DALTON

# Synthesis of tetranuclear cobalt–molybdenum butterfly clusters with alkyne ligands: crystal structure of $[Co_2Mo_2(\mu_4\text{-}C_2Me_2)(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_5)_2]$

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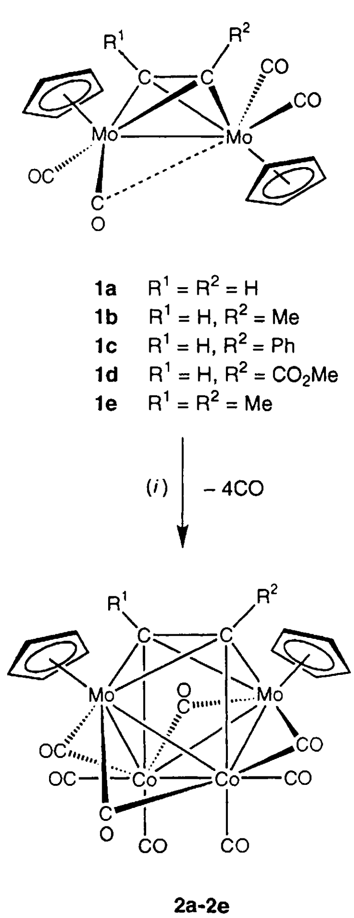
The dimolybdenum alkyne complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4(\eta\text{-}C_5H_5)_2]$ ($R^1 = R^2 =$ H, Me or $CO_2Me$; $R^1 =$ H, $R^2 =$ Me, Ph or $CO_2Me$) reacted with dicobalt octacarbonyl in refluxing toluene to give the 60-electron tetranuclear clusters $[Co_2Mo_2(\mu_4\text{-}R^1C_2R^2)(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_5)_2]$ in moderate to good yields. The crystal structure of the complex derived from but-2-yne ($R^1 = R^2 =$ Me) has been determined: monoclinic, space group *Cc*, $a = 34.74(2)$, $b = 8.7970(10)$, $c = 15.910(5)$ Å, $\beta = 102.93(4)°$, $Z = 8$. The cluster contains a butterfly-type core in which the two molybdenum atoms form the wingtips and the two cobalt atoms the hinge, with the alkyne ligand bridging the four metals to form an octahedral structure. All of the cobalt–molybdenum edges are asymmetrically bridged by carbonyl ligands which are bonded more strongly to molybdenum (average Mo–μ-CO 1.980 Å) than to cobalt (average Co–μ-CO 2.267 Å).

The rational synthesis of heterometallic clusters is a subject which has received considerable attention in recent years.[1] The application of the isolobal analogy by Stone[2] and the development of metal-exchange reactions by Vahrenkamp[3] are two examples of successful approaches to this problem. A further established strategy is the use of an assembling ligand to assist cluster build-up by the co-ordination of additional metal–ligand fragments. In this way mono- or di-nuclear complexes containing alkyne ligands can be employed as precursors for the construction of higher-nuclearity alkyne clusters.[4]

We have been examining the reactions of the dimolybdenum alkyne complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1** with a variety of reagents such as phosphines, thiols and elemental sulfur.[5] We have noted previously that the reactivity of complexes of type **1** differs markedly from those of its precursors $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, both of which have been extensively studied.[6] Usually the alkyne ligand is retained in the products, and in some cases different products are obtained depending on the identity of the alkyne substituents $R^1$ and $R^2$. Recently we reported that treatment of **1** with $[Ru_3(CO)_{12}]$ resulted in alkyne scission and formation of the hexanuclear bis(alkylidyne) clusters $[Mo_2Ru_4(\mu_3\text{-}CR^1)(\mu_3\text{-}CR^2)(CO)_{12}(\eta\text{-}C_5H_5)_2]$ in modest yield. This was so even when a terminal alkyne (*i.e.* $R^1 =$ H) was used, though the trinuclear vinylidene complexes $[Mo_2Ru(\mu_3\text{-}C{=}CHR^2)(CO)_7(\eta\text{-}C_5H_5)_2]$ were also produced as the major products in these reactions.[7] We were therefore prompted to examine cluster building by the reaction of **1** with other metal carbonyls, and in this paper we discuss the tetranuclear alkyne clusters obtained with $[Co_2(CO)_8]$.

## Results and Discussion

Heating a toluene solution of a dimolybdenum alkyne complex **1a**–**1e** with 1 equivalent of dicobalt octacarbonyl to reflux causes a rapid reaction in all cases (Scheme 1) readily monitored by a change from red to deep green. The products, the tetranuclear clusters $[Co_2Mo_2(\mu\text{-}R^1C_2R^2)(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_5)_2]$ **2a**–**2e** can be readily isolated by column chromatography as air-stable blue or green solids in moderate to good yields. Further experiments showed that **2a**–**2e** decompose in refluxing toluene over a period of 2 h; it is therefore important not to allow the reactions to proceed too long: a reaction time of around 30 min was used, though the yields reported are not optimised.



