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Synthesis and characterization of organotransition metal double μ_3-$RCCo_2M$ ($M = Mo$, W) cluster complexes containing bridged dicyclopentadienyl ligands. Crystal structure of $[\mu_3\text{-}MeCCo_2Mo(CO)_8]_2\,[\eta^5\text{-}C_5H_4C(O)\,CH_2]_2$

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Abstract

While the succinyl-bridged dicyclopentadienyl M/Na salts $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[M(CO)_3Na]_2$, prepared from $[\eta^5\text{-}C_5H_4C(O)CH_2]_2Na_2$ and $M(CO)_6$ ($M = Mo$, W), react with single clusters $\mu_3\text{-}RCCo_3(CO)_9$ (**2**, R = Me, Ph) to give the succinyl-bridged dicyclopentadienyl-bridged double clusters $[\mu_3\text{-}RCCo_2M(CO)_8]_2[\eta^5\text{-}C_5H_4C(O)CH_2]_2$ (**3a**–**d**, M = Mo, W; R = Me, Ph), the ether chain-bridged dicyclopentadienyl M/Na salts $[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5][M(CO)_3Na]_2$, generated from $[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5]Na_2$ and $M(CO)_6$ ($M = Mo$, W), react with single clusters **2** to afford the ether chain-bridged dicyclopentadienyl-bridged double clusters $[\mu_3\text{-}RCCo_2M(CO)_8]_2[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5]$ (**5a**–**d**, M = Mo, W; R = Me, Ph). Further treatment of **3a**, **b** (M = Mo, W; R = Me) with $NaBH_4$ has been shown to give the corresponding dihydroxy carbon chain-bridged dicyclopentadienyl-bridged double clusters $[\mu_3\text{-}MeCCo_2M(CO)_8]_2[\eta^5\text{-}C_5H_4CH(OH)CH_2]_2$ (**6a**, **b**, M = Mo, W). All the new clusters **3a**–**d**, **5a**–**d** and **6a**, **b** have been characterized by elemental analysis, IR and ^1H-NMR spectroscopy, as well as by X-ray diffraction techniques for **3a** (M = Mo, R = Me).

Keywords: Molybdenum; Tungsten; Cobalt; Bridged dicyclopentadienyl ligands; Clusters; X-ray structure

1. Introduction

Since the mid-1970s organotransition metal cluster complexes have drawn great attention, mainly because of the potential applications of organotransition cluster complexes in catalysis, as well as the novelty and diversity of their structures and properties [1–5]. In such cluster complexes we are particularly interested in those containing double cluster cores connected by functionally bridged dicyclopentadienyl ligands. This is because that such bridged double cluster complexes may undergo both the isolobal displacement reactions involved in their two cluster cores and the functional transformation reactions involved in the bridged dicyclopentadienyl ligands. In fact, such studies have led us to discover several new methods to synthesize series of transition metal cluster complexes, such as the noncyclic double clusters containing various bridged dicyclopentadienyl ligands and the single, double and triple cluster macrocycles [6–11]. In order to further develop the chemistry concerning such bridged double cluster complexes, we recently intitiated a study based on the reactions of the succinyl- and the ether chain-bridged dicyclopentadienyl M/Na salts $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[M(CO)_3Na]_2$ and $[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5][M(CO)_3Na]_2$ ($M = Mo$, W) with tetrahedral clusters $\mu_3\text{-}RCCo_3(CO)_9$ (R = Me, Ph). Herein we report the results obtained from this study, namely the synthesis and characterization of the double $\mu_3\text{-}RCCo_2M$

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(M = Mo, W) cluster complexes [μ_3-RCCo$_2$M(CO)$_8$]$_2$[η^5-C$_5$H$_4$C(O)CH$_2$]$_2$ (**3a**–**d**, M = Mo, W; R = Me, Ph), [μ_3-RCCo$_2$M(CO)$_8$]$_2$[η^5-C$_5$H$_4$CH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$C$_5$H$_4$-η^5] (**5a**–**d**, M = Mo, W; R = Me, Ph) and [μ_3-MeCCo$_2$M(CO)$_8$]$_2$[η^5-C$_5$H$_4$CH(OH)CH$_2$]$_2$ (**6a**, **b**, M = Mo, W), as well as the crystal structure of [μ_3-MeCCo$_2$Mo(CO)$_8$]$_2$[η^5-C$_5$H$_4$C(O)CH$_2$]$_2$ (**3a**) determined by X-ray diffraction analysis.

