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Alkyne scission in cobalt–molybdenum clusters: synthesis and structures of hexa- and heptanuclear alkylidyne clusters with unusual architectures †

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Heating $[Mo_2(\mu\text{-}RC{\equiv}CR)(CO)_4Cp_2]$ (R = CO_2Me; Cp = $\eta\text{-}C_5H_5$) with an excess of dicobalt octacarbonyl affords, in addition to the expected product $[Co_2Mo_2(\mu_4\text{-}C_2R_2)(\mu\text{-}CO)_4(CO)_4Cp_2]$, two clusters in which the alkyne ligand has been cleaved: hexanuclear $[Co_4Mo_2(\mu_4\text{-}CR)_2(\mu\text{-}CO)_2(CO)_8Cp_2]$ (**2**) and heptanuclear $[Co_5Mo_2(\mu_4\text{-}CR)(\mu_5\text{-}C)(CO)_{12}Cp_2]$ (**3**), both of which have been shown by X-ray diffraction to contain unusual edge-sharing bitetrahedral metal frameworks. An analogue of the latter, $[Co_5Mo_2(\mu_4\text{-}CH)(\mu_5\text{-}C)(CO)_{12}Cp_2]$ (**8**), was obtained from a similar reaction with R = H, but no counterpart of **2** could be isolated. Treatment of **3** with CO afforded the trinuclear cluster $[Co_2Mo(\mu_3\text{-}CCH_2CO_2Me)(CO)_8Cp]$ (**11**), presumably by carbido-alkylidyne coupling; the crystal structures of this cluster and of the related $[Co_2Mo(\mu_3\text{-}CMe)(CO)_8Cp]$ are also reported.

Introduction

The idea that the coordination and reactivity of organic fragments bonded to metal clusters may reflect those of the same fragments adsorbed on a metal surface during heterogeneous catalysis (the so-called cluster surface analogy) has provided the impetus for much research over the past 30 years.[1] In particular, species postulated as intermediates in the Fischer–Tropsch reaction, such as surface carbide (C), methylidyne (CH) and methylene (CH_2), have been considered desirable target ligands in cluster chemistry. Although some compounds containing methylidyne ligands are readily available {*e.g.* $[Co_3(\mu_3\text{-}CH)(CO)_9]$ from the reaction of dicobalt octacarbonyl with bromoform}, relatively few synthetic routes to clusters containing this archetypal hydrocarbon fragment have been established.[2] In many cases, other alkylidyne ligands such as ethylidyne (CMe), which can be made by hydrogenation and rearrangement of ethyne, and *p*-tolylmethylidyne (CC_6H_4Me-4), derived from the reagent $[W({\equiv}CC_6H_4Me\text{-}4)(CO)_2Cp]$, have been used instead of methylidyne itself. A very recent paper suggests, however, that the catalytic activity of the tricobalt methylidyne cluster is much greater than that of its higher homologues.[3]

We recently described the first example of a potentially valuable route to methylidyne complexes, namely the scission of the C≡C triple bond in ethyne ($HC{\equiv}CH \longrightarrow 2\ \mu_3\text{-}CH$) during the reaction of the dimolybdenum alkyne complex $[Mo_2(\mu\text{-}HC{\equiv}CH)(CO)_4Cp_2]$ with $[Ru_3(CO)_{12}]$ to afford $[Mo_2Ru_4(\mu_3\text{-}CH)_2(CO)_{12}Cp_2]$.[4] Cleavage of several other terminal alkynes and but-2-yne was also achieved, though the reaction failed for complexes of larger disubstituted alkynes such as diphenylacetylene or DMAD (dimethyl acetylenedicarboxylate, $MeO_2CC{\equiv}CCO_2Me$). We have also described an apparent example of alkyne scission in cobalt–molybdenum clusters, in the reaction of $[Co_2(\mu\text{-}C_2Ph_2)(CO)_6]$ with $[Mo_2(\mu\text{-}C_2Ph_2)(CO)_4Cp_2]$ to give the butterfly cluster $[Co_2Mo_2(\mu_3\text{-}CPh)_2(\mu_4\text{-}C_2Ph_2)(CO)_4Cp_2]$, though evidence was presented that coupling of the two alkynes to form a metallacyclopentadiene might occur before subsequent fragmentation to an alkyne and two benzylidyne ligands.[5] This reaction was very specific in that two aryl substituents were required on both alkynes for the reaction to work. As detailed in a recent review, approximately 20 other examples of alkyne scission have been observed in metal clusters, virtually all of which involve disubstituted alkynes.[6] In this paper, we describe the isolation and structural characterisation of two higher nuclearity cobalt–molybdenum clusters in which alkyne scission has again occurred, and show that the scission of ethyne itself can again be accomplished in this system.

Results and discussion

We recently reported that the dimolybdenum alkyne complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4Cp_2]$ (R^1 = H, R^2 = H, Me, Ph, CO_2Me; $R^1 = R^2$ = Me) react with 1 equivalent of dicobalt octacarbonyl in refluxing toluene to afford the blue or green tetranuclear butterfly clusters $[Co_2Mo_2(\mu_4\text{-}R^1C_2R^2)(CO)_8Cp_2]$ in moderate to good yields.[7] In some of these reactions, very small amounts of unidentified green or brown minor products were observed during chromatographic work-up. The only alkyne complex for which the reaction failed, presumably on steric grounds, was that with $R^1 = R^2$ = Ph, in which case the outcome consisted only of slow decomposition of the cobalt reagent and recovery of the dimolybdenum complex. However, we did notice subsequently that with the alkyne complex derived from DMAD (**1**; R = CO_2Me), the yield of the tetranuclear cluster was somewhat lower than usual. Conversely, from this reaction, we were able to isolate improved yields of two minor products, which has enabled us to characterise them crystallographically. They were found to be the hexanuclear bis(alkylidyne) cluster $[Co_4Mo_2(\mu_4\text{-}CCO_2Me)_2(\mu\text{-}CO)_2(CO)_8Cp_2]$ (**2**) and the heptanuclear carbide-alkylidyne cluster $[Co_5Mo_2(\mu_4\text{-}CCO_2Me)(\mu_5\text{-}C)(CO)_{12}Cp_2]$ (**3**) (Scheme 1). A third minor product, often present in these reactions, was identified as the known cluster $[Co_4(\mu\text{-}CO)_3(CO)_6(\eta\text{-}C_6H_5Me)]$ (**4**), which arises simply through heating $[Co_2(CO)_8]$ in toluene.[8] The remaining product of the reaction, $[Co_2Mo_2\{\mu_4\text{-}C_2(CO_2Me)_2\}(CO)_8Cp_2]$ (**5**) was characterised spectroscopically and is entirely analogous to the complexes reported earlier.[7] By employing an excess of cobalt carbonyl, the yields of **2** and **3** could be further improved at the expense of **5**.

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† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams in CHIME format. See http://www.rsc.org/suppdata/dt/b2/b204326m/

