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Pyrolysis of $Ru_3(\mu\text{-dppm})(CO)_9(PPh_3)$: formation of novel Ru_4 and Ru_3 clusters

Michael I. Bruce [a,*], Natasha N. Zaitseva [a], Brian W. Skelton [b], Allan H. White [b]

[a] *Department of Chemistry, University of Adelaide, Adelaide, S.A. 5005, Australia*
[b] *Department of Chemistry, University of Western Australia, Nedlands, W.A. 6907, Australia*

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Abstract

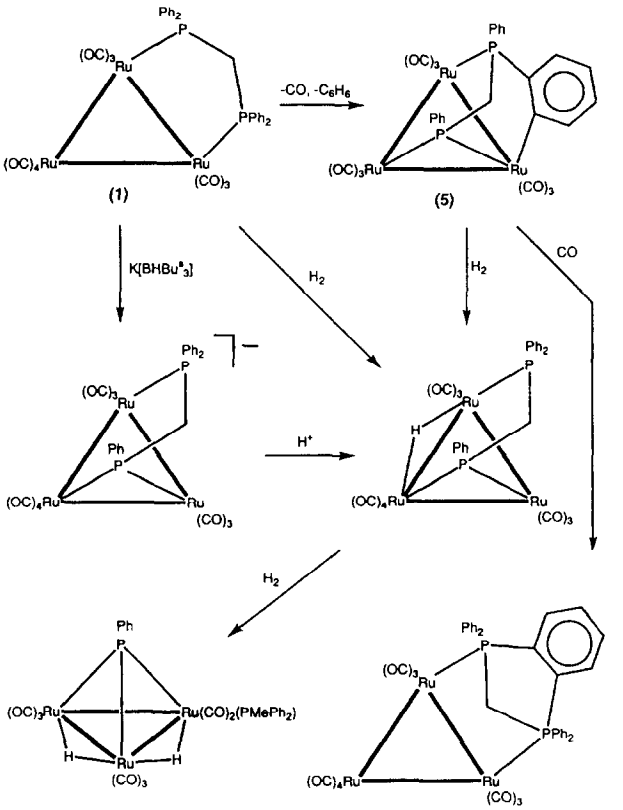
Heating $Ru_3(\mu\text{-dppm})(CO)_9(PPh_3)$ (**2**) for 90 min in refluxing toluene resulted in the formation of $Ru_4(\mu_4\text{-PPh})(\mu_4\text{-PPh}_2C_6H_4CO)(\mu\text{-PPh}_2CH_2)(CO)_8$ (**3**) and $Ru_3\{\mu_3\text{-PPh}(C_6H_4)\}(\mu\text{-PPh}_2CH_2)(\mu\text{-PPh}_2)(\mu\text{-CO})(CO)_6$ (**4**) as the major products (41%); other complexes identified were $Ru_3\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}(CO)_9$ (**5**) and $Ru_2(\mu\text{-PPhC}_6H_4\text{PPhCH}_2)(CO)_{6-n}(PPh_3)_n$ [$n = 1$(**6**), 0(**7**)]. The transformations involve oxidative addition of aromatic C–H and P–C bonds to the cluster, elimination of benzene and carbonylation of the aryl–Ru bond, as well as cluster disproportionation. X-ray structures of **3**, **4** and **6** are presented.

Keywords: Ruthenium; Carbonyl; Clusters; Pyrolysis; Crystal structure

1. Introduction

The complex $Ru_3(\mu\text{-dppm})(CO)_{10}$ (**1**) has proved to be a rich source of interesting chemistry [1]. Facile thermal transformations to a variety of complexes have been described by several groups and these are summarised in Scheme 1 [2]. Ready dephenylation to give the μ_3-bridging phosphido–phosphine ligand $PPhC_6H_4PPh_2$, metallation to give $PPh_2CH_2PPh(C_6H_4)$, a combination of the two reactions to give $PPhCH_2PPh(C_6H_4)$, and subsequent linking of the C_6H_4 and CH_2 fragments to give the bidentate phosphine $PPhC_6H_4PPhCH_2$, have all been found [2]. In related reactions, hydrogenation produced a double dephenylation to give the μ_3-PPh ligand [3], while cleavage of the cluster afforded isomeric binuclear complexes containing μ-$PPhC_6H_4PPhCH_2$ and μ-$PPhCH_2PPhC_6H_4$ ligands [4].

Pyrolysis of PPh_3 and $PMePh_2$ derivatives of $Ru_3(CO)_{12}$ has also given a variety of novel complexes, formed both by degradation of the tertiary phosphine and by cluster expansion reactions [5]. Features not seen in the reactions of **1** include formation and trapping of benzyne on the trinuclear cluster, further interaction of



Scheme 1.

* Corresponding author.

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the benzyne ligand with an extra one or two $Ru(CO)_3$ fragments, and stepwise carbonylation of the benzyne to give cluster-bound benzoyl and phthaloyl ligands [6].

Complex **1** is readily substituted by tertiary phosphines to give $Ru_3(\mu\text{-dppm})(CO)_9(PR_3)$, in which the entering phosphine substitutes a CO group on the $Ru(CO)_4$ fragment of **1** [7]. This paper describes the products obtained by pyrolysis of the mixed complex $Ru_3(\mu\text{-dppm})(CO)_9(PPh_3)$ (**2**), a reaction carried out to determine whether complex(es) containing fragments derived from both PPh_3 and dppm ligands would be formed.

2. Results

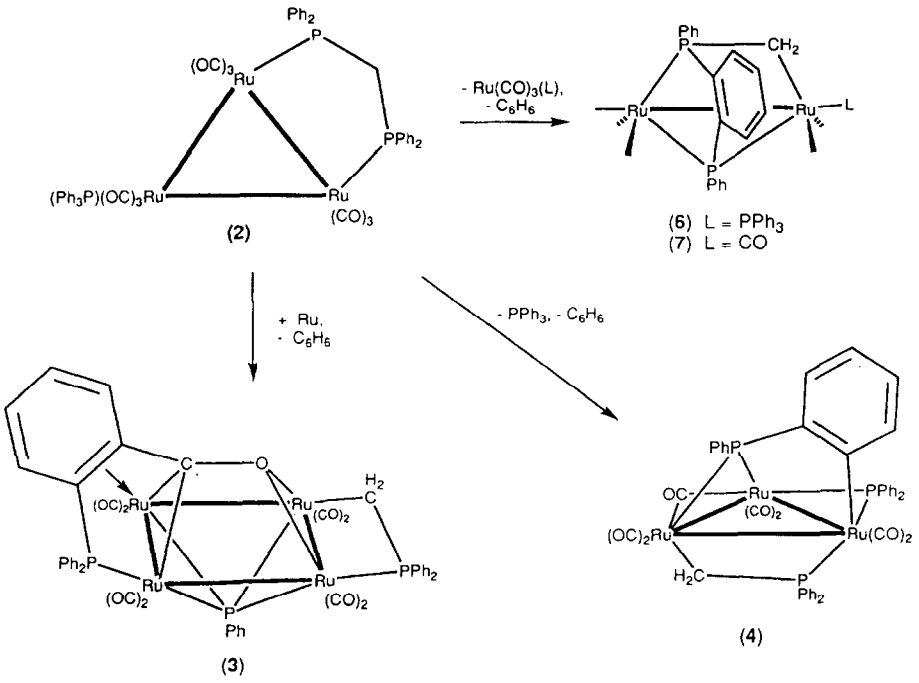
Complex **2** was heated in refluxing toluene for 90 min. Subsequent work-up by thin layer chromatography afforded five products, accounting for nearly 90% of **2**, which separated from a baseline. These are summarised in Scheme 2 and comprised orange $Ru_4(\mu_4\text{-PPh})(\mu_4\text{-PPh}_2C_6H_4CO)(\mu\text{-PPh}_2CH_2)(CO)_8$ (**3**), dark red $Ru_3\{\mu_3\text{-PPh}(C_6H_4)\}(\mu\text{-PPh}_2CH_2)(\mu\text{-PPh}_2)(\mu\text{-CO})(CO)_6$ (**4**), orange $Ru_3\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}(CO)_9$ (**5**; Scheme 1), yellow $Ru_2(\mu\text{-PPhC}_6H_4\text{PPhCH}_2)(CO)_5(PPh_3)$ (**6**), and pale yellow $Ru_2(\mu\text{-PPhC}_6H_4\text{PPhCH}_2)(CO)_6$ (**7**). Attempts to establish the sequence of reactions which led to the formation of these complexes were not successful: shorter reaction times result in the formation of the same products, but only 70% conversion was achieved, while under milder conditions, the same products were formed over a longer reaction time.

