Journal of Organometallic Chemistry, 423 (1992) 105–118
Elsevier Sequoia S.A., Lausanne
JOM 22228

Cluster chemistry

LXXVII. * Carbide clusters from $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and $Fe_2(CO)_9$: X-ray structures of $MRu_4(\mu_5\text{-}C)(\mu\text{-}dppm)(CO)_{13} \cdot 0.5CH_2Cl_2$ (M = Fe and Ru) and $FeRu_5(\mu_6\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{13}(PMe_2Ph)$

Chris J. Adams, Michael I. Bruce *

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001 (Australia)

Brian W. Skelton and Allan H. White

Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6009 (Australia)

(Received July 12, 1991)

Abstract

Five complexes have been isolated from the reaction between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**) and $Fe_2(CO)_9$, including the previously described isomer of (**1**), $Ru_5(\mu_5\text{-}C_2Ph)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)(CO)_{13}$, and the dicarbido complex $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}$. Three minor products were identified by X-ray crystallography as the phosphido-bridged pentanuclear clusters $MRu_4(\mu_5\text{-}C)(\mu\text{-}dppm)(CO)_{13}$ (M = Fe and Ru) and the hexanuclear $FeRu_5(\mu_6\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{14}$; the latter was structurally characterised as its mono-PMe_2Ph derivative. Likely routes leading to the formation of these complexes are discussed.

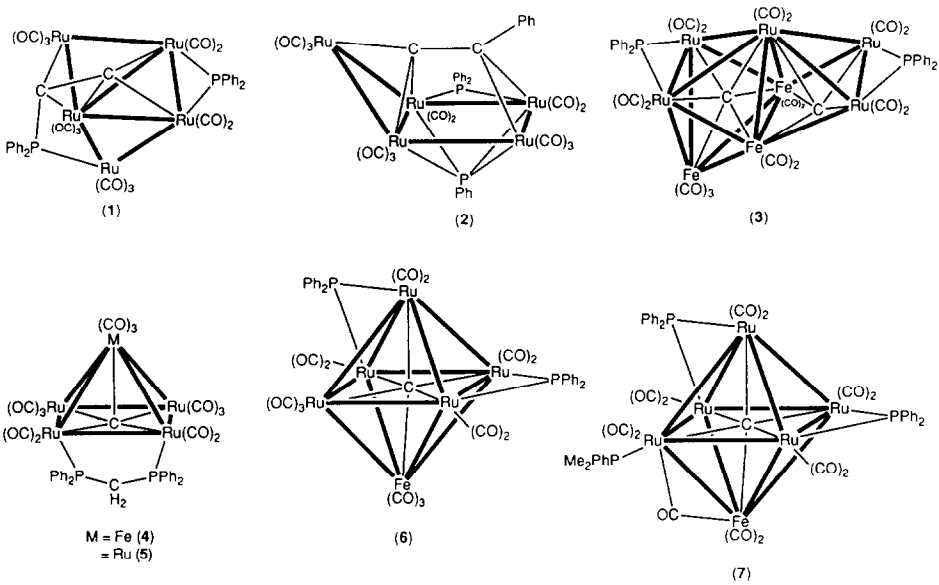
Introduction

The reactions of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**) are characterised by facile modification of the diphenylphosphino-acetylide ligand. Thus we have reported the formation of several complexes in which the C–H or P–C(*sp*) bonds have been cleaved, and in particular ones in which formal elimination of PPh to the cluster has occurred as in **2**, [2]. More recently, we have also described the formation of the octanuclear dicarbido cluster $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}$ (**3**), in which the C≡C bond of the ligand has also been broken [3]. In the latter reaction, the dppa ligand, from which **1** is derived, has been divided up thus:

$$Ph_2P\text{–}C{\equiv}C\text{–}PPh_2 \rightarrow Ph_2P + C + C + PPh_2$$

* For Part LXXVI see ref. 1.

0022-328X/92/$05.00 © 1992 – Elsevier Sequoia S.A. All rights reserved



From this reaction three other complexes were also obtained which have now been characterised by X-ray structural studies, together with an isomer of **1**, which we have described elsewhere [4].

Results and discussion

As described before [3], the reaction between **1** and $Fe_2(CO)_9$ was carried out in toluene for 40 h at 100 °C. In addition to **3** and an isomer of **1**, namely $Ru_5(\mu_5\text{-}C_2Ph)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)(CO)_{13}$ (**2**) [4], three complexes were obtained, two of which required repeated preparative TLC for complete separation. Since the compositions of these materials were not obvious from the normal analytical results, these compounds were characterised by X-ray crystallographic studies, and found to be the pentanuclear carbido clusters $MRu_4(\mu_5\text{-}C)(\mu\text{-dppm})(CO)_{13}$ (**4**; M = Fe) and (**5**; M = Ru) and the hexanuclear $FeRu_5(\mu_6\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{14}$ (**6**). In the latter case, crystals of the unsubstituted complex suitable for X-ray studies could not be obtained, and the structural study was carried out with the PMe_2Ph-substituted complex (**7**).

Molecular structures of $MRu_4(\mu_5\text{-}C)(\mu\text{-dppm})(CO)_{13}$ (4; M = Fe) and (5; M = Ru)

A plot of the two independent molecules of **5** is shown in Fig. 1; those of **4** are virtually identical. Collected structural parameters are given in Table 1. The two crystals were isomorphous; of the consistent, non-trivial and significant differences between the two independent molecules of each complex, perhaps the most interesting is in the angle Ru(4)–Ru(1)–P(1), presumably a consequence of the different pitch of phenyl ring 12 of the ligand.

Both complexes are derivatives of the well-known $M_5C(CO)_{15}$ structures, with the Fe atom occupying the apical site in the square pyramidal core in **4**; all metal