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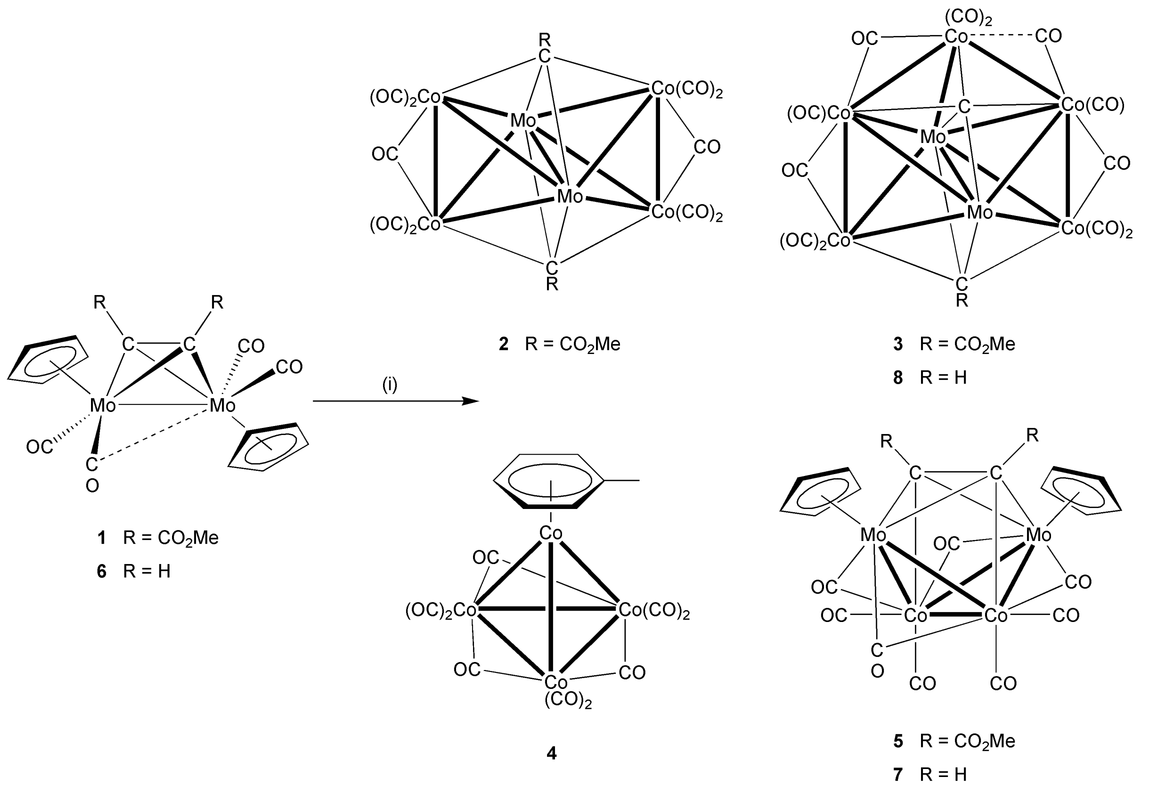


Scheme 1 Synthesis of the high nuclearity clusters. *Reagents and conditions*: (i) $[Co_2(CO)_8]$ (2.5 equiv.), toluene, reflux, 1 h. The Cp ligands on the Mo atoms in complexes **2**, **3** and **8** have been omitted for clarity.

Spectroscopic characterisation of brown, air-stable diamagnetic **2**, which was still formed in very low yield (3%), revealed IR absorptions for terminal (2038, 2011 cm^{-1}), bridging (1824 cm^{-1}) and ester (1656 cm^{-1}) carbonyl groups. Its ^{1}H NMR spectrum consisted of two singlets in a ratio of 5 : 3 due to Cp and methyl protons respectively, but the ^{13}C NMR spectrum contained a broad low field resonance at δ 312.5 indicative of the presence of an alkylidyne ligand.

The molecular structure of **2** is shown in Fig. 1 with selected bond lengths and angles collected in Table 1. This centrosymmetric cluster displays a highly unusual metal framework consisting of two edge-sharing tetrahedra, the shared edge being the original Mo–Mo bond; in this way, each molybdenum atom is joined to all four $Co(CO)_2$ units. Only a few examples of this geometry are known, most of which involve coinage metals.[9] The two which do not are the hexaosmium clusters $[Os_6(\mu\text{-}H)_2(\mu\text{-}CNMe_2)_2(\mu_3\text{-}SMe)_2(CO)_{12}]$[10] and $[Os_6(\mu\text{-}H)_2L_2(CO)_{15}]$, where L = the cyclic thioether $S(CH_2)_2O(CH_2)_2$.[11] Complex **2** has 84 electrons, but the electron counts for these compounds vary between 76 and 86, with the latter being the theoretically predicted value.[9,12]

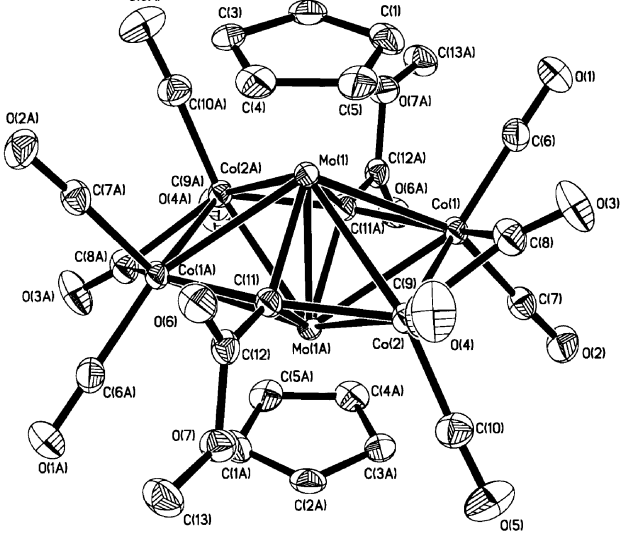


Fig. 1 Molecular structure of $[Co_4Mo_2(\mu_4\text{-}CCO_2Me)_2(\mu\text{-}CO)_2(CO)_8Cp_2]$ (**2**) in the crystal, showing the atomic numbering scheme.

The Mo–Mo bond length in **2** is 2.6447(6) Å, which appears typical for a ligand-bridged Mo–Mo bond in clusters; it is not as short as those found in $[Co_2Mo_2(\mu_3\text{-}CPh)_2(\mu_4\text{-}C_2Ph_2)(CO)_4Cp_2]$ [2.5507(11) Å][5] or $[Mo_2Ru_4(\mu_3\text{-}CMe)_2(CO)_{12}Cp_2]$ [2.5792(8) Å],[4] where some degree of multiple bonding is implied by the electron counts. The Co–Mo bond lengths range over 2.6328(6)–2.7189(7) Å, which is again typical, as is the Co–Co bond length [2.4744(8) Å], given that both Co–Co bonds are bridged by symmetrically bridging CO ligands; in addition each cobalt atom bears two terminal carbonyls. Both of the butterfly-like Co_2Mo_2 open faces are capped by μ_4-CCO_2Me ligands formed by scission of the original alkyne. The CO_2Me substituent on this ligand leans slightly to one side, as shown by the angles C(12)–C(11)–Co(2) and C(12)–C(11)–Co(1A) which are 104.6(2) and 99.6(2)°, respectively; similarly, the two angles C(12)–C(11)–Mo(1) and C(12)–C(11)–Mo(1A) also differ slightly [138.5(2) and 143.9(3)°, respectively]. The non-bonding C(11)–C(11A) distance, which is typically 1.33 Å in complexes of type **1**, has increased to 3.298 Å.

Heptanuclear cluster **3** was isolated as a dark brown air-stable solid in up to 47% yield. Its ^{1}H NMR spectrum comprised three peaks at δ 5.56, 4.97 and 3.71 with an intensity ratio of 5 : 5 : 3, revealing that the Cp ligands are inequivalent and that one of the ester groups has been lost. In the ^{13}C NMR spectrum, in addition to a peak at δ 285.5 due to the alkylidyne group, a second low field peak was observed at δ 475.0 due to the μ_5-carbide carbon atom.

The molecular structure of **3** is shown in Fig. 2, with selected bond lengths and angles collected in Table 2. The structure is complicated by the fact that there are three independent molecules (A–C) present in the unit cell, which differ significantly only in the arrangement of the carbonyl ligands;

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Mo(1)–C(11)	2.074(3)	Mo(1)–C(11)#1	2.152(3)
Mo(1)–Co(1)	2.6328(6)	Mo(1)–Co(2)#1	2.6396(7)
Mo(1)–Mo(1)#1	2.6447(6)	Mo(1)–Co(2)	2.6876(7)
Mo(1)–Co(1)#1	2.7189(7)	Co(1)–C(6)	1.785(4)
Co(1)–C(7)	1.817(4)	Co(1)–C(8)	1.897(4)
Co(1)–C(11)#1	2.019(3)	Co(1)–Co(2)	2.4744(8)
Co(2)–C(10)	1.779(4)	Co(2)–C(9)	1.796(4)
Co(2)–C(8)	1.920(4)	Co(2)–C(11)	1.999(3)
C(11)–C(12)	1.481(5)		
Co(1)–Mo(1)–Co(2)#1	96.19(3)	Co(1)–Mo(1)–Co(2)	55.418(18)
Co(2)#1–Mo(1)–Co(2)	120.476(17)	Co(1)–Mo(1)–Co(1)#1	120.795(17)
Co(2)#1–Mo(1)–Co(1)#1	54.98(2)	Co(2)–Mo(1)–Co(1)#1	93.07(3)
Co(2)–Co(1)–Mo(1)	63.413(19)	Co(2)–Co(1)–Mo(1)#1	60.881(18)
Mo(1)–Co(1)–Mo(1)#1	59.205(17)	Co(1)–Co(2)–Mo(1)#1	64.14(2)
Co(1)–Co(2)–Mo(1)	61.17(2)	Mo(1)#1–Co(2)–Mo(1)	59.524(17)
Co(1)–C(8)–Co(2)	80.80(16)	C(12)–C(11)–Co(2)	104.6(2)
C(12)–C(11)–Co(1)#1	99.6(2)	Co(2)–C(11)–Co(1)#1	155.14(18)
C(12)–C(11)–Mo(1)	138.5(2)	Co(2)–C(11)–Mo(1)	82.56(12)
Co(1)#1–C(11)–Mo(1)	83.24(13)	C(12)–C(11)–Mo(1)#1	143.9(3)
Co(2)–C(11)–Mo(1)#1	78.87(11)	Co(1)#1–C(11)–Mo(1)#1	78.19(12)
Mo(1)–C(11)–Mo(1)#1	77.45(11)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y, -z + 1$.

