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# Oxo ligands as assembling units in mixed-metal cluster chemistry: synthesis and X-ray structure of the bow-tie cluster $[Mo_2Ru_3(\mu_3\text{-}O)_2(\mu_3\text{-}CPh)(\mu\text{-}C_3Ph_3)(CO)_8(\eta\text{-}C_5H_5)_2]$

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**Abstract**

The thermal reaction of $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ with $[Ru_3(CO)_{12}]$ gives the pentanuclear cluster $[Mo_2Ru_3(\mu_3\text{-}O)_2(\mu_3\text{-}CPh)(\mu\text{-}C_3Ph_3)(CO)_8(\eta\text{-}C_5H_5)_2]$, which has been crystallographically characterised. The compound displays several unusual features: (i) a highly distorted bow-tie structure in which the two metal triangles are virtually perpendicular; (ii) the cleavage of the initial four carbon chain into a dimetalla-allyl fragment and an alkylidyne group; (iii) the presence of two triply-bridging oxo ligands; and (iv) the coordination of one of the phenyl groups of the $C_3Ph_3$ ligand to ruthenium.

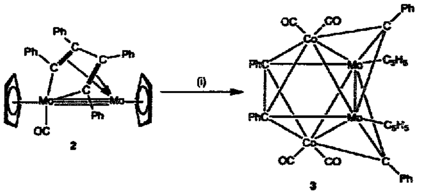
*Keywords:* Molybdenum; Ruthenium; Clusters; Alkyne; Alkylidyne; Crystal structure

## 1. Introduction

The interaction of hydrocarbon ligands with different metal–ligand fragments can be explored by studying their coordination and transformation on mixed-metal clusters [1]. One subject of current interest is the incorporation of higher oxidation state metal–oxo moieties into clusters with the intention of modelling hydrocarbon oxidation reactions, or the behaviour of metals on oxide supports with reference to widely used heterogeneous catalysts [2]. Although the number of clusters containing oxo ligands is slowly increasing, only in a very small number of cases does the oxo ligand play a demonstrable part in the assembly of the cluster. Perhaps the best documented example is the reaction of $[Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ with $[Fe_2(CO)_9]$, which gives $[Mo_2Fe(\mu_3\text{-}O)(CO)_7(\eta\text{-}C_5Me_5)_2]$ in the presence of oxygen and $[Mo_2Fe_2(\mu\text{-}CO)(\mu_4\text{-}CO)(CO)_9(\eta\text{-}C_5Me_5)_2]$ under strictly anaerobic conditions [3].

Recently we have employed the dimolybdenum complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1** ($R^1 = R^2$ = H, Me; $R^1$ = H, $R^2$ = Me, Ph, $CO_2Me$) as the starting materials for the synthesis of mixed-metal clusters. For example, **1** reacts 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 cases where $R^1$ = H, by the trinuclear vinylidene species $[Mo_2Ru(\mu_3\text{-}C{=}CHR^2)(CO)_7(\eta\text{-}C_5H_5)_2]$ [4]. In contrast, reaction of **1** with $[Co_2(CO)_8]$ gave high yields of the butterfly clusters $[Co_2Mo_2(\mu_4\text{-}R^1C{\equiv}CR^2)(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_5)_2]$ in which the alkyne ligand remained intact [5]. These results show that different rearrangements of the alkyne ligand occur depending on the metal–ligand fragments present.

We have now extended our studies to the complex $[Mo_2(\mu\text{-}C_4Ph_4)(CO)(\eta\text{-}C_5H_5)_2]$ **2**, which contains two



Scheme 1. Reagents and conditions: (i) $[Co_2(CO)_8]$, 1.1 equiv., toluene, reflux, 2 h, 49%.