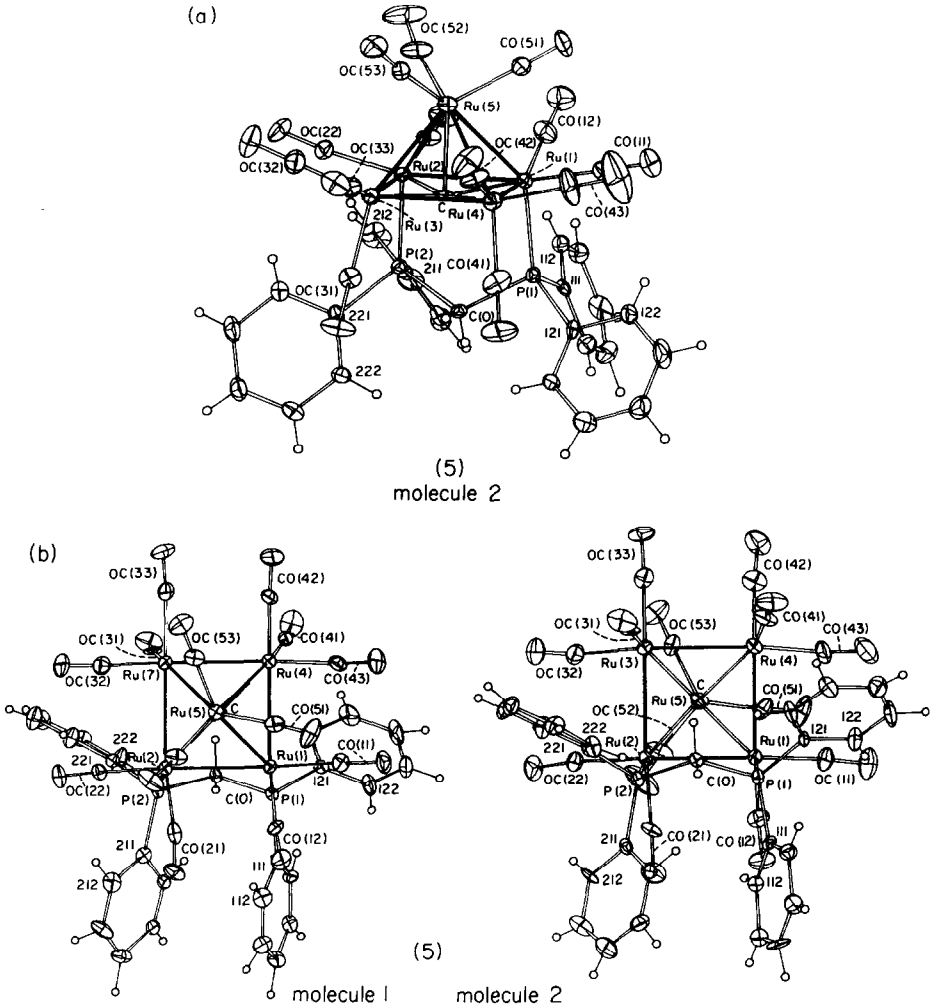


Fig. 1. Projections of $Ru_5C(\mu\text{-dppm})(CO)_{13}$ (**5**), (a) oblique and (b) normal to the Ru_4 plane, showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

atoms are Ru in **5**. Differences in the apical-basal M–Ru bond lengths are in accord with the differences in the atomic radii of Fe and Ru. Thus the average Fe–Ru length is 2.72(7) Å in **4**, compared with a value of 2.79(8) Å for the average Ru(ap)–Ru(bas) length in **5**, 2.82(2) (molecule 1) and 2.83(0) Å (molecule 2) in $Ru_5C(CO)_{15}$ [5] and 2.62(6) Å in $Fe_5C(CO)_{15}$ [6]. The carbido C atom occupies the usual site in the middle of the square face, but slightly below the mean planes in both cases (0.16(2) Å (×2) in **4**; 0.18(2) Å (×2) in **5**). The average Ru(bas)–C separations are 2.02 Å in **4**, 2.05 Å in **5**; as expected, the M(ap)–C distance is somewhat longer for the Ru_5 complex (2.00(2) Å (×2) in both molecules of **4**, 2.12(1), 2.11(1) Å in **5**).

The dppm ligand bridges an edge of the square and occupies an axial site on each Ru atom (Ru–P 2.314(6)–2.331(6) Å in **4**, 2.312(4)–2.320(4) Å in **5**). The

Table 1

Selected bond lengths (Å) and angles (°) for $MRu_4C(\mu\text{-dppm})(CO)_{13}$ (**4**, M = Fe; **5**, M = Ru)

	M = Fe (**4**)		M = Ru (**5**)	
Ru(1)–Ru(2)	2.858(3)	2.850(3)	2.854(1)	2.840(2)
Ru(1)–Ru(4)	2.859(3)	2.854(3)	2.869(2)	2.868(2)
Ru(2)–Ru(3)	2.866(3)	2.870(3)	2.866(2)	2.863(2)
Ru(3)–Ru(4)	2.834(3)	2.823(3)	2.837(2)	2.832(2)
M(5)–Ru(1)	2.760(3)	2.732(3)	2.821(2)	2.803(2)
M(5)–Ru(2)	2.718(3)	2.753(3)	2.808(2)	2.821(2)
M(5)–Ru(3)	2.713(3)	2.732(3)	2.800(2)	2.791(2)
M(5)–Ru(4)	2.713(3)	2.697(3)	2.768(2)	2.774(2)
Ru(1)–P(1)	2.320(6)	2.314(6)	2.316(4)	2.320(4)
Ru(2)–P(2)	2.331(6)	2.327(6)	2.312(4)	2.313(4)
Ru(1)–C	2.01(2)	2.03(2)	2.01(1)	2.08(1)
Ru(2)–C	2.03(2)	2.01(2)	2.06(1)	2.03(1)
Ru(3)–C	2.01(2)	2.00(2)	2.01(1)	1.94(1)
Ru(4)–C	2.05(2)	2.05(2)	2.03(2)	2.04(1)
M(5)–C	2.00(2)	2.00(2)	2.12(1)	2.11(1)
P(1)–C(0)	1.78(2)	1.89(2)	1.84(1)	1.85(1)
P(2)–C(0)	1.85(2)	1.78(2)	1.85(1)	1.82(1)
Ru(2)–Ru(1)–Ru(4)	90.62(7)	90.26(8)	90.53(5)	90.37(5)
Ru(1)–Ru(2)–Ru(3)	88.84(8)	89.19(8)	89.08(5)	89.47(5)
Ru(2)–Ru(3)–Ru(4)	90.97(8)	90.47(8)	90.94(5)	90.63(5)
Ru(3)–Ru(4)–Ru(1)	89.45(8)	90.07(8)	89.34(5)	89.52(5)
Ru(1)–M(5)–Ru(3)	94.1(1)	94.6(1)	91.09(6)	91.70(6)
Ru(2)–M(5)–Ru(4)	96.9(1)	95.7(1)	93.64(6)	92.73(6)
Ru(2)–Ru(1)–P(1)	90.7(2)	91.8(2)	91.1(1)	91.5(1)
Ru(4)–Ru(1)–P(1)	108.8(2)	103.1(2)	108.6(1)	102.8(1)
Ru(1)–Ru(2)–P(2)	95.3(2)	95.4(2)	95.6(1)	95.5(1)
Ru(3)–Ru(2)–P(2)	102.4(2)	102.1(2)	102.8(1)	102.6(1)
Ru(1)–C–Ru(3)	172(1)	171(1)	171.3(7)	170.6(8)
Ru(2)–C–Ru(4)	169(1)	170(1)	168.1(7)	169.0(8)
M(5)–C–Ru(1)	87.0(9)	85.3(8)	86.0(5)	83.8(5)
M(5)–C–Ru(2)	84.8(9)	86.7(8)	84.4(5)	85.7(5)
M(5)–C–Ru(3)	85.2(8)	86.2(8)	85.3(5)	86.8(5)
M(5)–C–Ru(4)	84.0(8)	83.5(8)	83.7(5)	83.9(5)
Ru(1)–P(1)–C(0)	110.4(7)	110.4(7)	109.8(5)	111.1(4)
Ru(2)–P(2)–C(0)	106.6(7)	108.4(7)	107.4(5)	108.2(5)
P(1)–C(0)–P(2)	118(1)	118(1)	116.2(8)	116.5(8)

For **4**:	Ru–CO	range 1.83–1.91, av. 1.86 Å
	Fe–CO	range 1.64–1.83, av. 1.79 Å
	C–O	range 1.12–1.20, av. 1.17 Å
	P–C(Ph)	range 1.81–1.83, av. 1.82 Å
	M–C–O	range 169–178, av. 174°
For **5**:	Ru–CO	range 1.79–1.91, av. 1.875 Å
	C–O	range 1.10–1.18, av. 1.15 Å
	P–C(Ph)	range 1.81–1.85, av. 1.83 Å
	Ru–C–O	range 170–180, av. 175°

bridged Ru–Ru edges do not differ significantly from the average Ru–Ru separation (2.85(5) Å), which are the same in both complexes. The remaining coordination sites are occupied by terminal CO groups.