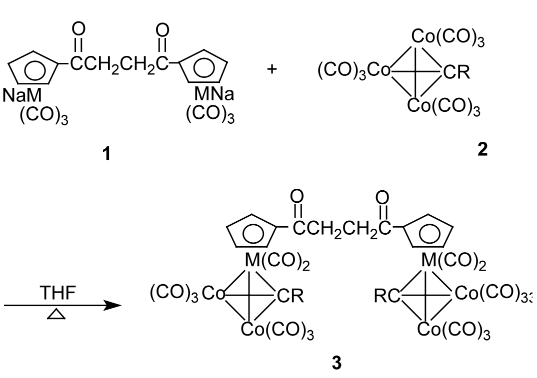
2. Results and discussion

2.1. Synthesis and characterization of *3a*–*d*, *4a*–*d* and *5a*, *b*

It was found that the succinyl-bridged dicyclopentadienyl M/Na salts (**1**, M = Mo, W), generated from [η^5-C$_5$H$_4$C(O)CH$_2$]$_2$Na$_2$ and M(CO)$_6$ (M = Mo, W) [12], reacted with two molecules of tetrahedral clusters μ_3-RCCo$_3$(CO)$_9$ (**2**, R = Me, Ph) in refluxing tetrahydrofuran (THF) to give a series of double tetrahedral μ_3-RCCo$_2$M cluster complexes each containing a succinyl-bridged dicyclopentadienyl ligand [μ_3-RCCo$_2$M(CO)$_8$]$_2$[η^5-C$_5$H$_4$C(O)CH$_2$]$_2$ (**3a**–**d**) (Scheme 1).

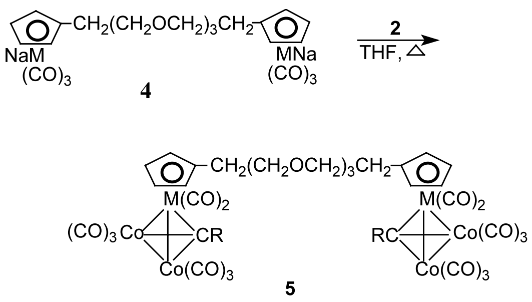
Similarly, it was also found that the ether chain-bridged dicyclopentadienyl M/Na salts (**4**, M = Mo, W), formed from [η^5-C$_5$H$_4$CH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$C$_5$H$_4$-η^5]Na$_2$ and M(CO)$_6$ (M = Mo, W) [8], reacted with two molecules of clusters **2** in THF at reflux to afford another series of double tetrahedral μ_3-RCCo$_2$M cluster compounds each containing an ether chain-bridged dicyclopentadienyl ligand [μ_3-RCCo$_2$M(CO)$_8$]$_2$[η^5-C$_5$H$_4$CH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$C$_5$H$_4$-η^5] (**5a**–**d**) (Scheme 2).

Interestingly, it was further found that clusters **3a**, **b** could react with an excess of NaBH$_4$ in MeOH at room temperature to produce two double μ_3-MeCCo$_2$M cluster complexes each containing a dihydroxy carbon chain-bridged dicyclopentadienyl ligand [μ_3-MeCCo$_2$M(CO)$_8$]$_2$[η^5-C$_5$H$_4$CH(OH)CH$_2$]$_2$ (**6a**, **b**) (Scheme 3).



	3a	3b	3c	3d
M	Mo	W	Mo	W
R	Me	Me	Ph	Ph

Scheme 1.

