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Cluster chemistry

LXXVIII. * Coupling of allene dimer and acetylide on an Ru₅ cluster. X-Ray structure of Ru₅(μ₅-PPh₂C₂C₆H₈)(μ-PPh₂)(CO)₁₀{P(OMe)₃}

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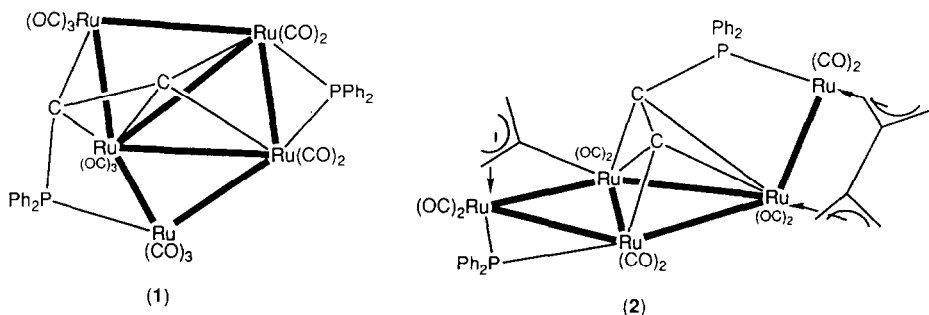
Abstract

The reaction between Ru₅(μ₅-C₂PPh₂)(μ-PPh₂)(CO)₁₃ (**1**) and allene afforded the novel cluster Ru₅(μ₅-PPh₂C₂C₆H₈)(μ-PPh₂)(CO)₁₁ (**3**), which contains a tertiary phosphine formed by coupling of an allene dimer with the C₂PPh₂ moiety in **1**. The metal core in **3**, which is an Ru₄ butterfly metallated at a wing-tip, interacts with the new ligand through the P atom, a 1,3-diene system, and the C₂ unit, which forms a C₂Ru₄ octahedron. Complex **3** was characterised by treatment with P(OMe)₃ and an X-ray structural study of the resulting title complex.

Introduction

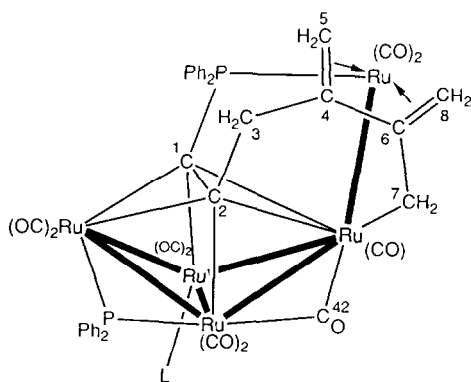
Continuing our studies of the interactions of the pentanuclear cluster complex Ru₅(μ₅-C₂PPh₂)(μ-PPh₂)(CO)₁₃ (**1**) with unsaturated hydrocarbons [2], we have examined its reaction with allene. While most of the products contain allene or its dimer interacting with the Ru₅ cluster, with interesting rearrangements of the metal skeleton, as found for example, in Ru₅(μ₄-C₂PPh₂)(μ-PPh₂)(μ-C₃H₄)(μ-C₆H₈)(CO)₁₀ (**2**) [3], one complex is formed by dimerisation of allene and coupling of the dimer with the acetylide function of the C₂PPh₂ ligand. This paper describes the structure of this unusual compound.

* For Part LXXVII see ref. 1.



Results

The reaction between allene and **1** was carried out in toluene in a sealed tube (90°C , 3.5 h). Separation by preparative TLC afforded several fast-moving products, which will be described elsewhere [3], together with a brown fraction, which contained a complex characterised by analytical and spectroscopic techniques as $\text{Ru}_5(\text{C}_2\text{PPh}_2)(\text{PPh}_2)(\text{CO})_{11}(\text{C}_3\text{H}_4)_2$ (**3**). Crystals suitable for an X-ray study could not be obtained directly, so we made a derivative by treatment of **3** with $\text{P}(\text{OMe})_3$ to give the black crystalline $\text{Ru}_5(\mu_5\text{-PPh}_2\text{C}_2\text{C}_6\text{H}_8)(\mu\text{-PPh}_2)(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}$ (**4**), the molecular structure of which was determined by X-ray crystallography.