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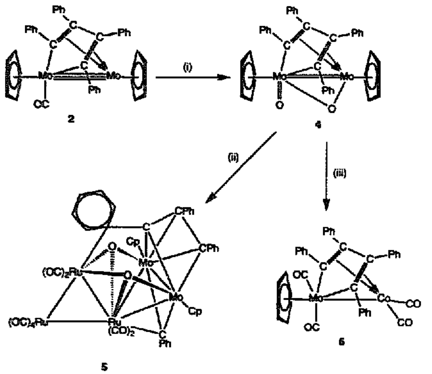

Scheme 2. Reagents and conditions: (i) $CH_2Cl_2$, air, room temperature, 1 h; (ii) $[Ru_3(CO)_{12}]$, 1 equiv., toluene, reflux, 2 h, 14.3%; (iii) $[Co_2(CO)_8]$, 3.1 equiv., toluene, reflux, 1.25 h, 29%.

diphenylacetylene molecules linked in the form of a metallacyclopentadiene ring [6]. In an unprecedented reaction with $[Co_2(CO)_8]$, the four carbon chain can be cleaved into an alkyne ligand and two capping alkylidyne groups to give the butterfly cluster $[Co_2Mo_2(\mu_3\text{-}CPh)_2(\mu_4\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ 3 (Scheme 1) [7]. In this paper we show that the oxidation product of 2, $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ 4, can also be used as the precursor to an unusual mixed-metal cluster in which the four-carbon chain is broken up in a different way.

## 2. Results and discussion

Complex 2 is readily prepared as a green air-sensitive crystalline solid by the reaction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with an excess of $C_2Ph_2$ in boiling octane (Scheme 2), as described in the classic paper on alkyne oligomerisation by Knox et al. [6]. Although they did

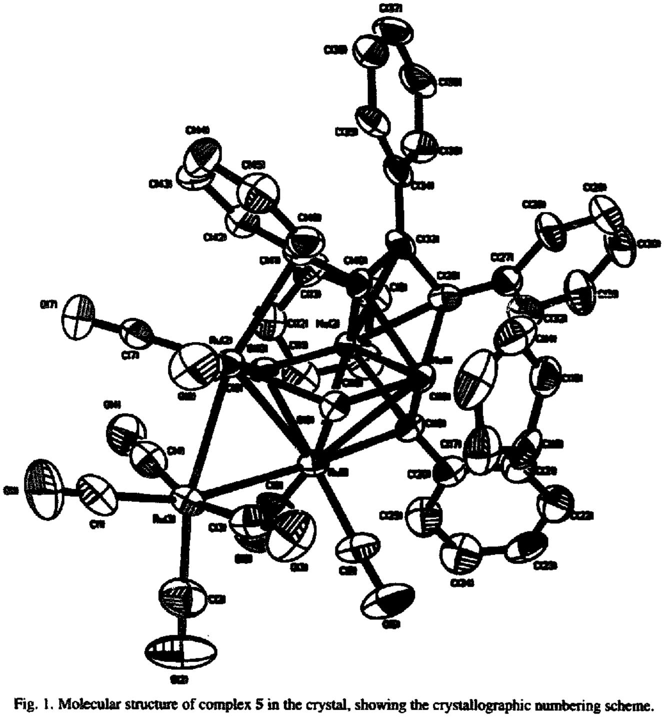

Fig. 1. Molecular structure of complex 5 in the crystal, showing the crystallographic numbering scheme.

not obtain the X-ray structure of the compound, its spectroscopic data correspond closely with those of the analogous dichromium species, which was crystallographically characterised. Exposure of $CH_2Cl_2$ solutions of 2 to air results in the rapid loss of the carbonyl ligand and formation of a brown compound which they formulated as $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ 4. We too have as yet been unable to obtain crystals of 4 (or its *p*-tolyl analogue) suitable for X-ray study, but we see no reason to doubt the proposed structure; however, it should be noted that a structure in which both oxo ligands are terminal is equally compatible with the spectroscopic data.

The reaction of complex 2 with $[Ru_3(CO)_{12}]$ (1 equiv., refluxing toluene, 2 h) afforded a large number of products which could neither be separated efficiently nor characterised. However, treatment of 4 with $[Ru_3(CO)_{12}]$ under similar conditions is more profitable, leading to the isolation of the red cluster 5 as the major product in a yield of 14.3% (Scheme 2). Its solution IR spectrum showed sharp peaks in the region associated with $Ru(CO)_x$ groups, and the incorporation of three ruthenium atoms was confirmed by the observation of a molecular ion in the mass spectrum at $m/z$ 1239. The $^1H$ NMR spectrum was unhelpful, consisting of just a singlet for the $\eta\text{-}C_5H_5$ ligands and the phenyl resonances, but the $^{13}C$ NMR spectrum contained a peak at 269.5 ppm which we considered indicative of an alkylidyne ligand (though its chemical shift is rather low compared to those in the other compounds we have made with alkylidyne ligands capping $Mo_2Ru$ faces). It therefore appeared that scission of the molybdacyclopentadiene unit had again occurred, and in order to establish the molecular structure of 5 a suitable crystal was subjected to X-ray diffraction analysis. The result is shown in Fig. 1, with selected bond lengths and angles collected in Tables 1 and 2 respectively.