**Scheme 1** Synthesis of the dicobalt–dimolybdenum clusters. (*i*) $[Co_2(CO)_8]$, heat, toluene

The solution IR spectra of compounds **2a**–**2e** are all very similar and contain peaks attributable to terminal and bridging carbonyl ligands. The molecular formulae of the clusters were readily apparent from the observation of molecular ions in their FAB mass spectra (in most cases accompanied by peaks due to the loss of up to five carbonyl ligands) and from their elemental analyses. Their $^1H$ NMR spectra are simple and all consist of one peak for the $C_5H_5$ ligands and appropriate signals for $R^1$ and $R^2$. The $C_5H_5$ ligands are still equivalent in **2b**–**2d** where

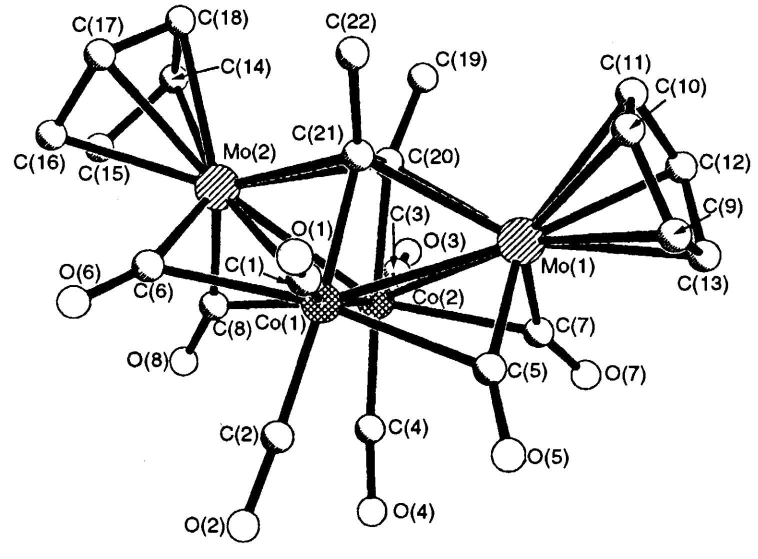


**Fig. 1** Molecular structure of $[Co_2Mo_2(\mu_4\text{-}C_2Me_2)(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_5)_2]$ **2e** in the crystal

the alkyne ligand is unsymmetrical (thus ruling out any structure where the alkyne lies parallel to the Mo $\cdots$ Mo axis). The spectra also point to the presence of intact alkyne ligands: isomerisation to a co-ordinated vinylidene is ruled out by **2b** (which displays two singlets for the propyne unit rather than the doublet and quartet expected for a μ-C=CHMe ligand), and the chemical shift of the CH protons in the terminal alkyne complexes **2a**–**2d** (around δ 8.5) is typical of four-electron-donor alkynes in similar butterfly clusters. The $^{13}C$ NMR spectra are not reported here since the effect of the quadrupolar $^{59}Co$ nucleus is to render all the signals except those due to the $C_5H_5$ ligands so broad as to be uninformative.

In order to establish the structure, suitable crystals of compound **2e** were grown by diffusion of light petroleum into a dichloromethane solution and subjected to X-ray diffraction. The molecular structure is shown in Fig. 1, and selected bond lengths and angles are collected in Table 1. It confirms that the complex is a member of a well known series of butterfly clusters with bridging alkyne ligands.[8] The butterfly consists of two cobalt atoms which form the hinge and two molybdenum atoms which act as the wingtips. The Co–Co hinge bond length is 2.5431(12) Å which can be compared with the values of 2.552(5) and 2.559(1) Å reported for the related butterfly clusters $[Co_4(\mu_4\text{-}C_2Et_2)(CO)_{10}]$ and $[Co_4(\mu_4\text{-}C_2H_2)(CO)_{10}]$ respectively.[9] The cobalt–molybdenum distances lie within the range 2.6861(13)–2.6929(11) Å which is comparable to those observed in other Co–Mo clusters where the bond is bridged by a ligand.[10,11] The Mo $\cdots$ Mo distance is 4.123(1) Å, well beyond the range of possible bonding and in fact the longest observed for this type of cluster. The dihedral angle of the butterfly (*i.e.* the angle of intersection of the two $MoCo_2$ planes) of 121.0° is also slightly larger than those in related clusters.[8]

Each molybdenum atom bears a cyclopentadienyl ring and each cobalt atom has two terminal carbonyl ligands. In addition each cobalt–molybdenum bond is spanned by an asymmetrically bridging carbonyl ligand which is more closely bonded to molybdenum [Mo–C 1.968(7) to 1.997(7) Å] than to cobalt [Co–C 2.253(7) to 2.284(7) Å]. It is also noticeable that the Mo–C–O angles for these carbonyls are in the range 157.8(6)–159.8(6) and thus show only a moderate deviation from linearity. These CO ligands can therefore justifiably be classed as semibridging even though they have asymmetry parameters in the range 0.136–0.152.[12] This is close to the nominal borderline with true bridging carbonyls, but in this case this is a deceptive view since no account is taken of the difference in radius between Co and Mo. The parameters for the carbonyls in compound **2e** can be contrasted with the situation in $[Co_2Mo_2(\mu\text{-}CO)_3(CO)_7(\eta\text{-}C_5H_5)_2]$ where the Co–CO and Mo–CO bonds of the two CO ligands bridging Co–Mo edges have average lengths of 1.94 and 2.20 Å respectively.[11]

The alkyne ligand lies parallel to the Co–Co bond and is bonded to all four metal atoms. The C(20)–C(21) distance of 1.425(8) Å is typical of those found in related butterfly clusters.[8] If the alkyne is regarded as a four-electron donor, all of these compounds have 60 cluster valence electrons and are thus formally electron deficient (an edge-opened tetrahedron is predicted to have 62 electrons). However an alternative visualisation is to regard the alkyne as two three-electron CR units which are part of the cluster framework, in which case the electron count is 62, as befits a *closo*-octahedral structure. Most of the other clusters of this type, for example the tetracobalt derivatives $[Co_4(\mu_4\text{-}R^1C{\equiv}CR^2)(CO)_{10}]$,[13] are also considered to have 60 electrons.

