

Studies of metal exchange reactions: the synthesis and structures of heteronuclear metal clusters containing the indenyl ligand (μ_3 -CR) $\text{Co}_2\text{M}(\text{CO})_8(\eta^5\text{-Ind})(\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5, \text{COOC}_2\text{H}_5; \text{M} = \text{Mo}, \text{W})$

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Abstract

The novel tetrahedral clusters (μ_3 -CR) $\text{Co}_2\text{M}(\text{CO})_8(\eta^5\text{-Ind})$ ($\text{M} = \text{Mo}, \text{W}; \text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5, \text{COOC}_2\text{H}_5$) **5–12** containing the indenyl ligand were isolated from reactions of tricobalt clusters (μ_3 -CR) $\text{Co}_3(\text{CO})_9$ ($\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5, \text{COOC}_2\text{H}_5$) and $\text{K}(\eta^5\text{-Ind})\text{M}(\text{CO})_3$ ($\text{M} = \text{Mo}, \text{W}$) under mild conditions. The cluster complex ($\mu_3\text{-CC}_6\text{H}_5$) $\text{CoMo}_2(\text{CO})_7(\eta^5\text{-Ind})(\eta^5\text{-Cp}^*)$ ($\text{Cp}^* = \text{C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3$) **16** was obtained via the stepwise metal exchange reaction of complex ($\mu_3\text{-CC}_6\text{H}_5$) $\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-Ind})$ **9** with $\text{Na}(\eta^5\text{-Cp}^*)\text{Mo}(\text{CO})_3$, but the reaction of ($\mu_3\text{-CC}_6\text{H}_5$) $\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-Cp}^*)$ **15** with $\text{K}(\eta^5\text{-Ind})\text{Mo}(\text{CO})_3$ yielded only **9**. The crystal structures of compounds **7**, **9** and **13** were established by single crystal X-ray diffraction methods and show structural evidence for “slippage” of the indenyl ring.

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1. Introduction

Applications of cluster complexes in catalysis has stimulated great interest in the preparation and properties of heteronuclear clusters [1–5]. We are interested in cluster complexes containing a chiral tetrahedral skeleton because evidence for asymmetric induction by cluster-catalyzed reactions would provide definitively the proof that the clusters do not fragment during catalysis [4]. Following the pioneering methods of Vahrenkamp [6] and Stone [7], the metal exchange reaction is now the relatively straightforward method for preparing chiral clusters containing a tetrahedral skeleton. The alkylidyne clusters $\text{Co}_2\text{M}(\mu_3\text{-CR})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) synthesized by metal exchange reactions with (μ_3 -CR) $\text{Co}_3(\text{CO})_9$ by using various neutral or anionic exchange reagents such as, $\text{Me}_2\text{AsM}(\text{CO})_3\text{Cp}$ [8–12], $[\text{M}(\text{CO})_3\text{Cp}]_2$

[13], $\text{ClM}(\text{CO})_3\text{Cp}$ [14,15] and $\text{NaCpM}(\text{CO})_3$ [6–18] ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) are excellent precursors for chiral tetrahedral-type cluster complexes. However, complexes containing the indenyl ligand (Ind), in place of the cyclopentadienyl (Cp) ligand, have rarely been introduced into the tetrahedral skeleton by the metal exchange reaction to date [19].

It is well established that the reactivity of the complexes containing the cyclopentadienyl ligand can be modified by the use of ‘substituted Cp ligands’ by using R groups with different steric and electronic properties. In this respect, the indenyl ligand ($\text{Ind} = \text{C}_9\text{H}_7$) provides a most interesting opportunity because Rerek and Basolo [20] showed that it can accelerate some substitution reactions by a factor up to 10^8 relative to the analogous complexes containing cyclopentadienyl ligand. This so called ‘indenyl effect’ [21–24] suggested to us the possibility of enhancing the reactivity of metal cluster complexes by introducing indenyl ligands into them. In order to explore the generality of the synthesis of

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complexes containing a indenyl ligand by metal exchange, we recently initiated a study based on the reactions of cluster complexes $(\mu_3\text{-CR})\text{Co}_3(\text{CO})_9$ (**1**, R = H; **2**, R = CH₃; **3**, R = C₆H₅; **4**, R = COOC₂H₅) with $\text{K}(\eta^5\text{-Ind})\text{M}(\text{CO})_3$ (M = Mo, W). Herein, we report the results obtained from this study, namely the synthesis and characterization of the alkylidyne Co_2M (M = Mo, W) cluster complexes containing indenyl ligand $(\mu_3\text{-CR})\text{Co}_2\text{M}(\text{CO})_8(\eta^5\text{-Ind})$ (**5–12**, M = Mo, W; R = H, CH₃, C₆H₅, COOC₂H₅), $(\mu_3\text{-CC}_6\text{H}_5)\text{CoMo}_2(\text{CO})_7(\eta^5\text{-Ind})(\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3)$ **16**, including the crystal structures of the compounds **7**, **9** and **13** determined by X-ray diffraction analysis.

2. Experimental

2.1. General information

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 were performed on 160/200 mesh silica gel. Infrared spectra were recorded as pressed KBr disks on a Nicolet FTIR 10 DX spectrometer. ¹H NMR spectra were recorded on a Bruker AM-400 MHz spectrometer in CDCl₃-deuterated solvent at ambient temperature. Chemical shifts are given in relative to SiMe₄ (0.0 ppm). Elemental analyses were performed on an 1106-type analyzer. The compounds $(\mu_3\text{-CR})\text{Co}_3(\text{CO})_9$ (**1**, R = H; **2**, R = CH₃; **3**, R = C₆H₅; **4**, R = COOC₂H₅) [25], $(\mu_3\text{-CC}_6\text{H}_5)\text{Co}_2\text{Mo}(\text{CO})_8[\eta^5\text{-CpC}(\text{O})\text{CH}_3]$ [26], $\text{Na}[\text{CpC}(\text{O})\text{CH}_3]$ [27], were prepared according to literature methods.

