

Study of metal exchange reactions in cobalt containing clusters

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Abstract

Treatment of the linked cluster $\{[(\mu_3\text{-C})\text{R}]\text{Co}_2\text{Mo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})]\}_2\text{C}_6\text{H}_4\text{-}p$ (**1a**, R = CO₂Et; **1b**, R = C₆H₅) with the substituted cyclopentadienyl tricarbonyl molybdenum anion $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{R}')^-]$ in THF gave rise to the formation of the single cluster complex $[(\mu_3\text{-C})\text{R}]\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{R}')$ (**2a**, R = CO₂Et, R' = H; **2b**, R = CO₂Et, R' = C(O)Me; **2c**, R = R' = CO₂Et; **2d**, R = C₆H₅, R' = CO₂Et) as the only product. However, reaction of cluster $\{(\mu_3\text{-Se})\text{RuCoMo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})]\}_2\text{C}_6\text{H}_4\text{-}p$ (**1c**) with $\text{NaMo}(\text{CO})_3[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{Me}]$ yielded the linked cluster compound $(\mu_3\text{-Se})\text{RuCoMo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{-}p\text{-C}_6\text{H}_4\text{-C}(\text{O})\text{C}_5\text{H}_4\text{-}\eta^5](\text{CO})_7\text{RuMo}_2(\mu_3\text{-Se})[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{Me}]$ (**3**). Further reactions of **2b** and cluster $[(\mu_3\text{-C})\text{CO}_2\text{Et}]\text{Co}_2\text{Mo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{-}p\text{-C}_6\text{H}_4\text{CO}_2\text{Me}]$ (**2e**), respectively, with the monoanion $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]^-$ gave four products **2a**, $[(\mu_3\text{-C})\text{CO}_2\text{Et}]\text{CoMo}_2(\text{CO})_7(\eta^5\text{-C}_5\text{H}_5)_2$ (**4**), $[(\mu_3\text{-C})\text{CO}_2\text{Et}]\text{CoMo}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{R})(\eta^5\text{-C}_5\text{H}_5)$ (**5a**, R = C(O)Me; **5b**, R = C(O)*p*-C₆H₄CO₂Me) and $[(\mu_3\text{-C})\text{CO}_2\text{Et}]\text{CoMo}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{R})_2$ (**6a**, R = C(O)Me). By contrast, treatment of cluster **2a** with the monoanion $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{R}')^-]$ afforded three cluster products **4**, **2** (**2b**, R = C(O)Me; **2e**, R = C(O)*p*-C₆H₄CO₂Me) and **5** (**5a**, R = C(O)Me; **5b**, R = C(O)*p*-C₆H₄CO₂Me). All the compounds were fully characterized by elemental and spectroscopic analyses. The molecular structures of clusters **2a** and **4** have been determined by single-crystal X-ray diffraction.

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1. Introduction

In recent years the isolobal displacement reactions, due to their theoretical interest and wide uses in rational synthesis of transition-metal cluster complexes, have attracted considerable attention [1–21]. So far, many examples are known in which a d^9 ML₃ fragment Co(CO)₃ can be displaced by an isolobal d^5 ML₅ fragment Cp*(CO)₂M (Cp* = Cp or substituted Cp, M = Cr, Mo or W). Some $(\mu_3\text{-X})\text{Co}_2\text{M}$ (X = C, S, Se, Te, P; M = Cr, Mo, W, Fe, Ni, Ru) and $(\mu_2\text{-X})\text{CoM}$ (M = Mo or W) tetrahedrane-type clusters were prepared by such procedures [1–21]. Our interests in higher-nuclearity cluster synthesis [17,22–24] prompted us to initiate a study in this area, and we found that metal exchange reaction in linked clusters compounds is

regioselective [15,17], and the Co(CO)₃ group in different cluster units has different reactivity [16], providing a potential application in the syntheses of polymeric species. It might be possible to prepare supramolecular cluster compounds in a molecular design manner by the metal exchange reactions of linked clusters.

In order to investigate metal exchange reactions in linked clusters more extensively, we carried out a study on reactions of $\{(\mu_3\text{-X})\text{Co}_2\text{Mo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})]\}_2\text{C}_6\text{H}_4\text{-}p$ (X = CCO₂Et, CC₆H₅ or Se) with $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{R}')^-]$ (R' = H, C(O)Me, CO₂Et). It was found that the two different d^5 ML₅ fragments of the type Cp*(CO)₂M can displace each other in Co(CO)₃ containing cluster compounds. The single cluster compound $(\mu_3\text{-X})\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{R}')$ can be separated as the only product in carbon atom capped clusters. However, the selenium atom capped cluster compound $\{(\mu_3\text{-Se})\text{RuCoMo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})]\}_2\text{C}_6\text{H}_4\text{-}p$ was found to react with $\text{NaMo}(\text{CO})_3[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{Me}]$ to yield the linked cluster compound $(\mu_3\text{-Se})\text{RuCoMo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{-}p\text{-C}_6\text{H}_4\text{-C}(\text{O})\text{C}_5\text{H}_4\text{-}\eta^5](\text{CO})_7\text{RuMo}_2(\mu_3\text{-}$

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Se)[η^5 -C₅H₄C(O)Me]. Further experiments indicated that the existence of bulky electron-withdrawing functional substitution (R') on the cyclopentadienyl ligand can decrease the reactivity of the [Mo(CO)₃(η^5 -C₅H₄R')] unit in metal exchange reactions. Nine novel cluster compounds were synthesized, and the crystal structures of **2a** and **4** were determined.