Of most interest is the finding that the PPh_3 ligand could be displaced, nearly 27% of the products (**5** and **7**) not containing this ligand and being identical to thermolysis products from **1**; only complex **6** contains an unchanged PPh_3 ligand. The major product is **3**, which contains four Ru atoms and three P atoms, one of which is in a ligand that can reasonably be derived from alteration of coordinated PPh_3. However, no linkage of fragments from PPh_3 and dppm appears to have occurred.

The complexes were identified as follows.

(a) $Ru_4(\mu_4\text{-PPh})(\mu_4\text{-PPh}_2C_6H_4CO)(\mu\text{-PPh}_2CH_2)(CO)_8$ *(3).* This cluster has a complex IR spectrum containing nine terminal ν(CO) bands; the mass spectrum shows a molecular ion which fragments by stepwise loss of up to nine CO groups, followed by three Ph groups. The molecular structure of **3** was determined by X-ray crystallography (see below).

(b) $Ru_3\{\mu_3\text{-PPh}(C_6H_4)\}(\mu\text{-PPh}_2CH_2)(\mu\text{-PPh}_2)(\mu\text{-CO})(CO)_6$ *(4).* As with **3**, the spectroscopic data were not sufficient to establish the molecular structure, which was determined by a single-crystal X-ray study (see below). The IR spectrum contained six terminal ν(CO) bands, while the ^{1}H NMR spectrum contained peaks at δ 0.89 and 5.72 assigned to the CH_2 protons of the



Scheme 2.

PPh_2CH_2 ligand. In the aromatic region, several multiplets were found, but could not be reliably assigned to any particular ligand.

(c) *$Ru_3\{\mu_3$-$PPhCH_2PPh(C_6H_4)\}(CO)_9$* **(5)**. This complex has been described before [2,8] and its identity was confirmed by comparison with an authentic sample (IR, MS).

(d) *$Ru_2(\mu$-$PPhC_6H_4PPhCH_2)(CO)_{6-n}(PPh_3)_n[n =$ 1* **(6)**, *0* **(7)**$]$. The IR spectrum of **6** contains only four ν(CO) bands. The stoichiometry was determined from

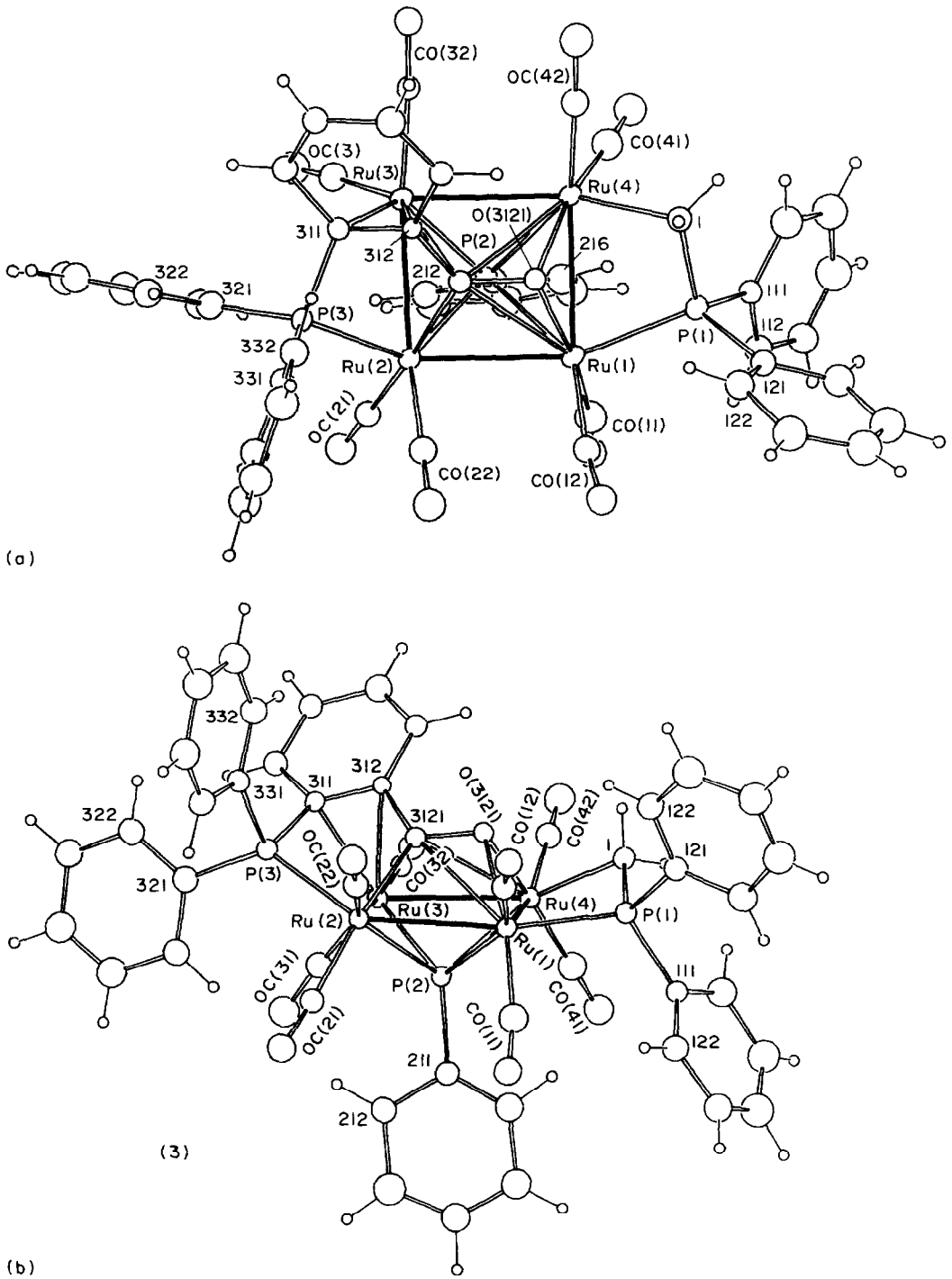
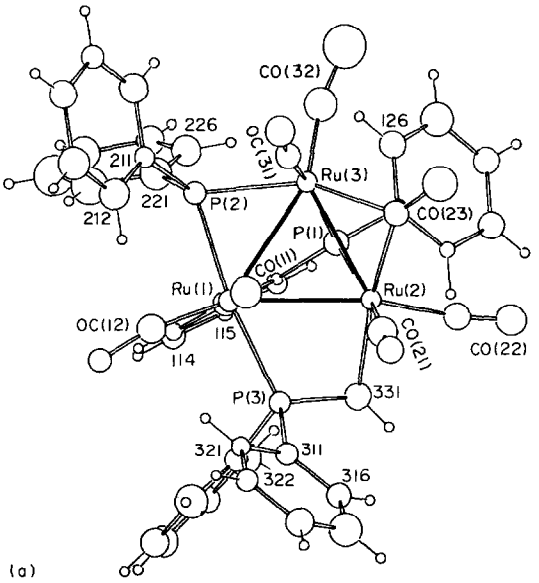