Table 1
Selected bond lengths (Å) for complex 5

| | | | |
|---|---|---|---|
| Mo(1)–O(9) | 1.947(6) | Mo(1)–C(19) | 2.059(10) |
| Mo(1)–C(40) | 2.154(10) | Mo(1)–C(26) | 2.263(10) |
| Mo(1)–C(15) | 2.367(12) | Mo(1)–C(14) | 2.372(12) |
| Mo(1)–C(18) | 2.426(11) | Mo(1)–C(16) | 2.434(11) |
| Mo(1)–C(17) | 2.443(12) | Mo(1)–Mo(2) | 2.6445(14) |
| Mo(1)–Ru(1) | 2.8095(13) | Mo(2)–O(10) | 2.001(7) |
| Mo(2)–C(19) | 2.084(10) | Mo(2)–C(26) | 2.220(11) |
| Mo(2)–C(40) | 2.313(10) | Mo(2)–C(10) | 2.357(11) |
| Mo(2)–C(9) | 2.362(11) | Mo(2)–C(13) | 2.388(11) |
| Mo(2)–C(12) | 2.412(11) | Mo(2)–C(11) | 2.419(10) |
| Mo(2)–C(33) | 2.512(10) | Mo(2)–Ru(1) | 2.7701(14) |
| Ru(1)–O(10) | 2.098(6) | Ru(1)–O(9) | 2.107(6) |
| Ru(1)–C(19) | 2.229(11) | Ru(1)–Ru(3) | 2.7930(13) |
| Ru(1)–Ru(2) | 2.9810(13) | Ru(2)–O(9) | 2.107(6) |
| Ru(2)–O(10) | 2.115(7) | Ru(2)–C(41) | 2.461(10) |
| Ru(2)–Ru(3) | 2.7455(14) | C(26)–C(33) | 1.470(14) |
| C(33)–C(40) | 1.40(2) | C(40)–C(41) | 1.493(14) |
| Ru(1)–CO (av.) | 1.876 | Ru(2)–CO (av.) | 1.845 |
| Ru(3)–CO (av.) | 1.936 | | |