2.2. Synthesis of complexes **1** and **2**

Indene (1.2 mL, 10 mmol) was added dropwise by syringe to a sample of the potassium sand (390 mg, 10 mmol) dispersed in DME (1,2-dimethoxyethane) (20 mL). The mixture was stirred at 0 °C for 0.5 h, and turned to bright-yellow during this time. After stirring for an additional 0.5 h $\text{M}(\text{CO})_6$ (10 mmol) (M = Mo or W) was added while warming to room temperature. This mixture was then refluxed under nitrogen for 12 h. A red solution containing $\text{K}(\eta^5\text{-Ind})\text{M}(\text{CO})_3$ (0.5 mol/mL) (M = Mo, W) was obtained and placed in cold storage for future use.

2.3. Synthesis of $(\mu_3\text{-CH})\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-Ind})$ (cluster **5**)

$\text{K}(\eta^5\text{-Ind})\text{Mo}(\text{CO})_3$ (2 mL, 1 mmol) in a DME solution was added by syringe to a sample of $(\mu_3\text{-CH})\text{Co}_3(\text{CO})_9$ (440 mg, 1 mmol) dissolved in THF (20 mL). The resulting mixture was stirred for 15 min and the solvent was then removed in vacuo. The residue was

separated by column chromatography on silica gel. After a small brown band was eluted with petroleum ether, petroleum ether/CH₂Cl₂ (3:1) afforded the main light green band and a trace of red band. After concentrating the solvent and crystallization from CH₂Cl₂–hexane at –20 °C, the cluster **5** (170 mg, 31% based on cluster **1**) was obtained as black crystals with a byproduct $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_3]_2$ as dark brown solid.

For **5**. *Anal.* Found: C, 38.18; H, 1.45. Calc. for C₂₄H₁₂O₈Co₂Mo: C, 38.04; H, 1.42%. IR: $\nu(\text{CO})$ 2077–1986 s, 1928 s, 1887 s cm⁻¹; (C₉H₇) 829 m, 749 m cm⁻¹. ¹H NMR: δ 5.61 (s, 1H, C₉H₇), 6.01 (s, 2H, C₉H₇), 7.33 (br, 4H, C₉H₇), 9.88 (s, 1H, μH). For **13**. *Anal.* Found: C, 48.25; H, 2.39. Calc. for C₂₄H₁₄O₆Mo₂: C, 48.49; H, 2.38%. IR: $\nu(\text{CO})$ 2020 w, 1957 s, 1910 s cm⁻¹. ¹H NMR: δ 4.30 (s, 2H, C₉H₇), 4.65 (s, 4H, C₉H₇), 6.58, 7.32 (m, 8H, C₉H₇).

Compounds **6–12** were prepared similarly.

For $(\mu_3\text{-CH})\text{Co}_2\text{W}(\text{CO})_8(\eta^5\text{-Ind})$ (**6**): A black solid (150 mg, 24%) and complex **14** as a brown solid. For **6**: *Anal.* found: C, 33.21; H, 1.18. Calc. for C₁₈H₈O₈Co₂W: C, 33.04; H, 1.23%. IR: $\nu(\text{CO})$ 2079–1985 s, 1921 s, 1876 s cm⁻¹, (C₉H₇) 835 m, 750 s cm⁻¹. ¹H NMR: δ : 5.61 (s, 1H, C₉H₇), 6.02 (s, 2H, C₉H₇), 7.33 (br, 4H, C₉H₇), 10.41 (s, 1H, μH). For **14**. *Anal.* found: C, 37.45; H, 1.81; Calc. for C₂₄H₁₄O₆W₂: C, 37.60; H, 1.84%. IR: $\nu(\text{CO})$ 2018 w, 1955 s, 1905 s cm⁻¹. ¹H NMR: δ 5.39 (s, 2H, C₉H₇), 5.73 (s, 4H, C₉H₇), 7.05, 7.46 (m, 8H, C₉H₇).

For $(\mu_3\text{-CCH}_3)\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-Ind})$ (**7**): A black solid (470 mg, 82%); *Anal.* found: C, 39.01; H, 1.65. Calc. for C₁₉H₁₀O₈Co₂Mo: C, 39.19; H, 1.73%. IR: $\nu(\text{CO})$ 2060–1999 s, 1975 s, 1931 s cm⁻¹; (C₉H₇) 825 m, 749 s cm⁻¹. ¹H NMR: δ 3.60 (s, 3H, CH₃), 5.35 (s, 1H, C₉H₇), 5.81 (s, 2H, C₉H₇), 7.20, 7.52 (br, 4H, C₉H₇).

For $(\mu_3\text{-CCH}_3)\text{Co}_2\text{W}(\text{CO})_8(\eta^5\text{-Ind})$ (**8**): A black solid (480 mg, 73%); *Anal.* found: C, 33.95; H, 1.47. Calc. for C₁₉H₁₀O₈Co₂W: C, 34.14; H, 1.51%. IR: $\nu(\text{CO})$ 2060–2001 s, 1975 s, 1930 s cm⁻¹; (C₉H₇) 831 m, 750 s cm⁻¹. ¹H NMR: δ 3.67 (s, 3H, CH₃), 5.36 (s, 1H, C₉H₇), 5.89 (s, 2H, C₉H₇), 7.18, 7.49 (br, 4H, C₉H₇).

