Tri-, Tetra-, Penta-, and Hexa-nuclear Phenylphosphinidene-capped Products from the Reaction of Dodecacarbonyltriruthenium with Phenylphosphine: Crystal Structures of $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$, $[Ru_5(\mu_4\text{-}PPh)\{\mu\text{-}PPh(OPr^n)\}(\mu\text{-}H)(CO)_{13}]$, $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$, and $[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]$ [†]

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The reaction of $[Ru_3(CO)_{12}]$ with $PPhH_2$ in toluene under reflux affords a range of products, the nature and yields of which are dependent on the reaction times and the molar ratios employed. Compounds isolated and characterised include not only the trinuclear derivatives $[Ru_3(\mu\text{-}PPhH)(\mu\text{-}H)(CO)_{10}]$, $[Ru_3(\mu_3\text{-}PPh)(\mu\text{-}H)_2(CO)_9]$, and $[Ru_3(\mu_3\text{-}PPh)_2(CO)_9]$ but the tetra-, penta-, and hexa-nuclear species $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$, $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}PPhH)_2(CO)_8]$, $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$, $[Ru_6(\mu\text{-}PPh)_2(CO)_n]$ (n = 14 or 15), $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$, and $[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]$ as well as the pentanuclear by-product $[Ru_5(\mu_4\text{-}PPh)\{\mu\text{-}PPh(OPr^n)\}(\mu\text{-}H)(CO)_{13}]$. Crystal-structure determinations have revealed that $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ contains an approximately square-planar array of ruthenium atoms capped on both sides by phenylphosphinidene ligands, that $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$ and $[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]$ have distorted trigonal-prismatic skeletal geometries, and that the ruthenium atom framework in $[Ru_5(\mu_4\text{-}PPh)\{\mu\text{-}PPh(OPr^n)\}(\mu\text{-}H)(CO)_{13}]$ adopts a square-pyramidal configuration with the basal plane being capped by a phenylphosphinidene ligand and a basal edge being bridged by a phosphido group.

The synthesis of metal cluster compounds containing bridging and/or capping monodentate ligands such as diphenylphosphido, PPh_2, and phenylphosphinidene, PPh, has received and continues to receive considerable attention, the function of these ligands being to stabilise the metal clusters to fragmentation during a chemical reaction. A method of synthesis of phosphinidene-capped metal carbonyl clusters involves the reaction of primary phosphines with the appropriate parent carbonyls. Thus Mays and co-workers[1] and Huttner and co-workers[2] have shown that reaction of $[Ru_3(CO)_{12}]$ with an equimolar amount of PRH_2 (R = Ph, $p\text{-}MeOC_6H_4$, or $p\text{-}BrC_6H_4$) under mild conditions produces $[Ru_3(\mu_3\text{-}PR)(\mu\text{-}H)_2(CO)_9]$ (**1**) in moderate yield. In particular, the former[1] established that treatment of $[Ru_3(CO)_{12}]$ with phenylphosphine in chloroform at *ca.* 60 °C leads to the formation of the bridged phosphido derivative $[Ru_3(\mu\text{-}PPhH)(\mu\text{-}H)(CO)_{10}]$ (**2**, R = Ph) which, on thermolysis in cyclohexane under reflux, gives compound (**1**) together with a small amount of $[Ru_3\{\mu_3\text{-}P(C_6H_4)H\}(\mu\text{-}H)_2(CO)_9]$. On the other hand Huttner and co-workers[2] found that $[Ru_3(\mu_3\text{-}PR)_2(CO)_9]$ (**3**) as well as (**1**) (R = $p\text{-}MeOC_6H_4$ or $p\text{-}BrC_6H_4$) is formed in the corresponding reaction in toluene at 60 °C. Products analogous to (**1**) and (**2**) have been isolated from the corresponding reactions involving $[Os_3(CO)_{12}]$ (R = Ph, $p\text{-}MeOC_6H_4$, or C_6H_{11})[1,3] and significantly the intermediate in the formation of $[Os_3(\mu\text{-}PRH)(\mu\text{-}H)(CO)_{10}]$, *viz.* $[Os_3(CO)_{11}(PRH_2)]$, could also be isolated.[1] Crystal-structure determinations on $[Ru_3(\mu\text{-}PPhH)(\mu\text{-}H)(CO)_{10}]$ and $[Ru_3(\mu_3\text{-}PR)(\mu\text{-}H)_2(CO)_9]$ (R = Ph or $p\text{-}MeOC_6H_4$) have confirmed the presence of a bridging phosphido group in compounds of type (**2**) and a capping phosphinidene group in compounds of type (**1**).[1,2]