After completing our structure determination of compound **2e** we discovered that the complex had been previously prepared in 7% yield by Schacht and Vahrenkamp[14] as a by-product in the metal-exchange reaction of $[Co_2Mo(\mu_3\text{-}CMe)(CO)_8(\eta\text{-}C_5H_5)]$ with $Na_2[Ru(CO)_4]$. They also determined the structure of a different crystalline modification in which the bond lengths are slightly different to those found by us, though the overall structural features of the molecule are the same.

It has been known for some years that the reaction of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $[Co_2(CO)_8]$ at room temperature produces $[CoMo(CO)_7(\eta\text{-}C_5H_5)]$ as the only heterometallic product, along with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and $[Co_4(CO)_{12}]$.[15] The rationale advanced involves the formation of an intermediate tetrahedral cluster, $[Co_2Mo_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$, which decomposes to give the observed product distribution. It is worth noting that a cluster of this formula has been isolated in low yield from the thermal reactions of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with either $[Co_2(CO)_8]$ or $[Co_4(CO)_9(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$ and proved stable enough for its structure to be determined; the related $[Co_3Mo(CO)_{11}(\eta\text{-}C_5H_5)]$ was also formed and structurally characterised.[11,16] The reactions of these species with alkynes do not appear to have been studied, but a common route to butterfly clusters with alkyne ligands is the opening of one edge of a tetrahedral cluster on reaction with an alkyne, *e.g.* treatment of $[W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ with $C_2Ph_2$ resulted in selective breaking of the W–W bond and formation of $[W_2Ir_2(\mu_4\text{-}C_2Ph_2)(CO)_8(\eta\text{-}C_5H_5)_2]$, closely related to the products of our reaction.[17] One possible mechanism for the formation of **2** might therefore be dissociation of the alkyne, formation of an