molecules A and B have three bridging carbonyls, whereas molecule C has four, one along each Co–Co bond (*vide infra*). The metal framework is similar to that in **2** in that four of the five cobalt atoms [Co(1), Co(2), Co(4) and Co(5)] are bonded to both molybdenum atoms in an edge-sharing bitetrahedral manner. A fifth cobalt, Co(3), which is bonded to Mo(2), Co(2) and Co(4), has now been incorporated. The Mo–Mo bond length [av. 2.7900 Å] is distinctly longer than in **2**, though the remaining Mo–Co and Co–Co distances are all comparable.

Instead of the two alkylidyne groups present in **2**, cluster **3** contains one μ_4-alkylidyne and one μ_5 (semi-exposed) carbide atom. The alkylidyne carbon, C(11), lies almost equidistant from the four metal atoms Mo(1), Mo(2), Co(1) and Co(5), in contrast to the slightly asymmetric disposition observed in **2**; consequently, the Co–C(11)–C(25) (av. 103.5°) and Mo–C(11)–C(25) angles (av. 137.8°) span smaller ranges. As a result of the longer Mo–Mo bond length, the Mo(1)–C(11)–Mo(2) bond angle is larger than in **2** [av. 84.2° compared to 77.45(11)°], whereas the Co(1)–C(11)–Co(5) angle is slightly reduced [av. 152.8° *vs.* 155.14(18)° in **2**]. The carbide carbon, C(12) is situated in a square-based pyramidal environment, with Mo(2) forming the apex of this pyramid and Mo(1) in the basal plane; the bond length to the apical Mo is significantly longer (av. 2.185 Å) than that to the basal one (av. 1.925 Å). As usual in such arrangements, the carbon atom lies slightly out of the basal plane, as shown by the Co(2)–C(12)–Co(4) and Mo(1)–C(12)–Co(3) angles being slightly less than 180° (av. 160.3 and 173.2°, respectively). The average C(11)–C(12) distance in **3** is 3.04 Å, which is somewhat smaller than in **2**.

Close inspection of the three independent molecules reveals little difference between A and B, but the presence of an additional bridging CO in C. In all three molecules, CO ligands C(15)–O(3) and C(22)–O(10) bridge their respective Co–Co edges symmetrically, whereas the coordination of C(17)–O(5) is unsymmetrical, as shown by the different Co–C(17) distances and Co–C(17)–O(5) bond angles, particularly in molecule C. In this molecule, C(20)–O(8) is also displaced into an asymmetric bridging mode along the Co(3)–Co(4) edge, while in molecules A and B it is terminally bound to Co(4) with an almost linear Co(4)–C(20)–O(8) angle. We have previously observed a similar phenomenon in the structure of $[Mo_2Ru_4(\mu_6\text{-}C)(\mu\text{-}O)(CO)_{12}Cp_2]$; presumably the energy difference between terminal and bridging carbonyls is small and can be influenced by crystal packing forces.[13] The solution fluxionality of the CO ligands in **3** has not been investigated owing to the broad nature of their ^{13}C NMR resonances (caused by bonding to the quadrupolar ^{59}Co nucleus).

Having successfully characterised clusters **2** and **3** derived from alkyne complex **1**, we decided to reinvestigate the reaction of the analogous complex **6** (containing ethyne itself) with $[Co_2(CO)_8]$ with the object of discovering whether any of the previously observed minor products were similar to **2** or **3** and arose from alkyne scission. In order to maximise the yields of higher nuclearity clusters, we used a 2.5-fold excess of dicobalt octacarbonyl, in contrast to our previously reported reaction, which used a 1 : 1 ratio of the two reagents. In addition to the major product, tetranuclear $[Co_2Mo_2(\mu_4\text{-}C_2H_2)(CO)_8Cp_2]$ (**7**) (42% yield), three minor products were isolated and characterised.

The most interesting of these was identified as $[Co_5Mo_2(\mu_4\text{-}CH)(\mu_5\text{-}C)(CO)_{12}Cp_2]$ (**8**), the methylidyne analogue of complex **3**. Its IR spectrum was very similar to that of **3**, and in the ^1H NMR spectrum, the Cp resonances were now accompanied by the characteristic low field signal (δ 12.52) due to a methylidyne proton. Weak resonances were observed at δ 466.0 and 283.2 in the ^{13}C NMR spectrum due to the carbide and methylidyne carbons, respectively. The molecular structure of **8** is shown in Fig. 3. The unit cell contains two independent molecules (A and B) which, in this case, differ only slightly; that shown is molecule A, and selected bond lengths and angles for this molecule are given in Table 3. For ease of comparison, the numbering system used is the same as that in **3**. The metal frameworks of the two clusters are virtually superimposable, with little change in metal–metal distances or angles. The arrangement of the carbonyl ligands in **8** resembles that found in molecule C of **3** in that there are two symmetrically bridging CO groups [C(15)–O(3) and C(22)–O(10)] and two which are unsymmetrically bridging, C(17)–O(5) and particularly C(20)–O(8). Scission of the original ethyne ligand is confirmed by the presence of the μ_5-carbide atom and the μ_4-methylidyne; bond lengths and angles in these ligands are again indistinguishable from those in **3**. The average non-bonding C(11)–C(12) distance in **8** is 3.025 Å.

The μ_4-methylidyne ligand in **8** is highly unusual. The only other example in the literature appears to be $[Ru_2Pt_2(\mu\text{-}H)(\mu_4\text{-}CH)(CO)_3(PR_3)_2Cp_2]$ (R = Cy, Pr^i), prepared by Stone *et al.* from $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2Cp_2]$ and $[Pt(\eta\text{-}C_2H_4)_2(PR_3)]$. Interestingly, when the acetonitrile complex $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(NCMe)Cp_2]$ was used instead, double C–H activation of the methylene ligand occurred to afford $[Ru_2Pt_2(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_2(PR_3)_2Cp_2]$.[14] A further example of methyl-

