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Dismantling a dinuclear metallacyclopentadiene: alkyne scission in cobalt–molybdenum clusters

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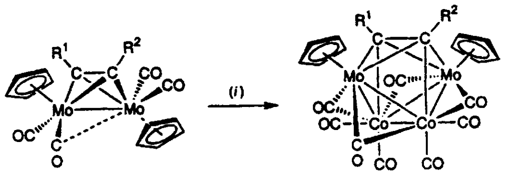
The alkyne complexes $[Mo_2(\mu\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Co_2(\mu\text{-}C_2Ph_2)(CO)_6]$ reacted together to give the butterfly cluster $[Co_2Mo_2(\mu_3\text{-}CPh)_2(\mu_4\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_5)_2]$, which can also be made from $[Mo_2(\mu\text{-}C_4Ph_4)(CO)(\eta\text{-}C_5H_5)_2]$ and $[Co_2(CO)_8]$; the possible role of the C_4Ph_4 complex as an intermediate in the former transformation is discussed.

Mixed-metal clusters offer organometallic chemists the opportunity to study the co-ordination and transformation of hydrocarbon ligands as a function of changing metal atom composition.[1] Recently we reported that the dimolybdenum alkyne complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1** ($R^1 = R^2 = H$ or Me; $R^1 = H$, $R^2 = Me$, Ph or CO_2Me) react with $[Ru_3(CO)_{12}]$ by scission of the alkyne ligand and formation of the bis(alkylidyne) clusters $[Mo_2Ru_4(\mu_3\text{-}CR^1)(\mu_3\text{-}CR^2)(CO)_{12}(\eta\text{-}C_5H_5)_2]$, accompanied, in the cases where $R^1 = H$, by the trinuclear vinylidene species $[Mo_2Ru(\mu_3\text{-}C{=}CHR^2)(CO)_7(\eta\text{-}C_5H_5)_2]$.[2] In contrast, reaction of **1** with $[Co_2(CO)_8]$ gave high yields of the butterfly clusters $[Co_2Mo_2(\mu_4\text{-}R^1C{\equiv}CR^2)(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_5)_2]$ **2** in which the alkyne ligand remained intact (Scheme 1).[3] However in this paper we show that a reaction which at first sight involves alkyne scission can be observed in a cobalt–molybdenum system for a particular set of alkyne substituents.

Heating a toluene solution of equimolar amounts of $[Mo_2(\mu\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Co_2(\mu\text{-}C_2Ph_2)(CO)_6]$ to reflux afforded the unusual butterfly cluster $[Co_2Mo_2(\mu_3\text{-}CPh)_2(\mu_4\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **3** in 22% yield after column chromatography (Scheme 2).† The compound was characterised spectroscopically and analytically,‡ by which we deduced that the dicobalt unit had been incorporated with retention of both diphenylacetylene ligands. However, the observation of a signal in the ^{13}C NMR spectrum at δ 363.9, characteristic of an alkylidyne group, indicated that alkyne scission had occurred. Consequently the molecular structure was determined by X-ray diffraction and is shown in Fig. 1.

The cluster consists of a butterfly-type core in which the two molybdenum atoms form the hinge and the cobalt atoms the wing-tips. The cobalt–molybdenum bond lengths are similar to those observed in **2** and in other Co–Mo clusters,[5] but the Mo–Mo distance is distinctly short, 2.5507(11) Å, a length usually considered indicative of some degree of metal–metal multiple bonding. The dihedral angle of the butterfly, *i.e.* the angle of intersection of the two $CoMo_2$ planes, is 103.2°. The four metal atoms are bridged by an alkyne molecule in a fashion also observed in **2** and a number of related butterfly clusters, *e.g.* the well known $[Co_4(\mu_4\text{-}R^1C{\equiv}CR^2)(CO)_{10}]$ (R^1, R^2 = H, Me, Ph, *etc.*).[6] If the alkyne ligand is considered to be a four electron donor, complex **3** is unique in having a total of only 58 electrons: butterfly clusters of this type, *e.g.* **2** almost always have 60 electrons (or, very rarely, 62).[6] The deficit is presumably accounted for by a formal double bond between the two Mo atoms, in accord with the short Mo–Mo distance. It is pertinent that in $[Mo_2Ru_4(\mu_3\text{-}CMe)_2(CO)_{12}(\eta\text{-}C_5H_5)_2]$, which is also electron-deficient (84 electrons as opposed to the more normal 86 for an octahedral cluster), the Mo–Mo distance is similar, 2.5792(8) Å.[2] The most closely related structural comparison for **3** is $[Co_2Mo_2(\mu_4\text{-}MeC_2CF_3)(\mu_3\text{-}S)_2(CO)_4(\eta\text{-}C_5H_5)_2]$, in which the Mo_2Co faces are capped by sulfur atoms,



