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Cluster chemistry

LXXXIX *. Oligomerization reactions of allene with $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$

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Abstract

Reactions between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**) and allene have given two isomers of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(CO)_{10}$ (**2**, **3**) containing the $\eta^3:\eta^3$-biallyl ligand, $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_9H_{12})(\mu\text{-}C_3H_4)(CO)_{10}$ (**7**) containing an allene trimer, and $Ru_5(\mu_5\text{-}C_8H_8PPh_2)(\mu\text{-}PPh_2)(CO)_{11}$ (**8**), in which an allene dimer has linked with the phosphino-acetylide ligand. Complex **2** reacted with $P(OMe)_3$ to give two isomers of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(CO)_9\{P(OMe)_3\}$ (**4** and **5**) both of which were shown to be structurally related to **2** and **3**; a third isomer, **6**, was obtained from similar reactions of **3** and $P(OMe)_3$. In complexes **2**–**6**, the metal cores consist of wing-tip spiked planar rhombi, one Ru–Ru separation of which is very long (3.19–3.38 Å); they contain μ-biallyl ligands formed by dimerization of two allene molecules. The metal core of **7** consists of a similar Ru_4 rhombus with the fifth Ru atom connected via the C_2PPh_2 and $\mu\text{-}C_9H_{12}$ ligands. The latter is formed from three allene molecules and is coordinated to a cluster Ru atom by a 1,3-diene unit and to the separated Ru atom by an η^3-allyl unit. All three complexes also contain a $\mu\text{-}\sigma,\eta^3\text{-}C_3H_4$ ligand. In **8**, incorporation of the acetylide carbons into the Ru_4 rhombus has given a C_2Ru_4 octahedron, of which a wing-tip Ru is also attached to the fifth Ru atom. A PPh_2 group bridges this Ru atom and a carbon of the cluster C_2 unit; the second carbon is linked to the C_6H_8 moiety which is attached to the cluster by σ and η^4 interactions. The results of single crystal X-ray studies of complexes **3**–**7** are reported.

1. Introduction

The open Ru_5 cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**; Scheme 1) contains a diphenylphosphino-acetylide ligand spanning the five metal atoms. Earlier accounts of its reactivity have shown that facile addition of unsaturated hydrocarbons (olefins, dienes) to the cluster-bound ligand can occur [2]. Thus it was of interest to examine the reaction between **1** and allene. Two products were pentanuclear complexes containing ligands formed by coupling of two or three allene molecules on the cluster, together with bridging $\sigma:\eta^3$-C_3H_4 ligands; the phosphino–acetylide ligand remains unchanged. A third product contains a novel tertiary phosphine ligand which has been formed by coupling of the allene and phosphino–acetylide ligands, as described earlier [3]. This paper describes these reactions in detail, together with some substitution products obtained with $P(OMe)_3$; X-ray studies helped to elucidate the structures of the initial allene complexes.

2. Results and discussion

The reactions between **1** and allene were carried out in toluene solution in a sealed tube heated at 90°C for several hours (Scheme 1). Three products were separated by TLC on silica gel, as described in the Experimental section. The complex $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}$

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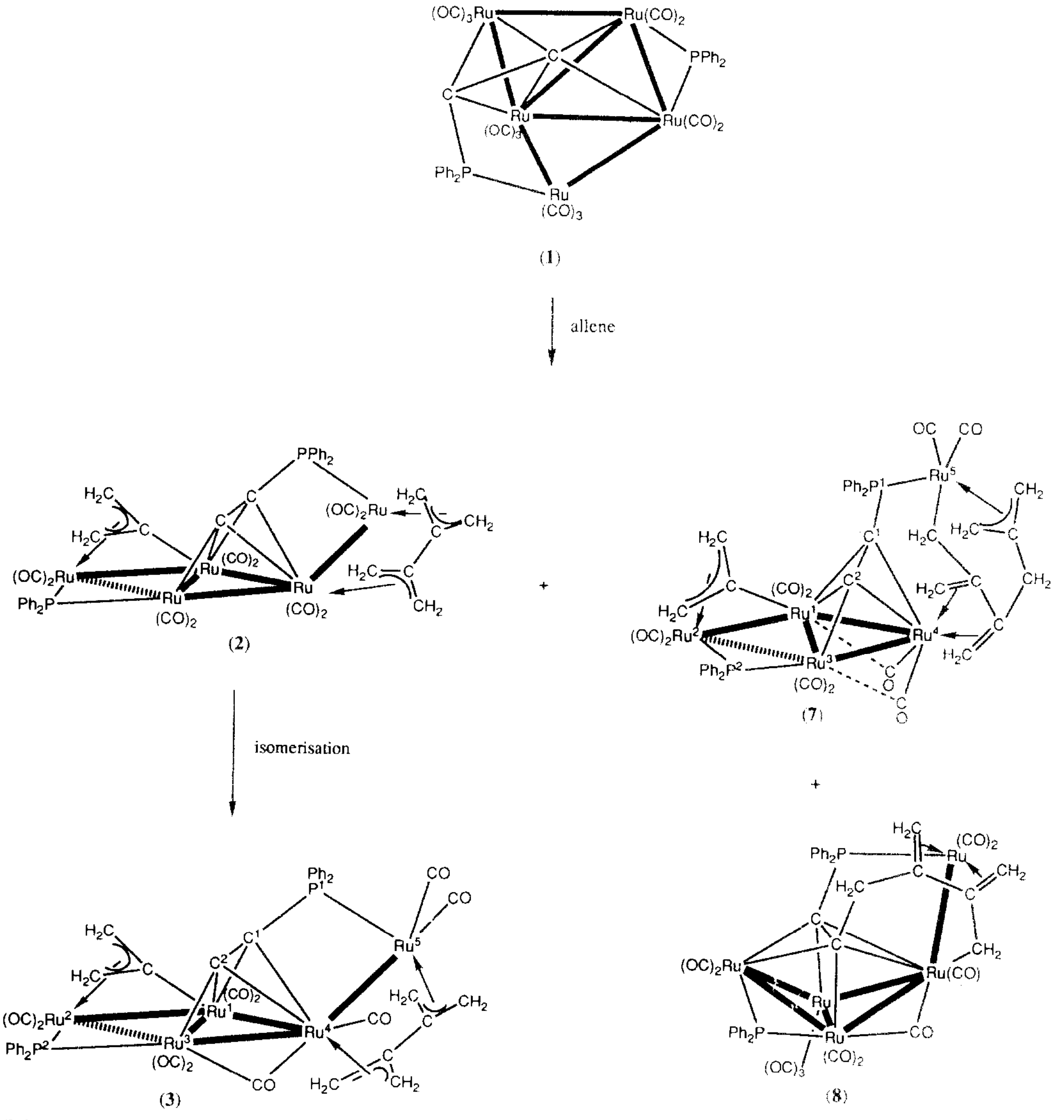
$PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(CO)_{10}$ (**2**) was obtained as red crystals that changed slowly in solution to an isomer, **3**, which contained a bridging CO group, as shown by a single-crystal X-ray study. Suitable crystals of **2** could not be obtained, but derivatization with $P(OMe)_3$ afforded three crystalline monosubstitution products, two of which (**4** and **5**; Scheme 2) were able to be fully characterized by X-ray crystallography. Complex **4** was the major product in the direct reaction of **2** with $P(OMe)_3$ and TMNO whereas complex **5** dominated when the acetonitrile derivative of **2** was treated with the phosphite. Spectroscopic studies suggest that **2** is the precursor of **4**. Isomer **3** reacted with $P(OMe)_3$ to produce a fourth monosubstituted complex (**6**; Scheme 3). An orange complex, $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_9H_{12})(\mu\text{-}C_3H_4)(CO)_{10}$ (**7**), was also obtained in 3% yield from the reaction between **1** and allene; this was shown to contain a planar Ru_4 cluster together with the fifth Ru atom, now separate, which interacts with the phosphino–acetylide and an allene trimer. Compound **8**, containing the coupled allene dimer–phosphino–acetylide ligand was also formed [3]. X-Ray structural characterizations of complexes **3**–**7** were made; since the first four are similar they are discussed together.

2.1. *Molecular structures of complexes 3–6*

The structures of the four complexes are shown in Figs. 1–4 and relevant bond parameters are collected in Table 1. The cluster core in each case consists of a



Scheme 1.

spiked planar rhombus, with the C_2PPh_2 ligand spanning four of the five metal atoms. The C_2 unit bridges the Ru_3 triangle formed by Ru(1)–Ru(3)–Ru(4) in the usual σ, 2π-($\perp$) fashion, while P(1) is attached to Ru(5). The Ru(2)–Ru(3) vector is bridged by P(2) of the μ-PPh_2 ligand, while Ru(3)–Ru(4) is bridged by CO(41) in all except **4**. The Ru(1)–Ru(2) vector is bridged by allene bonded in the $\sigma:\eta^3$ manner, as found in $Fe_2(\mu\text{-}\sigma:\eta^3\text{-}C_3H_4)(CO)_7$ [4], for example. The allene dimer bridges the Ru(4)–Ru(5) bond, being attached to each Ru by an η^3 interaction. This ligand has also been found in $Fe_2(\mu\text{-}\eta^3:\eta^3\text{-}C_6H_8)(CO)_6$ [5].

In the four complexes, the separations of like atoms are often significantly different. The Ru–Ru separations range from 2.860 to 3.382 Å over all complexes, indicative of a wide variety of Ru–Ru interaction strengths. Thus, the Ru(2)–Ru(3) separations [3.186(1)–3.382(2) Å] are substantially non-bonding, while the Ru(1)–Ru(2) separations are also greater than 3 Å; Ru(2) must be assumed to be held in position primarily by its strong interactions with the allylic group and the bridging PPh_2 ligand [Ru(2)–P(2) *ca.* 2.30 Å]. The Ru(2)–P(2)–Ru(3) angles range between 88.0° and 93.3(1)°, again consistent with a substantial non-bonding interaction between the two metal atoms. The shortest Ru–Ru separations in **3** and **4** are the diagonal separations across the rhombi [Ru(1)–Ru(3), 2.884(1), 2.860(1) Å, respectively], although in **5** and **6**, these have lengthened to 2.956(2) and 2.887(1) Å, respectively. The Ru(4)–Ru(5) separations range between 2.994 and 3.175 Å, the longest being found in **4** and **6**, in each of which the phosphite ligand is attached to Ru(4). Comparison of the cores in **3** and **6**, where the only chemical difference is replacement of a

TABLE 1. Selected bond lengths (Å) and angles (0) for complexes **3–6**

Bond	**3**	**4**	**5**	**6**
Ru(1)–Ru(2)	3.0588(9), 3.043(1)	3.119(2)	3.053(2)	3.0506(7)
Ru(1)–Ru(3)	2.884(1), 2.899(1)	2.860(1)	2.956(2)	2.887(1)
Ru(1)–Ru(4)	3.000(1), 2.9600(9)	2.945(1)	3.027(2)	2.9423(6)
Ru(2) · · · Ru(3)	3.273(1), 3.286(1)	3.186(1)	3.382(2)	3.2873(7)
Ru(3)–Ru(4)	2.9081(9), 2.954(1)	3.077(2)	2.926(2)	2.9619(7)
Ru(4)–Ru(5)	3.042(1), 3.062(1)	3.175(2)	2.994(2)	3.1462(7)
Ru–Ru (av.)	3.031	3.104	3.107	3.103
Ru(2)–P(2)	2.300(2), 2.298(2)	2.297(3)	2.306(4)	2.305(1)
Ru(3)–P(2)	2.309(2), 2.319(2)	2.288(3)	2.345(4)	2.311(1)
Ru(3)–P(3)	–	–	2.333(4)	–
Ru(4)–P(3)	–	2.308(4)	–	2.276(2)
Ru(5)–P(1)	2.296(2), 2.295(2)	2.268(2)	2.310(4)	2.291(1)
Ru(1)–C(102)	2.043(7), 2.046(8)	2.039(9)	2.06(1)	2.060(4)
Ru(2)–C(101)	2.215(9), 2.205(7)	2.19(1)	2.22(1)	2.205(5)
Ru(2)–C(102)	2.103(7), 2.078(7)	2.10(1)	2.08(1)	2.093(5)
Ru(2)–C(103)	2.297(8), 2.296(8)	2.28(1)	2.27(1)	2.288(5)
Ru(4)–C(201)	2.166(8), 2.174(9)	2.27(1)	2.20(1)	2.191(5)
Ru(4)–C(202)	2.179(6), 2.177(9)	2.22(1)	2.20(1)	2.182(6)
Ru(4)–C(203)	2.314(6), 2.342(8)	2.22(1)	2.33(1)	2.350(7)
Ru(5)–C(204)	2.146(8), 2.159(8)	2.14(1)	2.14(2)	2.180(6)
Ru(5)–C(205)	2.272(8), 2.27(1)	2.22(1)	2.31(1)	2.242(6)
Ru(5)–C(206)	2.213(7), 2.243(8)	2.30(1)	2.24(2)	2.237(6)
Ru(1)–C(1)	2.203(6), 2.182(6)	2.17(1)	2.20(1)	2.182(4)
Ru(1)–C(2)	2.188(5), 2.187(6)	2.17(1)	2.16(1)	2.232(4)
Ru(3)–C(2)	1.986(7), 1.973(6)	1.966(9)	1.94(1)	1.982(4)
Ru(4)–C(1)	2.457(8), 2.423(7)	2.422(9)	2.39(1)	2.426(4)
Ru(4)–C(2)	2.286(6), 2.293(8)	2.29(1)	2.30(1)	2.266(4)
Ru(3)–C(41)	2.433(7), 2.511(9)	–	2.32(1)	2.480(6)
Ru(4)–C(41)	1.943(9), 1.955(7)	–	1.98(1)	1.897(6)
P(1)–C(1)	1.763(7), 1.760(6)	1.76(1)	1.76(2)	1.755(4)
C(1)–C(2)	1.277(9), 1.293(9)	1.29(1)	1.32(2)	1.293(6)
C(101)–C(102)	1.39(1), 1.42(1)	1.43(2)	1.40(2)	1.421(8)
C(102)–C(103)	1.407(9), 1.418(9)	1.43(1)	1.40(2)	1.398(6)
C(201)–C(202)	1.40(1), 1.43(1)	1.41(2)	1.42(2)	1.419(8)
C(202)–C(203)	1.430(8), 1.433(9)	1.41(2)	1.39(2)	1.420(7)
C(202)–C(204)	1.49(1), 1.48(1)	1.49(2)	1.53(2)	1.476(8)
C(204)–C(205)	1.416(9), 1.420(9)	1.42(2)	1.39(2)	1.386(7)
C(204)–C(206)	1.39(1), 1.438(9)	1.39(2)	1.37(2)	1.413(6)