2. Experimental

2.1. General comments

All reactions were carried out under pure nitrogen using standard Schlenk techniques. All solvents were dried and deoxygenated according to standard procedures before use. Chromatographic separations and purification were performed on 160–200 mesh silica gel.

Infrared spectra were recorded as pressed KBr disks on a Nicolet FT-IR 10 DX spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AM 400 spectrometer in CDCl₃-deuterated solvent at ambient temperature. Chemical shifts were given on the δ scale relative to SiMe₄ (0.0 ppm). Elemental analyses were carried out on a Carlo Erba 1106 type analyzer.

Cluster complexes $\{[(\mu_3\text{-C})\text{R}] \text{Co}_2\text{Mo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})]\}_2\text{C}_6\text{H}_4\text{-}p$ (**1a**, R = CO₂Et; **1b**, R = C₆H₅), $\{(\mu_3\text{-Se})\text{RuCoMo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})]\}_2\text{C}_6\text{H}_4\text{-}p$ (**1c**), $[(\mu_3\text{-C})\text{CO}_2\text{Et}] \text{Co}_2\text{Mo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{-}p\text{-C}_6\text{H}_4\text{CO}_2\text{Me}]$ (**2e**) and NaMo(CO)₃(η^5 -C₅H₄R') (R' = H, C(O)Me, CO₂Et, C(O)-*p*-C₆H₄CO₂Me) were prepared according to literature methods or slight modifications thereof [21,14,25].

2.2. Reaction of **1a** with Na[Mo(CO)₃(η^5 -Cp*)]

Cluster **1a** (653 mg, 0.5 mmol) and NaMo(CO)₃(η^5 -C₅H₅) (134 mg, 0.5 mmol) were dissolved in 25 cm³ of THF and stirred at room temperature for 24 h. Then the solvent was pumped off and the residue was chromatographed on a 2 × 25 cm² silica gel column. After a small red band was eluted with petroleum ether, petroleum ether/CH₂Cl₂ (3:1) afforded the main black blue band, condensing the solvent and crystallization from CH₂Cl₂-hexane at -20 °C gave the cluster **2a** (115 mg, yield 39% based on **1a**) as black crystals. Anal. Found: C, 34.71; H, 1.73. Calc. for C₁₇H₁₀O₁₀Co₂Mo: C, 34.72; H, 1.71%. IR (cm⁻¹): (ν CO) 2076s, 2037vs, 2020vs, 1999vs, 1971s, 1955s, 1925m and (ν CO₂Et) 1669m. ¹H-NMR: δ 5.46 (s, 5H, C₅H₅), 4.35–4.29 (q, 2H, CH₂, *J* = 7.1 Hz), 1.38–1.34 (t, 3H, CH₃, *J* = 7.1 Hz). Finally, elution with CH₂Cl₂/ethyl ether (25:1) yielded the unreacted cluster **1a** (300 mg).

Similarly, only one product is formed from the reactions of cluster **1a** with other substituted cyclopentadienyl tricarbonyl molybdenum sodiums.

(1) From the reaction of **1a** with NaMo(CO)₃(η^5 -C₅H₄C(O)Me), 54 mg (yield 35% based on **1a**) of cluster **2b** as dark green crystals was obtained. Anal. Found: C, 36.21; H, 1.94. Calc. for C₁₉H₁₂O₁₁Co₂Mo: C, 36.22; H, 1.92%. IR (cm⁻¹): (ν CO) 2081s, 2032vs, 2011vs, 1997vs, 1984s, 1974s; (ν C=O) 1685m and (ν CO₂Et) 1664m. ¹H-NMR: δ 5.89 (s, 2H, H(2) and H(5)), 5.47 (s, 2H, H(3) and H(4)), 4.26 (s, 2H, CH₂), 2.28 (s, 3H, CH₃), 1.30 (s, 3H, CH₃).

(2) From the reaction of **1a** with NaMo(CO)₃(η^5 -C₅H₄CO₂Et), 35 mg (yield 37% based on **1a**) of cluster **2c** as a dark green solid was obtained. Anal. Found: C, 36.37; H, 2.14. Calc. for C₂₀H₁₄O₁₂Co₂Mo: C, 36.39; H, 2.14%. IR (cm⁻¹): (ν CO) 2091s, 2081s, 2035vs, 2014vs, 1942m, 1897m; (ν CO₂Et) 1725m and [ν (μ_3 -C)CO₂Et] 1674m. ¹H-NMR: δ 5.90 (s, 2H, H(2) and H(5)), 5.46 (s, 2H, H(3) and H(4)), 4.22 (s, 4H, 2CH₂), 1.17 (s, 6H, 2CH₃).