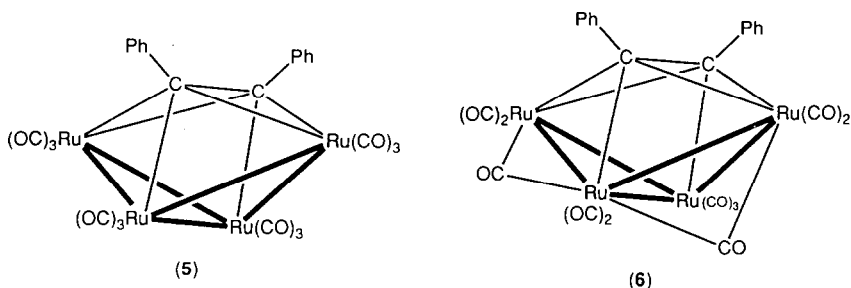


(3) L = CO
(4) L = $\text{P}(\text{OMe})_3$

Molecular structure of $\text{Ru}_5(\mu_5\text{-PPh}_2\text{C}_2\text{C}_6\text{H}_8)(\mu\text{-PPh}_2)(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}$ (**4**)

A molecule of **4** is depicted in Fig. 1 and selected bond parameters are given in Table 1. The structure is based on a butterfly Ru_4 skeleton, to one wing-tip atom of which is attached the fifth Ru atom. The Ru_4 skeleton supports two carbons of a $\mu_4\text{-}\eta^2$ -alkyne ligand formed by combination of the PPh_2C_2 fragment in **1** with one of the CH_2 groups of the allene dimer. The central C_2Ru_4 portion can also be described as a distorted *closo*-octahedron, as found, for example, in $\text{Ru}_4(\mu_4\text{-C}_2\text{Ph}_2)(\text{CO})_{12}$ (**5**) [4].

The Ru–Ru separations range from 2.706(1) to 3.012(1) Å, the longest involving the metallating Ru(5) atom. The hinge, Ru(1)–Ru(3) [2.903(1) Å], is longer than that found in **5** [2.85(1) Å] or the derived anion in the salt [NEt₄]₂[Ru₄(μ₄-C₂Ph₂)(μ-CO)₂(CO)₄] (**6**) [2.822(1) Å] [5]. The other non-bridged Ru–Ru bonds [Ru(1)–Ru(2) 2.828(1), Ru(1)–Ru(4) 2.767(1) Å] are also longer than those found in **5** or **6**. The CO-bridged Ru(3)–Ru(4) vector [2.779(1) Å] can be compared to similar bonds in **6** [2.752(1), 2.732(1) Å], while the PPh₂-bridged bond, which is the shortest, has precedent in Ru₄(μ₄-C=CHⁱPr)(μ₃-OR)(μ-PPh₂)(CO)₁₀ (R = H or Et) [6], in which the PPh₂-bridged Ru–Ru vector of the puckered rhombus is 2.703(1) Å. With coordination about Ru(5) of two CO groups, the tertiary phosphine and the diene giving an 18-electron configuration, the Ru(4)–Ru(5) interaction is best described as a two-electron donor bond from Ru(5) to Ru(4); the relatively large separation [3.012(1) Å] is consistent with this interpretation.



The PPh₂ group shows the usual asymmetry in bonding to Ru(2) and Ru(3) [2.247(3), 2.303(2) Å, respectively]. The P(OMe)₃ ligand occupies an axial position on Ru(1) [2.271(3) Å]. The phosphorus atom of the tertiary phosphino-alkyne is attached to Ru(5) [Ru(5)–P(1) 2.363(2) Å], as is the 1,3-diene system of the allene dimer [Ru(5)–C, 2.16–2.35(1) Å]. One of the CH₂ groups is σ-bonded to Ru(4) [Ru(4)–C(7) 2.169(9) Å], the other to the C₂ moiety of the original acetylide. The cluster-bound C≡C carbons show the usual lengthening to 1.47(1) Å [cf. 1.46(2) in **5**, 1.422(9) Å in **6**]. The Ru(3)–Ru(4) vector is semi-bridged by CO(42) [Ru(3)–C(42) 2.36(1), Ru(4)–C(42) 1.91(1) Å; Ru(3)–C(42)–O(42) 125.4(7), Ru(4)–C(42)–O(42) 153.7(8)°].