TABLE 1. (continued)

Bond	**3**	**4**	**5**	**6**
For **3**:				
Ru–CO	1.820–1.904(7), av. 1.882			
C–O	1.131–1.166(9), av. 1.145			
P–C(Ph)	1.817(7)–1.841(8), av. 1.830			
For **4**:				
Ru–CO	1.83–1.91(2), av. 1.88			
C–O	1.13–1.16(2), av. 1.14			
P–C(Ph)	1.81–1.87(1), av. 1.83			
P–OMe	1.584–1.604(9), av. 1.593			
For **5**:				
Ru–CO	1.83(2)–1.98(1), av. 1.88			
C–O	1.13–1.19(2), av. 1.15			
P–C(Ph)	1.81–1.87(1), av. 1.84			
P–OMe	1.58–1.61(1), av. 1.59			
For **6**:				
Ru–CO	1.842–1.917(5), av. 1.884			
C–O	1.127–1.152(6), av. 1.138			
P–C(Ph)	1.823–1.838(5), av. 1.832			
P–OMe	1.579(5)–1.600(4), av. 1.591			
Ru(1)–Ru(2)–Ru(3)	54.06(3), 54.35(3)	53.95(3)	54.41(4)	54.05(2)
Ru(1)–Ru(3)–Ru(2)	59.17(2), 58.55(2)	61.84(3)	57.11(5)	58.79(2)
Ru(1)–Ru(3)–Ru(4)	62.38(3), 60.75(3)	59.34(3)	61.94(4)	60.38(2)
Ru(1)–Ru(4)–Ru(3)	58.42(3), 58.70(3)	56.66(3)	59.53(5)	58.55(2)
Ru(2)–Ru(1)–Ru(3)	66.77(3), 67.10(3)	64.22(4)	68.49(5)	67.17(2)
Ru(3)–Ru(1)–Ru(4)	59.20(2), 60.55(2)	64.00(4)	58.53(5)	61.06(2)
Ru(1)–Ru(4)–Ru(5)	101.06(3), 100.26(3)	102.07(4)	99.74(6)	98.95(2)
Ru(3)–Ru(4)–Ru(5)	140.68(3), 138.39(3)	130.76(5)	146.00(6)	139.51(2)
Ru(2)–P(2)–Ru(3)	90.50(6), 90.75(9)	88.0(1)	93.3(1)	90.82(6)
Dihedral: Ru(1)–Ru(2)–Ru(3)/Ru(1)–Ru(3)–Ru(4)	3.51(4), 4.20(4)	4.30(4)	7.70(5)	2.49(4)

CO by $P(OMe)_3$ on Ru(3), shows that the major structural changes are in the Ru(1)–Ru(3) vector, *trans* to the phosphite, which is lengthened by *ca.* 0.07 Å and in the adjacent Ru(2) · · · Ru(3) non-bonded vector, which increases by more than 0.1 Å.

The Ru(1)–Ru(4) separations in the four complexes, which are spanned by the acetylide ligand, lie between 2.9423(6) and 3.027(2) Å. In related complexes there is a remarkable variation in the separation of ruthenium atoms bridged by acetylide ligands, which appears to be dependent on the nature of the other bridging groups (if present). Thus, values of 2.808(1) and 2.853(1) Å were found in $Ru_5(\mu\text{-H})(\mu_5\text{-}C_2PPh_2)(\mu\text{-Br})(\mu\text{-}PPh_2)(CO)_{13}$ [6] and $AuRu_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_2Ph)(CO)_{12}(PPh_3)$ [7], where this bond is also bridged by the H and $Au(PPh_3)$ groups, respectively. In $Ru_3(\mu\text{-X})(\mu_3\text{-}C_2{}^tBu)(CO)_9$, values of 2.792(3) (X = H [8]) and 2.820(1) Å (X = $Au(PPh_3)$ [9]) have been reported.

The Ru–P separations are within the normal ranges. As might be expected, however, attachment of the phosphite to Ru(3) results in a lengthening of the Ru(3)–P(2) bond from 2.309(2), 2.319(2) Å in **3** to 2.345(4) Å in **5**. The Ru(5)–P(1) separation is quite sensitive to its environment, ranging between 2.268(2) and 2.310(4) Å in the four complexes; the length appears to be inversely related to the Ru(4)–Ru(5) separation.

Considering the $\mu\text{-}C_3H_4$ ligand, the Ru(1)–C(102) σ-bond is between 2.04(1) and 2.06(1) Å; this central carbon is nearest to Ru(2) (2.08(1)–2.10 (1) Å). The outer carbons of the η^3-allyl group are between 2.19(1) and 2.30(1) Å from Ru(2). Similar values are found for the η^3-allyl groups in the $\mu\text{-}C_6H_8$ ligand, with the Ru–C(central) distances [2.14(1)–2.22(1) Å (av. 2.17 Å)] being shorter than the Ru–C(outer) separations [2.17(1)–2.33(1) Å (av. 2.25 Å)].

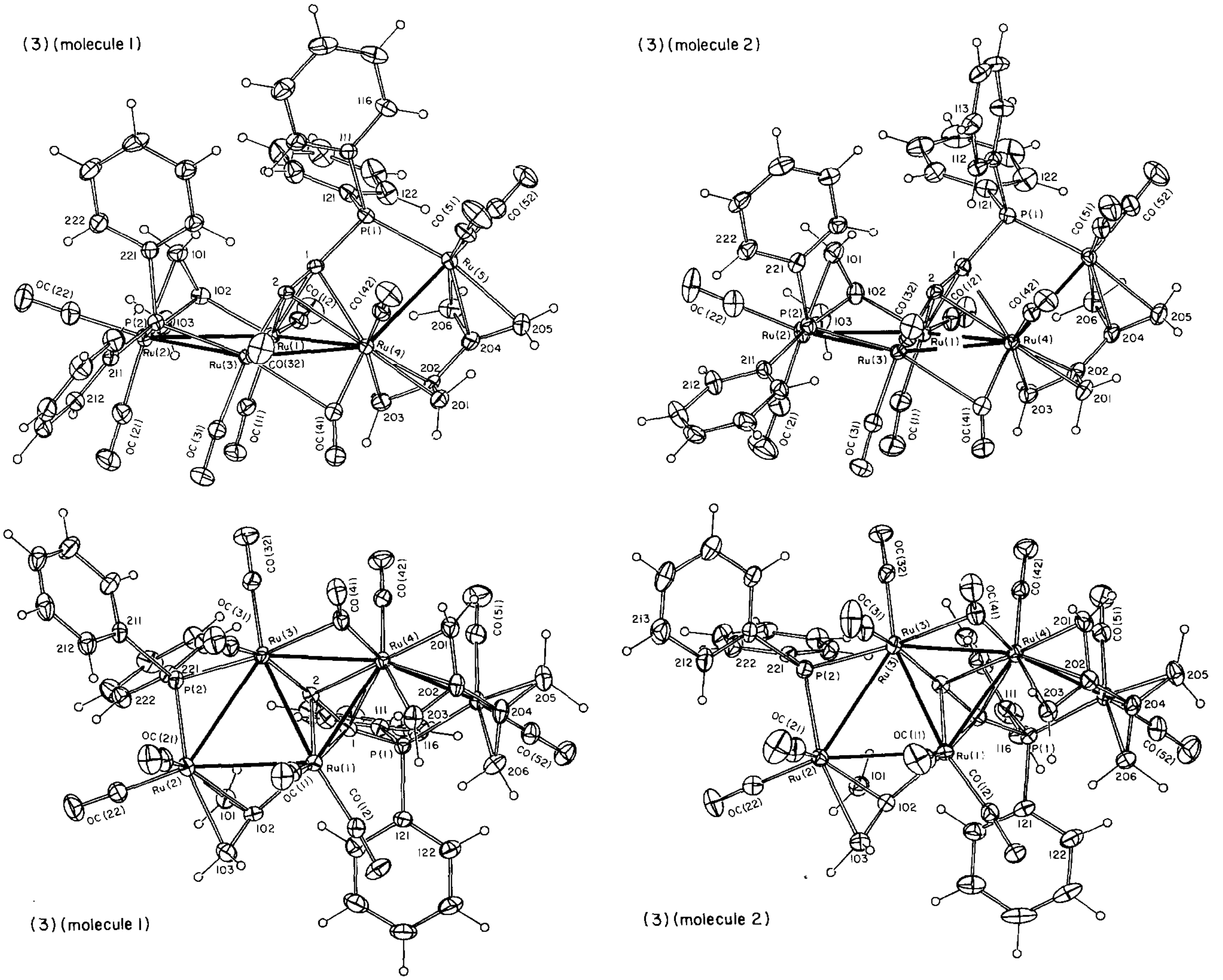
The acetylide ligand is σ-bonded to Ru(3) [separations 1.94(1)–1.986(7) Å] and π-bonded to Ru(1) and Ru(4); the attachment to Ru(1) appears to be stronger [Ru(1)–C(1) 2.17(1)–2.20(1), Ru(1)–C(2) 2.16(1)–2.232(4) Å] than to Ru(4) [Ru(4)–C(1)2.39(1)–2.46(1), Ru(4)–C(2) 2.266(4)–2.30(1) Å], no doubt because of the competition for metal electron density with the allylic group C(201)–C(202)–C(203). The C(1)–C(2) separation varies between 1.277(9) and 1.32 (2) Å in the four complexes.

Complex **3** contains nine terminal CO groups; one of these, on Ru(4) in **4** and on Ru(3) in **5** and **6**, has been replaced by the phosphite ligand. Complexes **3**, **5** and **6** each contain a CO group asymmetrically bridging the Ru(3)–Ru(4) vector [Ru(3)–C(41) 2.433 (7), 2.32(1), 2.480(6); Ru(4)–C(41) 1.943(9), 1.98(1), 1.897(6) Å; Ru(4)–C(41)–O(41) 154.0(5), 147(1), 157.3(5)°, respectively].

2.2. Molecular structure of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_9H_{12})(\mu\text{-}C_3H_4)(CO)_{10}$ (7)

The structure of **7** is shown in Fig. 5, and relevant bond parameters are listed in Table 2. The planar Ru_4 rhombus found in the previous four structures is still present, but the fifth Ru atom is now bonded only to P(1) of the phosphino–acetylide ligand and to four carbons of an allene trimer by a σ, η^3 system; one of the cluster Ru atoms is also bonded to this ligand by an η^4-1,3-diene moiety.

Within the Ru_4 rhombus, the Ru–Ru separations are generally similar to those found in complexes **3**–**6**.

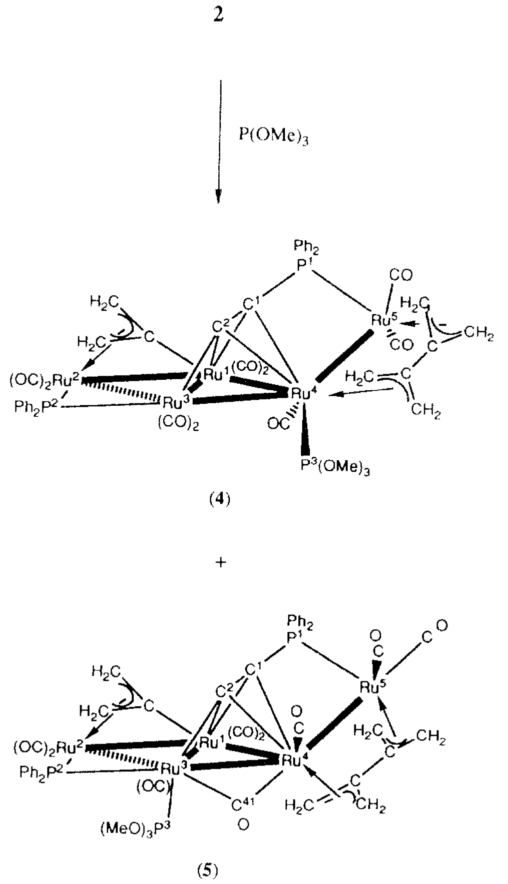

(3) (molecule 1)

(3) (molecule 2)

(3) (molecule 1)

(3) (molecule 2)

Fig. 1. Plots of molecules 1 and 2 of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(\mu\text{-}CO)(CO)_9$ (**3**) (a) oblique to and (b) normal to the Ru_4 "plane", showing the atom numbering scheme. For all Figures, non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.



Scheme 2.