Table 2
Selected bond angles (°) for complex 5

| | | | |
|---|---|---|---|
| C(40)–Mo(1)–C(26) | 59.6(4) | O(9)–Mo(1)–Mo(2) | 89.6(2) |
| C(19)–Mo(1)–Mo(2) | 50.8(3) | C(40)–Mo(1)–Mo(2) | 56.5(3) |
| C(26)–Mo(1)–Mo(2) | 53.1(3) | O(9)–Mo(1)–Ru(1) | 48.5(2) |
| C(19)–Mo(1)–Ru(1) | 51.7(3) | Mo(2)–Mo(1)–Ru(1) | 60.96(4) |
| C(26)–Mo(2)–C(40) | 57.9(4) | O(10)–Mo(2)–Mo(1) | 89.3(2) |
| C(19)–Mo(2)–Mo(1) | 49.9(3) | C(26)–Mo(2)–Mo(1) | 54.6(3) |
| C(40)–Mo(2)–Mo(1) | 51.0(2) | O(10)–Mo(2)–Ru(1) | 49.0(2) |
| C(19)–Mo(2)–Ru(1) | 52.4(3) | Mo(1)–Mo(2)–Ru(1) | 62.46(4) |
| O(10)–Ru(1)–O(9) | 76.6(3) | O(10)–Ru(1)–Mo(2) | 46.0(2) |
| O(9)–Ru(1)–Mo(2) | 83.1(2) | C(19)–Ru(1)–Mo(2) | 47.8(3) |
| Mo(2)–Ru(1)–Ru(3) | 130.25(4) | O(10)–Ru(1)–Mo(1) | 83.0(2) |
| O(9)–Ru(1)–Mo(1) | 43.8(2) | C(19)–Ru(1)–Mo(1) | 46.5(3) |
| Mo(2)–Ru(1)–Mo(1) | 56.58(3) | Ru(3)–Ru(1)–Mo(1) | 127.92(4) |
| O(10)–Ru(1)–Ru(2) | 45.2(2) | O(9)–Ru(1)–Ru(2) | 45.0(2) |
| Mo(2)–Ru(1)–Ru(2) | 81.25(4) | Ru(3)–Ru(1)–Ru(2) | 56.67(3) |
| Mo(1)–Ru(1)–Ru(2) | 79.49(4) | O(9)–Ru(2)–O(10) | 76.2(3) |
| C(8)–Ru(2)–C(41) | 100.5(4) | C(7)–Ru(2)–C(41) | 103.9(4) |
| O(9)–Ru(2)–C(41) | 80.5(3) | O(10)–Ru(2)–C(41) | 81.0(3) |
| O(9)–Ru(2)–Ru(3) | 85.3(2) | O(9)–Ru(2)–Ru(1) | 45.0(2) |
| O(10)–Ru(2)–Ru(1) | 44.7(2) | Ru(3)–Ru(2)–Ru(1) | 58.21(3) |
| Ru(2)–Ru(3)–Ru(1) | 65.12(3) | Mo(1)–O(9)–Ru(2) | 132.1(3) |
| Mo(1)–O(9)–Ru(1) | 87.7(3) | Ru(2)–O(9)–Ru(1) | 90.1(3) |
| Mo(2)–O(10)–Ru(1) | 85.0(2) | Mo(2)–O(10)–Ru(2) | 131.2(3) |
| Ru(1)–O(10)–Ru(2) | 90.1(3) | Mo(1)–C(19)–Mo(2) | 79.3(3) |
| Mo(1)–C(19)–Ru(1) | 81.8(4) | Mo(2)–C(19)–Ru(1) | 79.8(3) |
| Mo(2)–C(26)–Mo(1) | 72.3(3) | C(40)–C(33)–C(26) | 99.8(9) |
| C(41)–C(40)–Mo(1) | 132.3(7) | C(41)–C(40)–Mo(2) | 125.9(6) |
| Mo(1)–C(40)–Mo(2) | 72.5(3) | C(40)–C(41)–Ru(2) | 97.5(6) |

The compound consists of a pentanuclear cluster of metal atoms, and displays several notable features. The cluster has a bow-tie configuration consisting of an $Ru_3$ triangle fused to the $Mo_2$ unit through Ru(1). The $Ru_3$ plane is almost perpendicular to the $RuMo_2$ plane, the dihedral angle between them being 88°. Depending on the metal–ligand fragments involved, the dihedral angle in bow-tie clusters can range from close to zero, e.g. $[MFe_4(CO)_{16}]^{2-}$ (M = Pd, Pt) [8], to 21.2° in the archetypal $[Os_5(CO)_{19}]$ [9] and 55° in $[Fe_5(\mu_3\text{-}S)_2(CO)_{14}]^{2-}$ and $[H_2Os_5(\mu_3\text{-}S)_2(CO)_{14}]$ [10]. Examples of clusters in which the dihedral angle is close to 90° include $[GeCo_4(CO)_{14}]$ [11], $[PtRh_4(CO)_4(\eta\text{-}C_5Me_5)_4]$ [12] and $[MCr_4(\mu_3\text{-}S)_4(\mu\text{-}SBu^t)_2(\eta\text{-}C_5H_5)_4]$ (M = Cr, Co, Mn) [13]. Deeming and Martin have recently reported a cluster in which an anthracenylphosphine ligand bridges across a pentaruthenium bow-tie structure with a dihedral angle of 38.9° [14]. However, 5 appears to be the first example to contain simple ligands which bridge between the wings of the bow-tie, leading to the bond angles Ru(2)–Ru(1)–Mo(1) and Ru(2)–Ru(1)–Mo(2) being smaller than usual, 79.49(4) and 81.25(4)° respectively. The resulting geometry might also be visualised as an edge-bridged tetrahedron in which two of the basal edges have been opened.