2.3. Reaction of **1b** with NaMo(CO)₃(η^5 -C₅H₄CO₂Et)

A mixture of cluster **1b** (200 mg, 0.16 mmol) and NaMo(CO)₃(η^5 -C₅H₄CO₂Et) (55 mg, 0.16 mmol) in 25 cm³ of THF was stirred at reflux for 1 h. The workup was similar to that described in reaction of **1a** with NaMo(CO)₃(η^5 -C₅H₅). Single cluster **2d** (32 mg, yield 30% based on **1b**) as black crystals was obtained. Anal. Found: C, 41.57; H, 2.09%. Calc. for C₂₃H₁₄O₁₀Co₂Mo: C, 41.59; H, 2.12%. IR (cm⁻¹): (ν CO) 2085s, 2070s, 2021vs, 2000vs, 1979s, 1942m and (ν CO₂Et) 1719s. ¹H-NMR: δ 7.17 (s, 5H, C₆H₅), 5.81 (s, 2H, H(2) and H(5)), 5.22 (s, 2H, H(3) and H(4)), 4.24 (s, 2H, CH₂), 1.32 (s, 3H, CH₃). Unreacted **1b** (110 mg) was obtained from the last dark green band.

2.4. Reaction of **1c** with NaMo(CO)₃(η^5 -C₅H₄C(O)-Me)

Linked cluster **1c** (200 mg, 0.145 mmol) and NaMo(CO)₃(η^5 -C₅H₄C(O)Me) (40 mg, 0.145 mmol) were dissolved in 25 cm³ of THF and refluxed for 6 h. After removing the solvent, the residue was separated on a silica gel column. Elution with petroleum ether/CH₂Cl₂ (1:1) gave the single cluster **2f** (40 mg, yield 41.4% based on **1c**). IR (cm⁻¹): (ν CO) 2079s, 2048s, 2038s, 2014s, 1991s, 1893s, 1854m and (ν C(O)Me) 1686m. ¹H-NMR: δ 5.88–5.46 (q, 4H, C₅H₄), 2.40 (s, 3H, CH₃). Then a small red band and unreacted material **1c** (70 mg) were eluted. Finally, petroleum ether/CH₂Cl₂/ethyl ether (1:1:1) afforded the major purple band, from which linked cluster **3** (50 mg, yield 23% based on **1c**) as a red solid was obtained. Anal. Found: C, 32.16; H, 1.26. Calc. for C₄₀H₁₉O₁₈CoMo₃Ru₂Se₂: C, 32.15; H, 1.28%. IR (cm⁻¹): (ν CO) 2078s, 2039s, 1998vs, 1903s, 1863s and (ν C=O) 1679m, 1652m. ¹H-NMR: δ 7.82 (s, 4H, C₆H₄), 5.91–5.06 (m, 12H,

$3C_5H_4$), 2.29 (s, 3H, CH_3). ^{13}C -NMR: δ 229.65, 227.29, 227.17, 227.07, 226.55, 222.77, 192.96 (carbonyls bound to metals), 189.13, 188.91 (C=O), 140.98, 140.85, 128.29 (C_6H_4), 98.18–90.41 (m, $3C_5H_4$), 27.08 (CH_3).

2.5. Reaction of **2b** and $NaMo(CO)_3(\eta^5-C_5H_5)$

Compound **2b** (940 mg, 1.5 mmol) and $NaMo(CO)_3(\eta^5-C_5H_5)$ (402 mg, 1.5 mmol) were dissolved in THF (60 cm^3) and refluxed for 7 h. Then THF was removed and the residue was chromatographed on a silica gel column. Elution with petroleum ether/ CH_2Cl_2 (1:1) gave the first band, condensing the solvent and crystallization from CH_2Cl_2 -hexane at $-20^\circ C$ gave cluster **2a** (60 mg, yield 6.8%) as crystals. Then petroleum ether/ CH_2Cl_2 (1:2) yielded two dark green bands. Cluster **4** (120 mg, yield 12.05%) was obtained from the former band. Anal. Found: C, 38.11; H, 2.26. Calc. for $C_{21}H_{15}O_9CoMo_2$: C, 38.09; H, 2.28%. IR (cm^{-1}): (νCO) 2086m, 2045vs, 2005vs, 1980vs, 1964vs, 1906vs, 1846s and [$\nu(\mu_3-C)CO_2Et$] 1650(s). 1H -NMR: δ 5.29 (s, 10H, 2Cp), 4.29 (s, 2H, CH_2), 1.36 (s, 3H, CH_3). The latter band was the unreacted material **2b** (160 mg). Cluster **5a** (270 mg, yield 25.6%) as a dark green solid could be obtained from the fourth band eluted by CH_2Cl_2 . Anal. Found: C, 39.23; H, 2.45. Calc. for $C_{23}H_{17}O_{10}CoMo_2$: C, 39.23; H, 2.43%. IR (cm^{-1}): (νCO) 2044vs, 2008vs, 1985vs, 1967vs, 1925vs, 1870s, 1852s; (νCO) 1676m and [$\nu(\mu_3-C)CO_2Et$] 1650(s). 1H -NMR: δ 5.84 (s, 2H, H(2) and H(5)), 5.39 (s, 2H, H(3) and H(4)), 5.30 (s, 5H, Cp), 4.32 (s, 2H, CH_2), 2.32 (s, 3H, CH_3), 1.37 (s, 3H, CH_3). Finally, petroleum ether/ethyl ether/ CH_2Cl_2 (2:1:1) afforded the fifth band, from which cluster **6a** (60 mg, yield 5.4%) as a black solid was obtained. Anal. Found: C, 40.25; H, 2.59. Calc. for $C_{25}H_{19}O_{11}CoMo_2$: C, 40.24; H, 2.57%. IR (cm^{-1}): (νCO) 2058s, 2028vs, 2006vs, 1997vs, 1972s, 1915s, 1839s; ($\nu C=O$) 1692m, 1677m and [$\nu(\mu_3-C)CO_2Et$] 1665s. 1H -NMR: δ 5.76–5.41 (d, 8H, $2C_5H_4$), 5.41 (s, 5H, Cp), 4.37–4.31 (q, 2H, CH_2 , $J=6.88, 7.09, 6.89$ Hz), 2.34 (s, 6H, $2CH_3$), 1.40–1.36 (t, 3H, CH_3 , $J=7.12, 6.98$ Hz).

