Cluster chemistry
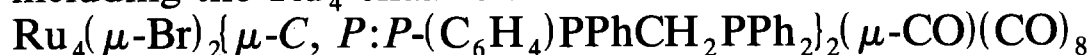
XCIII *. Reactions of $Ru_3(\mu\text{-dppm})(CO)_{10}$ with benzyl halides: isolation and crystal structures of some unusual transformation products, including the Ru_4 chain cluster $Ru_4(\mu\text{-Br})_2\{\mu\text{-}C, P:P\text{-}(C_6H_4)PPhCH_2PPh_2\}_2(\mu\text{-CO})(CO)_8$

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Abstract

Reactions between $Ru_3(\mu\text{-dppm})(CO)_{10}$ and $C_6X_5CH_2Br$ (X = H, Me or F) all gave as a minor product, the tetranuclear chain complex $Ru_4(\mu\text{-Br})_2\{\mu\text{-}C, P:P\text{-}(C_6H_4)PPhCH_2PPh_2\}_2(\mu\text{-CO})(CO)_8$, the structure of which was determined by an X-ray diffraction study. Other products identified were the same as those produced by pyrolysis of $Ru_3(\mu\text{-dppm})(CO)_{10}$; they include two new isomeric binuclear complexes $Ru_2(\mu\text{-CH}_2PPh(C_6H_4)PPh)(CO)_6$ and $Ru_2(\mu\text{-}(C_6H_4)PPhCH_2PPh)(CO)_6$, the former of which was identified by a single-crystal X-ray study.

Key words: Ruthenium; Cluster; Carbonyl

1. Introduction

The substituted trinuclear ruthenium carbonyl complex $Ru_3(\mu\text{-dppm})(CO)_{10}$ (1) was first reported in 1976 [2] and its crystal structure was determined several years later [3]. It was hoped that bridging of one of the Ru–Ru bonds by the bidentate tertiary phosphine ligand would stabilize the complex against the disproportionation reactions that take place with $Ru_3(CO)_{12}$ during reactions in which it might be expected to act as a catalyst. Some studies of the related complex $Ru_3(\mu\text{-dppm})_2(CO)_8$ have also been reported [4].

However, the dppm ligand in these complexes is not inert. Simple pyrolysis results in loss of a phenyl group

and metallation of one of the remaining phenyl groups to give $Ru_3\{\mu_3\text{-}(C_6H_4)PPhCH_2PPh\}(CO)_9$ (2); it is likely that metallation precedes dephenylation and that benzene is formed by combination of H + Ph on the cluster [5]. Dephenylation can also be achieved by treatment with a base such as $K[BH^sBu_3]$, whereupon the anion $[Ru(\mu_3\text{-PPhCH}_2PPh_2)(CO)_9]^-$ (3) is formed [6]. Again, it is supposed that there is initial formation of an anionic hydrido cluster, from which loss of benzene occurs. A considerable amount of derivative chemistry has been based on this anion [6–8]. The reaction of dihydrogen with 1 afforded the same dephenylated complex (4) as was obtained by protonation of 3 [5]; carbonylation of 2 gave a cluster (5) containing the novel diphosphine ligand $C_6H_4(PPh)_2CH_2$ [5].

These reactions often take place so readily as to result in formation of complex mixtures of products from reactions of 1. Nevertheless, the chemistry of 1

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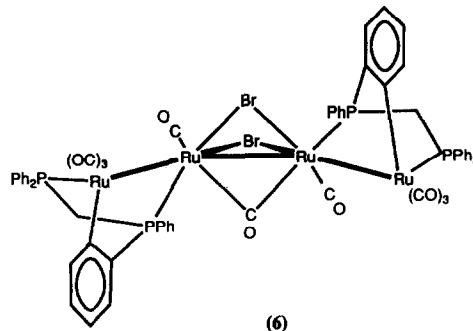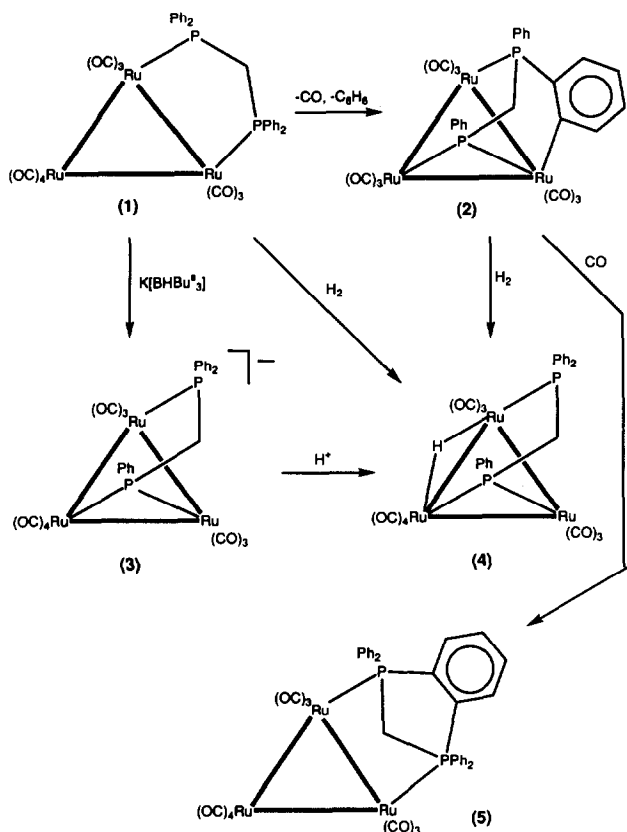
$C_6X_5CH_2Br$ (X = H, Me or F) all afforded mixtures containing small amounts (ca. 1–10%) of five complexes in addition to the metallated dephenylated complex $Ru_3\{\mu_3\text{-}(C_6H_4)PPhCH_2PPh\}(CO)_9$ (2), which was formed with up to 34% yield. Three of these minor products were identified as the isomeric binuclear derivatives $Ru_2\{\mu\text{-}CH_2PPh(C_6H_4)PPh\}(CO)_6$ (7) and $Ru_2\{\mu\text{-}C_6H_4PPh(CH_2)PPh\}(CO)_6$ (8) and the hydrido cluster $Ru_3(\mu\text{-}H)\{\mu\text{-}PPhCH_2PPh_2\}(CO)_9$ (4). However, the most striking of the new complexes was the deep-purple tetranuclear derivative $Ru_4(\mu\text{-}Br)_2\{\mu\text{-}C,P : P\text{-}(C_6H_4)PPhCH_2PPh_2\}_2(\mu\text{-}CO)(CO)_8$ (6), which was identified from a single-crystal X-ray diffraction study (see below). The IR $\nu(CO)$ spectrum contains six bands in the terminal CO region together with a weak absorption at 1837 cm^{-1} which can be assigned to the bridging CO group. The fast-atom bombardment (FAB) mass spectrum contains a molecular ion, which under-

