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Journal of Organometallic Chemistry 659 (2002) 142–150

Journal
of Organo
metallic
Chemistry

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Rational synthesis of tricobalt-molybdenum and -tungsten butterfly clusters with alkyne ligands

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Received 16 June 2002; accepted 15 July 2002

Abstract

The heterometallic alkyne complexes $[\text{CoM}(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_5\text{Cp}]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}, \text{CO}_2\text{Et}$; $\text{R}^1 = \text{H}, \text{R}^2 = \text{CO}_2\text{Me}$) react with dicobalt octacarbonyl in refluxing toluene to give the 60-electron tetranuclear clusters $[\text{Co}_3\text{M}(\mu_4\text{-R}^1\text{C}_2\text{R}^2)(\text{CO})_9\text{Cp}]$ in moderate to good yields. The clusters consist of a butterfly-type metal core in which the molybdenum (or tungsten) atom occupies a wing-tip position, as shown by X-ray analysis of three of the complexes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Tungsten; Alkyne; Cluster

1. Introduction

The rational synthesis of mixed-metal clusters remains a pertinent objective in modern organometallic chemistry. We recently showed that the reaction of the dimolybdenum alkyne complexes $[\text{Mo}_2(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_4\text{Cp}_2]$ (**1**) with dicobalt octacarbonyl in refluxing toluene provided a rational, rapid and efficient route to the 60-electron tetranuclear clusters $[\text{Co}_2\text{Mo}_2(\mu_4\text{-R}^1\text{C}_2\text{R}^2)(\mu\text{-CO})_4(\text{CO})_4\text{Cp}_2]$ (**2**) (Scheme 1) [1]. These clusters contain a butterfly metal core in which the two molybdenum atoms occupy the wing-tip positions and the two cobalt atoms the hinge. Prior to our work, only one of these complexes had been prepared previously, as a low yield by-product in a metal exchange reaction [2], though several analogous compounds have appeared since [3]. Examples of related clusters involving the other elements of Groups 6 and 9 have also been reported [4]. Among these, Chetcuti described the opening of a Co–Mo bond in tetrahedral $[\text{Co}_3\text{Mo}(\text{CO})_{11}(\eta\text{-C}_5\text{H}_4\text{Me})]$ with phenylacetylene to give the tricobalt-molybdenum butterfly cluster $[\text{Co}_3\text{Mo}(\mu_4\text{-HC}_2\text{Ph})(\text{CO})_9(\eta\text{-C}_5\text{H}_4\text{Me})]$ in 17% yield [5]. Since a simplistic view of the reaction

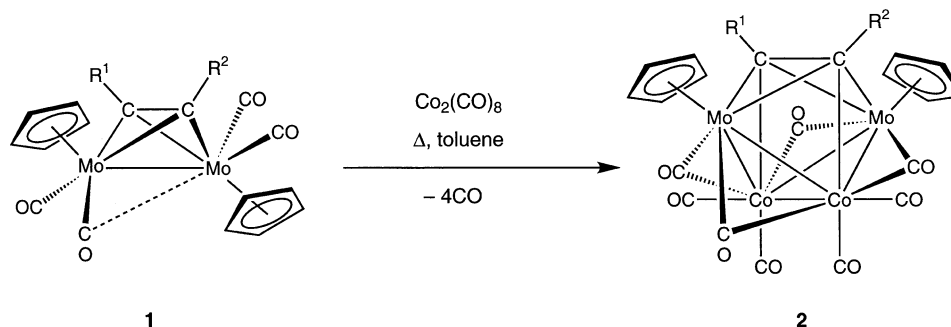
leading to **2** would involve the insertion of the dicobalt unit into the Mo–Mo bond, we were prompted to extend this strategy to the mixed-metal alkyne derivatives $[\text{CoM}(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_5\text{Cp}]$ ($\text{M} = \text{Mo}, \text{W}$) in the hope that it would provide a rational, high-yield synthesis of the corresponding Co_3M species.

2. Results and discussion

The starting complexes for this work, $[\text{CoM}(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_5\text{Cp}]$ ($\text{M} = \text{Mo}$: (**3a**) $\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$; (**3b**) $\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Et}$; (**3c**) $\text{R}^1 = \text{H}, \text{R}^2 = \text{CO}_2\text{Me}$) can be prepared in two ways. The first is through the reaction of alkynes with $[\text{CoMo}(\text{CO})_7\text{Cp}]$ [6,7], which itself can be prepared by photolysis of $[\text{Mo}_2(\text{CO})_6\text{Cp}_2]$ with $[\text{Co}_2(\text{CO})_8]$ [8]. We resorted to the second method, namely the isolobal displacement reaction of $[\text{Co}_2(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_6]$ with $\text{Na}[\text{Mo}(\text{CO})_3\text{Cp}]$, which is less economical in that half of the original cobalt is lost as $[\text{Co}(\text{CO})_4]^-$ but does not require photolysis [9]. After some variation of the conditions, we found that **3a–c** could be isolated in yields of 50–70% by heating the two reagents to reflux in THF solution for 30 min or by stirring at room temperature for 48 h; a typical procedure is given in Section 4 (Scheme 2). The tungsten analogues ($\text{M} = \text{W}$: (**3d**) $\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$; (**3e**) $\text{R}^1 =$

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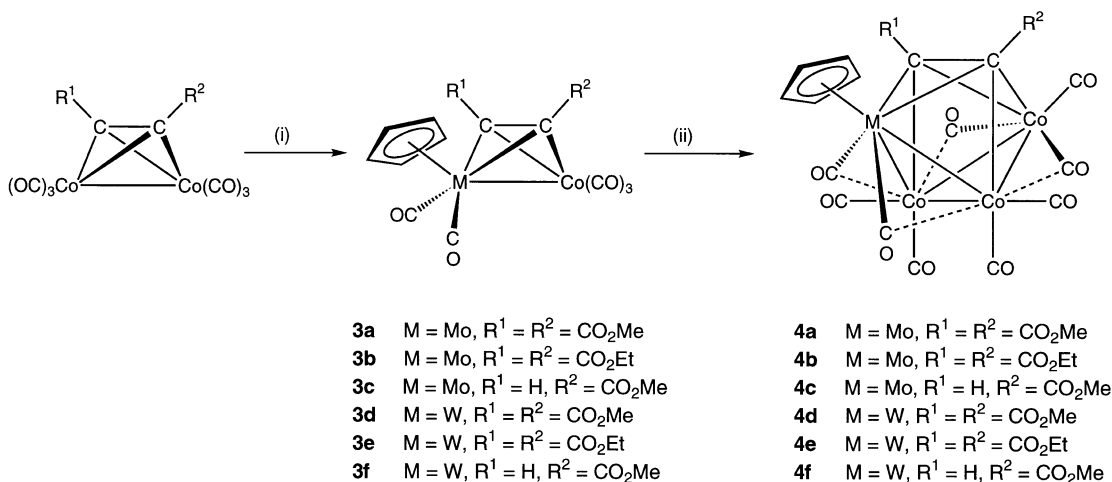
Scheme 1. Synthesis of $[\text{Co}_2\text{Mo}_2(\mu_4\text{-R}^1\text{C}_2\text{R}^2)(\mu\text{-CO})_4(\text{CO})_4\text{Cp}_2]$ [1].