The IR spectra of both complexes are similar, differences of only 1 or 2 cm^{-1} being found between corresponding bands in the all-terminal ν(CO) spectra. In the ^1H NMR spectrum, the CH_2 resonances of the dppm ligands were found at δ 3.81 and 4.13 for **4**, and δ 3.83 and 4.14 for **5**. The FAB mass spectra contained molecular ions at m/z 1223 and 1266, respectively, which decomposed by loss of up to thirteen CO groups.

Previous studies of the substitution of CO by tertiary phosphines in $Ru_5C(CO)_{15}$ have shown that the first PR_3 ligand replaces an axial CO on a basal Ru atom; the second goes into a similar site on the Ru atom diagonally opposite [7]. When chelating tertiary diphosphines are used, the substitution pattern appears to depend on the separation of the two P atoms (or bite). Thus for dppb, an X-ray structural study [8] showed that the phosphine bridged the square face, the two P atoms being attached to diagonally opposite Ru atoms, as also found for $Ru_5C(CO)_{13}(PPh_3)_2$ [7]. An associated IR study suggested that for diphosphines with shorter bridges, mixtures of isomers were formed, the diphosphine chelating one of the basal Ru atoms. In no case was any evidence adduced for an edge-bridging role for the diphosphine, even though such a coordination mode had been observed in Ru_3, Ru_4 and Ru_6 clusters previously.

The complexes described in the present work have been shown to have the edge-bridging structure. As far as we can tell, their IR spectra are similar to those shown by the dppm, dppe and dppp complexes reported earlier, and this raises the possibility that the latter also have the edge-bridging rather than chelating structure originally suggested or that a chelate-bridging equilibrium occurs, as found for $Ru_4(\mu\text{-H})_4(\mu\text{-LL})(CO)_{10}$ (LL = dppm, dppe) [9].

In the present case, the formation of dppm from the elements of dppa present in **1** is the first example we have come across, in this system, of reformation of a P–C bond to give a bidentate ligand

$$Ph_2PC{\equiv}C + PPh_2 \xrightarrow{2H} Ph_2PCH_2PPh_2 + C$$

The source of the hydrogen atoms is not obvious; however, we suspect that the $Fe_2(CO)_9$ contained residual water and, given the low yields of **4** and **5**, this provides a possible source of the required H atoms. A control experiment, running the original reaction with an added equivalent of water, showed that while the yield of **5** was marginally increased, neither **6** nor the isomer **2** was obtained; the yield of **3** was drastically reduced. The nature of the major product from this reaction has yet to be determined.

Molecular structure of $FeRu_5(\mu_6\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{13}(PMe_2Ph)$ (7)

Figure 2 depicts a molecule of **7** and Table 2 contains selected bond lengths and angles. As can be seen, the structure is based on that of the well-known $Ru_6C(CO)_{17}$ carbido cluster, with one of the rutheniums replaced by an iron atom. Two of the edges are bridged by PPh_2 groups, and the PMe_2Ph ligand occupies an equatorial site on Ru(3). Of the thirteen CO groups, only one, CO(62), is found bridging an M–M vector.

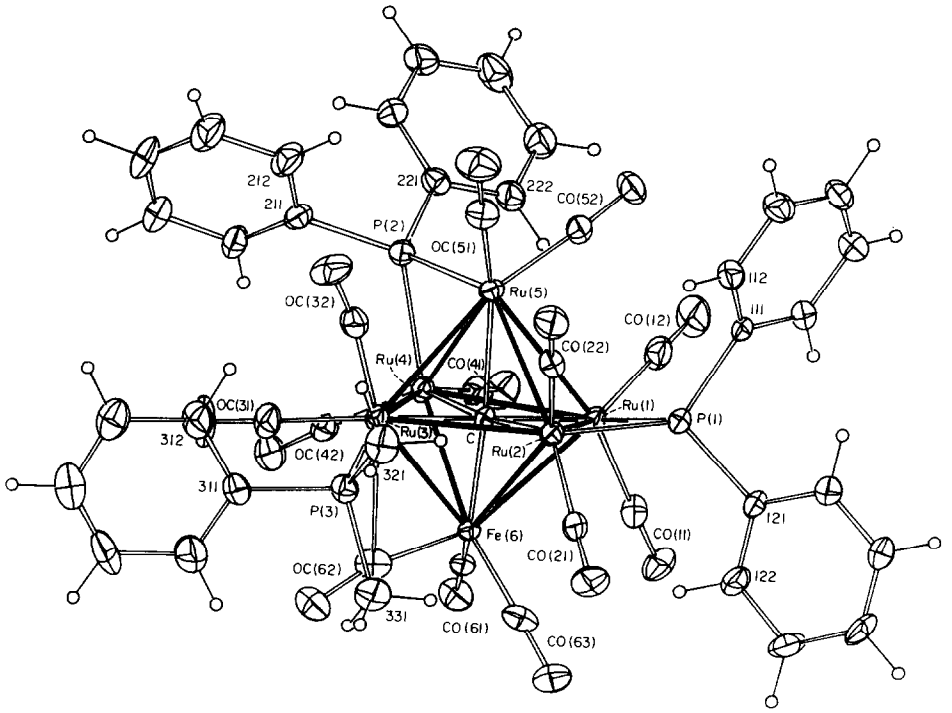


Fig. 2. Projection of a molecule of $FeRu_5C(\mu\text{-}PPh_2)_2(CO)_{13}(PMe_2Ph)$ (7), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

Table 2

Selected bond lengths (Å) and angles (°) for $FeRu_5C(\mu\text{-}PPh_2)_2(CO)_{13}(PMe_2Ph)$ (7)