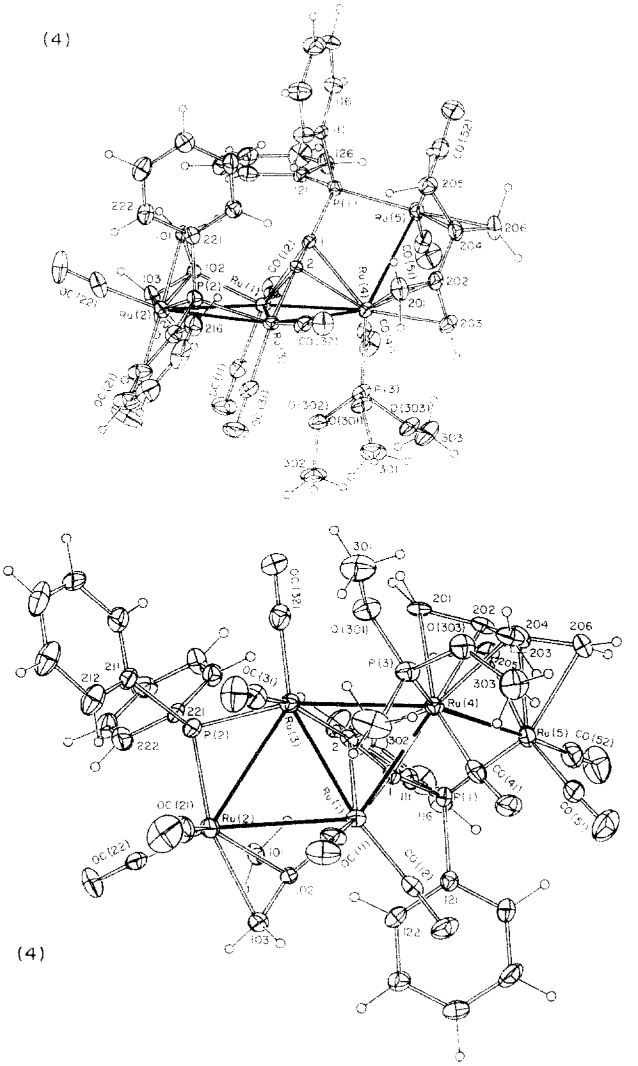
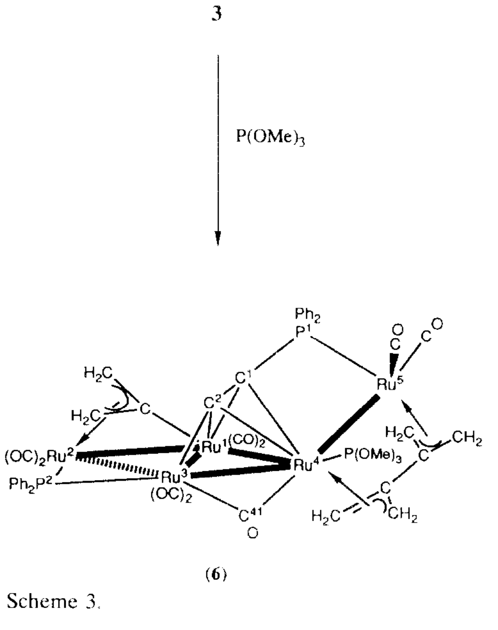


Fig. 2. A molecule of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(CO)_9\{P(OMe)_3\}$ (4) (a) oblique to and (b) normal to the Ru_4 "plane", showing the atom numbering scheme.

Thus, the bonded diagonal Ru(1)–Ru(3) is 2.968(1) Å, similar to that found in **5**. The Ru(1)–Ru(2) vector bridged by the C_3H_4 ligand is 3.073(2) Å, while that bridged by the PPh_2 group is substantially non-bonded at 3.249(2) Å. The μ-C_3H_4 ligand is σ-bonded to Ru(1) [Ru(1)–C(102) 2.05(1)] and π-bonded to Ru(2) [Ru(2)–C(102) 2.12(1), outer C 2.22, 2.30(1) Å]. The acetylide unit is more strongly attached than in **3**–**6**, with Ru(3)–C(2) shorter at 1.99(1) Å, and the C_2 unit also having a somewhat asymmetric interaction with Ru(1) and Ru(4) [Ru(1)–C(1) 2.25(1), Ru(1)–C(2) 2.18(1); Ru(4)–C(1) 2.37(1), Ru(4)–C(2) 2.28(1) Å]. The C(1)–C(2) separation is 1.26(2) Å. Coordination of the cluster Ru atoms is completed by two terminal CO groups on each of Ru(1), Ru(2) and Ru(3). Both the Ru(1)–Ru(4) [2.820(2) Å] and Ru(3)–Ru(4) [2.906(2) Å] bonds of the Ru(1)Ru(3)Ru(4) triangle are bridged asymmetrically by CO groups [Ru(4)–C(41,42) 1.98, 1.93(1), Ru(1)–C(42) 2.51(1), Ru(3)–C(41) 2.36 (1) Å;



Scheme 3.

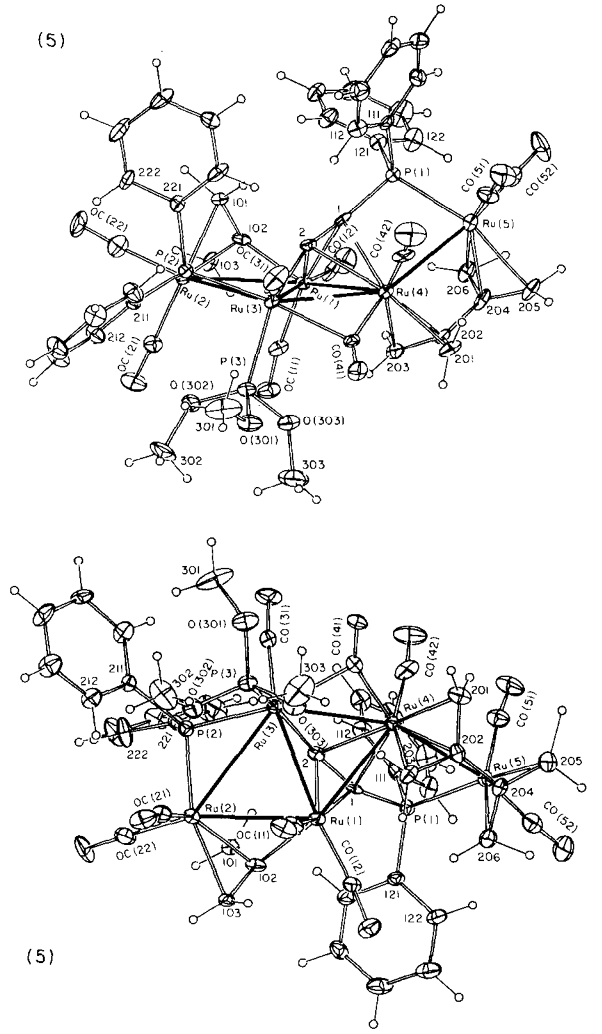


Fig. 3. A molecule of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(\mu\text{-}CO)(CO)_8\{P(OMe)_3\}$ (**5**) (a) oblique to and (b) normal to the Ru_4 "plane", showing the atom numbering scheme.

Ru(4)-C(41)-O(41) 148(1), Ru(4)-C(42)-O(42) 158(1)°].

The fifth Ru atom is attached to P(1) [2.338(3) Å], a CH_2 group [Ru(5)-C(2012) 2.20(1) Å], and allyl group [Ru(5)-C(204-206) 2.23-2.26(1) Å] of the C_9H_{12} ligand and to two CO groups. The C_9H_{12} ligand is also attached to Ru(4) via an η^4-1,3-diene moiety [Ru(4)-C 2.17-2.29(1) Å].

2.3. Spectroscopic properties

The IR spectra of complexes **2**–**7** contain complex absorptions in the terminal ν(CO) region, and for **3**, **5**, **6** and **7**, bands at 1899, 1861, 1876 and 1883 cm^{-1}, respectively, could be assigned to the bridging CO groups. The FAB mass spectra contain molecular ions, together with ions formed by loss of the CO groups. The ^1H NMR spectra of **2**–**6** are given in the Experimental section, while the ^{13}C NMR spectra are listed in Table 3; assignments of the hydrocarbon ligand resonances were achieved by a combination of double resonance and DEPT techniques, and show no unexpected features. Detailed comparison of the ^1H and ^{13}C NMR spectra reveals similarities between those of the pairs **2**, **4** and of **3**, **6**, particularly in respect of the resonances at δ 10.75 and 10.89 in the latter, assigned to CH_2 carbons of the C_6H_8 ligand. These were not present in the spectra of **2** and **4**, while in **5**, a resonance at δ 3.50 was found. It has not been possible to make a detailed assignment of these resonances; however the correspondences noted above suggest that the pairs **2**, **4** and **3**, **6** have similar structures as indicated in Schemes 1–3. Resonances of the C_2 carbons range between δ 42.73 and 50.10 [for C(1)] and between δ 162.80 and 175.[illegible]2 [for C(2)].

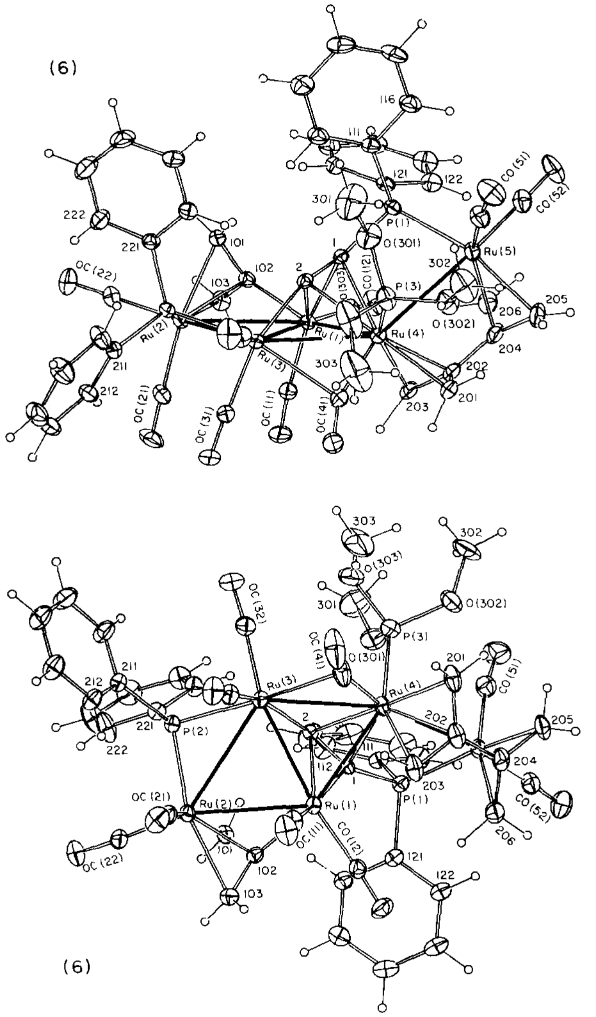


Fig. 4. A molecule of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(\mu\text{-}CO)(CO)_8\{P(OMe)_3\}$ (**6**) (a) oblique to and (b) normal to the Ru_4 "plane", showing the atom numbering scheme.

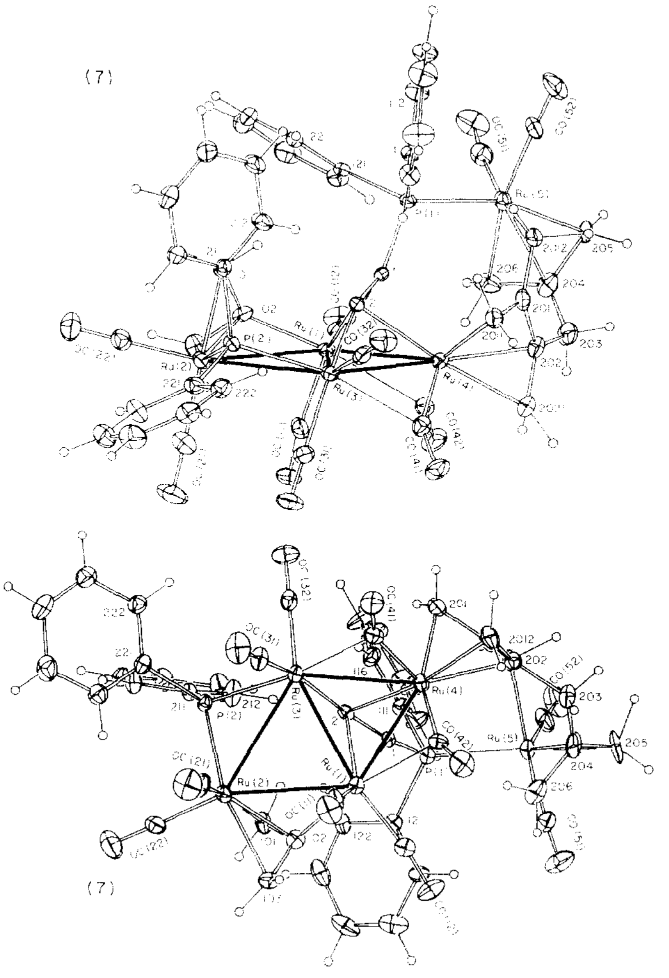


Fig. 5. A molecule of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_9H_{12})(\mu\text{-}C_3H_4)(CO)_{10}$ (7) (a) oblique to and (b) normal to the Ru_4 "plane", showing the atom numbering scheme.