$\text{R}^2 = \text{CO}_2\text{Et}$; (**3f**) $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CO}_2\text{Me}$ [6,7] were prepared in a similar manner from $\text{Na}[\text{W}(\text{CO})_3\text{Cp}]$. In the reactions leading to **3a**, **3d** and **3e**, all derived from disubstituted alkynes, small amounts of the dimetal-cyclopentadiene complexes $[\text{CoM}(\mu\text{-C}_4\text{R}_4)(\text{CO})_4\text{Cp}]$ ($\text{R} = \text{CO}_2\text{Me}$, CO_2Et) were also isolated, presumably arising through the reaction of the major products with free alkyne liberated by decomposition. In the case of **3f**, derived from the terminal alkyne, the only by-product was the alkylidyne cluster $[\text{Co}_2\text{W}(\mu_3\text{-CCH}_2\text{CO}_2\text{Me})(\text{CO})_8\text{Cp}]$. This may arise through addition of $[\text{HCo}(\text{CO})_4]$ (formed by protonation of $[\text{Co}(\text{CO})_4]^-$ on work-up) to the product [10].

Treatment of **3a** with one equivalent of $[\text{Co}_2(\text{CO})_8]$ in toluene solution at reflux for 1 h caused a colour change from orange-red to black. Column chromatography of the mixture gave a single product in 66% yield as a dark green–black zone. Identification of this compound as $[\text{Co}_3\text{Mo}(\mu_4\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{CO})_9\text{Cp}]$ (**4a**) followed from its IR spectrum, which showed peaks due to terminal and bridging carbonyls; its $^1\text{H-NMR}$ spectrum, which comprised two singlets in a ratio of 5:6 due to Cp and methyl protons, respectively; and its mass spectrum, which showed a molecular ion envelope centred on m/z

733. The $^{13}\text{C-NMR}$ spectrum was also in accord with the proposed structure. The related clusters **4b** ($\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Et}$) and **4c** ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CO}_2\text{Me}$) were prepared in 78 and 65% yields, respectively, in the same way; the $^1\text{H-NMR}$ spectrum of the latter showed a peak at δ 8.65 due to the alkyne proton, an appropriate value for an alkyne bridging a butterfly metal core (cf δ 8.30 for the Co_2Mo_2 analogue [1]). All three clusters are relatively air-stable and soluble in polar solvents but insoluble in saturated hydrocarbons. The tricobalt-tungsten clusters **4d–4f** were prepared in the same manner in somewhat lower yields. Their spectroscopic data mirrored those of the Mo analogues.

We noted two features in the $^{13}\text{C-NMR}$ spectra of the methyl propiolate complexes **4c** and **4f** that were different in comparison with the other clusters. Firstly, two sharp peaks were observed in the M–CO region whereas only one was seen for the other compounds. This may be a consequence of the inherently reduced symmetry caused by the unsymmetrical alkyne, and implies that, in solution at least, two carbonyl ligands are largely localised on M and are not subject to the broadening observed for those bonded to Co. Secondly, the signal due to the CH terminus of the alkyne could

Scheme 2. Synthesis of the new mixed metal clusters. Reagents and conditions: (i) $\text{Na}[\text{M}(\text{CO})_3\text{Cp}]$, THF, 30 min reflux or 2 days at room temperature (ii) $[\text{Co}_2(\text{CO})_8]$, toluene, reflux, 1 h.

not be observed, despite the fact that one would expect it to be more intense due to NOE effects (the assignment of all signals was checked by recording a ^1H -coupled spectrum). It seems unlikely that it is coincident with another peak in both compounds and we can only assume that it is broadened into the baseline by the quadrupolar Co nuclei. However, these inconsistencies led us to determine the molecular structures of both compounds (see below) to ensure that our structural assignments were correct.

Given the successful production of the Mo_2Co_2 clusters **2** from the dimolybdenum precursor **1**, and the formation of Co_3M clusters **4** from the CoM precursor **3**, we also briefly investigated the synthesis of the known homometallic complexes $[\text{Co}_4(\mu_4\text{-R}^1\text{C}_2\text{R}^2)(\text{CO})_{10}]$ (**5**) ($\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$, CO_2Et ; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CO}_2\text{Me}$) from $[\text{Co}_2(\mu\text{-R}^1\text{C}_2\text{R}^2)(\text{CO})_6]$ and $[\text{Co}_2(\text{CO})_8]$. However, this proved only partially successful: in refluxing toluene decomposition of both reagents and formation of a metal mirror occurred, though a low yield of **5** was obtained, and in refluxing light petroleum or heptane with a slight excess of dicobalt octacarbonyl, the yields of **5** were still only in the range 9–28%. Complexes of this type have been known for many years, and have generally been prepared by heating $[\text{Co}_2(\text{CO})_8]$ with alkynes or from preformed $[\text{Co}_4(\text{CO})_{12}]$ and alkynes [11]. The route described here does not appear to offer a viable alternative as the thermal decomposition of the reagents evidently predominates over the cluster formation reaction.

2.1. Crystal structure determinations

In order to compare the structural parameters of the new Co_3M clusters with the Co_2Mo_2 compounds prepared earlier, we determined the structures of three examples. Crystals of **4a** suitable for X-ray diffraction were grown by diffusion of light petroleum into a dichloromethane solution at 4 °C. The molecular structure is shown in Fig. 1, with selected bond lengths and angles collected in Table 1. As expected by analogy with the structure of **2** (the structure of which was determined for the complex with $\text{R}^1 = \text{R}^2 = \text{Me}$), the cluster consists of a butterfly of metal atoms in which the Mo atom occupies one of the wingtips. The two Mo–Co bonds are unequal in length, with Mo(1)–Co(1) [2.7378(7) Å] being longer than the CO-bridged Mo(1)–Co(3) [2.6467(7) Å]; the latter itself is slightly shorter than the average Mo–Co distance in **2** (2.689 Å) where all the bonds were bridged by CO ligands. In contrast the Co(1)–Co(2) and Co(2)–Co(3) distances are very similar, whereas the hinge bond, Co(1)–Co(3), is longer [2.5370(8) Å] and similar to the 2.5431(12) Å found in **2**. The alkyne ligand is bonded in the μ_4, η^2 -manner found in many related butterfly clusters [12].

