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Synthesis and X-ray crystal structure of the chiral trimetal carbonyl clusters (μ_3-CPh)FeCoMo(CO)$_8$(RCOCp)H (R = H, CH_3 or C_2H_5O) derived from the clusters (μ_3-CPh)Co$_2$Mo(CO)$_8$(RCOCp)

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Abstract

Three μ_3-phenylmethylidyne trimetal carbonyl clusters (μ_3-CPh)Co$_2$Mo(CO)$_8$(RCOCp) (**2**, R = H; **3**, R = CH_3; **4**, R = C_2H_5O) have been obtained from the reaction of the precursor (μ_3-CPh)Co$_3$(CO)$_9$ with the metal exchange reagents NaM(CO)$_3$(RCOCp) in THF under reflux. Reaction of (μ_3-CPh)CO$_2$Mo (CO)$_8$(RCOCp) clusters with Na$_2$[Fe(CO)$_4$] in THF under reflux followed by acidic treatment with 40% H_3PO_4 yielded three new chiral clusters (μ_3-CPh)FeCoMo(CO)$_8$(RCOCp)H (**5**, R = H; **6**, CH_3; **7**, C_2H_5O). Experimental results indicate that the electron-withdrawing groups RCO on cyclopentadienyl reduce the activity of the metal exchange reagents NaMo(CO)$_3$(RCOCp) and that the rate of the above reaction increases with increasing temperature. Cobalt carbonyl units Co(CO)$_3$ in the clusters PhCCo$_3$(CO)$_9$ and PhCCo$_2$Mo(CO)$_8$(RCOCp) may be exchanged by organometallic fragments Mo(CO)$_2$(RCOCp) and Fe(CO)$_3$, respectively. Clusters **5**–**7** were characterized by C/H analysis and IR and ^{1}H NMR spectroscopies and the crystal structures of **4** and **7** were determined. Cluster **4** is monoclinic with space group $P2_1/c$, $a = 11.356(2)$ Å, $b = 14.030(2)$ Å, $c = 16.076(3)$ Å, $\beta = 107.19(1)°$, $V = 2446.8(7)$ Å^3 and $Z = 4$; final $R = 0.048$ and $Rw = 0.057$ for 4751 reflections. Cluster **7** is monoclinic with space group $P2_1/c$, $a = 12.167(5)$ Å, $b = 14.032(7)$ Å, $c = 15.159(7)$ Å, $\beta = 105.21(3)°$, $V = 2497(2)$ Å^3 and $Z = 4$; final $R = 0.0468$ and $Rw = 0.0410$ for 3959 reflections.

Keywords: Carbonyl; Chirality; Cluster; Cyclopentadienyl; Transition metal; XRD crystal analysis

1. Introduction

Chiral tetrahedral clusters in which each of the four vertices is chemically different may be prepared by the exchange of the metal fragment in homonuclear and heteronuclear clusters [1–3]. Single pure antiomers of such clusters are useful as models for asymmetric catalysis.

A single antiomer of the chiral cluster was obtained by coordinating on optically active phosphide ligand the Fe atom of the chiral cluster [4]. It has been shown that such optically active clusters can undergo racemization by an opening-inversion-closing sequence under CO [5]. In order to avoid the risk of racemization resulting from action of CO on the cluster skeleton, we thought it preferable to introduce the optically active group into cyclopentadienyl ligand (such as R* OCOCp) followed by removal of R* O by hydrolysis.

Synthesis of the clusters PhCCo$_2$Mo(CO)$_8$Cp and PhCFeCoMo(CO)$_8$CpH through the exchange reaction of the metal carbonyl reagents NaMo(CO)$_3$Cp and Na$_2$[Fe(CO)$_4$] with PhCCo$_3$(CO)$_9$ and PhCCo$_2$-Mo(CO)$_8$Cp respectively has been reported by Blumhofer and Vahrenkamp [6], but their derivatives containing functionally substituted cyclopentadienyl and the X-ray crystal structural analysis of the tetrahedral chiral cluster core composed of C, Co, Fe and Mo have not been reported up to now. In this paper, we report the synthesis of three clusters PhCCo$_2$Mo(CO)$_8$(RCOCp)

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and three chiral clusters PhCCoFeMo(CO)$_8$(RCOCp)H (R = H, CH$_3$ or C$_2$H$_5$O) along with the crystal structures of the clusters PhCCo$_2$Mo(CO)$_8$(C$_2$H$_5$O$_2$CCp) and PhCCoFeMo(CO)$_8$(C$_2$H$_5$O$_2$CCp)H as revealed by X-ray crystallography.

2. Experimental details

2.1. General procedure and materials

All operations were carried out under pure dinitrogen using standard Schlenk and vacuum techniques. Hexane, benzene and tetrahydrofuran (THF) were predried over sodium wire and distilled from sodium–benzophenone under dinitrogen. NaMo(CO)$_3$(RCOCp) and PhCCo$_3$(CO)$_9$ were prepared according to literature procedures [7,8]. Column chromatography was carried out using 160–200 mesh silica gel.