For $(\mu_3\text{-CC}_6\text{H}_5)\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-Ind})$ (**9**): Black crystals (450 mg, 70%). *Anal.* Found: C, 44.90; H, 1.93. Calc. for C₂₄H₁₂O₈Co₂Mo: C, 44.73; H, 1.88%. IR: $\nu(\text{CO})$ 2078–2005 s, 1921 s, 1873 s cm⁻¹; (C₉H₇) 817 m, 750 s cm⁻¹. ¹H NMR: δ 5.50 (s, 2H, C₉H₇), 5.63 (s, 1H, C₉H₇), 6.93, 7.19 (br, 5H, C₆H₅), 7.18, 7.31 (br, 4H, C₉H₇).

For $(\mu_3\text{-CC}_6\text{H}_5)\text{Co}_2\text{W}(\text{CO})_8(\eta^5\text{-Ind})$ (**10**): A black solid (0.540 mg, 75%); *Anal.* found: C, 39.23; H, 1.60. Calc. for C₂₄H₁₂O₈Co₂W: C, 39.46; H, 1.66%. IR: $\nu(\text{CO})$ 2078–2005 s, 1921 s, 1873 s cm⁻¹; (C₉H₇) 817 m, 750 s cm⁻¹. ¹H NMR: δ 5.48 (s, 2H, C₉H₇), 5.70 (s, 1H, C₉H₇), 6.88, 7.07 (br, 5H, C₆H₅), 7.17, 7.29 (br, 4H, C₉H₇).

For $(\mu_3\text{-CCOOC}_2\text{H}_5)\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-Ind})$ (**11**): A black solid (300 mg, 46%); *Anal.* found: C, 39.15; H, 1.84. Calc. for C₂₁H₁₂O₁₀Co₂Mo: C, 39.39; H, 1.89%.

IR: $\nu(\text{CO})$ 2081–2003 s, 1921 s, 1873 s cm^{-1} ; $\nu(\text{C}=\text{O})$ 1674 s cm^{-1} ; (C_9H_7) 823 m, 752 m cm^{-1} . $^1\text{H NMR}$: δ 1.39 (s, 3H, CH_3), 4.38 (s, 2H, CH_2), 5.63 (s, 1H, C_9H_7), 5.84 (s, 2H, C_9H_7), 7.18, 7.49 (br, 4H, C_9H_7).

For $(\mu_3\text{-CCOOC}_2\text{H}_5)\text{Co}_2\text{W}(\text{CO})_8(\eta^5\text{-Ind})$ (**12**): A black solid (370 mg, 51%); *Anal.* found: C, 34.52; H, 1.68. Calc. for $\text{C}_{21}\text{H}_{12}\text{O}_{10}\text{Co}_2\text{W}$: C, 34.72; H, 1.67%. IR: $\nu(\text{CO})$ 2081–2001 s, 1925 s, 1880 s cm^{-1} ; $\nu(\text{C}=\text{O})$ 1656 s cm^{-1} ; (C_9H_7) 840 m, 754 m cm^{-1} . $^1\text{H NMR}$: δ 1.36 (s, 3H, CH_3), 4.35 (s, 2H, CH_2), 5.74 (br, 1H, C_9H_7), 5.91 (s, 2H, C_9H_7), 7.18, 7.49 (br, 4H, C_9H_7).

2.4. Metal exchange reactions of $(\mu_3\text{-CC}_6\text{H}_5)\text{Co}_3(\text{CO})_9$ using $\text{K}(\eta^5\text{-Ind})\text{Mo}(\text{CO})_3$, $\text{Na}(\eta^5\text{-Cp})\text{Mo}(\text{CO})_3$ and $\text{Na}(\eta^5\text{-CpMo}(\text{CO})_3(\text{Cp}^* = \text{C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3))$

The metal exchange reagent was synthesized by using appropriate amounts of NaCp, $\text{Na}[\text{C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3]$, KInd, with $\text{Mo}(\text{CO})_6$ (in order to realize a 0.5 mmol/mL DME solution) with refluxing overnight, respectively. To a 10 mL THF solution of $(\mu_3\text{-CC}_6\text{H}_5)\text{Co}_3(\text{CO})_9$ **3** (260 mg, 0.5 mmol), was added a solution containing the metal exchange reagent (1 mL, 0.5 mmol) by syringe. The mixture was stirred under room temperature and reaction progress was monitored by TLC.

2.5. Synthesis of $(\mu_3\text{-C}_6\text{H}_5)\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-Ind})$ (cluster **9**) (pathway 1)