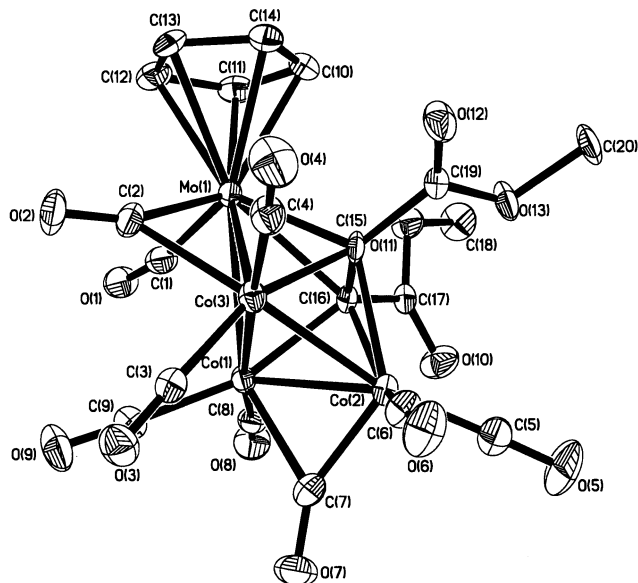


Fig. 1. Molecular structure of $[\text{Co}_3\text{Mo}(\mu_4\text{-MeO}_2\text{CC}_2\text{CO}_2\text{-Me})(\text{CO})_9\text{Cp}]$ (**4a**) in the crystal showing the atomic numbering scheme.

Table 1
Selected bond lengths (Å) and angles (°) for complex **4a**

Bond lengths			
Mo(1)–C(1)	2.003(5)	Mo(1)–C(2)	2.005(5)
Mo(1)–C(15)	2.217(4)	Mo(1)–C(16)	2.327(4)
Mo(1)–Co(3)	2.6467(7)	Mo(1)–Co(1)	2.7378(7)
Co(1)–C(9)	1.789(5)	Co(1)–C(8)	1.816(4)
Co(1)–C(16)	1.943(4)	Co(1)–C(7)	2.045(5)
Co(1)–Co(2)	2.4525(8)	Co(1)–Co(3)	2.5370(8)
Co(2)–C(6)	1.773(5)	Co(2)–C(5)	1.797(5)
Co(2)–C(7)	1.853(5)	Co(2)–C(16)	2.069(4)
Co(2)–C(15)	2.081(4)	Co(2)–Co(3)	2.4255(8)
Co(3)–C(3)	1.790(5)	Co(3)–C(4)	1.816(4)
Co(3)–C(15)	1.983(4)	Co(3)–C(2)	2.173(4)
C(15)–C(16)	1.441(6)		
Bond angles			
C(2)–Mo(1)–Co(3)	53.56(13)	C(1)–Mo(1)–Co(1)	62.92(13)
Co(3)–Mo(1)–Co(1)	56.191(19)	C(7)–Co(1)–Co(2)	47.60(13)
Co(2)–Co(1)–Co(3)	58.14(2)	Co(2)–Co(1)–Mo(1)	94.63(2)
Co(3)–Co(1)–Mo(1)	60.09(2)	C(7)–Co(2)–Co(1)	54.58(14)
Co(3)–Co(2)–Co(1)	62.67(2)	Co(2)–Co(3)–Co(1)	59.18(2)
C(2)–Co(3)–Mo(1)	47.93(13)	Co(2)–Co(3)–Mo(1)	97.64(3)
Co(1)–Co(3)–Mo(1)	63.72(2)	O(1)–C(1)–Mo(1)	168.7(4)
O(2)–C(2)–Mo(1)	155.6(4)	O(2)–C(2)–Co(3)	125.6(4)
Mo(1)–C(2)–Co(3)	78.51(16)	O(7)–C(7)–Co(2)	146.9(4)
O(7)–C(7)–Co(1)	135.2(4)	Co(2)–C(7)–Co(1)	77.82(18)
C(16)–C(15)–C(19)	126.1(4)	Co(2)–C(15)–Mo(1)	125.45(19)
C(15)–C(16)–C(17)	129.2(4)	Co(2)–C(16)–Mo(1)	120.57(19)

The molybdenum atom bears the Cp ligand and one carbonyl ligand, which is distinctly non-linear [Mo(1)–C(1)–O(1) 168.7(4)°], sufficiently so to describe it as semi-bridging to Co(1). Although asymmetry parameters [13] are of limited use here as two different metals are involved, the Co(1)–Mo(1)–C(1) angle of

62.92(13)° is below the value of 76.5° suggested by Crabtree and Lavin as diagnostic of semi-bridging CO's [14]. Each cobalt atom has two terminal carbonyl ligands, and there are two further bridging carbonyls. One of these bridges the Mo(1)–Co(3) edge, and is situated closer to Mo than Co [Mo(1)–C(2) 2.005(5), Co(3)–C(2) 2.173(4) Å] with a Mo(1)–C(2)–O(2) angle of 155.6(4)° and a Co(3)–Mo(1)–C(2) angle of 53.56(13)°. It can, therefore, be described as more strongly semibridging than C(1)–O(1), but is somewhat more symmetrically bonded than those in **2** where the average corresponding parameters were Mo–C 1.980 Å, Co–C 2.267 Å and Mo–C–O 158.7°. The second bridging carbonyl bridges the Co(1)–Co(2) edge and is also asymmetrically coordinated, with Co(1)–C(7) 2.045(5) Å and Co(2)–C(7) 1.853(5) Å. In addition the Co(2)–C(7)–O(7) angle, 146.9(4)°, is ca. 10° larger than the Co(1)–C(7)–O(7) angle of 135.2(4)°. These features are virtually identical to those observed by Chetcuti in the structure of [Co₃Mo(μ₄-HC₂Ph)(CO)₉(η-C₅H₄Me)] [5], and arise because of the formal imbalance in electron density between the wing-tips and the hinge metal atoms.

The molecular structure of **4c** is depicted in Fig. 2; selected bond lengths and angles are given in Table 2. The structure is subtly different to that of **4a**, in that a slightly different arrangement of semibridging carbonyl ligands is present in the solid state. The bonding parameters of the alkyne ligand are almost identical to those in **4a**, as is the arrangement of ligands around the molybdenum atom. However, both the carbonyl ligands bonded to the molybdenum now exhibit almost the same degree of semibridging: C(7)–O(2) semibridges to Co(3) [Mo(1)–C(7)–O(2) 163.4(3)°, Co(3)–Mo(1)–C(7)

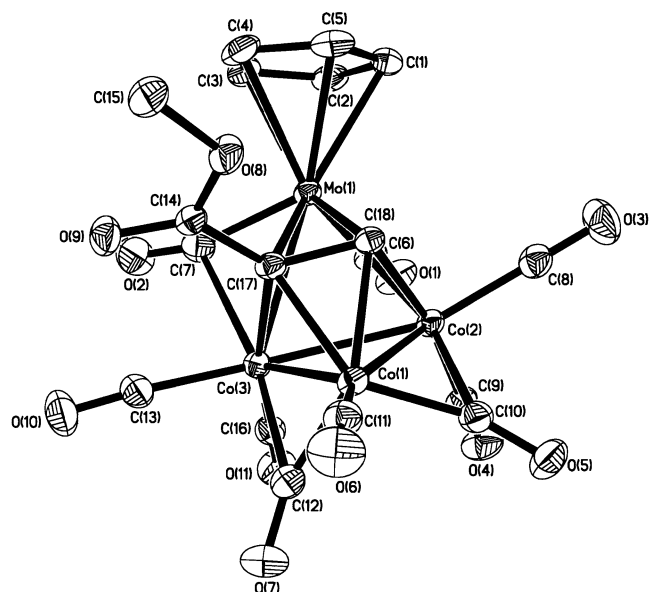


Fig. 2. Molecular structure of [Co₃Mo(μ₄-MeO₂CC₂H)(CO)₉Cp] (**4c**) in the crystal showing the atomic numbering scheme.