IR spectra were recorded on a Nicolet FT–IR 10 DX spectrophotometer; ^{1}H NMR spectra were recorded on Bruker AM-400 MHz spectrometer; C/H analyses were performed on a 1106-type analyzer.

2.2. Preparation of the clusters PhCCo$_2$Mo(CO)$_8$(RCOCp)(R = H (2), CH$_3$ (3) or C$_2$H$_5$O (4))

Mo(CO)$_6$ (0.34 g, 1.3 mmol) was added to a solution of 0.17 g (1.5 mmol) sodium formylcyclopentadienide NaCp(COH) in THF (20 ml). The mixture was heated under reflux for 16 h and cooled to room temperature. Then 0.25 g (1.0 mmol) PhCCo$_3$(CO)$_9$ (**1**) was added and the mixture was stirred for 6 h at 60°C. The solvent was removed under vacuum. The residue was chromatographed on a 20 × 2.5 cm silica gel column. Chromatographic workup (eluant benzene:hexane 1 : 1) gave two green and one red–purple fraction. The complexes obtained from the two green fractions were identified as the unfunctionalized PhCCo$_2$Mo(CO)$_8$Cp and a derivative **2**. The red–purple fraction contained the starting cluster **1**. Elution with benzene gave [Mo(CO)$_3$(HCOCp)]$_2$. Cluster **2** was recrystallized from hexane/benzene at −20°C to give a black crystalline product (0.15 g, 25.1%). C$_{21}$H$_{10}$Co$_2$MoO$_9$ Calc.: C, 40.65; H, 1.61%. Anal. Found: C, 40.53; H, 1.56%. IR (KBr disk): ν(CO) (C=O) 1689.8m, ν(CO) (terminal CO) 2071.7s, 2011.9vs, 1994.5s, 1977.2s, 1948.2s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 9.55 (s, 1H, HCO), 5.30, 5.76 (d, 4H, C$_5$H$_4$), 7.17–7.26 (m, 5H, C$_6$H$_5$).

Mo(CO)$_6$ (0.24 g, 0.9 mmol) sodium acetylcyclopentadienide NaCp(COCH$_3$) (0.13 g, 1.0 mmol), PhCCo$_3$(CO)$_9$ (**1**) (0.36 g, 0.7 mmol) and 20 ml of THF were used in preparation of the cluster (**3**). The reaction procedure and operations were the same as for cluster **2** above. Chromatographic separation with (eluant benzene : hexane = 1 : 1), gave a red band and the product **3** as a green band. The red fraction, separated with benzene, gave [Mo(CO)$_3$(CH$_3$COCp)]$_2$ and **1**. The cluster **3** was recrystallized in hexane/benzene at −20°C to give a black crystalline compound in yield 29.6% (0.21 g). C$_{22}$H$_{12}$Co$_2$MoO$_9$ Calc.: C, 41.64; H, 1.89; Anal. Found: C, 41.63; H, 1.691. IR (KBr disk): ν(CO) (C=O) 1685.9m, ν(CO) (terminal CO) 2069.8s, 2019.6vs, 2008.0vs, 1992.6s, 1973.3s cm^{-1}, ^{1}H NMR (CDCl$_3$): δ 2.30 (s, 3H, CH$_3$CO), 5.17, 5.76 (d, 4H, C$_5$H$_4$), 7.16–7.26 (m, 5H, C$_6$H$_5$).

Mo(CO)$_6$ (0.26 g, 1.0 mmol) sodium ethoxy carbonylcyclopentadienide NaCp(COOC$_2$H$_5$) (0.19 g, 1.2 mmol) cluster PhCCo$_3$(CO)$_9$ (**1**) (0.41 g, 0.8 mmol) and THF (20 ml) were used for preparation of the cluster **4**. The procedure and operations were the same as that described for the cluster **2**. Chromatographic workup (eluant benzene : hexane, 1 : 1) gave three fractions. They were the unreacted starting material **1**, byproduct PhCCo$_2$Mo(CO)$_8$Cp and the cluster **4**. The red–purple fraction, separated with benzene, was found to be complex [Mo(CO)$_3$(C$_2$H$_5$O$_2$CCp)]$_2$. Cluster **4** was obtained in yield 28.2% (0.22 g). C$_{23}$H$_{14}$Co$_2$MoO$_{10}$ Calc.: C, 41.56; H, 2.11%. Anal. Found: C, 41.66; H, 1.95%. IR (KBr disk): ν(CO)(C=O) 1718.7 s, ν(CO) (terminal CO) 2085.2m, 2069.8s, 2021.5vs, 2000.3vs, 1979.1s, 1942.5m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.30 (s, 3H, CH$_3$), 4.24 (s, 2H, OCH$_2$), 5.22, 5.80 (d, 4H, C$_5$H$_4$), 7.17–7.26 ppm (m, 5H, C$_6$H$_5$).

