

# Site-selective substitution and vinylidene–alkylidyne–vinylidene interconversion in dimolybdenum–ruthenium clusters

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The thermal reaction of the dimolybdenum–ruthenium vinylidene clusters  $[\text{Mo}_2\text{Ru}(\mu_3\text{-C=CHR})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_2]$  ( $\text{R} = \text{H}$  **1a**,  $\text{Me}$  **1b**,  $\text{Ph}$  **1c** or  $\text{CO}_2\text{Me}$  **1d**) with the tertiary phosphine  $\text{PPh}_2\text{Me}$  afforded the monosubstituted complexes  $[\text{Mo}_2\text{Ru}(\mu_3\text{-C=CHR})(\text{CO})_6(\text{PPh}_2\text{Me})(\eta\text{-C}_5\text{H}_5)_2]$  **2a–2d** in excellent yields. The products exist as single isomers in which site-selective substitution of a CO ligand has occurred exclusively at the ruthenium atom. The crystal structure of **2b** has been determined by X-ray diffraction; the geometry of the vinylidene ligand is identical to that previously found in the parent compound **1b**, but a slightly different pattern of semi-bridging carbonyls is present. The reactions of **1a** and **1b** with diphenylphosphine are more complex. Depending on the stoichiometry and conditions employed, three different types of cluster have been isolated: the substitution product  $[\text{Mo}_2\text{Ru}(\mu_3\text{-C=CH}_2)(\text{CO})_6(\text{PPh}_2\text{H})(\eta\text{-C}_5\text{H}_5)_2]$  **2e**; the 46-electron monophosphido compounds  $[\text{Mo}_2\text{Ru}(\mu_3\text{-CCH}_2\text{R})(\mu\text{-PPh}_2)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)_2]$  **3a**, **3b** and the saturated bis(phosphido) species  $[\text{Mo}_2\text{Ru}(\mu_3\text{-C=CHR})(\mu\text{-PPh}_2)_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  **4a**, **4b**. Separate experiments have established that these products are formed sequentially, thus demonstrating the conversion of the initial vinylidene into an alkylidyne ligand and then back to a vinylidene. The structures of **3b** and **4a** have been confirmed by X-ray diffraction, showing that the phosphido groups bridge one or both of the Mo–Ru edges respectively.

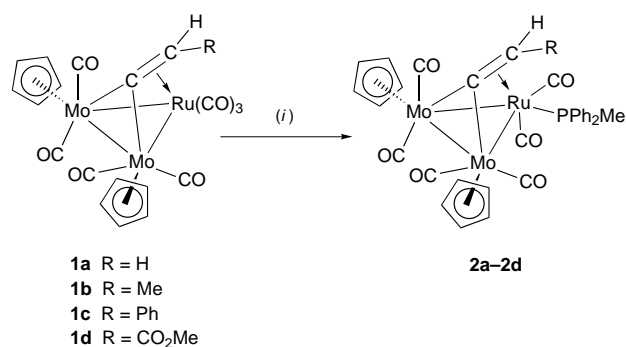
The chemistry of mixed-metal clusters has been under investigation for a number of years now,<sup>1</sup> and although much of this work has concentrated simply on the preparation of such compounds, studies of their reactivity are becoming more widespread as rational and efficient synthetic routes become available. We, in common with several other groups, are particularly interested in the co-ordination and transformation of small organic fragments on heterometallic frameworks in the belief that unusual reactivity patterns may be induced by the presence of two or more different metals, and that these metals may sometimes act in a co-operative manner.<sup>2</sup> Alkynes can serve as a convenient source of cluster-bound hydrocarbon fragments for investigation, since they can undergo a number of different activation processes which lead to ligands such as acetylide, vinyl, vinylidene, or alkylidyne.<sup>3</sup> In this paper we focus on the vinylidene ligand,  $\text{=C=CH}_2$ , which can be stabilised by co-ordination to mono-, di- and poly-nuclear complexes.<sup>4</sup> Multi-site bound vinylidenes are implicated as intermediates in the transformation of alkynes and alkenes into alkylidyne fragments on a variety of metal surfaces, and studies of their reactivity are therefore of relevance to heterogeneous catalysis.

Recently we reported that the readily available complexes  $[\text{Mo}_2(\mu\text{-HC}\equiv\text{CR})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  undergo rearrangement of the alkyne ligand on reaction with  $[\text{Ru}_3(\text{CO})_{12}]$  to give the trinuclear vinylidene clusters  $[\text{Mo}_2\text{Ru}(\mu_3\text{-C=CHR})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_2]$  ( $\text{R} = \text{H}$  **1a**,  $\text{Me}$  **1b**,  $\text{Ph}$  **1c** or  $\text{CO}_2\text{Me}$  **1d**) in reasonable yields (typically 45%).<sup>5,6</sup> We have now examined the reactivity of these clusters towards phosphines, and here report that they undergo site-selective substitution of a ruthenium-bound CO ligand by  $\text{PPh}_2\text{Me}$ , and also react with  $\text{PPh}_2\text{H}$  to give mono- and bis-phosphido-bridged clusters. This latter reaction also involves the sequential conversion of the vinylidene ligand first into an alkylidyne and then back to a vinylidene.

## Results and Discussion

### Site-selective substitution reactions with $\text{PPh}_2\text{Me}$

Clusters **1a–1d** react smoothly with 1 equivalent of  $\text{PPh}_2\text{Me}$  in refluxing toluene over a period of 30 min to produce the substitution products  $[\text{Mo}_2\text{Ru}(\mu_3\text{-C=CHR})(\text{CO})_6(\text{PPh}_2\text{Me})(\eta\text{-C}_5\text{H}_5)_2]$



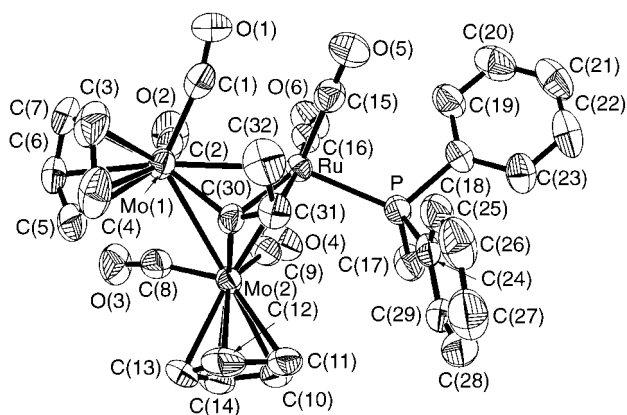
**Scheme 1** Synthesis of the phosphine-substituted clusters. Reagents and conditions: (i)  $\text{PPh}_2\text{Me}$ , refluxing toluene, 0.5 h

**2a–2d** in yields of around 90% in the case of complexes **2a–2c**, though rather lower for **2d** (increasing the reaction time does not improve the yield) (Scheme 1). Stirring a toluene solution of **1a** with 1 equivalent of  $\text{PPh}_2\text{Me}$  at room temperature for 18 d also gave **2a**, but in lower yield (71%); the thermal reaction is thus more convenient. If 2 equivalents of phosphine are used in refluxing toluene the same monosubstituted products are obtained exclusively.