2.6. Reaction of **2e** with $NaMo(CO)_3(\eta^5-C_5H_5)$

Treatment of **2e** (360 mg, 0.48 mmol) and $NaMo(CO)_3(\eta^5-C_5H_5)$ (134 mg, 0.48 mmol) in 40 cm^3 of THF at reflux with stirring for 10 h. The workup was similar to that described in reaction of **2b** and $NaMo(CO)_3(\eta^5-C_5H_5)$. Four bands were separated from the reaction as follows: Elution with petroleum ether/ CH_2Cl_2 (1:1) gave cluster **2a** (35 mg, yield 12.4%). The following two bands were cluster **4** (48 mg, yield 15.1%) and unreacted material **2e** (45 mg). Petroleum ether/ether/ CH_2Cl_2 (3:1:1) eluted the fourth band, 50 mg (yield 12.6%) of **5b** as black oil after removal of the

solvent. Anal. Found: C, 43.72; H, 2.59. Calc. for $C_{30}H_{21}O_{12}CoMo_2$: C, 43.71; H, 2.57%. IR (cm^{-1}): (νCO) 2053s, 2016vs, 1988vs, 1916s, 1848m; (νCO_2Me) 1723m and [$\nu(\mu_3-C)CO_2Et$] 1657s. 1H -NMR: δ 8.09–7.79 (d, 4H, C_6H_4), 5.93 (s, 2H, H(2) and H(5)), 5.40 (s, 2H, H(3) and H(4)), 5.25 (s, 5H, Cp), 4.20 (s, 2H, CH_2), 3.92 (s, 3H, CH_3), 1.29 (s, 3H, CH_3). ^{13}C -NMR δ 247.65 (μ_3-C), 228.83, 227.60, 203.61 (carbonyls bound to metals), 189.31, 181.10 (two ester carbons), 166.09 (C=O), 141.79, 133.21, 129.64, 128.03 (C_6H_4), 101.41, 99.64, 98.32, 96.35, 92.23 (C_5H_4 and C_5H_5), 61.33 (CH_2), 52.35 (O_2CH_3), 14.43 (CH_3).

2.7. Reaction of **2a** with $NaMo(CO)_3[\eta^5-C_5H_4C(O)-Me]$

Cluster **2a** (880 mg, 1.5 mmol) and $NaMo(CO)_3[\eta^5-C_5H_4C(O)Me]$ (465 mg, 1.5 mmol) were dissolved in 60 cm^3 of THF and stirred at reflux for 12 h. The workup was similar to that described in reaction of **2b** and $NaMo(CO)_3(\eta^5-C_5H_5)$. Clusters **2a** (198 mg, yield 12.1%), **2b** (50 mg, yield 5.3%) and **5a** (450 mg, yield 42.6%) were separated respectively.

2.8. Reaction of **2a** with $NaMo(CO)_3[\eta^5-C_5H_4C(O)-p-C_6H_4CO_2Me]$

A mixture of **2a** (880 mg, 1.5 mmol) and $NaMo(CO)_3[\eta^5-C_5H_4C(O)-p-C_6H_4CO_2Me]$ (645 mg, 1.5 mmol) in 60 cm^3 of THF was refluxed for 12 h. The workup was similar to that described in reaction of **2b** and $NaMo(CO)_3(\eta^5-C_5H_5)$. Clusters **2a** (375 mg, 4 (35 mg, yield 3.5%) and **5b** (585 mg, yield 47.3%) were obtained, respectively.

2.9. X-ray structure determination of **2a** and **4**

Crystals of **2a** and **4** used for X-ray determination were obtained from hexane/ CH_2Cl_2 at $-20^\circ C$. The data crystals were mounted in a thin glass capillary. Preliminary examination and data collection were performed with Mo-K $_{\alpha}$ radiation ($\lambda=0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The corrections for Lp factors and empirical absorption were applied to the intensity data. The structure was solved by direct method and expanded using Fourier technique. The non-hydrogen atoms were refined by the full-matrix least-squares method anisotropically, hydrogen atoms were included but not refined. All calculations were performed on macro VAX 3100 computer using the TEXSAN program system. Crystallographic data are collected in Table 1.