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

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mo(1)–C(7) | 1.968(7) | Mo(1)–C(5) | 1.983(8) | Co(2)–C(3) | 1.794(7) | Co(2)–C(4) | 1.796(7) |
| Mo(1)–C(13) | 2.283(8) | Mo(1)–C(20) | 2.305(6) | Co(2)–C(20) | 1.968(6) | Co(2)–C(7) | 2.268(7) |
| Mo(1)–C(12) | 2.308(8) | Mo(1)–C(11) | 2.322(8) | Co(2)–C(8) | 2.284(7) | O(1)–C(1) | 1.115(8) |
| Mo(1)–C(21) | 2.322(6) | Mo(1)–C(9) | 2.337(8) | O(2)–C(2) | 1.147(9) | O(3)–C(3) | 1.128(8) |
| Mo(1)–C(10) | 2.356(7) | Mo(1)–Co(2) | 2.6861(13) | O(4)–C(4) | 1.130(9) | O(5)–C(5) | 1.177(9) |
| Mo(1)–Co(1) | 2.689(2) | Mo(2)–C(6) | 1.971(7) | O(6)–C(6) | 1.173(8) | O(7)–C(7) | 1.168(8) |
| Mo(2)–C(8) | 1.997(7) | Mo(2)–C(20) | 2.279(6) | O(8)–C(8) | 1.157(8) | C(9)–C(10) | 1.359(13) |
| Mo(2)–C(21) | 2.284(6) | Mo(2)–C(17) | 2.317(7) | C(9)–C(13) | 1.41(2) | C(10)–C(11) | 1.348(12) |
| Mo(2)–C(16) | 2.327(8) | Mo(2)–C(18) | 2.329(7) | C(11)–C(12) | 1.358(14) | C(12)–C(13) | 1.43(2) |
| Mo(2)–C(14) | 2.344(7) | Mo(2)–C(15) | 2.352(8) | C(14)–C(15) | 1.397(11) | C(14)–C(18) | 1.402(11) |
| Mo(2)–Co(2) | 2.687(2) | Mo(2)–Co(1) | 2.6929(11) | C(15)–C(16) | 1.384(13) | C(16)–C(17) | 1.432(12) |
| Co(1)–C(2) | 1.789(7) | Co(1)–C(1) | 1.812(7) | C(17)–C(18) | 1.380(12) | C(19)–C(20) | 1.554(9) |
| Co(1)–C(21) | 1.972(6) | Co(1)–C(5) | 2.253(7) | C(20)–C(21) | 1.425(8) | C(21)–C(22) | 1.525(8) |
| Co(1)–C(6) | 2.263(7) | Co(1)–Co(2) | 2.5431(12) | | | | |
| C(7)–Mo(1)–C(5) | 87.3(3) | C(7)–Mo(1)–C(20) | 91.5(3) | C(20)–Co(2)–C(7) | 92.6(3) | C(3)–Co(2)–C(8) | 89.7(3) |
| C(5)–Mo(1)–C(20) | 119.3(3) | C(7)–Mo(1)–C(21) | 121.3(3) | C(4)–Co(2)–C(8) | 84.0(3) | C(20)–Co(2)–C(8) | 100.3(2) |
| C(5)–Mo(1)–C(21) | 98.4(2) | C(20)–Mo(1)–C(21) | 35.9(2) | C(7)–Co(2)–C(8) | 167.0(3) | C(3)–Co(2)–Co(1) | 165.5(2) |
| C(7)–Mo(1)–Co(2) | 55.8(2) | C(5)–Mo(1)–Co(2) | 87.7(2) | C(4)–Co(2)–Co(1) | 96.1(2) | C(20)–Co(2)–Co(1) | 73.2(2) |
| C(20)–Mo(1)–Co(2) | 45.67(14) | C(21)–Mo(1)–Co(2) | 66.10(14) | C(7)–Co(2)–Co(1) | 97.8(2) | C(8)–Co(2)–Co(1) | 85.6(2) |
| C(5)–Mo(1)–Co(1) | 55.2(2) | C(20)–Mo(1)–Co(1) | 65.8(2) | C(3)–Co(2)–Mo(1) | 117.7(2) | C(4)–Co(2)–Mo(1) | 113.5(2) |
| C(21)–Mo(1)–Co(1) | 45.61(14) | Co(2)–Mo(1)–Co(1) | 56.47(4) | C(20)–Co(2)–Mo(1) | 56.9(2) | C(7)–Co(2)–Mo(1) | 45.9(2) |
| C(6)–Mo(2)–C(8) | 88.6(3) | C(6)–Mo(2)–C(20) | 120.5(2) | C(8)–Co(2)–Mo(1) | 143.6(2) | Co(1)–Co(2)–Mo(1) | 61.83(4) |
| C(8)–Mo(2)–C(20) | 99.6(2) | C(6)–Mo(2)–C(21) | 89.7(2) | C(3)–Co(2)–Mo(2) | 105.3(2) | C(4)–Co(2)–Mo(2) | 124.1(2) |
| C(8)–Mo(2)–C(21) | 120.6(2) | C(20)–Mo(2)–C(21) | 36.4(2) | C(20)–Co(2)–Mo(2) | 56.1(2) | C(7)–Co(2)–Mo(2) | 145.5(2) |
| C(6)–Mo(2)–Co(2) | 102.2(2) | C(8)–Mo(2)–Co(2) | 56.1(2) | C(8)–Co(2)–Mo(2) | 46.5(2) | Co(1)–Co(2)–Mo(2) | 61.90(4) |
| C(20)–Mo(2)–Co(2) | 45.8(2) | C(21)–Mo(2)–Co(2) | 66.6(2) | Mo(1)–Co(2)–Mo(2) | 100.23(5) | O(1)–C(1)–Co(1) | 178.9(6) |
| C(6)–Mo(2)–Co(1) | 55.5(2) | C(8)–Mo(2)–Co(1) | 87.6(2) | O(2)–C(2)–Co(1) | 175.4(7) | O(3)–C(3)–Co(2) | 177.3(6) |
| C(20)–Mo(2)–Co(1) | 66.0(2) | C(21)–Mo(2)–Co(1) | 45.77(14) | O(4)–C(4)–Co(2) | 176.4(8) | O(5)–C(5)–Mo(1) | 157.8(6) |
| Co(2)–Mo(2)–Co(1) | 56.42(3) | C(2)–Co(1)–C(1) | 99.0(3) | O(5)–C(5)–Co(1) | 123.2(6) | Mo(1)–C(5)–Co(1) | 78.5(3) |
| C(2)–Co(1)–C(21) | 165.6(3) | C(1)–Co(1)–C(21) | 94.1(3) | O(6)–C(6)–Mo(2) | 159.8(6) | O(6)–C(6)–Co(1) | 121.5(5) |
| C(2)–Co(1)–C(5) | 85.4(3) | C(1)–Co(1)–C(5) | 88.3(3) | Mo(2)–C(6)–Co(1) | 78.7(2) | O(7)–C(7)–Mo(1) | 157.9(6) |
| C(21)–Co(1)–C(5) | 101.0(3) | C(2)–Co(1)–C(6) | 84.0(3) | O(7)–C(7)–Co(2) | 123.5(6) | Mo(1)–C(7)–Co(2) | 78.4(2) |
| C(1)–Co(1)–C(6) | 89.5(3) | C(21)–Co(1)–C(6) | 90.3(2) | O(8)–C(8)–Mo(2) | 159.4(6) | O(8)–C(8)–Co(2) | 123.0(5) |
| C(5)–Co(1)–C(6) | 168.6(3) | C(2)–Co(1)–Co(2) | 94.1(2) | Mo(2)–C(8)–Co(2) | 77.5(2) | C(21)–C(20)–C(19) | 126.1(5) |
| C(1)–Co(1)–Co(2) | 165.2(2) | C(21)–Co(1)–Co(2) | 73.8(2) | C(21)–C(20)–Co(2) | 107.1(4) | C(19)–C(20)–Co(2) | 126.8(4) |
| C(5)–Co(1)–Co(2) | 85.9(2) | C(6)–Co(1)–Co(2) | 98.8(2) | C(21)–C(20)–Mo(2) | 72.0(3) | C(19)–C(20)–Mo(2) | 117.4(4) |
| C(2)–Co(1)–Mo(1) | 123.9(2) | C(1)–Co(1)–Mo(1) | 104.8(2) | Co(2)–C(20)–Mo(2) | 78.1(2) | C(21)–C(20)–Mo(1) | 72.7(3) |
| C(21)–Co(1)–Mo(1) | 57.3(2) | C(5)–Co(1)–Mo(1) | 46.3(2) | C(19)–C(20)–Mo(1) | 113.9(4) | Co(2)–C(20)–Mo(1) | 77.4(2) |
| C(6)–Co(1)–Mo(1) | 144.8(2) | Co(2)–Co(1)–Mo(1) | 61.70(4) | Mo(2)–C(20)–Mo(1) | 128.2(3) | C(20)–C(21)–C(22) | 127.3(5) |
| C(2)–Co(1)–Mo(2) | 111.6(3) | C(1)–Co(1)–Mo(2) | 118.7(2) | C(20)–C(21)–Co(1) | 105.9(4) | C(22)–C(21)–Co(1) | 126.8(4) |
| C(21)–Co(1)–Mo(2) | 56.1(2) | C(5)–Co(1)–Mo(2) | 143.4(2) | C(20)–C(21)–Mo(2) | 71.6(3) | C(22)–C(21)–Mo(2) | 115.9(4) |
| C(6)–Co(1)–Mo(2) | 45.9(2) | Co(2)–Co(1)–Mo(2) | 61.68(4) | Co(1)–C(21)–Mo(2) | 78.1(2) | C(20)–C(21)–Mo(1) | 71.4(3) |
| Mo(1)–Co(1)–Mo(2) | 100.01(4) | C(3)–Co(2)–C(4) | 97.0(3) | C(22)–C(21)–Mo(1) | 116.5(4) | Co(1)–C(21)–Mo(1) | 77.1(2) |
| C(3)–Co(2)–C(20) | 94.2(3) | C(4)–Co(2)–C(20) | 168.0(3) | Mo(2)–C(21)–Mo(1) | 127.1(3) | | |
| C(3)–Co(2)–C(7) | 89.9(3) | C(4)–Co(2)–C(7) | 83.2(3) | | | | |

