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## Rupture of the triple C≡C and C≡O bonds in the mixed-metal clusters with Ni<sub>2</sub>Mo<sub>2</sub> and Mo<sub>4</sub>Co<sub>3</sub> cores. Synthesis and molecular structures of Cp<sub>4</sub>Ni<sub>2</sub>Mo<sub>2</sub>(μ<sub>3</sub>-CPh)<sub>2</sub>(μ<sub>3</sub>-CO)<sub>2</sub> and Cp<sub>4</sub>Mo<sub>4</sub>(μ<sub>3</sub>-OH)(μ<sub>3</sub>-CPh)<sub>2</sub>(μ<sub>6</sub>-C)Co<sub>3</sub>(μ-CO)<sub>3</sub>(CO)<sub>3</sub>

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### Abstract

Mixed-metal cluster Cp<sub>4</sub>Ni<sub>2</sub>Mo<sub>2</sub>(μ<sub>3</sub>-CPh)<sub>2</sub>(μ<sub>3</sub>-CO)<sub>2</sub> (I), in which the carbyne bridges under the "butterfly" Mo<sub>2</sub>Ni<sub>2</sub> (Mo–M 2.674(2), Mo–Ni 2.664(2) Å) wings are formed due to splitting of the C≡C bonds, has been synthesized by reaction of Cp<sub>2</sub>Ni<sub>2</sub>(Ph<sub>2</sub>C<sub>2</sub>) and Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> in refluxing *o*-xylene and characterized by X-ray structural analysis. In the reaction of CpNiCo(CO)<sub>3</sub>(Ph<sub>2</sub>C<sub>2</sub>) with Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>, the tolan (diphenylacetylene) molecule is transferred with formation of the well known Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>4</sub>(Ph<sub>2</sub>C<sub>2</sub>). An unusual seven-nuclear diamagnetic cluster Cp<sub>4</sub>Mo<sub>4</sub>(μ<sub>3</sub>-OH)(μ<sub>3</sub>-CPh)<sub>2</sub>(μ<sub>6</sub>-C)Co<sub>3</sub>(μ-CO)<sub>3</sub>(CO)<sub>3</sub> (III) in which the simultaneous rupture of C≡C and C≡O bonds takes place has been synthesized by reaction of Co<sub>2</sub>(CO)<sub>6</sub>(Ph<sub>2</sub>C<sub>2</sub>) with Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> in refluxing *o*-xylene. Cluster III is a combination of the distorted tetrahedral Cp<sub>4</sub>Mo<sub>4</sub>(μ<sub>3</sub>-CPh)<sub>2</sub>(μ-OH) (Mo–Mo 2.761(4)–2.939(4) Å) and triangular Co<sub>3</sub>(μ-CO)<sub>3</sub>(CO)<sub>3</sub> (Co–Co 2.463(3) Å) fragments bonded by μ<sub>6</sub>-carbide bridges and Co–Mo bonds (2.909(6)–2.946(5) Å).

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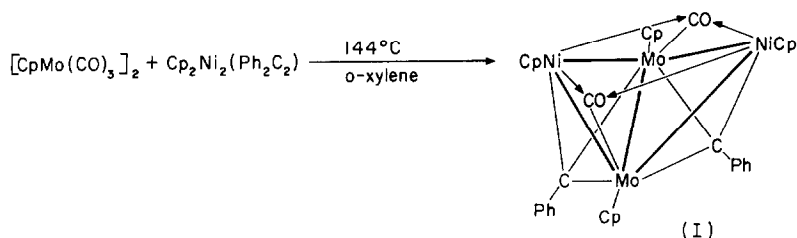
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## Introduction

Transformation of alkynes in the coordination sphere of transition metal atoms is usually accompanied by the formation of new M–H, M–C, C–H and C–C bonds [1]. This may occur with the rupture of the triple C≡C bonds [2] and formation of complexes with the bridging [3] or terminal [4] carbyne ligands. On the other hand, formation of the carbide heterometallic clusters as a result of rupture of the C≡O bond, *e.g.* in reactions with cobalt carbonyl [5] is also known. This article reports the rupture of the C≡C bond in the coordination sphere of a nickel–molybdenum-containing cluster and the simultaneous rupture of C≡C and C≡O bonds in the process of formation of a cobalt–molybdenum-containing cluster.

## Results and discussion

Refluxing of the tolan complex  $\text{Cp}_2\text{Ni}_2(\text{Ph}_2\text{C}_2)$  with  $[\text{CpMo}(\text{CO})_3]_2$  in *o*-xylene for 8 h results in the elimination of four CO groups and the formation of the complex  $\text{Cp}_4\text{Ni}_2\text{Mo}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CO})_2$  (I):



This has been isolated in the form of brown-black crystals, stable in air. In the IR spectra of cluster I, along with the absorption bands of the cyclopentadienyl rings and phenyl groups, stretching vibrations of the bridging CO groups ( $1775$ ,  $1810\text{ cm}^{-1}$ ) are also observed.