The ¹H and ¹³C NMR spectra of **3** and **4** are similar and well-resolved; they have been assigned as shown in Table 2. The diene protons (H_{5,8}) resonate between δ 2.09 and 3.4 and H₇ between δ 0.19 and 0.65, as expected for a metal-bonded CH₂ group. The resonances of the organic ligand carbons are found between δ 13.5 and 116.0, except for C₁ (occurring in the *ipso* C region at δ *ca.* 138) and C₂, found at δ 177 (for **3**) or 170.8 (for **4**). The bridging CO(42) resonates at δ *ca.* 216.

Formation of the organophosphine ligand can be envisaged to occur by simple coupling of one of the allylic carbons of a 2η³-C₆H₈ ligand (allene dimer) with C_β of the PPh₂C₂ group on the Ru₅ cluster; if, for example, a complex resembling **2** was the precursor, a simple reorientation of the two ligands would enable this coupling reaction to occur on the cluster (Scheme 1). The ¹H NMR spectra of **3** and **4** contain similar resonances and suggest that **3** also contains the coupled ligand.

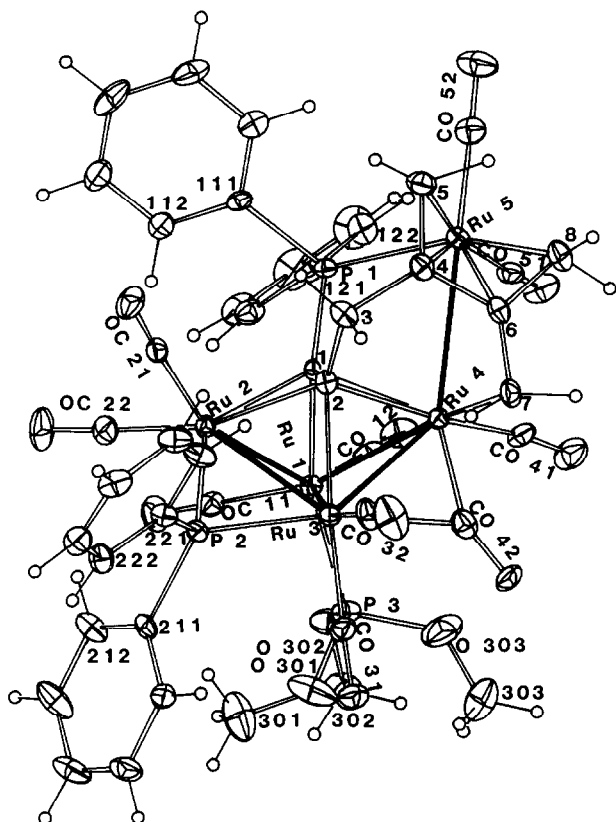


Fig. 1. Computer-generated plot of a molecule of $\text{Ru}_5(\mu_5\text{-PPh}_2\text{C}_2\text{C}_6\text{H}_8)(\mu\text{-PPh}_2)(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}$ (**4**), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

Conversion of **2** to **3** converts the allene dimer from a 6-electron donor to a 5-electron donor, and the phosphino-acetylide from a 5-electron donor to a 4-electron donor, i.e. a net loss of two electrons to the cluster. This is reflected in the total electron count for **3**, which is two short of the 50, required. However, if the cluster is considered as a metallated *closo*-octahedral C_2Ru_4 system, it has a total of 66 CVE, which is consistent with the observed geometry [7].

Experimental

General experimental conditions were similar to those described earlier [8]. Complex **1** was prepared by the literature method [9]. Allene (Matheson Gas) was used as received.