Complexes **2** were characterised spectroscopically. The IR,  $^1\text{H}$  NMR and mass spectral data all suggested replacement of one CO ligand of **1** by a phosphine ligand, and examination of the  $^{13}\text{C}$  NMR spectra proved unequivocally that the site of substitution was the ruthenium atom. Owing to the presence of the methyl substituent on the vinylidene, all seven CO ligands in **1b** are inequivalent and are clearly divided into the four bound to Mo ( $\delta$  233.8–222.8) and the three attached to Ru ( $\delta$  198.4–193.5). In the corresponding spectrum of **2b** the four carbonyls on Mo are still present, but there are now only two peaks observed for those attached to Ru, and moreover each of these peaks exhibits coupling to  $^{31}\text{P}$ . The presence of the vinylidene ligand is confirmed by resonances due to the  $\mu_3\text{-C}$  at  $\delta$  297.6 and the  $\beta$ -carbon at  $\delta$  95.0, very similar to their positions for **1b**. Analogous spectra were obtained for the other complexes of type **2**, though in the case of **2a** the  $^{31}\text{P}$  coupling to the Ru–CO groups was not well resolved. Each compound exists as a single

**Table 1** Selected bond lengths (Å) and angles (°) for complex **2b**·CH<sub>2</sub>Cl<sub>2</sub>

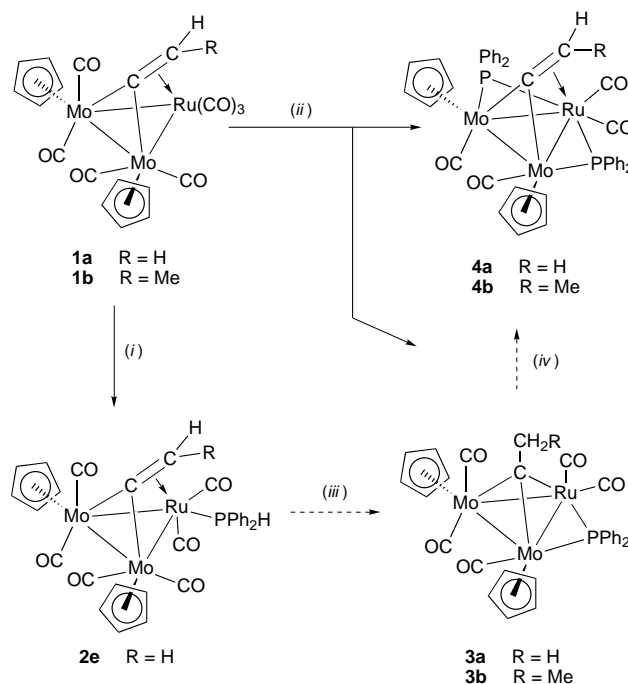
Ru–C(15)	1.872(7)	Ru–C(16)	1.907(7)
Ru–C(30)	2.100(6)	Ru–C(31)	2.345(6)
Ru–P	2.353(2)	Ru–Mo(2)	2.9642(12)
Ru–Mo(1)	2.9818(10)	Mo(1)–C(1)	1.975(8)
Mo(1)–C(2)	2.002(8)	Mo(1)–C(30)	2.093(6)
Mo(1)–Mo(2)	3.0064(11)	Mo(2)–C(8)	1.939(8)
Mo(2)–C(9)	1.985(7)	Mo(2)–C(30)	2.086(6)
C(30)–C(31)	1.395(8)	C(31)–C(32)	1.524(9)
C(30)–Ru–C(31)	36.0(2)	C(15)–Ru–P	90.4(2)
C(16)–Ru–P	92.3(2)	C(30)–Ru–Mo(2)	44.7(2)
C(31)–Ru–Mo(2)	73.0(2)	C(30)–Ru–Mo(1)	44.6(2)
C(31)–Ru–Mo(1)	73.5(2)	Mo(2)–Ru–Mo(1)	60.74(2)
C(1)–Mo(1)–Ru	67.1(2)	C(30)–Mo(1)–Ru	44.8(2)
C(30)–Mo(1)–Mo(2)	43.9(2)	Ru–Mo(1)–Mo(2)	59.34(2)
C(9)–Mo(2)–Ru	72.0(2)	C(30)–Mo(2)–Ru	45.1(2)
C(8)–Mo(2)–Mo(1)	64.3(2)	C(30)–Mo(2)–Mo(1)	44.1(2)
Ru–Mo(2)–Mo(1)	59.92(3)	O(1)–C(1)–Mo(1)	168.2(6)
O(2)–C(2)–Mo(1)	175.2(6)	O(3)–C(8)–Mo(2)	167.5(6)
O(4)–C(9)–Mo(2)	169.3(6)	O(5)–C(15)–Ru	178.3(6)
O(6)–C(16)–Ru	178.3(5)	C(31)–C(30)–Mo(2)	132.4(4)
C(31)–C(30)–Mo(1)	134.6(5)	Mo(2)–C(30)–Mo(1)	92.0(2)
C(31)–C(30)–Ru	81.6(4)	Mo(2)–C(30)–Ru	90.2(2)
Mo(1)–C(30)–Ru	90.7(2)	C(30)–C(31)–C(32)	124.1(6)
C(30)–C(31)–Ru	62.4(3)		

**Fig. 1** Molecular structure of complex **2b**·CH<sub>2</sub>Cl<sub>2</sub> in the crystal. The solvent of crystallisation has been omitted

isomer, in contrast to the situation in [Co<sub>2</sub>Ru(μ<sub>3</sub>-C=CHR)-(CO)<sub>5</sub>L] where two isomers exist depending on the orientation of the phosphine ligand with respect to the vinylidene substituent.<sup>7</sup>

Confirmation of the structure of complex **2b** was obtained through an X-ray diffraction study, the result of which is displayed in Fig. 1, with selected bond lengths and angles collected in Table 1. As expected, the structure is very similar to that of **1b** which we reported previously.<sup>6</sup> The two Mo–Ru bonds in **2b** are slightly longer than in **1b** but the Mo–Mo bond is if anything slightly shorter, while the geometry of the vinylidene ligand itself is, within experimental error, identical in both compounds. The phosphine ligand occupies a position essentially *trans* to one of the Mo–Ru bonds.

The molybdenum-bound CO ligands in complex **2b** deserve some comment. In the unsubstituted complex **1b** one carbonyl ligand attached to each Mo atom showed considerable non-linearity [Mo–C–O angles of 165.9(5) and 168.0(6)°], whereas the other was more linear with angles of 173.7(6) and 175.6(5)°. The former pair can be described as semi-bridging, one between the two Mo atoms and the other between Mo and Ru. The situation in **2b** is slightly different in that C(2)–O(2) is essentially linear, whereas C(1)–O(1), C(8)–O(3), and C(9)–O(4) are all significantly distorted, with Mo–C–O angles of 168.2(6), 167.5(6) and 169.3(6)° respectively. The long M–CO

**Scheme 2** Synthesis of the phosphido-bridged clusters. Reagents and conditions: (i) PPh<sub>2</sub>H, toluene, room temperature (r.t.), 24 d; (ii) PPh<sub>2</sub>H, refluxing toluene, 1–4; (iii) refluxing toluene, 1.25 h; (iv) PPh<sub>2</sub>H, refluxing toluene, 3 h

distances are Ru···C(1) 2.864, Mo(1)···C(8) 2.783 and Ru···C(9) 3.014 Å and hence the ligands have asymmetry parameters<sup>8</sup> of 0.450, 0.435 and 0.518 respectively. Another useful criterion is the M–M–C bond angle; Crabtree and Lavin<sup>9</sup> have suggested that in semi-bridging carbonyls this angle is less than 76.5°. In **2b** the relevant angles are C(1)–Mo(1)–Ru 67.1(2), C(8)–Mo(2)–Mo(1) 64.3(2) and C(9)–Mo(2)–Ru 72.0(2)°. It therefore appears that the first two CO ligands semi-bridge quite distinctly, and C(9)–O(4) rather more weakly. There seems no obvious electronic reason for this to occur, especially since two of the three CO's now semi-bridge to the Ru atom even though it has been rendered more electron rich through the replacement of a π-acceptor CO ligand by a phosphine. However the fact that all the bending occurs in the MMC plane (the angles around each carbonyl carbon add up to 360 ± 0.1°) and its occurrence in several different Mo<sub>2</sub>Ru clusters both argue against this being a simple crystal-packing phenomenon.