To a sample of $(\mu_3\text{-CC}_6\text{H}_5)\text{Co}_2\text{Mo}(\text{CO})_8[\eta^5\text{-CpC}(\text{O})\text{CH}_3]$ (**15**) (310 mg, 0.5 mmol) dissolved in THF (20 mL), was added a DME solution containing $\text{K}(\eta^5\text{-Ind})\text{Mo}(\text{CO})_3$ (1 mL, 0.5 mol) by syringe. The reaction was monitored by TLC. The reaction mixture was stirred for 2 h at reflux. The solvent was then removed in vacuo, and the residue was separated by column chromatography on silica gel. Chromatographic workup (petroleum ether/ether/ $\text{CH}_2\text{Cl}_2 = 4:1:1$) gave two green and one red fractions. The complexes obtained from the two green fractions were identified as the starting material **15** and complex **9** $(\mu_3\text{-CC}_6\text{H}_5)\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-Ind})$. Complex **9** was recrystallized from hexane/ CH_2Cl_2 at -20°C to give a black crystalline product (150 mg, 47%). Cluster **15**. *Anal.* found: C, 41.63; H, 1.691. Calc. for $\text{C}_{30}\text{H}_{19}\text{O}_8\text{CoMo}_2$: C, 41.64; H 1.89%. IR: $\nu(\text{CO})$ 2069 s, 2019 s, 2008 s, 1992 s, 1973 s cm^{-1} ; $\nu(\text{C}=\text{O})$ 1685 s cm^{-1} . $^1\text{H NMR}$: δ 2.30 (s, 3H, $\text{C}(\text{O})\text{CH}_3$), 5.17, 5.76 (d, 4H, C_5H_4), 7.16–7.26 (m, 5H, C_6H_5).

2.6. $(\mu_3\text{-CC}_6\text{H}_5)\text{CoMo}_2(\text{CO})_7(\eta^5\text{-Ind})[\eta^5\text{-CpC}(\text{O})\text{CH}_3]$ (**16**) (pathway 2)

$\text{Mo}(\text{CO})_6$ (160 mg, 0.6 mmol) was added to a solution of $\text{Na}[\text{CpC}(\text{O})\text{CH}_3]$ (80 mg, 0.6 mmol) in THF (20 mL). The mixture was heated to reflux for 12 h and then cooled to room temperature. Cluster **9** $(\mu_3\text{-$

$\text{CC}_6\text{H}_5)\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-Ind})$ (320 mg, 0.5 mmol) was then added and to the mixture and stirred for an additional 4 h at 60°C . The solvent was removed under vacuum. The chromatographic workup (petroleum ether/ CH_2Cl_2 /ether = 4:1:1) gave two green fractions. The complexes obtained from the two green fractions were identified as starting material cluster **9** and product **16**. Compound **16** was recrystallized from hexane/benzene at -20°C to give a black crystalline product (120 mg, 33%). *Anal.* found: C, 47.39; H, 2.48. Calc. for $\text{C}_{30}\text{H}_{19}\text{O}_8\text{CoMo}_2$: C, 47.25; H, 2.51%. IR: $\nu(\text{CO})$ 2084 s, 2031 s, 1998 s, 1923 s, 1874 s cm^{-1} ; $\nu(\text{C}=\text{O})$ 1684 s cm^{-1} ; (C_9H_7) 804 m, 749 w cm^{-1} . $^1\text{H NMR}$: δ 2.35 (s, 3H, $\text{C}(\text{O})\text{CH}_3$), 5.64, 5.51, 5.30 (s, 3H, C_9H_7), 5.15, 5.78 (br, 4H, C_5H_4), 6.90, 7.22 (br, 5H, C_6H_5), 7.16, 7.35 (br, 4H, C_9H_7).

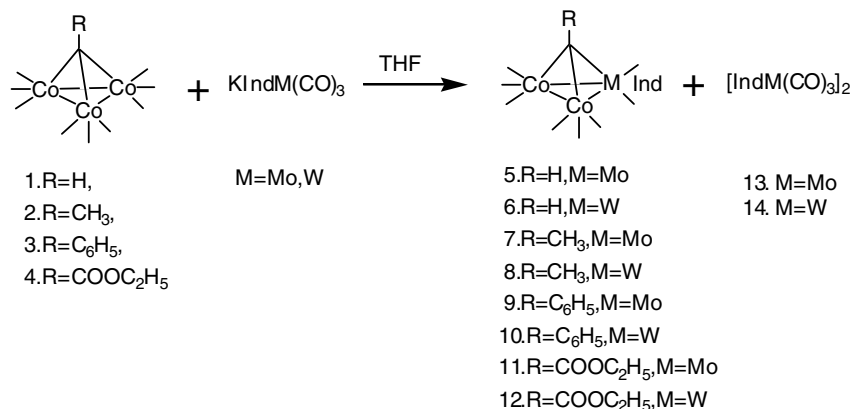
2.7. Crystallographic analyses

Crystals of **7**, **9**, **13** were grown by diffusion of a CH_2Cl_2 solution of the compounds into pentane at -20°C . The data crystals were mounted on glass fibers. Preliminary examination and data collection were performed with Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation on a CCD area detector equipped with graphite monochromator. Data were collected by the ω/ϕ scan technique. Absorption corrections were applied by using SADABS. The structures were solved by direct method using the SHELXS 97 program and refined by the full-matrix least-squares on F^2 by using the SHELXS 97 program. The non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated by using idealized geometries. The geometrical aspects of the structures were analyzed by using the PLATON program [28].

3. Results and discussion

3.1. Synthesis and characterization of **5–12** and **16**

All of the reactions are summarized in Scheme 1. The cluster complexes **5–12** were obtained by the displacement of a $\text{Co}(\text{CO})_3$ ($d^9\text{ML}_3$) vertex by using the isolobal fragments $(\eta^5\text{-Ind})\text{M}(\text{CO})_2$ ($\text{M} = \text{Mo}, \text{W}$) ($d^5\text{ML}_5$). The reactions of $\text{K}(\eta^5\text{-Ind})\text{M}(\text{CO})_3$ ($\text{M} = \text{Mo}, \text{W}$) with the alkylidyne tricobalt clusters **1–4** proceed at the room temperature in moderate yields 50–80%. The byproducts $[(\eta^5\text{-Ind})\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{13}, \text{Mo}; \text{14}, \text{W}$) were also fully characterized. It is found that the substitution at the apical carbon plays an important role on the metal exchange reaction process. When it is a methyl or phenyl group that is inert to the basicity of $\text{K}(\eta^5\text{-Ind})\text{M}(\text{CO})_3$ ($\text{M} = \text{Mo}, \text{W}$), then the reaction follows a simple route and the products are the corresponding clusters **7–10** and the red by-product $[(\eta^5\text{-Ind})\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$) in order of elution in the chromatographic separation. If