Fig. 1. Plots of a molecule of $Ru_4(\mu_4$-$PPh)(\mu_4$-$PPh_2C_6H_4CO)(\mu$-$PPh_2CH_2)(CO)_8$ **(3)** (a) perpendicular to and (b) oblique to the Ru_4 plane showing atom numbering scheme. In this and subsequent figures, non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

its mass spectrum, which contained a molecular ion at m/z 912 and ions formed by loss of between three and five CO groups. A single-crystal X-ray structural determination showed the complex was a PPh_3 substitution product of **7**, also obtained here, and previously reported as a by-product of a reaction of **1** with benzyl halides [4]. Complex **7** was identified by comparison (IR, MS) with an authentic sample.

2.1. Molecular structures

(a) $Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}PPh_2C_6H_4CO)(\mu\text{-}PPh_2CH_2)(CO)_8$ ***(3)***. Plots of a molecule of **3** are shown in Fig. 1



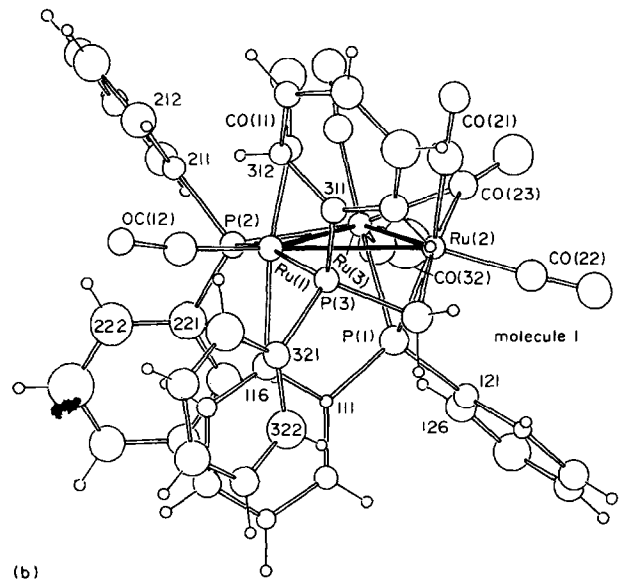


Fig. 2. Plots of molecule 1 of $Ru_3\{\mu_3\text{-}PPh(C_6H_4)\}(\mu\text{-}PPh_2CH_2)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_6$ (**4**) (a) perpendicular to and (b) oblique to the Ru_3 plane showing atom numbering scheme.

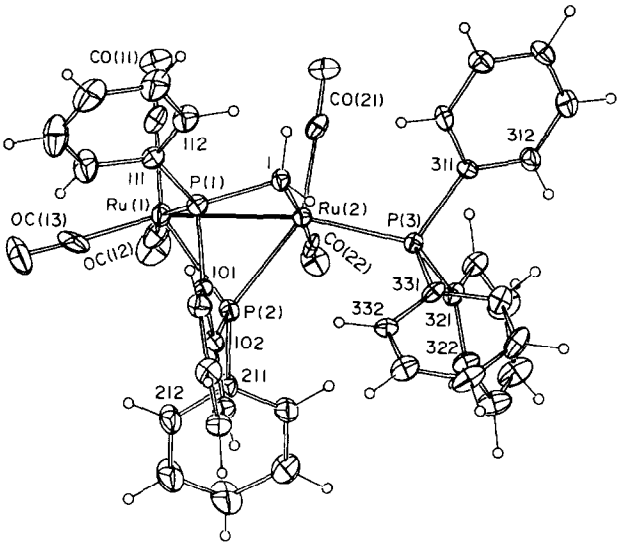


Fig. 3. Plot of a molecule of $Ru_2(\mu\text{-}PPhC_6H_4PPhCH_2)(CO)_5(PPh_3)$ (**6**) showing atom numbering scheme.

and significant structural parameters are collected in Table 1. The molecule is based on a rectangular Ru_4 core, which has unequal edges (two long, two short) ranging between 2.778(3) and 2.940(3) Å. One side is capped by the PPh group, with two long [Ru(1,4)–P(2) 2.412(7), 2.420(7) Å] and two short [Ru(2,3)–P(2) 2.363(7), 2.334(7) Å] bonds; similar μ_4-PR complexes often show a three short, one long pattern of M–P bonds. The Ru(1)–Ru(4) edge of the trapezium is bridged by a PPh_2CH_2 ligand with Ru(1)–P(1) [2.317(8) Å] and Ru(4)–C(1) [2.14(1) Å] separations somewhat shorter than those found in **5** and **7** (below).

The remaining organic group is a 2-diphenylphosphinobenzoyl ligand, which is attached by P(3) to Ru(2) [2.334(7) Å], to Ru(3) by an η^2-interaction with the C_6H_4 group [Ru(3)–C(311,312) 2.26(2), 2.31(2) Å] and to the Ru_4 core by the carbonyl group. The latter seems to be unprecedented, with C(3121) bridging the Ru(2)–Ru(3) edge [Ru(2,3)–C(3121) 2.09(2), 2.26(2) Å] and O(3121) bridging Ru(1)–Ru(4) [Ru(1,4)–O(3121) 2.17(2), 2.16(2) Å]. This mode of interaction is related to that found in $Ru_3(\mu\text{-}H)(\mu_3\text{-}O{=}CC_6H_4PPh_2)(\mu\text{-}dppm)(CO)_6$, in which the CO of the benzoyl group interacts with the Ru_3 core in a $2\eta^1$, η^2-mode [9]. The π-bonded Ru–C, O distances are 2.21(3) and 2.16(2) Å respectively, while the σ-bonded Ru–C, O distances are 2.04(2) and 2.09(2) Å respectively. In both cases, there are parallels between the coordination of the C=O group with the more familiar C≡C system.

(b) $Ru_3\{\mu_3\text{-}PPh(C_6H_4)\}(\mu\text{-}PPh_2CH_2)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_6$ ***(4)***. Fig. 2 shows a molecule of **4** and relevant bond parameters are collected in Table 2. The triangular metal core is capped by a $PPh(C_6H_4)$ ligand,

Table 1
Important bond lengths (Å) and angles (deg) in $Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}PPh_2C_6H_4CO)(\mu\text{-}PPh_2CH_2)(CO)_9$ (3)