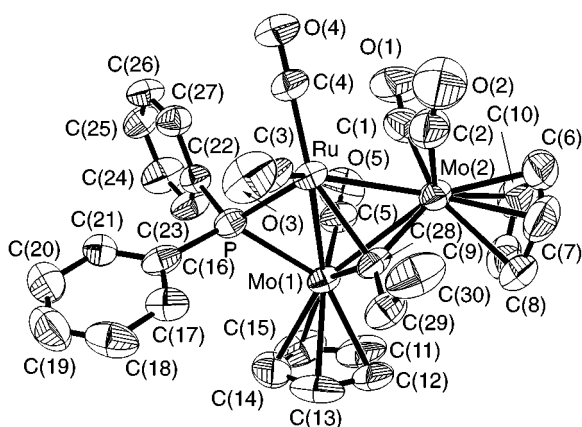
#### Reaction of the vinylidene clusters **1** with diphenylphosphine

Having established that the vinylidene clusters **1** reacted with a typical tertiary phosphine, we turned our attention to the secondary phosphine PPh<sub>2</sub>H with the objective of introducing a phosphido group into the molecule. At room temperature in toluene cluster **1a** reacted only very slowly with PPh<sub>2</sub>H to afford an analogous substitution product [Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CH<sub>2</sub>)(CO)<sub>6</sub>-(PPh<sub>2</sub>H)(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **2e** in a yield of 64% after 24 d (because of the long time-scale we did not attempt a similar reaction with **1b**, but a similar outcome can be predicted). Complex **2e** was identified spectroscopically, showing close similarity with **2a–2d** with the exception of the characteristic <sup>1</sup>H NMR signal due to the P–H functionality [δ 6.38 with a typically large *J*(PH) of 370 Hz].

On changing the reaction conditions to refluxing toluene a different product distribution was observed (Scheme 2). The monosubstituted complexes are presumably the initial products, but further reaction must occur rapidly. With strictly 1 equivalent of phosphine and short reaction times the major products were the green monophosphido alkyldiene clusters [Mo<sub>2</sub>Ru(μ<sub>3</sub>-CCH<sub>2</sub>R)(μ-PPh<sub>2</sub>)(CO)<sub>5</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **3a**, **3b**, accom-

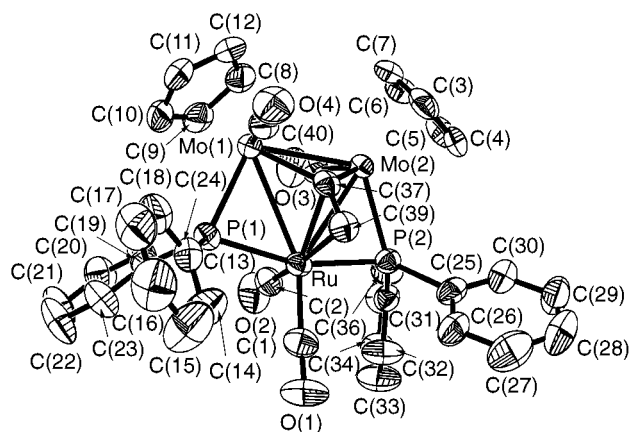
**Table 2** Selected bond lengths (Å) and angles (°) for complex **3b**·CHCl<sub>3</sub>

Mo(1)–C(5)	1.987(11)	Mo(1)–C(28)	1.999(8)
Mo(1)–P	2.381(2)	Mo(1)–Ru	2.7171(12)
Mo(1)–Mo(2)	3.0946(13)	Mo(2)–C(1)	1.977(11)
Mo(2)–C(2)	1.982(12)	Mo(2)–C(28)	2.087(10)
Mo(2)–Ru	2.7463(12)	Ru–C(3)	1.845(11)
Ru–C(4)	1.901(10)	Ru–C(28)	2.213(8)
Ru–P	2.312(2)	C(16)–C(17)	1.397(13)
C(28)–C(29)	1.546(13)	C(29)–C(30)	1.52(2)
C(28)–Mo(1)–Ru	53.4(2)	P–Mo(1)–Ru	53.45(6)
C(5)–Mo(1)–Mo(2)	71.6(3)	C(28)–Mo(1)–Mo(2)	41.8(3)
Ru–Mo(1)–Mo(2)	55.95(3)	C(1)–Mo(2)–Ru	74.8(3)
C(2)–Mo(2)–Ru	67.0(3)	C(28)–Mo(2)–Ru	52.4(2)
C(28)–Mo(2)–Mo(1)	39.7(2)	Ru–Mo(2)–Mo(1)	55.05(3)
C(28)–Ru–Mo(1)	46.5(2)	P–Ru–Mo(1)	55.82(6)
C(28)–Ru–Mo(2)	48.3(3)	Mo(1)–Ru–Mo(2)	69.00(3)
Ru–P–Mo(1)	70.74(7)	O(1)–C(1)–Mo(2)	168.9(11)
O(2)–C(2)–Mo(2)	165.4(11)	O(3)–C(3)–Ru	177.7(7)
O(4)–C(4)–Ru	177.8(9)	O(5)–C(5)–Mo(1)	170.2(9)
C(29)–C(28)–Mo(1)	128.7(7)	C(29)–C(28)–Mo(2)	127.4(7)
Mo(1)–C(28)–Mo(2)	98.4(4)	C(29)–C(28)–Ru	125.2(6)
Mo(1)–C(28)–Ru	80.1(3)	Mo(2)–C(28)–Ru	79.3(3)
C(30)–C(29)–C(28)	115.0(9)		

**Fig. 2** Molecular structure of complex **3b**·CHCl<sub>3</sub> in the crystal. The solvent of crystallisation has been omitted

panied by small amounts of the bis(phosphido) vinylidene clusters [Mo<sub>2</sub>Ru(μ-C=CHR)(μ-PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **4a**, **4b**. With more than 1 equivalent over longer reaction times **4** became the major products. By judicious choice of conditions it was possible to obtain yields in the region of 50% for each of these four compounds; however it did not prove possible to find conditions which led exclusively to either **3** or **4**, and some unreacted **1** was also usually recovered. A separate experiment showed that heating **2e** gave **3a**, and that **4b** is similarly formed sequentially from **3b** on treatment with further PPh<sub>2</sub>H.

The monophosphido species **3a** and **3b** each display three carbonyl absorptions in their IR spectra. Their <sup>1</sup>H NMR spectra show the incorporation of one phosphine ligand, and display signals appropriate for μ<sub>3</sub>-CMe or μ<sub>3</sub>-CEt units respectively, implying oxidative addition of the P–H functionality and migration of the resulting hydride ligand to the vinylidene fragment. This is confirmed by the <sup>31</sup>P NMR spectra, which each show one peak in a region typical of μ-PPh<sub>2</sub> groups. The <sup>13</sup>C NMR spectra contain peaks at δ 350.8 and 363.5 respectively, shifted considerably downfield from the region expected for vinylidenes but typical values for alkylidyne groups {cf. δ 353.8 for [Mo<sub>2</sub>Ru<sub>4</sub>(μ<sub>3</sub>-CMe)<sub>2</sub>(CO)<sub>12</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], in which the μ<sub>3</sub>-CMe groups also cap Mo<sub>2</sub>Ru faces}.<sup>6</sup> The spectra also contain signals for three Mo-bound CO ligands (one split into a doublet) and two Ru-bound CO ligands (again, one of which is split), showing the phosphido group to be located on one

**Fig. 3** Molecular structure of complex **4a**·CH<sub>2</sub>Cl<sub>2</sub> in the crystal. The solvent of crystallisation has been omitted

Mo–Ru edge. The mass spectra show molecular ions and carbonyl loss peaks for five CO ligands. The replacement of the μ<sub>3</sub>-C=CHR ligand and two CO's (totalling eight electrons) by the μ<sub>3</sub>-CCH<sub>2</sub>R and μ-PPh<sub>2</sub> ligands (totalling six) means that clusters **3** have only 46 electrons and are thus unsaturated.