has some interesting features that we have been studying in more detail. The reactions of halogens or of reactive organic halides with 1 have resulted in cluster break-up to give a binuclear ruthenium carbonyl fragment held together by the dppm ligand, while the third ruthenium is probably eliminated as a ruthenium carbonyl halide [9]. Thus from allyl halides, the complexes $Ru_2(\mu\text{-}X)(\mu\text{-}dppm)(\mu\text{-}C_3H_5)(CO)_4$ (X = Cl or Br) have been obtained. In seeking to understand more about this reaction, we have examined analogous reactions between 1 and the benzylic bromides, $C_6X_5CH_2Br$ (X = H, F or Me), only to find several more unusual transformation products of 1, none of which contain the benzylic group. These include the unusual tetranuclear open-chain cluster $Ru_4\{\mu\text{-}PPh_2 CH_2PPh(C_6H_4)\}(\mu\text{-}Br)_2(\mu\text{-}CO)(CO)_8$ (6) and two isomeric binuclear complexes $Ru_2\{\mu\text{-}CH_2PPh(C_6H_4)PPh_2\}(CO)_6$ (7) and $Ru_2\{\mu\text{-}C_6H_4PPh(CH_2)PPh_2\}(CO)_6$ (8), as well as some of the complexes mentioned above.

2. Results and discussion

As described in Section 3, reactions between $Ru_3(\mu\text{-}dppm)(CO)_{10}$ (1) and the benzyl bromides
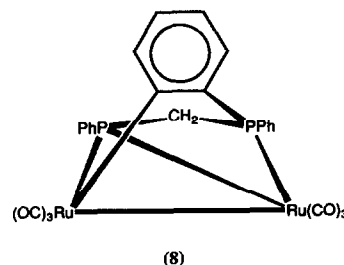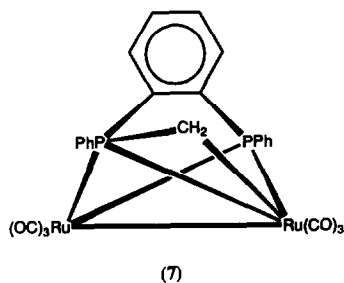
goes fragmentation by loss of up to nine CO groups and two Br atoms. In the ^{1}H NMR spectrum, the CH_2 and aromatic proton signals were found at $\delta = 3.29$ ppm and $\delta = 6.3$–7.9 ppm respectively.

2.1. Molecular structure of $Ru_4(\mu\text{-}Br)_2\{\mu\text{-}C,P : P\text{-}(C_6H_4)PPhCH_2PPh_2\}_2(\mu\text{-}CO)(CO)_8$ (6)

Plots of the two independent molecules of 6, each with quasi-2 symmetry, are shown in Fig. 1, and significant bond parameters are listed in Table 1. The half-molecules differ in the dispositions of the peripheral phenyl rings. The central feature is a non-linear Ru_4 chain (Ru(1)–Ru(2)–Ru(3), 143.79(7) and 148.36(8)°; Ru(2)–Ru(3)–Ru(4), 144.28(8), and 147.80(9)° (values for two independent molecules given)). The shorter central Ru(2)–Ru(3) vector (2.789(2) and 2.788(2) Å) is symmetrically bridged by a CO ligand and slightly asymmetrically by two Br atoms (Ru–Br distances, 2.590–2.635(2) and 2.600–2.629(3) Å); the longer Ru–Br bonds are *trans* to the terminal CO ligands on Ru(2) and Ru(3). The outer Ru–Ru vectors (2.845(2) and 2.846(2) Å; 2.869(3) and 2.863(2) Å) are each bridged by a metallated dppm ligand (Ru(1)–C(212), 2.10(2) and 2.17(2) Å; Ru(4)–C(312), 2.15(2) and 2.17(2) Å), with Ru–P distances to the inner Ru atoms

(2.252(5)–2.260(6) Å) considerably shorter than those to the outer Ru atoms (2.347(6)–2.384(6)(1) Å). In 2, the Ru–P and Ru–C(C_6H_4) distances are 2.351(1) Å and 2.158(3) Å respectively [5]. Coordination to each of the latter metal atoms is completed by three CO ligands, resulting in a 66-electron count for this open cluster.

Chains of four Ru atoms have been found before in a series of complexes obtained from $Ru_3(CO)_{12}$ and monoazabutadienes or diazabutadienes [10–12]. These compounds are centrosymmetric 66-electron clusters in which the Ru_4 chain is almost linear (angles at inner Ru atoms, 176.48(6) for $Ru_4H_2(\mu\text{-}R\text{-}dab)_2(\mu\text{-}CO)_2(CO)_6$ (9) (R = CH_2^tBu)) [10] and 174.55(2) for $Ru_4(\mu\text{-}CHMe=CHCH=N^iPr)$ $(CO)_8$ (10) [11]). In the former, the outer Ru atoms are each bonded to a terminal H atom. For 9 and 10, the Ru–Ru separations are 2.806(2) and 2.7819(5) Å (outer), and 2.745(2) and 2.7084(4) Å respectively.

Complex 6 was never obtained with yields of greater than about 3%. We have not been able to obtain evidence for its formation in reactions of either 1 or the metallated complex with possible sources of Br, such as Br_2, HBr, N-bromosuccinimide or allyl bromide. Possibly reaction occurs by addition of the benzyl