2.4. *Coupling of allene dimer with acetylide*

Complex **8** is formed by coupling of the C_6H_8 and C_2PPh_2 ligands to give a novel tertiary phosphine. In this complex, which has been fully described elsewhere [3], the Ru_4 system takes up a butterfly conformation as a result of the interaction with the C_2 unit; the resulting C_2Ru_4 octahedron is spiked by the fifth Ru atom.

3. Discussion

The complexes isolated from reactions between **1** and allene have been formed by attack of the unsaturated hydrocarbon on the cluster framework. Coordination of one allene molecule, in the common $\mu\text{-}\sigma:\eta^3$ mode, has been found previously with iron carbonyl complexes, such as $Fe_2(\mu\text{-}\sigma:\eta^3\text{-}C_3H_4)(CO)_7$ obtained from allene with an excess of $Fe_2(CO)_9$ [4]. So-called 'head-to-head' linkage of two allene molecules at transition metal centres has been observed with complexes of Pd (in $\{Pd(acac)\}_2(\mu\text{-}C_6H_8)$, a minor product from the reaction of allene with $Pd(acac)(\eta\text{-}C_3H_5)$ [10]), or of Fe, in $Fe_2(\mu\text{-}C_6H_8)(CO)_6$, obtained from allene and $Fe_3(CO)_{12}$ [5]. Trimerization of allene in reactions with $Fe_3(CO)_{12}$ has been reported [5b,11], one of the three products (**9**) containing the same ligand as we have found in **7**.

The formation of complex **2** from **1** involves loss of CO and addition of ligands derived from the allene, with the net addition of four electrons to the cluster. Formally, cleavage of two Ru–Ru bonds would be expected. The observed cluster core consists of a planar rhombus with one long, essentially non-bonding, Ru · · · Ru edge; the fifth Ru atom remains attached by virtue of the bridging C_6H_8 ligand, although the Ru(4)–Ru(5) separation is also relatively long. This enables this complex to retain a compact core, yet bond efficiently to the new ligands which are formed. It is a moot point whether there is any bonding interaction between Ru(2) and Ru(3); occupation of a M–M antibonding orbital partially localized on these metal atoms may result in the observed lengthening, the two

TABLE 2. Selected bond lengths (Å) and angles (°) for $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_9H_{12})(\mu\text{-}C_3H_4)(CO)_{10}$ (7)

Ru(1)–Ru(2)	3.073(2)	Ru(4)–C(2021)	2.17(1)
Ru(1)–Ru(3)	2.968(2)	Ru(4)–C(202)	2.21(1)
Ru(1)–Ru(4)	2.820(2)	Ru(4)–C(201)	2.29(1)
Ru(2) · · · Ru(3)	3.249(2)	Ru(4)–C(2011)	2.18(1)
Ru(3)–Ru(4)	2.906(2)	Ru(1)–C(42)	2.51(1)
Ru(3)–P(2)	2.326(3)	Ru(3)–C(41)	2.36(1)
Ru(2)–P(2)	2.295(4)	Ru(4)–C(42)	1.93(1)
Ru(5)–P(1)	2.338(3)	Ru(4)–C(41)	1.98(1)
Ru(1)–C(1)	2.25(1)	P(1)–C(1)	1.81(1)
Ru(1)–C(2)	2.18(1)	C(1)–C(2)	1.26(2)
Ru(4)–C(1)	2.37(1)	C(102)–C(103)	1.40(2)
Ru(4)–C(2)	2.28(1)	C(101)–C(102)	1.44(2)
Ru(3)–C(2)	1.99(1)	C(204)–C(206)	1.40(2)
Ru(1)–C(102)	2.05(1)	C(204)–C(205)	1.47(2)
Ru(2)–C(103)	2.30(1)	C(202)–C(2021)	1.43(2)
Ru(2)–C(102)	2.12(1)	C(201)–C(202)	1.43(2)
Ru(2)–C(101)	2.22(1)	C(201)–C(2011)	1.43(2)
Ru(5)–C(2012)	2.20(1)	C(202)–C(203)	1.50(2)
Ru(5)–C(204)	2.25(1)	C(201)–C(2012)	1.48(2)
Ru(5)–C(206)	2.26(1)	C(203)–C(204)	1.49(2)
Ru(5)–C(205)	2.23(1)		
Ru–CO	1.81–1.95(1), av. 1.88		
C–O	1.12–1.17(2), av. 1.15		
P–C(Ph)	1.82–1.86(1), av. 1.83		
Ru(1)–Ru(2)–Ru(3)	55.93(4)	Ru(1)–Ru(4)–Ru(3)	62.42(4)
Ru(1)–Ru(3)–Ru(2)	59.03(4)	Ru(2)–Ru(1)–Ru(3)	65.05(4)
Ru(1)–Ru(3)–Ru(4)	57.36(4)	Ru(3)–Ru(1)–Ru(4)	60.22(4)
Dihedral:	Ru(1)–Ru(2)–Ru(3)/ Ru(1)–Ru(3)–Ru(4) 0.00(3)°		

Ru atoms remaining in relatively close association by virtue of the bridging PPh_2 ligand.

The slow isomerization of **2** to **3** corresponds to a rotation of the biallyl ligand around the Ru(4)–Ru(5) vector with concomitant semi-bridging of the Ru(3)–Ru(4) bond by a CO ligand. The reasons for this subtle rearrangement of electron density are not clear. The reaction of **2** with $P(OMe)_3$ afforded the substituted derivatives of both **2** and **3**; again, subtle effects are at work to direct the entering phosphite ligand to either Ru(4) in (in **4**) or Ru(3) (in **5**). Complex **3** reacted with $P(OMe)_3$ to give a third isomer, **6**, which contains the biallyl ligand in the same orientation as found in **5**, but with the phosphite coordinated to Ru(4).

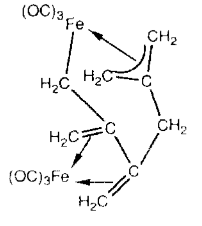
In **3**–**6**, which all have similar cores, the ligands supply 40 electrons to the metal framework, so that the cluster valence electron (CVE) count is 80, which is consistent with a core with five Ru–Ru bonds. These complexes provide further examples of the importance of the bridging ligands in deciding the geometry of clusters; in the present case, relevant earlier examples include the planar 64 CVE clusters in $Ru_4(\mu\text{-}PPh_2)_2(CO)_{13}$ and $Ru_4(\mu\text{-}PPh_2)_4(CO)_{10}$ [12]. The latter have average Ru–Ru separations of 3.106 and 3.101 Å, respectively, compared with values between 3.102 and 3.107 Å for **3**–**6**. Complex **7** is a planar 64 CVE rhomboidal cluster; in this case, the lengthening of Ru(3)–Ru(4) to 3.249(2) Å and the Ru(3)–P(1)–Ru(4) angle of 89.4(1)° result in an average Ru–Ru separation of 3.180 Å, providing a more extreme example of this effect. It is notable that in **8**, where the ligands contribute only 34 electrons to the cluster, the tighter Ru-spiked C_2Ru_4 polyhedron is adopted, where a favourable electron count can be achieved by incorporation of the C atoms into the cluster.

Coordination of allene to two metal centres in the $\mu\text{-}\sigma$, η^3 mode has been found previously in several systems, among them $Fe_2(\mu\text{-}\sigma, \eta^3\text{-}C_3H_4)(CO)_7$ [4] and $MNi\{\mu\text{-}\sigma, \eta^3\text{-}C(CH_2)(CMe_2)\}(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$ (M = Mo, W) [13]. Ready dimerization of allene occurs at transition metal centres, complexes containing $\mu\text{-}\eta^3$, $\eta^3\text{-}C_6H_8$ (biallyl) ligands analogous to those found here having been reported for Mn [14], Fe [5], Ni [13] and Pd [10]. The essential reactions involve oxidative addition of allene across an M–M bond to give the σ, $\eta^3\text{-}C_3H_4$ ligand and insertion of a second

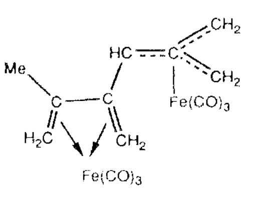
TABLE 3. ^{13}C NMR chemical shift data for complexes **2**–**6**[a]

	2	**3**	**4**	**5**	**6**
$\mathrm{CC}(\mathit{C}\mathrm{H}_2)_2$	35.28 (d, 15.1), 38.38 (2 × C), 41.76	10.75, 31.36, 37.47 (d, 14.4), 39.18	33.23 (d, 7.9), 37.33 (2 × C; d, 17.4), 41.46 (d, 14.1)	3.50, 33.19, 34.83 (d, 15.1), 42.31	10.89 (d, 36.7), 30.77, 34.84 (d, 14.8), 40.02 (d, 4.1)
$\mathrm{RuC}(\mathit{C}\mathrm{H}_2)_2$	61.06, 66.46 (d, 17.3)	62.36, 65.59 (d, 17.4)	60.43, 65.32 (d, 17.7)	62.48 (d, 17.2), 64.30	61.98, 65.18 (d, 17.3)
$\mathrm{C}\mathit{C}(\mathrm{CH}_2)_2$	93.09, 94.97	93.98 (2 × C)	90.27, 95.79	79.00, 94.16	70.54 (d, 3.4), 94.40
$\mathrm{Ru}\mathit{C}(\mathrm{CH}_2)_2$	167.18	167.20	168.51	167.07	169.91 (d, 3.6)
$\mathrm{P}\mathit{C}\mathrm{C}$	48.19 (d, 47.0)	50.10 (d, 43.1)	42.73 (dd, 52.1 5.4)	48.02 (d, 46.4)	47.99 (d, 47.6)
$\mathrm{PC}\mathit{C}$	169.55 (t, 15.0)	175.52 (t, 3.5)	162.80 (br)	174.02 (dt, 121, 3.7)	175.49 (t, 3.1)
$P(OMe)_3$	–	–	55.02 (d, 11.0)	52.69 (d, 8.1)	53.13 (d, 9.8)
PPh (*ipso* C)	137.86 (d, 50.8), 142.98 (d, 34.4), 143.81 (d, 34.3), 144.31 (d, 41.4)	137.68 (d, 46.6), 143.25 (d, 35.9)	138.60 (d, 54.7), 144.89 (d, 32.2)	133.50 (d, 57.3), 138.37 (d, 45.2), 145.25 (dd, 31.8, 2.6), 147.17 (d, 34.1)	134.00 (d, 59.8), 137.06 (d, 50.1), 143.30 (d, 33.0), 144.54 (d, 34.1)
Ph	127.61–135.29	127.66–135.26	127.65–136.16	127.06–135.75	127.48–135.59
CO	190.94 (d, 6.9), 192.10 (d, 4.8), 195.72 (d, 10.7), 198.11 (d, 4.2), 198.14, 199.14 (d, 11.2), 199.21, 200.11 (d, 2.2) 201.04 (d, 8.4), 205.13 (d, 18.6)	191.52 (d, 5.6), 192.99, 193.74 (d, 6.1), 197.00 (d, 10.8), 197.31 (d, 3.5), 198.84 (d, 10.7), 200.16 (d, 13.4), 201.02 (d, 8.4), 203.22 (d, 16.5)	191.65 (d, 6.0), 196.20 (d, 4.6) 198.32 (dd, 10.6, 7.0), 199.83 (d, 3.5), 200.42 (d, 3.8), 201.49 (d, 9.4), 202.15-202.63 (2 × d), 203.24	194.25, 194.39 (d, 7.2), 197.20 (dd, 16.2, 7.7), 198.73 (d, 3.5), 199.61 (d, 10.0), 201.82 (d, 7.6), 202.02, 202.35 (d, 11.3), 212.14 (dd, 20.2, 9.2)	195.28 (d, 7.6), 198.03 (d, 3.6), 198.49 (d, 10.0), 200.46 (t, 6.7), 201.39 (d, 3.4), 201.67 (d, 8.5), 207.20 (dd, 15.4, 9.3)

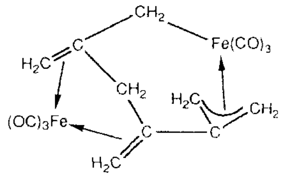
[a] Chemical shifts (ppm), multiplicity and J(CP) (Hz) given; resonances without multiplicity indicated are singlets.



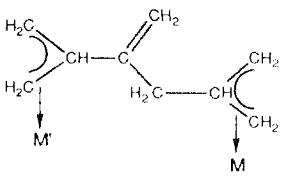
(9a)



(9b)



(9c)



(10)

molecule of allene into the M–C σ bond to generate the C_6H_8 ligand [15].

Trimerization of allene to give various C_9H_{12} ligands has also been described previously. In the iron carbonyl-allene system, three isomeric binuclear complexes have been characterized by X-ray studies as **9a–c** [5b,11]; the C_9H_{12} ligand in **9a** is the same as that found in 7. A fourth mode of attachment is found in **10** (MM′ = $Pd_2(\mu\text{-}O_2CMe)_2$ [16]; M = $Mo(CO)_2(\eta\text{-}C_5H_4Me)$, M′ = $Ni(\eta\text{-}C_5H_5)$ [13]). All are derived from the same hydrocarbon skeleton.

The common structural features found in the various complexes isolated during this work suggest that they are formed from common intermediates, although we have been unable to detect any species which contain only one allene ligand. Further reaction of the complexes containing C_6H_8 ligands may be with a third molecule of allene to give 7, or by intramolecular coupling to give **8**. However, we have not been able to convert **2** or **3** into **7** by reaction with excess allene, nor have we been able to find conditions under which the allene dimer and phosphino-acetylide ligands combine to give complex **8**.

