which is consistent with IR bands in the range 1918–2065 cm^{-1}. The substituent MeO_2C is conjugated very well with the π-system of the cyclopentadienyl ring, since the dihedral angle between the plane of the cyclopentadienyl ring and that of O(27)–C(26)–O(28) is quite small (4.71°) and the bond length C(21)–C(26) (1.47(2) Å) is much

TABLE II Atomic coordinates and equivalent isotropic temperature factors for **1c**

Atom	*x/a*	*y/b*	*z/c*	*B (eq)*
W(1)	0.02972(3)	0.03351(5)	0.19102(3)	2.42(2)
W(2)	0.25285(3)	0.53384(5)	0.45348(3)	2.62(2)
Se(1)	−0.05310(9)	0.1447(1)	0.26346(9)	4.61(8)
Se(2)	0.15742(7)	0.4115(1)	0.50346(8)	3.18(6)
Co(1)	−0.0686(1)	−0.0472(2)	0.2827(1)	3.8(1)
Co(2)	0.1361(1)	0.5978(2)	0.5330(1)	3.20(8)
Fe(1)	0.0464(1)	0.0692(2)	0.3366(1)	3.11(9)
Fe(2)	0.2426(1)	0.4743(2)	0.5957(1)	3.34(9)
O(1)	0.1528(7)	0.221(1)	0.1959(7)	6.7(7)
O(2)	0.1622(5)	−0.129(1)	0.2453(6)	4.9(5)
O(3)	−0.2080(6)	−0.065(2)	0.1878(8)	11(1)
O(4)	−0.1263(7)	−0.082(2)	0.4207(7)	8.6(9)
O(5)	0.0055(7)	−0.264(1)	0.2675(7)	6.3(7)
O(6)	−0.0157(8)	0.135(1)	0.4660(7)	7.7(8)
O(7)	0.1288(6)	−0.122(1)	0.4030(7)	5.6(6)
O(8)	0.1678(9)	0.236(1)	0.3536(8)	9(1)
O(9)	0.3744(6)	0.691(1)	0.5366(7)	5.9(6)
O(10)	0.3819(6)	0.350(1)	0.4740(7)	6.2(7)
O(11)	0.0163(6)	0.659(1)	0.4214(7)	6.0(7)
O(12)	0.2122(7)	0.818(1)	0.5625(8)	6.7(7)
O(13)	0.0358(8)	0.588(1)	0.6453(8)	8.0(8)
O(14)	0.3612(7)	0.302(1)	0.6287(8)	8.0(8)
O(15)	0.1561(8)	0.382(2)	0.7062(8)	9(1)
O(16)	0.3187(8)	0.651(1)	0.6829(8)	8.1(8)
C(1)	0.1063(9)	0.152(1)	0.1977(8)	4.2(7)
C(2)	0.1135(7)	−0.067(1)	0.2308(8)	3.2(6)
C(3)	−0.1544(9)	−0.060(2)	0.223(1)	7(1)
C(4)	−0.1033(8)	−0.067(2)	0.369(1)	6(1)
C(5)	−0.0222(8)	−0.179(2)	0.2732(9)	4.2(8)
C(6)	0.010(1)	0.110(2)	0.416(1)	5.2(9)
C(7)	0.0981(7)	−0.047(1)	0.3752(7)	3.0(6)
C(8)	0.120(1)	0.171(2)	0.345(1)	5.3(9)
C(9)	0.3267(8)	0.633(1)	0.5109(9)	3.9(7)
C(10)	0.3330(8)	0.412(1)	0.4699(9)	4.3(8)
C(11)	0.0638(8)	0.635(1)	0.4644(8)	4.0(7)
C(12)	0.1849(8)	0.732(2)	0.5514(9)	4.4(8)
C(13)	0.0748(9)	0.590(1)	0.603(1)	4.7(8)
C(14)	0.317(1)	0.371(1)	0.614(1)	5.1(9)
C(15)	0.188(1)	0.419(2)	0.664(1)	5(1)
C(16)	0.2884(8)	0.584(2)	0.6478(9)	4.5(8)
C(21)	0.0645(7)	0.006(1)	0.0804(7)	2.5(5)
C(22)	0.0230(7)	−0.090(1)	0.0975(7)	3.0(6)
C(23)	−0.0530(8)	−0.059(1)	0.1024(8)	3.5(7)
C(24)	−0.0588(7)	0.059(1)	0.0905(8)	3.6(7)
C(25)	0.0135(8)	0.097(1)	0.0772(8)	3.8(7)
C(26)	0.1438(8)	0.003(1)	0.0624(8)	3.2(6)
O(27)	0.1646(5)	0.0999(9)	0.0362(6)	3.9(5)
O(28)	0.1838(6)	−0.081(1)	0.0682(7)	5.4(6)
C(29)	0.2386(8)	0.096(2)	0.008(1)	6(1)
C(31)	0.3094(7)	0.571(1)	0.3549(8)	3.6(7)
C(32)	0.2587(7)	0.479(1)	0.3381(7)	3.3(6)
C(33)	0.1861(8)	0.521(1)	0.3395(7)	3.8(7)
C(34)	0.1890(8)	0.635(1)	0.3576(9)	3.9(7)
C(35)	0.2659(7)	0.669(1)	0.3668(8)	3.4(6)
C(36)	0.3949(8)	0.574(1)	0.355(1)	4.1(7)
C(37)	0.4187(5)	0.4730(9)	0.3309(7)	5.0(6)
C(38)	0.4348(5)	0.649(1)	0.3728(7)	5.5(6)
C(39)	0.500(1)	0.458(2)	0.331(1)	7(1)