Bond lengths			
Ru(1)–Ru(2)	2.855(3)	Ru(2)–C(3121)	2.09(2)
Ru(1)–Ru(4)	2.786(4)	Ru(3)–C(3121)	2.26(3)
Ru(2)–Ru(3)	2.778(3)	Ru(3)–C(311)	2.26(2)
Ru(3)–Ru(4)	2.940(3)	Ru(3)–C(312)	2.31(2)
Ru(1)–P(1)	2.317(8)	Ru(4)–C(1)	2.14(3)
Ru(1)–P(2)	2.412(7)	Ru(1)–O(3121)	2.17(2)
Ru(2)–P(2)	2.363(7)	Ru(4)–O(3121)	2.16(2)
Ru(2)–P(3)	2.309(8)	P(1)–C(1)	1.74(3)
Ru(3)–P(2)	2.334(7)	P(3)–C(311)	1.82(2)
Ru(4)–P(2)	2.420(7)	O(3121)–C(3121)	1.31(3)
		C(311)–C(312)	1.35(3)
Bond angles			
Ru(2)–Ru(1)–Ru(4)	89.7(1)	Ru(1)–P(1)–C(1)	101.7(9)
Ru(1)–Ru(2)–Ru(3)	91.9(1)	Ru(4)–C(1)–P(1)	98(1)
Ru(2)–Ru(3)–Ru(4)	88.1(1)	P(3)–C(311)–C(312)	116(2)
Ru(3)–Ru(4)–Ru(1)	90.0(1)	C(311)–C(312)–C(3121)	113(2)
		C(312)–C(3121)–O(3121)	118(2)

and each of the three edges is bridged by a different ligand. A PPh_2CH_2 ligand bridges Ru(1)–Ru(2), which is the longest Ru–Ru separation at 2.981 Å [Ru(1)–P(3) 2.36, Ru(2)–C(331) 2.12 Å], while Ru(1)–Ru(3) carries a μ-PPh_2 group [Ru(1,3)–P(2) 2.33, 2.33 Å]; the third Ru–Ru vector is bridged by CO(23). The Ru_3 triangle is capped by a $PPh(C_6H_4)$ ligand [Ru(1)–C(112) 2.13; Ru(2,3)–P(1) 2.34, 2.33 Å]. Coordination is completed by two terminal CO groups on each ruthenium atom.

(c) $Ru_2(\mu\text{-}PPhC_6H_4PPhCH_2)(CO)_5(PPh_3)$ (6). A plot of a molecule of **6** is shown in Fig. 3 and salient bond distances and angles, together with those of **7**, are listed in Table 3. The $PPhC_6H_4PPhCH_2$ ligand bridges the two ruthenium atoms via P(2) [Ru(1,2)–P(2) 2.339(5), 2.362(4) Å] and the P(1)–C(1) fragment [Ru(1)–P(1) 2.370(5), Ru(2)–C(1) 2.25(2) Å]. The PPh_3 ligand is attached to Ru(2) [Ru(2)–P(3) 2.346(4) Å] approximately *trans* to the Ru–Ru bond [Ru(1)–Ru(2)–P(3) 162.8(1)°]. Neglecting the Ru–Ru bond, the two ruthenium have nearly trigonal bipyramidal geometries; there are no significant differences between similar parameters in the structures of **6** and **7**.

Table 2
Significant bond lengths (Å) and angles (deg) for $Ru_3(\mu_3\text{-}PPh(C_6H_4))(\mu\text{-}PPh_2CH_2)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_6$ (4) [a]

Bond lengths		*Average*
Ru(1)–Ru(2)	2.943(6), 3.019(6)	2.981
Ru(1)–Ru(3)	2.912(5), 2.913(6)	2.913
Ru(2)–Ru(3)	2.744(6), 2.722(6)	2.733
Ru(1)–P(2)	2.33(2), 2.33(1)	2.33
Ru(1)–P(3)	2.36(2), 2.36(2)	2.36
Ru(2)–P(1)	2.32(1), 2.36(1)	2.34
Ru(3)–P(1)	2.33(2), 2.33(1)	2.33
Ru(3)–P(2)	2.35(2), 2.30(1)	2.33
Ru(1)–C(112)	2.13(3), 2.13(3)	2.13
Ru(2)–C(23)	2.02(5), 2.24(6)	2.13
Ru(2)–C(331)	2.21(5), 2.03(4)	2.12
Ru(3)–C(23)	2.12(5), 1.97(6)	2.05
P(1)–C(111)	1.75(4), 1.77(4)	1.76
P(3)–C(331)	1.76(6), 1.75(4)	1.76
Bond angles		
Ru(1)–P(3)–C(331)	112(2), 107(2)	110
Ru(2)–C(331)–P(3)	92(2), 102(2)	97
Ru(1)–C(112)–C(111)	119(2), 121(2)	120
P(1)–C(111)–C(112)	113(2), 117(3)	115

[a] Two values for each entry are for molecules 1 and 2.

3. Discussion

The major feature of interest in the present work is the formation of the tetranuclear complex **3** as the major product. The ligands present in **3** are formally formed by loss of benzene from the dppm and PPh_3 combination. The benzoyl phosphine can be formed by insertion of CO in a metallated phenyl–Ru bond, as found for the benzyne ligand in $Ru_3(\mu_3\text{-}C_6H_4)(\mu\text{-}PPh_2)_2(CO)_7$ reported earlier [5]. Metallation of PPh_3 to give the $PPh_2(C_6H_4)$ ligand is a common reaction in mononuclear metal–PPh_3 complexes, but is not so common in clusters. Further interaction of the C_6H_4 ring by η^2-coordination to Ru(2) appears to result from the close approach of this ring to the metal atom, which is forced by the μ_4-coordination of the acyl group to the Ru_4 face. Formally, the dppm ligand has been cleaved at the P–CH_2 bond to give a PPh_2CH_2 ligand, which bridges one Ru–Ru edge, and a PPh_2 group. Under the reaction conditions, this has further dephenylated (probably by elimination of benzene formed by combination of the

Table 3
Important bond lengths and angles in $Ru_2(\mu\text{-}PPhC_6H_4PPhCH_2)(CO)_{6-n}(PPh_3)_n$ [n = 1(6), 0(7) [7d]]

	L = CO	L = PPh_3		L = CO	L = PPh_3
Bond lengths					
Ru(1)–Ru(2)	2.8110(7)	2.834(2)	Ru(1)–C(13)	1.937(6)	1.88(2)
Ru(1)–P(1)	2.356(1)	2.370(5)	Ru(2)–C(21)	1.921(5)	1.85(2)
Ru(1)–P(2)	2.332(1)	2.339(5)	Ru(2)–C(22)	1.899(5)	1.89(2)
Ru(2)–P(2)	2.343(1)	2.362(4)	Ru(2)–C(23)	1.917(7)	
Ru(2)–P(3)		2.346(4)	P(1)–C(1)	1.786(4)	1.76(1)
Ru(2)–C(1)	2.232(6)	2.25(2)	P(1)–C(101)	1.827(4)	1.78(1)
Ru(1)–C(11)	1.916(6)	1.91(2)	P(2)–C(102)	1.815(4)	1.81(2)
Ru(1)–C(12)	1.907(6)	1.92(2)			
Bond angles					
Ru(2)–Ru(1)–P(1)	72.52(4)	71.9(1)	Ru(1)–P(2)–Ru(2)	73.92(3)	74.2(1)
Ru(1)–Ru(2)–C(1)	80.0(1)	79.1(3)			
Ru(1)–P(1)–C(1)	103.5(2)	103.8(6)	Ru(2)–C(1)–P(1)	99.4(2)	99.6(7)

Ph group with the H from the metallated PPh_3 ligand, through the intermediacy of an undetected cluster hydride) to give the μ_4-PPh ligand found capping one side of the Ru_4 rectangle. The latter has been formed by disproportionation of the original Ru_3 cluster, formally again by incorporation of a ruthenium carbonyl fragment liberated during the formation of the binuclear complexes **6** and **7**.