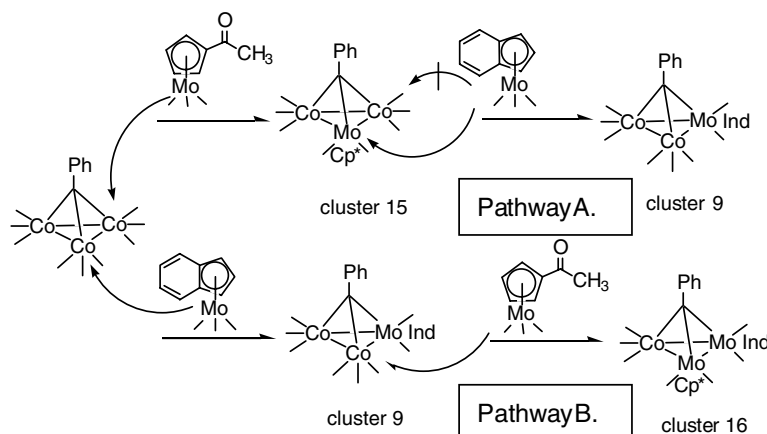


Scheme 1.

the substitution is an ester group, the products including the by-product are complicated and include the target clusters **11** and **12** and two unidentified deep green bands in trace amounts. Similarly, the products from the reaction involving $\text{ClCCO}_3(\text{CO})_9$ are too complicated to isolate. It is worth to pointing out that if the substituent is a ferrocenyl group, the tricobalt cluster $(\mu_3\text{-CFC})\text{Co}_3(\text{CO})_9$ decomposes quickly at room temperature. Generally, the replacement of a cyclopentadienyl ligand with indenyl ligand will enhance the reactivity of the complex [21–24]. In order to investigate the reactivity of indenyl metal exchange reagents, the reagents for the indenyl exchange reactions were compared with those obtained from the metal exchange reaction of $\text{Na}(\text{CpMo}(\text{CO})_3)$ ($\text{Cp}^* = \text{C}_5\text{H}_5$ or $\text{C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3$) with the tricobalt cluster **3** ($\mu_3\text{-CC}_6\text{H}_5$) $\text{Co}_3(\text{CO})_9$. We compared the reactivity of $\text{K}(\eta^5\text{-Ind})\text{Mo}(\text{CO})_3$, $\text{Na}(\eta^5\text{-Cp})\text{Mo}(\text{CO})_3$ and $\text{Na}[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3]\text{Mo}(\text{CO})_3$ toward tricobalt cluster **3** in THF at room temperature. The metal exchange reaction, monitored by the disappearance of the tricobalt cluster and the formation of heteronuclear cluster by TLC, was found require 10–15 min for the $\text{K}(\eta^5\text{-Ind})\text{Mo}(\text{CO})_3$, 20–25 min for $\text{Na}(\eta^5\text{-Cp})\text{Mo}(\text{CO})_3$ and no reaction was observed for

$\text{Na}[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3]\text{Mo}(\text{CO})_3$ even after stirring for 15 h. Therefore, the metal exchange reactivity of three reagents decreases in order of $\text{K}(\eta^5\text{-Ind})\text{Mo}(\text{CO})_3 \approx \text{Na}(\eta^5\text{-Cp})\text{Mo}(\text{CO})_3 > \text{Na}[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3]\text{Mo}(\text{CO})_3$.

In order to investigate the stepwise metal exchange reaction, we performed the two reactions: (1) reaction of the cluster complex **15** with $\text{K}(\eta^5\text{-Ind})\text{Mo}(\text{CO})_3$, and (2) reaction of cluster complex **9** with $\text{Na}[\eta^5\text{-CpC}(\text{O})\text{CH}_3]\text{Mo}(\text{CO})_3$, see Scheme 2. In principle, the target complex, **16** ($\mu_3\text{-CC}_6\text{H}_5$) $\text{CoMo}_2(\text{CO})_7(\eta^5\text{-Ind})[\eta^5\text{-CpC}(\text{O})\text{CH}_3]$ could be obtained by following both pathways A and B in Scheme 2. Interestingly, in the pathway A, the $(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2$ ($d^5\text{ML}_5$) unit displaces the isolobal unit $[\eta^5\text{-CpC}(\text{O})\text{CH}_3]\text{Mo}(\text{CO})_2$ ($d^5\text{ML}_5$) instead of $\text{Co}(\text{CO})_3$ ($d^9\text{ML}_3$, a good leaving group in many double exchange reactions) to give the cluster **9**. By pathway B the $\text{Co}(\text{CO})_3$ ($d^9\text{ML}_3$) unit is replaced by the $\text{Mo}(\text{CO})_2[\eta^5\text{-CpC}(\text{O})\text{CH}_3]$ ($d^5\text{ML}_5$) unit, which is consistent with the literature [21]. It is believed that the metal–metal exchange reaction of the tricobalt clusters involves fragmentation–reconstruction, addition–elimination or elimination–addition mechanisms [29]. The leaving ability of $\text{Co}(\text{CO})_3$ unit and the nucleophilicity of the isolobal exchange reagent

Scheme 2. Synthesis of the double exchange product $(\mu_3\text{-CC}_6\text{H}_5)\text{CoMo}_2(\text{CO})_7(\eta^5\text{-Ind})[\eta^5\text{-CpC}(\text{O})\text{CH}_3]$.

is the central feature of these metal–metal exchange reactions [12,30–37].