The structure of complex I has been solved by X-ray structural analysis (Fig. 1, Tables 1–3). Molecule I has a “butterfly” mixed-metal core with a dihedral angle of  $123^\circ$  between the planes of two similar  $\text{NiMo}_2$  triangles. Bond lengths Ni–Mo(1), Ni’–Mo(2) and Mo(1)–Mo(2) in the “butterfly” core are equal to  $2.664(2)$ ,  $2.665(2)$  and  $2.674(2)\text{ \AA}$  respectively. The core of the cluster is supplemented by  $\mu_3$ -bridging CPh groups located under each  $\text{NiMo}_2$  triangle (with mean bond lengths of Ni–C  $1.937(9)\text{ \AA}$  and Mo–C  $2.053(9)$  and  $2.088(9)\text{ \AA}$ ) and by two asymmetrically bonded  $\mu_3$ -CO groups which form short Mo–C bonds ( $1.96(4)$  and  $1.98(2)\text{ \AA}$ ) and elongated Ni–C bonds (mean  $2.48(1)\text{ \AA}$ ) with each  $\text{NiMoNi}'$  fragment in the cavity of the mixed-metal core.

In the  $^1\text{H}$  NMR spectrum of cluster I there are two sharp singlets corresponding to  $\eta^5\text{-C}_5\text{H}_5$  protons ( $\delta = 5.285$  and  $4.977\text{ ppm}$ ) and a complex multiplet ( $\delta = 6.78\text{--}7.32\text{ ppm}$ ) corresponding to phenyl rings. Formally I is the product of the splitting of the initial tolan nickel-containing compound into two carbyne  $\text{CpNi}\equiv\text{CPh}$  fragments and their bonding to the dimolybdenum fragment. Although the bis-alkyne-dimolybdenum  $\text{Cp}_2\text{Mo}_2(\text{CO})_2(\text{R}_2\text{C}_2)_2$  complex has not been described, a niobium analogue  $\text{Cp}_2\text{Nb}_2(\text{CO})_2(\text{Ph}_2\text{C}_2)_2$  containing a double Nb=Nb bond with a bond length of  $2.73\text{ \AA}$  is known [6]. On the other hand, the analogous rupture of

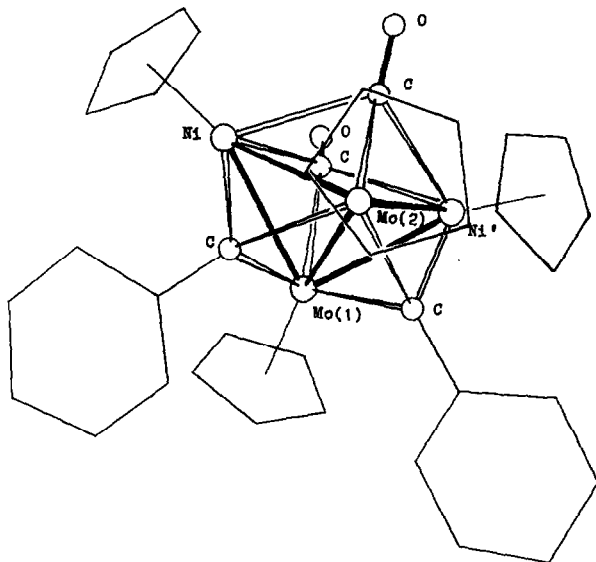


Fig. 1. The molecular structure of  $\text{Cp}_4\text{Ni}_2\text{Mo}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CO})_2$ .

Table 1

Atomic coordinates for  $\text{Cp}_4\text{Ni}_2\text{Mo}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CO})_2$  ( $\times 10^5$  for Ni and Mo,  $\times 10^4$  for O, C, H)