intermediate tetrahedral cluster, and then reco-ordination of the alkyne.* We were able to rule this out, however, by a cross-over reaction between a mixture of [$Mo_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2$] and [$Mo_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(\eta\text{-}C_5H_4Me)_2$] with 2 equivalents of cobalt carbonyl (the alkyne substituents were selected to allow easy separation of the products by chromatography, since those with $CO_2Me$ groups elute in much more polar solvent mixtures). This produced only the expected products **2e** and [$Co_2Mo_2\{\mu_4\text{-}C_2(CO_2Me)_2\}(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_4Me)_2$]; there was no scrambling of the alkyne ligands or the cyclopentadienyls, showing that the dimolybdenum alkyne unit remains intact throughout the cluster-building process. Moreover we did not observe any heterodinuclear products in any of our reactions. It therefore appears that the formation of **2** approximates to the simple insertion of a dicobalt unit into the Mo–Mo bond.

It is interesting to compare the synthesis of compound **2** with that of the related butterfly cluster [$Co_2Ru_2(\mu_4\text{-}C_2Ph_2)(\mu_3\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2$], which is made by the reaction of the transversely bonded alkyne complex [$Ru_2(\mu\text{-}CO)(\mu\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2$] with [$Co_2(CO)_8$] at room temperature.[19] Despite the similar synthetic route, in this complex it is the $Ru_2$ unit which forms the hinge of the butterfly with the cobalt atoms as the wingtips. On the other hand, in the iron complexes [$Co_2Fe_2(\mu_4\text{-}R^1C_2R^2)(\mu_3\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2$], prepared by the reaction of [$Co_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_6$] with [$Fe_2(CO)_4(\eta\text{-}C_5H_5)_2$] in refluxing octane, the metal-atom distribution is reversed.[20] Moreover in [$Co_4(\mu_4\text{-}R^1C_2R^2)(\mu\text{-}CO)(CO)_4(\eta\text{-}C_5H_5)_2$], formed by treatment of the same dicobalt alkyne complexes with [$Co(CO)_2(\eta\text{-}C_5H_5)$], the hinge is formed by one $Co(CO)_2$ and one $Co(\eta\text{-}C_5H_5)$ unit.[21] Clearly the factors affecting the distribution of the different metal–ligand fragments in these clusters are complicated and deserve further investigation.

Preliminary studies on the reactivity of complex **2e** have been carried out which show that the cluster is stable for long periods (24 h) in refluxing tetrahydrofuran, but decomposes relatively rapidly (2 h) in refluxing heptane or toluene to insoluble material and very low yields of two unidentified brown compounds. Remarkably, when **2e** is heated in refluxing toluene with 1 equivalent of [$Ru_3(CO)_{12}$] the major product is [$Mo_2Ru_4(\mu_3\text{-}CMe)_2(CO)_{12}(\eta\text{-}C_5H_5)_2$]. It therefore appears that dissociation of the dicobalt unit is the major reaction

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* Alkyne exchange is known to occur in complexes of type **1** under certain conditions, but simple alkyne displacement does not occur below 150 °C.[18]