1   2

Scheme 1 (*i*) $[Co_2(CO)_8]$ 1 equivalent, toluene, reflux 30 min

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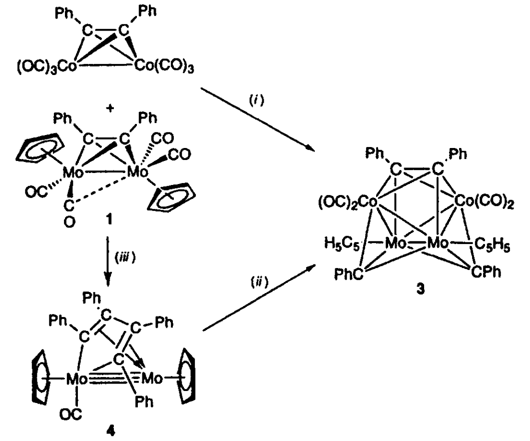
† General experimental techniques and instrumentation were as given in ref. 3. Synthesis of **3** from **1**. The complexes $[Mo_2(\mu\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (100 mg, 0.163 mmol) and $[Co_2(\mu\text{-}C_2Ph_2)(CO)_6]$ (76 mg, 0.163 mmol) were dissolved in toluene (150 cm^3). The solution was heated to reflux for 18 h with a slow purge of argon passing through it. After removal of the solvent, the residue was adsorbed onto silica and chromatographed. Elution with CH_2Cl_2–light petroleum (b.p. 60–80 °C) (1 : 9) afforded a yellow band of **3** (32.5 mg, 22%). Further elution with a 1 : 4 mixture of the same solvents gave 58.5 mg of recovered **1**.

Synthesis of **3** from **4**. A solution of **4** (221.4 mg, 0.314 mmol) and $[Co_2CO)_8]$ (119 mg, 0.348 mmol) in toluene (150 cm^3) was heated to reflux for 2 h. Column chromatography as above gave **3** (138.5 mg, 48.6%) as the first yellow-brown zone.

‡ Spectroscopic data for **3**. IR (CH_2Cl_2): ν(CO) 2010w, 1993s, 1954m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.45–6.82 (m, 20 H, Ph), 5.04 (s, 10 H, $\eta\text{-}C_5H_5$). ^{13}C NMR ($CDCl_3$): δ 363.9 (μ_3-C), 202.0 (CO), 165.5 (C_{ipso} of μ_3-CPh), 154.9 (C_2Ph_2), 153.6 (C_{ipso} of C_2Ph_2), 131.4–123.6 (m, Ph), 101.3 ($\eta\text{-}C_5H_5$). Mass spectrum: m/z 797 ($M^+ - 4CO$) (Found: C, 53.60; H, 3.20. Calc. for $C_{42}H_{30}Co_2Mo_2O_4{\cdot}0.5CH_2Cl_2$: C, 53.60; H, 3.25%).

Crystal data for $\mathbf{3}{\cdot}0.5CH_2Cl_2$: $C_{42.5}H_{31}ClCo_2Mo_2O_4$, $M = 950.86$, crystallises from dichloromethane and light petroleum, crystal dimensions 0.67 × 0.43 × 0.35 mm. Monoclinic, space group $C2/c$, $a = 18.226(4)$, $b = 11.304(2)$, $c = 35.932(7)$ Å, $\beta = 94.42(3)°$, $U = 7381(3)$ Å^3, $Z = 8$, $D_c = 1.711$ g cm^{-3}, Mo-Kα radiation ($\bar{\lambda} = 0.710\,73$ Å), μ(Mo-Kα) = 1.662 mm^{-1}, $F(000) = 3784$.

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. Of the 6055 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 4003 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0467$ ($wR2 = 0.2023$, for all 4781 data, 467 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −1.003 and 0.885 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^{\,2}) + (0.0607P)^2 + 68.4545P]$ where $P = (F_o^{\,2} + 2F_c^{\,2})/3$ was used in the latter stages of refinement. A disordered dichloromethane solvent molecule was successfully refined at half occupancy. Complex scattering factors were taken from the program package SHELXL 93[4] as implemented on the Viglen 486dx computer. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/249.



Scheme 2 (*i*) Toluene, reflux 18 h; (*ii*) $[Co_2(CO)_8]$ 1.1 equivalents, toluene, reflux 2 h; (*iii*) C_2Ph_2 3 equivalents, octane, reflux 18 h