Reaction of $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$ with allene

A solution of $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$ (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 carefully venting the excess pressure the solvent was removed and the residue purified by preparative

Table 1

Selected bond lengths (Å) and angles (°) for Ru₅(μ₅-PPh₂C₂C₆H₈)(μ-PPh₂)(CO)₁₀[P(OMe)₃] (4)

Ru(1)–Ru(2)	2.828(1)	Ru(1)–C(1)	2.165(8)
Ru(1)–Ru(3)	2.903(1)	Ru(2)–C(1)	2.238(7)
Ru(1)–Ru(4)	2.767(1)	Ru(2)–C(2)	2.198(8)
Ru(2)–Ru(3)	2.706(1)	Ru(3)–C(2)	2.245(9)
Ru(3)–Ru(4)	2.779(1)	Ru(4)–C(1)	2.265(8)
Ru(4)–Ru(5)	3.012(1)	Ru(4)–C(2)	2.192(9)
Ru(1)–P(3)	2.271(3)	Ru(4)–C(7)	2.169(9)
Ru(2)–P(2)	2.247(3)	Ru(5)–C(4)	2.26(1)
Ru(3)–P(2)	2.303(2)	Ru(5)–C(5)	2.32(1)
Ru(5)–P(1)	2.363(2)	Ru(5)–C(6)	2.35(1)
Ru(3)–C(42)	2.36(1)	Ru(5)–C(8)	2.16(1)
Ru(4)–C(42)	1.91(1)		
P(1)–C(1)	1.837(8)	C(1)–C(2)	1.47(1)
Ru–CO	range 1.86–1.914(9), av. 1.89 Å		
C–O	range 1.13–1.18(1), av. 1.14 Å		
P–C(Ph)	range 1.83–1.873(9), av. 1.85 Å		
P–OMe	range 1.541–1.62(1), av. 1.586 Å		
Dihedrals:	Ru(1)–Ru(2)–Ru(3)/Ru(1)–Ru(3)–Ru(4) 68.24(4)°		
	Ru(1)–Ru(3)–Ru(4)/Ru(4)–Ru(5) 45.22(3)°		
	Ru(2)–C(1)–C(2)/Ru(4)–C(1)–C(2) 42.7(2)°		

Table 2

¹H and ¹³C NMR spectra of 3 and 4

Assignment	3	4
H _{3a,b}	1.52, 2.98 (AB q, <i>J</i> 16.0)	1.45, 3.13 (AB q, <i>J</i> 16.0)
H _{5a,b}	2.67, 2.86 (s)	2.81
H _{7a,b}	0.19, 0.65 (dd, <i>J</i> 6.5, 6.5)	0.08 (dd, <i>J</i> 2.1, 5.4), 0.56 (t, <i>J</i> 6.5)
H _{8a,b}	2.09, 3.40 (s)	2.01 (d, <i>J</i> 2.1), 3.41 (s)
Ph	7.23–7.46, 7.70–7.75, 7.85–7.94 (m)	7.18–7.49, 7.84–8.05 (m)
P–OMe	–	3.31 (d, <i>J</i> 12)
C ₁	137.84 (d, <i>J</i> 51.9)	138.71 (d, <i>J</i> 52.2)
C ₂	177.93 (s)	170.83 (d, <i>J</i> 5.2)
C _{3,7}	13.62 (d, <i>J</i> 27.5), 13.94 (d, <i>J</i> 3.1)	14.25 (d, <i>J</i> 28.1), 15.06 (s)
C _{4,6}	93.86 (d, <i>J</i> 3.4), 116.01 (s)	92.84 (d, <i>J</i> 3.4), 115.94 (s)
C _{5,8}	57.95 (d, <i>J</i> 13.4), 69.17 (s)	57.79 (d, <i>J</i> 14.75), 67.68 (s)
P–OMe	–	52.64 (d, <i>J</i> 7.2)
Ph	128.19–128.43, 130.24–131.12, 131.73, 131.88, 132.42, 132.57, 133.73, 133.92	127.71–127.97, 129.74–130.19, 131.47–131.92, 133.40–133.78
<i>ipso</i> C	139.68, 139.84, 139.96, 140.34 (2×d), 142.79 (d, <i>J</i> 32.6), 146.07 (d, <i>J</i> 26.9), 146.20 (d, <i>J</i> 25.7)	139.56, 139.96, 140.01, 140.22 (2×d), 143.20, 144.39 (d, <i>J</i> 32.2)
CO	193.91, 194.15 (d, <i>J</i> 6.6), 195.04, 196.63 (dd, <i>J</i> 5.1, 12.4), 198.43, 198.78 (d, <i>J</i> 5.3), 199.27, 202.33 (d, <i>J</i> 5.8)	195.08, 195.16, 195.34, 195.38 (m), 196.27, 199.20 (d, <i>J</i> 5.5), 200.01, 200.21, 200.34, 200.63, 203.49 (d, <i>J</i> 5.4), 205.60 (d, <i>J</i> 24.5)
μ-CO	215.98 (d, <i>J</i> 25.1)	216.30, 217.84 (d, <i>J</i> 25.1)