Table 2
Selected bond lengths (Å) and angles (°) for complex **4c**

<i>Bond lengths</i>			
Mo(1)–C(7)	1.990(4)	Mo(1)–C(6)	2.000(3)
Mo(1)–C(18)	2.225(3)	Mo(1)–C(17)	2.254(3)
Mo(1)–Co(3)	2.7165(6)	Mo(1)–Co(2)	2.7190(6)
Co(1)–C(11)	1.779(4)	Co(1)–C(12)	1.812(3)
Co(1)–C(10)	1.813(3)	Co(1)–C(17)	2.083(3)
Co(1)–C(18)	2.085(3)	Co(1)–Co(2)	2.4160(7)
Co(1)–Co(3)	2.4415(7)	Co(2)–C(8)	1.793(4)
Co(2)–C(9)	1.809(3)	Co(2)–C(18)	1.963(3)
Co(2)–C(10)	2.146(3)	Co(2)–C(6)	2.484(3)
Co(2)–Co(3)	2.6147(6)	Co(3)–C(16)	1.799(3)
Co(3)–C(13)	1.809(4)	Co(3)–C(17)	1.952(3)
Co(3)–C(12)	2.155(3)	Co(3)–C(7)	2.393(4)
C(17)–C(18)	1.437(4)		
<i>Bond angles</i>			
C(7)–Mo(1)–Co(3)	58.73(10)	C(6)–Mo(1)–Co(2)	61.31(9)
Co(3)–Mo(1)–Co(2)	57.506(14)	C(10)–Co(1)–Co(2)	58.95(11)
C(12)–Co(1)–Co(3)	58.66(11)	Co(2)–Co(1)–Co(3)	65.130(18)
C(10)–Co(2)–Co(1)	46.38(9)	Co(1)–Co(2)–Co(3)	57.907(19)
Co(1)–Co(2)–Mo(1)	95.402(18)	C(6)–Co(2)–Mo(1)	44.93(8)
Co(3)–Co(2)–Mo(1)	61.200(16)	C(12)–Co(3)–Co(1)	45.92(9)
Co(1)–Co(3)–Co(2)	56.964(18)	C(7)–Co(3)–Mo(1)	45.30(9)
Co(1)–Co(3)–Mo(1)	94.870(19)	Co(2)–Co(3)–Mo(1)	61.294(16)
O(1)–C(6)–Mo(1)	165.4(3)	O(1)–C(6)–Co(2)	120.6(2)
Mo(1)–C(6)–Co(2)	73.76(11)	O(2)–C(7)–Mo(1)	163.4(3)
O(2)–C(7)–Co(3)	120.6(3)	Mo(1)–C(7)–Co(3)	75.98(12)
O(5)–C(10)–Co(1)	154.0(3)	O(5)–C(10)–Co(2)	131.4(3)
Co(1)–C(10)–Co(2)	74.68(12)	O(7)–C(12)–Co(1)	153.0(3)
O(7)–C(12)–Co(3)	131.6(3)	Co(1)–C(12)–Co(3)	75.42(12)
C(18)–C(17)–C(14)	125.9(3)	Co(1)–C(17)–Mo(1)	122.52(14)
Co(1)–C(18)–Mo(1)	123.85(15)		

58.73(10)°] and C(6)–O(1) to Co(2) [Mo(1)–C(6)–O(1) 165.4(3)°, Co(2)–Mo(1)–C(6) 61.31(9)°]. In keeping with this, the two Mo–Co bond lengths are also now identical within experimental error. The wingtip cobalt atom Co(1) now bears only one terminal carbonyl ligand, but has bridging carbonyls to each of the other two cobalts. Both C(10)–O(5) and C(12)–O(7) exhibit an almost identical degree of semibridging character, which is less than that seen for C(7)–O(7) in **4a** above; thus the average Co(1)–C distance for these two carbonyls is 2.150 Å, the average Co(1)–C–O angle 153.5°, the average Co(hinge)–C distance 1.813 Å and the average Co(hinge)–C–O angle 131.5°.

The crystal structure of **4f** was also determined and a view is shown in Fig. 3, with selected bond lengths and angles given in Table 3. The gross features of the molecule are very similar to those of **4c**; the two W–Co bond lengths are identical within experimental error and the Co(1)–Co(2) and Co(2)–Co(3) bonds are very similar in length, whereas the unbridged hinge bond Co(1)–Co(3) is much longer. The arrangement of the carbonyl ligands is also very similar to that in **4c**. Thus the two carbonyl ligands attached to the tungsten atom are both weakly semibridging: C(14)–O(9) to Co(3), with a W(1)–C(14)–O(9) angle of 169.0(4)° and a

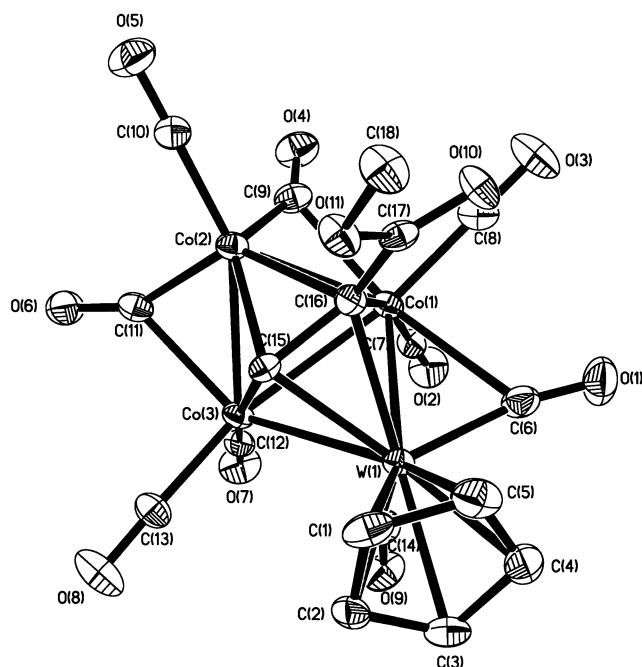


Fig. 3. Molecular structure of $[\text{Co}_3\text{W}(\mu_4\text{-MeO}_2\text{CC}_2\text{H})(\text{CO})_9\text{Cp}]$ (**4f**) in the crystal showing the atomic numbering scheme.