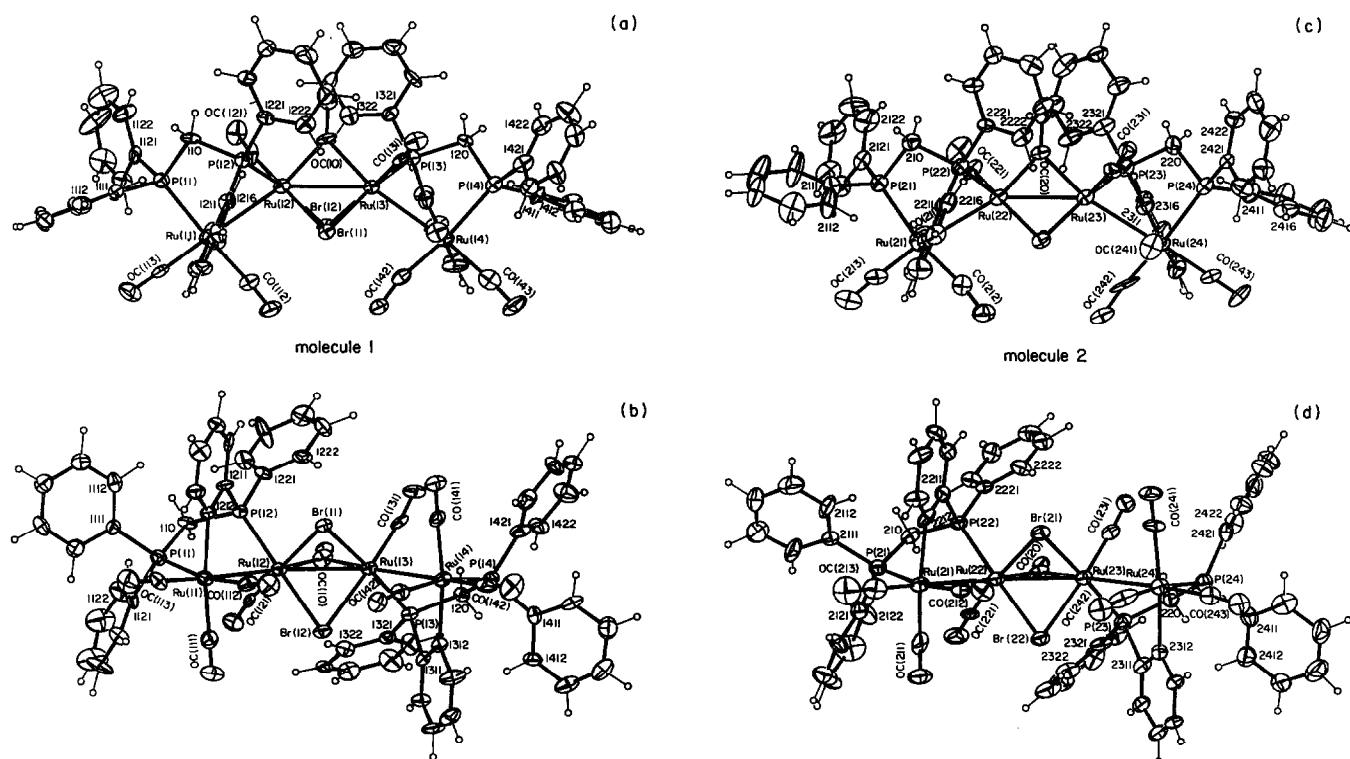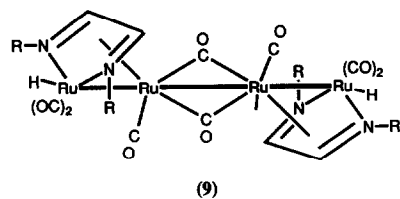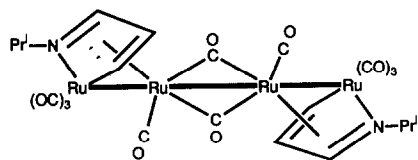Fig. 1. Two views of of molecules 1 and 2 of $Ru_4\{\mu\text{-}(C_6H_4)PPhCH_2PPh_2\}(\mu\text{-}Br)_2(\mu\text{-}CO)(CO)_8$ (6), showing the atom-numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

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bromide to give an intermediate which loses $C_6X_5CH_3$ (by combination of the $C_6X_5CH_2$ group with the H from dppm) and dimerizes via the Br atoms.

The other minor products have also been found in the products of thermolysis of $Ru_3(\mu\text{-dppm})(CO)_{10}$

itself. As mentioned above, Bonnet and coworkers [5] have described the formation of **2** by pyrolysis of **1**. In our study, this complex was also obtained as the major product. The previously unreported binuclear species **7** and **8** were isolated with about 10% yields and were characterized by an X-ray study of the former and by comparison of the nuclear magnetic resonance (NMR) and mass spectra of the two complexes. Their IR spectra are similar in the CO region (six bands between 2070 and 1970 cm^{-1}) and both FAB mass spectra contain molecular ions. Both fragmented to give the expected series $[M - nCO]^+$ ($n = 1$–6). Their NMR spectra serve to characterize them further. The Ru-bonded CH_2 group in **7** resonates as an AB quartet at $\delta = 0.15$ and 0.82 ppm, showing the high-field shift characteristic of metal-bonded alkyl groups. In the spectrum of **8**, the CH_2 protons are found at the more usual position of $\delta = 3.80$ and 3.98 ppm. In the ^{13}C NMR spectra, the CH_2 carbons are found at $\delta = -17.5$ and 43.0 ppm, the former again being characteristic of the metal-bonded alkyl (cf. the value of $\delta = -20.8$

TABLE 1. Important bond parameters for $Ru_4\{\mu\text{-(}C_6H_4)PPhCH_2PPh_2\}(\mu\text{-Br})_2(\mu\text{-CO})(CO)_8$ (**6**) (values for molecules 1 and 2 given).

	Bond lengths (Å)		Bond lengths (Å)
Ru(1)–Ru(2)	2.845(2), 2.869(3)	Ru(1)–C(212)	2.10(2), 2.17(2)
Ru(2)–Ru(3)	2.789(2), 2.788(2)	Ru(4)–C(312)	2.15(2), 2.17(2)
Ru(3)–Ru(4)	2.846(2), 2.863(2)	Ru(2)–C(0)	2.04(2), 1.98(2)
Ru(2)–Br(1)	2.615(3), 2.629(3)	Ru(3)–C(0)	2.08(2), 2.04(2)
Ru(2)–Br(2)	2.592(2), 2.610(3)	Ru(2)–C(21)	1.80(2), 1.81(2)
Ru(3)–Br(1)	2.590(3), 2.600(3)	Ru(3)–C(31)	1.86(2), 1.81(2)
Ru(3)–Br(2)	2.635(2), 2.626(3)	Ru(1)–C(11)	1.99(2), 1.97(2)
Ru(1)–P(1)	2.354(5), 2.384(6)	Ru(1)–C(12)	1.96(2), 1.90(2)
Ru(2)–P(2)	2.258(5), 2.263(5)	Ru(1)–C(13)	1.83(2), 1.81(2)
Ru(3)–P(3)	2.252(5), 2.260(6)	Ru(4)–C(41)	1.93(2), 2.00(2)
Ru(4)–P(4)	2.347(6), 2.364(6)	Ru(4)–C(42)	1.84(2), 1.77(3)
		Ru(4)–C(43)	1.90(2), 1.91(2)

	Bond angles (°)		
Ru(2)–Br(1)–Ru(3)	64.79(7), 64.42(8)	P(1)–Ru(1)–Ru(2)	92.3(1), 92.9(2)
Ru(2)–Br(2)–Ru(3)	64.49(7), 64.34(7)	P(2)–Ru(2)–Ru(1)	76.8(1), 76.1(2)
Ru(1)–Ru(2)–Ru(3)	143.79(7), 148.36(8)	Ru(4)–P(4)–C(20)	108.0(6), 106.3(7)
Ru(2)–Ru(3)–Ru(4)	144.28(8), 147.80(9)	Ru(3)–P(3)–C(20)	115.0(6), 113.2(7)
Ru(1)–P(1)–C(10)	109.4(6), 107.6(7)	P(4)–Ru(4)–Ru(3)	94.3(1), 93.9(2)
Ru(2)–P(2)–C(10)	114.4(5), 114.3(6)	P(3)–Ru(3)–Ru(4)	77.0(1), 75.4(1)
Ru(2)–C(0)–Ru(3)	85.1(6), 87.8(7)		