2.3. Preparation of the clusters PhCCoFeMo(CO)$_8$(RCOCp)H (R = H (5), CH$_3$ (6) or C$_2$H$_5$O (7))

To a solution of 0.25 g (1.2 mmol) Na$_2$[Fe(CO)$_4$] in 20 ml THF was added 0.28 g (0.45 mmol) of the cluster PhCCo$_2$Mo(CO)$_8$(HCOCp). The mixture was refluxed for 6 h cooled to room temperature and 12 ml 40% H$_3$PO$_4$ added. The mixture was stirred for 5 min and extracted with 30 ml benzene. The organic layer was separated, concentrated to ca. 5 ml and chromatographed on a 40 × 2.5 cm silica gel column: first fraction (eluant hexane : benzene, 1 : 1, deep green); 84 mg Fe$_3$(CO)$_{12}$; second fraction (eluant : hexane :benzene 3 : 1; green), cluster **2** (trace); third fraction (eluant benzene, red) cluster **5** (yield: 0.1 g, 35%). C$_{21}$H$_{11}$CoFeMoO$_9$ Calc.: C, 33.98; H, 1.78. Anal. Found: C, 34.15; H, 1.96%. IR (KBr disk): ν(CO) (C=O) 1688.5m (C=O), ν(CO)(terminal CO) 2068.5s, 2025.4vs, 1997.6vs, 1958.3s, 1946.7s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.31, 5.47, 5.79 and 5.86 (q, 4H, C$_5$H$_4$), 7.17–7.36 (m, 5H, C$_6$H$_5$), 9.54 (s, 1H, HCO), −16.53 ppm (s, 1H, Fe–H).

PhCCo$_2$Mo(CO)$_8$(CH$_3$COCp) Cluster (0.34 g, 0.53 mmol), Na$_2$[Fe(CO)$_4$] (0.29 g, 1.37 mol), THF (20 ml) and 40% H$_3$PO$_4$ (14 ml) were used for preparation of the cluster **6**. All operations were the same as cluster **5**.

Chromatographic isolation yielded 64 mg $Fe_3(CO)_{12}$ (eluant hexane : benzene, 1 : 1; deep green), cluster **3** (eluant hexane : benzene, 3 : 1, green) and cluster **6** (eluant benzene, red). The crystalline complex **6** (yield: 0.14 g, 41%) was obtained from hexane/benzene at −20°C. $C_{22}H_{13}CoFeMoO_9$ Calc.: C, 41.77%; H, 2.06%; Anal. Found: C, 41.52; H, 1.84%. IR (KBr disk): ν(CO)(C=O) 1687.6m, ν(CO) (terminal CO) 2066.4s, 2014.6vs, 2011.5vs, 1978.5s, 1945.4m cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3), 5.32, 5.46, 5.75 and 5.90 (q, 4H, C_5H_4), 7.16–7.36 (m, 5H, C_6H_5), −16.49 ppm (s, 1H, Fe–H).

$PhCCo_2Mo(CO)_8(C_2H_5OCOCp)$ cluster (0.30 g, 0.47 mmol) $Na_2[Fe(CO)_4]$ (0.26 g, 1.21 mol), THF (20 ml) and 40% H_3PO_4 (12 ml) were used for preparation of the cluster **7**. All operations were as above. Chromatographic separation yielded 78 mg $Fe_3(CO)_{12}$ (eluant hexane : benzene, 1 : 1; deep green), cluster **4** (eluant hexane : benzene, 3 : 1; green) and cluster **7** (eluant benzene; red). The crystalline complex **7** (0.14 g, 44%) was obtained from hexane/benzene at −20°C. $C_{23}H_{15}CoFeMoO_{10}$ calc.: C, 41.69; H, 2.17%. Anal. found: C, 41.65; H, 2.31%. IR (KBr disk): ν(CO)(C=O) 1719.2m, ν(CO) (terminal CO) 2065.0s, 2015.0vs, 1998.3vs, 1958.5s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30 (t, 3H, CH_3), 4.28 (q, 2H, OCH_2), 5.51, 5.62, 5.69 and 5.89 (q, 4H, C_5H_4), 7.16–7.48 (m, 5H, C_6H_5), −16.33 ppm (s, 1H, Fe–H).

2.4. X-ray crystallography

The black crystals used for X-ray determination were obtained from their hexane/benzene solution at −20°C. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71069 Å) on Enraf-nonius CAD4 and R3M/E four circle diffractometers equipped with graphite monochromators for clusters **4** and **7**, respectively.