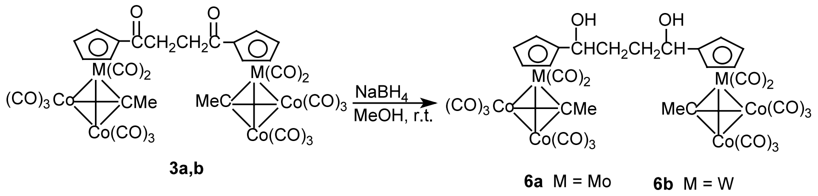


	5a	5b	5c	5d
M	Mo	W	Mo	W
R	Me	Me	Ph	Ph

Scheme 2.

Products **3a**–**d**, **5a**–**d** and **6a**, **b**, to our knowledge, are the first reported double μ_3-RCCo$_2$M cluster complexes containing such bridged dicyclopentadienyl ligands, although the single clusters μ_3-RCCo$_2$M(η^5-C$_5$H$_5$)(CO)$_8$ (M = Mo, W) were previously prepared by reaction between tetrahedral clusters μ_3-RCCo$_3$(CO)$_9$ and the M/Na salts (η^5-C$_5$H$_5$)M(CO)$_3$Na [13]. Apparently, while products **6a**, **b** were generated by reduction of the succinyl-bridged dicyclopentadienyl ligands of **3a**, **b** with NaBH$_4$, products **3a**–**d** and **5a**–**d** can be regarded as derived from a double isolobal displacement of the two Co(CO)$_3$(d^{9}ML$_3$) structural units in two molecules of the parent clusters **2** by a bridging double d^{5}ML$_5$ isolobal fragment [M(CO)$_2$]$_2$[η^5-C$_5$H$_4$C(O)CH$_2$]$_2$ or [M(CO)$_2$]$_2$[η^5-C$_5$H$_4$CH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$C$_5$H$_4$-η^5] generated in situ from M/Na salts **1** or **4** [6,14]. It is noteworthy that all the synthesized double clusters have been characterized by elemental analysis and IR and ^{1}H-NMR spectroscopy. The C/H analytical data for **3a**–**d**, **5a**–**d** and **6a**, **b** are consistent with their compositions. The IR spectra of **3a**–**d**, **5a**–**d** and **6a**, **b** displayed several absorption bands in the range 2082–1925 cm^{-1} for their carbonyls attached to transition metals. In addition, while the IR spectra of **3a**–**d** showed one absorption band in the region 1680–1676 cm^{-1} for their ketonic carbonyls of succinyl groups, those of **5a**–**d** exhibited one absorption band in the range 1117–1105 cm^{-1} for their C–O–C functionalities of the ether chain and those of **6a**, **b** displayed one absorption band at 3432 cm^{-1} for their dihydroxy functionalities in the bridged dicyclopentadienyl ligand.

It is known that ^{1}H-NMR spectra of a monosubstituted cyclopentadienyl ring in transition metal complexes vary greatly in complexity, such as a single resonance, an A$_2$B$_2$ or A$_2$BB′ pattern or a multiplet pattern,mainly depending on the nature of the substituent and the transition metal moieties [6,15]. For example, in the ^{1}H-NMR spectra of **3a**–**d** the four



Scheme 3.

protons for each of the bridged Cp rings displayed two singlets in the range 5.35–6.02 ppm, the upfield singlet being assigned to H^3 and H^4 protons remote from the electron-withdrawing succinyl bridge and the downfield one to H^2 and H^5 close to the bridge [6,15], whereas the ^{1}H-NMR spectra of the four protons for each of the bridged Cp rings in **5a**, **b** showed only one broad singlet at 5.30 and 5.32 ppm, respectively. In addition, while the ^{1}H-NMR spectra of the four protons for each of the bridged Cp rings in **5c**,**d** exhibited two singlets in the region 5.41–5.68 ppm, the upfield singlet being attributed to H^2 and H^5 close to the electron-donating ether chain and the downfield one to H^3 and H^4 remote from the ether chain [6,15], the ^{1}H-NMR spectra of those protons in **6a**, **b** diplayed one multiplet between 5.10 and 5.70 ppm. Finally, it should be noted that the ^{1}H-NMR spectra of **3a**–**d**, **5a**–**d** and **6a**, **b** also showed the other corresponding signals assignable to their respective hydrogen-containing groups, such as CH_2, CH, OH, CH_3 and C_6H_5.