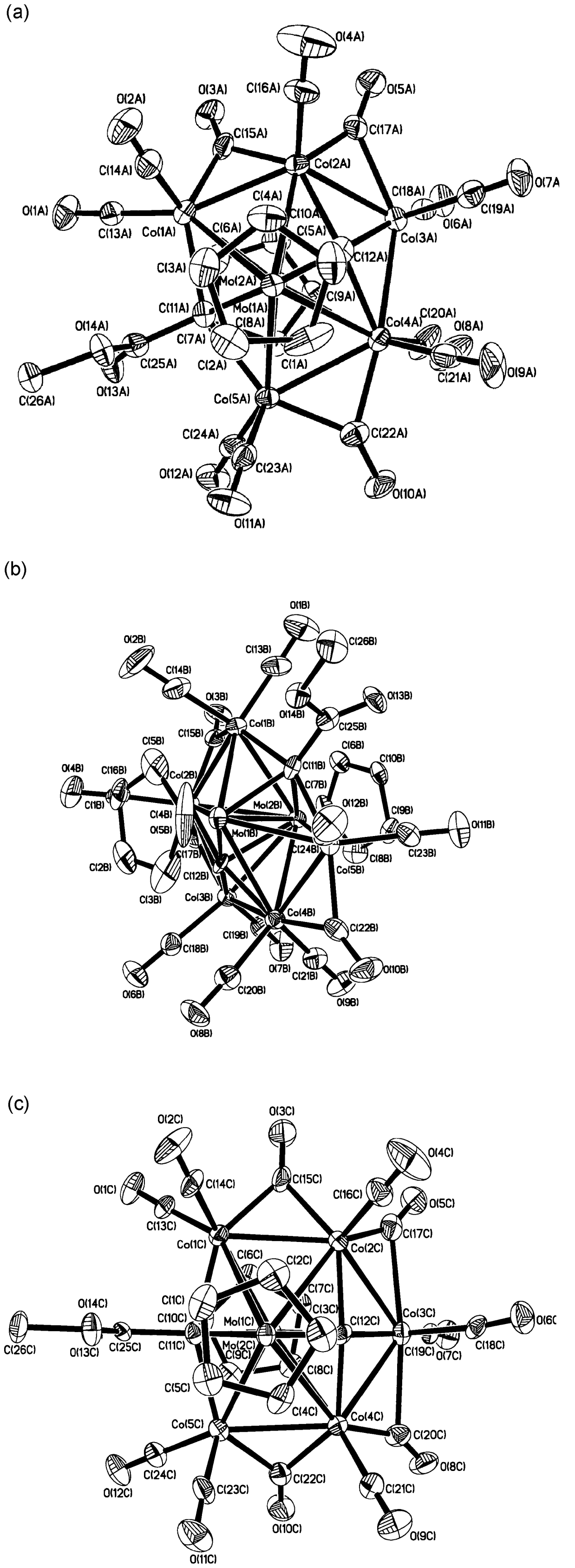


Fig. 2 Molecular structures of the three independent molecules present in the unit cell of $[Co_5Mo_2(\mu_4\text{-}CCO_2Me)(\mu_5\text{-}C)(CO)_{12}Cp_2]$ (**3**) in the crystal, showing the atomic numbering scheme. Molecules A and C are viewed along the Mo–Mo bond to show the different arrangement of CO ligands.

Table 2 Selected bond lengths (Å) and angles (°) for the three independent molecules of complex **3**

	Molecule A	Molecule B	Molecule C
Co(1)–C(15)	1.921(7)	1.926(7)	1.918(7)
Co(1)–C(11)	2.056(6)	2.039(6)	2.075(6)
Co(1)–Co(2)	2.4530(13)	2.4597(12)	2.4891(12)
Co(1)–Mo(2)	2.6825(10)	2.6690(10)	2.6534(10)
Co(1)–Mo(1)	2.6947(10)	2.6746(10)	2.6595(10)
Co(2)–C(17)	1.823(7)	1.846(7)	1.796(7)
Co(2)–C(15)	1.900(7)	1.863(7)	1.895(7)
Co(2)–C(12)	1.936(6)	1.950(6)	1.944(6)
Co(2)–Co(3)	2.4805(13)	2.4829(12)	2.5603(12)
Co(2)–Mo(2)	2.7228(10)	2.7121(10)	2.6954(10)
Co(2)–Mo(1)	2.8562(10)	2.8461(10)	2.8244(10)
Co(3)–C(12)	1.851(6)	1.832(6)	1.846(6)
Co(3)–C(17)	2.053(7)	1.987(7)	2.299(7)
Co(3)–C(20)	—	—	2.195(7)
Co(3)–Co(4)	2.6365(13)	2.6519(12)	2.5278(12)
Co(3)–Mo(2)	2.8145(11)	2.8223(11)	2.8080(10)
Co(4)–C(20)	1.763(7)	1.812(7)	1.795(7)
Co(4)–C(22)	1.945(7)	1.924(7)	1.918(7)
Co(4)–C(12)	1.953(6)	1.946(6)	1.922(6)
Co(4)–Co(5)	2.5211(13)	2.5193(12)	2.4762(12)
Co(4)–Mo(2)	2.6801(10)	2.6790(10)	2.6921(10)
Co(4)–Mo(1)	2.8108(11)	2.8002(10)	2.8339(10)
Co(5)–C(22)	1.908(7)	1.892(7)	1.933(7)
Co(5)–C(11)	2.076(6)	2.073(6)	2.062(6)
Co(5)–Mo(1)	2.6222(10)	2.6126(10)	2.6704(10)
Co(5)–Mo(2)	2.6799(10)	2.6993(10)	2.6471(10)
Mo(1)–C(12)	1.922(6)	1.923(6)	1.929(6)
Mo(1)–C(11)	2.041(6)	2.071(6)	2.019(6)
Mo(1)–Mo(2)	2.7988(8)	2.7821(8)	2.7893(8)
Mo(2)–C(11)	2.109(6)	2.100(6)	2.142(6)
Mo(2)–C(12)	2.187(6)	2.169(6)	2.198(6)
C(11)–C(25)	1.508(9)	1.501(9)	1.493(8)
Av. Co–CO (terminal)	1.782	1.783	1.790
Mo(2)–Co(1)–Mo(1)	62.73(2)	62.75(3)	63.34(2)
Co(1)–Co(2)–Co(3)	127.23(5)	127.22(4)	125.53(4)
Mo(2)–Co(2)–Mo(1)	60.17(2)	60.01(2)	60.65(2)
Co(2)–Co(3)–Co(4)	96.91(4)	96.85(4)	96.80(4)
Co(5)–Co(4)–Co(3)	124.99(4)	125.39(4)	126.10(4)
Mo(2)–Co(4)–Mo(1)	61.24(2)	60.98(3)	60.57(2)
Mo(1)–Co(5)–Mo(2)	63.71(3)	63.14(3)	63.28(2)
C(12)–Mo(1)–C(11)	99.7(2)	99.6(2)	101.5(2)
C(11)–Mo(2)–C(12)	89.7(2)	91.2(2)	89.6(2)
C(25)–C(11)–Mo(1)	136.7(4)	137.2(5)	136.5(4)
C(25)–C(11)–Co(1)	103.3(4)	106.1(4)	102.8(4)
C(25)–C(11)–Co(5)	103.0(4)	100.6(4)	105.3(4)
Co(1)–C(11)–Co(5)	153.6(3)	153.2(4)	151.6(3)
C(25)–C(11)–Mo(2)	138.5(5)	138.8(5)	139.3(4)
Mo(1)–C(11)–Mo(2)	84.8(2)	83.7(2)	84.1(2)
Co(3)–C(12)–Mo(1)	173.3(4)	174.1(4)	172.3(4)
Co(2)–C(12)–Co(4)	160.2(3)	161.1(3)	159.6(3)
Mo(1)–C(12)–Mo(2)	85.6(2)	85.5(2)	84.8(2)
O(3)–C(15)–Co(2)	140.0(6)	141.8(5)	140.3(6)
O(3)–C(15)–Co(1)	140.1(6)	137.2(5)	138.2(6)
Co(2)–C(15)–Co(1)	79.9(3)	80.9(3)	81.5(3)
O(5)–C(17)–Co(2)	149.3(6)	144.9(6)	157.1(6)
O(5)–C(17)–Co(3)	131.3(5)	134.4(5)	126.4(5)
Co(2)–C(17)–Co(3)	79.3(3)	80.6(3)	76.3(3)
O(8)–C(20)–Co(4)	170.4(8)	176.9(7)	153.3(6)
O(8C)–C(20C)–Co(3C)	—	—	128.4(5)
Co(4C)–C(20C)–Co(3C)	—	—	77.9(3)
O(10)–C(22)–Co(5)	140.0(6)	139.0(6)	139.6(6)
O(10)–C(22)–Co(4)	138.2(6)	138.3(6)	140.4(6)
Co(5)–C(22)–Co(4)	81.7(3)	82.6(3)	80.0(3)

idyne to carbide conversion was provided by the same group's synthesis of Os_3Pt and Os_3Pt_2 carbido clusters from $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ and $[Pt(\eta\text{-}C_2H_4)_2(PCy_3)]$.[15] To our knowledge, **8** is, however, the first cluster to contain both carbide and methylidyne ligands.