The structural diversity of the ligands present in **4** is remarkable, although each has been found previously in other complexes formed by pyrolysis of ruthenium carbonyl clusters containing PPh_3 or dppm. The simplest way to account for the formation of this compound is by oxidative addition of an *ortho* C–H group of one of the *P*-phenyl groups of the PPh_3 ligand across an Ru–Ru bond [as found with $Os_3(CO)_{10}(PPh_3)_2$ [5a]] to give μ-H and μ-$PPh_2C_6H_4$ ligands, followed by elimination of benzene, formed by combination of the cluster-bound H atom with one of the Ph groups of the $PPh_2C_6H_4$ ligand. The resulting phosphido group is found bridging Ru(2)–Ru(3). Alteration of the dppm ligand occurs by oxidative addition of a P–CH_2 bond across the cluster, to give PPh_2 and PPh_2CH_2 ligands. While this is not a common route for dppm, which usually prefers to add a phenyl C–H bond and then to eliminate benzene, evidently this process is blocked by the PPh_3 ligand in the

Table 4
Crystal data and refinement details for **3**, **4** and **6**

Compound	**3**	**4**	**6**
Formula	$C_{46}H_{31}O_9P_3Ru_4$	$C_{44}H_{31}O_7P_3Ru_3$	$C_{42}H_{31}O_5P_3Ru_2$
MW	1225.0	1067.9	910.8
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*Pbca* (No. 61)	$Pca2_1$ (No. 29)	$P\bar{1}$ (No. 2)
a (Å)	21.060(19)	22.112(7)	18.890(9)
b (Å)	30.115(14)	12.847(9)	10.93(1)
c (Å)	15.107(8)	29.378(12)	10.520(5)
α (deg)			66.29(5)
β (deg)			83.39(3)
γ (deg)			78.88(3)
V (Å^3)	9581	8346	1950
Z	8	8	2
D_c (g cm^{-3})	1.70	1.70	1.55
F(000)	4800	4224	912
Crystal size (mm^3)	0.57 × 0.07 × 0.18	0.24 × 0.11 × 0.06	0.08 × 0.37 × 0.10
A^* (min, max)	1.10, 1.21	1.07, 1.15	1.07, 1.11
μ (cm^{-1})	13.9	12.4	9.4
$2\theta_{max}$ (deg)	55	45	50
N	10007	5199	6824
N_o	2722	2114	3998
R	0.075	0.074	0.075
R_w	0.078	0.071	0.081

Table 5
Non-hydrogen positional and isotropic displacement parameters (3)

Atom	x	y	z	U_{eq} Å^2
Ru(1)	0.3657(1)	0.35621(6)	0.8784(2)	0.0363(8)
Ru(2)	0.27507(9)	0.39084(6)	0.7559(2)	0.0345(7)
Ru(3)	0.3648(1)	0.39436(7)	0.6213(2)	0.0363(8)
Ru(4)	0.46011(9)	0.36428(6)	0.7503(2)	0.0363(7)
C(11)	0.325(2)	0.303(1)	0.911(2)	0.08(1)
O(11)	0.2959(9)	0.2729(6)	0.923(1)	0.068(6)
C(12)	0.329(1)	0.3840(9)	0.982(2)	0.054(9)
O(12)	0.3128(9)	0.3991(6)	1.044(1)	0.065(6)
C(21)	0.206(1)	0.3524(8)	0.740(2)	0.050(7)
O(21)	0.1623(9)	0.3312(6)	0.732(1)	0.070(6)
C(22)	0.237(1)	0.414(1)	0.855(2)	0.057(9)
O(22)	0.214(1)	0.4316(7)	0.915(2)	0.077(7)
C(31)	0.326(1)	0.365(1)	0.525(2)	0.059(9)
O(31)	0.301(1)	0.3438(7)	0.470(1)	0.081(7)
C(32)	0.436(1)	0.4050(8)	0.545(2)	0.038(7)
O(32)	0.4758(9)	0.4120(6)	0.497(1)	0.057(6)
C(41)	0.497(1)	0.313(1)	0.712(2)	0.07(1)
O(41)	0.521(1)	0.2813(7)	0.686(1)	0.077(7)
C(42)	0.526(1)	0.3945(9)	0.699(2)	0.058(8)
O(42)	0.567(1)	0.4124(7)	0.661(1)	0.083(7)
C(1)	0.515(1)	0.3698(8)	0.869(2)	0.043(7)
P(1)	0.4641(4)	0.3400(2)	0.9386(5)	0.040(3)
C(111)	0.489(1)	0.2819(8)	0.939(2)	0.040(7)
C(112)	0.451(1)	0.250(1)	0.973(2)	0.059(9)
C(113)	0.471(2)	0.206(1)	0.979(2)	0.07(1)
C(114)	0.524(2)	0.195(1)	0.946(3)	0.10(1)
C(115)	0.566(2)	0.224(1)	0.911(2)	0.09(1)
C(116)	0.548(2)	0.271(1)	0.909(2)	0.07(1)
C(121)	0.478(1)	0.3577(9)	1.052(2)	0.048(8)
C(122)	0.464(1)	0.4011(9)	1.074(2)	0.062(9)
C(123)	0.471(2)	0.415(1)	1.166(2)	0.09(1)
C(124)	0.499(2)	0.387(1)	1.227(2)	0.09(1)
C(125)	0.514(2)	0.346(1)	1.205(3)	0.09(1)
C(126)	0.505(2)	0.329(1)	1.116(2)	0.07(1)
P(2)	0.3536(3)	0.3371(2)	0.7243(4)	0.034(2)
C(211)	0.338(1)	0.2780(9)	0.699(2)	0.050(8)
C(212)	0.286(1)	0.2693(9)	0.646(2)	0.055(8)
C(213)	0.272(2)	0.222(1)	0.631(2)	0.09(1)
C(214)	0.307(2)	0.191(1)	0.676(2)	0.07(1)
C(215)	0.356(2)	0.199(1)	0.730(2)	0.08(1)
C(216)	0.370(1)	0.246(1)	0.740(2)	0.070(9)
P(3)	0.2497(3)	0.4487(2)	0.6623(5)	0.038(3)
C(311)	0.330(1)	0.4651(7)	0.630(2)	0.035(7)
C(312)	0.375(1)	0.4616(7)	0.694(2)	0.027(6)
C(3121)	0.361(1)	0.4253(7)	0.757(2)	0.038(6)
O(3121)	0.4050(8)	0.4150(5)	0.815(1)	0.036(4)
C(313)	0.431(1)	0.4879(8)	0.691(2)	0.042(7)
C(314)	0.439(1)	0.5159(9)	0.622(2)	0.066(9)
C(315)	0.395(1)	0.5188(9)	0.555(2)	0.049(8)
C(316)	0.340(1)	0.4937(9)	0.551(2)	0.050(8)
C(321)	0.201(1)	0.447(1)	0.568(2)	0.058(9)
C(322)	0.182(1)	0.4855(9)	0.524(2)	0.062(9)
C(323)	0.146(2)	0.484(1)	0.447(2)	0.07(1)
C(324)	0.127(2)	0.442(1)	0.413(2)	0.08(1)
C(325)	0.146(2)	0.405(1)	0.453(2)	0.08(1)
C(326)	0.183(1)	0.404(1)	0.533(2)	0.063(9)
C(331)	0.216(1)	0.4974(8)	0.723(2)	0.042(7)
C(332)	0.252(1)	0.5347(9)	0.732(2)	0.061(9)
C(333)	0.226(2)	0.571(1)	0.784(2)	0.08(1)
C(334)	0.163(2)	0.566(1)	0.819(2)	0.08(1)
C(335)	0.132(2)	0.528(1)	0.806(2)	0.08(1)
C(336)	0.157(1)	0.4941(9)	0.754(2)	0.062(8)