Atom	x	y	z
Mo(1)	17826(6)	42033(6)	0
Mo(2)	19959(6)	28242(6)	0
Ni	12426(8)	34145(8)	11328(10)
O(1)	433(7)	2369(7)	0
O(2)	209(13)	4183(13)	0
C(1)	976(10)	2654(10)	0
C(2)	768(22)	4071(23)	0
C(3)	2208(5)	3577(5)	851(5)
C(4)	2806(6)	3697(5)	1367(6)
C(5)	2729(8)	3967(10)	2139(8)
C(6)	3362(11)	4138(9)	2573(9)
C(7)	4007(7)	3988(8)	2296(9)
C(8)	4060(7)	3860(7)	1558(8)
C(9)	3477(6)	3712(7)	1106(7)
C(10)	4910(8)	2608(7)	0
C(11)	4806(6)	2201(6)	683(7)
C(12)	4631(5)	1542(6)	419(8)
C(13)	3030(9)	2226(8)	0
C(14)	2662(8)	1994(7)	663(7)
C(15)	2112(7)	1658(6)	411(9)
C(16)	237(8)	3235(12)	1537(13)
C(19)	653(10)	2686(12)	1758(11)
C(17)	1187(11)	2973(11)	2332(10)
C(18)	938(13)	3631(10)	2315(12)
C(20)	578(12)	4038(11)	1815(17)

Table 2

Bond lengths (Å) in  $\text{Cp}_4\text{Ni}_2\text{Mo}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CO})_2$ 

Mo(1)–Mo(2)	2.674(2)	O(1)–C(1)	1.17(2)
Mo(1)–Ni	2.664(2)	O(2)–C(2)	1.09(5)
Mo(1)–C(2)	1.96(4)	C(3)–C(4)	1.48(1)
Mo(1)–C(3)	2.053(9)	C(4)–C(5)	1.42(2)
Mo(1)–C(10)	2.32(1)	C(4)–C(9)	1.36(2)
Mo(1)–C(11)	2.37(1)	C(5)–C(6)	1.46(2)
Mo(1)–C(12)	2.39(1)	C(6)–C(7)	1.35(2)
Mo(2)–Ni	2.665(2)	C(7)–C(8)	1.29(2)
Mo(2)–C(1)	1.98(2)	C(8)–C(9)	1.39(2)
Mo(2)–C(3)	2.088(9)	C(10)–C(11)	1.42(1)
Mo(2)–C(13)	2.29(2)	C(11)–C(12)	1.38(2)
Mo(2)–C(14)	2.33(1)	C(12)–C(12)	1.43(2)
Mo(2)–C(15)	2.35(1)	C(13)–C(14)	1.41(2)
Ni–C(1)	2.48(1)	C(14)–C(15)	1.31(2)
Ni–C(2)	2.48(3)	C(15)–C(15)	1.41(2)
Ni–C(3)	1.937(9)	C(16)–C(19)	1.37(3)
Ni–C(16)	2.08(2)	C(16)–C(20)	1.74(3)
Ni–C(17)	2.22(2)	C(19)–C(17)	1.52(3)
Ni–C(18)	2.14(2)	C(17)–C(18)	1.35(3)
Ni–C(19)	2.09(2)	C(18)–C(20)	1.35(3)
Ni–C(20)	2.10(2)		

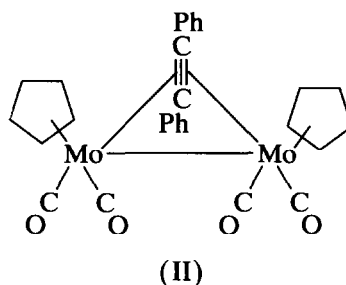
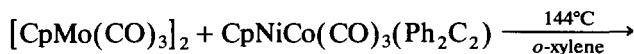
Table 3

Bond angles (deg) in  $\text{Cp}_4\text{Ni}_2\text{Mo}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CO})_2$ 