The structure of the cluster 4 was solved by Patterson method. The positions of Co and Mo atoms were determined by heavy atom method. The remaining nonhydrogen atoms were located by Fourier syntheses. The structure was refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The crystal and refinement data of cluster **4** are listed in Table 1.

The structure of cluster **7** was solved by the direct method. The positions of Fe, Co and Mo atoms were obtained from the E map. The remaining nonhydrogen atoms were located by Fourier syntheses. The structure was refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The crystal and refinement data of cluster **7** are listed in Table 1. It was difficult to differentiate between Co and Fe atoms. These were found first by X-ray energy dispersive analysis and then by the method of optimum *R* factor: when the Fe and Co atoms interchange with

Table 1
Crystal and refinement data for the clusters **4** and **7**

Cluster	**4**	7
Formula	$C_{23}H_{14}Co_2MoO_{10}$	$C_{23}H_{15}CoFeMoO_{10}$
*M*r	664.16	662.05
System	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
F(000)	1312	1312
a (Å)	11.356(2)	12.167(2)
b (Å)	14.030(2)	14.032(7)
c (Å)	14.076(3)	15.159(7)
β (°)	106.82(2)	107.19(1)
V (Å^3)	2446.8(7)	2497 (2)
Z	4	4
Dc (g cm^{-3})	1.80	1.76
Crystal dimension (Å^3)	0.60 × 0.45 × 0.35	0.72 × 0.40 × 0.24
Absorption coefficient (cm^{-1})	18.84	17.64
Temperature (°C)	23	21
Scan rate (° min^{-1})	5.49	7
2θ range (°)	2 -50	2 -46
Total no. reflections	4751	3959
No. observation [$I > 3\sigma(I)$]	3499	2728
No. independent reflections	4572	3875
No. variables	326	369
R	0.048	0.0468
Rw	0.057	0.041
Goodness of fit indicator	1.76	1.04
Max residual (e Å^{-3})	0.98	0.82

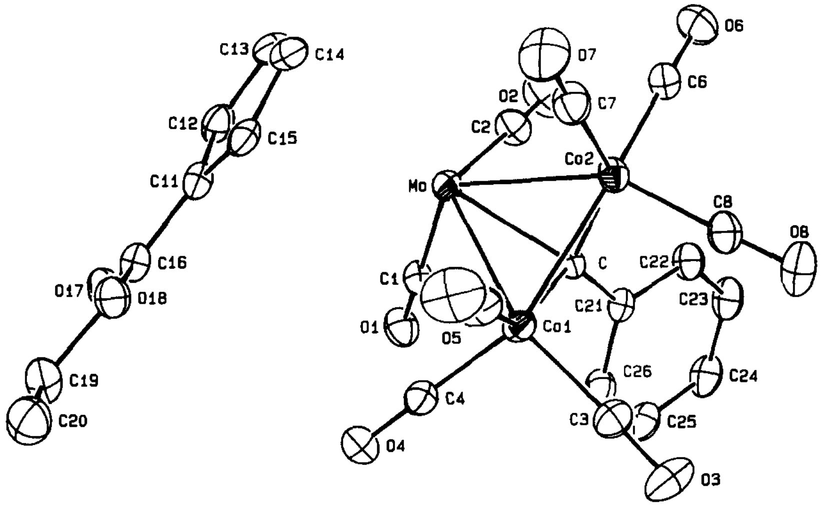

Fig. 1. The crystal structure of cluster **4**.

each other, the final R value changes from 0.1058 to 0.1069.

3. Results and discussion

The reaction of NaCp(RCOCp) with $Mo(CO)_6$ gave the complexes $NaMo(CO)_3(RCOCp)$ [8,9]. The clusters $PhCCo_2Mo(CO)_8(RCOCp)$ were prepared by heating a solution of **1** with $NaMo(CO)_3(RCOCp)$ in THF for 5–6 h under reflux. The anticipated clusters were obtained in 25–30% yields with the red–purple byproducts $[Mo(CO)_3(RCOCp)]_2$ and black complexes $PhCCo_2Mo(CO)_8Cp$ which were identified by elemental analysis, IR and ^1H NMR. The reaction of the clusters $PhCCo_2Mo(CO)_8$ (RCOCp) with $Na_2[Fe(CO)_4]$ followed by treatment with 40% H_3PO_4 gave the clusters $PhCCoFeMo(CO)_8(RCOCp)H$ in 34–45% yields along with the by product $Fe_3(CO)_{12}$. The reaction routes were as follows:

$$PhCCo_3(CO)_9 + NaMo(CO)_3(RCOCp)$$
$$(\mathbf{1})$$
$$\xrightarrow[\text{THF}]{\text{refluxing}} PhCCo_2Mo(CO)_8(RCOCp)$$
$$R = H\ (\mathbf{2}),\ CH_3\ (\mathbf{3})\ \text{or}\ C_2H_5O\ (\mathbf{4})$$
$$\xrightarrow[(2)\ 40\%H_3PO_4]{(1)\ Na_2[Fe(CO)_4]} PhCCoFeMo(CO)_8(RCOCp)H$$
$$R = H(\mathbf{5}), CH_3\ (\mathbf{6})\ \text{or}\ C_2H_5O\ (\mathbf{7})$$