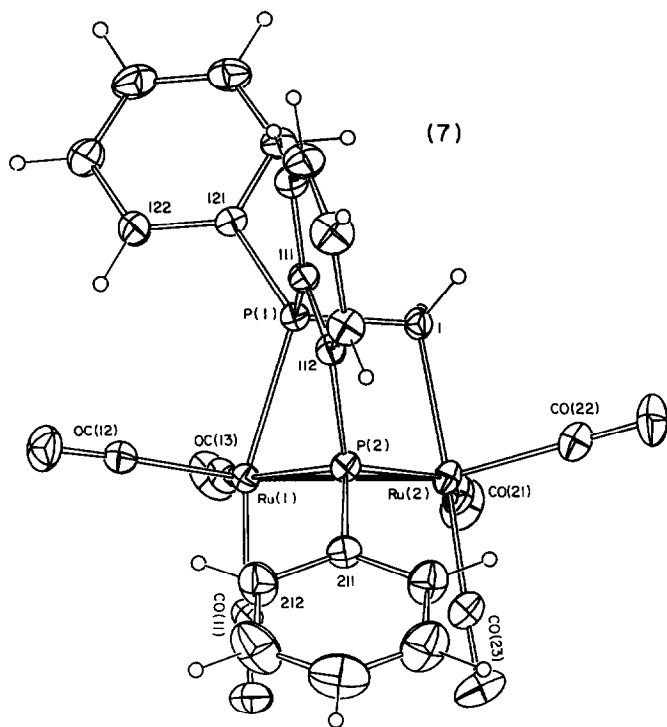|	Phosphine ring torsion angles (molecules 1 and 2) (°)		Phosphine ring torsion angles (molecules 1 and 2) (°)
P(1)–Ru(1)–Ru(2)–P(2)	42.9(2), 43.4(2)	P(4)–Ru(4)–Ru(3)–P(3)	40.0(2), 42.6(2)
Ru(1)–Ru(2)–P(2)–C(10)	−62.4(6), −63.8(8)	Ru(4)–Ru(3)–P(3)–C(20)	−59.3(6), −63.3(7)
Ru(2)–P(2)–C(10)–P(1)	56(1), 58(1)	Ru(3)–P(3)–C(20)–P(4)	57(1), 61(1)
P(2)–C(10)–P(1)–Ru(1)	−7(1), −9(1)	P(3)–C(20)–P(4)–Ru(4)	−10(1), −12(1)
C(10)–P(1)–Ru(1)–Ru(2)	−27.7(6), −26.9(7)	C(20)–P(4)–Ru(4)–Ru(3)	−23.7(6), −24.6(6).

Fig. 2. Molecular structure of Ru₂{μ-CH₂PPh(C₆H₄)PPh}(CO)₆ (7).

positions, the latter now being σ bonded to the metal atom.

2.2. Molecular structure of Ru₂{μ-CH₂PPh(C₆H₄)-PPh}(CO)₆ (7)

Figure 2 depicts a molecule of **7**, and important bond distances and angles are given in Table 2. The binuclear complex consists of an Ru₂ centre (2.8110(7) Å) bridged by the novel phosphino-phosphide ligand, which is attached to Ru(2) by the CH₂ group (Ru(2)–C(1), 2.232(6) Å) and to Ru(1) by P(1) (2.356(1) Å), while atom P(2) bridges both Ru atoms (Ru(1, 2)–P(2), 2.332(1) and 2.343(1) Å). The Ru(2)–C(1) distance (2.232(6) Å) is similar to those found in Ru₂(μ-dmpm)₂{μ-2,η¹-C₂H₂(CO₂Me)₂}(CO)₄ [14], while angle Ru(2)–C(1)–P(1) is only 99.4(2)°. The angle subtended at P(2) by the two Ru atoms is 73.92(3)°, consistent with a strong Ru–Ru interaction. Three CO ligands on each Ru atom complete their coordination environments, each attaining an 18-electron configuration.

3. Experimental details

3.1. General comments

General experimental conditions were similar to those described in an earlier paper [15].

3.2. Pyrolysis of Ru₃(μ-dppm)(CO)₁₀ in refluxing tetrahydrofuran

A tetrahydrofuran (THF) (40 cm³) solution of Ru₃(μ-dppm)(CO)₁₀ (251 mg, 0.259 mmol) was refluxed for 20 h. Following removal of solvent in vacuo, the residue was dissolved in CH₂Cl₂ (2.0 cm³) and

ppm found for [Ru₂(μ-dmpm)₂(Me)(CO)₅][OTf] [13]. Of the six CO resonances found for **7**, three are coupled to ³¹P and can be assigned as shown; for **8**, only one of the four CO resonances is so coupled. These data are consistent with the solid state structure of **7** (see below) and with the fact that **8** is an isomer in which the CH₂ and C₆H₄ groups have exchanged

TABLE 2. Important bond parameters in Ru₂{μ-CH₂PPh(C₆H₄)PPh}(CO)₆ (7)

	Bond distance (Å)		Bond distance (Å)
Ru(1)–Ru(2)	2.8110(7)	Ru(2)–C(21)	1.921(5)
Ru(1)–P(1)	2.356(1)	Ru(2)–C(22)	1.899(5)
Ru(1)–P(2)	2.332(1)	Ru(2)–C(23)	1.917(7)
Ru(2)–P(2)	2.343(1)	P(1)–C(1)	1.786(4)
Ru(2)–C(1)	2.232(6)	P(1)–C(111)	1.827(4)
Ru(1)–C(11)	1.916(6)	P(1)–C(121)	1.814(6)
Ru(1)–C(12)	1.907(5)	P(2)–C(112)	1.815(4)
Ru(1)–C(13)	1.937(6)	P(2)–C(211)	1.811(6)

	Bond angle (°)		Bond angle (°)
Ru(2)–Ru(1)–P(1)	72.52(4)	P(2)–C(112)–C(111)	114.3(3)
Ru(1)–Ru(2)–C(1)	80.0(1)	P(1)–C(111)–C(112)	114.1(3)
Ru(1)–P(2)–Ru(2)	73.92(3)	Ru(1)–P(1)–C(111)	107.8(2)
Ru(1)–P(1)–C(1)	103.5(2)	Ru(1)–P(2)–C(112)	109.3(2)
Ru(2)–C(1)–P(1)	99.4(2)	Ru(2)–P(2)–C(112)	117.2(1)

separated into five fractions by preparative thin layer chromatography (TLC) (light petroleum : acetone, 4 : 1).