Mo(2)–Mo(1)–Ni	59.91(4)	Mo(2)–Ni–C(3)	51.0(3)
Mo(2)–Mo(1)–Ni	59.91(4)	C(1)–Ni–C(2)	67.3(9)
Mo(2)–Mo(1)–C(2)	91.1(3)	C(1)–Ni–C(3)	95.6(5)
Mo(2)–Mo(1)–C(3)	50.3(3)	C(2)–Ni–C(3)	94.3(9)
Mo(2)–Mo(1)–C(3)	50.3(3)	Mo(2)–C(1)–Ni	72.5(5)
Ni–Mo(1)–Ni	93.11(6)	Mo(2)–C(1)–Ni	72.5(5)
Ni–Mo(1)–C(2)	63.0(1)	Mo(2)–C(1)–O(1)	162.0(1)
Ni–Mo(1)–C(3)	46.3(3)	Ni–C(1)–Ni	102.8(6)
Ni–Mo(1)–C(3)	109.7(3)	Ni–C(1)–O(1)	117.0(1)
C(2)–Mo(1)–C(3)	109.0(1)	Mo(1)–C(2)–Ni	73(1)
C(2)–Mo(1)–C(3)	109.0(1)	Mo(1)–C(2)–Ni	73(1)
C(3)–Mo(1)–C(3)	90.1(4)	Mo(1)–C(2)–O(2)	161.0(3)
Mo(1)–Mo(2)–Ni	59.85(4)	Ni–C(2)–Ni	102(1)
Mo(1)–Mo(2)–Ni	59.85(4)	Ni–C(2)–O(2)	117(3)
Mo(1)–Mo(2)–C(1)	90.7(5)	Mo(1)–C(3)–Mo(2)	80.5(3)
Mo(1)–Mo(2)–C(3)	49.2(3)	Mo(1)–C(3)–Ni	83.7(4)
Mo(1)–Mo(2)–C(3)	49.2(3)	Mo(2)–C(3)–Ni	82.9(4)
Ni–Mo(2)–Ni	93.05(6)	C(1)–Mo(2)–C(3)	107.8(5)
Ni–Mo(2)–C(1)	62.3(5)	C(1)–Mo(2)–C(3)	107.8(5)
Ni–Mo(2)–C(3)	46.1(3)	C(3)–Mo(2)–C(3)	88.2(4)
Ni–Mo(2)–C(3)	108.5(3)	Mo(1)–Ni–Mo(2)	60.24(4)
Mo(1)–Ni–C(1)	81.2(4)	Mo(1)–Ni–C(2)	44.7(8)
Mo(1)–Ni–C(3)	50.0(3)	Mo(2)–Ni–C(1)	45.2(4)
Mo(2)–Ni–C(2)	81.3(8)		

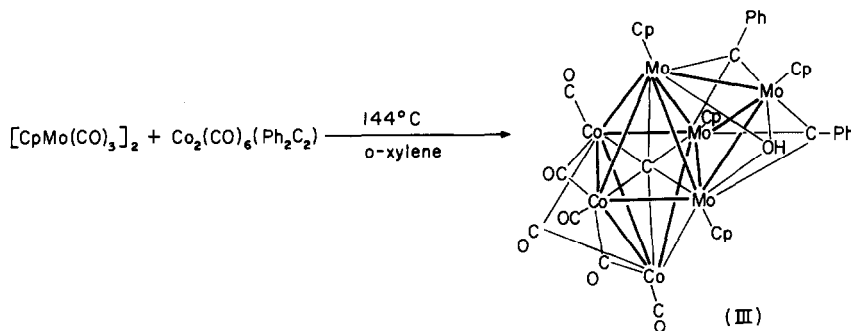
the C=C bond has been observed previously in the case of the tungsten–osmium tetrahedral cluster  $\text{CpWOS}_3(\text{CO})_{10}(\mu_3\text{-C}_2\text{R}_2)(\text{H})$ , where  $\text{R} = p\text{-tolyl}$  [7].

We then made an attempt to use a mixed nickel–cobalt tolan complex  $\text{CpNiCo}(\text{CO})_3(\text{Ph}_2\text{C}_2)$  in the reaction with  $[\text{CpMo}(\text{CO})_3]_2$ ; however, this has only led to transmetalation with the formation of the known binuclear molybdenum–tolan complex  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{Ph}_2\text{C}_2)$  (II) [8].



Complex II was identified by means of X-ray structural analysis which confirmed the results of the earlier structural investigations [8].

Finally, interaction under the same conditions of  $\text{Co}_2(\text{CO})_6(\text{Ph}_2\text{C}_2)$  with  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  leads to the formation of the seven-nuclear cluster  $\text{Cp}_4\text{Mo}_4(\mu_3\text{-CPh})_2 \cdot (\mu_3\text{-OH})(\mu_6\text{-C})\text{Co}_3(\mu\text{-CO})_3(\text{CO})_3$  (III):



Cluster III has been isolated in the form of brown-black diamagnetic crystals, stable in air. Characteristic stretching vibration bands of the bridging ( $1800$  and  $1825\text{ cm}^{-1}$ ) and terminal ( $1940\text{--}2015\text{ cm}^{-1}$ ) CO groups and vibration bands of the cyclopentadienyl  $\text{C}_5\text{H}_5$  rings and phenyl groups are present in the IR spectrum. The structure of III has been solved by X-ray structural analysis (Fig. 2, Tables 4–6). Cluster III contains a tetrahedral fragment  $\text{Cp}_4\text{Mo}_4$  with the following bond lengths:  $\text{Mo}(1)\text{--}\text{Mo}(2)$   $2.792(5)$ ,  $\text{Mo}(1)\text{--}\text{Mo}(3)$   $2.939(4)$ ,  $\text{Mo}(2)\text{--}\text{Mo}(3)$   $2.761(4)$  and  $\text{Mo}(3)\text{--}\text{Mo}(3a)$   $2.930(3)$  Å. Two faces of this tetrahedron are coordinated by  $\mu_3\text{-CPh}$  ( $\text{Mo}\text{--}\text{C}$   $2.09(3)\text{--}2.14(3)$  Å) ligands and the third face has a bridging  $\mu_3\text{-OH}$  ( $\text{Mo}\text{--}\text{O}$   $1.96(3)\text{--}2.05(2)$  Å) ligand. Over the fourth face of the tetrahedron there is a carbide carbon atom and the  $\text{Co}_3(\mu\text{-CO})_3(\text{CO})_3$  ( $\text{Co}\text{--}\text{Co}$   $2.463(3)$ ,  $\text{Co}\text{--}\text{C}$   $1.94(3)$  Å) triangle which forms, with the  $\text{Mo}_3$  face, a  $\mu_6\text{-C}$  centred octahedron