Table 6
Non-hydrogen positional and isotropic displacement parameters (4)

Atom	x	y	z	U_{eq} Å^2
Ru(11)	0.6918(2)	0.5150(3)	0.5(−) *	0.050(2)
Ru(12)	0.5712(2)	0.4256(3)	0.4836(2)	0.042(2)
Ru(13)	0.6232(2)	0.5439(3)	0.4163(2)	0.045(2)
C(111)	0.711(2)	0.395(4)	0.469(2)	0.05(2)
O(111)	0.736(2)	0.313(3)	0.453(1)	0.10(2)
C(112)	0.761(3)	0.540(4)	0.526(2)	0.09(2)
O(112)	0.810(1)	0.536(2)	0.548(1)	0.06(1)
C(121)	0.596(3)	0.286(5)	0.480(2)	0.10(2)
O(121)	0.612(2)	0.194(3)	0.475(1)	0.07(1)
C(122)	0.490(2)	0.389(4)	0.490(2)	0.08(2)
O(122)	0.439(2)	0.369(3)	0.490(1)	0.10(1)
C(123)	0.564(2)	0.415(4)	0.415(2)	0.07(2)
O(123)	0.534(2)	0.378(4)	0.386(2)	0.13(2)
C(131)	0.670(2)	0.468(4)	0.380(2)	0.07(2)
O(131)	0.696(2)	0.422(3)	0.352(1)	0.09(1)
C(132)	0.598(3)	0.628(5)	0.375(2)	0.11(3)
O(132)	0.572(3)	0.661(5)	0.338(2)	0.20(3)
P(11)	0.5636(6)	0.605(1)	0.4760(7)	0.069(7)
C(1111)	0.596(2)	0.682(3)	0.5185(9)	0.01(1)
C(1112)	0.655(2)	0.652(2)	0.530(1)	0.06(2)
C(1113)	0.687(1)	0.708(3)	0.563(1)	0.03(1)
C(1114)	0.661(2)	0.794(3)	0.5841(8)	0.06(2)
C(1115)	0.602(2)	0.825(2)	0.5724(9)	0.03(1)
C(1116)	0.570(1)	0.769(4)	0.540(1)	0.04(2)
C(1121)	0.489(1)	0.661(3)	0.463(1)	0.05(2)
C(1122)	0.438(2)	0.634(2)	0.490(1)	0.03(1)
C(1123)	0.383(2)	0.682(3)	0.481(1)	0.07(2)
C(1124)	0.377(1)	0.756(3)	0.447(1)	0.07(2)
C(1125)	0.427(2)	0.783(2)	0.4203(9)	0.11(3)
C(1126)	0.483(2)	0.736(4)	0.429(1)	0.07(2)
P(12)	0.7125(6)	0.628(1)	0.4399(5)	0.054(7)
C(1211)	0.779(1)	0.602(4)	0.406(1)	0.04(2)
C(1212)	0.824(2)	0.533(3)	0.420(1)	0.10(2)
C(1213)	0.876(2)	0.520(3)	0.393(1)	0.11(3)
C(1214)	0.882(1)	0.577(3)	0.352(1)	0.08(2)
C(1215)	0.837(2)	0.646(3)	0.339(1)	0.05(2)
C(1216)	0.785(2)	0.659(3)	0.366(1)	0.09(2)
C(1221)	0.718(6)	0.758(3)	0.451(1)	0.11(3)
C(1222)	0.774(4)	0.793(8)	0.466(1)	0.15(3)
C(1223)	0.782(2)	0.90(1)	0.479(1)	0.17(4)
C(1224)	0.734(6)	0.966(3)	0.476(1)	0.10(2)
C(1225)	0.677(4)	0.932(8)	0.461(1)	0.08(2)
C(1226)	0.669(3)	0.83(1)	0.448(1)	0.09(2)
P(13)	0.6476(6)	0.428(1)	0.5623(5)	0.050(6)
C(1311)	0.671(4)	0.297(3)	0.575(1)	0.05(2)
C(1312)	0.729(3)	0.267(5)	0.563(1)	0.04(2)
C(1313)	0.747(1)	0.163(7)	0.568(1)	0.05(2)
C(1314)	0.707(4)	0.090(3)	0.586(1)	0.09(2)
C(1315)	0.649(3)	0.120(5)	0.599(1)	0.12(3)
C(1316)	0.630(2)	0.224(7)	0.594(1)	0.06(2)
C(1321)	0.664(2)	0.491(3)	0.619(1)	0.06(2)
C(1322)	0.631(1)	0.575(4)	0.635(1)	0.12(3)
C(1323)	0.648(2)	0.623(2)	0.676(1)	0.07(2)
C(1324)	0.698(2)	0.586(3)	0.7008(9)	0.10(2)
C(1325)	0.731(1)	0.502(4)	0.684(1)	0.08(2)
C(1326)	0.714(2)	0.454(2)	0.643(1)	0.12(3)
C(1331)	0.568(2)	0.427(4)	0.559(2)	0.08(2)
Ru(21)	0.4481(2)	1.0019(3)	0.7195(1)	0.031(1)
Ru(22)	0.3213(2)	1.0813(3)	0.7353(2)	0.044(2)
Ru(23)	0.3749(2)	0.9610(3)	0.8000(2)	0.044(2)
C(211)	0.472(2)	1.127(3)	0.753(1)	0.02(1)
O(211)	0.487(1)	1.185(2)	0.776(1)	0.034(9)

Table 6 (continued)