Table 3

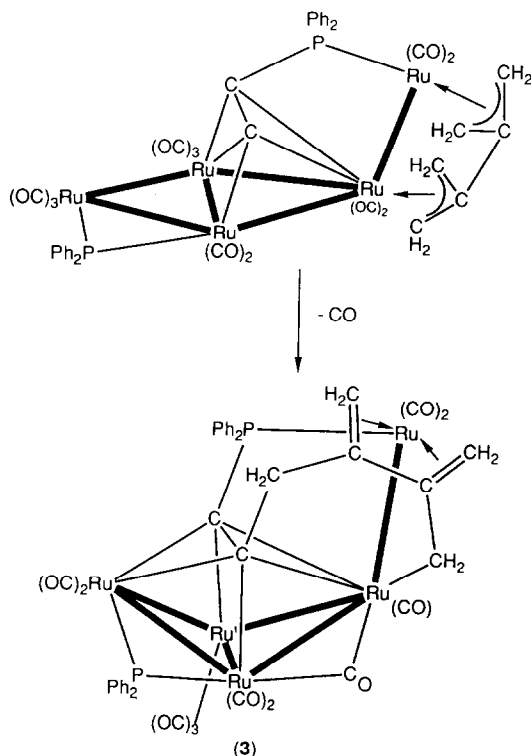
Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters for $\text{Ru}_5(\mu_5\text{-PPH}_2\text{C}_2\text{C}_6\text{H}_8)(\mu\text{-PPH}_2)(\text{CO})_{10}[\text{P}(\text{OMe})_3]_3$ (**4**)