Table 1
Crystal and refinement data for cluster **2a** and **4**

Cluster	2a	4
Empirical formula	C ₁₇ H ₁₀ O ₁₀ Co ₂ Mo	C ₂₁ H ₁₅ O ₉ CoMo ₂
Formula weight	588.05	662.14
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions		
<i>a</i> (Å)	8.1316(16)	8.4906(17)
<i>b</i> (Å)	8.1440(16)	9.2475(18)
<i>c</i> (Å)	16.321(3)	14.862(3)
α (°)	98.21(3)	89.15(3)
β (°)	91.12(3)	87.13(3)
γ (°)	107.03(3)	76.90(3)
Volume (Å ³)	1020.7(4)	1135.1(4)
<i>Z</i>	2	2
<i>D</i> _{calc} (Mg m ⁻³)	1.913	1.937
Absorption coefficient (mm ⁻¹)	2.262	1.860
<i>F</i> (0 0 0)	576	648
Crystal size (mm ³)	0.65 × 0.65 × 0.30	0.625 × 0.40 × 0.125
θ Range for data collection (°)	2.53–25.97	2.26–25.97
Reflections collected	4094	4718
Unique reflections	3950 [<i>R</i> _{int} = 0.0391]	4410 [<i>R</i> _{int} = 0.0229]
Refinement method		
Data/restraints/parameters	3950/0/272	4410/0/229
Goodness-of-fit on <i>F</i> ²	1.164	1.048
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0290, <i>wR</i> ₂ = 0.0699	<i>R</i> ₁ = 0.0392, <i>wR</i> ₂ = 0.1000
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0315, <i>wR</i> ₂ = 0.0709	<i>R</i> ₁ = 0.0433, <i>wR</i> ₂ = 0.1024
Largest diff. peak and hole (e Å ⁻³)	0.363 and -0.495	1.193 and -1.173

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad wR_2 = \frac{[\sum \omega (|F_o| - |F_c|)^2 / \sum \omega F_o^2]^{1/2}}{\sum \omega F_o^2}$$

3. Results and discussion

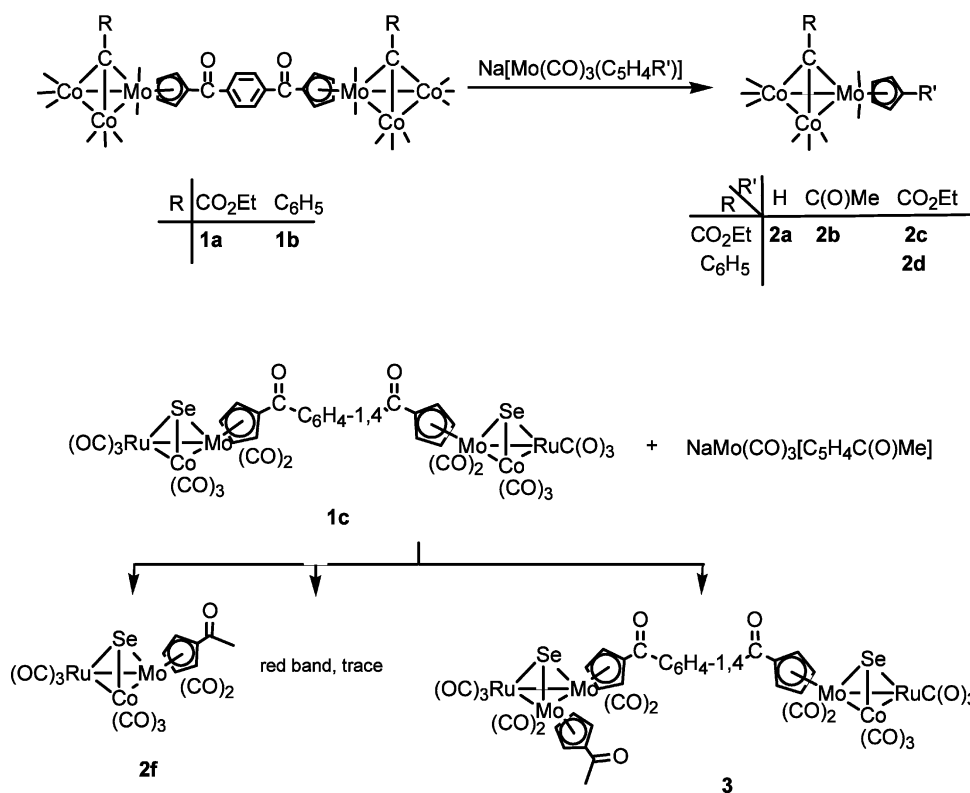
It is known that the metal exchange reactions of bridging bis(cyclopentadienyl) transition metal reagents with tetrahedral clusters such as FeCo₂(CO)₉(μ₃-S) and RuCo₂(CO)₉(μ₃-S) can link the two clusters together [9,20]. If the linked cluster could be treated with a bridging metal exchange reagent further, a new methodology for higher-nuclearity cluster compound would come into being. Metal exchange reactions in linked clusters have been studied recently [15–19], we wish to report the investigation of metal exchange reactions of {[(μ₃-C)R]Co₂M(CO)₈[η⁵-C₅H₄C(O)]}₂C₆H₄-*p* and {(μ₃-Se)RuCoMo(CO)₈[η⁵-C₅H₄C(O)]}₂C₆H₄-*p* with [Mo(CO)₃(η⁵-C₅H₄R')]⁻ in this report. All the work is described in Schemes 1–3.