Table 1
Selected bond lengths (Å) and angles (°) for **3a**

Bond lengths			
Co(1)–C(9)	1.943(6)	Co(1)–C(3)	1.785(8)
Co(2)–Mo(1)	2.6600(11)	Co(1)–Co(2)	2.4836(13)
Mo(1)–C(1)	1.989(7)	Co(1)–Mo(1)	2.6949(12)
C(10)–C(9)	1.501(8)	Co(2)–C(9)	1.920(6)
Bond angles			
C(9)–Mo(1)–Co(2)	45.67(16)	C(9)–Co(1)–Co(2)	49.60(17)
C(9)–Mo(1)–Co(1)	45.68(16)	C(9)–Co(1)–Mo(1)	51.34(17)
Co(2)–Mo(1)–Co(1)	55.26(3)	C(9)–Co(2)–Co(1)	50.38(18)
Co(2)–C(9)–Co(1)	80.0(2)	C(9)–Co(2)–Mo(1)	52.16(17)
Co(2)–C(9)–Mo(1)	82.2	Co(1)–Co(2)–Mo(1)	63.08(3)

2.2. Crystal structure of 3a

Fortunately, the crystal structure of **3a** was successfully determined by X-ray diffraction techniques, which has not only unequivocally confirmed the structure of **3a**, but also has further provided some important structural information about **3a**–**d**, **5a**–**d** and **6a**, **b**. The crystal structure of **3a** is shown in Fig. 1, whereas the bond lengths and angles are presented in Table 1. As seen intuitively in Fig. 1, the molecule of **3a** comprises two identical tetrahedral CCo_2Mo subcluster cores, each carrying one methyl group attached to carbon atom, two carbonyls bound to Mo atom and two sets of three carbonyls attached to two Co atoms. In addition, the two subcluster cores are connected through Mo atoms to two η^5-cyclopentadienyl rings of the succinyl-bridged dicyclopentadienyl ligand in a trans fashion. In fact, this molecule is centrosymmetric and somewhat similar to double cluster $[MoCoFe(\mu_3\text{-}S)(CO)_8]_2[\eta^5\text{-}C_5H_4C(O)CH_2]_2$ [6]. For **3a**, the bond lengths of Co(1)–Co(2) (2.4836(13) Å), Co(1)–C(9) (1.943(6) Å), Co(1)–Mo(1) (2.6949(12) Å), Co(2)–Mo(1) (2.6600(11) Å), Mo(1)–C(9) (2.120(6) Å) in the cluster core are close to the corresponding those in starting single tetrahedral cluster $\mu_3\text{-}MeCCo_3(CO)_9$ [16], single tetrahedral C_2Mo_2 cluster $[\eta^5\text{-}MeO_2CC_5H_4](CO)_2Mo]_2(\mu\text{-}\eta^2,\eta^2\text{-}C_2H_2)$ [17] and double tetrahedral MoCoFeS cluster $[MoCoFe(\mu_3\text{-}S)(CO)_8]_2[\eta^5\text{-}C_5H_4C(O)CH_2]_2$ [6]. Since the dihedral