Atom	x	y	z	U_{eq} (\AA^2)
Ru(1)	0.29647(5)	0	0.26542(7)	0.0304(3)
Ru(2)	0.27501(5)	0.15663(4)	0.20270(7)	0.0297(3)
Ru(3)	0.18900(5)	0.10840(5)	0.40596(7)	0.0314(3)
Ru(4)	0.37616(5)	0.04139(5)	0.51576(7)	0.0298(3)
Ru(5)	0.60115(5)	0.09034(5)	0.55525(7)	0.0344(4)
C(11)	0.2632(7)	-0.0032(6)	0.0852(9)	0.041(5)
O(11)	0.2504(7)	-0.0122(5)	-0.0224(6)	0.072(5)
C(12)	0.3984(7)	-0.0797(5)	0.2859(9)	0.043(5)
O(12)	0.4570(5)	-0.1281(4)	0.2940(8)	0.062(5)
C(21)	0.3146(7)	0.2604(6)	0.1927(8)	0.041(5)
O(21)	0.3403(6)	0.3226(4)	0.1912(7)	0.064(5)
C(22)	0.2609(7)	0.1577(6)	0.023(1)	0.050(6)
O(22)	0.2544(7)	0.1618(5)	-0.0871(7)	0.082(6)
C(31)	0.0616(7)	0.0548(6)	0.406(1)	0.048(6)
O(31)	-0.0143(5)	0.0249(4)	0.4121(7)	0.065(5)
C(32)	0.1529(8)	0.1743(6)	0.5347(9)	0.051(6)
O(32)	0.1270(7)	0.2122(6)	0.6120(7)	0.089(6)
C(41)	0.4191(7)	-0.0550(6)	0.581(1)	0.049(6)
O(41)	0.4336(6)	-0.1151(5)	0.6200(9)	0.078(5)
C(42)	0.2451(8)	0.0142(6)	0.5620(9)	0.053(6)
O(42)	0.1915(5)	-0.0174(5)	0.6257(7)	0.066(5)
C(51)	0.6215(7)	-0.0149(6)	0.560(1)	0.044(5)
O(51)	0.6408(6)	-0.0782(4)	0.5626(9)	0.074(5)
C(52)	0.7433(8)	0.1072(6)	0.568(1)	0.053(6)
O(52)	0.8321(6)	0.1190(5)	0.5751(9)	0.084(6)
C(1)	0.4029(6)	0.0928(5)	0.3264(7)	0.026(4)
C(2)	0.3533(6)	0.1471(5)	0.4036(8)	0.032(4)
C(3)	0.4093(7)	0.2130(5)	0.4809(9)	0.040(5)
C(4)	0.4971(7)	0.1895(5)	0.5881(8)	0.039(5)
C(5)	0.5967(8)	0.2201(6)	0.595(1)	0.052(6)
C(6)	0.4782(7)	0.1308(5)	0.6820(8)	0.041(5)
C(7)	0.3801(7)	0.1022(7)	0.6960(8)	0.046(5)
C(8)	0.5792(8)	0.1006(7)	0.7533(9)	0.054(6)
P(1)	0.5445(2)	0.0971(1)	0.3306(2)	0.030(1)
C(111)	0.5806(6)	0.1800(5)	0.2345(9)	0.034(5)
C(112)	0.5317(7)	0.1918(6)	0.109(1)	0.046(6)
C(113)	0.5629(9)	0.2485(7)	0.036(1)	0.063(7)
C(114)	0.645(1)	0.2948(6)	0.086(1)	0.081(9)
C(115)	0.694(1)	0.2836(7)	0.211(1)	0.072(8)
C(116)	0.6614(8)	0.2256(6)	0.284(1)	0.051(6)
C(121)	0.5874(7)	0.0196(5)	0.2350(9)	0.040(5)
C(122)	0.6745(8)	-0.0207(6)	0.280(1)	0.050(6)
C(123)	0.711(1)	-0.0778(8)	0.211(1)	0.09(1)
C(124)	0.658(1)	-0.0964(7)	0.094(1)	0.083(9)
C(125)	0.573(1)	-0.0563(7)	0.041(1)	0.070(8)
C(126)	0.5350(8)	0.0002(6)	0.1129(9)	0.050(6)
P(2)	0.1110(2)	0.1802(1)	0.2336(2)	0.032(1)
C(211)	-0.0034(7)	0.1407(5)	0.1267(9)	0.038(5)
C(212)	0.0057(8)	0.1160(7)	0.007(1)	0.060(6)
C(213)	-0.0805(9)	0.0856(8)	-0.072(1)	0.081(8)
C(214)	-0.1735(8)	0.0787(7)	-0.031(1)	0.072(7)

Table 3 (continued)

Atom	x	y	z	U_{eq} (\AA^2)
C(215)	-0.1836(7)	0.1047(7)	0.090(1)	0.061(6)
C(216)	-0.0974(7)	0.1368(6)	0.1698(9)	0.046(6)
C(221)	0.0707(7)	0.2790(5)	0.2607(9)	0.037(5)
C(222)	-0.0167(8)	0.3116(6)	0.188(1)	0.046(6)
C(223)	-0.0397(8)	0.3873(6)	0.211(1)	0.053(6)
C(224)	0.0197(8)	0.4284(6)	0.303(1)	0.057(6)
C(225)	0.1067(8)	0.3964(6)	0.372(1)	0.056(6)
C(226)	0.1323(7)	0.3219(6)	0.352(1)	0.050(6)
P(3)	0.1791(2)	-0.0955(2)	0.2697(3)	0.047(1)
O(301)	0.0599(6)	-0.0872(6)	0.234(1)	0.102(7)
C(301)	0.004(1)	-0.066(1)	0.126(1)	0.12(1)
O(302)	0.2056(6)	-0.1635(4)	0.1795(8)	0.068(5)
C(302)	0.154(1)	-0.2324(7)	0.158(1)	0.081(8)
O(303)	0.1854(8)	-0.1372(6)	0.4078(9)	0.102(7)
C(303)	0.115(1)	-0.1758(8)	0.459(1)	0.10(1)