When the linked cluster {[(μ₃-C)R]Co₂Mo(CO)₈[η⁵-C₅H₄C(O)]}₂C₆H₄-*p* (**1a–b**) was allowed to react with monoanion [Mo(CO)₃(η⁵-C₅H₄R')]⁻ in 1:1 molecular ratio, the [Mo(CO)₂Cp*] fragment in Co₂Mo(μ₃-C) core was replaced by the [Mo(CO)₂(η⁵-C₅H₄R')] isolobal

fragment to yield the single cluster [(μ₃-C)R]Co₂Mo(CO)₈(η⁵-C₅H₄R') (**2a**, R = CO₂Et, R' = H; **2b**, R = CO₂Et, R' = C(O)Me; **2c**, R = R' = CO₂Et; **2d**, R = C₆H₅, R' = CO₂Et) as the only product. It was not found that the Co(CO)₃ fragment in Co₂Mo(μ₃-C) core was replaced by the [Mo(CO)₃(η⁵-C₅H₄R')]⁻ anion to give the linked cluster [(μ₃-C)R]Co₂Mo(CO)₈[η⁵-C₅H₄C(O)-*p*-C₆H₄-C(O)C₅H₄-η⁵](CO)₇CoMo₂[(μ₃-C)R](η⁵-C₅H₄R). However, the reaction of {(μ₃-Se)RuCoMo(CO)₈[η⁵-C₅H₄C(O)]}₂C₆H₄-*p* (**1c**) was found to react with NaMo(CO)₃[η⁵-C₅H₄C(O)Me] to yield the linked cluster (μ₃-Se)RuCoMo(CO)₈[η⁵-C₅H₄C(O)-*p*-C₆H₄-C(O)C₅H₄-η⁵](CO)₇RuMo₂(μ₃-Se)[η⁵-C₅H₄C(O)Me] (**3**) successfully, although a small amount of the single cluster (μ₃-Se)RuCoMo(CO)₈[η⁵-C₅H₄C(O)Me] (**2f**) also was formed.

In order to investigate the self-displacement of the two Cp*(CO)₂M species further, experiments described in Schemes 2 and 3 were carried out. The separation of cluster **2a** confirmed that the two different *d*⁵ ML₅ fragment of the type Cp*(CO)₂M could displace each other in the system involving Co(CO)₃ containing cluster compounds. This phenomenon has been found in cobalt containing clusters capped by the sulfido ligand [8]. It is found that this occurred in carbon and selenium capped metal clusters in this report. Further study found that functional substitution on the cyclopentadienyl ligand could influence the product's yield. Their electron-withdrawing effect can reduce the reactivity of the fragment M(CO)₂(η⁵-C₅H₄R) unit in the metal exchange reaction. This indicated that the fragment M(CO)₂(η⁵-C₅H₅) is more reactive than the fragment M(CO)₂(η⁵-C₅H₄R). Therefore, there are two routes to prepare the cluster [(μ₃-C)R]CoMo₂(CO)₈(η⁵-C₅H₄R')(η⁵-C₅H₅): reaction of [(μ₃-C)R]Co₂Mo(CO)₈(η⁵-C₅H₄R') with [Mo(CO)₃(η⁵-C₅H₅)]⁻, and reaction of [(μ₃-C)R]Co₂Mo(CO)₈(η⁵-C₅H₅) and [Mo(CO)₃(η⁵-C₅H₄R')]⁻. The suitable preparation route should be the latter route as described in Scheme 3.

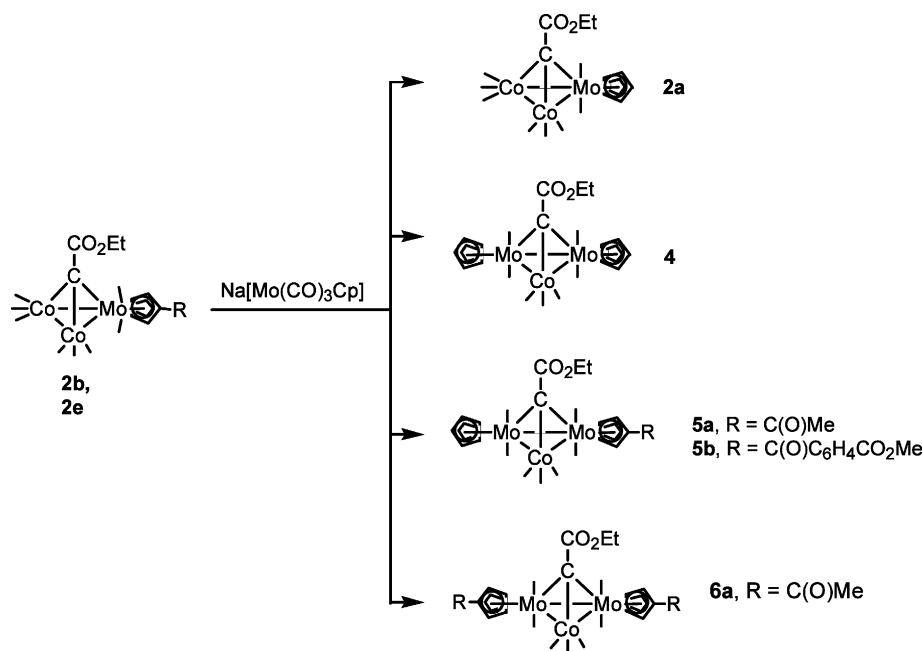
Except of **2a**, **2b**, **2f** and **2e**, the compounds **1a–b**, **2c**, **2d**, **3**, **4**, **5a–b** and **6a** are all new and were fully characterized by elemental analysis, IR and NMR spectroscopies. In their IR spectra, carbonyl absorption bands appear in the range of 2091–1839 cm⁻¹, in good agreement with literature [11,17,20,26,27]. Bridging or semi-bridging carbonyls might also exist due to one or two absorption bands present between 1900 and 1839 cm⁻¹. The IR spectra of **2a–d**, **3**, **5a–b** and **6a** also show one absorption band at ca. 1660 cm⁻¹, which is characteristic of the CO₂Et group attached to the capped carbon atom. The frequency around 1720 cm⁻¹ in IR spectra of **2c** and **2d** is the ester absorption attached to cyclopentadienyl ligand. The absorption bands in the range of 1692–1653 cm⁻¹ in IR spectra of