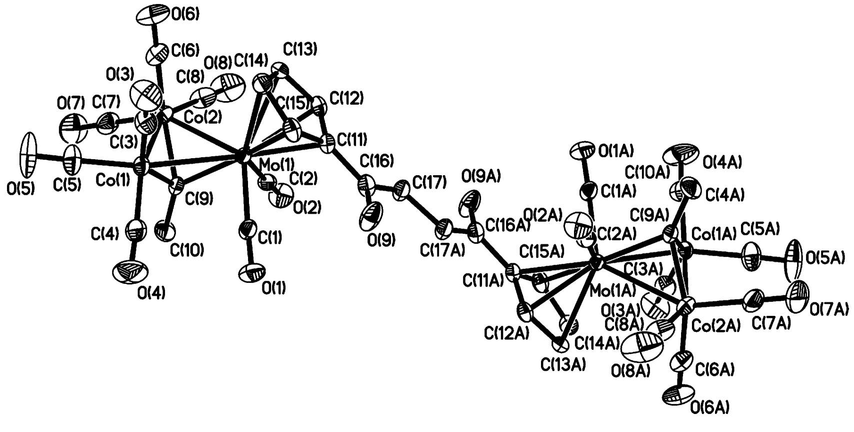


Fig. 1. ORTEP drawing of **3a** with the atom labeling scheme.

angle between the Cp ring and the plane O(9)–C(16)–C(17) is rather small (5.2°), the π-system of half of the succinyl bridge would be regarded as conjugated with the Cp ring π-system and thus the bond length of C(11)–C(16) (1.470(8) Å) becomes shorter than a normal C–C single bond.

3. Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. THF and diglyme were distilled from Na–benzophenone ketyl under nitrogen. $[\eta^5\text{-}C_5H_4C(O)CH_2]_2Na_2$ [18], $[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3\text{-}CH_2C_5H_4\text{-}\eta^5]Na_2$ [8], μ_3-MeCCo$_3$(CO)$_9$ and μ_3-PhCCo$_3$(CO)$_9$ [19] were prepared according to literature procedures. Products were isolated by preparative TLC and further recrystallized from CH_2Cl_2 and hexane mixed solvent. IR spectra were recorded on a Nicolet Magna 560 FTIR infrared spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AC-P200 NMR spectrometer. C/H analyses were performed on an Elementar Vario EL analyzer. Melting points (m.p.) were determined on a Yanaco MP-500 apparatus and were uncorrected.

3.1. Preparation of $[\mu_3\text{-MeCCo}_2\text{Mo(CO)}_8]_2[\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2]_2$ (**3a**)

A 100 ml three-necked flask equipped with a stir-bar, a serum cap and a reflux condenser topped with a nitrogen inlet tube was charged with 0.528 g (2.0 mmol) of Mo(CO)$_6$, 0.258 g (1.0 mmol) of $[\eta^5\text{-}C_5H_4C(O)CH_2]_2Na_2$ and 20 ml of diglyme. The reaction mixture was stirred at reflux for 4 h. After evaporation of diglyme under vacuum, 0.912 mg (2 mmol) of μ_3-MeCCo$_3$(CO)$_9$ and 30 ml of THF were added, the mixture was stirred at reflux for 10 h. Solvent was removed under reduced pressure. The residue was subjected to preparative TLC separation using CH_2Cl_2 as eluent. The main green band afforded 0.442 g (39%) of **3a** as a green solid, m.p. > 290 °C. Anal. Found: C, 35.66; H, 1.89. $C_{34}H_{18}Co_4Mo_2O_{18}$ Calc.: C, 35.76; H, 1.59%. IR (KBr disk): $\nu_{C\equiv O}$ 2071s, 2015vs, 1992vs, 1948s; $\nu_{C=O}$ 1678m cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 3.00 (s, 4H, 2CH$_2$), 3.74 (s, 6H, 2CH$_3$), 5.53 (s, 4H, 2H^3, 2H^4), 5.82 (s, 4H, 2H^2, 2H^5) ppm.