The bond lengths within the triruthenium fragment are normal, with the Ru(1)–Ru(2) bond, which is bridged by the two oxo ligands, longer than the other two. As expected, the average Ru–CO distance is greater for Ru(3), which has four carbonyl ligands bound to it, than for Ru(1) and Ru(2), which only have two. The Mo–Mo bond is rather short, 2.6445(14) Å, but this has been observed previously in clusters containing bridging organic fragments and does not necessarily indicate any degree of multiple bonding between them [15]. The Mo–Mo bond in 3, which we proposed to be a double bond, is shorter still, 2.5507(11) Å [7]. Each molybdenum atom is bonded to a cyclopentadienyl ring, which is somewhat tilted away from the central portion of the molecule: two of the carbon atoms of each ring have short Mo–C distances whereas the other three are longer.

The two open faces formed by Mo(1), Ru(1) and Ru(2) and Mo(2), Ru(1) and Ru(2) are capped by two $\mu_3$-oxo ligands, O(9) and O(10). The Mo(1)–O(9) bond length of 1.947(6) Å is slightly shorter than the corresponding Mo(2)–O(10) distance of 2.001(7) Å. This presumably reflects the fact that Mo(1) is formally electron deficient compared to Mo(2) due to the asymmetric coordination of the dimetalla-allyl fragment.

This three-carbon dimetalla-allyl ligand and the capping alkylidyne ligand have arisen through the cleavage of the initial $C_4$ chain of the metallacyclopentadiene. The metal–carbon bond distances in the latter, which as expected caps the $Mo_2Ru$ face, are almost identical to those found in $[Mo_2Ru_4(\mu_3\text{-}CMe)_2(CO)_{12}(\eta\text{-}C_5H_5)_2]$ [4], with the average Mo–C(19) distance of 2.07 Å being shorter than the Ru(1)–C(19) distance of 2.229(11) Å. The dimetalla-allyl ligand bridges the Mo–Mo bond, σ-bonded to Mo(1) through the two terminal carbons and $\eta^3$-bonded to Mo(2). Such ligands are well known both in dinuclear complexes and clusters.

The final unusual feature in 5 is the presence of an interaction between one of the phenyl groups of the $C_3Ph_3$ ligand and the rather electron-deficient atom Ru(2). This is reminiscent of the labile interaction observed in the unsaturated complex $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$ [16], and a closely related example has been observed very recently in the triruthenium cluster $[Ru_3(\mu_3\text{-}HCCPhCOCPhCPh)(dppm)(CO)_6]$ where the terminal C–Ph bond of the diphenylacetylene portion of the bridging ligand is loosely coordinated to one Ru [17]. The $C_{ipso}$–Ru distance of 2.343(7) Å in that complex is shorter than the Ru(2)–C(41) separation of 2.461(10) Å found in 5. Ignoring the coordination of C(41) and regarding the oxo ligands as four-electron donors, complex 5 has a total of 78 electrons which is the expected number for a bow-tie cluster [18].

With the benefit of the structure determination, the observation of only one peak for the cyclopentadienyl ligands in the room temperature $^1H$ and $^{13}C$ NMR spectra of 5 implies the operation of a fluxional process which renders the two Mo atoms equivalent. The most likely candidate is a flipping of the central carbon C(33) of the dimetalla-allyl fragment between the two molybdenum atoms in a σ,π rearrangement. Cooling the $^1H$ NMR sample to 226 K did not cause any change in the $C_5H_5$ signal, but some changes were evident in the phenyl region. A broad doublet at δ 6.20 had collapsed and reappeared as two broad peaks at δ 5.91 and 6.42, while an apparent triplet at δ 6.90 had broadened. This is consistent with the effect of slowing the fluxionality of the dimetalla-allyl fragment, causing the pairwise equivalence of protons on the phenyl ring coordinated to Ru to break down.

In conclusion, the oxo ligands present in 4 clearly play a large part in the assembly of cluster 5, and we are currently examining similar reactions with other suitable metal fragments. However, the complexity of the processes which can occur is shown by the fact that the only tractable product obtained from the reaction of 4 with $[Co_2(CO)_8]$ is the known dinuclear mixed-metal complex $[CoMo(\mu\text{-}C_4Ph_4)(CO)_4(\eta\text{-}C_5H_5)]$ 6 [19], the fate of the molybdenum oxo moiety being unknown (Scheme 2). Once again, however, the reactivity of oxo complex 4 is completely different from that of its carbonyl precursor 2.