Atom	x	y	z	U_{eq} Å^2
C(212)	0.524(2)	0.984(4)	0.691(1)	0.04(2)
O(212)	0.570(2)	0.971(3)	0.679(1)	0.08(1)
C(221)	0.348(2)	1.219(3)	0.746(1)	0.03(1)
O(221)	0.348(2)	1.311(3)	0.754(1)	0.08(1)
C(222)	0.240(2)	1.113(4)	0.731(2)	0.07(2)
O(222)	0.189(2)	1.129(3)	0.720(1)	0.12(2)
C(223)	0.308(3)	1.059(4)	0.810(2)	0.09(2)
O(223)	0.277(2)	1.117(3)	0.833(1)	0.09(1)
C(231)	0.422(2)	1.047(5)	0.843(2)	0.10(2)
O(231)	0.445(2)	1.091(3)	0.867(1)	0.09(1)
C(232)	0.353(2)	0.872(4)	0.846(2)	0.05(2)
O(232)	0.344(1)	0.810(3)	0.874(1)	0.06(1)
P(21)	0.3149(5)	0.8982(9)	0.7410(4)	0.028(5)
C(2111)	0.354(2)	0.832(3)	0.6969(9)	0.08(2)
C(2112)	0.411(2)	0.870(2)	0.686(1)	0.02(1)
C(2113)	0.445(1)	0.823(3)	0.651(1)	0.06(2)
C(2114)	0.420(2)	0.738(3)	0.6269(9)	0.07(2)
C(2115)	0.363(2)	0.701(2)	0.638(1)	0.09(2)
C(2116)	0.329(1)	0.748(3)	0.673(1)	0.03(1)
C(2121)	0.246(1)	0.829(3)	0.747(1)	0.06(2)
C(2122)	0.199(2)	0.848(2)	0.715(1)	0.05(2)
C(2123)	0.144(2)	0.797(3)	0.720(1)	0.08(2)
C(2124)	0.134(1)	0.729(3)	0.756(1)	0.07(2)
C(2125)	0.180(2)	0.710(2)	0.7879(9)	0.05(2)
C(2126)	0.236(1)	0.760(3)	0.783(1)	0.09(2)
P(22)	0.4639(6)	0.883(1)	0.7783(5)	0.038(6)
C(2211)	0.528(1)	0.899(3)	0.816(1)	0.07(2)
C(2212)	0.576(2)	0.963(3)	0.8040(9)	0.08(2)
C(2213)	0.623(1)	0.982(2)	0.835(1)	0.03(1)
C(2214)	0.621(1)	0.937(3)	0.879(1)	0.06(2)
C(2215)	0.572(2)	0.873(3)	0.891(1)	0.11(3)
C(2216)	0.526(1)	0.854(2)	0.860(1)	0.09(2)
C(2221)	0.464(6)	0.738(2)	0.770(1)	0.06(2)
C(2222)	0.519(4)	0.690(9)	0.758(1)	0.05(2)
C(2223)	0.521(3)	0.58(1)	0.7525(9)	0.03(1)
C(2224)	0.470(6)	0.521(2)	0.7590(9)	0.04(1)
C(2225)	0.415(3)	0.569(9)	0.7713(9)	0.04(2)
C(2226)	0.412(3)	0.68(1)	0.7768(9)	0.06(2)
P(23)	0.4054(6)	1.096(1)	0.6585(5)	0.051(6)
C(2311)	0.428(4)	1.235(2)	0.658(1)	0.05(2)
C(2312)	0.485(3)	1.271(6)	0.671(1)	0.03(1)
C(2313)	0.500(2)	1.376(7)	0.666(1)	0.09(2)
C(2314)	0.457(4)	1.446(2)	0.649(1)	0.05(2)
C(2315)	0.400(3)	1.410(6)	0.6359(9)	0.07(2)
C(2316)	0.385(2)	1.304(7)	0.640(1)	0.07(2)
C(2321)	0.428(2)	1.050(3)	0.6018(9)	0.05(2)
C(2322)	0.391(1)	0.980(3)	0.578(1)	0.09(2)
C(2323)	0.408(2)	0.950(3)	0.534(1)	0.09(2)
C(2324)	0.460(2)	0.989(3)	0.5136(9)	0.09(2)
C(2325)	0.497(1)	1.058(3)	0.538(1)	0.18(4)
C(2326)	0.481(2)	1.089(3)	0.582(1)	0.12(3)
C(2331)	0.327(2)	1.095(3)	0.667(1)	0.02(1)

* Defines origin.

present case. The PPh_2CH_2 ligand is also found in complexes **6** and **7** (see above).

The $PPh(C_6H_4)$ ligand is relatively uncommon and recent examples occur in the tetranuclear clusters $RhRu_3(\mu\text{-H})\{\mu\text{-PPh}(C_6H_4)\}(\mu\text{-CO})(CO)_6(PPh_3)_2$ [10] and $Ru_4(\mu\text{-H})\{\mu_4\text{-PPh}(C_6H_4)\}(\mu\text{-PPh}_2)(CO)_{10}$ [11]. In the former, however, the $P\text{–}C_6H_4$ part of the ligand interacts further with the Rh atom by an $\eta^3(P, 2C)$-mode; in the latter, the phosphorus atom of this ligand exhibits an unusual five-coordination.

Clearly, the mild conditions employed in the present reactions can lead to a variety of interesting complexes formed by facile modification of the tertiary phosphine ligands — further examples will no doubt emerge as additional studies are carried out.

4. Experimental

General reaction conditions were similar to those reported in an earlier paper [9b]. The complex $Ru_3(\mu$-

Table 7
Non-hydrogen positional and isotropic displacement parameters (**6**)

Atom	*x*	*y*	*z*	U_{eq} Å^2
Ru(1)	0.15657(7)	1.2327(1)	0.2073(1)	0.0445(6)
Ru(2)	0.28740(6)	1.0495(1)	0.2271(1)	0.0335(5)
C(11)	0.200(1)	1.389(2)	0.104(2)	0.058(8)
O(11)	0.2298(8)	1.479(1)	0.039(1)	0.092(8)
C(12)	0.130(1)	1.221(2)	0.042(2)	0.064(9)
O(12)	0.1146(8)	1.211(1)	−0.055(1)	0.101(8)
C(13)	0.063(1)	1.301(2)	0.258(2)	0.08(1)
O(13)	0.0058(7)	1.348(2)	0.283(2)	0.13(1)
C(21)	0.3462(9)	1.173(2)	0.117(2)	0.050(8)
O(21)	0.3818(7)	1.255(1)	0.047(1)	0.075(7)
C(22)	0.2702(8)	1.006(1)	0.078(2)	0.043(7)
O(22)	0.2591(6)	0.984(1)	−0.015(1)	0.067(6)
C(1)	0.2996(7)	1.122(1)	0.395(1)	0.041(7)
P(1)	0.2091(2)	1.1893(4)	0.4182(4)	0.043(2)
C(111)	0.2001(9)	1.312(2)	0.500(2)	0.049(8)
C(112)	0.2570(9)	1.326(2)	0.556(2)	0.064(9)
C(113)	0.252(1)	1.410(2)	0.629(2)	0.08(1)
C(114)	0.186(1)	1.476(2)	0.649(2)	0.09(1)
C(115)	0.129(1)	1.462(2)	0.594(3)	0.11(1)
C(116)	0.134(1)	1.383(2)	0.516(2)	0.09(1)
C(101)	0.1749(7)	1.049(1)	0.551(2)	0.040(7)
C(102)	0.1525(7)	0.959(2)	0.505(2)	0.045(7)
C(103)	0.1291(8)	0.840(2)	0.604(2)	0.054(8)
C(104)	0.1237(9)	0.815(2)	0.744(2)	0.063(9)
C(105)	0.1468(9)	0.904(2)	0.789(2)	0.063(9)
C(106)	0.1703(8)	1.020(2)	0.694(2)	0.051(8)
P(2)	0.1723(2)	0.9969(4)	0.3226(4)	0.041(2)
C(211)	0.1253(8)	0.889(2)	0.279(2)	0.048(7)
C(212)	0.0524(9)	0.914(2)	0.269(2)	0.09(1)
C(213)	0.018(1)	0.832(3)	0.232(3)	0.12(2)
C(214)	0.056(1)	0.730(3)	0.205(3)	0.11(2)
C(215)	0.128(1)	0.697(2)	0.219(2)	0.09(1)
C(216)	0.1642(9)	0.781(2)	0.255(2)	0.07(1)
P(3)	0.3811(2)	0.8660(4)	0.3110(4)	0.035(2)
C(311)	0.4722(7)	0.909(1)	0.282(1)	0.037(6)
C(312)	0.5324(8)	0.848(2)	0.228(2)	0.052(8)
C(313)	0.5977(9)	0.886(2)	0.215(2)	0.061(9)
C(314)	0.6075(8)	0.990(2)	0.251(2)	0.057(9)
C(315)	0.5487(9)	1.051(2)	0.308(2)	0.054(8)
C(316)	0.4827(7)	1.013(2)	0.320(2)	0.048(8)
C(321)	0.3848(8)	0.741(1)	0.233(2)	0.043(7)
C(322)	0.3609(9)	0.619(2)	0.307(2)	0.055(8)
C(323)	0.360(1)	0.530(2)	0.246(2)	0.08(1)
C(324)	0.389(1)	0.556(2)	0.115(2)	0.08(1)
C(325)	0.413(1)	0.677(2)	0.037(2)	0.08(1)
C(326)	0.4130(9)	0.769(2)	0.094(2)	0.052(8)
C(331)	0.3831(8)	0.755(1)	0.493(1)	0.041(7)
C(332)	0.3239(8)	0.758(1)	0.583(2)	0.043(7)
C(333)	0.326(1)	0.665(2)	0.715(2)	0.062(9)
C(334)	0.383(1)	0.566(2)	0.769(2)	0.066(9)
C(335)	0.442(1)	0.565(2)	0.681(2)	0.067(9)
C(336)	0.4436(9)	0.657(2)	0.549(2)	0.055(8)

dppm)$(CO)_9(PPh_3)$ was made as described elsewhere [7d].