3.2. Preparation of $[\mu_3\text{-MeCCo}_2\text{W(CO)}_8]_2[\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2]_2$ (**3b**)

The same procedure as that for **3a** was followed, but 0.704 g (2.0 mmol) of W(CO)$_6$ was used in place of Mo(CO)$_6$. The main green band afforded 0.246 g (9%) of **3b** as green solid, m.p. > 290 °C. Anal. Found: C, 30.55; H, 1.38. $C_{34}H_{18}Co_4O_{18}W_2$ Calc.: C, 30.97; H, 1.38%. IR (KBr disk): $\nu_{C\equiv O}$ 2074s, 2016vs, 1993vs, 1942s; $\nu_{C=O}$ 1680m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 3.01 (s, 4H, 2CH$_2$), 3.64 (s, 6H, 2CH$_3$), 5.63 (s, 4H, 2H^3, 2H^4), 5.79 (s, 4H, 2H^2, 2H^5) ppm.

3.3. Preparation of $[\mu_3\text{-PhCCo}_2\text{Mo(CO)}_8]_2[\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2]_2$ (**3c**)

The same procedure as that for **3a** was followed, but 1.036 g (2.0 mmol) of μ_3-PhCCo$_3$(CO)$_9$ was used instead of μ_3-MeCCo$_3$(CO)$_9$. The main green band afforded 0.647 g (51%) of **3c** as a green solid, m.p. > 290 °C. Anal. Found: C, 41.56; H, 1.67. $C_{44}H_{22}Co_4Mo_2O_{18}$ Calc.: C, 41.74; H, 1.75%. IR (KBr disk): $\nu_{C\equiv O}$ 2075s, 2026vs, 1995vs, 1985vs, 1952s; $\nu_{C=O}$ 1678m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 3.01 (s, 4H, 2CH$_2$), 5.60 (s, 4H, 2H^3, 2H^4), 6.02 (s, 4H, 2H^2, 2H^5). 7.34 (s, 10H, 2C$_6$H$_5$) ppm.

3.4. Preparation of $[\mu_3\text{-PhCCo}_2\text{W(CO)}_8]_2[\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2]_2$ (**3d**)

The same procedure as that for **3a** was followed, but 0.704g (2.0 mmol) of W(CO)$_6$ and 1.036 g (2.0 mmol) of μ_3-PhCCo$_3$(CO)$_9$ were used instead of Mo(CO)$_6$ and μ_3-MeCCo$_3$(CO)$_9$. The main green band gave 0.125 g (9%) of **3d** as a green solid, m.p. > 290 °C. Anal. Found: C, 36.50; H, 1.67. $C_{44}H_{22}Co_4O_{18}W_2$ Calc.: C, 36.65; H, 1.54%. IR(KBr disk): $\nu_{C\equiv O}$ 2082s, 2034vs, 1985vs, 1946s; $\nu_{C=O}$ 1676m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.89 (s, 4H, 2CH$_2$), 5.35 (s, 4H, 2H^3, 2H^4), 5.80 (s, 4H, 2H^2, 2H^5), 7.24(s, 10H, 2C$_6$H$_5$) ppm.

3.5. Preparation of $[\mu_3\text{-MeCCo}_2\text{Mo(CO)}_8]_2[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5]$ (**5a**)

The same procedure as that for **3a** was followed, but 0.258 g (1.0 mmol) of $[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3\text{-}CH_2C_5H_4\text{-}\eta^5]Na_2$ was used instead of $[\eta^5\text{-}C_5H_4C\text{-}(O)CH_2]_2Na_2$. The main green band afforded 0.277g (23%) of **5a** as a green solid, m.p. > 290 °C. Anal. Found: C, 37.42; H, 2.47. $C_{38}H_{30}Co_4Mo_2O_{19}$ Calc.: C, 37.46; H, 2.48%. IR (KBr disk): $\nu_{C\equiv O}$ 2074s, 2025vs, 1997vs, 1938s; $\nu_{C\text{–}O\text{–}C}$ 1113m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.64 (br, s, 4H, 2CH$_2$Cp), 3.65 (s, 12H, 6CH$_2$O), 3.71 (s, 6H, 2CH$_3$). 5.30(br, s, 8H, 2C$_5$H$_4$) ppm.