4. Conclusions

The structures of complexes isolated from reactions between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and allene show that previously observed dimerization and trimerization reactions of this hydrocarbon occur on this metal cluster, and provide further examples of the reactivity of cluster-bound ligands and the ability of medium-sized cluster frameworks to alter their architecture to accommodate the organic ligands.

5. Experimental details

5.1. *General conditions*

All reactions were carried out under dry, high purity nitrogen by use of standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7. Preparative TLC was carried out on glass plates (20–20 cm^2) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

5.1.1. *Reagents*

Complex **1** was prepared by the published method [17]. $Me_3NO \cdot 2H_2O$ (TMNO; Aldrich) was dehydrated by sublimation (100°C/0.1 mm). Allene (Matheson) and $P(OMe)_3$ (Aldrich) were used as received.

5.1.2. *Instrumentation*

IR: Perkin-Elmer 1700X FT IR; 683 double beam, NaCl optics; NMR: Bruker CXP300 or ACP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz). FAB MS: VG ZAB 2HF (FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

5.2. *Reaction of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1) with allene*

A solution of **1** (250 mg, 0.20 mmol) and allene (1.26 g, 31.5 mmol) in toluene (10 ml) was heated in a Carius tube for 3.5 h at 90°C (tube oven). After cooling to room temperature and careful release of the excess pressure, the solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 4:1). An orange band (R_f 0.6) was recrystallized from CH_2Cl_2/MeOH to give red crystals of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_9H_{12})(\mu\text{-}C_3H_4)(CO)_{10}$ (**7**) (10 mg, 3%). Anal. Found: C, 43.38; H, 3.19, *M*, 1341 (mass spectrometry). $C_{48}H_{36}O_{10}P_2Ru_5$ calc.: C, 43.02; H, 2.71%; *M*, 1341. IR: (cyclohexane): ν(CO) 2080w, 2071vw, 2052s, 2024vs, 2022(sh), 2011s, 2002m, 1997m, 1994(sh), 1973s, 1961m, 1953(sh), 1941w, 1919m, 1883m cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 15.14 (d, $J(CP) = 8.1$ Hz, CH_2); 36.02 (s, CH_2), 39.54 (d, $J(CP) = 19.3$ Hz, CH_2); 47.03 (s, CH_2); 50.17 (s, CH_2); 54.01 (s, CH_2); 61.04 (s, CH_2); 66.64 (d, $J(CP) = 25.2$ Hz, CH_2); 101.21 (s, $CC(CH_2)_2$); 123.60 (s, $C=CH_2$); 127.31–135.86 (m, Ph); 142.32, 142.50, 142.78, 142.99 (2 × d (overlapping, *ipso* C); 146.36 (d, $J(CP) = 3.5$ Hz, C=CH_2); 161.53 (s, $Ru(CH_2)_2$); 177.07 (dd, $J(CP) = 11.0, 4.9$ Hz, PCC); 193.07–210.40 (m, CO). FAB MS: m/z 1341, M^+; 1313–1061, $[M - nCO]^+$ ($n = 1 - 10$); 901, $[Ru_5\{C_2(PPh_2)_2\}]^+$. A red band (R_f 0.45) was recrystallized from CH_2Cl_2/MeOH to yield red crystals of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(CO)_{10}$ (**2**) (132 mg, 51%), m.p. > 300°C (dec.). Anal. Found: C, 41.41; H, 2.32; *M*, 1301 (mass spectrometry). $C_{45}H_{32}O_{10}P_2Ru_5$ calc.: C, 41.57; H, 2.48%; *M*, 1301. IR (cyclohexane): ν(CO) 2054m, 2034 vs, 2018m, 1977s, 1962(sh), 1939w, 1893w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.48 (1H, dd, $J = 7.2$, 4.5 Hz); 0.96 (1H, d, $J = 2.3$ Hz); 1.25 (1H, s);

TABLE 4. Non-hydrogen positional and isotropic displacement parameters for $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(CO)_{10}$ (**3**)

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
Ru(11)	0.74782(3)	0.29265(3)	0.74677(3)	0.0370(5)
Ru(12)	0.59086(3)	0.41335(3)	0.80316(4)	0.0439(6)
Ru(13)	0.76644(3)	0.45605(3)	0.69122(4)	0.0369(5)
Ru(14)	0.90678(3)	0.33232(3)	0.63496(4)	0.0373(5)
Ru(15)	0.97028(3)	0.20877(3)	0.51196(4)	0.0426(6)
C(111)	0.7335(4)	0.2930(4)	0.8691(4)	0.050(7)
O(111)	0.7307(3)	0.2904(3)	0.9434(3)	0.072(6)
C(112)	0.7503(4)	0.1812(4)	0.7724(4)	0.050(7)
O(112)	0.7456(3)	0.1163(3)	0.7895(4)	0.079(7)
C(121)	0.5884(4)	0.4325(5)	0.9171(5)	0.065(9)
O(121)	0.5850(3)	0.4388(4)	0.9888(3)	0.090(7)
C(122)	0.4843(4)	0.4564(4)	0.8201(5)	0.061(8)
O(122)	0.4166(3)	0.4860(4)	0.8296(4)	0.093(8)
C(131)	0.7538(4)	0.4857(4)	0.8034(5)	0.054(8)
O(131)	0.7505(3)	0.4999(3)	0.8712(4)	0.082(7)
C(132)	0.8045(4)	0.5465(4)	0.6157(5)	0.057(8)
O(132)	0.8283(3)	0.6012(3)	0.5688(4)	0.090(7)
C(141)	0.9015(4)	0.4073(4)	0.7079(5)	0.053(8)
O(141)	0.9272(3)	0.4350(3)	0.7462(4)	0.080(7)
C(142)	0.9411(4)	0.4041(4)	0.5237(4)	0.048(7)
O(142)	0.9608(3)	0.4501(3)	0.4608(3)	0.079(7)
C(151)	1.0077(4)	0.2860(4)	0.4058(5)	0.059(8)
O(151)	1.0314(4)	0.3282(3)	0.3407(4)	0.100(8)
C(152)	0.9991(4)	0.1291(4)	0.4449(5)	0.057(8)
O(152)	1.0187(3)	0.0775(3)	0.4048(3)	0.078(7)
C(11)	0.7963(4)	0.3069(4)	0.5968(4)	0.038(6)
C(12)	0.7805(3)	0.3757(3)	0.6172(4)	0.034(6)
P(11)	0.8369(1)	0.2418(1)	0.5177(1)	0.038(2)
C(1111)	0.8051(4)	0.2938(4)	0.4146(4)	0.041(7)
C(1112)	0.7423(4)	0.3589(4)	0.4136(4)	0.052(8)
C(1113)	0.7141(5)	0.3889(5)	0.3375(5)	0.070(9)
C(1114)	0.7490(5)	0.3517(5)	0.2629(5)	0.08(1)
C(1115)	0.8112(5)	0.2883(5)	0.2636(5)	0.08(1)
C(1116)	0.8389(5)	0.2595(4)	0.3390(5)	0.059(8)
C(1121)	0.7793(4)	0.1642(4)	0.5577(4)	0.046(7)
C(1122)	0.8150(5)	0.0849(4)	0.5698(5)	0.064(9)
C(1123)	0.7709(5)	0.0262(5)	0.5962(6)	0.09(1)
C(1124)	0.6901(5)	0.0480(5)	0.6102(6)	0.08(1)
C(1125)	0.6524(5)	0.1262(5)	0.5994(6)	0.08(1)
C(1126)	0.6959(4)	0.1848(5)	0.5732(5)	0.064(9)
P(12)	0.6351(1)	0.5207(1)	0.6993(1)	0.041(2)
C(1211)	0.6096(4)	0.6209(4)	0.7270(5)	0.047(7)
C(1212)	0.5740(4)	0.6347(4)	0.8146(5)	0.059(8)
C(1213)	0.5561(4)	0.7105(5)	0.8339(6)	0.08(1)
C(1214)	0.5749(5)	0.7732(5)	0.7636(6)	0.08(1)
C(1215)	0.6098(5)	0.7610(4)	0.6776(6)	0.08(1)
C(1216)	0.6272(5)	0.6855(4)	0.6575(5)	0.065(9)
C(1221)	0.6106(4)	0.5464(3)	0.5902(4)	0.040(6)
C(1222)	0.5315(4)	0.5704(4)	0.5913(5)	0.058(8)
C(1223)	0.5097(4)	0.5956(5)	0.5099(6)	0.08(1)
C(1224)	0.5687(5)	0.5944(5)	0.4270(5)	0.070(9)
C(1225)	0.6459(4)	0.5711(4)	0.4270(5)	0.061(8)
C(1226)	0.6684(4)	0.5468(4)	0.5064(4)	0.050(7)
C(1101)	0.5951(4)	0.3523(4)	0.6956(5)	0.052(8)
C(1102)	0.6292(4)	0.3018(4)	0.7625(4)	0.043(7)
C(1103)	0.5765(4)	0.2831(4)	0.8499(5)	0.063(9)
C(1201)	1.0257(4)	0.2928(4)	0.6541(5)	0.055(8)
C(1202)	0.9890(4)	0.2270(4)	0.6842(5)	0.050(7)
C(1203)	0.9191(4)	0.2322(4)	0.7608(4)	0.056(8)
C(1204)	1.0132(4)	0.1617(4)	0.6310(5)	0.054(8)
C(1205)	1.0840(4)	0.1572(5)	0.5571(6)	0.070(9)
C(1206)	0.9600(5)	0.1156(4)	0.6378(5)	0.062(9)
Ru(21)	1.32814(3)	0.17897(3)	0.83939(4)	0.0436(6)
Ru(22)	1.34207(4)	0.08920(4)	0.69331(4)	0.0523(6)
Ru(23)	1.29531(3)	0.02046(3)	0.91521(4)	0.0389(5)
Ru(24)	1.27562(3)	0.12655(3)	1.04060(4)	0.0387(5)
Ru(25)	1.16655(3)	0.28223(3)	1.09641(4)	0.0444(6)
C(211)	1.4386(4)	0.1350(5)	0.8004(5)	0.067(9)
O(211)	1.5058(3)	0.1073(4)	0.7864(4)	0.103(8)
C(212)	1.3434(4)	0.2837(4)	0.8125(5)	0.060(9)
O(212)	1.3551(4)	0.3470(3)	0.7905(4)	0.085(7)
C(221)	1.4473(5)	0.0252(5)	0.6676(6)	0.08(1)
O(221)	1.5111(3)	−0.0125(4)	0.6482(5)	0.12(1)
C(222)	1.3221(5)	0.0815(5)	0.5884(5)	0.08(1)
O(222)	1.3089(5)	0.0782(4)	0.5239(4)	0.12(1)
C(231)	1.3950(4)	−0.0554(5)	0.8960(5)	0.066(9)
O(231)	1.4562(3)	−0.0973(4)	0.8880(5)	0.110(9)
C(232)	1.2312(4)	−0.0511(4)	0.9985(5)	0.048(7)
O(232)	1.1894(3)	−0.0905(3)	1.0442(3)	0.074(6)
C(241)	1.3520(4)	0.0238(4)	1.0389(5)	0.061(9)
O(241)	1.3992(3)	−0.0269(3)	1.0621(4)	0.091(8)
C(242)	1.1914(4)	0.0812(4)	1.1292(5)	0.048(7)
O(242)	1.1477(3)	0.0492(3)	1.1879(4)	0.074(6)
C(251)	1.0832(4)	0.2299(4)	1.1761(5)	0.059(8)
O(251)	1.0302(3)	0.2036(3)	1.2249(4)	0.086(7)
C(252)	1.1041(5)	0.3814(5)	1.1179(5)	0.068(9)
O(252)	1.0674(4)	0.4429(3)	1.1304(4)	0.102(8)
C(21)	1.2056(4)	0.2024(4)	0.9276(4)	0.042(7)
C(22)	1.2252(4)	0.1271(4)	0.9250(4)	0.042(7)
P(21)	1.1343(1)	0.2856(1)	0.9664(1)	0.039(2)
C(2111)	1.0352(4)	0.2690(4)	0.9827(4)	0.041(7)
C(2112)	1.0194(4)	0.1935(4)	1.0126(5)	0.050(8)
C(2113)	0.9422(4)	0.1830(5)	1.0316(5)	0.060(9)
C(2114)	0.8823(4)	0.2457(5)	1.0206(5)	0.067(9)
C(2115)	0.8968(4)	0.3215(5)	0.9916(6)	0.076(9)
C(2116)	0.9738(4)	0.3321(4)	0.9718(5)	0.061(8)
C(2121)	1.1403(4)	0.3708(4)	0.8716(5)	0.051(7)
C(2122)	1.1413(5)	0.4435(4)	0.8870(6)	0.07(1)
C(2123)	1.1353(6)	0.5095(5)	0.8172(7)	0.10(1)
C(2124)	1.1296(5)	0.5035(5)	0.7361(6)	0.10(1)
C(2125)	1.1295(5)	0.4302(5)	0.7217(6)	0.08(1)
C(2126)	1.1341(5)	0.3653(4)	0.7893(5)	0.063(9)
P(22)	1.2793(1)	−0.0104(1)	0.7894(1)	0.044(2)
C(2211)	1.3257(4)	−0.1121(4)	0.7704(5)	0.049(7)
C(2212)	1.3671(5)	−0.1254(5)	0.6834(5)	0.07(1)
C(2213)	1.4006(5)	−0.2039(5)	0.6673(6)	0.08(1)
C(2214)	1.3961(4)	−0.2664(5)	0.7388(6)	0.08(1)
C(2215)	1.3558(5)	−0.2539(4)	0.8264(6)	0.07(1)
C(2216)	1.3212(4)	−0.1769(4)	0.8417(5)	0.057(8)