**Table 2** Crystal data and structure refinement for complex **2e**

| | |
|---|---|
| Empirical formula | $C_{22}H_{16}Co_2Mo_2O_8$ |
| $M$ | 718.09 |
| $T$/K | 293(2) |
| $\lambda$/Å | 0.710 73 |
| Crystal system | Monoclinic |
| Space group | $Cc$ |
| $a$/Å | 34.74(2) |
| $b$/Å | 8.7970(10) |
| $c$/Å | 15.910(5) |
| $\beta$/° | 102.93(4) |
| $U$/Å$^3$ | 4739(3) |
| $Z$ | 8 |
| $D_c$/Mg m$^{-3}$ | 2.013 |
| $\mu$/mm$^{-1}$ | 2.455 |
| $F$(000) | 2800 |
| Crystal size/mm | 0.73 × 0.44 × 0.34 |
| $\theta$ Range for data collection/° | 2.39–22.50 |
| $h,k,l$ Ranges | $-1$ to 37, $-1$ to 9, $-17$ to 16 |
| Reflections collected | 4117 |
| Independent reflections | 3113 ($R_{int}$ = 0.0363) |
| Data, restraints, parameters | 3113, 0, 307 |
| Goodness of fit on $F^2$ | 1.189 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0463$, $wR2 = 0.1136$ |
| (all data) | $R1 = 0.0520$, $wR2 = 0.1178$ |
| Largest difference peak and hole/e Å$^{-3}$ | 0.552, $-1.392$ |

**Table 3** Atomic coordinates ( × 10$^4$) for complex **2e**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Mo(1) | 719(1) | 2732(1) | 1056(1) |
| Mo(2) | 1832(1) | 1285(1) | 911(1) |
| Co(1) | 1412(1) | 3872(1) | 861(1) |
| Co(2) | 1109(1) | 1679(1) | −105(1) |
| O(1) | 1638(2) | 6051(6) | 2275(3) |
| O(2) | 1522(2) | 5848(8) | −553(4) |
| O(3) | 890(2) | −1327(7) | −838(4) |
| O(4) | 934(2) | 3362(9) | −1731(4) |
| O(5) | 714(2) | 6075(6) | 428(5) |
| O(6) | 2294(1) | 4316(6) | 1004(4) |
| O(7) | 210(2) | 1963(9) | −741(4) |
| O(8) | 1778(2) | 1309(7) | −1064(3) |
| C(1) | 1555(2) | 5227(7) | 1732(5) |
| C(2) | 1464(2) | 5060(9) | −20(5) |
| C(3) | 970(2) | −151(9) | −573(4) |
| C(4) | 1012(2) | 2738(9) | −1094(4) |
| C(5) | 794(2) | 4807(9) | 632(5) |
| C(6) | 2058(2) | 3346(8) | 947(4) |
| C(7) | 466(2) | 2200(9) | −142(5) |
| C(8) | 1723(2) | 1377(7) | −374(5) |
| C(9) | 311(3) | 4103(13) | 1765(7) |
| C(10) | 535(2) | 3188(10) | 2370(5) |
| C(11) | 453(3) | 1725(11) | 2149(6) |
| C(12) | 172(3) | 1636(15) | 1404(7) |
| C(13) | 80(3) | 3166(18) | 1130(6) |
| C(14) | 2062(2) | −1224(9) | 1095(6) |
| C(15) | 2298(3) | −465(11) | 627(6) |
| C(16) | 2498(2) | 653(12) | 1165(7) |
| C(17) | 2378(2) | 604(11) | 1969(6) |
| C(18) | 2108(2) | −562(9) | 1914(5) |
| C(19) | 1099(2) | −663(7) | 1392(4) |
| C(20) | 1205(2) | 932(7) | 1091(4) |
| C(21) | 1377(2) | 2153(7) | 1635(4) |
| C(22) | 1506(2) | 2143(8) | 2617(4) |

pathway under thermal conditions, and in the absence of other reagents leads to decomposition. Treatment of **1e** with 2 equivalents of cobalt carbonyl did not lead to any higher-nuclearity clusters and the yield of **2e** was unchanged.

## Experimental

All reactions were carried out under dry argon using standard Schlenk techniques. Work-up procedures can be carried out without special precautions as the products described are relatively air stable and decompose only slowly in solution.

Toluene and light petroleum (b.p. 60–80 °C) were dried by distillation from sodium. Dichloromethane and other solvents were used as received unless otherwise stated. Chromatographic separations were performed under a slight positive pressure of argon on silica columns (Merck Kieselgel 60, 230–400 mesh) of varying length. Thin-layer chromatography (TLC) was carried out on commercial Merck plates coated with a 0.20 mm layer of silica.

Infrared spectra were recorded in $CH_2Cl_2$ solution on a Perkin-Elmer 1600 FT-IR machine using 0.5 mm NaCl cells, $^1H$ and $^{13}C$ NMR spectra in $CDCl_3$ solution on a Bruker AC250 machine with automated sample-changer or an AMX400 spectrometer. Chemical shifts are given on the $\delta$ scale relative to $SiMe_4$ (0.0 ppm). Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in fast atom bombardment mode with *m*-nitrobenzyl alcohol as matrix. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry.