3.6. Preparation of $[\mu_3\text{-MeCCo}_2\text{W(CO)}_8]_2[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5]$ (**5b**)

The same procedure as that for **3a** was followed, but 0.704 g (2.0 mmol) of W(CO)$_6$ and 0.258 g (1.0 mmol) of $[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5]Na_2$ were used instead of Mo(CO)$_6$ and $[\eta^5\text{-}C_5H_4C(O)CH_2]_2Na_2$. The main green band produced 0.194 g (14%) of **5b** as a green solid, m.p. > 290 °C. Anal. Found: C, 32.48; H, 2.40. $C_{38}H_{30}Co_4O_{19}W_2$ Calc.: C, 32.74; H, 2.17%. IR (KBr disk): $\nu_{C\equiv O}$ 2070s, 2022vs, 1992vs, 1925s; ν_{C-O-C} 1117m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.64 (br, s, 4H, $2CH_2Cp$), 3.60 (s, 12H, $6CH_2O$), 3.77 (s, 6H, $2CH_3$). 5.32(br, s, 8H, $2C_5H_4$) ppm.

3.7. Preparation of $[\mu_3\text{-}PhCCo_2Mo(CO)_8]_2[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5]$ *(**5c**)*

The same procedure as that for **3a** was followed, but 0.258 g (1.0 mmol) of $[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3\text{-}CH_2C_5H_4\text{-}\eta^5]Na_2$ and 1.036 g (2.0 mmol) of $\mu_3\text{-}PhCCo_3(CO)_9$ were used instead of $[\eta^5\text{-}C_5H_4C(O)\text{-}CH_2]_2Na_2$ and $\mu_3\text{-}MeCCo_3(CO)_9$. The main green band afforded 0.123 g (9%) of **5c** as a green solid, m.p. > 290 °C. Anal. Found: C, 42.75; H, 2.67. $C_{48}H_{34}Co_4Mo_2O_{19}$ Calc.: C, 42.95; H, 2.55%. IR (KBr disk): $\nu_{C\equiv O}$ 2074s, 2010vs, 1998vs, 1926s; ν_{C-O-C} 1105m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.57 (br, s, 4H, $2CH_2Cp$), 3.54 (s, 12H, $6CH_2O$), 5.41 (s, 4H, $2H^2$, $2H^5$), 5.55 (s, 4H, $2H^3$, $2H^4$). 7.32 (s, 10H, $2C_6H_5$).

3.8. Preparation of $[\mu_3\text{-}PhCCo_2W(CO)_8]_2[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5]$ *(**5d**)*

The same procedure as that for **3a** was followed, but 0.704 g (2.0 mmol) of $W(CO)_6$, 0.258 g (1.0 mmol) of $[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5]Na_2$ and 1.036 g (2.0 mmol) of $\mu_3\text{-}PhCCo_3(CO)_9$ were used instead of $Mo(CO)_6$, $[\eta^5\text{-}C_5H_4C(O)CH_2]_2Na_2$ and $\mu_3\text{-}MeC\text{-}Co_3(CO)_9$. The main green band afforded 0.176 g (12%) of **5d** as a green solid, m.p. > 290 °C. Anal. Found: C, 37.83; H, 2.52. $C_{48}H_{34}Co_4O_{19}W_2$ Calc.: C, 37.97; H, 2.26%. IR (KBr disk): $\nu_{C\equiv O}$ 2074s, 2034vs, 1993vs, 1942s; ν_{C-O-C} 1117m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.67 (br, s, 4H, $2CH_2Cp$), 3.56 (s, 12H, $6CH_2O$), 5.57 (s, 4H, $2H^2$, $2H^5$), 5.68 (s, 4H, $2H^3$, $2H^4$). 7.26 (s, 10H, $2C_6H_5$) ppm.