TABLE 4. (continued)

C(2221)	1.1755(4)	−0.0065(4)	0.7978(4)	0.046(7)
C(2222)	1.1559(5)	−0.0490(4)	0.7483(5)	0.063(9)
C(2223)	1.0778(5)	−0.0442(5)	0.7546(6)	0.07(1)
C(2224)	1.0171(5)	0.0012(5)	0.8115(6)	0.07(1)
C(2225)	1.0340(4)	0.0449(5)	0.8583(5)	0.062(9)
C(2226)	1.1122(4)	0.0407(4)	0.8527(5)	0.053(8)
C(2101)	1.2365(5)	0.1888(4)	0.7098(5)	0.061(9)
C(2102)	1.3065(4)	0.2063(4)	0.7143(5)	0.055(8)
C(2103)	1.3695(5)	0.2141(5)	0.6321(5)	0.07(1)
C(2201)	1.3234(4)	0.1233(4)	1.1512(5)	0.058(9)
C(2202)	1.3325(4)	0.1956(4)	1.0856(5)	0.054(8)
C(2203)	1.3867(4)	0.1850(4)	0.9975(5)	0.056(8)
C(2204)	1.2847(4)	0.2745(4)	1.1060(5)	0.050(8)
C(2205)	1.2333(4)	0.2827(5)	1.1950(5)	0.064(9)
C(2206)	1.2720(4)	0.3408(4)	1.0332(5)	0.057(8)

1.36 (1H, d, $J = 2.2$ Hz); 1.74 (1H, d, $J = 2.2$ Hz); 1.81 (1H, dd, $J = 7.8$, 3.4 Hz); 2.00 (1H, s); 2.56 (1H, s (br)); 2.59 (1H, dd, $J = 3.7$, 2.8 Hz); 2.99 (1H, d, $J = 3.5$ Hz); 3.39 (1H, s (br), CH_2); 3.95 (1H, t, $J = 3.1$ Hz) (all CH_2 protons); 7.28–8.20 (20H, m, Ph). FAB MS; (m/z) 1301, M^+; 1273–1021, $[M - n\text{CO}]^+$ ($n = 1$–10); 901, $[Ru_5\{C_2(PPh_2)_2\}]^+$; 824, $[901 - Ph]^+$. A brown band (R_f 0.40) was recrystallized from CH_2Cl_2/MeOH to yield black crystals of $Ru_5(\mu 5\text{-}C_8H_8PPh_2)(\mu\text{-}PPh_2)(CO)_{11}$ (**8**) (68 mg, 26%) [3].

5.3. *Reaction of 2 with $P(OMe)_3$*

TMNO (*ca.* 8 mg, 0.11 mmol) was added to a mixture of **2** (80 mg, 0.062 mmol) and $P(OMe)_3$ (210 ml of a 0.355 mmol/ml solution in tetrahydrofuran, 0.075 mmol) in tetrahydrofuran (20 ml) until no starting material remained. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 2:1) to yield two major bands. An orange band (R_f 0.70) was recrystallized from CH_2Cl_2/MeOH to yield orange crystals of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(\mu\text{-}CO)(CO)_8\{P(OMe)_3\}$ (**5**) (5 mg, 6%), m.p. 198–199°C (dec.). Anal. Found: C, 40.47; H, 2.96; M, 1397 (mass spectrometry). $C_{47}H_{41}O_{12}P_3Ru_5$ calc.: C, 40.34; H, 2.96%; M, 1397. IR (cyclohexane): ν(CO) 2029m, 2016vs, 1998m, 1988s, 1962m, 1953m, 1947m, 1860m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −1.20 (1H, d, $J = 2.7$ Hz); 1.09 (1H, s); 1.70 (1H, s); 1.75 (1H, s); 1.95 (1H, s); 1.98 (1H, q, $J = 3.5$ Hz); 2.30 (1H, s; 2.56 (1H, d, $J = 3.5$ Hz); 2.67 (1H, s); 2.95 (1H, s); 3.44 (1H, s) (all CH_2 protons); 3.27 (9H, d, J(HP) = 11.1 Hz, $P(OMe)_3$); 7.20–8.20 (20H, m, Ph). FAB MS: m/z 1397, M^+; 1369–1201, $[M - n\text{CO}]^+$ ($n = 1$–7); 1304, $[M - 30Me]^+$. The major dark red band (R_f 0.50) was recrystallized from CH_2Cl_2/MeOH to yield black crystals of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(CO)_9\{P(OMe)_3\}$ (**4**) (27 mg, 31%), m.p. > 320°C (dec.). Anal. Found: C, 38.79; H, 3.00; M, 1397 (mass spectrometry). $C_{47}H_{41}O_{12}P_3Ru_5 \cdot CH_2Cl_2$ calc.: C, 38.93, H, 2.93%; M, 1397. IR (cyclohexane): ν(CO) 2034m, 2018vs, 1997m, 1966s, 1945m, 1919w, 1911sh

TABLE 5. Non-hydrogen coordinates and isotropic thermal parameters for $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(CO)_9\text{-}\{P(OMe)_3\}$ (4)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.92395(7)	0.56889(4)	0.72599(5)	0.0393(5)
Ru(2)	0.92316(7)	0.67318(4)	0.81906(6)	0.0472(6)
Ru(3)	0.74615(7)	0.62782(4)	0.68377(5)	0.0409(5)
Ru(4)	0.76041(7)	0.51983(4)	0.60859(5)	0.0399(5)
Ru(5)	0.75890(8)	0.40415(4)	0.67654(6)	0.0509(6)
C(11)	0.9899(8)	0.6170(5)	0.6770(6)	0.057(8)
O(11)	1.0363(6)	0.6428(4)	0.6490(5)	0.086(6)
C(12)	1.0287(7)	0.5211(4)	0.7407(5)	0.043(6)
O(12)	1.0955(6)	0.4945(3)	0.7486(5)	0.074(6)
C(21)	0.965(1)	0.7274(5)	0.7603(8)	0.075(9)
O(21)	0.9945(8)	0.7594(4)	0.7282(7)	0.127(9)
C(22)	0.9508(8)	0.7111(5)	0.9110(8)	0.068(8)
O(22)	0.9685(7)	0.7321(4)	0.9705(6)	0.115(8)
C(31)	0.7738(9)	0.6865(5)	0.6268(7)	0.064(8)
O(31)	0.7924(8)	0.7214(3)	0.5927(5)	0.095(7)
C(32)	0.6129(9)	0.6378(5)	0.6424(6)	0.061(8)
O(32)	0.5308(6)	0.6429(3)	0.6185(5)	0.079(6)
C(41)	0.8816(9)	0.4989(4)	0.5942(6)	0.056(7)
O(41)	0.9476(6)	0.4828(4)	0.5757(5)	0.081(6)
C(51)	0.8694(9)	0.3847(5)	0.6418(7)	0.071(8)
O(51)	0.9363(7)	0.3685(4)	0.6244(6)	0.107(8)
C(52)	0.756(1)	0.3403(5)	0.7273(7)	0.073(9)
O(52)	0.7501(8)	0.3029(4)	0.7605(6)	0.113(8)
C(1)	0.8202(7)	0.5132(4)	0.7502(5)	0.038(6)
C(2)	0.7738(7)	0.5569(4)	0.7290(5)	0.032(6)
P(1)	0.8284(2)	0.4490(1)	0.7886(2)	0.040(2)
C(111)	0.7622(8)	0.4453(4)	0.8632(6)	0.041(6)
C(112)	0.7009(9)	0.4831(5)	0.8730(7)	0.060(8)
C(113)	0.641(1)	0.4761(5)	0.9239(8)	0.074(9)
C(114)	0.646(1)	0.4294(6)	0.9642(8)	0.08(1)
C(115)	0.710(1)	0.3918(5)	0.9571(7)	0.075(9)
C(116)	0.7696(9)	0.3993(5)	0.9075(7)	0.064(8)
C(121)	0.9528(8)	0.4362(4)	0.8453(6)	0.041(6)
C(122)	1.0018(8)	0.4721(4)	0.9013(6)	0.050(7)
C(123)	1.0974(8)	0.4635(5)	0.9432(7)	0.058(7)
C(124)	1.1431(9)	0.4182(5)	0.9322(7)	0.063(8)
C(125)	1.0961(9)	0.3804(5)	0.8802(8)	0.075(9)
C(126)	0.9990(9)	0.3899(4)	0.8382(7)	0.059(8)
P(2)	0.7567(2)	0.6831(1)	0.7880(2)	0.045(2)
C(211)	0.6956(8)	0.7473(4)	0.7609(6)	0.050(7)
C(212)	0.748(1)	0.7912(5)	0.7509(8)	0.076(9)
C(213)	0.696(1)	0.8391(5)	0.7255(8)	0.09(1)
C(214)	0.597(1)	0.8417(5)	0.7101(8)	0.10(1)
C(215)	0.551(1)	0.7986(6)	0.7200(8)	0.09(1)
C(216)	0.597(1)	0.7513(5)	0.7459(8)	0.072(9)
C(221)	0.6929(8)	0.6631(4)	0.8611(6)	0.044(7)
C(222)	0.7141(9)	0.6888(5)	0.9327(7)	0.064(8)
C(223)	0.6631(9)	0.6773(5)	0.9859(7)	0.074(9)
C(224)	0.5920(8)	0.6387(5)	0.9710(7)	0.065(8)
C(225)	0.5709(9)	0.6135(5)	0.9001(7)	0.067(8)
C(226)	0.6225(8)	0.6253(4)	0.8467(7)	0.053(7)
P(3)	0.7559(2)	0.5822(1)	0.5127(2)	0.053(2)

TABLE 5. (continued)

Atom	x	y	z	U_{eq} (Å^2)
O(301)	0.6622(6)	0.6193(3)	0.4903(4)	0.064(5)
C(301)	0.627(1)	0.6497(6)	0.4219(8)	0.09(1)
O(302)	0.8522(6)	0.6164(3)	0.5271(4)	0.070(6)
C(302)	0.884(1)	0.6477(6)	0.4708(8)	0.10(1)
O(303)	0.7452(6)	0.5617(3)	0.4250(4)	0.066(5)
C(303)	0.814(1)	0.5279(6)	0.4052(7)	0.10(1)
C(101)	0.9228(8)	0.6017(4)	0.8887(6)	0.047(7)
C(102)	0.9839(7)	0.5973(4)	0.8364(6)	0.037(6)
C(103)	1.0690(8)	0.6296(4)	0.8537(7)	0.059(7)
C(201)	0.5960(7)	0.5227(5)	0.5893(7)	0.061(8)
C(202)	0.6241(7)	0.4732(5)	0.5663(6)	0.051(7)
C(203)	0.6714(8)	0.4758(5)	0.5060(6)	0.062(8)
C(204)	0.6150(9)	0.4222(5)	0.6060(7)	0.061(8)
C(205)	0.6090(9)	0.4214(5)	0.6851(7)	0.061(8)
C(206)	0.6349(9)	0.3753(5)	0.5728(7)	0.070(8)
C(1′)	1.257(1)	0.7631(5)	1.016(1)	0.10(1)
C(11′)	1.195(2)	0.7847(8)	1.063(1)	0.18(2)
C(2′)	1.218(1)	0.7474(5)	0.9397(9)	0.11(1)
C(3′)	1.279(1)	0.7273(6)	0.8958(9)	0.11(1)
C(4′)	1.379(1)	0.7238(6)	0.927(1)	0.14(2)
C(5′)	1.411(1)	0.7403(6)	1.003(1)	0.12(1)
C(6′)	1.355(1)	0.7587(6)	1.049(1)	0.11(1)
C(1″)	0.3494(8)	0.5194(5)	0.8108(6)	0.17(2)
C(11″)	0.347(2)	0.4784(7)	0.8633(9)	0.23(2)
C(2″)	0.4045(7)	0.5143(6)	0.7565(7)	0.15(2)
C(3″)	0.4065(9)	0.5553(8)	0.7040(7)	0.19(2)
C(4″)	0.353(1)	0.6014(6)	0.7057(7)	0.23(3)
C(5″)	0.298(1)	0.6065(5)	0.7600(9)	0.28(4)
C(6″)	0.2960(6)	0.5655(6)	0.8124(7)	0.16(2)

cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −0.02 (1H, q, $J = 2.6$ Hz); 0.88 (1H, s, (br)); 0.97 (1H, s (br)); 1.37–1.53 (3H, m); 1.89 (1H, s); 2.46 (1H, s (br)); 2.67 (1H, s (br)); 2.98 (1H, d, $J = 3.3$ Hz); 3.59 (1H, d, $J = 3.5$ Hz); 3.95 (1H, t, $J = 2.9$ Hz) (all CH_2 protons), 3.50 (9H, d, J(HP) = 11.1 Hz, $P(OMe)_3$); 6.97–8.17 (20H, m, Ph). FAB MS: m/z 1397, M$^+$; 1369-1201, $[M - nCO]^+$ (n = 1–7); 1304, $[M - 3OMe]^+$.