Ru(1)–Ru(2)	2.790(2)	Ru(2)–P(1)	2.295(4)
Ru(1)–Ru(4)	2.940(2)	Ru(4)–P(2)	2.295(4)
Ru(1)–Ru(5)	2.966(2)	Ru(5)–P(2)	2.346(4)
Ru(2)–Ru(3)	2.939(2)	Ru(3)–P(3)	2.368(4)
Ru(2)–Ru(5)	2.919(2)	Ru(1)–C	2.08(1)
Ru(3)–Ru(4)	2.928(2)	Ru(2)–C	2.00(1)
Ru(3)–Ru(5)	2.940(2)	Ru(3)–C	2.05(1)
Ru(4)–Ru(5)	2.776(2)	Ru(4)–C	2.07(1)
Fe(6)–Ru(1)	2.824(2)	Ru(5)–C	2.10(1)
Fe(6)–Ru(2)	2.900(2)	Fe(6)–C	1.88(1)
Fe(6)–Ru(3)	2.754(2)	Fe(6)–C(62)	1.73(2)
Fe(6)–Ru(4)	2.771(2)	Ru(3)–C(62)	2.59(1)
Ru(1)–P(1)	2.293(3)	C(62)–O(62)	1.21(2)
Ru(1)–C–Ru(3)	179.2(6)	Ru(3)–C(62)–O(62)	119 (1)
Ru(5)–C–Fe(6)	172.3(6)	Fe(6)–C(62)–O(62)	164 (1)
Ru(2)–C–Ru(4)	173.4(7)		
Fe–CO	1.75, 1.76(2)		
Ru–CO	range 1.83–1.93(2), av. 1.88 Å		
C–O	range 1.11–1.18(2), av. 1.145 Å		
P–C(Ph)	range 1.81–1.85(1), av. 1.83 Å		

Table 3

Crystal data and refinement details for **4**, **5**, and **7**

Compound	**4**	**5**	**7**
Formula	$C_{39}H_{22}FeO_{13}P_2Ru_4 \cdot 0.5CH_2Cl_2$	$C_{39}H_{22}O_{13}P_2Ru_5 \cdot 0.5CH_2Cl_2$	$C_{46}H_{31}FeO_{13}P_3Ru_5$
MW	1263.1	1308.4	1445.9
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)
a (Å)	10.729(4)	10.796(6)	21.314(8)
b (Å)	39.935(7)	39.891(12)	11.016(4)
c (Å)	10.046(1)	10.054(4)	10.719(4)
α (deg)	90	90	85.34(3)
β (deg)	93.20(2)	93.50(4)	85.97(3)
γ (deg)	90	90	81.40(3)
U (Å^3)	4298	4321	2477
Z	4	4	2
D_c (g cm^{-3})	1.95	2.01	1.94
$F(000)$	2452	2524	2808
Crystal size (mm)	0.30×0.15×0.08	0.19×0.13×0.28	0.29×0.48×0.23
A^*(min, max)	1.18, 1.29	1.20, 1.30	1.42, 1.63
μ (cm^{-1})	17.5	17.8	17.5
$2\theta_{max}$ (deg)	45	50	50
N	7658	7688	8486
N_o	5348	6456	6129
R	0.064	0.047	0.067
R_w	0.067	0.052	0.075

There do not seem to be any other examples of structurally characterised Ru_6C clusters with bridging phosphido ligands. The Ru–Ru bonds in **7** fall into short and long categories. The former comprise Ru(1)–Ru(2) and Ru(4)–Ru(5) [2.790(2), 2.776(2) Å], the edges bridged by the μ-PPh_2 groups (cf. 2.721(1) Å in $Ru_5C(\mu$-$H)(\mu$-$PPh_2)(CO)_{13}$ [9]). Of the latter, P(1) symmetrically bridges the two metal atoms [2.293, 2.295(3) Å], while P(2) is less symmetrically situated, with Ru(4)–P(2) [2.295(4) Å] rather shorter than Ru(5)–P(2) [2.346(4) Å]. The longer Ru–Ru bonds lie between 2.928 and 2.966(2) Å [av. 2.94 Å], with bonds to the PMe_2Ph-substituted Ru(3) atom between 2.928 and 2.940(2) Å. In $Ru_6C(CO)_{17}$ [10] and $Ru_6C(CO)_{16}(PEtPh_2)$ [11], the average Ru–Ru separations are 2.90 and 2.91 Å, respectively, although bonds to the substituted ruthenium atom in the latter average 2.96 Å. Bonds from the iron atom to the four rutheniums forming the square plane range from 2.754 to 2.900(2) Å, the shortest bearing the semi-bridging CO group [Fe(6)–C(62) 1.73(2), Ru(3)–C(62) 2.59(1) Å, Fe(6)–C(62)–O(62) 164(1)°]. The other distances reflect the asymmetry in attachment of the iron atom to the Ru_4 square face, also shown by the non-linear arrangement of Fe(6)–C–Ru(5) [172.3(6)°]. The PMe_2Ph ligand is attached to Ru(3) [2.368(4) Å]. The interstitial carbide is approximately at the centre of the octahedron and is bonded to all six metal atoms [Fe–C 1.88(1), Ru–C 2.00–2.10(1) Å]; Ru(2)–C–Ru(4) is also noticeably non-linear, at 173.3(7)°.

We assume that the precursor **6** is $FeRu_5C(\mu$-$PPh_2)_2(CO)_{14}$, as suggested by its FAB mass spectrum, which shows a molecular ion at m/z 1336 and fragment ions

Table 4

Non-hydrogen atomic coordinates and isotropic thermal parameters for $FeRu_4C(\mu\text{-dppm})(CO)_{13}$ (**4**) and $Ru_5C(\mu\text{-dppm})(CO)_{13}$ (**5**)