3.9. Preparation of $[\mu_3\text{-}MeCCo_2Mo(CO)_8]_2[\eta^5\text{-}C_5H_4CH(OH)CH_2]_2$ *(**6a**)*

A 100 ml three-necked flask equipped with a stir-bar, a serum cap with a nitrogen inlet tube was charged with 0.640 g (0.56 mmol) of $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[\mu_3\text{-}MeC\text{-}Co_2Mo(CO)_8]_2$, 0.129 g (3.36 mmol) of $NaBH_4$ and 20 ml of MeOH. The reaction mixture was stirred at room temperature (r.t.) for 2 h. After evaporation of the solvent under vacuum, The residue was subjected to preparative TLC separation using CH_2Cl_2–Et_2O (v/v = 30:1) as eluent. The main green band afforded 0.275 g (43%) of **6a** as a green solid, m.p. (dec.) 70 °C. Anal. Found: C, 35.80; H, 1.69. $C_{34}H_{22}Co_4Mo_2O_{18}$ Calc.: C, 35.63; H, 1.94%. IR (KBr disk): $\nu_{C\equiv O}$ 2069s, 2022vs, 1996vs, 1934s; ν_{OH} 3432 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.78(br, s, 4H, $2CH_2$), 2.52 (br, s, 2H, 2OH), 3.70 (s, 6H, $2CH_3$), 4.20–4.75 (m, 2H, 2CH), 5.12–5.50 (m, 8H, $2C_5H_4$) ppm.

3.10. Preparation of $[\mu_3\text{-}MeCCo_2W(CO)_8]_2[\eta^5\text{-}C_5H_4CH(OH)CH_2]_2$ *(**6b**)*

The same procedure as that for **6a** was followed, but 0.370 g (0.28 mmol) of $[\eta^5\text{-}C_5H_4C(O)CH_2]_2[\mu_3\text{-}MeC\text{-}Co_2W(CO)_8]_2$ was used instead of $[\eta^5\text{-}C_5H_4C\text{-}(O)CH_2]_2[\mu_3\text{-}MeCCo_2Mo(CO)_8]_2$. The main green band afforded 0.074 g (20%) of **6b** as a green solid, m.p. (dec.) 80 °C. Anal. Found: C, 30.99; H, 1.77. $C_{34}H_{22}Co_4\text{-}O_{18}W_2$ Calc.: C, 30.89; H, 1.68%. IR (KBr disk): $\nu_{C\equiv O}$ 2077s, 2020vs, 1992vs, 1937s; ν_{OH} 3432 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.92 (br, s, 4H, $2CH_2$), 2.24 (br,s, 2H, 2OH), 3.70 (s, 6H, $2CH_3$), 4.22–4.78 (m, 2H, 2CH), 5.20–5.68 (m, 8H, $2C_5H_4$) ppm.

*3.11. X-ray structure determination of **3a***

Single crystals of **3a** suitable for X-ray diffraction analysis were grown by slow evaporation of its CH_2Cl_2–hexane solution at about 4 °C. A crystal measuring 0.30 × 0.25 × 0.20 mm was mounted on a Bruker SMART 1000 automated diffractometer with a graphite monochromator with Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Details of the crystal data, data collections and structure refinements are summarized in Table 2.

The structure was solved by direct methods and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-

Table 2
Crystal data and structural refinements details for **3a**

Formula	$C_{34}H_{18}Co_4Mo_2O_{18}$
Formula weight	1142.1189
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.617(3)
b (Å)	8.861(3)
c (Å)	15.497(5)
α (°)	105.001(5)
β (°)	91.426(5)
γ (°)	117.767(5)
V (Å^3)	996.6(5)
Z	4
D_{calc} (g cm^{-3})	1.903
F(000)	558
μ (Mo–K$_\alpha$) (mm^{-1})	2.311
Temperature (K)	298(2)
Scan type	ω–2θ
$2\theta_{max}$ (°)	50.04
Data/restraints/parameters	3510/0/262
R	0.0410
R_w	0.0813
Goodness-of-fit	0.997
Largest difference peak and hole (e Å^{-3})	0.480 and −0.577

hydrogen atoms. The calculations were performed using the SHELXTL-97 program.

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 188955. 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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