The crystal structure of the μ<sub>3</sub>-CEt complex **3b** was determined and is shown in Fig. 2, with selected bond lengths and angles collected in Table 2. Whereas the Mo–Mo distance of 3.0946(13) Å is virtually identical to those observed in the structures of **1b** and **2b**, both Mo–Ru distances are considerably shorter [Mo(1)–Ru 2.7171(12) and Mo(2)–Ru 2.7463(12) Å]. Since these distances lengthen again in the bis(phosphido) cluster **4a** (see below) this shortening may reflect the electronic unsaturation of the cluster. The phosphido ligand bridges the Mo(1)–Ru edge and is slightly closer to the ruthenium atom. The angle between the Mo<sub>2</sub>Ru and MoRuP planes is 19.0°, with the phosphorus atom pointing away from the capping alkylidyne. The alkylidyne ligand itself is bonded relatively symmetrically above the metal triangle; the Mo–C(28) bonds of 1.999(8) and 2.087(10) Å are slightly shorter than the Ru–C(28) bond of 2.213(8) Å, these distances being very similar to those found in [Mo<sub>2</sub>Ru<sub>4</sub>(μ<sub>3</sub>-CMe)<sub>2</sub>(CO)<sub>12</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>].<sup>6</sup>

As in complexes **1b** and **2b**, the CO ligands attached to ruthenium are linear, whereas those attached to molybdenum display semi-bridging character. Of these C(5)–O(5) is the weakest, with a bond angle of 170.2(9)°; it bridges from Mo(1) to Mo(2) with a long Mo(2)···C(5) distance of 3.104 Å. Both carbonyls attached to Mo(2) are more strongly semi-bridging with Ru, reflected in both their deviation from linearity [168.9(11) and 165.4(11)°] and the shorter semi-bridging lengths: Ru···C(1) 2.933 and Ru···C(2) 2.686 Å. The angles C(1)–Mo(2)–Ru and C(2)–Mo(2)–Ru are 74.8(3) and 67.0(3)° respectively.

The IR spectra of complexes **4** show four bands, and their <sup>1</sup>H NMR spectra show the incorporation of two phosphine ligands, confirmed by the <sup>31</sup>P NMR spectra which each display two doublets in the appropriate region for μ-PPh<sub>2</sub> groups. The reinstatement of the vinylidene ligand is also evident from the presence in the <sup>1</sup>H NMR spectrum of two complex multiplets for the =CH<sub>2</sub> protons in **4a**, and a doublet of quartets and a doublet for the =CHMe group of **4b**. In the <sup>13</sup>C NMR spectra the μ<sub>3</sub>-C of the vinylidene ligand appear as apparent triplets at δ 267.9 for **4a** and at δ 258.4 for **4b**, shifted some 40 ppm upfield from their positions for **1** and **2**. The spectra also show the presence of two Mo–CO and two Ru–CO ligands, which were visible as carbonyl loss peaks in the mass spectra.

The structure of complex **4a** was determined crystallographically and is illustrated in Fig. 3, with selected bond lengths and angles shown in Table 3. In this compound the metal triangle is virtually equilateral, since the Mo–Mo bond of 2.9177(13) Å is somewhat shorter than in **1–3** and the Mo–Ru

**Table 3** Selected bond lengths (Å) and angles (°) for complex **4a**·CH<sub>2</sub>Cl<sub>2</sub>

Ru–C(2)	1.892(10)	Ru–C(1)	1.887(10)
Ru–C(38)	2.191(8)	Ru–C(39)	2.300(8)
Ru–P(1)	2.387(3)	Ru–P(2)	2.397(3)
Ru–Mo(2)	2.9139(11)	Ru–Mo(1)	2.9839(13)
Mo(1)–C(40)	1.896(11)	Mo(1)–C(38)	2.090(9)
Mo(1)–P(1)	2.393(2)	Mo(1)–Mo(2)	2.9177(13)
Mo(2)–C(37)	1.963(10)	Mo(2)–C(38)	2.081(8)
Mo(2)–P(2)	2.373(2)	C(38)–C(39)	1.386(12)
C(38)–Ru–C(39)	35.8(3)	P(1)–Ru–P(2)	162.63(8)
C(38)–Ru–Mo(2)	45.4(2)	C(39)–Ru–Mo(2)	73.0(2)
P(2)–Ru–Mo(2)	51.96(6)	C(38)–Ru–Mo(1)	44.4(2)
C(39)–Ru–Mo(1)	74.5(2)	P(1)–Ru–Mo(1)	51.46(6)
Mo(2)–Ru–Mo(1)	59.29(3)	C(38)–Mo(1)–Mo(2)	45.5(2)
C(38)–Mo(1)–Ru	47.2(2)	P(1)–Mo(1)–Ru	51.29(6)
Mo(2)–Mo(1)–Ru	59.16(3)	C(38)–Mo(2)–Ru	48.6(2)
P(2)–Mo(2)–Ru	52.73(6)	C(37)–Mo(2)–Mo(1)	79.2(3)
C(38)–Mo(2)–Mo(1)	45.7(2)	Ru–Mo(2)–Mo(1)	61.55(3)
Mo(2)–P(2)–Ru	75.30(7)	Ru–P(1)–Mo(1)	77.25(8)
O(1)–C(1)–Ru	177.1(10)	O(2)–C(2)–Ru	176.4(9)
O(3)–C(37)–Mo(2)	172.2(8)	C(39)–C(38)–Mo(2)	128.7(7)
C(39)–C(38)–Mo(1)	137.1(7)	Mo(2)–C(38)–Mo(1)	88.8(3)
C(39)–C(38)–Ru	76.4(5)	Mo(2)–C(38)–Ru	86.0(3)
Mo(1)–C(38)–Ru	88.3(3)	C(38)–C(39)–Ru	67.8(5)
O(4)–C(40)–Mo(1)	174.9(8)		

**Table 4** Distribution of cyclopentadienyl ligands in complexes **1–4**. For definition of  $\theta$  see text

Complex	$\theta/^\circ$	
	For Mo(1)–C <sub>5</sub> H <sub>5</sub>	For Mo(2)–C <sub>5</sub> H <sub>5</sub>
<b>1b</b>	10.0	17.8
<b>2b</b>	10.0	11.9
<b>3b</b>	6.9	3.9
<b>4a</b>	–12.9	15.0

bonds [Ru–Mo(1) 2.9839(13) and Ru–Mo(2) 2.9139(11) Å] are somewhat longer than in **3** but similar to those in **1** and **2**. On going from **3** to **4**, the alkyldiene ligand and one CO (together donating five electrons) are replaced by the vinylidene and a  $\mu$ -PPh<sub>2</sub> unit, totalling seven electrons; hence, **4** is once again electronically saturated with a 48-electron count. The two phosphido ligands bridge the two Mo–Ru edges symmetrically, and lie virtually in the plane of the metal triangle: the angle between the Mo<sub>2</sub>Ru and MoRuP plane is 1.7° for P(1) while the corresponding angle for P(2) is 3.1°. The two CO ligands attached to Ru are as expected linear; however the deviations from linearity of the Mo–CO ligands are also less than in **1–3**, the angles being Mo(1)–C(40)–O(4) 174.9(8)° and Mo(2)–C(37)–O(3) 172.2(8)°. It therefore appears that they are only very weakly semi-bridging, if at all.