Unexpectedly, the two other minor products were identified as the known trinuclear ethylidyne clusters $[Co_2Mo(\mu_3\text{-}CMe)(CO)_8Cp]$ (**9**)[16,17] and $[CoMo_2(\mu_3\text{-}CMe)(CO)_7Cp_2]$ (**10**),[18] see Chart 1, by comparison of their spectroscopic data with published values. Both of these compounds have been prepared from $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ by treatment with a variety of metal exchange reagents, *e.g.* $[Mo_2(CO)_6Cp_2]$, $[MoH(CO)_3Cp]$ or

Table 3 Selected bond lengths (Å) and angles (°) for molecule A of complex **8**

Mo(1)–C(12)	1.911(4)	Mo(1)–C(11)	2.008(5)
Mo(1)–Co(5)	2.6383(8)	Mo(1)–Co(1)	2.6919(7)
Mo(1)–Mo(2)	2.7948(5)	Mo(1)–Co(4)	2.8262(8)
Mo(1)–Co(2)	2.8394(8)	Mo(2)–C(11)	2.109(4)
Mo(2)–C(12)	2.189(4)	Mo(2)–Co(4)	2.6696(7)
Mo(2)–Co(5)	2.6729(8)	Mo(2)–Co(1)	2.6882(7)
Mo(2)–Co(2)	2.7149(8)	Mo(2)–Co(3)	2.7916(8)
Co(1)–C(14)	1.772(5)	Co(1)–C(13)	1.790(5)
Co(1)–C(15)	1.923(5)	Co(1)–C(11)	2.045(5)
Co(1)–Co(2)	2.4706(9)	Co(2)–C(16)	1.787(5)
Co(2)–C(17)	1.822(5)	Co(2)–C(15)	1.887(5)
Co(2)–C(12)	1.940(4)	Co(2)–Co(3)	2.5134(9)
Co(3)–C(18)	1.789(5)	Co(3)–C(19)	1.804(5)
Co(3)–C(12)	1.850(4)	Co(3)–C(17)	2.082(5)
Co(3)–C(20)	2.517(5)	Co(3)–Co(4)	2.6029(10)
Co(4)–C(20)	1.775(5)	Co(4)–C(21)	1.796(5)
Co(4)–C(22)	1.927(5)	Co(4)–C(12)	1.965(4)
Co(4)–Co(5)	2.5163(9)	Co(5)–C(23)	1.765(5)
Co(5)–C(24)	1.773(6)	Co(5)–C(22)	1.899(5)
Co(5)–C(11)	2.059(4)	Av. Co–CO (terminal)	1.785
C(12)–Mo(1)–C(11)	100.09(17)	C(11)–Mo(2)–C(12)	88.71(16)
Mo(2)–Co(1)–Mo(1)	62.592(17)	Co(1)–Co(2)–Co(3)	126.37(3)
Mo(2)–Co(2)–Mo(1)	60.370(18)	Co(2)–Co(3)–Co(4)	97.28(3)
Co(5)–Co(4)–Co(3)	125.08(3)	Mo(2)–Co(4)–Mo(1)	61.053(17)
Mo(1)–Co(5)–Mo(2)	63.495(19)	Co(1)–C(11)–Co(5)	155.6(3)
Mo(1)–C(11)–Mo(2)	85.46(18)	Co(3)–C(12)–Mo(1)	172.6(3)
Co(2)–C(12)–Co(4)	159.2(2)	Mo(1)–C(12)–Mo(2)	85.65(16)
O(5)–C(17)–Co(2)	149.8(4)	O(5)–C(17)–Co(3)	130.3(4)
Co(2)–C(17)–Co(3)	79.84(19)	O(8)–C(20)–Co(4)	165.5(5)
O(8)–C(20)–Co(3)	122.1(4)	Co(4)–C(20)–Co(3)	72.34(18)

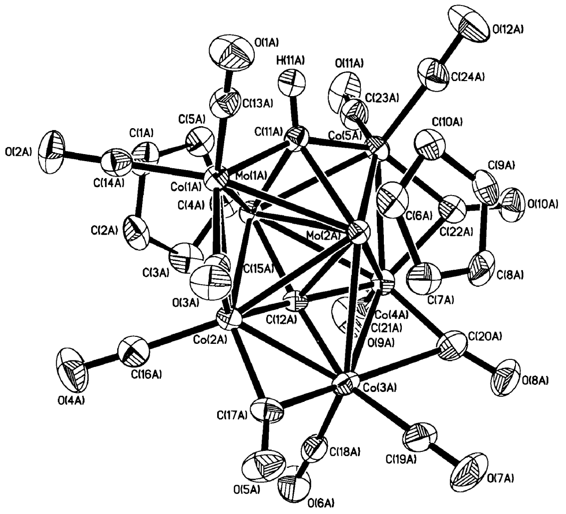
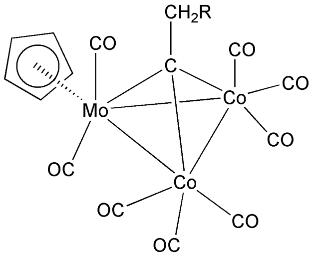
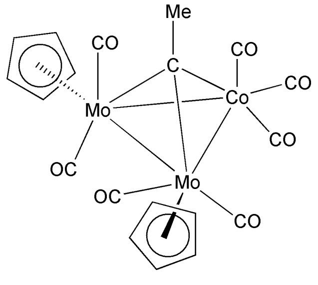


Fig. 3 Molecular structure of molecule A, one of the two independent molecules present in the unit cell of [$Co_5Mo_2(\mu_4\text{-}CH)(\mu_5\text{-}C)(CO)_{12}Cp_2$] (**8**) in the crystal, showing the atomic numbering scheme.



9 R = H
11 R = CO_2Me



10

Chart 1

Na[$Mo(CO)_3Cp$]. Presumably, in this case, the ethylidyne ligand arises through rearrangement of the alkyne and addition of an extra hydrogen atom, though the mechanism is clearly complex, especially given that **9** is the only compound isolated from any of these reactions that involves cleavage of the original Mo–Mo bond. The crystal structure of **10** has been previously determined, but that of **9** has not. The molecular structure of **9** is, therefore, shown in Fig. 4, with selected bond lengths and angles collected in Table 4. The cluster consists of a triangle of two cobalt atoms and one molybdenum, with each cobalt bearing three terminal CO groups and the Mo atom two CO ligands and the Cp ring. The triangle is capped by an ethylidyne ligand which leans over slightly towards the dicobalt unit as a result of the shorter Co–C(9) bonds. As expected, the geometry of the molecule is very similar to that of the benzylidyne cluster [$Co_2Mo(\mu_3\text{-}CPh)(CO)_8Cp$] determined by Vahrenkamp.[16]

We next addressed the origin of the μ_5-carbide atom in the heptanuclear clusters **3** and **8**. The obvious inference is that it arises from the original alkyne by removal of one of the substituents, but it might also be formed by the cleavage of a carbonyl ligand, itself a known process in cluster chemistry.[19] In the absence of ^{13}C labelling studies, we cannot prove conclusively that it is the former, but we believe that the following experiment provides an indication that this is the case. When the dimolybdenum alkyne complex [$Mo_2(\mu\text{-}HC{\equiv}CCO_2Me)(CO)_4Cp_2$], derived from methyl propiolate, was heated with [$Co_2(CO)_8$] under similar conditions, the only heptanuclear cluster formed was **3**, with no trace of **8** present. One might expect the CH bond of the methylidyne group to be cleaved in preference to the CCO_2Me group, giving the observed product. Conversely, if the carbide atom arose from a carbonyl ligand, a mixture of **3** and **8** might be anticipated.