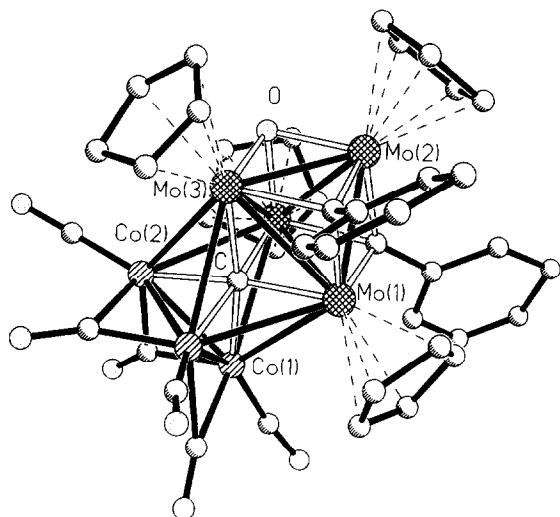


Fig. 2. The molecular structure of  $\text{Cp}_4\text{Mo}_4(\mu_3\text{-OH})(\mu_3\text{-CPh})_2(\mu_6\text{-C})\text{Co}_3(\mu\text{-CO})_3(\text{CO})_3$ .

$\text{Mo}_3\text{Co}_3(\mu_6\text{-C})$  with Mo–Co distances of 2.909(6)–2.946(5) and Mo–C distances of 2.03(3)–2.06(3) Å.

The hydrogen atom of the OH group has not been located; however, its existence has been confirmed by the singlet signal in the  $^1\text{H}$  NMR spectrum ( $\delta = 15.16$  ppm relative to tetramethylsilane).

The mechanism of cluster III formation is not yet clear; however, the tetramolybdenum fragment may be anticipated to be formed by the original transmetallation of the cobalt–tolan containing complex with formation of the well-known complex II, which then interacts with  $[\text{CpMo}(\text{CO})_2]_2$ , presumably in accordance with the scheme analogous to the synthesis of cluster I occurring with rupture of the  $\text{C}\equiv\text{C}$  bond. On the other hand the split  $\text{Co}_2(\text{CO})_6$  fragments form a triangular fragment  $\text{Co}_3(\text{CO})_9(\mu_3\text{-CO})$ . This may be bonded to the molybdenum atom *via* the isocarbonyl group, analogous to the previously described interaction of  $(\text{CpCrOCMe}_3)_2$  and  $\text{Co}_2(\text{CO})_8$ , resulting in a cluster in which fragment  $\text{Co}_3(\text{CO})_9$  is bonded to one of the chromium atoms of the dimer  $(\text{CpCrOCMe}_3)_2$  *via* the isocarbonyl group with a considerably loosened C–O bond (1.247(6) Å) [9]. Then, in the system  $\text{Cp}_4\text{Mo}_4\text{-OCCo}_3$ , rupture of the  $\text{C}\equiv\text{O}$  bond with formation of a  $\mu_6$ -carbide atom and a  $\mu_3$ -OH group under the face of the decarbonylated tetrahedron  $\text{Mo}_4$  takes place. It is noteworthy that this rupture of the two-electron-donating molecule CO increases the number of electrons which are introduced into the core to 9 (4 electrons of the C carbide atom, 5 electrons of the hydroxide bridge). Thus the electron deficit which appears on decarbonylation of the fragments is compensated for.