Atom	**4**			**5**		
	x	*y*	*z*	*x*	*y*	*z*
Molecule 1						
Ru(1)	0.9413(2)	1/2	0.1322(2)	0.9397(1)	1/2	0.1347(1)
Ru(2)	0.9758(2)	0.42911(5)	0.1471(2)	0.9734(1)	0.42911(3)	0.1503(1)
Ru(3)	1.0567(2)	0.43651(5)	0.4223(2)	1.0546(1)	0.43634(3)	0.4255(1)
Ru(4)	1.0333(2)	0.50705(5)	0.4034(2)	1.0317(1)	0.50707(3)	0.4070(1)
M(5)	1.1633(3)	0.47157(8)	0.2272(3)	1.1694(1)	0.47247(4)	0.2285(1)
C	0.987(2)	0.4675(6)	0.280(2)	0.984(1)	0.4681(4)	0.285(1)
C(11)	0.929(2)	0.5472(7)	0.126(3)	0.925(2)	0.5470(4)	0.132(2)
O(11)	0.913(2)	0.5761(4)	0.122(2)	0.911(1)	0.5757(3)	0.124(2)
C(12)	0.973(2)	0.5044(6)	−0.048(2)	0.975(1)	0.5023(4)	−0.052(2)
O(12)	1.007(2)	0.5065(5)	−0.156(2)	1.006(1)	0.5056(3)	−0.155(1)
C(21)	0.966(2)	0.4327(7)	−0.043(3)	0.964(1)	0.4323(4)	−0.034(2)
O(21)	0.967(2)	0.4314(5)	−0.157(2)	0.967(1)	0.4305(3)	−0.145(1)
C(22)	1.031(2)	0.3868(6)	0.133(2)	1.034(1)	0.3854(4)	0.140(2)
O(22)	1.072(2)	0.3594(5)	0.125(2)	1.073(1)	0.3588(3)	0.125(1)
C(31)	0.916(3)	0.4238(7)	0.510(3)	0.915(2)	0.4241(5)	0.511(1)
O(31)	0.821(2)	0.4193(6)	0.568(2)	0.826(1)	0.4192(4)	0.568(1)
C(32)	1.135(3)	0.3954(8)	0.408(3)	1.127(2)	0.3950(5)	0.413(2)
O(32)	1.186(2)	0.3712(6)	0.402(2)	1.179(1)	0.3691(3)	0.407(1)
C(33)	1.146(2)	0.4429(6)	0.585(2)	1.149(2)	0.4432(4)	0.595(2)
O(33)	1.206(2)	0.4426(5)	0.686(2)	1.207(1)	0.4447(4)	0.689(1)
C(41)	0.897(2)	0.5137(6)	0.508(3)	0.894(1)	0.5149(4)	0.514(2)
O(41)	0.815(2)	0.5160(5)	0.580(2)	0.812(1)	0.5172(4)	0.582(2)
C(42)	1.151(2)	0.5138(7)	0.540(3)	1.151(2)	0.5139(4)	0.548(2)
O(42)	1.220(2)	0.5180(6)	0.634(2)	1.224(1)	0.5195(4)	0.634(1)
C(43)	1.063(3)	0.5527(7)	0.369(3)	1.060(2)	0.5538(5)	0.371(2)
O(43)	1.096(2)	0.5803(5)	0.356(2)	1.088(2)	0.5808(3)	0.355(2)
C(51)	1.214(2)	0.5112(6)	0.156(2)	1.218(1)	0.5137(5)	0.160(2)
O(51)	1.255(2)	0.5354(5)	0.110(2)	1.254(1)	0.5383(4)	0.111(2)
C(52)	1.213(3)	0.4477(7)	0.108(3)	1.220(2)	0.4442(5)	0.095(2)
O(52)	1.266(2)	0.4310(5)	0.024(2)	1.269(1)	0.4272(4)	0.019(1)
C(53)	1.290(3)	0.4652(8)	0.341(3)	1.303(1)	0.4641(5)	0.346(2)
O(53)	1.386(2)	0.4599(5)	0.404(2)	1.393(1)	0.4590(4)	0.414(1)
C(0)	0.687(2)	0.4556(5)	0.209(2)	0.686(1)	0.4548(3)	0.214(1)
P(1)	0.7263(5)	0.4933(2)	0.1271(6)	0.7261(3)	0.4939(1)	0.1291(4)
C(111)	0.632(2)	0.4908(5)	−0.029(2)	0.635(1)	0.4918(4)	−0.030(2)
C(112)	0.685(2)	0.4816(6)	−0.143(2)	0.685(1)	0.4815(5)	−0.148(2)
C(113)	0.616(2)	0.4762(7)	−0.264(2)	0.611(2)	0.4772(5)	−0.257(2)
C(114)	0.483(2)	0.4798(6)	−0.263(3)	0.485(2)	0.4821(4)	−0.261(2)
C(115)	0.432(2)	0.4911(6)	−0.150(2)	0.433(1)	0.4913(4)	−0.144(2)
C(116)	0.502(2)	0.4949(6)	−0.026(2)	0.507(1)	0.4964(4)	−0.035(1)
C(121)	0.639(2)	0.5248(6)	0.216(2)	0.640(1)	0.5253(4)	−0.223(1)
C(122)	0.621(3)	0.5573(7)	0.164(3)	0.623(2)	0.5562(5)	0.163(2)
C(123)	0.552(2)	0.5806(7)	0.220(3)	0.559(2)	0.5802(5)	0.225(2)
C(124)	0.499(3)	0.5746(7)	0.332(3)	0.506(2)	0.5738(5)	0.344(2)
C(125)	0.518(3)	0.5439(8)	0.393(3)	0.522(2)	0.5432(6)	0.403(2)
C(126)	0.583(2)	0.5181(6)	0.329(2)	0.588(2)	0.5181(5)	0.339(2)
P(2)	0.7646(5)	0.4165(1)	0.1591(6)	0.7652(4)	0.4165(1)	0.1602(4)
C(211)	0.678(2)	0.4025(5)	0.010(2)	0.683(1)	0.4017(4)	0.010(1)
C(212)	0.739(2)	0.3805(7)	−0.080(3)	0.740(2)	0.3804(5)	−0.077(2)

Table 4 (continued)