Table 4 Selected bond lengths (Å) and angles (°) for complex **9**

Mo(1)–C(9)	2.102(5)	Mo(1)–Co(1)	2.6465(8)
Mo(1)–Co(2)	2.7095(9)	Co(1)–C(9)	1.933(5)
Co(1)–Co(2)	2.4812(10)	Co(2)–C(9)	1.942(5)
C(15)–C(9)	1.498(7)		
Co(1)–Mo(1)–Co(2)	55.18(2)	Co(2)–Co(1)–Mo(1)	63.70(2)
Co(1)–Co(2)–Mo(1)	61.12(2)	Co(1)–C(9)–Co(2)	79.61(19)
Co(1)–C(9)–Mo(1)	81.86(19)	Co(2)–C(9)–Mo(1)	84.03(18)

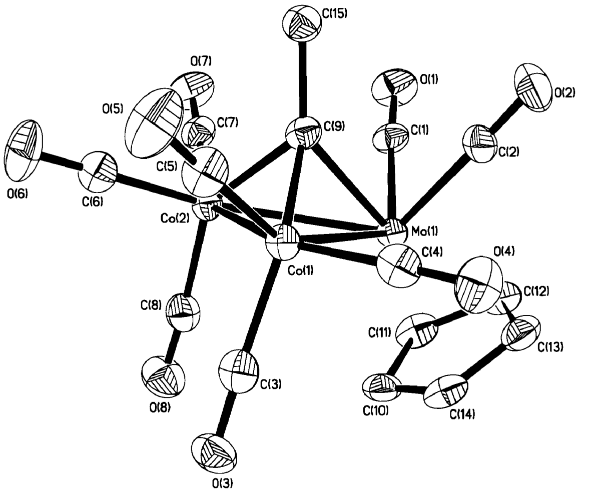


Fig. 4 Molecular structure of $[Co_2Mo(\mu_3\text{-CMe})(CO)_8Cp]$ (**9**) in the crystal, showing the atomic numbering scheme.

Given the structural similarity between clusters **2** and **3**, it is attractive to postulate that **3** might be formed by attachment of an additional cobalt carbonyl fragment to **2**, with concomitant loss of the ester functionality from one of the alkylidyne groups and formation of the μ_5-C ligand. Although heating isolated **2** with additional $[Co_2(CO)_8]$ under similar conditions does give **3**, the yield is rather poor, which does not tally with the yields of the two complexes obtained from the original reaction: the conversion of **2** to **3** would have to be extremely efficient, since the yield of **2** is very low, but that of **3** is surprisingly high for a reaction of this complexity. It therefore appears more likely that the two clusters are formed by independent pathways rather than sequentially.

We also examined the role of the tetranuclear cluster $[Co_2Mo_2\{\mu_4\text{-}C_2(CO_2Me)_2\}(CO)_8Cp_2]$ (**5**) as a possible intermediate to the higher nuclearity species. Indeed, when heated with an excess of $[Co_2(CO)_8]$ (5 equivalents), **5** produced both **2** (10%) and **3** (58.5%) in yields which indicate that some, if not all, of the products in the original reaction could arise in this way. A similar reaction with $[Co_2Mo_2(\mu_4\text{-HC}{\equiv}CCO_2Me)(CO)_8Cp_2]$ again gave **3**, but in the case of $[Co_2Mo_2(\mu_4\text{-}C_2H_2)(CO)_8Cp_2]$ (**7**), no trace of **8** was observed (and indeed no products at all were formed). These results may reflect the differing propensities of ethyne and DMAD to undergo cleavage, which, in turn, will depend on the stabilities of the resulting μ_4-CH and μ_4-CCO_2Me alkylidyne ligands.

Recently, Chi and co-workers have reported the preparation of several carbido-alkylidyne clusters *via* the cleavage of coordinated acetylide ligands (μ-C≡CR ⟶ μ-C + μ-CR).[20] In some cases, these reactions are reversible: simply adding CO regenerates the C≡C bond. We were therefore prompted to examine the reactivity of **3** towards CO to see whether an acetylide ligand could be formed from the carbide and alkylidyne units. In the event, treatment of **3** with CO (15 atm, 80 °C) in a sealed vessel unexpectedly gave a 74% yield of the alkylidyne cluster $[Co_2Mo(\mu_3\text{-}CCH_2CO_2Me)(CO)_8Cp]$ (**11**); the fate of the remaining metal atoms is unknown. Clearly, the formation of **11** requires not only the coupling of the carbide and alkylidyne, but also the addition of two hydrogen atoms, the source of which is unknown. Treatment of **3** with dihydrogen under similar conditions was unproductive (only unchanged starting material and decomposition were recovered), and carrying out the carbonylation reaction in toluene-d_8 still produced **11**, which contained no detectable deuterium. The structure of molecule **11** in the crystal is shown in Fig. 5, with selected bond lengths and angles given in Table 5. As might be expected, the structural parameters are very similar to those of **9**. In the solid state, the CO_2Me substituent of the alkylidyne occupies a position above one of the Mo–Co bonds, presumably to minimise steric repulsions with the carbonyl ligands.

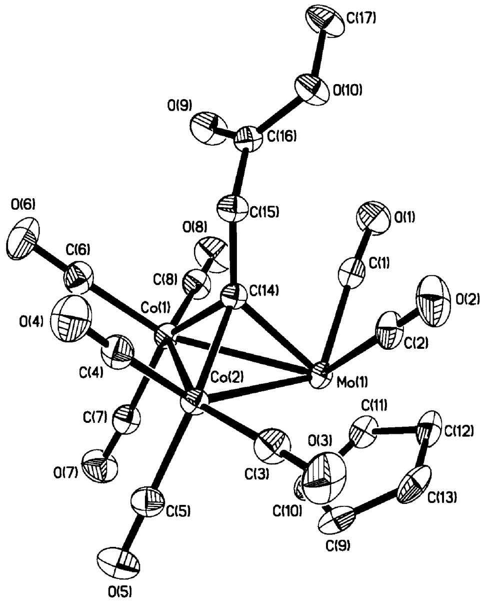


Fig. 5 Molecular structure of $[Co_2Mo(\mu_3\text{-}CCH_2CO_2Me)(CO)_8Cp]$ (**11**) in the crystal, showing the atomic numbering scheme.

Conclusion

The scission of the alkyne ligand in $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4Cp_2]$ can indeed be effected by reaction with dicobalt octacarbonyl, in yields that vary dramatically with the substituents R^1 and R^2. This system provides the second example of the scission of ethyne itself on a metal cluster. The product clusters contain either two alkylidyne ligands or one alkylidyne and one carbide, apparently formed by loss of one of the original alkyne substituents, and exhibit very unusual metal frameworks. Further exploration of alkyne cleavage in **1** as a route to otherwise inaccessible higher nuclearity mixed-metal alkylidyne clusters is under way in our laboratory; the stability of the dimolybdenum unit and the fact that the alkylidyne ligands produced can cap faces which contain both MoCp vertices is, we believe, an important factor in the success of these reactions.[21]

Experimental

General experimental techniques were as described in a recent paper from this laboratory.[13] Infrared spectra were recorded in

Table 5 Selected bond lengths (Å) and angles (°) for complex **11**

Co(1)–C(14)	1.923(2)	Co(1)–Co(2)	2.4945(4)
Co(1)–Mo(1)	2.7020(4)	Co(2)–C(14)	1.938(2)
Co(2)–Mo(1)	2.6695(4)	Mo(1)–C(14)	2.109(2)
C(14)–C(15)	1.518(3)		
Co(2)–Co(1)–Mo(1)	61.670(11)	Co(1)–Co(2)–Mo(1)	62.993(12)
Co(2)–Mo(1)–Co(1)	55.337(11)	Co(1)–C(14)–Co(2)	80.51(9)
Co(1)–C(14)–Mo(1)	84.04(9)	Co(2)–C(14)–Mo(1)	82.44(9)

dichloromethane solutions on a Perkin–Elmer 1600 FT–IR machine. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution on a Bruker AC250 machine with an automated sample-changer or an AMX400 spectrometer. Chemical shifts are given on the δ scale relative to $SiMe_4 = 0.0$ ppm. The $^{13}C\{^1H\}$ 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 fast atom bombardment mode with *m*-nitrobenzyl alcohol as matrix; the figures reported are the highest intensity peak of each isotope envelope. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry, University of Sheffield. Light petroleum refers to the fraction boiling in the range 60–80 °C.