Table 3
Selected bond lengths (Å) and angles (°) for complex **4f**

<i>Bond lengths</i>			
W(1)–C(6)	1.971(6)	W(1)–C(14)	2.000(5)
W(1)–C(15)	2.192(5)	W(1)–C(16)	2.244(5)
W(1)–Co(1)	2.7166(7)	W(1)–Co(3)	2.7194(7)
Co(1)–C(7)	1.796(5)	Co(1)–C(8)	1.799(6)
Co(1)–C(16)	1.955(5)	Co(1)–C(9)	2.129(5)
Co(1)–Co(2)	2.4345(10)	Co(1)–C(6)	2.458(5)
Co(1)–Co(3)	2.6109(9)	Co(2)–C(10)	1.779(5)
Co(2)–C(9)	1.806(6)	Co(2)–C(11)	1.808(5)
Co(2)–C(16)	2.083(5)	Co(2)–C(15)	2.088(5)
Co(2)–Co(3)	2.4087(9)	Co(3)–C(13)	1.795(5)
Co(3)–C(12)	1.796(5)	Co(3)–C(15)	1.962(5)
Co(3)–C(11)	2.109(5)	C(15)–C(16)	1.442(7)
<i>Bond angles</i>			
C(6)–W(1)–Co(1)	60.80(15)	C(14)–W(1)–Co(3)	63.99(15)
Co(1)–W(1)–Co(3)	57.41(2)	C(9)–Co(1)–Co(2)	46.02(15)
Co(2)–Co(1)–Co(3)	56.90(3)	Co(2)–Co(1)–W(1)	94.45(3)
C(6)–Co(1)–W(1)	44.42(13)	Co(3)–Co(1)–W(1)	61.35(2)
C(11)–Co(2)–Co(3)	57.94(16)	C(9)–Co(2)–Co(1)	58.04(17)
Co(3)–Co(2)–Co(1)	65.24(3)	C(11)–Co(3)–Co(2)	46.60(13)
Co(2)–Co(3)–Co(1)	57.86(3)	Co(2)–Co(3)–W(1)	94.98(3)
Co(1)–Co(3)–W(1)	61.24(2)	O(1)–C(6)–W(1)	166.5(5)
O(1)–C(6)–Co(1)	118.7(4)	W(1)–C(6)–Co(1)	74.78(18)
O(4)–C(9)–Co(2)	152.1(5)	O(4)–C(9)–Co(1)	131.9(4)
Co(2)–C(9)–Co(1)	75.9(2)	O(6)–C(11)–Co(2)	152.7(4)
O(6)–C(11)–Co(3)	131.8(4)	Co(2)–C(11)–Co(3)	75.47(19)
O(9)–C(14)–W(1)	169.0(4)	Co(2)–C(15)–W(1)	124.3(2)
C(15)–C(16)–C(17)	126.4(5)	Co(2)–C(16)–W(1)	122.0(2)

Co(3)–W(1)–C(14) angle of $63.99(15)^\circ$, and C(6)–O(1) slightly more strongly to Co(1) with a W(1)–C(6)–O(1) angle of $166.5(5)^\circ$ and a Co(1)–W(1)–C(6) angle of

$60.80(15)^\circ$. Both Co(wingtip)–Co(hinge) bonds are bridged by asymmetrically bridging CO's with very similar bonding parameters.

3. Conclusions

The reaction of the mixed-metal alkyne complexes $[\text{CoM}(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_5\text{Cp}]$ with dicobalt octacarbonyl provides a convenient high-yield route to the tricobalt-molybdenum and -tungsten alkyne clusters $[\text{Co}_3\text{M}(\mu_4\text{-R}^1\text{C}_2\text{R}^2)(\text{CO})_9\text{Cp}]$. Although in this report we have restricted ourselves to complexes containing strongly bound electron-withdrawing alkynes, there seems no reason why the reaction could not be extended to other alkyne complexes of the same type. Together with our previous report, this paper demonstrates that the cluster expansion reaction with $[\text{Co}_2(\text{CO})_8]$ is a general one for the series $[\text{Co}_{2-n}\text{Mo}_n(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_{6-n}\text{Cp}_n]$ where $n = 1$ or 2 , but the application of the same method to the homometallic case ($n = 0$) is limited by the thermal instability of the reagents.

4. Experimental

4.1. General

General experimental techniques were as described in a recent paper from this laboratory [15]. Infra-red (IR) spectra were recorded in hexane or CH_2Cl_2 solution on a Perkin–Elmer 1600 FTIR machine using 0.5 mm NaCl cells. ^1H and ^{13}C -NMR spectra were obtained in CDCl_3 solution on a Bruker AC250 machine with automated sample-changer or an AMX400 spectrometer. Chemical shifts are given on the δ scale relative to $\text{SiMe}_4 = 0.0$ ppm. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in either electron impact or fast atom bombardment mode with *m*-nitrobenzyl alcohol as matrix. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry. Light petroleum refers to the fraction boiling in the range $60\text{--}80^\circ\text{C}$. The salts $\text{Na}[\text{M}(\text{CO})_3\text{Cp}] \cdot 2\text{DME}$ were prepared by the literature method [16]. The compounds $[\text{Co}_2(\mu\text{-R}^1\text{C}_2\text{R}^2)(\text{CO})_6]$ were prepared in $60\text{--}70\%$ yield by stirring dicobalt octacarbonyl with one equivalent of the appropriate alkyne in light petroleum at room temperature (r.t.), and purified by column chromatography.

4.2. Preparation of $[\text{CoMo}(\mu\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{CO})_5\text{Cp}]$ (**3a**)

The compound $\text{Na}[\text{Mo}(\text{CO})_3\text{Cp}] \cdot 2\text{DME}$ (1.39 g, 3.1 mmol) and an equimolar amount of the dicobalt alkyne complex $[\text{Co}_2(\mu\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{CO})_6]$ (1.33 g, 3.1 mmol) were added to THF (100 ml). The solution was heated to reflux for 30 min. After cooling, the solvent was removed under vacuum. Column chromatography gave an orange band which was eluted with dichloromethane–acetone (49:1). The orange solid was further purified by rechromatography in dichloromethane. Yield: 796 mg, 51%; IR (hexanes): 2074, 2035, 2016, 2001, 1977, 1715 cm^{-1} [17]. $^1\text{H-NMR}$: δ 5.47 (s, 5H, Cp), 3.80 (s, 6H, Me). Mass spectrum: m/z 502 $[\text{M}^+]$.

A further orange–brown band was then eluted with a 19:1 mixture of the same solvents and identified as $[\text{CoMo}\{\mu\text{-C}_4(\text{CO}_2\text{Me})_4\}(\text{CO})_4\text{Cp}]$ (160 mg, 8%). IR (CH_2Cl_2): 2097, 2057, 2006, 1966, 1723 cm^{-1} . $^1\text{H-NMR}$: δ 5.19 (s, 5H, Cp), 3.82 (s, 6H, Me), 3.69 (s, 6H, Me). Mass spectrum: m/z 618 $[\text{M}^+]$ [6,7].