The clusters $PhCCo_2Mo(CO)_8(RCOCp)$ are air-stable black solids, but $PhCCoFeMo(CO)_8(RCOCp)H$ clusters are air-sensitive. This is in accord with the higher instability of heterometallic clusters compared with homometallic ones. Elemental analyses, IR and ^1H NMR data for these clusters are consistent with the structures presented in Figs. 1 and 2. According to literature [6], the clusters $PhCCo_2Mo(CO)_8Cp$ were obtained in 61% yield by reaction of $PhCCo_3(CO)_9$ with $NaMo(CO)_3Cp$ at room temperature. But under the same reaction conditions, only a trace amount of $PhCCo_2Mo(CO)_8(RCOCp)$ and a great quantity of the starting cluster **1** were found by TLC. This may be the result of the reduced nucleophilicity of $NaMo(CO)_3$-(RCOCp) compared with $NaMo(CO)_3Cp$. We also found that reaction of compound **1** with $NaMo(CO)_3(RCOCp)$ was accelerated at higher temperatures: the yield under reflux is better than at room temperature. The byproduct $PhCCo_2Mo(CO)_8Cp$ yielded during reaction is due to the trace amount of unreacted NaCp mixed in NaCp(RCOCp). Results show that metal units $Co(CO)_3$ in the compounds **1**–**4** may be exchanged by the metal units $Mo(CO)_2(RCOCp)$ and $Fe(CO)_3$, respectively on heating. This result, which is consistent with literature reports [1,6,10] further exhibits the generality of this kind of the metal exchange reaction.

For the IR spectra of the cluster, characteristic carbonyl absorption peaks of RCO groups appear at about

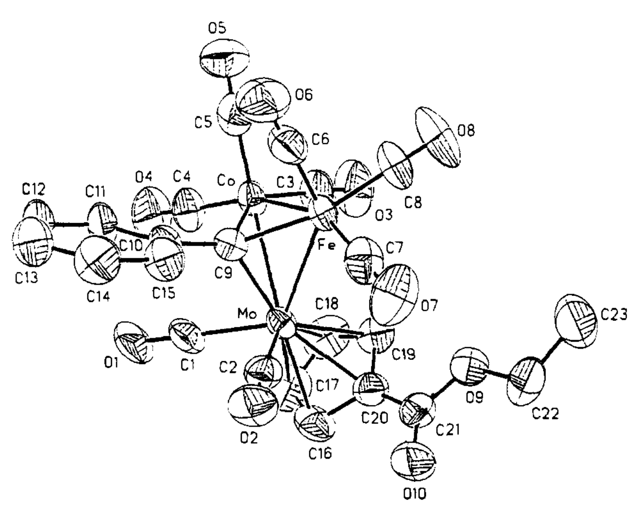

Fig. 2. The crystal structure of cluster **7**.

1700 cm^{-1}. A large number of stronger absorption bands between 2085.2–1940.5 cm^{-1} were assigned to characteristic terminal carbonyl.

For the ^{1}H NMR assignment of the clusters, the multiplets in the range 7.15–7.37 ppm were assigned to protons of bridge Ph. For clusters **2**–**4** the upfield single between 5.17–5.30 ppm, in which each one stands for two protons, were assigned to two *m*-H atoms of the substituent cyclopentadienyl, and the downfield singlet between 5.76–5.80 ppm to *o*-H, resulting from the different deshielding effects of electron-withdrawing groups RCO to *o*-H and *m*-H. For the clusters **5**–**7**, four singlets instead of two singlets appear at 5.31–5.90 ppm. These were assigned to four protons on cyclopentadienyl. This indicates the difference of electron environment around each proton in the cyclopentadienyl group when $Co(CO)_3$ in the clusters **5**–**7** is displaced by $Fe(CO)_3$. This result is similar to that obtained for the chiral cluster $SCoFeW(CO)_8(CH_3COCp)$ in which the ^{1}H–^{13}C chemical shift correlated NMR spectrum indicates that each proton in the cyclopentadienyl group is directly correlated to its carbon. The ^{1}H NMR spectra of the clusters **5**–**7** show proton peaks at −16.53, −16.49 and −16.33 ppm assigned to proton bonded to Fe atom.