TABLE III Selected bond lengths (Å) and angles (°) for **1c**

W(1)–Se(1)	2.484(2)	W(1)–Co(1)	2.751(2)
W(1)–Fe(1)	2.789(2)	Se(1)–Fe(1)	2.305(3)
Se(1)–Co(1)	2.323(3)	Co(1)–Fe(1)	2.574(3)
W(1)–C(1)	1.94(1)	C(21)–C(26)	1.47(2)
C(21)–C(22)	1.41(2)	C(26)–O(28)	1.21(2)
C(26)–O(27)	1.32(2)		
C(1)–W(1)–C(2)	85.7(6)	Se(1)–W(1)–Co(1)	52.38(7)
Se(1)–W(1)–Fe(1)	51.44(6)	CO(1)–W(1)–Fe(1)	55.37(7)
Fe(1)–Se(1)–Co(1)	67.59(9)	Fe(1)–Se(1)–W(1)	71.13(7)
Co(1)–Se(1)–W(1)	69.72(7)	C(3)–Co(1)–C(4)	102.5(7)
Se(1)–Co(1)–Fe(1)	55.87(8)	Se(1)–Co(1)–W(1)	57.90(7)
Fe(1)–Co(1)–W(1)	63.07(7)	C(6)–Fe(1)–C(7)	94.5(7)
C(25)–C(21)–C(22)	106(1)	Se(1)–Fe(1)–Co(1)	56.53(9)
Se(1)–Fe(1)–W(1)	57.43(7)	CO(1)–Fe(1)–W(1)	61.55(7)
O(28)–C(26)–O(27)	124(1)	O(28)–C(26)–C(21)	124(1)

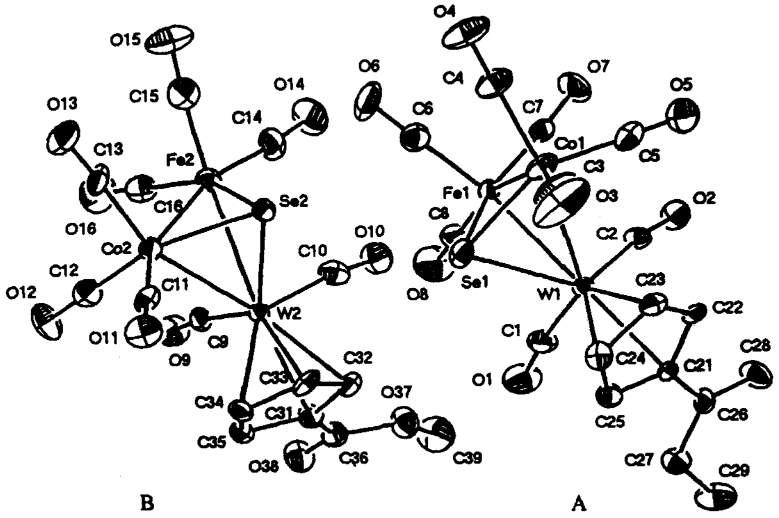


FIGURE 1 Molecular structure of **1c**, showing atom labeling scheme.

shorter than a normal C–C single bond. Bond lengths in the WCoFeSe cluster core are Se(1)–Fe(1) = 2.305(3) Å,[14] Fe(1)–Co(1) = 2.574(3) Å,[1] Co(1)–W(1) = 2.751(2) Å,[1] W(1)–Fe(1) = 2.789(2) Å[1] Se(1)–W(1) = 2.484(2) Å,[15] and Se(1)–Co(1) = 2.323(3) Å,[16] which are similar to those corresponding bond lengths reported in the literature, respectively.

Supplementary Material

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

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