The product from band 1 ($R_f = 0.78$) was recrystallized (CH_2Cl_2–C_6H_{14}) to give pale-yellow crystals of $Ru_2\{\mu$-$CH_2PPh(C_6H_4)PPh\}(CO)_6$ (**7**) (23.2 mg (13%)) identified by X-ray crystallography (melting point (m.p.), 208–210°C (decomposition)). Found ($M^+= 677$): C, 44.41; H, 2.35. $C_{25}H_{16}O_6P_2Ru_2$ calc ($M = 677$): C, 44.38; H, 2.38%. IR (cyclohexane): ν(CO) 2069s, 2036s, 2007s, 1988m, 1983m, 1972m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.15 (dd, 1H, J(PH) = 11 Hz, J(HH) = 4 Hz, CH$_2$); 0.82 (m, 1H, CH$_2$); 6.73 (t, 1H, J(HH) = 8 Hz, C$_6$H$_4$): 6.95 (t, 1H, J(HH) = 8 Hz, C$_6$H$_4$); 7.06 (m, 1H, C$_6$H$_4$); 7.24 (m, 1H, C$_6$H$_4$); 7.58–7.70 (m, 8H, Ph); 7.98 (m, 2H, Ph) ppm. ^{13}C NMR (CDCl$_3$): δ −17.5 (dd, J(PP) = 13 Hz, J(PC) = 6 Hz, CH$_2$); 126.7–135.8 (m, Ph); 141.5 (m, C$_6$H$_4$); 146.4 (m, C$_6$H$_4$); 195.9 (dd, J(PC) = 10 Hz, J(PC) = 3 Hz, CO); 196.4 (m, CO); 197.2 (dd, J(PC) = 13 Hz, J(PC) = 3 Hz, CO); 198.6 (dd, J(PP) = 83 Hz, J(PC) = 11 Hz, CO); 202.6 (dd, J(PC) = 45 Hz, J(PC) = 14 Hz, CO); 203.5 (s, CO); 204.4 (s, CO) ppm. FAB mass spectroscopy (MS); m/z 677 (M$^+$), 649–509 ([M − nCO]$^+$ (n = 1–6), 432 ([M − 6CO − Ph]$^+$).

Band 2 ($R_f = 0.59$) did not afford X-ray quality crystals, but the formula $Ru_2\{\mu$-$(C_6H_4)PPhCH_2$-$PPh\}(CO)_6$ (**8**) was assigned to the product (1.5 mg (1%)) on the basis of spectroscopic data. Found ($M^+= 677$): C, 44.40; H, 2.44%. $C_{25}H_{16}O_6P_2Ru_2$ calc. ($M = 676.5$): C, 44.38; H, 2.38%. IR (cyclohexane): ν(CO) 2071s, 2036s, 2010s, 1992m, 1985m, 1974ms cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.80 (m, 1H, CH$_2$, ABXY pattern); 3.98 (m, 1H, CH$_2$, ABXY pattern); 6.19 (t, 1H, J(HH) = 8 Hz, C$_6$H$_4$), 6.69 (t, 1H, C$_6$H$_4$); 6.98 (m, 1H, C$_6$H$_4$); 7.47–7.81 (m, 10H, Ph); 7.96 (d, 1H, J(HH) = 8 Hz, C$_6$H$_4$) ppm. ^{13}C NMR (CDCl$_3$): δ 43.0 (dd, J(PC) = 29 Hz, J(PC) = 10 Hz, CH$_2$); 122.5 (s, C$_6$H$_4$); 122.6–132.6 (m, Ph or C$_6$H$_4$); 146.3 (s, Ph or C$_6$H$_4$); 147.1 (s, Ph); 195.9 (m, CO); 197.1 (s, CO); 203.7 (s, CO); 204.5 (s, CO) ppm. FAB MS: m/z 677 (M$^+$), 649–509 ([M − nCO]$^+$ (n = 1–6)), 432 ([M − 6CO − Ph]$^+$).

Bands 3 ($R_f = 0.53$), 4 ($R_f = 0.45$) and 5 ($R_f = 0.32$) contained $Ru_3(\mu$-H)(μ_3-PPhCH$_2$PPh$_2$)(CO)$_9$ (**4**) (14.9 mg (7%)), $Ru_3\{\mu_3$-$(C_6H_4)PPhCH_2PPh\}(CO)_9$ (**2**) (75.2 mg (34%)) and $Ru_3(\mu$-dppm)(CO)$_{10}$ (**1**) (1.5 mg (1%)), all identified from their IR ν(CO) spectra.

3.3. Reactions of Ru$_3$(μ-dppm)(CO)$_{10}$

3.3.1. With C$_6$F$_5$CH$_2$Br
A mixture of Ru$_3$(μ-dppm)(CO)$_{10}$ (225 mg, 0.233 mmol) and C$_6$F$_5$CH$_2$Br (0.20 cm^3, 350 mg, 1.324 mmol) in refluxing THF (40 cm^3) was heated under reflux for 36 h. Following removal of solvent and the excess of C$_6$F$_5$CH$_2$Br in vacuo, the residue was dissolved in

CH$_2$Cl$_2$ (2.0 cm^3) and separated into nine fractions by preparative TLC (light petroleum : acetone, 4 : 1).

Bands 1–3 and 5 contained **7** (6.4 mg (6%)), **4** (5.8 mg (4%)), **2** (68.2 mg (34%)) and **1** (51.6 mg (23%)) respectively. Bands 4 and 6–8 contained small amounts (about 1–3 mg each) of unidentified complexes. Band 9 ($R_f = 0.17$) gave purple crystals (from CH$_2$Cl$_2$–MeOH) of Ru$_4$(μ-Br)$_2\{\mu$-PPhCH$_2$PPh(C$_6$H$_4$)$\}_2$(μ-CO)(CO)$_8$ (**6**) (7.2 mg (3%)) (m.p. 161–167 °C (decomposition)). Found ($M^+= 1583$): C, 44.72; H, 2.65. $C_{59}H_{42}O_9P_4$-Br$_2$Ru$_4$ calc. ($M = 1583$): C, 44.81; H, 2.87%. IR (cyclohexane): ν(CO) 2071ms, 2055m, 2017vs, 1983s, 1968m, 1946m, 1936m, 1836w cm^{-1}. ^{1}H NMR (CDCl$_3$): 3.92 (m, 2H, CH$_2$), 6.34 (m, 2H, C$_6$H$_4$); 6.50 (m, 1H, C$_6$H$_4$); 6.80 (m, 2H, C$_6$H$_4$); 6.91 (m, 1H, C$_6$H$_4$); 7.33–7.79 (m, 30H, Ph); 7.92 (m, 2H, C$_6$H$_4$) ppm. FAB MS: m/z 1583 (M$^+$), 1527 ([M − 2CO]$^+$), 1471–1331 ([M − nCO]$^+$ (n = 4–9)), 1251, 1171, ([M − 9CO − nBr]$^+$ (n = 1, 2)).

3.3.2. With C$_6$H$_5$CH$_2$Br
A solution of Ru$_3$(μ-dppm)(CO)$_{10}$ (88 mg, 0.091 mmol) and C$_6$H$_5$CH$_2$Br (155 mg, 0.091 mmol) was heated in refluxing THF (40 cm^3) for 20 h. Following removal of solvent and excess C$_6$H$_5$CH$_2$Br in vacuo, the residue was dissolved in CH$_2$Cl$_2$ (2.0 cm^3) and separated into seven fractions by preparative TLC (light petroleum : acetone, 4 : 1).