The orientation of the cyclopentadienyl ligands in complex **4a** is different compared to those of the other Mo<sub>2</sub>Ru clusters. Table 4 shows the angle  $\theta$  between the centroid of the C<sub>5</sub>H<sub>5</sub> ligand and the Mo<sub>2</sub>Ru plane, with a positive value indicating displacement towards the capping organic fragment and a negative value away from it. In complexes **1b**, **2b** and **3b** both C<sub>5</sub>H<sub>5</sub> ligands are displaced towards this fragment, whereas in **4a** one lies on each side of the trimetallic plane. Relatively easy passage of a  $\eta$ -C<sub>5</sub>H<sub>5</sub> ring from one side to the other during a reaction is a known phenomenon, and indeed some clusters display such a movement as a fluxional process.<sup>10</sup>

The pathway for the sequential formation of complexes **3** and **4** is assumed to involve production of the terminally substituted complex **2** as the initial step. Oxidative addition of the P–H bond, migration of the H to the  $\beta$ -carbon of the vinylidene ligand, and displacement of one Mo-bound CO ligand by the phosphido group would yield **3**. The co-ordinatively unsatur-

ated nature of **3** would allow addition of a further PPh<sub>2</sub>H ligand, either at the ruthenium atom or at the second Mo atom. Repetition of the oxidative-addition step, this time with elimination of H<sub>2</sub> to regenerate the vinylidene ligand, and loss of CO would produce **4**. Interconversion of vinylidene and alkyldiene ligands on clusters by the addition or elimination of dihydrogen is a well established mode of reactivity.<sup>11</sup> In some cases the process is reversible, and Vahrenkamp and co-workers<sup>12</sup> have compared such transformations for a range of trinuclear heterometallic clusters with FeCoMo, RuCoMo or RuCoW cores, and found that the vinylidene tends to be the most favoured form. As far as we are aware, however, the use of the oxidative addition of a secondary phosphine to provide the hydrogen atom for addition to the vinylidene fragment has not been recorded. Attempts are currently under way in our laboratory to exploit the unsaturated nature of **3** in reactions with other ligands such as alkynes.

## Experimental

General experimental techniques were as described in recent publications from this laboratory.<sup>13</sup> 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. All the products described are relatively air-stable, and work-up procedures can be carried out without special precautions.

Infrared spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> solution on a Perkin-Elmer 1600 FT-IR machine using 0.5 mm NaCl cells, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra in CDCl<sub>3</sub> 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<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> ( $\delta$  0.0). The <sup>13</sup>C-<sup>1</sup>H NMR spectra were recorded using an attached proton-test technique (MOD pulse sequence). Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in fast atom bombardment mode with 3-nitrobenzyl alcohol as matrix. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry. The complexes [Mo<sub>2</sub>Ru( $\mu$ -C=CHR)(CO)<sub>7</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] were prepared as described previously.<sup>6</sup>

## Preparations

**[Mo<sub>2</sub>Ru( $\mu$ -C=CH<sub>2</sub>)(CO)<sub>6</sub>(PPh<sub>2</sub>Me)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] 2a.** A solution of [Mo<sub>2</sub>Ru( $\mu$ -C=CH<sub>2</sub>)(CO)<sub>7</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **1a** (200 mg, 0.31 mmol) in toluene (150 cm<sup>3</sup>) was treated with PPh<sub>2</sub>Me (0.058 cm<sup>3</sup>, 0.31 mmol) and heated to reflux for 30 min after which time it had turned dark red from its initial orange. The solvent was removed and the residue absorbed onto a small amount of silica. Chromatography produced a very small amount of unchanged complex **1a** eluted in light petroleum (b.p. 60–80 °C)–CH<sub>2</sub>Cl<sub>2</sub> (4:1). Finally a dark red band of complex **2a** (236.2 mg, 0.29 mmol, 93.2%) was eluted with a 1:1 mixture of the same solvents. M.p. 172–174 °C. IR:  $\nu$ (CO) 2012s, 1952s, 1905w, 1840w and 1782w cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.71–7.32 (m, 10 H, Ph), 5.16 (s, 5 H,  $\eta$ -C<sub>5</sub>H<sub>5</sub>), 4.95 (s, 5 H,  $\eta$ -C<sub>5</sub>H<sub>5</sub>), 4.35 (m, 2 H, C=CH<sub>2</sub>) and 2.19 (d, 3 H,  $J$  = 12, Me); <sup>13</sup>C NMR  $\delta$  298.7 ( $\mu$ -C), 242.6, 230.5, 228.8, 227.2 (all Mo–CO), 201.4 (d, Ru–CO), 199.3 (d, Ru–CO), 137.8 (d,  $J$  = 40,  $C_{ipso}$ ), 137.0 (d,  $J$  = 41,  $C_{ipso}$ ), 132.0–128.2 (m, Ph), 92.2 ( $\eta$ -C<sub>5</sub>H<sub>5</sub>), 90.3 ( $\eta$ -C<sub>5</sub>H<sub>5</sub>), 73.0 (CH<sub>2</sub>) and 17.2 (d, Me,  $J$  = 27 Hz); <sup>31</sup>P NMR  $\delta$  20.4 (Found: C, 42.63; H, 3.00. Calc. for C<sub>31</sub>H<sub>25</sub>Mo<sub>2</sub>O<sub>6</sub>PRu·CH<sub>2</sub>Cl<sub>2</sub>: C, 42.57; H, 2.99%); mass spectrum  $m/z$  818 ( $M^+$ ).

In a separate experiment a solution of complex **1a** (100 mg, 0.155 mmol) and PPh<sub>2</sub>Me (0.03 cm<sup>3</sup>) in toluene (50 cm<sup>3</sup>) was stirred at room temperature for 18 d. Chromatography as above gave unchanged **1a** (17.4 mg) followed by a red band of **2a** (89.8 mg, 70.9%).

**[Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CHMe)(CO)<sub>6</sub>(PPh<sub>2</sub>Me)(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] 2b.** In a similar reaction a solution of [Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CHMe)(CO)<sub>7</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **1b** (200 mg, 0.31 mmol) and PPh<sub>2</sub>Me (0.057 cm<sup>3</sup>, 0.31 mmol) in toluene (75 cm<sup>3</sup>) was heated to reflux for 2 h. Chromatography as above produced an orange band of unchanged complex **1b** (21.4 mg, 0.03 mmol, 10.7% recovery) followed by a dark red band of **2b** (218.9 mg, 0.26 mmol, 87%). M.p. 192 °C. IR ν(CO) 2011s, 1958s, 1937 (sh), 1866w and 1817w cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.58–7.36 (m, 10 H, Ph), 5.12 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 4.79 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 4.36 (m, 1 H, CHMe), 2.00 (d, 3 H, PPh<sub>2</sub>Me, *J* = 12) and 1.75 (d, 3 H, CHMe, *J* = 6); <sup>13</sup>C NMR 297.6 (μ<sub>3</sub>-C), 237.3, 233.8, 231.1, 224.9 (all Mo–CO), 203.2 (d, *J* = 11, Ru–CO), 199.1 (d, *J* = 12, Ru–CO), 138.7 (d, *J* = 46, C<sub>ipso</sub>), 134.8 (d, *J* = 42, C<sub>ipso</sub>), 133.3–128.5 (m, Ph), 95.0 (CHMe), 90.7 (η-C<sub>5</sub>H<sub>5</sub>), 90.4 (η-C<sub>5</sub>H<sub>5</sub>), 27.7 (CHMe) and 20.2 (d, *J* = 29 Hz, PPh<sub>2</sub>Me); <sup>31</sup>P NMR δ 25.1 (Found: C, 45.69; H, 2.91. Calc. for C<sub>32</sub>H<sub>27</sub>Mo<sub>2</sub>O<sub>6</sub>PRu: C, 46.21; H, 3.25%); mass spectrum *m/z* 833 (*M*<sup>+</sup>).