TLC (light petroleum/acetone 4:1). A brown band (R_f 0.40) was crystallised ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) to yield black crystals of $\text{Ru}_5(\mu_5\text{-PPh}_2\text{C}_2\text{C}_6\text{H}_8)(\mu\text{-PPh}_2)(\text{CO})_{11}$ (**3**) (63 mg, 25%), m.p. 204–206 °C (dec.). Anal. Found: C, 39.85; H, 2.80%; M^+ , 1288. $\text{C}_{43}\text{H}_{28}\text{O}_{11}\text{P}_2\text{Ru}_5$ calc.: C, 40.10; H, 2.19%; M , 1288. IR: $\nu(\text{CO})$ (cyclohex-



Scheme 1

ane) 2058m, 2028vs, 2003s, 1983m, 1966m, 1942vw cm^{-1} . $^1\text{H NMR}$: δ (CDCl_3) 0.19 (1H, dd, $J(\text{HH}) = 5.7$ Hz, $J(\text{HP}) = 2.3$ Hz), 0.65 (1H, t, $J(\text{HH}) = 6.7$ Hz, $J(\text{HP}) = 6.7$ Hz) (H_7); 1.52 (1H, d, $J(\text{HH}) = 16.0$ Hz), 2.98 (1H, d, $J(\text{HH}) = 16.0$ Hz) (H_3); 2.08 (1H, d, $J(\text{HH}) = 2.5$ Hz), 2.66 (1H, d, $J(\text{HH}) = 2.3$ Hz), 2.86 (1H, d, $J(\text{HH}) = 2.0$ Hz), 3.41 (1H, s (br)) ($\text{H}_{5,8}$); 7.28–7.48, 7.67–7.94 (20H, m, Ph). $^{13}\text{C NMR}$: δ (CDCl_3) 13.62 (d, $J(\text{CP}) = 27.5$ Hz, C_7), 13.94 (d, $J(\text{CP}) = 3.1$ Hz, C_3), 57.95 (d, $J(\text{CP}) = 13.4$ Hz), 69.17 (s, $\text{C}_{5,8}$), 93.86 (d, $J(\text{CP}) = 3.4$ Hz), 116.01 (s, $\text{C}_{4,6}$), 128.19–133.92 (m, Ph), 137.90–146.37 (m, *ipso* C and C_1), 177.93 (s, C_2), 193.91 (s, CO), 194.15 (d, $J(\text{CP}) = 6.8$ Hz, CO), 195.04 (s, CO), 196.67 (dd, $J(\text{CP}) = 12.4, 5.1$ Hz, CO), 198.43 (s, CO), 198.78 (d, $J(\text{CP}) = 5.3$ Hz, CO), 199.27 (s, CO), 202.33 (d, $J(\text{CP}) = 5.8$ Hz, CO), 215.98 (d, $J(\text{CP}) = 25.1$ Hz, $\mu\text{-CO}$). FAB MS (m/z): 1288, M^+ ; 1260–980, $[M - n\text{CO}]^+$ ($n = 1-11$); 900, $[\text{Ru}_5(\text{dppa}^*)]^+$; 823, $[\text{Ru}_5(\text{dppa}^*) - \text{Ph}]^+$.

Reaction of $\text{Ru}_5(\mu_5\text{-PPh}_2\text{C}_2\text{C}_6\text{H}_8)(\mu\text{-PPh}_2)(\text{CO})_{11}$ with $\text{P}(\text{OMe})_3$