Table 2
Positional parameters and B_{eq} for the cluster **4**

Atom	x	y	z	B_{eq}
Mo	0.12916(4)	0.05893(3)	0.21961(3)	3.76(2)
Co(1)	0.36379(6)	0.01796(5)	0.30660(4)	4.03(3)
Co(2)	0.32251(7)	0.16746(4)	0.22008(4)	4.13(3)
O(1)	0.0942(4)	−0.1536(3)	0.1602(3)	6.2(2)
O(2)	0.0291(5)	0.1068(3)	0.0221(3)	8.0(2)
O(3)	0.6010(5)	−0.0475(4)	0.2895(4)	8.3(3)
O(4)	0.2862(4)	−0.1635(3)	0.3607(3)	7.0(2)
O(5)	0.4191(5)	0.1138(4)	0.4760(3)	9.1(3)
O(6)	0.2181(5)	0.2864(3)	0.0679(3)	7.5(2)
O(7)	0.2976(5)	0.3016(3)	0.3538(3)	8.4(3)
O(8)	0.5788(5)	0.1864(4)	0.2235(3)	7.8(3)
O(17)	−0.0265(4)	−0.1345(3)	0.3358(3)	6.2(2)
O(18)	0.1034(4)	−0.0569(2)	0.4459(2)	5.1(2)
C	0.2893(5)	0.0375(3)	0.1817(3)	3.7(2)
C(1)	0.1084(5)	−0.0762(4)	0.1819(3)	4.5(2)
C(2)	0.0674(6)	0.0896(4)	0.0935(4)	5.4(2)
C(3)	0.5112(4)	−0.0194(4)	0.2974(4)	5.5(3)
C(4)	0.3141(5)	−0.0928(4)	0.3381(4)	5.2(2)
C(5)	0.3957(6)	0.0770(4)	0.4101(4)	5.8(3)
C(6)	0.2576(5)	0.2396(4)	0.1276(4)	5.1(2)
C(7)	0.3161(6)	0.2493(4)	0.3023(4)	5.6(3)
C(8)	0.4789(6)	0.1777(4)	0.2220(4)	5.2(3)
C(11)	0.0219(5)	0.0252(4)	0.3185(4)	4.6(2)
C(12)	−0.0663(5)	0.0446(4)	0.2357(4)	5.7(3)
C(13)	−0.0520(6)	0.1417(5)	0.2167(5)	6.8(3)
C(14)	0.0399(6)	0.1818(4)	0.2846(5)	6.0(3)
C(15)	0.0888(5)	0.1116(4)	0.3477(4)	4.8(2)
C(16)	0.0297(5)	−0.0650(4)	0.3652(4)	4.6(2)
C(19)	0.1151(6)	−0.1412(4)	0.5007(4)	6.1(3)
C(20)	0.2073(7)	−0.1195(5)	0.5854(4)	7.2(3)
C(21)	0.3184(5)	−0.0140(3)	0.1107(3)	4.1(2)
C(22)	0.3178(6)	0.0315(4)	0.0337(4)	5.1(2)
C(23)	0.3411(6)	−0.0186(5)	−0.0342(4)	6.1(3)
C(24)	0.3679(6)	−0.1132(5)	−0.0273(4)	6.2(3)
C(25)	0.3704(6)	−0.1600(4)	0.0487(5)	6.1(3)
C(26)	0.3462(6)	−0.1107(4)	0.1169(4)	5.2(2)

Table 3
Atomic coordinates $(\times 10^4)$ and isotropic thermal parameters $(\mathrm{A}^2 \times 10^3)$

Atom	x	y	z	U [a]
Mo	1273(1)	9454(1)	2151(1)	41(1)
Co	3015(1)	8275(1)	2170(1)	46(1)
Fe	3504(1)	9775(1)	3105(1)	45(1)
O(1)	666(5)	9044(5)	43(3)	95(2)
O(2)	1146(4)	11616(3)	1643(4)	74(2)
O(3)	2587(7)	7054(4)	3512(4)	111(3)
O(4)	2097(6)	7052(4)	592(4)	100(3)
O(5)	5422(5)	7918(5)	2303(4)	103(3)
O(6)	5662(4)	10307(5)	2737(4)	95(3)
O(7)	3111(6)	11691(4)	3711(4)	94(3)
O(8)	4372(7)	8821(5)	4870(4)	18(3)
O(9)	1058(4)	10523(4)	4502(3)	65(2)
O(10)	−133(5)	11407(4)	3450(4)	84(2)
C(1)	883(6)	9196(5)	811(4)	61(3)
C(2)	1219(5)	10824(5)	1825(4)	53(2)
C(3)	2758(7)	7530(5)	3066(5)	69(3)
C(4)	2423(7)	7540(5)	1189(5)	65(3)
C(5)	4479(7)	8068(5)	2245(5)	70(3)
C(6)	4824(6)	10079(6)	2885(5)	64(3
C(7)	3284(6)	10953(5)	3465(5)	62(3)
C(8)	4045(7)	9195(6)	4197(5)	72(3)
C(9)	2845(5)	9602(4)	1791(4)	40(2)
C(10)	3161(5)	10090(4)	1020(4)	43(2)
C(11)	9235(7)	9608(5)	243(4)	58(3)
C(12)	3497(8)	10094(6)	−472(5)	73(3)
C(13)	3698(8)	11036(7)	−429(6)	79(4)
C(14)	3664(7)	11538(5)	348(6)	71(3)
C(15)	3399(6)	11064(5)	1064(5)	59(3)
C(16)	−578(6)	9716(7)	2234(6)	72(3)
C(17)	−517(7)	8750(7)	1971(6)	85(4)
C(18)	209(7)	8241(5)	2678(7)	79(4)
C(19)	638(6)	8871(5)	3393(5)	58(3)
C(20)	160(6)	9798(5)	3129(5)	55(2)
C(21)	317(6)	10678(5)	3680(5)	58(3)
C(22)	1313(9)	11341(6)	5118(6)	80(4)
C(23)	2216(8)	11048(8)	5928(6)	100(4)