Complexes **3b** (57% yield) and **3c** (66%) were prepared in a similar way except that the reactions were stirred for 48 h at r.t. rather than refluxed for 30 min. No other products were isolated from these reactions.

4.3. Synthesis of $[\text{CoW}(\mu\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{CO})_5\text{Cp}]$ (**3d**)

This complex was prepared in a similar way to the above from $\text{Na}[\text{W}(\text{CO})_3\text{Cp}] \cdot 2\text{DME}$ (1.08 g, 2.0 mmol) and $[\text{Co}_2(\mu\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{CO})_6]$ (0.86 g, 2.0 mmol) in THF (30 ml, reflux for 30 min). Column chromatography produced two orange bands. The first, eluted with dichloromethane and acetone (49:1) consisted of the desired product **3d** [6,7]. Yield: 659.5 mg, 55%. IR (CH_2Cl_2): 2070, 2028, 2009, 1996, 1965, 1701 cm^{-1} . $^1\text{H-NMR}$: δ 5.49 (s, 5H, Cp), 3.77 (s, 6H, Me). Mass spectrum: m/z 589 $[\text{M}^+]$. The second, eluted with a 24:1 mixture of the same solvents, was identified as $[\text{CoW}\{\mu\text{-C}_4(\text{CO}_2\text{Me})_4\}(\text{CO})_4\text{Cp}]$. Yield 22.8 mg, 1.6%. IR (CH_2Cl_2): 2056, 2005, 1953, 1726, 1707 cm^{-1} . $^1\text{H-NMR}$: δ 5.27 (s, 5H, Cp); 3.82 (s, 6H, Me); 3.69 (s, 6H, Me) [6,7].

The known complex **3e** (52%) [7] was obtained in the same manner. The complex $[\text{CoW}\{\mu\text{-C}_4(\text{CO}_2\text{Et})_4\}(\text{CO})_4\text{Cp}]$ (3.5% yield) was obtained as a by-product; this compound has been reported previously [7] but no characterising data were given. Orange solid, IR (CH_2Cl_2) 2055vs, 2004s, 1950m, 1723m, 1690w sh cm^{-1} . $^1\text{H-NMR}$ δ 5.28 (s, 5H, Cp), 4.27 (q, 4H, $J=7$ Hz, CH_2), 4.14 (q, 2H, $J=7$ Hz, CH_2), 4.13 (q, 2H, $J=7$ Hz, CH_2), 1.30 (t, 6H, $J=7$ Hz, Me), 1.25 (t, 6H, $J=7$ Hz, Me). Anal. Found: C, 39.34; H, 3.25. Calc. for $\text{C}_{25}\text{H}_{25}\text{CoO}_{12}\text{W}$: C, 39.50; H, 3.31%.

Mass spectrum m/z 760 $[\text{M}^+]$, 732 (M–CO), 715, 687, 676, 648, 631.

The known complex **3f** (44%) [6] was prepared in an analogous manner except that the mixture was refluxed for 45 mins. In this preparation a small dark green–black band was eluted before the major product and identified as the alkylidyne cluster $[\text{Co}_2\text{W}(\mu_3\text{-CCH}_2\text{CO}_2\text{Me})(\text{CO})_8\text{Cp}]$ (1.4% yield) on the basis of its spectroscopic data: IR (CH_2Cl_2): 2077w, 2070m, 2030s, 2014s, 2000s, 1941m, 1731w cm^{-1} ; $^1\text{H-NMR}$ δ 5.45 (s, 5H, Cp), 4.83 (s, 2H, CH_2), 3.71 (s, 3H, Me). Mass spectrum: m/z 647, 619, 591, 563, 535, 507, 479, 451 $[\text{M}^+ - n\text{CO}]$, $n=1-8$. The molybdenum analogue of this compound has recently been prepared by us [18].

4.4. Synthesis of $[\text{Co}_3\text{Mo}(\mu_4\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{CO})_9\text{Cp}]$ (**4a**)

A solution of $[\text{CoMo}(\mu\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{CO})_5\text{Cp}]$ (**3a**) (1.18 g, 2.3 mmol) and dicobalt octacarbonyl (0.80 g, 2.3 mmol) in toluene (50 ml) was heated to reflux for 1 h. The solution was cooled and the solvent was removed. Column chromatography of the mixture using light petroleum–dichloromethane (1:4) as eluent gave a large dark-green band of the product (1.14 g, 66%). M.p. > 250 °C. IR (CH_2Cl_2): 2082ms, 2052vs, 2045vs, 1876m, 1811w, 1700w cm^{-1} . $^1\text{H-NMR}$: δ 5.40 (s, 5H, Cp), 3.70 (s, 6H, Me). $^{13}\text{C-NMR}$: δ 243.5 (s, Mo–CO), 207.5, 199.0, 191.4 (br, Co–CO), 172.2 (s, CO_2Me), 148.1 (s, $\text{C}\equiv\text{C}$), 96.6 (s, Cp), 52.9 (s, Me). Anal. Found: C, 32.45; H, 1.65. Calc. for $\text{C}_{20}\text{H}_{11}\text{Co}_3\text{MoO}_{13}$: C, 32.78; H, 1.50%. Mass spectrum: m/z 733, 706, 678, 650, 622, 594, 566 $[\text{M}^+ - n\text{CO}]$, $n=0-6$.

4.5. Synthesis of $[\text{Co}_3\text{Mo}(\mu_4\text{-EtO}_2\text{CC}_2\text{CO}_2\text{Et})(\text{CO})_9\text{Cp}]$ (**4b**)

In a similar manner to the above, $[\text{CoMo}(\mu\text{-EtO}_2\text{CC}_2\text{CO}_2\text{Et})(\text{CO})_5\text{Cp}]$ (**3b**) (1.80 g, 3.4 mmol) and dicobalt octacarbonyl (1.16 g, 3.4 mmol) reacted in refluxing toluene (1 h) to give $[\text{Co}_3\text{Mo}(\mu_4\text{-EtO}_2\text{CC}_2\text{CO}_2\text{Et})(\text{CO})_9\text{Cp}]$ (**4b**) (2.011 g, 78%) after chromatography; the product was eluted as a dark green band with CH_2Cl_2 . M.p. 179–181 °C. IR (CH_2Cl_2): 2082s, 2051vs, 2041vs, 1876m, 1809w, 1695w cm^{-1} . $^1\text{H-NMR}$: δ 5.42 (s, 5H, Cp), 4.13 (q, 4H, $J=7$ Hz, CH_2), 1.27 (t, 6H, $J=7$ Hz, Me). $^{13}\text{C-NMR}$: δ 243.6 (s, Mo–CO), 207.5, 199.5, 192.2 (br, Co–CO), 171.7 (s, CO_2Et), 149.0 (s, $\text{C}\equiv\text{C}$), 96.6 (s, Cp), 62.3 (s, CH_2), 13.9 (s, Me). Anal. Found: C, 34.67; H, 1.89. Calc. for $\text{C}_{22}\text{H}_{15}\text{Co}_3\text{MoO}_{13}$: C, 34.76; H, 1.99%. Mass spectrum: m/z 762, 734, 706, 678, 650, 622, 594, 566, 538, 510 $[\text{M}^+ - n\text{CO}]$, $n=0-9$, 476, 446.