4.1. Pyrolysis of $Ru_3(\mu$-dppm)$(CO)_9(PPh_3)$

A solution of $Ru_3(\mu$-dppm)$(CO)_9(PPh_3)$ (150 mg, 0.125 mmol) in toluene (10 ml) was heated at reflux point for 1.5 h. After cooling the solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 (2 ml) and separated by thin layer chromatography (silica gel; acetone/hexane 3:7) into six coloured bands and a baseline.

The product from band 1 (R_f 0.60) was recrystallised (CH_2Cl_2/MeOH) to give pale yellow crystals of $Ru_2(\mu$-$PPhC_6H_4PPhCH_2)(CO)_6$ (**7**) (8 mg, 9.4%), identified by an X-ray study and by comparison with an authentic sample [4]. IR (cyclohexane): ν(CO) 2069s, 2053w, 2036vs, 2007vs, 1988m, 1982m, 1972m, 1960(sh) cm^{-1}.

The second red band (R_f 0.50) gave dark red crystals of **4** (10 mg, 8%). IR (cyclohexane): ν(CO) 2053vs, 2027s, 2001vs, 1989m, 1983vw, 1919w, 1916w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 0.89 (m, 1H, CH_2), 5.72 (m, 1H, CH_2), 6.19–8.06 (m, 29H, $5Ph + C_6H_4$). FAB MS (m/z): 1069, M^+; 1041–873, $[M-n CO]^+$ ($n = 1$–7); 796–642, $[M-7CO-nPh]^+$ ($n = 1$–3).

Band 3 (R_f 0.45) gave yellow crystals (from C_6H_6) of $Ru_2(\mu$-$PPhC_6H_4PPhCH_2)(CO)_5(PPh_3)$ (**6**) (12 mg, 11%). IR (CH_2Cl_2): ν(CO) 2046vs, 1986vs, 1957m (br), 1932w (br) cm^{-1}. FAB MS (m/z): 912, M^+; 828–772, $[M-nCO]^+$ ($n = 3$–5) (most intense peak for $n = 5$). Further crystallisation afforded $Ru_3\{\mu_3$-$PPhCH_2PPh(C_6H_4)\}(CO)_9$ (**5**) as orange crystals, identified form its IR ν(CO) spectrum.

A dark orange band (R_f 0.41) was recrystallised from CH_2Cl_2 to give orange crystals of $Ru_4(\mu_4$-$PPh)(\mu_4$-$PPh_2C_6H_4CO)(\mu$-$PPh_2CH_2)(CO)_8$ (**3**) (67 mg, 41%). IR (cyclohexane): ν(CO) 2042w, 2026vs, 2014(sh), 2000m, 1991m, 1976m, 1968w, 1960vw, 1951w cm^{-1}. FAB MS (m/z): 1226, M^+; 1198–974, $[M-nCO]^+$ ($n = 1$–9); 897–743, $[M-9CO-nPh]^+$ ($n = 1$–3).

Two other minor bands were not identified.

4.2. 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 Kα radiation, $\lambda = 0.71073$ 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, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.0 program system [12] implemented by Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables. Tables of H-atom coordinates and thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

4.3. Abnormal features / variations in procedure

All three determinations recorded in this paper are, for various reasons, inferior, serving only to establish non-hydrogen atom stereochemistries and confirming stoichiometry at that level. The only dimensions with any useful degree of precision are those associated with the heavy atoms. Specifically: for **3**, data were very weak; O(3121) was assigned as such from chemical considerations. Anisotropic thermal parameter forms were refined for Ru and P only. For **4**, data were very weak and limited in extent, refinement problems being compounded by pseudosymmetry. Ru and P only were refined with anisotropic thermal parameter forms, phenyl rings being treated as rigid bodies. The chirality of the asymmetric unit was assigned by a ratio test. For **6**, specimens were compound/twinned aggregates with wide line widths.

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References

[1] A.J. Deeming, in E.W. Abel, F.G.A. Stone and G. Wilkinson (eds.), *Comprehensive Organometallic Chemistry*, Elsevier, Oxford, 2nd edn., 1995, Chapter 12, p. 683.

[2] N. Lugan, J.-J. Bonnet and J.A. Ibers, *J. Am. Chem. Soc.*, *107* (1985) 4484.

[3] M.I. Bruce, E. Horn, O. bin Shawkataly, M.R. Snow, E.R.T. Tiekink and M.L. Williams, *J. Organomet. Chem.*, 316 (1986) 187.

[4] M.I. Bruce, J.R. Hinchliffe, R.J. Surynt, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *469* (1994) 89.

[5] (a) C.W. Bradford and R.S. Nyholm, *J. Chem. Soc., Dalton Trans.*, (1973) 529; (b) M.I. Bruce, G. Shaw and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1972) 2094; (c) M.I. Bruce, J.M. Guss, R. Mason, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, 251 (1983) 261; (d) S.A.R. Knox, B.R. Lloyd, D.A.V. Morton, S.M. Nicholls, A.G. Orpen, J.M. Viñas, M. Weber and G.K. Williams, *J. Organomet. Chem.*, *394* (1990) 385.

[6] J.P.H. Charmant, H.A.A. Dickson, N.J. Grist, J.B. Keister, S.A.R. Knox, D.A.V. Morton, A.G. Orpen and J.M. Viñas, *J. Chem. Soc., Chem. Commun.*, (1991) 1393.

[7] (a) D.F. Foster, J. Harrison, B.S. Nicholls and A.K. Smith, *J. Organomet. Chem.*, *295* (1985) 99; (b) B. Ambwani, S.K. Chawla and A.J. Poë, *Inorg. Chim. Acta*, *133* (1987) 93; (c) B. Ambwani, S. Chawla and A.J. Poë, *Polyhedron*, *7* (1988) 1939; (d) M.I. Bruce, P.A. Humphrey, R.J. Surynt and E.R.T. Tiekink, *Aust. J. Chem.*, *47* (1994) 477.

[8] M.I. Bruce, P.A. Humphrey, B.W. Skelton, A.H. White and M.L. Williams, *Aust. J. Chem.*, *38* (1985) 1301.

[9] (a) C.J. Adams, M.I. Bruce, O. Kühl, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *445* (1993) C6; (b) C.J. Adams, M.I. Bruce, P.A. Duckworth, P.A. Humphrey, O. Kühl, E.R.T. Tiekink, W.R. Cullen, P. Braunstein, S. Coco Cea, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *467* (1994) 251.

[10] H. Jungbluth, G. Süss-Fink, M.A. Pellinghelli and A. Tiripicchio, *Organometallics*, *9* (1990) 1670.

[11] J.F. Corrigan, S. Doherty, N.J. Taylor and A.J. Carty, *J. Am. Chem. Soc.*, *114* (1992) 7557.

[12] S.R. Hall and J.M. Stewart (eds.), *XTAL Users' Manual, Vers. 3.0*, Universities of Western Australia and Maryland, 1990.