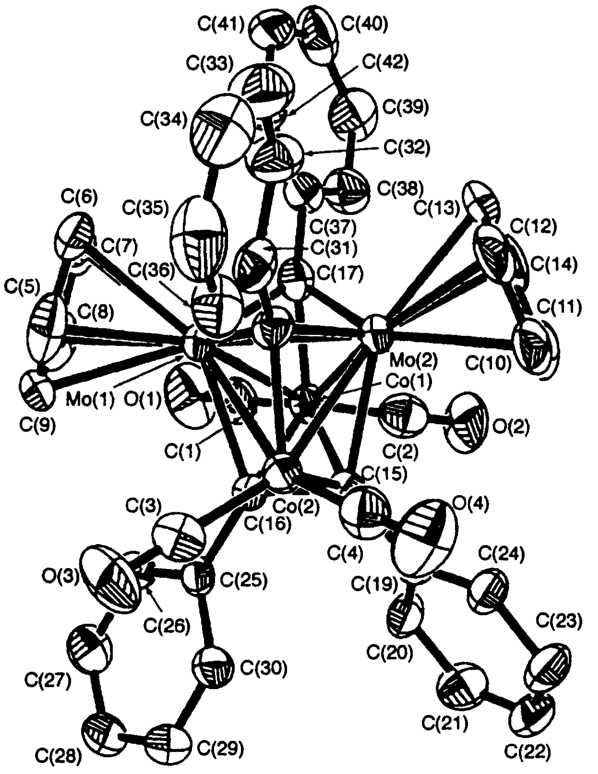


Fig. 1 Molecular structure of $[Co_2Mo_2(\mu_3\text{-}CPh)_2(\mu_4\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **3**. Selected bond lengths (Å): Mo(1)–Mo(2) 2.5507(11), Mo(1)–Co(1) 2.6225(12), Mo(1)–Co(2) 2.6165(12), Mo(2)–Co(1) 2.6169(12), Mo(2)–Co(2) 2.6181(12), Mo(1)–C(16) 2.261(7), Mo(2)–C(15) 2.271(6), average Co–μ_4-C_2Ph_2 2.081, Co(1)–C(17) 1.953(8), Co(2)–C(18) 1.958(7), average Mo–μ_3-CPh 2.061

which are four-electron donors, thus giving a 60-electron count. The Mo–Mo distance in this case was 2.717(1) Å.[7]

Each of the two outer Mo_2Co faces in **3** is capped by a benzylidyne ligand (μ_3-CPh) derived by cleavage of one of the orginal alkyne molecules. The bond lengths within these fragments are comparable to those in related Mo_2Co alkylidyne clusters.[8] The preference of these ligands for the Mo_2Co faces, a result of the strong Mo–C bonds,[9] has been previously noted and may be responsible for the reversal of the metal atom distribution in **3** compared to that in compound **2**, where a similar ligand would have to bridge a Co_2Mo face.

The rather low yield of **3** seemed to be limited by the stability of the dicobalt complex under the reaction conditions, as much of the dimolybdenum complex was recovered unchanged. Attempts to produce complexes analogous to **3** starting from either dicobalt or dimolybdenum precursors bearing different alkyne ligands proved unsuccessful (except for di-*p*-tolylacetylene, which does give an analogous cluster). Moreover in some syntheses of **3** we noticed the presence of small amounts of tetraphenylcyclopentadienone (C_4Ph_4CO), which raised the possibility that the two alkyne ligands may link together before being split up into an alkyne and two alkylidynes.

To explore this idea we extended our studies to the formally unsaturated molybdacyclopentadiene complex $[Mo_2(\mu\text{-}C_4Ph_4)(CO)(\eta\text{-}C_5H_5)_2]$ **4**, which contains two linked diphenylacetylene molecules and is readily accessible in one step from $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ as described by Knox *et al.*[10] Remarkably, treatment of **4** with $[Co_2(CO)_8]$ (1.1 equivalents) in refluxing toluene for 2 h provided **3** in 49% yield, representing the unprecedented scission of a four-carbon chain into three smaller fragments (Scheme 2).[11]

We therefore propose that the pathway of the original reaction involves dissociation of C_2Ph_2 from the dicobalt complex, combination of this free alkyne with **1** to form **4**, followed by further reaction with the released dicobalt fragment to give **3**. In support of this are three further facts: (*i*) the dimolybdenum alkyne complex **1** derived from diphenylacetylene ($R^1 = R^2 = Ph$) is known to react with further C_2Ph_2 to give **4**;[10] (*ii*) complex **4** can only be made when all the alkyne substituents are aryl; (*iii*) presumably for steric reasons, compound **1** ($R^1 = R^2 = Ph$) does not react with $[Co_2(CO)_8]$ to give a cluster of type **2**. The relevance of these facts is shown by the reaction of $[Mo_2(\mu\text{-}PhC{\equiv}CH)(CO)_4(\eta\text{-}C_5H_5)_2]$ with $[Co_2(\mu\text{-}C_2Ph_2)(CO)_6]$, which gave $[Co_2Mo_2(\mu_4\text{-}PhC{\equiv}CH)(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_5)_2]$: in this case the dimolybdenum complex cannot react with the released C_2Ph_2 to give a complex of type **4**, but it can react with the dicobalt fragment to give a cluster of type **2**. The corresponding reaction of $[Mo_2(\mu\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ with $[Co_2(\mu\text{-}PhC{\equiv}CH)(CO)_6]$ gave only decomposition products.

Acknowledgements

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