Me_3NO (ca. 4 mg, 0.05 mmol) was added to a solution of **2** (53 mg, 0.041 mmol) and $\text{P}(\text{OMe})_3$ (120 ml of a 0.355 mM solution in tetrahydrofuran, 0.043 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 one major black band (R_f 0.60), which was crystallised ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) to yield $\text{Ru}_5(\mu_5\text{-PPh}_2\text{C}_2\text{C}_6\text{H}_8)(\mu\text{-PPh}_2)(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}$ (**4**) (33 mg, 59%), m.p. 192–194 °C (dec.). Anal. Found: C, 39.05; H, 2.80%; M^+ , 1384. $\text{C}_{45}\text{H}_{37}\text{O}_{13}\text{P}_3\text{Ru}_5$ calc.: C, 39.05; H, 2.69%; M , 1384, IR: $\nu(\text{CO})$ (cyclohexane) 2035sh, 2023vs, 1998sh, 1994s, 1976m, 1959s, 1954sh, 1915vw, 1868w cm^{-1} . $^1\text{H NMR}$: δ (CDCl_3) 0.08 (1H, dd, $J(\text{HH}) = 5.6$ Hz, $J(\text{HP}) = 2.4$ Hz), 0.56 (1H, t, $J(\text{HH}) = 5.6$ Hz) (H_7); 1.45 (1H, d, $J(\text{HH}) = 16.0$ Hz), 3.13 (1H, d, $J(\text{HH}) = 16.0$ Hz) (H_3); 2.01 (1H, d, $J(\text{HH}) = 2.0$ Hz), 2.81 (2H, s), 3.41 (1H, s) ($\text{H}_{5,8}$); 3.31 (9H, d, $J(\text{HP}) = 12.0$ Hz, $\text{P}(\text{OMe})_3$); 7.18–7.49, 7.84–8.05 (20H, 2 \times m, Ph). $^{13}\text{C NMR}$: δ (CDCl_3) 14.25 (d, $J(\text{CP}) = 28.1$ Hz, C_7), 15.05 (s, (br), C_3), 52.64 (d, $J(\text{CP}) = 7.2$ Hz, $\text{P}(\text{OMe})_3$), 57.57 (d, $J(\text{CP}) = 14.8$ Hz), 67.68 (s, $\text{C}_{5,8}$), 92.84 (d, $J(\text{CP}) = 3.4$ Hz), 115.94 (s, $\text{C}_{4,6}$), 127.71–133.78 (m, Ph), 138.37–144.60 (m, *ipso* C and C_1), 170.83 (d, $J(\text{CP}) = 5.2$ Hz, C_2), 195.12 (d, $J(\text{CP}) = 6.3$ Hz, CO), 195.36 (d, $J(\text{CP}) = 3.2$ Hz, CO), 196.27 (s, CO), 199.20 (d, $J(\text{CP}) = 5.5$ Hz, CO), 200.10 (m, CO), 200.63 (s, CO), 203.49 (d, $J(\text{CP}) = 5.4$ Hz, CO), 205.60 (d, $J(\text{CP}) = 24.5$ Hz, CO), 217.84 (d, $J(\text{CP}) = 25.1$ Hz, $\mu\text{-CO}$). FAB MS: 1384, M^+ ; 1356–1160, $[M - n\text{CO}]^+$ ($n = 1-8$).

Crystallography

A unique data set was measured at ca. 295 K within the limit $2\theta_{\text{max}} = 50^\circ$ using an Enraf–Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo-K_α radiation, λ 0.7107(3) Å); 4325 independent reflections were obtained, 3912 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. Conventional residuals R, R' on $|F|$ arc 0.031, 0.034 (both chiralities), using statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) +$

$0.0004\sigma^4(I_{\text{diff}})$. Computation used the XTAL 3.0 program system [10] implemented by S.R. Hall; neutral atom complex scattering factors were employed.

Crystal and refinement data

$\text{Ru}_5(\mu_5\text{-PPh}_2\text{C}_2\text{C}_6\text{H}_8)(\mu\text{-PPh}_2)(\text{CO})_{10}\{\text{P}(\text{OMe})_3\} \equiv \text{C}_{45}\text{H}_{37}\text{O}_{13}\text{P}_3\text{Ru}_5$, $M = 1384.1$. Monoclinic, space group $P2_1$, No. 4, $a = 13.002(5)$, $b = 17.536(6)$, $c = 10.525(4)$ Å, $\beta = 99.36(3)^\circ$, $V = 2368$ Å³, $Z = 2$, $\rho_c = 1.94$ g cm⁻³, $F(000) = 1352$. Crystal dimensions: $0.29 \times 0.34 \times 0.20$ mm, $\mu(\text{Mo-K}\alpha) = 15.6$ cm⁻¹, $A^*(\text{min, max}) = 1.20, 1.38$.

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