**[Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CHPh)(CO)<sub>6</sub>(PPh<sub>2</sub>Me)(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] 2c.** A solution of [Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CHPh)(CO)<sub>7</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **1c** (180 mg, 0.25 mmol) and PPh<sub>2</sub>Me (0.047 cm<sup>3</sup>, 0.25 mmol) in toluene (125 cm<sup>3</sup>) was heated to reflux for 15 min after which time the solution had turned dark red. Chromatography as above produced a very small amount of unchanged complex **1c** followed by a dark red band of **2c** (213.6 mg, 0.24 mmol, 96.1%). Finally an unidentified green band (43.4 mg) was eluted with CH<sub>2</sub>Cl<sub>2</sub>. Data for **2c**: m.p. 183–185 °C; IR ν(CO) 2013s, 1964s, 1941 (sh), 1872w and 1823w cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.56–7.16 (m, 15 H, Ph), 5.40 (d, 1 H, CHPh, *J* = 12), 4.99 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 4.82 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 2.06 (d, *J* = 12, 3 H, PPh<sub>2</sub>Me); <sup>13</sup>C NMR δ 300.6 (μ<sub>3</sub>-C), 236.6, 232.9, 232.4, 223.8 (all Mo–CO), 202.9 (d, *J* = 11, Ru–CO), 197.8 (d, *J* = 12, Ru–CO), 144.3 (C<sub>ipso</sub> of CHPh), 139.1 (d, *J* = 47, C<sub>ipso</sub> of PPh<sub>2</sub>Me), 133.1 (d, *J* = 40, C<sub>ipso</sub> of PPh<sub>2</sub>Me), 131.9–126.2 (m, Ph), 103.4 (CHPh), 91.6 (η-C<sub>5</sub>H<sub>5</sub>), 91.2 (η-C<sub>5</sub>H<sub>5</sub>) and 20.1 (d, *J* = 31 Hz, Me); <sup>31</sup>P NMR δ 24.4 (Found: C, 49.63; H, 3.27. Calc. for C<sub>37</sub>H<sub>29</sub>Mo<sub>2</sub>O<sub>6</sub>PRu: C, 49.72; H, 3.25%); mass spectrum *m/z* 894 (*M*<sup>+</sup>).

**[Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CHCO<sub>2</sub>Me)(CO)<sub>6</sub>(PPh<sub>2</sub>Me)(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] 2d.** A solution of [Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CHCO<sub>2</sub>Me)(CO)<sub>7</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **1d** (94 mg, 0.13 mmol) in toluene (70 cm<sup>3</sup>) was treated with PPh<sub>2</sub>Me (0.025 cm<sup>3</sup>, 0.13 mmol) and heated to reflux for 30 min, turning dark red in the process. Chromatography produced a very small amount of unchanged complex **1d** followed by a dark red band of **2d** (64 mg, 0.07 mmol, 54.7%) which was eluted with light petroleum–CH<sub>2</sub>Cl<sub>2</sub> (1:3). M.p. 148–150 °C. IR ν(CO) 2018s, 1968s, 1946 (sh), 1882w and 1828w cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.57–7.15 (m, 10 H, Ph), 5.28 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 4.79 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 3.64 (s, 3 H, CO<sub>2</sub>Me), 3.27 (s, 1 H, CH), 2.15 (d, *J* = 12, PPh<sub>2</sub>Me); <sup>13</sup>C NMR 303.7 (μ<sub>3</sub>-C), 239.4, 231.3, 228.3, 226.3 (all Mo–CO), 201.7 (d, *J* = 12, Ru–CO), 198.5 (d, *J* = 11, Ru–CO), 172.1 (CO<sub>2</sub>Me), 137.5 (d, *J* = 45, C<sub>ipso</sub>), 135.1 (d, *J* = 43, C<sub>ipso</sub>), 131.8–128.4 (m, Ph), 91.9 (η-C<sub>5</sub>H<sub>5</sub> rings coincident), 82.9 (CH), 51.2 (CO<sub>2</sub>Me) and 18.6 (d, *J* = 30 Hz, PPh<sub>2</sub>Me); <sup>31</sup>P NMR δ 19.6 (Found: C, 45.55; H, 3.44. Calc. for C<sub>33</sub>H<sub>27</sub>Mo<sub>2</sub>O<sub>8</sub>PRu: C, 45.26; H, 3.09%); mass spectrum *m/z* 877 (*M*<sup>+</sup>).

**[Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CH<sub>2</sub>)(CO)<sub>6</sub>(PPh<sub>2</sub>H)(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] 2e.** A solution of complex **1a** (89.9 mg, 0.139 mmol) and PPh<sub>2</sub>H (0.024 cm<sup>3</sup>) in toluene (20 cm<sup>3</sup>) was stirred at room temperature and monitored periodically by IR spectroscopy and TLC. Towards the end of the reaction period (24 d) some decomposition was noted and so the reaction was terminated at this point. Chromatography gave an orange band of returned **1a** (10.3 mg), eluted with CH<sub>2</sub>Cl<sub>2</sub>–light petroleum (1:4), followed by a red band of **2e** (71.8 mg, 64%) which was eluted in a 3:7 mixture of the same solvents. M.p. 78 °C (decomp.). IR ν(CO) 2015s, 1954m, 1905w and 1826m cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.76–7.37 (m, 10 H, Ph), 6.38 (d, *J* = 370, 1 H, P–H), 5.16 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>),

5.07 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>) and 4.05 (m, 2 H, CH<sub>2</sub>); <sup>13</sup>C NMR δ 296.4 (μ<sub>3</sub>-C), 241.4, 231.2, 228.7, 227.0 (all Mo–CO), 200.6 (d, *J* = 10, Ru–CO), 200.1 (d, *J* = 9, Ru–CO), 134.1 (d, *J* = 47, C<sub>ipso</sub>), 133.9 (d, *J* = 44 Hz, C<sub>ipso</sub>), 133.9–128.7 (m, Ph), 91.9 (C<sub>5</sub>H<sub>5</sub>), 90.2 (C<sub>5</sub>H<sub>5</sub>) and 75.3 (CH<sub>2</sub>); <sup>31</sup>P δ NMR 35.0 (Found: C, 44.56; H, 2.88. Calc. for C, 44.83; H, 2.86%); mass spectrum *m/z* 803 (*M*<sup>+</sup>).