Reaction of $[Mo_2(\mu\text{-}MeO_2CC{\equiv}CCO_2Me)(CO)_4Cp_2]$ (1) with $[Co_2(CO)_8]$

A solution of the dimolybdenum alkyne complex **1** (2.22 g, 3.86 mmol) and dicobalt octacarbonyl (6.60 g, 19.3 mmol) in toluene (100 cm^3) was heated to reflux for 1 h. After cooling, a small amount of silica was added and the solvent was removed. The residue was loaded onto a chromatography column. Elution with light petroleum and dichloromethane (3 : 2) afforded an olive-green band [IR ν(CO) 2074, 2030, 2012, 1997, 1820 cm^{-1}] identified as $[Co_4(CO)_9(\eta\text{-toluene})]$ (**4**) (480.5 mg, 9%) by comparison with the published data.[8]

Elution with a 2 : 3 mixture of the same solvents produced a dark brown band of $[Co_5Mo_2(\mu_5\text{-}C)(\mu_4\text{-}CCO_2Me)(CO)_{12}Cp_2]$ (**3**) (1.877 g, 47%), which was obtained as dark brown crystals suitable for X-ray diffraction by diffusion of light petroleum into a CH_2Cl_2 solution at 4 °C. A second smaller brown band, identified as $[Co_4Mo_2(\mu_4\text{-}CCO_2Me)_2(CO)_{10}Cp_2]$ (**2**) (98.6 mg, 3%), was then eluted with a 1 : 4 mixture of light petroleum and dichloromethane. Dark brown crystals suitable for X-ray diffraction were grown in the same manner as above. Continued elution of the column with CH_2Cl_2 afforded a green band consisting of the tetranuclear alkyne complex $[Co_2Mo_2\{\mu_4\text{-}C_2(CO_2Me)_2\}(CO)_8Cp_2]$ (**5**) (230.2 mg, 7%).

Data for 3. M.p. > 250 °C. IR: ν(CO) 2068m, 2031vs, 2014sh, 1859m, 1823m, 1659w cm^{-1}. ^{1}H NMR: δ 5.55 (s, 5 H, Cp), 4.97 (s, 5 H, Cp), 3.71 (s, 3 H, Me). ^{13}C NMR: δ 475.0 (br s, μ_5-C), 285.5 (br s, μ_4-C), 220.0–190.0 (v br, CO), 176.3 (s, *C*O$_2$Me), 99.1 (s, Cp), 93.2 (s, Cp), 53.1 (s, Me). Found: C, 30.08; H, 0.92; calc. for $C_{26}H_{13}Co_5Mo_2O_{14}$: C, 30.15; H, 1.26%. Mass spectrum: *m*/*z* 1037, 1008, 982, 952, 921, 895, 867, 838 ($M^+ - n$CO, $n = 0$–7).

Data for 2. M.p. > 250 °C. IR: ν(CO) 2038vs, 2011s, 1824m, 1656w cm^{-1}. ^{1}H NMR: δ 5.71 (s, 10 H, Cp), 3.73 (s, 6 H, Me). ^{13}C NMR: δ 312.5 (br s, μ_4-C), 203.5 (br s, CO), 173.8 (s, *C*O$_2$Me), 97.3 (s, Cp), 51.9 (s, Me). Found: C, 31.64; H, 1.46; calc. for $C_{26}H_{16}Co_4Mo_2O_{14}$: C, 31.87; H, 1.65%. Mass spectrum: *m*/*z* 982, 897, 867, 838 ($M^+ - n$CO, $n = 0$, 3–5).

Data for 5. M.p. > 250 °C. IR: ν(CO) 2066vs, 2044vs, 2026sh, 1846s, 1806m, 1709w, 1683w cm^{-1}. ^{1}H NMR: δ 5.31 (s, 10 H, Cp); 3.65 (s, 6 H, Me). ^{13}C NMR: δ 245.2 (s, CO), 173.7 (s, *C*O$_2$Me), 146.0 (s, *C*CO$_2$Me), 96.7 (s, Cp), 52.1 (s, Me). Found: C, 35.63; H, 1.64; calc. for $C_{24}H_{16}Co_2Mo_2O_{12}$: C, 35.76; H, 2.00%. Mass spectrum: *m*/*z* 807, 780, 751, 723, 694, 666, 638 ($M^+ - n$CO, $n = 0$–6).

A similar reaction between **1** (1.63 g, 2.83 mmol) and $[Co_2(CO)_8]$ (0.967 g, 2.83 mmol) in refluxing toluene (150 cm^3) for 1 h, followed by the same chromatographic work-up, afforded $[Co_4(CO)_9(\eta\text{-toluene})]$ (31.0 mg, 4%); cluster **3** (277.0 mg, 9%); cluster **2** (trace); and **5** (952.6 mg, 42%).

Reaction of $[Mo_2(\mu\text{-}HC{\equiv}CH)(CO)_4Cp_2]$ (6) with $[Co_2(CO)_8]$

The complex $[Mo_2(\mu\text{-}HC_2H)(CO)_4Cp_2]$ (0.227 g, 0.49 mmol) and 2.5 equiv. of dicobalt octacarbonyl (0.420 g, 1.22 mmol) were dissolved in toluene (20 cm^3). The solution was heated to reflux for 1 h. The solvent was removed and the residue absorbed onto a small amount of silica. Column chromatography gave the following bands:

(i) A green band, eluted with light petroleum–dichloromethane (4 : 1) which was identified as $[Co_2Mo(\mu_3\text{-}CMe)(CO)_8Cp]$ (**9**) (55.5 mg, 22%) by comparison with published data.[17] IR: ν(CO) 2077w, 2068m, 2025s, 2009s, 1999s, 1944w cm^{-1}. ^{1}H NMR: δ 5.39 (s, 5 H, Cp), 3.73 (s, 3 H, Me). Mass spectrum: *m*/*z* 503, 475, 447, 419, 391 ($M^+ - n$CO, $n = 0$–4). Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution in light petroleum.

(ii) On some occasions (particularly at lower Co : Mo ratios), a second green band was eluted with the same solvent mixture in yields of up to 7%; this compound was identified as $[CoMo_2(\mu_3\text{-}CMe)(CO)_7Cp_2]$ (**10**) by comparison with published data.[18] IR: ν(CO) 2035ms, 1992s, 1975sh, 1945sh, 1916m, 1848w cm^{-1}. ^{1}H NMR: δ 5.27 (s, 5 H, Cp), 3.77 (s, 3 H, Me). Mass spectrum: *m*/*z* 605, 576, 548, 520, 492, 464, 436, 406 ($M^+ - n$CO, $n = 0$–7).

(iii) A brown band, eluted in light petroleum–dichloromethane (3 : 2) and identified as $[Co_5Mo_2(\mu_5\text{-}C)(\mu_4\text{-}CH)(CO)_{12}Cp_2]$ (**8**) (127.1 mg, 26%). Crystals suitable for X-ray study were grown by diffusion of light petroleum into a CH_2Cl_2 solution at 4 °C.

(iv) A dark blue band, eluted in a 1 : 4 mixture of the same solvents and identified as $[Co_2Mo_2(\mu_4\text{-}C_2H_2)(CO)_8Cp_2]$ (**7**) (143.0 mg, 42%), as reported previously.[7]

Data for 8. M.p. > 250 °C. IR: ν(CO) 2064m, 2028sh, 2021vs, 1983sh, 1853m, 1817m cm^{-1}. ^{1}H NMR: δ 12.52 (s, 1 H, CH), 5.35 (s, 5 H, Cp), 4.62 (s, 5 H, Cp). ^{13}C NMR: δ 466.0 (br s, μ_5-C), 283.2 (s, μ_4-C), 214.0 (br, CO), 96.8 (s, Cp), 92.3 (s, Cp). Found: C, 29.24; H, 0.91; calc. for $C_{24}H_{11}Co_5Mo_2O_{12}$: C, 29.48; H, 1.13%. Mass spectrum: *m*/*z* 979, 951, 923, 895, 866, 837, 810, 792 ($M^+ - n$CO, $n = 0$–7).