## 3. Experimental section

General experimental techniques were as described in recent publications from this laboratory [20]. 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. The products described are relatively air-stable, and work-up procedures can be carried out without special precautions.

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 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 $SiMe_4 = 0.0$ ppm. Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in fast atom bombardment mode with 3-nitrobenzyl alcohol as matrix. The elemental analysis was carried out by the Microanalytical Service of the Department of Chemistry.

### 3.1. Preparation of $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ 4 [6]

A solution of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (2.0 g, 4.08 mmol) and diphenylacetylene (2.54 g, 14.3 mmol)

Table 3
Crystal data and structure refinement for complex **5**

| | |
|---|---|
| Identification code | 1123 |
| Empirical formula | $C_{46}H_{30}Mo_2O_{10}Ru_3$ |
| Formula weight | 1237.79 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | $a = 10.123(2)$ Å, $\alpha = 104.70(2)°$ |
| | $b = 11.251(2)$ Å, $\beta = 94.40(2)°$ |
| | $c = 19.049(4)$ Å, $\gamma = 91.52(2)°$ |
| Volume | 2090.0(7) Å$^3$ |
| $Z$ | 2 |
| Density (calc.) | 1.967 Mg m$^{-3}$ |
| Absorption coefficient | 1.703 mm$^{-1}$ |
| $F(000)$ | 1204 |
| Crystal size | 0.54 × 0.34 × 0.30 mm |
| $\theta$ range for data collection | 1.87 to 22.50° |
| Index ranges | $-1 \le h \le 10$, $-11 < k \le 11$, $-20 \le l \le 20$ |
| Reflections collected | 6496 |
| Independent reflections | 5397 ($R_{int} = 0.0661$) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 5385/0/550 |
| Goodness-of-fit on $F^2$ | 1.123 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0480$, $wR_2 = 0.1206$ |
| $R$ indices (all data) | $R_1 = 0.0662$, $wR_2 = 0.1415$ |
| Largest diff. peak and hole | 0.871 and −1.034 e Å$^{-3}$ |

in freshly distilled octane (150 cm$^3$) was heated to reflux for 18 h, producing a green solution of [$Mo_2(\mu$-$C_4Ph_4)(CO)(\eta$-$C_5H_5)_2$] **2**. The octane was removed under vacuum and the residue dissolved in dichloromethane (100 cm$^3$) and stirred vigorously in air for 1 h, turning brown. After addition of a small amount of silica, the solvent was removed and the residue chromatographed. A series of weak bands was obtained on elution with light petroleum changing progressively to a 1:1 $CH_2Cl_2$–light petroleum mixture. A large orange–brown band of product **4** (1.2576 g, 43%) was eluted with $CH_2Cl_2$ and acetone (9:1). The spectroscopic properties of the compound were identical to those reported in the literature [6].

### 3.2. Synthesis of [$Mo_2Ru_3(\mu_3$-$O)_2(\mu_3$-$CPh)(\mu$-$C_3Ph_3)(CO)_8(\eta$-$C_5H_5)_2$] 5

A solution of [$Mo_2(O)(\mu$-$O)(\mu$-$C_4Ph_4)(\eta$-$C_5H_5)_2$] (250 mg, 0.352 mmol) and [$Ru_3(CO)_{12}$] (225 mg, 0.352 mmol) in toluene (150 cm$^3$) was heated to reflux for 2 h, with monitoring of the reaction by spot TLC. After this time the solvent was removed in vacuo and