**[Mo<sub>2</sub>Ru(μ<sub>3</sub>-CMe)(μ-PPh<sub>2</sub>)(CO)<sub>5</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] 3a.** Diphenylphosphine (0.054 cm<sup>3</sup>, 0.31 mmol) was added by microsyringe to a solution of [Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CH<sub>2</sub>)(CO)<sub>7</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **1a** (200 mg, 0.31 mmol) in toluene (60 cm<sup>3</sup>). The solution was heated to reflux for 2 h, monitoring by TLC. After this time silica was added and the solvent removed using a rotary evaporator. The solid residue was loaded onto a chromatography column and the products separated. Elution with CH<sub>2</sub>Cl<sub>2</sub>–light petroleum (1:3) produced an orange band of complex **1a** (13.5 mg, 6.8% recovery), followed by a red band of [Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CH<sub>2</sub>)(μ-PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **4a** (49.6 mg, 0.053 mmol, 17.2%). A small unidentified orange band was eluted with a 3:7 mixture of the same solvents. Finally, [Mo<sub>2</sub>Ru(μ<sub>3</sub>-CMe)(μ-PPh<sub>2</sub>)(CO)<sub>5</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **3a** (121.5 mg, 0.16 mmol, 50.6%) was eluted as a green band with CH<sub>2</sub>Cl<sub>2</sub>–light petroleum (2:3). Data for **3a**: m.p. 217 °C; IR ν(CO) 2002s, 1939m and 1863w cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.80–6.75 (m, 10 H, Ph), 5.49 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 5.39 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>) and 3.49 (d, *J* = 1, 3 H, Me); <sup>13</sup>C NMR 350.8 (d, *J* = 3, μ<sub>3</sub>-C), 235.1 (d, *J* = 2, Mo–CO), 233.2 (s, Mo–CO), 227.8 (d, *J* = 13, Mo–CO), 205.8 (s, Ru–CO), 198.8 (d, *J* = 4, Ru–CO), 147.2 (d, *J* = 30, C<sub>ipso</sub>), 138.6 (d, *J* = 40 Hz, C<sub>ipso</sub>), 133.7–127.5 (m, Ph), 94.6 (s, η-C<sub>5</sub>H<sub>5</sub>), 92.0 (s, η-C<sub>5</sub>H<sub>5</sub>) and 55.8 (s, Me); <sup>31</sup>P NMR δ 188.5 (Found: C, 41.41; H, 2.74. Calc. for C<sub>29</sub>H<sub>23</sub>Mo<sub>2</sub>O<sub>5</sub>PRu·CH<sub>2</sub>Cl<sub>2</sub>: C, 41.86; H, 2.91%); mass spectrum *m/z* 777, 748, 720, 692, 664, 633 (*M*<sup>+</sup> – *n*CO, *n* = 0–5).

In a separate experiment a solution of complex **2e** (71.8 mg, 0.08 mmol) was heated to reflux in toluene (50 cm<sup>3</sup>) for 1.25 h. Separation by chromatography as above gave trace amounts of **1a** and **4a** followed by **3a** (60.1 mg, 87%).

**[Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CH<sub>2</sub>)(μ-PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] 4a.** On a separate occasion a reaction containing the same quantities of reagents as above was refluxed for 4 h. Separation of the products by chromatography as above gave an orange band consisting of a mixture of unchanged complex **1a** and [Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CH<sub>2</sub>)(μ-PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **4a**, followed by a dark green band of [Mo<sub>2</sub>Ru(μ<sub>3</sub>-CMe)(μ-PPh<sub>2</sub>)(CO)<sub>5</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **3a** (48.4 mg, 0.062 mmol, 20.1%). The two components of the orange band were separated by rechromatography. Elution with CH<sub>2</sub>Cl<sub>2</sub>–petroleum ether (3:17) gave orange **1a** (69.6 mg, 34.8% recovery), and a 1:4 mixture of the same solvents eluted red **4a** (142 mg, 0.152 mmol, 49.2%). Data for **4a**: m.p. > 250 °C; IR ν(CO) 2011s, 1963m, 1881m and 1855m cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.85–6.71 (m, 20 H, Ph), 5.39 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 4.89 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 3.72 (m, 1 H of CH<sub>2</sub>) and 2.97 (m, 1 H of CH<sub>2</sub>); <sup>13</sup>C δ NMR 267.9 (t, *J* = 5, μ<sub>3</sub>-C), 237.8 (d, *J* = 10, Mo–CO), 236.7 (d, *J* = 12, Mo–CO), 205.1 (t, *J* = 5, Ru–CO), 194.7 (t, *J* = 1, Ru–CO), 145.0 (d, *J* = 30, C<sub>ipso</sub>), 144.8 (d, *J* = 38, C<sub>ipso</sub>), 143.6 (d, *J* = 26, C<sub>ipso</sub>), 135.9 (d, *J* = 35, C<sub>ipso</sub>), 135.6–127.3 (m, Ph), 91.6 (s, η-C<sub>5</sub>H<sub>5</sub>), 86.7 (s, η-C<sub>5</sub>H<sub>5</sub>) and 79.9 (s, CH<sub>2</sub>); <sup>31</sup>P NMR δ 200.3 (d, *J* = 83 Hz) and 166.1 (d) (Found: C, 51.55; H, 3.53. Calc. for C<sub>40</sub>H<sub>32</sub>Mo<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Ru: C, 51.56; H, 3.44%); mass spectrum *m/z* 932, 905, 876, 848 and 818 (*M*<sup>+</sup> – *n*CO, *n* = 0–4).

**[Mo<sub>2</sub>Ru(μ<sub>3</sub>-CEt)(μ-PPh<sub>2</sub>)(CO)<sub>5</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] 3b.** A solution of complex **1b** (404 mg, 0.61 mmol) in toluene (50 cm<sup>3</sup>) was treated with PPh<sub>2</sub>H (0.107 cm<sup>3</sup>, 0.61 mmol) from a microsyringe and then heated to reflux for 2 h. After the solvent was removed and the residue absorbed on silica, the products were separated by chromatography. Elution with CH<sub>2</sub>Cl<sub>2</sub>–light petroleum

**Table 5** Summary of crystallographic data for complexes **2b**·CH<sub>2</sub>Cl<sub>2</sub>, **3b**·CHCl<sub>3</sub> and **4a**·CH<sub>2</sub>Cl<sub>2</sub>\*

	<b>2b</b> ·CH <sub>2</sub> Cl <sub>2</sub>	<b>3b</b> ·CHCl <sub>3</sub>	<b>4a</b> ·CH <sub>2</sub> Cl <sub>2</sub>
Formula	C <sub>33</sub> H <sub>29</sub> Cl <sub>2</sub> Mo <sub>2</sub> O <sub>6</sub> PRu	C <sub>31</sub> H <sub>26</sub> Cl <sub>3</sub> Mo <sub>2</sub> O <sub>5</sub> PRu	C <sub>41</sub> H <sub>34</sub> Cl <sub>2</sub> Mo <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Ru
<i>M</i>	916.38	908.79	1016.47
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	<i>Pbca</i>	<i>P2<sub>1</sub>/n</i>	<i>P1</i>
<i>a</i> /Å	16.435(7)	15.337(3)	12.897(4)
<i>b</i> /Å	17.387(5)	10.145(2)	13.221(3)
<i>c</i> /Å	24.389(8)	21.754(6)	13.410(3)
<i>α</i> /°			79.150(10)
<i>β</i> /°		97.71(2)	89.60(3)
<i>γ</i> /°			85.89(3)
<i>U</i> /Å <sup>3</sup>	6969(4)	3354(2)	2239.9(10)
<i>Z</i>	8	4	2
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.747	1.800	1.507
<i>μ</i> /mm <sup>-1</sup>	1.377	1.505	1.111
<i>F</i> (000)	3616	1784	1008
Crystal size/mm	1.1 × 0.7 × 0.4	0.55 × 0.42 × 0.32	0.72 × 0.42 × 0.35
<i>θ</i> Range for data collection/°	1.90 to 22.46	1.89 to 22.50	1.99 to 22.50
Index ranges	-1 ≤ <i>h</i> ≤ 17, -1 ≤ <i>k</i> ≤ 18, -1 ≤ <i>l</i> ≤ 26	-1 ≤ <i>h</i> ≤ 16, -1 ≤ <i>k</i> ≤ 10, -23 ≤ <i>l</i> ≤ 23	-1 ≤ <i>h</i> ≤ 13, -13 ≤ <i>k</i> ≤ 13, -14 ≤ <i>l</i> ≤ 14
Reflections collected	5534	5581	6757
Independent reflections ( <i>R<sub>int</sub></i> )	4505 (0.0497)	4344 (0.0582)	5825 (0.0220)
Absorption correction	<i>ψ</i> Scans	None	None
Maximum, minimum transmission	0.84, 0.66	—	—
Data, restraints, parameters	4505, 0, 406	4337, 0, 388	5825, 2, 454
Goodness of fit on <i>F</i> <sup>2</sup>	1.067	1.025	1.301
Final <i>R</i> 1, <i>wR</i> 2 indices [ <i>I</i> > 2σ( <i>I</i> ) (all data)]	0.0410, 0.0976	0.0566, 0.1410	0.0547, 0.1744
Largest difference peak, hole/e Å <sup>-3</sup>	1.066, -0.922	1.076, -0.710	1.584, -0.941