Bands 1–5 contained **7** (5.8 mg (9%)), **8** (4.2 mg (7%)), **4** (2.0 mg (3%)), **2** (24.4 mg (31%)) and **1** (1.1 mg (1%)). Band 6 ($R_f = 0.20$) contained a purple complex, but this was not identified (0.5 mg (0.3%)). IR (cyclohexane): ν(CO) 2072 ms, 2055 m, 2016 s, 1982 ms, 1945 m, 1923 m, 1837 w cm^{-1}. FAB MS: m/z 1597 (M$^+$), 1457 ([M − 5CO]$^+$), 1429 ([M − 6CO]$^+$). Band 7 ($R_f = 0.18$) contained **6** (3.0 mg (2%)).

3.3.3. With C$_6$Me$_5$CH$_2$Br
A THF (40 cm^3) solution of Ru$_3$(μ-dppm)(CO)$_{10}$ (152 g, 0.157 mmol) and C$_6$Me$_5$CH$_2$Br (250 mg, 1.04 mmol) was refluxed for 30 h. Following removal of solvent in vacuo, the residue was dissolved in CH$_2$Cl$_2$ (about 2.0 cm^3) and separated into seven fractions by preparative TLC (light petroleum : acetone, 4 : 1). Band 1 ($R_f = 0.98$) contained C$_6$Me$_6$, identified from its mass spectrum (m/z = 162) (19.6 mg (8%)). Bands 2–7 contained **7** (6.4 mg (6%)), **8** (3.6 mg (3%)), **4** (5.4 mg (4%)), **2** (34.0 mg (25%)), **1** (20.6 mg (14%)) and **6** (7.2 mg (3%)).

3.4. Structure determinations
Unique room-temperature diffractometer data sets (T ca. 295 K; $2\theta/\theta$ scan mode with $2\theta_{max} = 50°$; monochromatic Mo Kα radiation with $\lambda = 0.7107_3$ Å)

TABLE 3. Positional parameters for non-hydrogen atoms in Ru$_4${μ-(C$_6$H$_4$)PPhCH$_2$PPh$_2$}(μ-Br)$_2$(μ-CO)(CO)$_8$ (6) (values for molecules 1 and 2 given)