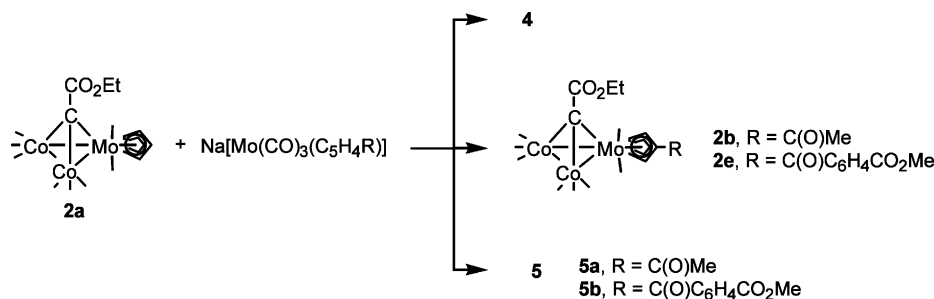
Scheme 1.

1b, **5a**, **6a** and **3** are carbonyl absorption frequencies on the cyclopentadienyl ligand. For the ¹H-NMR assignment of these clusters, the multiplets in the range of δ 5.99–5.06 are assigned to the protons on cyclopentadienyl ring. The ¹H-NMR signals around δ 1.30 and 4.30 in **2a–d**, **4**, **5a–b** and **6a** spectra are the resonances of

ethyl protons on the (μ_3 -C)CO₂Et group. In the ¹H-NMR spectra of **3**, **5a** and **6a**, the singlet at δ 2.30 is due to the acetyl protons attached to cyclopentadienyl ligand. ¹³C-NMR spectra of **3** and **5b** confirmed their structures. The resonances downfield between δ 229.65 and 192.96 are assigned to the carbonyl ligands bound



Scheme 2.



Scheme 3.

to the transition metal atoms. The signals at δ 141.79–128.29 arise from the carbon atoms in the benzene ring. The chemical shifts of cyclopentadienyl carbons are observed in the range of δ 101.41–90.41.

The crystal structures of **2a** and **4** were determined by single-crystal X-ray structure analyses. Selected bond distances and angles are listed in Tables 2 and 3. Figs. 1 and 2 show the molecular structures of **2a** and **4**.

As seen in Fig. 1, cluster **2a** has a tetrahedral skeleton composed of C, Mo and two Co atoms. One CO_2Et group is attached to the capped carbon atom. The Co atom is coordinated by three terminal CO ligands, and the Mo atom is coordinated by two terminal CO ligands and one cyclopentadienyl ligand. Bridging carbon atom to the two Co atoms and one Mo atom with bond lengths $\text{C}(14)\text{--Co}(1) = 1.914(2)$ Å, $\text{C}(14)\text{--Co}(2) = 1.919(3)$ Å and $\text{C}(14)\text{--Mo} = 2.094(3)$ Å, respectively, are in accord with previous literature and our reports [11,16,27]. The bond distance of $\text{C}(14)\text{--C}(15)$ is 1.478(4) Å, slightly shorter than a normal C–C single bond length (1.544 Å). This is because the C(14) atom is capped by three transition metal atoms, which also provide a reasonable explanation for the attached CO_2Et absorption frequency being as low as at 1660 cm^{-1} .

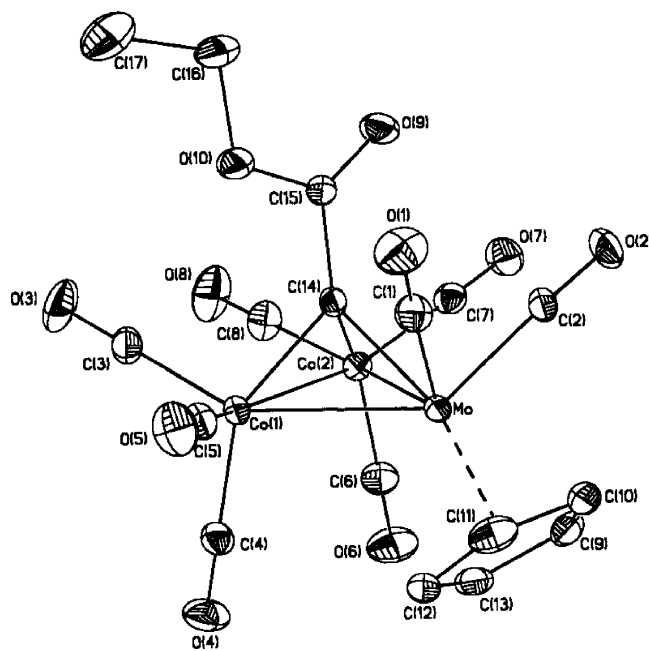
As seen in Fig. 2, cluster **4** also has a tetrahedral skeleton composed of C, two Mo atoms and one Co atom. Selected bond angles and lengths of the tetrahedra are approximately the same as those in the literature