Table 4
Atomic coordinates (× 10$^4$) and equivalent isotropic displacement parameters (Å$^2$ × 10$^3$) for complex **5**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Mo(1) | 3409(1) | 6620(1) | 1771(1) | 29(1) |
| Mo(2) | 2347(1) | 8426(1) | 2699(1) | 27(1) |
| Ru(1) | 900(1) | 6203(1) | 2224(1) | 31(1) |
| Ru(2) | 2650(1) | 5623(1) | 3413(1) | 30(1) |
| Ru(3) | 167(1) | 4513(1) | 2991(1) | 38(1) |
| O(1) | 402(12) | 2883(10) | 4070(6) | 84(3) |
| O(2) | −2595(11) | 3701(12) | 2217(7) | 109(4) |
| O(3) | 1677(11) | 2749(9) | 1840(5) | 69(3) |
| O(4) | −665(9) | 6811(9) | 4099(5) | 61(2) |
| O(5) | −238(11) | 4609(9) | 760(5) | 77(3) |
| O(6) | −1887(8) | 7040(8) | 2418(5) | 58(2) |
| O(7) | 2073(9) | 5919(8) | 4968(5) | 57(2) |
| O(8) | 3865(10) | 3234(8) | 3444(5) | 65(3) |
| O(9) | 2783(6) | 5466(6) | 2295(3) | 30(2) |
| O(10) | 1770(7) | 7221(6) | 3241(4) | 32(2) |
| C(1) | 289(13) | 3465(12) | 3673(8) | 56(3) |
| C(2) | −1569(14) | 3983(14) | 2503(8) | 66(4) |
| C(3) | 1108(12) | 3427(11) | 2271(7) | 46(3) |
| C(4) | −373(11) | 5952(12) | 3681(7) | 46(3) |
| C(5) | 209(13) | 5180(11) | 1328(7) | 51(3) |
| C(6) | −834(13) | 6737(10) | 2339(7) | 45(3) |
| C(7) | 2309(10) | 5825(10) | 4377(7) | 36(3) |
| C(8) | 3373(11) | 4149(11) | 3430(6) | 39(3) |
| C(9) | 2385(12) | 10587(10) | 2909(7) | 47(3) |
| C(10) | 1102(12) | 10108(10) | 2569(7) | 48(3) |
| C(11) | 437(12) | 9611(10) | 3052(7) | 48(3) |
| C(12) | 1293(12) | 9758(11) | 3675(7) | 48(3) |
| C(13) | 2482(13) | 10332(10) | 3613(6) | 44(3) |
| C(14) | 5382(13) | 6093(16) | 1192(7) | 64(4) |
| C(15) | 4542(14) | 6578(12) | 724(6) | 54(3) |
| C(16) | 3432(13) | 5717(12) | 468(6) | 51(3) |
| C(17) | 3641(15) | 4755(11) | 807(7) | 58(4) |
| C(18) | 4831(17) | 4984(15) | 1246(7) | 70(5) |
| C(19) | 1690(10) | 7503(10) | 1631(5) | 32(2) |
| C(20) | 899(11) | 7828(10) | 1025(6) | 38(3) |
| C(21) | 1527(12) | 8059(11) | 439(6) | 47(3) |
| C(22) | 805(14) | 8379(12) | −133(7) | 56(3) |
| C(23) | −516(14) | 8454(12) | −145(7) | 57(4) |
| C(24) | −1158(13) | 8237(13) | 419(8) | 60(4) |
| C(25) | −474(12) | 7947(13) | 988(7) | 57(4) |
| C(26) | 4104(10) | 8627(9) | 2102(6) | 32(2) |
| C(27) | 4559(11) | 9468(10) | 1676(6) | 35(3) |
| C(28) | 5909(11) | 9585(12) | 1583(7) | 47(3) |
| C(29) | 6371(13) | 10372(13) | 1211(8) | 60(4) |
| C(30) | 5536(15) | 11092(13) | 918(8) | 66(4) |
| C(31) | 4198(15) | 10984(13) | 990(7) | 62(4) |
| C(32) | 3702(12) | 10179(11) | 1357(7) | 49(3) |
| C(33) | 4838(9) | 8557(10) | 2786(6) | 34(3) |
| C(34) | 5835(10) | 9440(10) | 3267(6) | 36(3) |
| C(35) | 6786(10) | 8991(11) | 3703(6) | 42(3) |
| C(36) | 7754(11) | 9784(12) | 4154(6) | 49(3) |
| C(37) | 7809(12) | 11015(13) | 4184(7) | 56(4) |
| C(38) | 6880(13) | 11460(12) | 3743(7) | 55(4) |
| C(39) | 5904(11) | 10693(11) | 3306(7) | 46(3) |
| C(40) | 4285(10) | 7446(10) | 2859(5) | 29(2) |
| C(41) | 4677(9) | 6921(10) | 3486(6) | 31(2) |
| C(42) | 4484(12) | 7531(12) | 4200(6) | 49(3) |
| C(43) | 5164(11) | 7219(13) | 4785(7) | 54(3) |
| C(44) | 6022(13) | 6326(14) | 4678(7) | 59(4) |
| C(45) | 6202(12) | 5635(12) | 3975(7) | 50(3) |
| C(46) | 5508(11) | 5921(10) | 3390(6) | 43(3) |