\* Details in common: 293(2) K; λ(Mo-α) 0.710 73 Å.

(1:4) produced an orange band of **1b** (230.1 mg, 57% recovery). Elution with a 3:7 mixture of these solvents produced a red band of [Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CHMe)(μ-PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **4b** (75.3 mg, 0.08 mmol, 13.0%), followed by an unidentified green band (40.3 mg). Finally, [Mo<sub>2</sub>Ru(μ<sub>3</sub>-CEt)(μ-PPh<sub>2</sub>)(CO)<sub>5</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **3b** (275.5 mg, 0.35 mmol, 57%) was eluted using CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (2:3). Data for **3b**: m.p. >250 °C; IR ν(CO) 2002s, 1937s and 1864m cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.80–6.76 (m, 10 H, Ph), 5.53 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 5.36 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 4.04 [ddq, *J*(HH) = 7, *J*(PH) = 1, 1 H of CH<sub>2</sub>], 3.49 (dq, *J* = 7, 1 H of CH<sub>2</sub>) and 0.86 (t, *J* = 7, 3 H, Me); <sup>13</sup>C NMR δ 363.5 (s, μ<sub>3</sub>-C), 234.2 (s, Mo–CO), 233.1 (s, Mo–CO), 228.2 (d, *J* = 13, Mo–CO), 205.7 (s, Ru–CO), 199.4 (d, *J* = 4, Ru–CO), 146.7 (d, *J* = 30, *C<sub>ipso</sub>*), 139.0 (d, *J* = 40 Hz, *C<sub>ipso</sub>*), 133.4–127.7 (m, Ph), 94.6 (s, η-C<sub>5</sub>H<sub>5</sub>), 91.7 (s, η-C<sub>5</sub>H<sub>5</sub>), 58.4 (s, CH<sub>2</sub>) and 18.8 (s, Me); <sup>31</sup>P NMR δ 188.7 (Found: C, 45.35; H, 3.07. Calc. for C<sub>30</sub>H<sub>25</sub>Mo<sub>2</sub>O<sub>5</sub>PRu: C, 45.63; H, 3.17%); mass spectrum *m/z* 790, 762, 734, 704, 676 and 646 (*M*<sup>+</sup> - *n*CO, *n* = 0–5).

[Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CHMe)(μ-PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **4b**. To a solution of complex **1b** (750 mg, 1.14 mmol) in toluene (150 cm<sup>3</sup>) was added PPh<sub>2</sub>H (0.198 cm<sup>3</sup>, 1.14 mmol). The mixture was heated to reflux for 2 h with TLC monitoring. After this time 0.5 equivalent of PPh<sub>2</sub>H (0.099 cm<sup>3</sup>) was added and the reaction refluxed for one more hour (total reaction time 3 h). Chromatography as above, eluting with CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (1:4), produced a large red-brown band of [Mo<sub>2</sub>Ru(μ<sub>3</sub>-C=CHMe)(μ-PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] **4b** (500.5 mg, 0.530 mmol, 46.5%). Elution with a 2:3 mixture of these solvents produced a brown band (53.2 mg) which could not be identified. Data for **4b**: m.p. 214 °C; IR ν(CO) 2008s, 1958m, 1879m and 1847m cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.94–6.41 (m, 20 H, Ph), 5.48 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 4.89 (s, 5 H, η-C<sub>5</sub>H<sub>5</sub>), 4.52 [dq, *J*(HH) = *J*(PH) = 7, 1 H, CH] and 0.60 (d, 3 H, Me); <sup>13</sup>C δ NMR 258.4 (t, *J* = 4, μ<sub>3</sub>-C), 237.6 (d, *J* = 10, Mo–CO), 235.2 (d, *J* = 12, Mo–CO), 205.9 (s, Ru–CO), 195.8 (t, *J* = 8, Ru–CO), 146.6 (d, *J* = 30, *C<sub>ipso</sub>*), 145.0 (d, *J* = 39, *C<sub>ipso</sub>*), 143.6 (d, *J* = 24, *C<sub>ipso</sub>*), 137.5 (d, *J* = 36, *C<sub>ipso</sub>*), 135.8–127.1 (m, Ph), 98.0 (apparent d, *J* = 4,

CHMe), 92.2 (s, η-C<sub>5</sub>H<sub>5</sub>), 86.9 (s, η-C<sub>5</sub>H<sub>5</sub>) and 22.5 (s, Me); <sup>31</sup>P NMR δ 202.1 (d, *J* = 79 Hz) and 176.9 (d) (Found: C, 52.06; H, 3.80. Calc. for C<sub>41</sub>H<sub>34</sub>Mo<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Ru: C, 52.06; H, 3.60%); mass spectrum *m/z* 946, 918, 890, 862 and 833 (*M*<sup>+</sup> - *n*CO, *n* = 0–4).

In a separate experiment a solution of complex **3b** (73.3 mg, 0.09 mmol) in toluene (50 cm<sup>3</sup>) was treated with PPh<sub>2</sub>H (0.016 cm<sup>3</sup>, 1 equivalent) and heated to reflux for 3 h. Separation by column chromatography as above gave a red band of **4b** (46.9 mg, 53%) as the only isolable product.

### Crystallography

The crystal data for the three structures are summarised in Table 5. Three-dimensional room-temperature X-ray data were collected on a Siemens P4 diffractometer by the ω-scan method. The reflections were corrected for Lorentz-polarisation effects, and in the case of complex **2b** for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.66 and 0.84), and the independent reflections for which  $|F|/\sigma(|F|) > 4.0$  were used in refinement. The structures were solved by direct methods and refined by full-matrix least squares on *F*<sup>2</sup>. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at the *R* values shown with allowance for the thermal anisotropy of all non-hydrogen atoms. Weighting schemes  $w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 4.8327P]$  for **2b**,  $1/[\sigma^2(F_o^2) + (0.0924P)^2 + 7.9997P]$  for **3b** and  $1/[\sigma^2(F_o^2) + (0.0942P)^2 + 5.5981P]$  for **4a** where  $P = (F_o^2 + 2F_c^2)/3$  were used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL 93<sup>14</sup> as implemented on a Viglen 486dx computer.

CCDC reference number 186/615. Tables of structure factors are available from the authors.

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