Table 2
Selected bond lengths (Å) and angles ($^\circ$) for cluster **2a**

Bond lengths			
Mo–C(14)	2.094(3)	Co(1)–Co(2)	2.4952(9)
Mo–Co(1)	2.6635(9)	Co(2)–C(14)	1.919(3)
Mo–Co(2)	2.7158(11)	C(14)–C(15)	1.478(4)
Bond angles			
Co(1)–C(14)	1.914(2)		
C(14)–Mo–Co(1)	45.51(7)	C(14)–Co(2)–Co(1)	49.29(7)
C(14)–Mo–Co(2)	44.73(7)	C(14)–Co(2)–Mo	50.20(8)
Co(1)–Mo–Co(2)	55.26(3)	Co(1)–C(14)–Co(2)	81.25(10)
C(14)–Co(1)–Co(2)	49.46(8)	Co(1)–C(14)–Mo	83.16(9)
C(14)–Co(1)–Mo	51.33(8)	Co(2)–C(14)–Mo	85.06(10)
Co(2)–Co(1)–Mo	63.43(3)	Co(1)–Co(2)–Mo	61.30(3)

Table 3
Selected bond lengths (Å) and angles ($^\circ$) for cluster **4**

Bond lengths			
Mo(1)–C(8)	2.098(3)	Mo(2)–Co	2.7207(10)
Mo(1)–Co	2.7248(9)	Co–C(8)	1.936(3)
Mo(1)–Mo(2)	2.9572(9)	C(8)–C(9)	1.477(5)
Mo(2)–C(8)	2.097(4)		
Bond angles			
C(8)–Mo(1)–Co	45.05(10)	C(8)–Co–Mo(2)	50.12(11)
C(8)–Mo(1)–Mo(2)	45.15(10)	Mo(2)–Co–Mo(1)	65.78(3)
Co–Mo(1)–Mo(2)	57.04(3)	Co–C(8)–Mo(2)	84.75(14)
C(8)–Mo(2)–Co	45.13(10)	Co–C(8)–Mo(1)	84.88(13)
C(8)–Mo(2)–Mo(1)	45.19(9)	Mo(2)–C(8)–Mo(1)	89.66(13)
Co–Mo(2)–Mo(1)	57.18(2)		

Fig. 1. Molecular structure of compound **2a**.

[11,16,27]. The bridging carbon atom is bonded to the Co and Mo atoms with bond lengths are $\text{C}(8)\text{--Co} = 1.936(3)$ Å, $\text{C}(8)\text{--Mo}(1) = 2.098(3)$ Å and $\text{C}(8)\text{--Mo}(2) = 2.097(4)$ Å. The acute angles in the tetrahedra about the basal metal atoms range from $57.04(3)$ to $65.78(3)^\circ$ and those of the carbon atom average 86.43° , a slightly deviation from a perfect tetrahedral geometry.

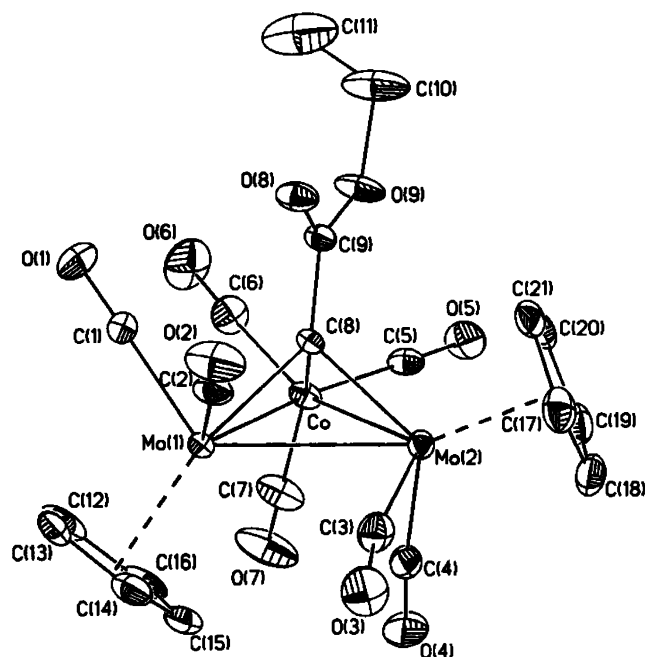


Fig. 2. Molecular structure of compound 4.

4. Supplementary material

Crystallographic data for the structure analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 201060 for cluster **2a** and No. 201061 for cluster **4**. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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- Cluster **1b**: $\{[(\mu_3\text{-C})\text{C}_6\text{H}_5]\text{Co}_2\text{Mo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})]\}_2\text{-C}_6\text{H}_4\text{-}p$, IR (νCO) 2085(s), 2076(s), 2050(vs), 2038(vs), 2022(vs), 1992(vs), 1983(vs), 1963(s), 1921(s), 1881(s) cm^{-1} ; ($\nu\text{C=O}$)1653(m) cm^{-1} . $^1\text{H-NMR}$: δ 7.70 (s, 4H, C_6H_4), 7.14 (s, 10H, $2\text{C}_6\text{H}_5$), 5.76–5.22 (d, 8H, $2\text{C}_5\text{H}_4$). Anal. Calc. For $\text{C}_{24}\text{H}_{11}\text{O}_9\text{Co}_2\text{Mo}$: C, 43.87; H, 1.69. Found: C, 43.86; H, 1.72.