Atom	Molecule 1				Molecule 2 [a]			
	x	y	z	U (Å²)	x	y	x	U (Å²)
Ru(11)	1.0	0.62163(5)	0.5	0.0566(6)	0.24975(8)	0.41369(6)	0.16147(8)	0.0703(7)
Ru(12)	0.86689(8)	0.62265(5)	0.50038(7)	0.0516(6)	0.34965(8)	0.36041(5)	0.12318(8)	0.0600(6)
Ru(13)	0.76561(7)	0.57058(5)	0.52792(7)	0.0488(6)	0.38942(8)	0.27718(6)	0.07961(8)	0.0602(6)
Ru(14)	0.73162(8)	0.48528(5)	0.57729(8)	0.0569(6)	0.35614(9)	0.18669(6)	0.03426(8)	0.0677(7)
Br(11)	0.84586(9)	0.53885(7)	0.45912(9)	0.0567(8)	0.3264(1)	0.28204(7)	0.1758(1)	0.0695(9)
Br(12)	0.8701(1)	0.58515(7)	0.61412(9)	0.0647(8)	0.2907(1)	0.32162(8)	0.0162(1)	0.0728(9)
C(10)	0.7717(9)	0.6357(6)	0.4894(9)	0.063(8)	0.4323(8)	0.3384(7)	0.1043(8)	0.062(8)
O(10)	0.7350(5)	0.6642(4)	0.4714(5)	0.064(5)	0.4875(6)	0.3517(4)	0.1070(6)	0.080(6)
C(111)	1.0094(9)	0.6444(7)	0.592(1)	0.074(9)	0.236(1)	0.4375(7)	0.071(1)	0.10(1)
O(111)	1.0148(8)	0.6563(6)	0.6430(7)	0.129(9)	0.2245(8)	0.4502(6)	0.0201(7)	0.121(8)
C(112)	0.9944(9)	0.5588(6)	0.5300(8)	0.068(9)	0.208(1)	0.3571(7)	0.1386(9)	0.080(9)
O(112)	0.9947(7)	0.5231(4)	0.5439(7)	0.098(7)	0.1794(7)	0.3241(5)	0.1310(8)	0.106(7)
C(113)	1.0848(9)	0.6181(6)	0.4958(9)	0.066(8)	0.181(1)	0.4418(8)	0.184(1)	0.10(1)
O(113)	1.1375(7)	0.6167(6)	0.4910(8)	0.116(8)	0.1362(8)	0.4580(7)	0.199(1)	0.16(1)
C(121)	0.8807(8)	0.6799(7)	0.5304(8)	0.073(9)	0.3636(9)	0.4113(6)	0.0784(8)	0.070(8)
O(121)	0.8853(7)	0.7168(5)	0.5537(7)	0.102(7)	0.3771(8)	0.4415(5)	0.0495(7)	0.118(8)
C(131)	0.6944(9)	0.5602(5)	0.4638(8)	0.052(7)	0.4547(8)	0.2472(7)	0.1294(8)	0.065(8)
O(131)	0.6540(7)	0.5554(5)	0.4200(6)	0.088(6)	0.4982(6)	0.2311(4)	0.1624(7)	0.086(6)
C(141)	0.7179(9)	0.4692(6)	0.4854(9)	0.065(8)	0.3734(9)	0.1690(6)	0.1288(9)	0.076(9)
O(141)	0.7086(7)	0.4586(5)	0.4320(6)	0.090(7)	0.3813(8)	0.1596(5)	0.1794(6)	0.117(8)
C(142)	0.819(1)	0.4804(6)	0.5897(9)	0.070(9)	0.279(1)	0.2068(8)	0.041(1)	0.12(1)
O(142)	0.8740(6)	0.4705(4)	0.6030(6)	0.082(6)	0.2225(7)	0.2179(5)	0.0414(8)	0.115(8)
C(143)	0.720(1)	0.4255(7)	0.6077(9)	0.09(1)	0.3309(9)	0.1278(7)	0.000(1)	0.081(9)
O(143)	0.7152(8)	0.3886(5)	0.6234(8)	0.125(9)	0.3141(8)	0.0946(5)	−0.0250(8)	0.120(8)
P(11)	0.9956(2)	0.6918(2)	0.4442(2)	0.056(2)	0.3195(3)	0.4753(2)	0.1989(3)	0.069(2)
C(1111)	1.0505(8)	0.6942(6)	0.3876(8)	0.055(7)	0.304(1)	0.5075(7)	0.2678(9)	0.075(9)
C(1112)	1.0365(8)	0.6773(6)	0.3211(9)	0.067(8)	0.291(1)	0.4904(8)	0.321(1)	0.14(2)
C(1113)	1.082(1)	0.6762(7)	0.283(1)	0.077(9)	0.275(2)	0.514(1)	0.372(1)	0.16(2)
C(1114)	1.1420(9)	0.6931(8)	0.306(1)	0.08(1)	0.276(1)	0.5608(8)	0.367(1)	0.15(2)
C(1115)	1.155(1)	0.7110(9)	0.368(1)	0.10(1)	0.291(2)	0.5795(8)	0.314(1)	0.19(2)
C(1116)	1.1115(9)	0.7123(7)	0.4090(9)	0.08(1)	0.306(2)	0.5541(9)	0.266(1)	0.17(2)
C(1121)	1.0130(9)	0.7449(6)	0.490(1)	0.072(9)	0.327(1)	0.5187(7)	0.1395(9)	0.078(9)
C(1122)	0.987(1)	0.7852(7)	0.469(1)	0.10(1)	0.382(1)	0.5334(8)	0.129(1)	0.14(2)
C(1123)	1.003(2)	0.8234(9)	0.502(1)	0.16(2)	0.382(1)	0.565(1)	0.079(1)	0.16(2)
C(1124)	1.044(2)	0.8213(8)	0.561(1)	0.17(2)	0.326(1)	0.5859(8)	0.047(1)	0.14(1)
C(1125)	1.073(1)	0.7846(9)	0.581(1)	0.13(1)	0.272(1)	0.5698(9)	0.060(1)	0.13(1)
C(1126)	1.0604(9)	0.7445(7)	0.547(1)	0.08(1)	0.271(1)	0.5389(7)	0.105(1)	0.09(1)
C(110)	0.9167(8)	0.6990(5)	0.3942(8)	0.051(7)	0.4010(9)	0.4513(7)	0.2238(9)	0.074(9)
P(12)	0.8734(2)	0.6458(2)	0.3979(2)	0.051(2)	0.3942(3)	0.3893(2)	0.2219(2)	0.062(2)
C(1211)	0.9216(8)	0.6061(6)	0.3625(7)	0.055(7)	0.3452(9)	0.3762(6)	0.2802(9)	0.065(8)
C(1212)	0.9780(8)	0.5954(6)	0.4045(7)	0.052(7)	0.2804(9)	0.3845(7)	0.2581(9)	0.073(9)
C(1213)	1.0169(9)	0.5650(7)	0.3761(9)	0.073(9)	0.240(1)	0.3722(8)	0.297(1)	0.10(1)
C(1214)	1.001(1)	0.5467(7)	0.316(1)	0.08(1)	0.260(1)	0.3531(9)	0.361(1)	0.11(1)
C(1215)	0.9437(9)	0.5588(7)	0.2766(9)	0.072(9)	0.323(1)	0.3459(7)	0.381(1)	0.09(1)
C(1216)	0.9044(8)	0.5886(6)	0.2991(9)	0.060(8)	0.365(1)	0.3562(6)	0.3420(9)	0.08(1)
C(1221)	0.8000(8)	0.6546(6)	0.3407(8)	0.057(7)	0.4740(8)	0.3704(6)	0.2568(7)	0.051(7)
C(1222)	0.7566(9)	0.6193(7)	0.3293(8)	0.072(8)	0.482(1)	0.3235(7)	0.269(1)	0.09(1)
C(1223)	0.698(1)	0.6233(7)	0.286(1)	0.09(1)	0.542(1)	0.3074(7)	0.293(1)	0.08(1)
C(1224)	0.684(1)	0.6648(9)	0.256(1)	0.11(1)	0.594(1)	0.3346(9)	0.305(1)	0.10(1)
C(1225)	0.7269(9)	0.6994(8)	0.267(1)	0.14(1)	0.584(1)	0.3825(7)	0.295(1)	0.09(1)
C(1226)	0.7829(9)	0.6949(7)	0.307(1)	0.081(9)	0.5247(8)	0.3983(7)	0.2682(9)	0.070(9)
P(13)	0.7054(2)	0.5909(2)	0.6020(2)	0.051(2)	0.4322(3)	0.2698(2)	−0.0120(3)	0.067(2)
C(1311)	0.7388(8)	0.5633(7)	0.6806(8)	0.064(8)	0.374(1)	0.2501(7)	−0.0824(9)	0.076(9)
C(1312)	0.7478(8)	0.5172(6)	0.6724(8)	0.053(7)	0.3360(8)	0.2124(6)	−0.0654(8)	0.056(8)
C(1313)	0.771(1)	0.4937(7)	0.7311(9)	0.09(1)	0.2933(9)	0.1963(7)	−0.1156(9)	0.076(9)
C(1314)	0.779(1)	0.5142(8)	0.7888(9)	0.09(1)	0.282(1)	0.2139(7)	−0.1768(9)	0.09(1)
C(1315)	0.769(1)	0.5611(8)	0.7937(8)	0.09(1)	0.320(1)	0.2487(7)	−0.1904(9)	0.09(1)
C(1316)	0.7468(9)	0.5865(6)	0.7412(8)	0.067(8)	0.366(1)	0.2680(7)	−0.1426(9)	0.078(9)
C(1321)	0.6977(8)	0.6521(6)	0.6214(7)	0.052(7)	0.469(1)	0.3176(7)	−0.0406(8)	0.077(9)
C(1322)	0.7496(9)	0.6786(7)	0.6250(9)	0.075(9)	0.430(1)	0.3543(8)	−0.0630(9)	0.09(1)

TABLE 3 (continued)

Atom	Molecule 1				Molecule 2 [a]			
	x	y	z	U (Å^2)	x	y	x	U (Å^2)
C(1323)	0.749(1)	0.7256(6)	0.6390(8)	0.072(9)	0.456(1)	0.3942(9)	−0.087(1)	0.12(1)
C(1324)	0.693(1)	0.7436(7)	0.647(1)	0.09(1)	0.521(1)	0.3971(8)	−0.088(1)	0.12(1)
C(1325)	0.641(1)	0.7176(7)	0.644(1)	0.10(1)	0.559(1)	0.3617(8)	−0.068(1)	0.11(1)
C(1326)	0.6426(8)	0.6729(7)	0.632(1)	0.08(1)	0.534(1)	0.3198(8)	−0.0445(9)	0.09(1)
C(120)	0.6250(8)	0.5688(6)	0.5865(8)	0.047(7)	0.493(1)	0.2263(6)	−0.0052(9)	0.072(9)
P(14)	0.6268(3)	0.5075(2)	0.5811(2)	0.058(2)	0.4577(3)	0.1711(2)	0.0092(3)	0.073(2)
C(1411)	0.5966(9)	0.4868(5)	0.6513(9)	0.066(8)	0.457(1)	0.1375(7)	−0.066(1)	0.10(1)
C(1412)	0.6079(9)	0.5069(7)	0.7151(8)	0.069(9)	0.446(1)	0.1562(8)	−0.125(1)	0.11(1)
C(1413)	0.584(1)	0.4890(7)	0.767(1)	0.09(1)	0.441(1)	0.1292(8)	−0.182(1)	0.14(1)
C(1414)	0.553(1)	0.4482(7)	0.758(1)	0.09(1)	0.440(2)	0.084(1)	−0.179(1)	0.16(2)
C(1415)	0.540(1)	0.4254(8)	0.699(1)	0.11(1)	0.448(1)	0.0621(8)	−0.121(1)	0.13(1)
C(1416)	0.564(1)	0.4458(7)	0.6479(9)	0.09(1)	0.455(1)	0.0914(9)	−0.062(1)	0.12(1)
C(1421)	0.562(1)	0.4909(6)	0.5164(8)	0.068(9)	0.5191(9)	0.1428(6)	0.0691(9)	0.066(8)
C(1422)	0.506(1)	0.5116(6)	0.508(1)	0.081(9)	0.582(1)	0.1514(8)	0.072(1)	0.10(1)
C(1423)	0.455(1)	0.4940(9)	0.465(1)	0.12(1)	0.628(1)	0.1253(8)	0.115(1)	0.11(1)
C(1424)	0.460(1)	0.4588(8)	0.427(1)	0.09(1)	0.608(1)	0.0895(8)	0.150(1)	0.12(1)
C(1425)	0.515(1)	0.4375(7)	0.432(1)	0.09(1)	0.548(1)	0.0807(8)	0.148(1)	0.10(1)
C(1426)	0.568(1)	0.4532(7)	0.476(1)	0.09(1)	0.500(1)	0.1058(8)	0.106(1)	0.10(1)