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

3.1. X-ray crystal structure analysis

The atomic coordinates and thermal parameters of nonhydrogen atoms for the clusters **4** and **7** are given in Tables 2 and 3. Selected bond angles and lengths are listed in Tables 4 and 5.

As seen in Fig. 1, cluster **4** has tetrahedral skeleton composed of C, Mo and two Co atoms. The Co atom was coordinated by three terminal CO ligands. The Mo atom is coordinated by two terminal CO ligands and one carbonylcyclopentadienyl ligand. Bridging carbon

Table 4
Selected bond angles and lengths of the cluster **4** [a]

Bond angles			
Co–Mo–Co′	55.33(2)	C$_B$–Mo–Co′	46.3(1)
C$_B$–Mo–Co′	45.7(1)	Co′–Co–Mo	62.15(3)
C$_B$–Co–Mo	51.1(1)	C$_B$–Co–Co′	49.7(1)
Co–Co′–Mo	62.53(3)	C$_B$–Co′–Mo	51.4(2)
C$_B$–Co′–Co	50.7(1)	Co–C$_B$–Mo	82.6(2)
Co–C$_B$–Co′	79.6(2)	Co′–C$_B$–Mo	82.9(2)
C′–C$_B$–Mo	135.0(3)	C′–C$_B$–Co	130.3(3)
C′–C$_B$–Co′	126.9(4)	O–C–Mo	178.4ave
O–C–Co	177.3ave	O–C–Co′	178.4ave
Co–Mo–C$_{Cp}$	91.8(1)–147.7(2)	Co′–Mo–C$_{Cp}$	92.4(2)–149.2(2)
C$_B$–Mo–C$_{Cp}$	134.9(2)–163.4(2)	C$_{Cp}$–C$_{Cp}$–C$_{Cp}$	106.9(5)–109.2(5)
C$_B$–C–C(11)	121.5(4)	C$_B$–C–C(26)	121.6(4)
O(17)–C(16)–O(18)	124.8(5)	O(17)–C(16)–C(11)	124.5(5)
O(18)–C(16)–O(11)	110.8(4)	C(16)–O(18)–C(19)	116.2(4)
Bond lengths			
Mo–Co	2.6801(9)	Mo–Co′	2.6707(9)
Co–Co′	2.484(1)	Mo–C$_B$	2.103(5)
Co–C$_B$	1.954(5)	Co′–C$_B$	1.926(4)
C′–C$_B$	1.468(7)		
Co–C(CO)	1.792ave	Co′–C(CO)	1.784 av.
O–C(Mo)	1.132ave	O–C(Co)	1.135 av.
O–C(Co′)	1.132ave	Mo–C(CO)	1.985 av.
Mo–C$_{Cp}$	2.318(6)–2.390(6)	C$_{Cp}$–C$_{Cp}$	1.39(1)–1.46(1)
C$_B$–C′	1.468(7)	C(11)–C(16)	1.460(7)
O(17)–C(16)	1.186(6)	O(18)–C(16)	1.325(6)
O(18)–C(19)	1.458(7)	C(19)–C(20)	1.48(1)

[a] Angles are in degrees, lengths in Å. Estimated standard deviations in the least significant figure are given in parentheses. C$_{Cp}$ represents each carbon atom in cyclopentadienyl composed of C(11)–C(15) atoms for **4**. Co, Co′, C$_B$ and C′ represent Co(1), Co(2), the bridge C and the C atom of the benzenyl link to bridge C respectively.