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Note to Table 4:
$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

the residue absorbed onto a small amount of silica and loaded onto a silica chromatography column. Elution with light petroleum produced an orange–yellow zone of $[Ru_3(CO)_{12}]$ which was recovered. Elution with $CH_2Cl_2$–light petroleum (1:4) produced a red band which consisted of cluster 5 (62.4 mg, 0.05 mmol, 14.3%). No other tractable products were eluted.

Data for 5. M.p. 230–233 °C. IR: $\nu$(CO) 2074 s, 2034 w, 2005 vs, 1939 w, 1920 m $cm^{-1}$. $^1H$ NMR $\delta$ 7.80–6.80 (m, 16H, Ph), 6.25–6.14 (m, 4H, Ph), 5.78 (s, 10H, $\eta$-$C_5H_5$) ppm. $^{13}C$ NMR $\delta$ 269.5 ($\mu_3$-C), 201.5 (2CO), 201.2 (2CO), 200.0 (2CO), 191.4 (CO), 191.3 (CO), 160.9 ($C_{ipso}$ of $\mu_3$-CPh), 145.9 ($C_{ipso}$), 142.3 ($\mu$-CPh), 141.1 ($C_{ipso}$), 140.0 ($\mu$-CPh), 130.8–124.4 (m, Ph), 105.0 ($\eta$-$C_5H_5$), 102.3 ($C_{ipso}$ of Ph bonded to Ru), 92.4 (CPh). Anal. Found: C, 42.56; H, 2.40. $C_{46}H_{30}Mo_2O_{10}Ru_3 \cdot CH_2Cl_2$ Calc.: C, 42.66; H, 2.42%. Mass spectrum $m/z$ 1239 ($M^+$).

### 3.3. *Reaction of* $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ *with* $[Co_2(CO)_8]$

Dicobalt octacarbonyl (288 mg, 0.842 mmol) was added to a solution of $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ (190 mg, 0.268 mmol) in toluene (175 $cm^3$). The mixture was heated to reflux for 1.25 h, at which point TLC monitoring indicated complete reaction. Column chromatography, eluting with $CH_2Cl_2$–light petroleum (1:9) produced an unidentified green–brown dicobalt complex (22.8 mg). IR $\nu$(CO) 2073 m, 2029 s, 2012 m, 1820 m $cm^{-1}$. $^1H$ NMR $\delta$ 7.55–6.97 (m, Ph). Mass spectrum $m/z$ 580, 552, 524, 496, 468. Elution with a 1:4 mixture of the same solvents gave a bright orange band containing $[CoMo(\mu\text{-}C_4Ph_4)(CO)_4(\eta\text{-}C_5H_5)]$ 6 (53.6 mg, 0.078 mmol, 29%), identified by comparison of its IR, NMR and mass spectra with literature data [19]. A large amount of decomposition was observed at the top of the column.

### 3.4. *Crystal structure determination of complex 5*

Details of the crystal data and refinement parameters are given in Table 3; atomic coordinates and equivalent isotropic displacement parameters in Table 4. Three-dimensional, room temperature X-ray data were collected in the range $3.5° < 2\theta < 45°$ on a Siemens P4 diffractometer by the $\omega$-scan method. Of the 6496 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 4354 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 on $F^2$. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0480$ ($wR_2 = 0.1415$ for all 5385 unique data, 550 parameters, mean and maximum $\delta/\sigma$ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density $-1.034$ and 0.871 e Å$^{-3}$. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 20.3642P]$ 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 [21] as implemented on the Viglen 486dx computer.

Full listings of bond lengths and angles, anisotropic thermal parameters and hydrogen atom position parameters have been deposited with the Cambridge Crystallographic Data Centre. Structure factor tables are available from the authors.

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