[a] Read 2 for the first digit of the atom number, Ru(11) defines the origin.

TABLE 4. Positional parameters for $Ru_2\{\mu\text{-}CH_2PPh(C_6H_4)PPh\}(CO)_6$ (7)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.84124(4)	0.41883(1)	0.34916(3)	0.0389(2)
Ru(2)	0.91868(4)	0.31131(2)	0.29587(3)	0.0428(2)
C(11)	1.0114(6)	0.4527(2)	0.3566(4)	0.053(3)
O(11)	1.1155(4)	0.4711(2)	0.3629(4)	0.085(3)
C(12)	0.7238(5)	0.4869(2)	0.3142(4)	0.052(2)
O(12)	0.6569(5)	0.5287(2)	0.2931(4)	0.085(3)
C(13)	0.9460(5)	0.4124(2)	0.5315(5)	0.052(2)
O(13)	1.0088(5)	0.4086(2)	0.6371(3)	0.082(2)
C(21)	1.0603(5)	0.2929(2)	0.4702(5)	0.057(2)
O(21)	1.1411(4)	0.2828(2)	0.5740(3)	0.087(2)
C(22)	0.8952(5)	0.2392(2)	0.2154(4)	0.057(2)
O(22)	0.8830(5)	0.1957(2)	0.1705(4)	0.091(3)
C(23)	1.0662(6)	0.3388(2)	0.2630(5)	0.060(3)
O(23)	1.1507(4)	0.3537(2)	0.2389(4)	0.097(3)
C(1)	0.7445(5)	0.2837(2)	0.3350(4)	0.043(2)
P(1)	0.6583(1)	0.35181(5)	0.3219(1)	0.0387(5)
C(111)	0.5073(4)	0.3529(2)	0.1554(4)	0.044(2)
C(112)	0.5543(4)	0.3648(2)	0.0727(4)	0.043(2)
C(113)	0.4508(5)	0.3631(2)	−0.0569(4)	0.058(2)
C(114)	0.3033(6)	0.3509(3)	−0.1011(5)	0.075(3)
C(115)	0.2563(5)	0.3400(2)	−0.0191(5)	0.070(3)
C(116)	0.3578(5)	0.3397(2)	0.1092(4)	0.054(2)
C(121)	0.5697(4)	0.3540(2)	0.4127(4)	0.043(2)
C(122)	0.5540(6)	0.4057(2)	0.4591(5)	0.065(3)
C(123)	0.4907(7)	0.4073(3)	0.5316(6)	0.081(4)
C(124)	0.4430(6)	0.3576(3)	0.5572(5)	0.078(3)
C(125)	0.4597(6)	0.3064(2)	0.5139(5)	0.067(3)
C(126)	0.5220(6)	0.3045(2)	0.4409(5)	0.058(3)
P(2)	0.7532(1)	0.37956(5)	0.1497(1)	0.0412(5)
C(211)	0.7752(5)	0.4140(2)	0.0304(4)	0.051(2)
C(212)	0.7532(8)	0.4722(2)	0.0106(6)	0.083(4)
C(213)	0.767(1)	0.4989(3)	−0.0819(7)	0.115(6)
C(214)	0.7998(9)	0.4671(4)	−0.1539(7)	0.116(5)
C(215)	0.8239(9)	0.4103(4)	−0.1363(7)	0.106(5)
C(216)	0.8109(7)	0.3827(3)	−0.0429(5)	0.078(3)

TABLE 5. Crystal data and refinement details for 6 and 7

Complex	6	7
Formula	$C_{59}H_{40}Br_2O_9P_4Ru_4$	$C_{25}H_{16}O_6P_2Ru_2$
M	1583.0	676.5
Crystal system	Monoclinic	Monoclinic
Space group	Cc $(C_s^4;$ No. 9$)$	$P2_1/c$ $(C_{2h}^5;$ No. 14$)$
a (Å)	21.363(6)	10.546(2)
b (Å)	29.332(8)	23.182(4)
c (Å)	20.737(4)	12.491(2)
U (Å^3)	12787	2585
Z	8	4
D_c (g cm^{-3})	1.62	1.74
$F(000)$	6192	1328
Crystal size (mm $\times$ mm $\times$ mm)	0.14 $\times$ 0.20 $\times$ 0.48	0.43 $\times$ 0.20 $\times$ 0.33
$A^*_{min,max}$ [a]	1.38; 1.56	1.27; 1.54
μ (cm^{-1})	23.3	13.3
$2\theta_{max}$ ($^\circ$)	50	50
N	11228	4554
N_0	5900	3809
R	0.046 [a]	0.030
R_w	0.040 [a]	0.037

[a] Preferred hand.

yielded N independent reflections, N_0 with $I > 3\sigma(I)$ being considered "observed" and used in the large-block full-matrix least-squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms (but see below); $(x, y, z, U_{iso})_H$ were constrained at estimated values. Conventional residuals R and R_w on $|F|$ at convergence are quoted; statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were used. Neutral atom complex scattering factors were employed; computation used the XTAL 3.0 program system [16] implemented by S.R. Hall. Pertinent results are given in Figs. 1 and 2 and Tables 3–5. Lists of hydrogen and thermal parameters and complete non-hydrogen geometries have been deposited with the Cambridge Crystallographic Data Centre.

3.4.1. Abnormal features and variations in procedure for 6

Although extensive, data were weak; anisotropic thermal parameters were refined only for all non-hydrogen atoms, but the dubious credibility of, for example, that for C(242) of molecule 2 (Fig. 1) suggests that the model refinement is on the limit of overparametrization $(n_v = 1404)$ and derivative parameters should be viewed with appropriate circumspection.

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