4.6. Synthesis of $[Co_3Mo(\mu_4-HC_2CO_2Me)(CO)_9Cp]$ (**4c**)

In a similar manner to the above, a solution of $[CoMo(\mu-HC_2CO_2Me)(CO)_5Cp]$ (**3c**) (0.58 g, 1.3 mmol) and dicobalt octacarbonyl (0.45 g, 1.3 mmol) in toluene was heated to reflux for 1 h. Column chromatography gave $[Co_3Mo(\mu_4-HC_2CO_2Me)(CO)_9Cp]$ (**4c**) (0.5686 g, 65%) as a dark brown zone on elution with light petroleum– CH_2Cl_2 (1:4). M.p. 161–163 °C. IR (CH_2Cl_2): 2078ms, 2048vs, 2035vs, 1868m, 1811w, 1693w cm^{-1} . 1H -NMR: δ 8.65 (s, 1H, CH), 5.37 (s, 5H, Cp), 3.70 (s, 3H, Me). ^{13}C -NMR: δ 244.2 (s, Mo–CO); 241.4 (s, Mo–CO) 207.2, 200.5, 191.0 (br, Co–CO); 173.3 (s, CO_2Me), 145.7 (s, $C\equiv C$), 94.4 (s, Cp), 52.6 (s, Me). Anal. Found: C, 31.69; H, 1.23. Calc. for $C_{18}H_9Co_3MoO_{11}$: C, 32.08; H, 1.35%. Mass spectrum: m/z 675, 647, 618, 592, 564, 536, 508, 480, 452 [$M^+ - nCO$, $n = 0-8$], 421, 392, 366.

4.7. Synthesis of $[Co_3W(\mu_4-MeO_2CC_2CO_2Me)(CO)_9Cp]$ (**4d**)

A solution of $[CoW(\mu-MeO_2CC_2CO_2Me)(CO)_5Cp]$ (**3d**) (0.98 g, 1.67 mmol) and dicobalt octacarbonyl (0.57 g, 1.67 mmol) in toluene (30 ml) was heated to reflux for 1 h. The solution was cooled and the solvent was removed. The residue was separated by column chromatography.

Elution with light petroleum–dichloromethane (3:2) gave an olive-green band which was identified as $[Co_4(CO)_9(\eta^6-toluene)]$ (12.6 mg) [19]. A second green band was eluted with a 1:4 mixture of the same solvents and is tentatively identified as $[Co_5W_2(\mu_5-C)(\mu_4-CCO_2Me)(CO)_{12}Cp_2]$ (7.6 mg) by comparison with its Mo analogue [18]. Elution of the column with CH_2Cl_2 afforded a dark green band of $[Co_3W(\mu_4-MeO_2CC_2CO_2Me)(CO)_9Cp]$ (**4d**) (741.2 mg, 54%). M.p. (dec.) 204 °C. IR (CH_2Cl_2): 2078s, 2041vs, 1988m, 1873m, 1810w, 1788w, 1704w cm^{-1} . 1H -NMR: δ 5.50 (s, 5H, Cp), 3.70 (s, 6H, Me). ^{13}C -NMR: δ 227.9 (s, W–CO), 210–192 (br m, Co–CO), 173.0 (s, CO_2Me), 136.9 (s, $C\equiv C$), 94.2 (s, J_{WC} 89, Cp), 53.0 (s, Me). Anal. Found: C, 29.21; H, 1.07. Calc. for $C_{20}H_{11}Co_3O_{13}W$: C, 29.30; H, 1.35%. Mass spectrum: m/z 819, 791, 763, 735, 707, 680, 652 [$M^+ - nCO$, $n = 0-6$].

Unchanged **3d** (204.8 mg, 21% recovery) was then eluted as an orange band with dichloromethane–acetone (99:1).

4.8. Synthesis of $[Co_3W(\mu_4-EtO_2CC_2CO_2Et)(CO)_9Cp]$ (**4e**)

A solution of complex **3e** (1.207 g, 1.95 mmol) and dicobalt octacarbonyl (0.668 g, 1.95 mmol) in toluene (40 ml) was heated to reflux for 1 h. Chromatographic

work-up as above, eluting with light petroleum–dichloromethane (3:2), gave a small olive-green band which was tentatively identified as $[Co_5W_2(\mu_5-C)(\mu_4-CCO_2Et)(CO)_{12}Cp_2]$ (5.4 mg) on the basis of its IR and NMR spectra [18]. A dark green band of $[Co_3W(\mu_4-EtO_2CC_2CO_2Et)(CO)_9Cp]$ **4e** (562.6 mg, 34%) was eluted with a 1:4 mixture of the same solvents. M.p. 150–152 °C. IR (CH_2Cl_2): 2078s, 2043vs, 1988w, 1876m, 1813w, 1695w cm^{-1} . 1H -NMR: δ 5.52 (s, 5H, Cp), 4.13 (q, 4H, $J = 7$ Hz, CH_2), 1.28 (t, 6H, $J = 7$ Hz, Me). ^{13}C -NMR: δ 227.9 (s, J_{WC} 85, W–CO), 212–191 (br m, Co–CO), 172.4 (s, CO_2Et), 137.8 (s, $C\equiv C$), 94.2 (s, J_{WC} 92, Cp), 62.4 (s, CH_2), 13.9 (s, Me). Anal. Found: C, 31.10; H, 1.61. Calc. for $C_{22}H_{15}Co_3O_{13}W$: C, 31.16; H, 1.78%. Mass spectrum: m/z 848, 819, 791, 763, 735, 708, 680, 652, 624 [$M^+ - nCO$, $n = 0-8$].

Unchanged **3e** (355.0 mg, 29% recovery) was then eluted as an orange band with dichloromethane–acetone (99:1).

4.9. Synthesis of $[Co_3W(\mu_4-HC_2CO_2Me)(CO)_9Cp]$ (**4f**)

In a similar manner to the above, complex **3f** (0.293 g, 0.55 mmol) reacted with $[Co_2(CO)_8]$ (0.188 g, 0.55 mmol) in toluene (20 ml) at reflux over a period of 1.5 h. Column chromatography of the residue with light petroleum–dichloromethane (2:3) gave a dark green band due to the alkylidyne cluster $[Co_2W(\mu_3-CCH_2CO_2Me)(CO)_8Cp]$, characterised as above.