Atom	**4**			**5**		
	x	*y*	*z*	*x*	*y*	*z*
C(213)	0.679(3)	0.3691(7)	−0.194(3)	0.680(2)	0.3694(5)	−0.187(2)
C(214)	0.554(2)	0.3794(7)	−0.225(3)	0.560(2)	0.3779(5)	−0.229(2)
C(215)	0.498(2)	0.3990(6)	−0.141(2)	0.505(2)	0.3991(4)	−0.137(2)
C(216)	0.558(2)	0.4105(6)	−0.024(2)	0.560(1)	0.4109(4)	−0.031(2)
C(221)	0.713(2)	0.3858(6)	0.278(2)	0.713(1)	0.3854(4)	0.279(1)
C(222)	0.593(3)	0.3857(7)	0.326(3)	0.594(2)	0.3867(5)	0.317(2)
C(223)	0.556(2)	0.3607(7)	0.406(3)	0.554(2)	0.3610(5)	0.406(2)
C(224)	0.631(2)	0.3365(6)	0.447(3)	0.627(2)	0.3369(5)	0.445(2)
C(225)	0.745(3)	0.3355(7)	0.404(3)	0.746(2)	0.3352(5)	0.410(2)
C(226)	0.795(2)	0.3599(6)	0.321(2)	0.791(2)	0.3609(5)	0.329(2)
Molecule 2						
Ru(1)	0.8398(2)	0.66178(5)	0.5970(2)	0.8422(1)	0.66225(3)	0.6005(1)
Ru(2)	0.8688(2)	0.73241(5)	0.6257(2)	0.8704(1)	0.73269(3)	0.6300(1)
Ru(3)	0.9442(2)	0.72259(5)	0.9016(2)	0.9465(1)	0.72305(3)	0.9051(1)
Ru(4)	0.9194(2)	0.65261(6)	0.8704(2)	0.9217(1)	0.65273(3)	0.8753(1)
M(5)	1.0568(3)	0.68862(8)	0.7050(3)	1.0668(1)	0.68890(4)	0.7078(1)
C	0.879(2)	0.6934(5)	0.752(2)	0.882(1)	0.6941(4)	0.762(1)
C(11)	0.845(2)	0.6180(7)	0.559(3)	0.851(2)	0.6173(5)	0.567(2)
O(11)	0.854(2)	0.5880(6)	0.530(2)	0.854(2)	0.5899(4)	0.538(2)
C(12)	0.866(3)	0.6649(7)	0.413(3)	0.873(2)	0.6641(5)	0.428(2)
O(12)	0.891(2)	0.6646(5)	0.306(2)	0.895(1)	0.6645(4)	0.309(1)
C(21)	0.865(2)	0.7340(6)	0.439(2)	0.866(1)	0.7345(5)	0.440(2)
O(21)	0.859(2)	0.7367(5)	0.325(2)	0.862(1)	0.7364(4)	0.326(1)
C(22)	0.925(2)	0.7773(6)	0.627(2)	0.927(2)	0.7778(4)	0.633(2)
O(22)	0.966(2)	0.8045(5)	0.614(2)	0.965(1)	0.8044(3)	0.620(1)
C(31)	0.798(2)	0.7332(6)	0.992(2)	0.801(2)	0.7341(5)	0.996(1)
O(31)	0.713(2)	0.7406(5)	1.043(2)	0.714(1)	0.7404(4)	1.051(1)
C(32)	1.014(3)	0.7641(7)	0.894(3)	1.021(2)	0.7670(5)	0.894(2)
O(32)	1.064(2)	0.7911(6)	0.895(2)	1.070(2)	0.7914(4)	0.901(2)
C(33)	1.030(3)	0.7158(8)	1.070(3)	1.041(2)	0.7162(5)	1.063(2)
O(33)	1.097(2)	0.7127(5)	1.165(2)	1.097(1)	0.7134(4)	1.164(1)
C(41)	0.785(3)	0.6453(7)	0.972(3)	0.787(2)	0.6461(6)	0.984(2)
O(41)	0.707(2)	0.6414(6)	1.044(2)	0.704(1)	0.6424(5)	1.047(1)
C(42)	1.035(3)	0.6450(8)	1.014(3)	1.040(2)	0.6451(6)	1.014(2)
O(42)	1.111(2)	0.6379(6)	1.098(2)	1.114(1)	0.6387(4)	1.092(2)
C(43)	0.919(4)	0.608(1)	0.826(4)	0.935(3)	0.6087(5)	0.830(2)
O(43)	0.941(3)	0.5790(9)	0.803(3)	0.949(3)	0.5802(5)	0.814(2)
C(51)	1.099(3)	0.6563(8)	0.661(3)	1.123(2)	0.6474(5)	0.646(2)
O(51)	1.150(2)	0.6279(6)	0.609(2)	1.160(1)	0.6222(4)	0.614(2)
C(52)	1.106(3)	0.7132(8)	0.584(3)	1.125(2)	0.7176(6)	0.572(2)
O(52)	1.160(2)	0.7317(6)	0.503(2)	1.167(1)	0.7310(5)	0.488(2)
C(53)	1.185(2)	0.6974(6)	0.817(2)	1.198(1)	0.7002(4)	0.830(2)
O(53)	1.270(2)	0.7027(5)	0.886(2)	1.284(1)	0.7061(4)	0.898(1)
C(0)	0.580(2)	0.7064(6)	0.684(2)	0.584(1)	0.7058(3)	0.689(1)
P(1)	0.6251(5)	0.6658(2)	0.6034(6)	0.6284(4)	0.6664(1)	0.6072(4)
C(111)	0.526(2)	0.6663(6)	0.448(2)	0.529(1)	0.6659(4)	0.456(1)
C(112)	0.572(2)	0.6781(6)	0.330(2)	0.575(1)	0.6767(4)	0.339(2)
C(113)	0.493(2)	0.6810(7)	0.220(3)	0.499(2)	0.6804(5)	0.217(2)
C(114)	0.371(2)	0.6713(6)	0.224(2)	0.378(2)	0.6712(5)	0.227(2)
C(115)	0.327(3)	0.6602(7)	0.331(3)	0.329(2)	0.6595(5)	0.342(2)
C(116)	0.402(2)	0.6569(6)	0.450(2)	0.404(2)	0.6572(4)	0.461(2)
C(121)	0.551(2)	0.6340(6)	0.704(2)	0.554(1)	0.6353(3)	0.713(1)
C(122)	0.566(3)	0.6004(7)	0.681(3)	0.576(2)	0.6018(4)	0.687(2)

Table 4 (continued)

Atom	4			5		
	x	*y*	*z*	*x*	*y*	*z*
C(123)	0.514(3)	0.5771(7)	0.757(3)	0.519(2)	0.5782(5)	0.757(2)
C(124)	0.434(3)	0.5863(7)	0.854(3)	0.442(2)	0.5859(5)	0.856(2)
C(125)	0.413(2)	0.6169(7)	0.876(3)	0.421(2)	0.6185(5)	0.881(2)
C(126)	0.474(2)	0.6417(7)	0.802(3)	0.478(2)	0.6434(4)	0.811(2)
P(2)	0.6567(5)	0.7437(2)	0.6355(6)	0.6607(4)	0.7439(1)	0.6374(4)
C(211)	0.576(2)	0.7585(6)	0.480(2)	0.579(1)	0.7580(4)	0.487(1)
C(212)	0.626(2)	0.7825(7)	0.407(3)	0.633(2)	0.7826(4)	0.408(2)
C(213)	0.562(3)	0.7938(8)	0.289(3)	0.568(2)	0.7937(6)	0.296(2)
C(214)	0.449(3)	0.7818(7)	0.256(3)	0.456(2)	0.7813(5)	0.260(2)
C(215)	0.387(2)	0.7590(6)	0.329(3)	0.398(2)	0.7589(5)	0.330(2)
C(216)	0.451(2)	0.7472(6)	0.445(2)	0.460(2)	0.7468(4)	0.446(1)
C(221)	0.603(2)	0.7743(5)	0.752(2)	0.604(2)	0.7742(4)	0.754(2)
C(222)	0.481(2)	0.7722(6)	0.791(2)	0.484(2)	0.7735(4)	0.792(2)
C(223)	0.435(2)	0.7961(6)	0.877(2)	0.440(2)	0.7974(5)	0.874(2)
C(224)	0.508(2)	0.8220(7)	0.922(3)	0.513(2)	0.8230(5)	0.922(2)
C(225)	0.623(3)	0.8254(8)	0.886(3)	0.632(2)	0.8249(5)	0.882(2)
C(226)	0.671(2)	0.8000(7)	0.801(3)	0.681(2)	0.8004(5)	0.805(2)
Solvent						
Cl(1)	0.952(1)	0.3072(4)	−0.254(2)	0.959(1)	0.3050(3)	−0.250(1)
Cl(2)	1.143(2)	0.3562(5)	−0.242(2)	1.152(1)	0.3546(3)	−0.223(1)
C	1.093(5)	0.316(1)	−0.182(5)	1.013(4)	0.346(1)	−0.294(5)

corresponding to the loss of up to 14 CO groups. Substitution of a CO group in **6** by PMe_2Ph occurs without change in the metal core geometry, even though the reaction is accompanied by a colour change from orange to dark brown. Substitution of CO by PR_3 in red $Ru_6C(CO)_{17}$ has been reported to occur under mild conditions, giving dark brown mono- and di-substituted complexes, the bridging CO groups being attached to the ruthenium atom adjacent to that bearing the $PEtPh_2$ ligand [11].

In the formation of **6** from **1**, the original dppa ligand suffers a net loss of one carbon atom:

$$Ph_2P\text{-}C{\equiv}C + PPh_2 \xrightarrow{-C} Ph_2P + C + PPh_2$$

At this time we are not able to comment further on the fate of this atom.

Experimental

General reaction conditions were similar to those employed previously in related studies [12]; complex **1** was made by the literature method [13].