Table 5
Selected bond angles and lengths of the cluster 7 [a]

Bond angles			
Co–Mo–Fe	55.2(1)	Mo–Co–Fe	63.9(1)
Mo–Fe–Co	60.9(1)	Co–Mo–C(9)	45.9(1)
Fe–Mo–C(9)	45.0(1)	Fe–Co–C(9)	50.0(2)
Mo–Co–C(9)	51.9(2)	Mo–Fe–C(9)	50.3(2)
Co–Fe–C(9)	49.5(2)	Co–C(9)–Fe	80.5(2)
Mo–C(9)–Fe	84.7(2)	Mo–C(9)–Co	82.2(2)
Fe–C(9)–C(10)	128.4(4)	Co–C(9)–C(10)	129.9(5)
Mo–C(9)–C(10)	132.8(4)		
Co–C–O	177.9ave	Fe–C–O	177.8ave
Mo–C–O	178.4ave		
Co–Mo–C$_{Cp}$	93.0(2)–150.9(3)	Fe–Mo–C$_{Cp}$	97.0(2)–152.6(2)
C(9)–Mo–C$_{Cp}$	37.8(2)–161.4(3)	C$_{Cp}$–C$_{Cp}$–C$_{Cp}$	97.5(7)–110.1(7)
C(9)–C(10)–C(11)	122.2(6)	C(9)–C(10)–C(15)	120.4(6)
C(16)–C(15)–C(21)	124.5(7)	C(19)–C(20)–C(21)	127.9(6)
O(9)–C(21)–O(10)	123.6(7)	O(9)–C(21)–C(20)	110.7(6)
O(10)–C(21)–C(20)	125.7(6)	O(9)–C(22)–C(23)	107.5(7)
Bond lengths			
Co–Mo	2.683(1)	Co–Fe	2.520(1)
Fe–Mo	2.7576(1)	Co–C(9)	1.944(6)
Fe–C(9)	1.957(6)	Mo–C(9)	2.132(6)
Co–C(CO)	1.794ave	Fe–C(CO)	1.789ave
Mo–C(CO)	1.988ave	(C–O)$_{Co}$	1.133ave
(C–O)$_{Fe}$	1.135ave	(C–O)$_{Mo}$	1.144ave
Mo–C$_{Cp}$	2.345ave	C$_{Cp}$–C$_{Cp}$	1.413ave
C(9)–C(10)	1.489(9)	C(20)–C(21)	1.466(10)
O(9)–C(21)	1.349(8)	O(9)–C(22)	1.462(10)
O(10)–C(21)	1.178(9)	C(22)–C(23)	1.475(12)

[a] Distances are in Å. Estimated standard deviations in the least significant figure are given in parentheses. C$_{Cp}$ represents each carbon atom in cyclopentadienyl composed of C(16)–C(20) atoms for 7.

atoms bond to two Co and one Mo atom with bond lengths 1.926(4), 1.954(5) and 2.103(5) Å for bonds C_B–Co′, C_B–Co and C_B–Mo. Selected bond angles and lengths of the parent $PhCCo_2Mo(CO)_8Cp$ in Ref. [11] have been compared with those of cluster **4**. It was found that respective bond angles and lengths in the cluster cores are approximately equal. In both cases the bond angles Mo–Co–Co in the triangular base CoCoMo that is basically equal to each other are larger than angle Co–Mo–Co. So triangular base CoCoMo is an isosceles triangle.

As seen in Fig. 2, cluster **7** also has tetrahedral skeleton composed of C, Co, Fe and Mo atoms. Bridge carbon atom are bonded to Co, Fe and Mo atoms with bond lengths of 1.944(6), 1.957(6) and 2.132(6) Å, respectively. Fe and Co atoms are coordinated by three carbonyl ligands, Mo by two carbonyl and one carbonylcyclopentadienyl ligands. Selected bond angles and lengths for clusters **4** and $PhCCo_2Mo(CO)_8Cp$ were compared with those of cluster **7**. It was found that respective bond angles and lengths in their cluster cores were approximately equal to each other. This is because Fe and Co atoms have identical coordination, atom number and chemical lengths.

From Tables 4 and 5 it may be seen that the bond lengths (Å) of O(17)–C(16) (1.186(6)), O(18)–C(16) (1.325(6)) and O(18)–C(19) (1.458(6)) in the group C_2H_5OCO of cluster **4** and O(10)–C(21) (1.178(9)), O(9)–C(21) (1.349(8)) and O(9)–C(22) (1.462(10)) in the group C_2H_5OCO of cluster **7** exhibit the increasing magnitudes. This is due to the π-system of the O(17)–C(16) or O(10)–C(21)) bond and the large π-conjugate system composed of the lone pair electron of the O(18) (or O(9)) atom and the π-systems of O(17)–C(16) (or O(10)–C(21)) and cyclopentadienyl.

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[11] Precursor $PhCCo_2Mo(CO)_8Cp$ principal bond lengths: Co–Co = 2.483(1), Co–Mo = 2.677(1), Co–C = 1.933(3), Mo–C = 2.104(7)(Å). Bond angles: CoMoCo = 55.28(3), CoCoMo = 62.36(2), CoCMo = 83.0(2), CoCCo = 79.9(3)°.