The complex $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and the alkyne complexes **1a**–**1e** were prepared by literature methods or slight modifications thereof.[22,23]

### Preparations

**$[Co_2Mo_2(\mu\text{-}C_2H_2)(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_5)_2]$ 2a.** A solution of $[Co_2(CO)_8]$ (256.3 mg, 0.75 mmol) and $[Mo_2(\mu\text{-}C_2H_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (344.7 mg, 0.75 mmol) in toluene (50 cm$^3$) was refluxed for 30 min. A change from red to deep green was observed and TLC monitoring showed the disappearance of the starting complexes. After addition of a small amount of silica the solvent was removed and the residue chromatographed. Elution with light petroleum produced faint green and pink bands, and with light petroleum–$CH_2Cl_2$ (4:1) a red-brown band was collected which proved to be a mixture of remaining **1a** and an unidentified brown compound. A further unidentified brown product (27.5 mg) was eluted with a 1:1 mixture of the same solvents. Elution with a 1:9 mixture produced a large blue band of cluster **2a** (220.4 mg, 0.319 mmol, 42.6%), m.p. > 350 °C. IR: ν(CO) 2058s, 2029s, 2012 (sh), 1944w, 1838m and 1796m cm$^{-1}$. $^1H$ NMR: $\delta$ 8.02 (s, 2 H, CH) and 5.48 (s, 10 H, $\eta\text{-}C_5H_5$) (Found: C, 34.65; H, 1.60. Calc. for

$C_{20}H_{12}Co_2Mo_2O_8$: C, 34.80; H, 1.75%). Mass spectrum: *m/z* 691, 664 and 634 ($M^+ - n$CO, $n$ = 0–2).

**[$Co_2Mo_2$(μ-$HC_2$Me)(μ-CO)$_4$(CO)$_4$(η-$C_5H_5$)$_2$] 2b.** In a similar reaction to the above, a solution of [$Co_2(CO)_8$] (275.3 mg, 0.80 mmol) and [$Mo_2$(μ-$HC_2$Me)(CO)$_4$(η-$C_5H_5$)$_2$] (381.0 mg, 0.80 mmol) in toluene (75 cm$^3$) was refluxed for 35 min, turning deep green. Chromatography as above produced several faint bands and the major product **2b** which was eluted as a blue band in light petroleum–$CH_2Cl_2$ (3:7) (156.2 mg, 0.22 mmol, 27.7%), m.p. 198–200 °C. IR: ν(CO) 2058s, 2029s, 1995 (sh), 1831m and 1790m cm$^{-1}$. $^1$H NMR: δ 8.47 (s, 1 H, CH), 5.37 (s, 10 H, $C_5H_5$) and 2.49 (s, 3 H, Me) (Found: C, 36.00; H, 1.85. Calc. for $C_{21}H_{14}Co_2Mo_2O_8$: C, 35.80; H, 2.00%). Mass spectrum: *m/z* 705, 678, 649, 620, 592 and 564 ($M^+ - n$CO, $n$ = 0–5).

**[$Co_2Mo_2$(μ-$HC_2$Ph)(μ-CO)$_4$(CO)$_4$(η-$C_5H_5$)$_2$] 2c.** In a similar way, the reaction of [$Co_2(CO)_8$] (123.8 mg, 0.36 mmol) with [$Mo_2$(μ-$HC_2$Ph)(CO)$_4$(η-$C_5H_5$)$_2$] (202.4 mg, 0.38 mmol) in refluxing toluene for 30 min produced, on chromatography, minor bands which were sequentially brown, pink, dark green, red **1c**, and brown. The major product, cluster **2c**, was eluted with light petroleum–$CH_2Cl_2$ (1:1) as a green band (149.6 mg, 0.195 mmol, 54.3%), m.p. 228–230 °C. IR: ν(CO) 2055s, 2024s, 1991m, 1840m and 1799m cm$^{-1}$. $^1$H NMR: δ 8.36 (s, 1 H, CH), 7.23–6.50 (m, 5 H, Ph) and 5.05 (s, 10 H, $C_5H_5$) (Found: C, 40.70; H, 2.05. Calc. for $C_{26}H_{16}Co_2Mo_2O_8$: C, 40.75; H, 2.10%). Mass spectrum: *m/z* 767, 739, 711, 682, 654 and 627 ($M^+ - n$CO, $n$ = 0–5).

**[$Co_2Mo_2$(μ-$HC_2CO_2$Me)(μ-CO)$_4$(CO)$_4$(η-$C_5H_5$)$_2$] 2d.** Heating a solution of [$Co_2(CO)_8$] (291.2 mg, 0.85 mmol) and [$Mo_2$(μ-$HC_2CO_2$Me)(CO)$_4$(η-$C_5H_5$)$_2$] (438.5 mg, 0.85 mmol) in toluene (100 cm$^3$) for 45 min caused a change to deep green. Chromatography as above produced minor green and brown bands. The major product, cluster **2d**, was then eluted as a large green band in $CH_2Cl_2$ (484.4 mg, 0.65 mmol, 76.2%), m.p. > 350 °C. IR: ν(CO) 2063s, 2039s, 2018 (sh), 1843m, 1801m and 1674w cm$^{-1}$. $^1$H NMR: δ 8.30 (s, 1 H, CH), 5.33 (s, 10 H, $C_5H_5$), and 3.62 (s, 3 H, Me) (Found: C, 35.15; H, 1.85. Calc. for $C_{22}H_{14}Co_2Mo_2O_{10}$: C, 35.30; H, 1.85%). Mass spectrum: *m/z* 749 and 721 ($M^+$, $M^+$ − CO).