## Experimental

All operations concerning the synthesis and isolation of the products were carried out in an argon flow. The hydrocarbon solvents were purified by distillation

Table 4

Atomic coordinates for  $\text{Cp}_4\text{Mo}_4(\mu_3\text{-OH})(\mu_3\text{-CPh})_2(\mu_6\text{-C})\text{Co}_3(\mu\text{-CO})_3(\text{CO})_3$  ( $\times 10^4$  for Mo and Co,  $\times 10^3$  for O, C, H)

Atom	x	y	z
Mo(1)	728(4)	2801(2)	2500
Mo(2)	-1861(4)	3262(2)	2500
Mo(3)	-1466(3)	2225(1)	1863(1)
Co(1)	1141(4)	1625(2)	1964(2)
Co(2)	-703(7)	1150(3)	2500
O	-277(3)	248(1)	250
O(1)	38(3)	38(1)	156(1)
O(2)	-271(4)	23(2)	250
O(3)	357(4)	118(2)	250
O(4)	288(2)	167(1)	95(1)
C	-14(4)	198(2)	250
C(1)	34(3)	82(1)	185(1)
C(2)	-179(5)	56(2)	250
C(3)	255(5)	142(2)	250
C(4)	220(3)	168(1)	134(1)
CA(1)	-49(3)	308(1)	184(1)
CA(2)	2(3)	340(1)	126(1)
CA(3)	-14(3)	400(1)	120(1)
CA(4)	24(3)	433(1)	66(1)
CA(5)	80(3)	395(2)	23(1)
CA(6)	99(3)	331(1)	35(1)
CA(7)	61(3)	303(1)	84(1)
C(11)	311(5)	275(2)	250
C(12)	275(3)	308(1)	201(1)
C(13)	207(3)	360(1)	222(1)
C(21)	-216(5)	433(2)	250
C(22)	-287(3)	405(1)	200(1)
C(23)	-391(3)	368(1)	220(1)
C(31)	-219(3)	240(1)	91(1)
C(32)	-338(3)	236(1)	123(1)
C(33)	-339(3)	179(1)	146(1)
C(34)	-221(3)	142(1)	123(2)
C(35)	-149(3)	193(1)	88(1)
CB(1)	535(5)	958(2)	91(2)
CB(2)	381(4)	964(2)	58(2)
CB(3)	346(4)	901(2)	20(2)
CB(4)	422(4)	855(2)	19(2)
CB(5)	548(4)	851(2)	43(2)
CB(6)	579(4)	895(2)	79(2)

over a suspension of sodium in an argon flow. Complexes  $[\text{CpMo}(\text{CO})_3]_2$ ,  $\text{Cp}_2\text{Ni}_2(\text{Ph}_2\text{C}_2)$ ,  $\text{CpNiCo}(\text{CO})_3(\text{Ph}_2\text{C}_2)$  and  $\text{Co}_2(\text{CO})_6(\text{Ph}_2\text{C}_2)$  were synthesized in accordance with well-known techniques [10–13]. IR spectra were measured with a Specord 75 IR instrument in KBr pellets. X-Ray crystal data for complexes I and III were obtained with a four-circular automatic diffractometer, Hilger and Watts ( $\lambda(\text{Mo-K}_\alpha)$ ,  $\theta$ - $2\theta$  scanning) and for complexes II with the Syntex P2<sub>1</sub> ( $\lambda(\text{Mo-K}_\alpha)$ ,  $\theta$ - $2\theta$  scanning,  $T = -100^\circ\text{C}$ ). Crystal data are summarized in Table 7. Structures I and III were solved by direct methods and refined in an anisotropic full-matrix

Table 5

Bond lengths (Å) in  $\text{Cp}_4\text{Mo}_4(\mu_3\text{-OH})(\mu_3\text{-CPh})_2(\mu_6\text{-C})\text{Co}_3(\mu\text{-CO})_3(\text{CO})_3$ 

Mo(1)–Mo(2)	2.792(5)	Mo(2)–O	1.96(3)
Mo(1)–Mo(3)	2.939(4)	Mo(3)–O	2.05(2)
Mo(1)–Co(1)	2.923(5)	O(1)–C(1)	1.19(4)
Mo(2)–Mo(3)	2.761(4)	O(2)–C(2)	1.17(6)
Mo(3)–Mo(3a)	2.930(3)	O(3)–C(3)	1.16(6)
Mo(3)–Co(1a)	2.946(5)	O(4)–C(4)	1.14(4)
Mo(3)–Co(2)	2.909(6)	CA(1)–CA(2)	1.59(4)
Co(1)–Co(1a)	2.464(6)	CA(2)–CA(3)	1.35(4)
Co(1)–Co(2)	2.462(7)	CA(2)–CA(7)	1.41(4)
Mo(1)–C	2.03(3)	CA(3)–CA(4)	1.49(4)
Mo(1)–CA(1)	2.05(3)	CA(4)–CA(5)	1.41(4)
Mo(2)–CA(1)	2.09(3)	CA(5)–CA(6)	1.47(4)
Mo(3)–C	2.06(3)	CA(6)–CA(7)	1.35(4)
Mo(3)–CA(1)	2.14(3)		
Co(1)–C	1.94(3)		
Co(2)–C	1.93(3)		
Co(1)–C(1)	1.97(3)		
Co(2)–C(1)	1.96(3)		
Co(1)–C(3)	1.93(4)		
Co(1a)–C(4)	1.79(3)		
Co(2)–C(2)	1.70(5)		

approximation for non-hydrogen atoms. All the calculations were performed with an Eclipse S/200 computer using the INEXTL program package [14].