All the new cluster complexes are green in solution and black in solid state. Elemental analyses, IR and ^1H NMR data for these clusters are consistent with the corresponding structures. All the clusters exhibit a strong infrared absorption band in the range from 2080 to 1850 cm^{-1} , assigned to terminal carbonyl ligands coordinated to metal atoms. The absorptions at 2085–2000 cm^{-1} and 1980–1820 cm^{-1} correspond to the carbonyl ligands on cobalt atoms and M (M = Mo, W) atoms, respectively. These characteristic carbonyl absorption bands indicate the integrity of CCo_2M skeleton. In the IR spectrum of **16**, the different composition of cluster skeleton (CCoMo_2) results in a sharp change in the position of the carbonyl absorption band. The vibrational absorptions of these C=O groups appear in the range 1674–1684 cm^{-1} . Finally, the absorptions of indenyl group were observed at 850 and 710 cm^{-1} , which is in accord with the literature [38].

The ^1H NMR spectra of all complexes show the expected resonances of the hydrogen atoms on their hydrocarbon ligands. The three protons of the C5 ring of the indenyl moiety of **5–12** display as two broad signals in ratio of 2:1 in the range δ 5.50–5.70 ppm. The resonances (A_2B type) of these protons indicate that the indenyl ligand resides in a symmetric environment.

The aromatic protons of indenyl moiety appear as multiplets in the range δ 7.10–7.50 ppm. In addition, for **5** and **6**, the ^1H NMR spectra display one singlet at the range of δ 9.88–10.44 ppm for the proton on central carbon atom. The ^1H NMR spectra of **7** and **8** show a singlet at about δ 3.65 ppm for methyl group. The ^1H NMR spectra of **9** and **10** show multiplets in the range of δ 6.90–7.38 ppm assigned to the C_6H_4 protons. The ^1H NMR spectra of **11** and **12** show broad signals at around δ 1.39 ppm and 4.38 ppm in ratio of 3:2, respectively; assigned to the protons CH_3 and CH_2 groups. For cluster complex **16**, the proton signal of methyl group appears as singlet at δ 2.35 ppm and the protons of substituted cyclopentadienyl ring appears as two broad signals which overlap the signals of C_9H_7 protons in the range of δ 5.30–5.78 ppm. It should be noticed that $\text{AA}'\text{B}$ type singlets of the protons in the five-membered ring reveal that the indenyl ligand is located in an asymmetric environment, due to the chiral tetrahedral skeleton CCoMoIndMoCp^* [19,39].

3.2. The X-ray structure analyses

The complexes $(\mu_3\text{-CR})\text{Co}_2\text{Mo}(\text{CO})_8(\eta^5\text{-Ind})$ (**7**, R = CH_3 and **9**, R = C_6H_5) and $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_3]_2$ **13** have been characterized by single-crystal X-ray diffraction studies. The crystallographic data are collected in

Table 1
Summary of the crystallographic data for compounds **7**, **9** and **13**

Cluster	7	9	13
Empirical formula	$\text{C}_{19}\text{H}_{10}\text{O}_8\text{Co}_2\text{Mo}$	$\text{C}_{24}\text{H}_{12}\text{O}_8\text{Co}_2\text{Mo}$	$\text{C}_{24}\text{H}_{14}\text{O}_6\text{Mo}_2$
Formula weight	580.07	642.14	590.23
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
Unit cell dimensions			
<i>a</i> (Å)	8.7884(6)	8.6335(10)	7.3504(7)
<i>b</i> (Å)	9.4183(7)	10.0038(11)	14.4726(14)
<i>c</i> (Å)	12.4581(9)	27.420(3)	19.9447(19)
α (°)	79.969(1)	90.00	90.00
β (°)	87.485(1)	96.304(2)	90.00
γ (°)	87.019(1)	90.00	90.00
Volume (Å ³)	1013.41(13)	2353.9(5)	2121.7(4)
<i>Z</i>	2	4	4
Density (cal.) (g/cm ³)	1.901	1.812	1.848
μ (Mo K α) (mm ⁻¹)	2.271	1.965	1.222
<i>F</i> (000)	568	1264	1160
θ range for data collection (°)	1.66–28.24	2.17–28.31	2.17–28.31
Limiting indices	$-10 \leq h \leq 11$ $-11 \leq k \leq 12$ $-16 \leq l \leq 14$	$-11 \leq h \leq 10$ $-13 \leq k \leq 13$ $-21 \leq l \leq 35$	$-9 \leq h \leq 9$ $-19 \leq k \leq 12$ $-26 \leq l \leq 26$
Reflections collected/unique	6219/4053 [$R_{\text{int}} = 0.0613$]	13936/5464 [$R_{\text{int}} = 0.1010$]	12826/4929 [$R_{\text{int}} = 0.1084$]
Goodness-of-fit on F^2	0.993	0.913	0.935
Final <i>R</i> indices, R_1	0.0414	0.0451	0.0440
wR_2 [$I > 2\sigma(I)$]	0.1003	0.0976	0.0846
Largest diff. peak and hole (e Å ⁻³)	1.060 and -1.072	0.897 and -0.580	1.128 and -0.603

$$R^1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR^2 = \left[\frac{\sum w|F_o| - |F_c|^2}{\sum wF_o^2} \right]^{1/2}$$