Reaction between 1 and $Fe_2(CO)_9$

A reaction between $Fe_2(CO)_9$ (300 mg, 0.82 mmol) and **1** (220 mg, 0.17 mmol) was carried out in toluene (10 ml) at 100 °C for 40 h. After cooling, the residue remaining after removal of solvent was separated by preparative TLC (silica gel; light petroleum/acetone 4 : 1) into six coloured bands. A light brown band (R_f 0.6)

Table 5

Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters for $FeRu_5C(\mu\text{-}PPh_2)_2(CO)_{13}(PMe_2Ph)$ (7)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.32838(5)	0.9032(1)	0.3550(1)	0.0406(4)
Ru(2)	0.34828(5)	0.66010(9)	0.28885(9)	0.0386(4)
Ru(3)	0.21358(5)	0.6667(1)	0.2417(1)	0.0427(4)
Ru(4)	0.19100(5)	0.9146(1)	0.3311(1)	0.0413(4)
Ru(5)	0.25065(5)	0.7248(1)	0.48674(9)	0.0431(4)
Fe(6)	0.27704(8)	0.8521(2)	0.1325(1)	0.0327(6)
C	0.2701(5)	0.785(1)	0.299(1)	0.038(4)
C(11)	0.3596(7)	1.027(1)	0.249(1)	0.060(6)
O(11)	0.3782(5)	1.1034(9)	0.187(1)	0.076(5)
C(12)	0.3380(7)	0.999(2)	0.492(2)	0.069(7)
O(12)	0.3422(6)	1.058(1)	0.569(1)	0.113(7)
C(21)	0.4020(7)	0.606(1)	0.153(1)	0.058(6)
O(21)	0.4361(5)	0.571(1)	0.071(1)	0.081(5)
C(22)	0.3582(6)	0.508(1)	0.375(1)	0.050(5)
O(22)	0.3651(5)	0.411(1)	0.425(1)	0.080(5)
C(31)	0.1263(7)	0.699(1)	0.197(1)	0.066(6)
O(31)	0.0755(5)	0.716(1)	0.172(1)	0.103(6)
C(32)	0.1940(7)	0.542(1)	0.360(1)	0.065(6)
O(32)	0.1774(6)	0.462(1)	0.422(1)	0.093(5)
C(41)	0.1988(6)	1.075(1)	0.370(1)	0.053(5)
O(41)	0.1993(5)	1.1737(9)	0.394(1)	0.076(5)
C(42)	0.1172(6)	0.974(1)	0.242(1)	0.059(6)
O(42)	0.0754(5)	1.015(1)	0.187(1)	0.084(5)
C(51)	0.2502(7)	0.579(1)	0.582(1)	0.065(6)
O(51)	0.2509(6)	0.487(1)	0.645(1)	0.103(6)
C(52)	0.2870(6)	0.778(1)	0.621(1)	0.053(5)
O(52)	0.3082(5)	0.806(1)	0.7095(9)	0.085(5)
C(61)	0.2516(6)	1.009(1)	0.095(1)	0.052(6)
O(61)	0.2351(5)	1.1117(9)	0.059(1)	0.071(4)
C(62)	0.2252(7)	0.804(1)	0.036(1)	0.060(6)
O(62)	0.1938(5)	0.792(1)	−0.051(1)	0.078(5)
C(63)	0.3408(8)	0.846(1)	0.018(1)	0.066(6)
O(63)	0.3814(5)	0.847(1)	−0.059(1)	0.093(6)
P(1)	0.4193(2)	0.7640(3)	0.3717(3)	0.042(1)
C(111)	0.4459(5)	0.730(1)	0.531(1)	0.044(5)
C(112)	0.4441(6)	0.617(1)	0.596(1)	0.060(6)
C(113)	0.4633(7)	0.599(1)	0.716(1)	0.068(6)
C(114)	0.4863(7)	0.692(2)	0.770(1)	0.083(8)
C(115)	0.4896(7)	0.804(2)	0.710(1)	0.071(7)
C(116)	0.4696(7)	0.820(1)	0.587(1)	0.063(6)
C(121)	0.4930(6)	0.789(1)	0.282(1)	0.045(5)
C(122)	0.4913(6)	0.838(2)	0.162(1)	0.070(6)
C(123)	0.5453(8)	0.850(2)	0.086(1)	0.085(7)
C(124)	0.6037(7)	0.807(2)	0.135(2)	0.081(8)
C(125)	0.6068(7)	0.755(2)	0.254(2)	0.077(7)
C(126)	0.5521(7)	0.745(1)	0.326(1)	0.064(6)
P(2)	0.1505(2)	0.8417(3)	0.5218(3)	0.046(1)
C(211)	0.0767(7)	0.772(1)	0.526(1)	0.055(6)
C(212)	0.0737(8)	0.662(2)	0.595(2)	0.079(7)
C(213)	0.016(1)	0.613(2)	0.598(2)	0.11(1)
C(214)	−0.0352(8)	0.676(2)	0.542(2)	0.097(9)
C(215)	−0.0301(7)	0.780(2)	0.474(2)	0.086(8)

Table 5 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(216)	0.0255(7)	0.830(1)	0.469(1)	0.064(6)
C(221)	0.1367(6)	0.936(1)	0.655(1)	0.051(5)
C(222)	0.1809(7)	1.013(1)	0.672(1)	0.065(6)
C(223)	0.1733(8)	1.083(2)	0.774(2)	0.081(8)
C(224)	0.1206(9)	1.081(2)	0.858(2)	0.092(9)
C(225)	0.0776(8)	1.005(2)	0.839(1)	0.085(8)
C(226)	0.0847(7)	0.936(2)	0.739(1)	0.077(7)
P(3)	0.2404(2)	0.5065(3)	0.1045(3)	0.052(1)
C(311)	0.1706(7)	0.452(1)	0.053(1)	0.054(5)
C(312)	0.1361(8)	0.381(1)	0.133(2)	0.073(7)
C(313)	0.0815(9)	0.340(2)	0.095(2)	0.085(8)
C(314)	0.062(1)	0.372(2)	−0.020(2)	0.11(1)
C(315)	0.093(1)	0.446(3)	−0.096(2)	0.18(2)
C(316)	0.148(1)	0.486(2)	−0.060(2)	0.12(1)
C(321)	0.2832(7)	0.367(1)	0.170(2)	0.074(7)
C(331)	0.2870(7)	0.530(1)	−0.042(1)	0.076(7)