5.4. Reaction of 2 with MeCN

TMNO (*ca.* 8 mg, 0.11 mmol) was added to a solution of **2** (53 mg, 0.040 mmol) in CH_2Cl_2 (20 ml) and MeCN (2 ml) until no starting material remained. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 3 : 1) to yield three bands. The major orange band (R_f 0.30) was recrystallized from CH_2Cl_2/MeOH to yield $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(\mu\text{-}CO)(CO)_8\text{-}(NCMe)$ (49 mg, 94%). Anal. Found: C, 41.60; H, 2.65; N, 107; M, 1314 (mass spectrometry). $C_{46}H_{35}NO_9P_2Ru_5$ calc.: C, 42.08; H, 2.69; N 1.07%; M, 1314. ^{1}H NMR ($CDCl_3$): δ 0.54 (1H, s (br)); 0.98 (1H, d, J(HP) = 2.6 Hz); 1.05 (1H, s); 1.25 (1H, s); 1.39 (1H, s); 1.69 (1H, dd, $J = 7.4$, 3.2 Hz); 1.78 (1H, s); 1.83 (1H, s(br)); 2.36 (1H, s (br)); 2.58 (1H, s (br)); 2.86 (1H, d, $J = 2.7$ Hz), 3.83 (1H, s (br)) (all CH_2 protons); 1.76 (3H, s, $NCCH_3$); 7.20–8.28 (20H, m, Ph). IR (cyclohexane): ν(CO) 2033vs, 2017sh, 2011s, 2001m, 1989w, 1966s,

TABLE 6. Non-hydrogen positional and isotropic displacement parameters for $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(\mu\text{-}CO)(CO)_8\{P(OMe)_3\}$ (**5**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.13602(6)	0.41418(9)	0.18961(6)	0.0325(7)
Ru(2)	0.15397(7)	0.58510(9)	0.10461(6)	0.0351(7)
Ru(3)	0.29407(6)	0.49120(8)	0.20829(6)	0.0300(7)
Ru(4)	0.26444(7)	0.31497(8)	0.26882(6)	0.0335(7)
Ru(5)	0.21369(7)	0.12541(9)	0.24187(6)	0.0412(8)
C(11)	0.0920(8)	0.504(1)	0.2426(7)	0.05(1)
O(11)	0.0626(6)	0.5533(8)	0.2804(5)	0.066(8)
C(12)	0.0424(9)	0.352(1)	0.1832(7)	0.06(1)
O(12)	−0.0185(7)	0.3188(9)	0.1746(6)	0.082(9)
C(21)	0.1212(9)	0.686(1)	0.1574(8)	0.05(1)
O(21)	0.932(6)	0.7441(8)	0.1848(6)	0.069(8)
C(22)	0.1486(9)	0.651(1)	0.0251(9)	0.06(1)
O(22)	0.1452(7)	0.6895(9)	−0.0268(6)	0.09(1)
C(31)	0.4007(8)	0.491(1)	0.2052(6)	0.036(9)
O(31)	0.4693(6)	0.4815(9)	0.2030(5)	0.078(9)
C(41)	0.3271(8)	0.414(1)	0.3091(7)	0.036(8)
O(41)	0.3705(6)	0.4371(7)	0.3528(5)	0.058(7)
C(42)	0.363(1)	0.266(1)	0.2509(7)	0.06(1)
O(42)	0.4249(7)	0.243(1)	0.2383(7)	0.10(1)
C(51)	0.318(1)	0.085(1)	0.2343(8)	0.06(1)
O(51)	0.3772(7)	0.0504(9)	0.2284(6)	0.08(1)
C(52)	0.170(1)	0.019(1)	0.2133(8)	0.06(1)
O(52)	0.1474(9)	−0.0514(8)	0.1959(8)	0.11(1)
C(1)	0.2138(7)	0.309(1)	0.1524(6)	0.034(8)
C(2)	0.2541(8)	0.384(1)	0.1629(6)	0.034(9)
P(1)	0.2059(2)	0.1936(3)	0.1347(2)	0.035(2)
C(111)	0.2878(9)	0.165(1)	0.0806(6)	0.040(9)
C(112)	0.3515(9)	0.219(1)	0.0747(8)	0.05(1)
C(113)	0.417(1)	0.190(1)	0.0412(9)	0.07(1)
C(114)	0.417(1)	0.105(1)	0.0127(8)	0.06(1)
C(115)	0.354(1)	0.052(1)	0.0176(9)	0.07(1)
C(116)	0.2891(9)	0.080(1)	0.0508(8)	0.06(1)
C(121)	0.1207(7)	0.179(1)	0.0779(7)	0.038(9)
C(122)	0.0607(9)	0.120(1)	0.0926(8)	0.06(1)
C(123)	−0.002(1)	0.108(1)	0.048(1)	0.09(2)
C(124)	−0.007(1)	0.157(1)	−0.0112(9)	0.07(1)
C(125)	0.0482(9)	0.218(1)	−0.0278(7)	0.05(1)
C(126)	0.1116(9)	0.229(1)	0.0166(8)	0.06(1)
P(2)	0.2882(2)	0.5890(3)	0.1134(2)	0.036(2)
C(211)	0.3419(8)	0.6979(9)	0.1216(7)	0.035(9)
C(212)	0.3040(9)	0.778(1)	0.1281(9)	0.06(1)
C(213)	0.343(1)	0.856(1)	0.134(1)	0.07(1)
C(214)	0.423(1)	0.857(1)	0.131(1)	0.08(1)
C(215)	0.4638(8)	0.777(1)	0.1246(9)	0.06(1)
C(216)	0.422(1)	0.698(1)	0.1190(9)	0.06(1)
C(221)	0.3362(8)	0.546(1)	0.0375(7)	0.037(9)
C(222)	0.340(1)	0.597(1)	−0.0225(8)	0.08(1)
C(223)	0.370(1)	0.568(2)	−0.0805(9)	0.09(2)
C(224)	0.4032(9)	0.483(2)	−0.0839(8)	0.07(1)
C(225)	0.403(1)	0.431(1)	−0.0276(9)	0.07(1)
C(226)	0.3698(9)	0.463(1)	0.0333(8)	0.06(1)
P(3)	0.2814(2)	0.6052(3)	0.2897(2)	0.043(3)

TABLE 6. (continued)

O(301)	0.3516(6)	0.6386(8)	0.3377(5)	0.070(8)
C(301)	0.423(1)	0.671(2)	0.313(1)	0.12(2)
O(302)	0.2413(6)	0.6951(7)	0.2632(5)	0.061(8)
C(302)	0.235(1)	0.778(1)	0.299(1)	0.12(2)
O(303)	0.2264(6)	0.5692(7)	0.3498(5)	0.065(8)
C(303)	0.214(1)	0.610(1)	0.414(1)	0.11(2)
C(101)	0.1491(7)	0.4625(9)	0.0396(7)	0.035(8)
C(102)	0.0980(7)	0.461(1)	0.0943(7)	0.037(9)
C(103)	0.0347(8)	0.520(1)	0.0913(7)	0.045(9)
C(201)	0.2266(9)	0.272(1)	0.3776(7)	0.06(1)
C(202)	0.1895(9)	0.264(1)	0.3500(7)	0.04(1)
C(203)	0.1533(9)	0.344(1)	0.3307(7)	0.05(1)
C(204)	0.1561(8)	0.171(1)	0.3313(8)	0.05(1)
C(205)	0.1942(9)	0.095(1)	0.3568(7)	0.06(1)
C(206)	0.0972(9)	0.163(1)	0.2823(8)	0.06(1)

1951m, 1944sh, 1921m, 1867m cm^{-1}. FAB MS: m/z 1314, M$^+$; 1273, [M − NCMe]$^+$; 1245–1021 [M − NCMe − nCO]$^+$ (n = 1–9).

5.5. Reaction of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(\mu\text{-}CO)(CO)_8(NCMe)$ with $P(OMe)_3$

A solution of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}\eta\text{-}C_3H_4)(\mu\text{-}CO)(CO)_8(NCMe)$ (42 mg, 0.032 mmol) and $P(OMe)_3$ (5 mg, 0.040 mmol) in CH_2Cl_2 (15 ml) was stirred at room temperature for 16 h. The solvent was removed and the residue purified by preparative TLC (light petrol/acetone 3:1) to yield two major bands; a red band (R_f 0.35) was recrystallized from CH_2Cl_2/MeOH to yield **4** (11 mg, 25%) and the major orange band (R_f 0.40) was further purified by preparative TLC (light petroleum/CH_2Cl_2 5:2) to yield **5** (26 mg, 58%).

5.6. Isomerization of 2

A solution of **2** (40 mg, 0.030 mmol) in CH_2Cl_2 (5 ml) was left at ambient temperature for 21 days. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 4:1) producing one major band (R_f 0.6) which was recrystallized from toluene/hexane to yield red crystals of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(CO)_{10}$ (**3**) (36 mg, 90%), m.p. 218–220°C. Anal. Found: C, 41.73; H, 2.58; M, 1301 (mass spectrometry). $C_{45}H_{32}O_{10}P_2Ru_5$ calc.: C, 41.41; H, 3.32%; M, 1301. IR (cyclohexane): ν(CO) 2052m, 2029vs, 2018m, 2001s, 1980m, 1968m, 1953sh, 1899m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −0.65 (1H, d, J = 3.5 Hz); 0.96 (1H, s); 1.48 (1H, dd, J = 6.2, 3.7 Hz); 1.56 (1H, s); 1.70 (1H, dd, J = 7.6, 3.4 Hz); 1.96 (1H, s); 2.55 (1H, s(br)); 2.65 (1H, t, J = 2.5 Hz); 2.87 (1H, d, J = 3.6 Hz); 3.12 (1H, t, J = 3.4 Hz); 3.23 (1H, s (br)); 3.74 (1H, t, J = 3.2 Hz) (all CH_2 protons); 7.21–8.15 (20H, m, Ph). FAB MS: m/z 1301, M; 1273–1021, [M − nCO]$^+$ (n = 1–10). A trace amount of starting material (R_f 0.4) was also recovered.

TABLE 7. Non-hydrogen positional and isotropic displacement parameters for $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(\mu\text{-}CO)(CO)_8\{P\text{-}(OMe)_3\}$ (**6**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.80538(2)	0.88124(3)	0.36733(4)	0.0372(1)
Ru(2)	0.80127(2)	0.65662(3)	0.35722(4)	0.0378(1)
Ru(3)	0.85924(2)	0.86719(3)	0.64023(4)	0.0378(1)
Ru(4)	0.85123(2)	1.07494(3)	0.61619(4)	0.0446(2)
Ru(5)	0.74941(2)	1.21210(3)	0.54447(4)	0.0465(2)
C(11)	0.8725(2)	0.8319(4)	0.2889(5)	0.054(2)
O(11)	0.9142(2)	0.8098(3)	0.2406(4)	0.080(2)
C(12)	0.7720(2)	0.9119(3)	0.2037(5)	0.051(2)
O(12)	0.7525(2)	0.9235(3)	0.0996(4)	0.073(2)
C(21)	0.8782(2)	0.6185(4)	0.3119(5)	0.051(2)
O(21)	0.9221(2)	0.5945(3)	0.2751(4)	0.077(2)
C(22)	0.7685(2)	0.5193(4)	0.3081(5)	0.055(2)
O(22)	0.7482(2)	0.4345(3)	0.2814(4)	0.087(2)
C(31)	0.9366(2)	0.8151(4)	0.6155(5)	0.051(2)
O(31)	0.9827(1)	0.7871(3)	0.6007(4)	0.075(2)
C(32)	0.8778(2)	0.8955(4)	0.8381(5)	0.058(2)
O(32)	0.8887(2)	0.9049(3)	0.9553(4)	0.092(2)
C(41)	0.9277(2)	1.0275(4)	0.6738(7)	0.081(3)
O(41)	0.9810(2)	1.0307(3)	0.7099(7)	0.134(3)
C(51)	0.7336(3)	1.2730(4)	0.7291(6)	0.066(3)
O(51)	0.7186(2)	1.3181(3)	0.8304(4)	0.095(2)
C(52)	0.6860(3)	1.2774(4)	0.4767(6)	0.066(3)
O(52)	0.6462(2)	1.3173(3)	0.4377(5)	0.098(2)
P(1)	0.69205(5)	1.05220(9)	0.4826(1)	0.0385(5)
C(111)	0.6353(2)	1.0353(3)	0.5829(4)	0.042(2)
C(112)	0.6293(2)	0.9517(4)	0.6249(5)	0.060(3)
C(113)	0.5807(3)	0.9370(5)	0.6875(6)	0.075(3)
C(114)	0.5397(2)	1.0075(5)	0.7099(6)	0.076(3)
C(115)	0.5454(2)	1.0909(5)	0.6704(6)	0.077(3)
C(116)	0.5932(2)	1.1061(4)	0.6077(6)	0.064(3)
C(121)	0.6443(2)	0.9876(3)	0.3009(5)	0.042(2)
C(122)	0.6318(2)	1.0418(4)	0.2083(5)	0.054(2)
C(123)	0.5927(3)	0.9933(5)	0.0743(5)	0.067(3)
C(124)	0.5675(2)	0.8912(4)	0.0295(5)	0.063(2)
C(125)	0.5801(2)	0.8361(4)	0.1174(5)	0.058(2)
C(126)	0.6181(2)	0.8840(4)	0.2540(5)	0.049(2)
C(1)	0.7491(2)	0.9716(3)	0.5051(4)	0.035(2)
C(2)	0.7852(2)	0.9318(3)	0.5836(4)	0.036(2)
P(2)	0.81909(5)	0.69788(9)	0.6004(1)	0.0378(5)
C(211)	0.8737(2)	0.6325(3)	0.6915(5)	0.045(2)
C(212)	0.9140(2)	0.5730(4)	0.6227(5)	0.054(2)
C(213)	0.9579(2)	0.5286(4)	0.6928(6)	0.069(3)
C(214)	0.9615(3)	0.5427(5)	0.8310(6)	0.077(3)
C(215)	0.9223(3)	0.6008(5)	0.9024(6)	0.085(3)
C(216)	0.8777(3)	0.6458(4)	0.8330(6)	0.070(3)
C(221)	0.7510(2)	0.6833(3)	0.6738(5)	0.044(2)
C(222)	0.7234(3)	0.5840(4)	0.6482(7)	0.083(3)
C(223)	0.6728(3)	0.5697(5)	0.7042(8)	0.101(4)
C(224)	0.6503(3)	0.6529(5)	0.7846(6)	0.076(3)
C(225)	0.6757(2)	0.7515(4)	0.8084(6)	0.063(2)
C(226)	0.7269(2)	0.7670(4)	0.7543(5)	0.052(2)
P(3)	0.83730(7)	1.1468(1)	0.8417(2)	0.0639(6)