Reaction of $[Mo_2(\mu\text{-}HC{\equiv}CCO_2Me)(CO)_4Cp_2]$ with $[Co_2(CO)_8]$

The dimolybdenum alkyne complex $[Mo_2(\mu\text{-}HC{\equiv}CCO_2Me)(CO)_4Cp_2]$ (0.260 g, 0.50 mmol) and 2.5 equiv. of dicobalt octacarbonyl (0.430 g, 1.25 mmol) were dissolved in toluene (20 cm^3). The solution was heated to reflux for 1 h. The solvent was removed and the residue absorbed on a small amount of silica for chromatography. The following bands were observed:

(i) Olive-green $[Co_4(CO)_9(\eta\text{-toluene})]$ (111.9 mg, 31%), eluted with light petroleum–dichloromethane (3 : 2);

Table 6 Summary of crystallographic data for complexes **2**, **3** and **8** and for the trinuclear clusters **9** and **11**

	2	**3**	**8**	**9**	**11**
Empirical formula	$C_{26}H_{16}Co_4Mo_2O_{14}$	$C_{26}H_{13}Co_5Mo_2O_{14}$	$C_{24}H_{11}Co_5Mo_2O_{12}$	$C_{15}H_8Co_2MoO_8$	$C_{17}H_{10}Co_2MoO_{10}$
Formula weight	979.99	1035.89	977.86	530.01	588.05
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.4754(19)	17.768(2)	10.6072(10)	7.9482(16)	7.9324(5)
b/Å	9.740(2)	17.468(2)	16.1964(16)	8.1591(17)	9.0316(5)
c/Å	10.003(2)	29.337(4)	16.4925(16)	14.264(3)	15.5819(9)
a/°	113.584(4)	90	99.395(2)	102.893(4)	96.5350(10)
β/°	117.660(4)	94.388(3)	92.574(2)	92.936(4)	96.7060(10)
γ/°	94.207(4)	90	92.924(2)	108.181(4)	115.9990(10)
V/Å^3	710.2(3)	9079(2)	2787.7(5)	849.3(3)	979.32(10)
Z	1	12	4	2	2
μ/mm^{-1}	3.211	3.544	3.834	2.698	2.358
Reflections collected	4518	57159	17776	5414	7667
Independent reflections [R(int)]	3210 [0.0407]	21967 [0.1025]	12614 [0.0477]	3843 [0.0526]	4448 [0.0471]
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0448, 0.1221	0.0491, 0.0817	0.0377, 0.0685	0.0465, 0.1015	0.0329, 0.0900
$R1$, $wR2$ (all data)	0.0494, 0.1251	0.1110, 0.0963	0.0635, 0.0749	0.0670, 0.1079	0.0345, 0.0919

(ii) Dark brown $[Co_5Mo_2(\mu_5\text{-}C)(\mu_4\text{-}CCO_2Me)(CO)_{12}Cp_2]$ **3** (91.5 mg, 18%), eluted with a 2 : 3 mixture of the same solvents and characterised as above;

(iii) Dark green $[Co_2Mo_2(\mu_4\text{-}HC{\equiv}CCO_2Me)(CO)_8Cp_2]$ (289.4 mg, 77%) eluted with CH_2Cl_2; the characterisation of this complex was reported previously.[7]

Reaction of $[Co_4Mo_2(\mu_4\text{-}CCO_2Me)_2(CO)_{10}Cp_2]$ (2) with $[Co_2(CO)_8]$

Cluster **2** (0.11 g, 0.11 mmol) and 2 equiv. of dicobalt octacarbonyl (0.07 g, 0.23 mmol) were dissolved in toluene (15 cm^3) and heated to reflux for 1.25 h. After removal of the solvent, the residue was chromatographed as above to give olive-green $[Co_4(CO)_9(\eta\text{-toluene})]$ (16.9 mg, 26%), the cluster $[Co_5Mo_2(\mu_5\text{-}C)(\mu_4\text{-}CCO_2Me)(CO)_{12}Cp_2]$ **3** (13.4 mg, 11%) and finally unchanged **2** (46.9 mg, 42% recovery).

Reaction of $[Co_2Mo_2\{\mu_4\text{-}C_2(CO_2Me)_2\}(CO)_8Cp_2]$ (5) with $[Co_2(CO)_8]$

A solution of cluster **5** (100 mg, 0.12 mmol) and an excess of dicobalt octacarbonyl (212 mg, 0.62 mmol) in toluene (10 cm^3) was heated to reflux for 1 h. Chromatographic work-up initially afforded remaining $[Co_2(CO)_8]$ (16.9 mg, 8% recovery) and $[Co_4(CO)_9(\eta\text{-toluene})]$ (60.9 mg, 34%). Elution with dichloromethane–light petroleum (2 : 3) produced a dark brown band of **3** (75.2 mg, 58.5%). A second smaller brown band, identified as **2** (12.4 mg, 10%), was then eluted with a 1 : 4 mixture of the same solvents. Elution with dichloromethane–acetone (99 : 1) afforded a small amount of remaining **5** (7.0 mg, 7% recovery).

Reaction of $[Co_2Mo_2(\mu_4\text{-}HC{\equiv}CCO_2Me)(CO)_8Cp_2]$ with $[Co_2(CO)_8]$

In a similar manner to the above, a toluene solution (10 cm^3) of the cluster $[Co_2Mo_2(\mu_4\text{-}HC{\equiv}CCO_2Me)(CO)_8Cp_2]$ (100.0 mg, 0.13 mmol) and dicobalt octacarbonyl (229.0 mg, 0.67 mmol) was heated to reflux for 2.5 h. Chromatography gave $[Co_4(CO)_9(\eta\text{-toluene})]$ (41.0 mg, 21.5%) and **3** (14.5 mg, 10%), with recovery of 82.9 mg (83%) of the starting cluster.

Reaction of $[Co_2Mo_2(\mu_4\text{-}C_2H_2)(CO)_8Cp_2]$ with $[Co_2(CO)_8]$

A similar reaction between $[Co_2Mo_2(\mu_4\text{-}C_2H_2)(CO)_8Cp_2]$ (100.0 mg, 0.14 mmol) and $[Co_2(CO)_8]$ (248.0 mg, 0.72 mmol) in boiling toluene (10 cm^3) for 2.5 h gave only $[Co_4(CO)_9(\eta\text{-toluene})]$ (19.2 mg, 9%) and the starting tetranuclear cluster (79.2 mg, 79% recovery).

Reaction of $[Co_5Mo_2(\mu_4\text{-}CCO_2Me)(\mu_5\text{-}C)(CO)_{12}Cp_2]$ 3 with CO

Complex **3** (0.200 g, 0.19 mmol) was dissolved in toluene (30 cm^3) in a glass tube. The solution was placed under a pressure of 15 atm of carbon monoxide in a Fisher–Porter apparatus and then heated to 80 °C for 48 h with stirring. After cooling, the pressure was released and the solvent was removed under vacuum. Column chromatography with an eluant of light petroleum and diethyl ether (4 : 1) gave a brown band of recovered starting material (19.5 mg, 9.8%). Further elution with the same solvent mixture produced a green zone consisting of $[Co_2Mo(\mu_3\text{-}CCH_2CO_2Me)(CO)_8Cp]$ (**11**) (84.5 mg, 74%). A crystal suitable for X-ray diffraction was grown by slow diffusion of light petroleum into a solution of the compound in diethyl ether at −10 °C.

Data for 11. M.p. 139–142 °C. IR: ν(CO) 2081w, 2071m, 2030s, 2015s, 2002s, 1947w, 1731w cm^{-1}. ^{1}H NMR: δ 5.38 (s, 5 H, Cp), 4.75 (s, 2 H, CH_2), 3.72 (s, 3 H, Me). ^{13}C NMR: δ 269.6 (br s, μ_3-C), 208.1 (br, CO), 171.0 (s, CO_2Me), 90.9 (s, Cp), 61.0 (s, CH_2), 51.6 (s, Me). Found: C, 34.09; H, 1.68; calc. for $C_{17}H_{10}Co_2MoO_{10}$: C, 34.72; H, 1.71%. Mass spectrum: m/z 561, 533, 505, 477, 449, 421, 393, 365 ($M^+ - n$CO, $n = 0$–7).

Reaction of $[Co_5Mo_2(\mu_4\text{-}CCO_2Me)(\mu_5\text{-}C)(CO)_{12}Cp_2]$ 3 with H_2

A similar reaction of **3** (0.200 g, 0.19 mmol) with H_2 (15 atm) at 80 °C for 48 h gave recovered starting material (88.1 mg, 44%) as the only isolable product on chromatography as above.

Crystal structure determinations of complexes 2, 3, 8, 9 and 11

The crystal data for the five structures are collected in Table 6. General procedures were as described in previous publications;[7,13] a Bruker Smart CCD area detector with an Oxford Cryosystems low temperature system was used for data collection. Complex scattering factors were taken from the program package SHELXTL,[22] as implemented on a Viglen Pentium computer.

CCDC reference numbers 185243–185247.

See http://www.rsc.org/suppdata/dt/b2/b204326m/ for crystallographic data in CIF or other electronic format.

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