Table 1. Selected bond distances and angles are listed in Tables 2–4. The atomic positional and thermal parameters for the two structures are available in the supplementary material. As can be seen in Figs. 1 and 2, the structures of **7** and **9** both contain tetrahedral CCo₂Mo cluster cores, similar to those found in other carbon bridged compounds such as (μ_3 -CC₆H₅)Co₂Mo(CO)₈ (η^5 -CpR), where R = H, C(O)CH₃, or COOCH₃ [26,31]. Compound **7** has tetrahedral skeleton composed of C, Mo and two Co atoms, a methyl group attached to carbon atom C(9), two carbonyls coordinated to Mo

atom and two sets of three carbonyls attached to two Co atoms. The indenyl ligand is connected to the cluster skeleton through the Mo atom. The carbon atom is bonded to the two cobalt atoms and one molybdenum atom with bond lengths 1.911(4), 1.943(4) and 2.091(4) (Å), respectively. The bond angles Mo–Co–Co (62.65°, 62.13°) in the triangular Co₂Mo base are equal and are larger than the angle Co–Mo–Co (55.20°), making it an isosceles triangle. The average value of the Mo–C distances to the five-membered ring of the indenyl ligand is 2.367 Å.

Table 2
Selected bond distances (Å) and angles (°) for cluster **7**

Mo–C9	2.091(4)	Mo–Ring(Ind)	2.0351(3)
Mo–C13	2.304(5)	Mo–Co1	2.677(1)
Mo–C12	2.309(4)	Mo–Co2	2.690(1)
Mo–C11	2.348(4)	Co1–C9	1.911(4)
Mo–C14	2.424(4)	Co1–Co2	2.487(1)
Mo–C19	2.450(4)	Co2–C9	1.943(4)
Mo–Cg(Ind)	2.0411(18)	Co2–Co1–Mo	62.656(16)
C1–Mo–C2	83.44(15)	C9–Co2–Co1	49.24(10)
C9–Mo–Co1	45.20(10)	C9–Co2–Mo	50.57(10)
C9–Mo–Co2	45.89(9)	Co1–Co2–Mo	62.136(16)
Co1–Mo–Co2	55.208(16)	Co1–C9–Co2	80.36(14)
C9–Co1–Co2	50.40(9)	Co2–C9–Mo	83.54(14)
C9–Co1–Mo	50.94(10)	Co1–C9–Mo	83.84(14)

Table 3
Selected bond distances (Å) and angles (°) for cluster **9**

Mo–C18	2.086(4)	Mo–Ring(Ind)	2.0351(3)
Mo–C11	2.305(7)	Mo–Co1	2.721(1)
Mo–C12	2.309(5)	Mo–Co2	2.725(1)
Mo–C10	2.349(5)	Co1–C18	1.928(4)
Mo–C13	2.399(4)	Co1–Co2	2.502(2)
Mo–C9	2.439(5)	Co2–C18	1.935(3)
Mo–Cg(Ind)	2.0411(18)	Co2–Co1–Mo	62.74(2)
C1–Mo–C2	82.2(2)	C18–Co2–Co1	49.51(10)
C18–Mo–Co1	44.92(9)	C18–Co2–Mo	49.72(9)
C18–Mo–Co2	45.04(9)	Co1–Co2–Mo	62.56(2)
Co1–Mo–Co2	54.69(2)	Co1–C18–Co2	80.73(14)
C18–Co1–Co2	49.76(11)	Co1–C18–Mo	85.25(13)
C18–Co1–Mo	49.83(10)	Co2–C18–Mo	85.24(12)

Table 4
Selected bond distances (Å) and angles (°) for complex **13**

Mo1–C4	2.297(6)	Mo2–C16	2.316(6)
Mo1–C5	2.341(6)	Mo2–C17	2.334(6)
Mo1–C6	2.365(6)	Mo2–C18	2.375(6)
Mo1–C12	2.382(6)	Mo2–C24	2.383(6)
Mo1–C7	2.426(5)	Mo2–C19	2.439(5)
Mo1–Ring(Ind)	2.0280	Mo2–Ring(Ind)	2.0355(4)
Mo1–Mo2	3.2469(6)	C13–Mo2–C15	77.69(24)
C3–Mo1–C2	104.80(23)	C13–Mo2–C14	104.91(24)
C3–Mo1–C1	77.71(24)	C15–Mo2–C14	80.20(26)
C2–Mo1–C1	77.27(25)	C17–C16–C24	106.83(48)
C5–C4–C12	108.83(50)	C16–C17–C18	110.31(50)
C4–C5–C6	107.95(51)	C17–C18–C19	108.07(49)
C5–C6–C7	108.36(50)	C18–C19–C24	107.21(48)
C12–C7–C6	107.57(48)	C19–C24–C16	107.48(44)
C7–C12–C4	107.14(44)		

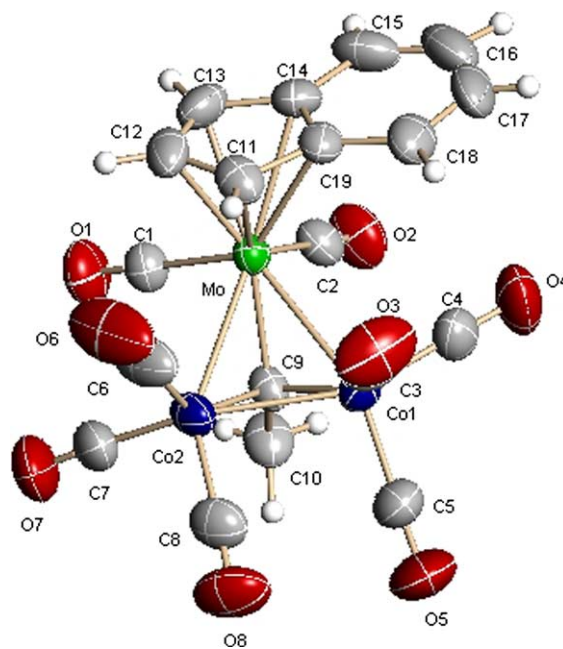


Fig. 1. The molecular structure of **7** showing 50% probability thermal ellipsoids.