#### $\text{Cp}_4\text{Ni}_2\text{Mo}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CO})_2$ (I)

$\text{Cp}_2\text{Mo}_2(\text{CO})_6$  (1.38 g, 2.82 mmol) in 20 ml of *o*-xylene was added to a solution of 1.2 g (2.82 mmol) of  $\text{Cp}_2\text{Ni}_2(\text{Ph}_2\text{C}_2)$  in 30 ml of *o*-xylene. The red-brown solution thus obtained was refluxed for 8 h in an argon flow; its colour gradually changed to dark brown. The solution was then concentrated at 60°C/0.1 Torr to a volume of 10 ml and chromatographed on an  $\text{Al}_2\text{O}_3$  column (5 × 20 cm), the dark-brown zone being eluted by benzene. The dark-brown solution thus obtained was concentrated at 60°C/0.1 Torr to a volume of 15 ml and stored for a day at 5°C. The black-brown prisms precipitated were isolated by decantation of the solution, washed in acetone and dried under vacuum. Yield: 0.39 g (17%). IR spectrum ( $\nu$ ): 670w, 690m, 800m, 1010w, 1050m, 1775s, 1810s  $\text{cm}^{-1}$ .

#### $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{Ph}_2\text{C}_2)$ (II)

$\text{Cp}_2\text{Mo}_2(\text{CO})_6$  (0.5 g, 1.15 mmol) in 20 ml of *o*-xylene was added to a solution of 0.5 g (1.15 mmol) of  $\text{CpNiCo}(\text{CO})_3(\text{Ph}_2\text{C}_2)$  in 30 ml of *o*-xylene; the mixture was refluxed for 6 h in an argon flow; the colour of the solution gradually changed from red-brown to dark brown. The solution was then concentrated at 60°C/0.1 Torr to a volume of 10 ml, and the residue was chromatographed on an  $\text{SiO}_2$  column (5 × 20 cm), the red-brown zone being eluted by a hexane/benzene (7:3) mixture. The red-brown solution thus obtained was concentrated at 60°C/0.1 Torr to a volume of 10 ml and stored for 24 h at –5°C. The precipitated red-brown crystals were isolated by decantation, washed with pentane and dried under vacuum.



Table 6

Bond angles (deg) in  $\text{Cp}_4\text{Mo}_4(\mu_3\text{-OH})(\mu_3\text{-CPh})_2(\mu_6\text{-C})\text{Co}_3(\mu\text{-CO})_3(\text{CO})_3$ 