TABLE 7. (continued)

O(301)	0.7684(2)	1.1131(3)	0.8515(4)	0.082(2)
C(301)	0.7441(5)	1.1099(7)	0.9648(8)	0.142(5)
O(302)	0.8495(2)	1.2716(3)	0.9050(4)	0.080(2)
C(302)	0.8488(4)	1.3376(5)	1.0482(7)	0.123(4)
O(303)	0.8757(2)	1.1175(3)	0.9674(4)	0.120(2)
C(303)	0.9398(4)	1.1516(7)	1.028(1)	0.192(6)
C(101)	0.7086(2)	0.7101(3)	0.3460(5)	0.045(2)
C(102)	0.7445(2)	0.7444(3)	0.2655(5)	0.042(2)
C(103)	0.7543(2)	0.6679(4)	0.1436(5)	0.053(2)
C(201)	0.9164(2)	1.2132(4)	0.6536(7)	0.069(3)
C(202)	0.8796(2)	1.1782(4)	0.5117(6)	0.060(2)
C(203)	0.8889(2)	1.0795(4)	0.4193(6)	0.063(3)
C(204)	0.8320(2)	1.2395(4)	0.4684(6)	0.059(2)
C(205)	0.8237(3)	1.3363(4)	0.5591(6)	0.069(3)
C(206)	0.7830(3)	1.1907(4)	0.3458(5)	0.063(2)
C(01)	0.5965(6)	0.314(1)	0.053(1)	0.28(1)
C(02)	0.5820(9)	0.430(2)	0.111(4)	0.68(4)
C(03)	0.5551(7)	0.418(2)	0.190(2)	0.40(2)
C(04)	0.520(1)	0.528(1)	0.242(3)	0.58(2)
C(05)	0.5391(6)	0.589(2)	0.360(2)	0.37(2)
C(06)	0.4987(7)	0.656(1)	0.421(2)	0.32(2)

5.7. Reaction of 3 with $P(OMe)_3$

TMNO (*ca.* 8 mg, 0.11 mmol) was added to a mixture of **3** (50 mg, 0.038 mmol) and $P(OMe)_3$ (5 mg, 0.040 mmol) in CH_2Cl_2 (20 cm^3) until no starting material remained. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 3:1) to yield three major bands. The major orange band (R_f 0.70) was recrystallized from CH_2Cl_2/MeOH to yield $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(\mu\text{-}CO)(CO)_8\{P(OMe)_3\}$ (**6**) (43 mg, 81%). Anal. Found: C, 41.73; H, 2.58; *M*, 1397 (mass spectrometry). $C_{47}H_{41}O_{12}P_3Ru_5$ calc.: C, 40.44; H, 2.96%; *M*, 1397, IR (cyclohexane): ν(CO) 2039s, 2011vs, 1996s, 1971s, 1959s. 1945m, 1926vw, 1874m (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.73 (1H, dd, $J = 9.3$, 3.4 Hz); 0.95 (1H, s (br)); 1.44 (1H, s (br)); 2.05 (1H, dd, $J = 8.3$, 3.4 Hz); 2.09 (s); 2.59 (1H, s (br)); 2.74 (1H, t, $J = 2.2$ Hz); 2.85 (1H, d, $J = 3.9$ Hz); 2.97 (1H, d, $J = 1.7$ Hz); 3.05 (1H, t, $J = 2.9$ Hz); 3.65 (1H, s (br)) (all CH_2 protons); 3.43 (9H, d, J(HP) = 10.6 Hz, $P(OMe)_3$); 7.22–8.18 (20H, m, Ph). FAB MS; m/z 1397, M^+; 1369–1145, $[M\text{-}nCO]^+$ ($n = 1$–9).

5.8. Crystallography

Unique data sets were measured at *ca.* 295 K within the specified $2\theta_{max}$ limits using an Enraf-Nonius CAD4 diffractometer (2θ–θ scan mode; monochromatic Mo Kα radiation, λ 0.7107$_3$ Å); N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values (after location of these atoms in difference maps in the case of the core ligands). Conventional residuals R, R' on $|F|$ are

TABLE 8. Non-hydrogen positional and isotropic displacement parameters for $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_9H_{12})(\mu\text{-}C_3H_4)(CO)_{10}$ (**7**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.3783(1)	0.07081(7)	0.89098(3)	0.0338(3)
Ru(2)	0.2533(1)	−0.10627(7)	0.85285(3)	0.0368(3)
Ru(3)	0.1137(1)	0.01960(7)	0.91516(3)	0.0329(3)
Ru(4)	0.2617(1)	0.18256(7)	0.94517(3)	0.0370(4)
Ru(5)	0.3497(1)	0.42537(7)	0.87951(3)	0.0421(4)
C(11)	0.465(1)	−0.0280(9)	0.9193(4)	0.056(5)
O(11)	0.526(1)	−0.0813(7)	0.9386(3)	0.078(4)
C(12)	0.536(1)	0.1230(9)	0.8780(4)	0.046(5)
O(12)	0.6363(9)	0.1486(8)	0.8677(3)	0.074(4)
C(21)	0.297(1)	−0.202(1)	0.8894(5)	0.060(6)
O(21)	0.333(1)	−0.2610(8)	0.9106(4)	0.098(6)
C(22)	0.217(1)	−0.187(1)	0.8126(4)	0.056(6)
O(22)	0.191(1)	−0.2380(8)	0.7867(3)	0.096(6)
C(31)	0.126(1)	−0.0891(9)	0.9488(4)	0.052(5)
O(31)	0.130(1)	−0.1512(7)	0.9684(3)	0.085(5)
C(32)	−0.056(1)	0.0554(9)	0.9250(3)	0.048(5)
O(32)	−0.163(1)	0.0820(7)	0.9294(3)	0.070(4)
C(41)	0.183(1)	0.087(1)	0.9766(4)	0.048(5)
O(41)	0.162(1)	0.0616(7)	1.0068(3)	0.071(4)
C(42)	0.445(1)	0.1414(9)	0.9569(4)	0.044(5)
O(42)	0.549(1)	0.1328(8)	0.9743(3)	0.078(5)
C(51)	0.465(1)	0.459(1)	0.8421(4)	0.059(6)
O(51)	0.527(1)	0.4857(8)	0.8192(4)	0.091(5)
C(52)	0.236(2)	0.5201(9)	0.8575(4)	0.065(6)
O(52)	0.169(1)	0.5778(7)	0.8458(4)	0.102(6)
C(1)	0.245(1)	0.1939(8)	0.8761(3)	0.028(4)
C(2)	0.175(1)	0.1264(8)	0.8856(3)	0.031(4)
P(1)	0.2463(3)	0.2977(2)	0.84680(9)	0.031(1)
C(111)	0.072(1)	0.3247(8)	0.8296(3)	0.037(4)
C(112)	0.052(1)	0.392(1)	0.7999(4)	0.050(5)
C(113)	−0.076(2)	0.424(1)	0.7874(4)	0.068(6)
C(114)	−0.183(1)	0.388(1)	0.8024(5)	0.077(7)
C(115)	−0.164(1)	0.325(1)	0.8322(5)	0.073(7)
C(116)	−0.038(1)	0.291(1)	0.8451(4)	0.048(5)
C(121)	−0.306(1)	0.2564(8)	0.8021(3)	0.034(4)
C(122)	0.220(1)	0.2175(8)	0.7713(3)	0.044(5)
C(123)	0.270(2)	0.189(1)	0.7389(4)	0.067(6)
C(124)	0.407(2)	0.195(1)	0.7346(4)	0.079(7)
C(125)	0.490(2)	0.229(1)	0.7647(5)	0.077(7)
C(126)	0.445(1)	0.2600(9)	0.7989(4)	0.046(5)
P(2)	0.0359(3)	−0.0798(2)	0.8644(1)	0.035(1)
C(211)	−0.082(1)	−0.0292(8)	0.8245(3)	0.037(4)
C(212)	−0.078(1)	0.0634(9)	0.8145(4)	0.057(5)
C(213)	−0.162(2)	0.099(1)	0.7842(4)	0.067(6)
C(214)	−0.255(1)	0.043(1)	0.7626(4)	0.059(6)
C(215)	−0.262(1)	−0.048(1)	0.7728(4)	0.051(5)
C(216)	−0.178(1)	−0.0846(9)	0.8036(4)	0.050(5)
C(221)	−0.068(1)	−0.1771(9)	0.8768(4)	0.044(5)
C(222)	−0.188(1)	−0.162(1)	0.8931(4)	0.049(5)
C(223)	−0.273(1)	−0.236(1)	0.8974(4)	0.059(6)
C(224)	−0.240(2)	−0.322(1)	0.8878(5)	0.075(7)
C(225)	−0.116(2)	−0.340(1)	0.8713(5)	0.075(7)
C(226)	−0.034(1)	−0.2666(9)	0.8672(4)	0.057(6)

TABLE 8. (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(101)	0.261(1)	0.0095(9)	0.8106(3)	0.048(5)
C(102)	0.379(1)	0.0035(9)	0.8385(3)	0.045(5)
C(103)	0.462(1)	−0.073(1)	0.8345(4)	0.054(5)
C(201)	0.192(1)	0.3338(9)	0.9472(4)	0.050(5)
C(2011)	0.087(1)	0.2691(9)	0.9502(4)	0.049(5)
C(2012)	0.191(1)	0.4085(9)	0.9177(4)	0.046(5)
C(202)	0.310(1)	0.3176(9)	0.9736(4)	0.045(5)
C(2021)	0.299(2)	0.247(1)	1.0023(4)	0.059(6)
C(203)	0.428(1)	0.382(1)	0.9737(4)	0.059(6)
C(204)	0.481(1)	0.413(1)	0.9371(4)	0.065(6)
C(205)	0.478(2)	0.510(1)	0.9234(4)	0.079(7)
C(206)	0.527(1)	0.349(1)	0.9112(5)	0.063(6)
C(01) *	−0.060(6)	0.395(3)	1.026(1)	0.17(3)
Cl(11) *	0.059(2)	0.478(2)	1.0224(6)	0.27(2)
Cl(12) *	−0.164(2)	0.412(2)	0.9909(7)	0.30(2)

* Site occupancy factor = 0.5.

quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system [18] implemented by S.R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables. In the figures, 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. Projections oblique and normal to the Ru_4 "plane" are shown, giving numbering schemes.

5.8.1. Abnormal features / variations in procedure

3: Two independent molecules comprise the asymmetric unit, differing significantly in the dispositions of the pendant phenyl rings (Fig. 1) and in their bonding parameters (Table 1).

4: Solvent thermal motion was very high, but seemingly without disorder or fractional site occupancy on the basis of refinement behaviour.

6: Solvent population was constrained at unity, despite high apparent thermal motion, on the basis of refinement behaviour.

7: Solvent population was constrained at 0.5 on the basis of refinement behaviour.

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TABLE 9. Crystal data and refinement details for complexes **3**–**7**

Compound	**3**	**4**	**5**	**6**	**7**
Formula	$C_{45}H_{32}O_{10}P_2Ru_5$	$C_{47}H_{41}O_{12}P_3Ru_5 \cdot 2C_7H_8$	$C_{47}H_{41}O_{12}P_3Ru_5$	$C_{47}H_{41}O_{12}P_3Ru_5 \cdot C_6H_{14}$	$C_{48}H_{40}O_{10}P_2Ru_5 \cdot 0.5\ CH_2Cl_2$
MW	1300.1	1580.4	1396.1	1482.1	1386.6
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No.2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	18.120(5)	14.231(3)	17.168(9)	22.040(4)	10.042(3)
b (Å)	17.772(6)	25.391(7)	14.889(9)	13.751(2)	14.426(7)
c (Å)	15.777(3)	17.676(9)	19.373(16)	10.253(3)	34.411(11)
α (°)	74.59(2)	–	–	109.90(1)	–
β (°)	70.48(2)	105.61(3)	91.99(6)	101.58(2)	96.66(3)
γ (°)	73.58(2)	–	–	93.27(1)	–
U (Å^3)	4510	6151	4949	2836	4951
Z	4	4	4	2	4
D_c (g cm^{-3})	1.91	1.71	1.87	1.74	1.86
$F(000)$	2528	3136	2736	1468	2716
Crystal size (mm^3)	0.20 × 0.30 × 0.23	0.21 × 0.14 × 0.19	0.18 × 0.20 × 0.08	0.25 × 0.19 × 0.36	0.52 × 0.05 × 0.12
A^* (min, max)	1.14, 1.20	1.16, 1.27	1.12, 1.25	1.25, 1.42	1.08, 1.25
μ (cm^{-1})	15.9	12.0	14.9	14.1	15.0
$2\theta_{max}$ (°)	50	50	50	50	50
N	15 319	10 216	8668	9960	8545
N_o	11 252	5080	4251	7813	5903
R	0.038	0.050	0.054	0.031	0.068
R_w	0.040	0.047	0.049	0.035	0.074

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