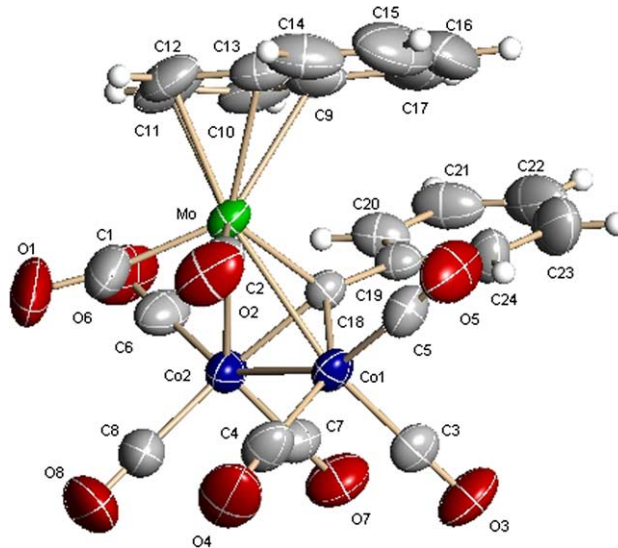


Fig. 2. solid-state molecular structure of **9** showing 50% probability thermal ellipsoids.

Table 5
Slippage parameters of the various indenyl ligands

Entry	Compound	Δ (Å)	σ (°)	Ψ (°)	Ω (°)	Reference
1	7	0.156	57.84	4.38	5.3	This work
2	9	0.144	49.5	4.05	2.6	This work
3	13	0.100	86.9	2.8	3.8	This work
4	[MoCp(Ind)(NCMe)(CO)] [BF ₄] ₂ η ⁵ -Cp	0.065	9.7	1.9	None	[42]
5	[MoCp(Ind)(NCMe)(CO)] [BF ₄] ₂ η ⁵ -Ind	0.194	2.6	5.6	5.1	[42]
6	(η ⁵ -Cp)(η ³ -Ind)Mo(CO) ₂ η ⁵ -Cp	0.120	0.6	3.4	2.1	[42]
7	(η ⁵ -Cp)(η ³ -Ind)Mo(CO) ₂ η ³ -Ind	0.947	6.0	24.1	21.4	[42]
8	[η ⁵ -Ind] ₂ Ni	0.418	13.9	13.9	13.1	[43]
9	[η ⁵ -Ind] ₂ Fe	0.043	2.2	2.2	0.8	[43]

The structure of **9** is similar to **7** except for the substitution on the apical carbon. The apical carbon atom is bonded to two cobalt atoms and one molybdenum atom with bond lengths of 1.928(4), 1.935(3) and 2.086(4) Å. Selected bond distances and angles for the cluster complex (μ₃-CC₆H₅)Co₂Mo(CO)₈(η⁵-Cp) [31] compare favorably with those of cluster **9**. The molecular structures of the compounds of **7** and **9** indicate ring slippage of indenyl ligand. Employing the slip parameters of Faller, Crabtree and Habib [40], the “slip” parameters of the indenyl ligand in **7** and **9** listed in Table 5. Both indenyl ligands in **7** and **9** exhibit “slip-fold” distortion from ideal pentahapto coordination of the Mo(CO)₂ fragment (Table 5, entries **1**, **2**). These variations are typical for indenyl ligand coordinated to transition metals, as comparison with attests of the mixed ring complex (Table 5, entries **4–6**), canonical trihapto (Table 5, entries **7**, **8**) and pentahapto complexes (Table 5, entry **9**). Thus, the indenyl ligands coordinated to the basal Mo atom of the cluster skeleton exhibit the pentahapto coordination.

The molecular structure of **13** is shown in Fig. 3. The structure is similar to that of the Cp homologue, [(η⁵-Cp)Mo(CO)₃]₂, **17** [41]. The metal–metal bond distance in **13**, 3.2469(6) Å is slightly longer than that in **17**, 3.235(1) Å.

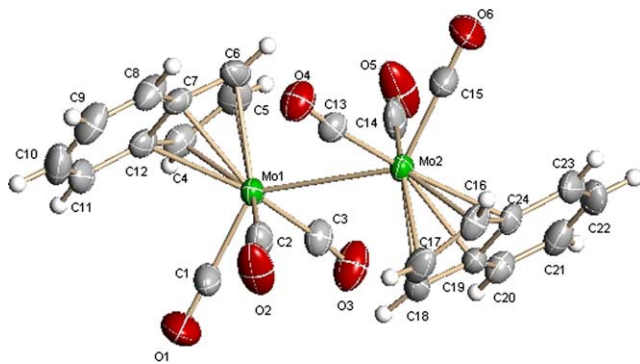


Fig. 3. Solid-state molecular structure of **13** showing 50% probability thermal ellipsoids.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, deposit numbers CCDC 190825, 190818 and 215773. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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