Mo(1)–Mo(2)–Mo(3)	63.9(1)	Mo(3)–Mo(3a)–Co(1)	85.5(1)
Mo(1)–Mo(2)–O	96.3(7)	Mo(3)–Mo(3a)–Co(2)	59.8(1)
Mo(1)–Mo(3)–Mo(2)	58.6(1)	Mo(3)–Mo(3a)–O	44.3(6)
Mo(1)–Mo(3)–Mo(3a)	60.1(9)	Mo(3)–Mo(3a)–C	44.5(8)
Mo(1)–Mo(3a)–Co(1)	59.6(1)	Mo(3)–Co(1)–Co(1a)	94.5(2)
Mo(1)–Mo(3)–Co(2)	84.9(1)	Mo(3)–Co(1)–Co(2)	64.4(2)
Mo(1)–Mo(3)–O	89.9(6)	Mo(3a)–Co(1)–C	44.0(8)
Mo(1)–Mo(3)–C	43.6(8)	Mo(3)–Co(2)–Co(1)	65.9(2)
Mo(1)–Co(1)–Mo(3a)	60.1(1)	Mo(3)–Co(2)–Co(1a)	95.5(2)
Mo(1)–Co(1)–Co(1a)	65.1(1)	Mo(3)–Co(2)–C	44.8(8)
Mo(1)–Co(1)–Co(2)	93.9(2)	Mo(3)–Co(2)–Mo(3a)	60.5(1)
Mo(1)–Co(1)–C	43.7(8)	Mo(3)–O–Mo(3a)	91.4(9)
Mo(1)–C–Mo(3)	92(1)	Mo(3)–C–Mo(3a)	91(1)
Mo(1)–C–Co(1)	95(1)	Mo(3)–C–Co(1a)	95(1)
Mo(1)–C–Co(2)	172(2)	Mo(3)–C–Co(1)	171(2)
Mo(2)–Mo(1)–Mo(3)	57.5(1)	Mo(3)–C–Co(2)	94(1)
Mo(2)–Mo(1)–Co(1)	117.4(1)	Co(1)–Mo(1)–Co(1a)	49.9(1)
Mo(2)–Mo(1)–C	86.2(8)	Co(1)–Mo(1)–C	41.5(8)
Mo(2)–Mo(3)–Mo(3a)	57.96(9)	Co(1)–Mo(3a)–Co(2)	49.7(1)
Mo(2)–Mo(3)–Co(2)	117.3(2)	Co(1)–Mo(3a)–O	129.7(6)
Mo(2)–Mo(3)–O	45.0(6)	Co(1)–Mo(3a)–C	41.1(8)
Mo(2)–Mo(3)–C	86.5(8)	Co(1)–Co(1a)–Co(2)	60.0(2)
Mo(2)–Mo(3a)–Co(1)	117.7(1)	Co(1)–Co(1a)–C	50.7(8)
Mo(2)–O–Mo(3)	87.2(9)	Co(1)–Co(2)–Co(1a)	60.1(2)
Mo(3)–Mo(1)–Mo(3a)	59.81(9)	Co(1)–Co(2)–C	50.8(8)
Mo(3)–Mo(1)–Co(1)	60.3(1)	Co(1)–C–Co(1a)	79(1)
Mo(3)–Mo(1)–Co(1a)	85.7(1)	Co(1)–C–Co(2)	79(1)
Mo(3)–Mo(1)–C	44.4(8)	Co(2)–Mo(3)–O	92.3(6)
Mo(3)–Mo(2)–Mo(3a)	64.1(1)	Co(2)–Mo(3)–C	41.5(8)
Mo(3)–Mo(2)–O	47.8(6)	Co(2)–Co(1)–C	50.3(8)
		O–Mo(3)–C	88.8(9)

Table 7

Crystal data for  $\text{Cp}_4\text{Ni}_2\text{Mo}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CO})_2$  (I) and  $\text{Cp}_4\text{Mo}_4(\mu_3\text{-OH})(\mu_3\text{-CPh})_2(\mu_6\text{-C})\text{Co}_3(\mu\text{-CO})_3(\text{CO})_3$  (III)

	I	III
Crystal system	Tetrahedral	Rhombohedral
Space group	$I4/m$	$Pbcm$
$a$ (Å)	19.164(1)	10.031(2)
$b$ (Å)	19.164(1)	22.265(4)
$c$ (Å)	17.074(8)	236001(2)
$V$ (Å <sup>3</sup> )	6270.6	5137.4
$Z$	4 <sup>a</sup>	8
$2\theta$ (°)	56	56
Number of reflections measured	5320	2856
Number of reflections with $I > 3\sigma$ included in refinement	2719	1275
$R_1$	0.070	0.097
$R_w$	0.071	0.085

<sup>a</sup> The molecule is located in the crystallographic plane  $\text{Cp}_4\text{Ni}_2\text{Mo}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CO})_2$  (I).

Yield: 0.23 g (33.5%). IR spectrum ( $\nu$ ): 700w, 765m, 810m, 1010m, 1585w, 1830s, 1890s, 1900vs, 1960s  $\text{cm}^{-1}$ .

*Cp<sub>4</sub>Mo<sub>2</sub>( $\mu_3$ -OH)( $\mu_3$ -CPh)<sub>2</sub>( $\mu_6$ -C)Co<sub>3</sub>( $\mu$ -CO)<sub>3</sub>(CO)<sub>3</sub> (III)*

Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> (0.5 g, 1.02 mmol) in 20 ml of *o*-xylene was added to a solution of 0.53 g (1.14 mmol) of Co<sub>2</sub>(CO)<sub>6</sub>(Ph<sub>2</sub>C<sub>2</sub>) in 30 ml of *o*-xylene; the cherry-red solution thus obtained was refluxed for 10 h in an argon flow; the colour of the solution gradually changed to dark brown. The dark black-brown crystals precipitated were isolated from the solution by decantation, washed in pentane and dried under vacuum. The yield was 0.23 g (25.7%). IR spectrum ( $\nu$ ): 700m, 743m, 815s, 1010m, 1800m, 1800vs, 1825s, 1940vs, 1970vs, 2015s  $\text{cm}^{-1}$ .

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