A black band of $[Co_3W(\mu_4-HC_2CO_2Me)(CO)_9Cp]$ (**4f**) was then eluted with a 2:3 mixture of the same solvents. After removal of the solvent the product was washed with light petroleum to remove further $[Co_2W(\mu_3-CCH_2CO_2Me)(CO)_8Cp]$ (total yield 48.3 mg, 13%) to leave **4f**. Yield 114.9 mg, 27%. M.p. 169–171 °C. IR (CH_2Cl_2): 2078s, 2045s, 2033s, 1872m, 1817m, 1797m, 1692m cm^{-1} . 1H -NMR: δ 8.19 (s, 1H, CH), 5.50 (s, 5H, Cp), 3.70 (s, 3H, Me). ^{13}C -NMR: δ 229.7 (s, W–CO), 224.6 (s, W–CO), 207.2 (br, Co–CO), 194.2 (br, Co–CO), 174.3 (s, CO_2Me), 132.6 (s, $C\equiv C$), 92.1 (s, Cp), 52.7 (s, Me). Anal. Found: C, 28.09; H, 1.11. Calc. for $C_{18}H_9Co_3O_{11}W$: C, 28.38; H, 1.19%. Mass spectrum: m/z 762, 734, 706, 678, 650, 622, 594, 566, 538 [$M^+ - nCO$, $n = 0-8$].

A suitable crystal for X-ray diffraction was grown by slow diffusion of light petroleum into a solution of the compound in dichloromethane at -10 °C.

4.10. Synthesis of $[Co_4(\mu_4-R^1C_2R^2)(CO)_{10}]$ (**5**)

A solution of $[Co_2(\mu-MeO_2CC_2CO_2Me)(CO)_6]$ (207.3 mg, 0.48 mmol) and 1.5 equivalents of dicobalt octacarbonyl (266.0 mg, 0.73 mmol) in heptane (20 ml) was heated to reflux for 3 h. The solution was cooled and the solvent removed. Column chromatography of the mix-

Table 4
Summary of crystallographic data for complexes **4a**, **4c** and **4f**

	4a	4c	4f
Empirical formula	C ₂₀ H ₁₁ Co ₃ MoO ₁₃	C ₁₈ H ₉ Co ₃ MoO ₁₁	C ₁₈ H ₉ Co ₃ O ₁₁ W
Formula weight	732.02	673.98	761.89
<i>T</i> (K)	150(2)	293(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.8291(8)	8.9624(14)	8.9202(8)
<i>b</i> (Å)	16.3202(14)	9.8531(15)	9.7790(8)
<i>c</i> (Å)	16.2230(13)	12.7808(19)	12.7934(11)
α (°)	90	96.632(3)	96.3200(10)
β (°)	93.423(2)	108.601(3)	108.4760(10)
γ (°)	90	102.435(3)	102.254(2)
<i>V</i> (Å ³)	2333.4(3)	1023.7(3)	1015.23(15)
<i>Z</i>	4	2	2
<i>D</i> _{calc} (Mg m ⁻³)	2.084	2.187	2.492
μ (mm ⁻¹)	2.689	3.048	8.116
<i>F</i> (000)	1432	656	720
Crystal size (mm)	0.16 × 0.14 × 0.10	0.45 × 0.34 × 0.34	0.35 × 0.30 × 0.15
θ Range for data collection (°)	1.77 to 28.29	1.72 to 28.27	1.71 to 28.30
Index ranges	-11 ≤ <i>h</i> ≤ 11, -21 ≤ <i>k</i> ≤ 18, -19 ≤ <i>l</i> ≤ 21	-11 ≤ <i>h</i> ≤ 11, -12 ≤ <i>k</i> ≤ 11, -13 ≤ <i>l</i> ≤ 17	-11 ≤ <i>h</i> ≤ 7, -12 ≤ <i>k</i> ≤ 12, -16 ≤ <i>l</i> ≤ 16
Reflections collected	14304	6467	8587
Independent reflections	5642 [<i>R</i> _{int} = 0.1218]	4606 [<i>R</i> _{int} = 0.0281]	4657 [<i>R</i> _{int} = 0.0478]
Completeness to θ (%)	97.3	90.7	92.3
Absorption correction	Semi-empirical	Empirical	Empirical
Max./min. transmission	0.7747 and 0.6729	0.4239 and 0.3409	0.3757 and 0.1634
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5642/0/334	4606/0/298	4657/0/299
Goodness-of-fit on <i>F</i> ²	1.061	1.107	1.061
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0438, <i>wR</i> ₂ = 0.1073	<i>R</i> ₁ = 0.0352, <i>wR</i> ₂ = 0.0950	<i>R</i> ₁ = 0.0327, <i>wR</i> ₂ = 0.0815
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0619, <i>wR</i> ₂ = 0.1317	<i>R</i> ₁ = 0.0378, <i>wR</i> ₂ = 0.0968	<i>R</i> ₁ = 0.0370, <i>wR</i> ₂ = 0.0838
Largest difference in peak and hole (e Å ⁻³)	0.904 and -1.552	1.265 and -1.579	2.449 and -1.456

ture was performed, giving a brown band due to residual [Co₂(CO)₈] (94.7 mg, 36% recovery), eluted with light petroleum–dichloromethane (4:1); a dark blue band of [Co₄(μ -MeO₂CC₂CO₂Me)(CO)₁₀] (57.5 mg, 18%), eluted with a 2:3 mixture of the same solvents [20,21]; and finally an orange band of residual [Co₂(μ -MeO₂CC₂CO₂Me)(CO)₆] (49.2 mg, 24%).

Reactions of [Co₂(CO)₈] with [Co₂(μ -EtO₂CC₂-CO₂Et)(CO)₆] or [Co₂(μ -HC₂CO₂Me)(CO)₆] were conducted in the same way to give the analogous tetracobalt derivatives [Co₄(μ -EtO₂CC₂CO₂Et)(CO)₁₀] [20] and [Co₄(μ -HC₂CO₂Me)(CO)₁₀] in yields of 9 and 28%, respectively. Small amounts of the two starting complexes were recovered in each case. The latter complex has not been previously reported: m.p. 114–117 °C. IR (CH₂Cl₂): 2099w, 2062vs, 2048vs, 2004m, 1875m, 1706w cm⁻¹. ¹H-NMR: δ 8.72 (s, 1H, CH), 3.74 (s, 3H, Me). Anal. Found: C, 26.43; H, 0.71. Calc. for C₁₄H₄Co₄O₁₂·CH₂Cl₂: C, 26.31; H, 0.88%. Mass spectrum: *m/z* 600, 572, 544, 516, 488, 460, 432, 404, 376, 348, 320 [*M*⁺ - *n*CO, *n* = 0–10].

4.11. Crystal structure determinations of **4a**, **4c** and **4f**

Details of the crystal structure determinations are given in Table 4. Data collected were measured on a Bruker Smart CCD area detector with an Oxford Cryosystems low temperature system. The general procedures for structure solution were as described in a recent paper [22]. Complex scattering factors were taken from the program package SHELXTL [23] as implemented on the Viglen Pentium computer.

5. Supplementary material

Crystallographic data for the structure determinations have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 186784–186786. 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](http://www.ccdc.cam.ac.uk)).

Acknowledgements

We acknowledge the EPSRC for the award of a studentship (to L.V.Y.G.) and we also thank Andrea Riddiough for the data collection and structure solution of complex **4f**.

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