**[$Co_2Mo_2$(μ-$C_2Me_2$)(μ-CO)$_4$(CO)$_4$(η-$C_5H_5$)$_2$] 2e.** Dicobalt octacarbonyl (1.0081 g, 2.95 mmol) and [$Mo_2$(μ-$C_2Me_2$)(CO)$_4$(η-$C_5H_5$)$_2$] (1.4413 g, 2.95 mmol) were dissolved in toluene (200 cm$^3$) and the solution was heated to reflux for 30 min, causing a change to green. After addition of a small amount of silica the solvent was removed *in vacuo*, and the resulting powder loaded onto a chromatography column. Elution with light petroleum, changing progressively to light petroleum–$CH_2Cl_2$ (3:2), produced several minor bands. These were, in sequence, brown-grey, orange, red, red (due to remaining **1e**), red-brown (48.9 mg), dark brown (37.4 mg) and green-brown (25.8 mg). Elution with a 1:3 mixture of the same solvents yielded a large blue band of cluster **2e** (1.2633 g, 1.76 mmol, 59.7%). A further red band (110.8 mg) was eluted in $CH_2Cl_2$ but decomposed before characterisation could be attempted. Complex **2e**: m.p. 223 °C; IR ν(CO) 2057s, 2029s, 1995 (sh), 1827m and 1787m cm$^{-1}$; $^1$H NMR δ 5.30 (s, 10 H, $C_5H_5$) and 2.67 (s, 6 H, Me) (Found: C, 36.75; H, 2.20. Calc. for $C_{22}H_{16}Co_2Mo_2O_8$: C, 36.75; H, 2.25%); mass spectrum *m/z* 718, 690, 663, 634, 606 and 580 ($M^+ - n$CO, $n$ = 0–5).

### Crossover reaction

A mixture of [$Mo_2$(μ-$C_2Me_2$)(CO)$_4$(η-$C_5H_5$)$_2$] (413.7 mg, 0.85 mmol), [$Mo_2${μ-$C_2(CO_2Me)_2$}(CO)$_4$(η-$C_5H_4$Me)$_2$] (514.8 mg, 0.85 mmol) and [$Co_2(CO)_8$] (577.3 mg, 1.69 mmol) was dissolved in toluene and heated to reflux for 40 min, causing a change to green-brown. After removal of the solvent, chromatography yielded several minor bands (orange, brown, pale green, brown) which were discarded, followed by the two major products. Complex **2e** was eluted with $CH_2Cl_2$–light petroleum (3:1) as a blue-green band (294.2 mg, 0.41 mmol, 48%). The complex [$Co_2Mo_2${μ$_4$-$C_2(CO_2Me)_2$}(μ-CO)$_4$(CO)$_4$-(η-$C_5H_4$Me)$_2$] **2f** was eluted with $CH_2Cl_2$–acetone (19:1) as a dark brown band (207.3 mg, 0.25 mmol, 29.4%). The NMR spectra of these two products showed no scrambling of the alkyne or cyclopentadienyl ligands. Complex **2f**: m.p. > 350 °C; IR ν(CO) 2063s, 2040s, 2019 (sh), 1845m and 1804m cm$^{-1}$; $^1$H NMR δ 5.19 (br s, 8 H, $C_5H_4$Me), 3.74 (s, 6 H, $CO_2$Me) and 2.10 (s, 6 H, Me) (Found: C, 37.55; H, 2.45. Calc. for $C_{26}H_{20}Co_2Mo_2O_{12}$: C, 37.40; H, 2.40%); mass spectrum *m/z* 834, 806, 777, 749, 721, 693 and 665 ($M^+ - n$CO, $n$ = 0–6).

### Reaction of [$Co_2Mo_2$(μ$_4$-$C_2Me_2$)(μ-CO)$_4$(CO)$_4$(η-$C_5H_5$)$_2$] with [$Ru_3(CO)_{12}$]

A solution of complex **2e** (101.9 mg, 0.14 mmol) and ruthenium carbonyl (86.5 mg, 0.14 mmol) in toluene (50 cm$^3$) was heated to reflux for 3 h. Column chromatography of the residue produced a weak yellow band of unchanged [$Ru_3(CO)_{12}$], eluted in light petroleum, followed by a blue band of [$Mo_2Ru_4$(μ$_3$-CMe)$_2$(CO)$_{12}$(η-$C_5H_5$)$_2$] (32.3 mg, 0.03 mmol, 28.5%) which was eluted with $CH_2Cl_2$–light petroleum (1:4) and identified by comparison of its IR and NMR spectra with those of an authentic sample.[7] Minor red and brown bands were also eluted from the column but could not be identified.

### Crystallography

The crystal data for complex **2e** are collected in Table 2 and fractional atomic coordinates in Table 3. Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the ω-scan method. The 2742 independent reflections (of 4117 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.126 and 0.239). The structure was solved by Patterson synthesis and refined by full-matrix least squares on $F^2$. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R$ = 0.0463 ($wR2$ = 0.1178, for all 3113 data, 307 parameters, mean and maximum δ/σ 0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −1.392 and 0.552 e Å$^{-3}$. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0782P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL 93[24] as implemented on a Viglen 486dx computer.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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