was recrystallised (CH_2Cl_2/MeOH) to give $Ru_5(\mu_5\text{-}C_2Ph)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)(CO)_{13}$ (**2**) (20 mg, 9%), identified by comparison (IR, TLC) with an authentic sample [4]. An orange band (R_f 0.4) was recrystallised (CH_2Cl_2/MeOH) to give $FeRu_5(\mu_6\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{14}$ (**6**) (85 mg, 37%), m.p. > 300 °C (dec.). Anal. Found: C, 34.66; H, 1.62%; [M + H], 1336. $C_{39}H_{20}FeO_{14}P_2Ru_5$ calc.: C, 35.08; H, 1.51%; M, 1335. IR: ν(CO) (cyclohexane) 2066m, 2029s, 2021vs, 2007w, 1996w, 1971w cm^{-1}. FAB MS (m/z): 1336, M^+; 1308–944, $[M - n\text{CO}]^+$ (n = 1–14). A brown band (R_f 0.3) was recrystallised (CH_2Cl_2/MeOH) to give $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}$ (**2**) (92 mg, 35%) [3]. A purple band (R_f 0.2) was recrystallised (CH_2Cl_2/MeOH) to give $Ru_5(\mu_5\text{-}C)(\mu\text{-dppm})(CO)_{13} \cdot 0.5CH_2Cl_2$ (**5**) (9 mg, 4%), m.p. 230–231 °C (dec.). Anal. Found: C, 36.03; H, 1.74%; M (mass spectrometry), 1266. $C_{39}H_{22}O_{13}P_2Ru_5 \cdot 0.5CH_2Cl_2$ calc.: C, 36.26; H, 1.77%; M, 1266. IR: ν(CO) (cyclohexane) 2074m, 2046sh, 2039s, 2026vs, 2009s, 2002s, 1996sh, 1988sh, 1967m, 1951w cm^{-1}. ^{1}H NMR: $\delta(CDCl_3)$ 3.83 (1H, q, J(PH, HH) = 11.5 Hz, CH_2), 4.14 (1H, q, J(PH, HH) = 11.7 Hz, CH_2), 7.23–7.39 (20H, m, Ph). FAB MS (m/z): 1266, M^+; 1182–902, $[M - n\text{CO}]^+$ (n = 3–13). A green band (R_f 0.15) was recrystallised (CH_2Cl_2/MeOH) to give $FeRu_4(\mu_5\text{-}C)(\mu\text{-dppm})(CO)_{13} \cdot 0.5CH_2Cl_2$ (**4**) (2 mg, 1%). Anal. Found: C, 37.36; H, 1.79%; M (mass spectrometry), 1223. $C_{33}H_{22}FeO_{13}P_2Ru_4 \cdot 0.5CH_2Cl_2$ calc.: C, 37.32; H, 1.81%; M, 1223. IR: ν(CO) (cyclohexane) 2077m, 2074m, 2048m, 2040s, 2031sh, 2025vs, 2018sh, 2009s, 2003s, 1996m, 1967m cm^{-1}. ^{1}H NMR: $\delta(CDCl_3)$ 3.81 (1H, q, J(PH, HH) = 11.7 Hz, CH_2), 4.13 (1H, q, J(PH, HH) = 12.1 Hz, CH_2), 7.22–7.39 (20H, m, Ph). FAB MS (m/z): 1223, M^+; 1195–859, $[M - n\text{CO}]^+$ (n = 1–13). Some starting complex **1** was recovered from the band at R_f0.5 (23 mg, 10%): total mass balance, 96%.

Reaction between 6 and PMe_2Ph

A mixture of **6** (70 mg, 0.057 mmol) and PMe_2Ph (8 mg, 0.065 mmol) was dissolved in CH_2Cl_2 (20 ml) and Me_3NO was added until no starting material remained (TLC). The solution was filtered through a short plug of silica gel and

the solvent was evaporated. The residue was purified by preparative TLC (silica gel; light petroleum/acetone 5:2) to give one major product in a dark brown band (R_f 0.35). This was recrystallised (CH_2Cl_2/MeOH) to give black crystals of $FeRu_5(\mu_6\text{-}C)(\mu\text{-}PPh_2)(CO)_{13}(PMe_2Ph)$ (7) (48 mg, 64%). Anal. Found: C, 37.18; H, 2.17%; *M* (mass spectrometry), 1446. $C_{46}H_{31}FeO_{13}P_3Ru_5 \cdot 0.5CH_2Cl_2$ calc.: C, 37.52; H, 2.17%; *M*, 1446. IR (cyclohexane): ν(CO) 2044w, 2017sh, 2011vs, 1997m, 1991m, 1978w, 1959w, 1953w, 1943vw cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.64 (3H, d, J(PH) = 9.5 Hz, PMe), 1.99 (3H, d, J(PH) = 9.9 Hz, PMe), 7.01–7.76 (25H, m, Ph). FAB MS (*m/z*): 1446, M^+; 1418–1082, $[M - nCO]^+$ (n = 1–13).

Crystallography

Unique data sets were measured at *ca.* 295 K within the specified $2\theta_{max}$ limits using an Enraf–Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo-K_α 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. Conventional residuals R, R' on $|F|$ are quoted, using a statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$. Computation used the XTAL 2.6 program system [14] implemented by S.R. Hall; neutral atom complex scattering factors were employed.

Abnormal features / variations in procedure

Useful specimens of all samples were obtained only with difficulty, that of **5** being twinned. In consequence of the long cell axes, the extended counter arm of the diffractometer was used to assist resolution. In **4** and **5** difference map artefacts were modelled as dichloromethane of solvation, with occupancy set at 0.5. In **4**, Ru, Fe, P and Cl only were refined with anisotropic thermal parameters; for O and C the isotropic form was used on account of the weakness of the data. In **5**, two thermal motion tensors C(2115,6) were ill-behaved and were refined using the isotropic form. For both structures, the residuals were independent of chirality.

Acknowledgements

We thank the Australian Research Council for financial support and Johnson Matthey Technology Centre for a generous loan of $RuCl_3 \cdot nH_2O$.

References

1 Part LXXVI: C.J. Adams, M.I. Bruce, B.W. Skelton and A.H. White, J. Organomet. Chem., 423 (1992) 97.
2 M.I. Bruce, M.J. Liddell and E.R.T. Tiekink, J. Organomet. Chem., 391 (1990) 81.
3 C.J. Adams, M.I. Bruce, B.W. Skelton and A.H. White, Inorg. Chem., submitted.
4 C.J. Adams, M.I. Bruce, B.W. Skelton and A.H. White, J. Organomet. Chem., 420 (1991) 87.
5 B.F.G. Johnson, J. Lewis, J.N. Nicholls, J. Puga, P.R. Raithby, M.J. Rosales, M. McPartlin and W. Clegg, J. Chem. Soc., Dalton Trans., (1983) 277.
6 E.H. Braye, L.F. Dahl, W. Hübel and D.L. Wampler, J. Am. Chem. Soc., 84 (1962) 4633.
7 J.G. Evans, B.P. Gracey, L.R. Gray and M. Webster, J. Organomet. Chem., 240 (1982) C61.

8 M.R. Churchill, R.A. Lashewycz, J.R. Shapley and S.I. Richter, Inorg. Chem., 19 (1980) 1277.
9 S.L. Cook, J. Evans, L.R. Gray and M. Webster, J. Chem. Soc., Dalton Trans., (1986) 2149.
10 A. Sirigu, M. Bianchi and E. Benedetti, Chem. Commun., (1969) 596.
11 S.C. Brown, J. Evans and M. Webster, J. Chem. Soc., Dalton Trans., (1981) 2263.
12 C.J. Adams, M.I. Bruce, M.J. Liddell, B.K. Nicholson, B.W. Skelton and A.H. White, J. Organomet. Chem., 420 (1991) 105.
13 M.I. Bruce, M.L. Williams, J.M. Patrick and A.H. White, J. Chem. Soc., Dalton Trans., (1985) 1229.
14 S.R. Hall and J.M. Stewart (Eds.), XTAL Users' Manual, Version 2.6, Universities of Western Australia and Maryland, 1989.