As part of a programme investigating the potential of the phenylphosphinidene ligand, PPh, for stabilising homo- and hetero-nuclear metal cluster compounds of unusual geometry and stereochemistry we carried out a detailed examination of the reaction of $[Ru_3(CO)_{12}]$ with $PPhH_2$ with the initial object of developing high-yield syntheses of $[Ru_3(\mu\text{-}PPhH)(\mu\text{-}H)(CO)_{10}]$ and $[Ru_3(\mu_3\text{-}PPh)(\mu\text{-}H)_2(CO)_9]$ for subsequent conversion to $[Ru_3(\mu\text{-}PPhH)(CO)_{10}]^-$ and $[Ru_3(\mu_3\text{-}PPh)(\mu\text{-}H)(CO)_9]^-$, potential precursors for the synthesis of higher nuclearity clusters.[4] It soon became clear that the reaction in toluene under reflux affords not only a wide range of products, the nature and yields of which are dependent on the reaction time and the molar ratios employed, but that the majority of these are of nuclearity greater than three. The results of this investigation are reported here; some of these results have been the subject of two preliminary communications.[5,6]

Results and Discussion

Reaction of $[Ru_3(CO)_{12}]$ *with an Equimolar Amount of* $PPhH_2$.—The reaction of equimolar quantities of $[Ru_3(CO)_{12}]$ and $PPhH_2$ in toluene under reflux was found to produce a reaction mixture which gave a large number of bands on column chromatographic treatment, eight of which [in order of elution, yellow, green, brown (i), green-brown, brown (ii), purple, dark green, and brown (iii)] were distinct and could be separated. However, the residues of three of these [green-brown, brown (ii), and brown (iii)] could not be isolated in crystalline form and as a consequence could not be characterised. A ninth band was also observed but only for those reactions with very short

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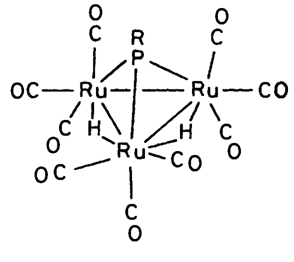
[†] μ-Carbonyl-decacarbonyl-di-μ_4-phenylphosphido-*cyclo*-tetraruthenium (4*Ru–Ru*), 1,1,2,2,3,3,3,4,4,4,5,5,5-tridecacarbonyl-1,2-μ-hydrido-1,2,3,4-μ_4-phenylphosphido-1,2-μ-phenyl(propoxy)phosphido-*cyclo*-pentaruthenium (8 *Ru–Ru*), dodecacarbonyl-1,2,5;3,4,6-di-μ_3-phenylphosphido-1,4,5,6;2,3,5,6-di-μ_4-phenylphosphido-*cyclo*-hexaruthenium (8 *Ru–Ru*), and dodecacarbonyl-1,2,6;3,4,5-di-μ_3-phenylphosphido-1,2,3,4; 2,3,5,6; 1,4,5,6-tri-μ_4-phenylphosphido-*cyclo*-hexaruthenium (6 *Ru–Ru*) respectively.

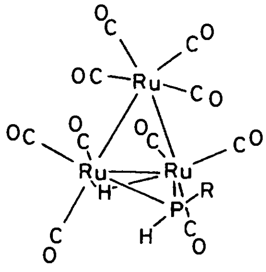
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Selected interatomic distances (Å) and angles (°) for $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ (**4**) with estimated standard deviations in parentheses

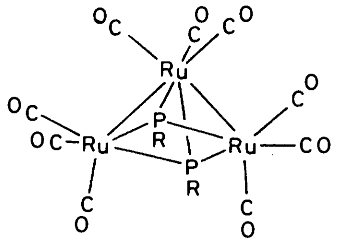
Molecule A		Molecule B		Molecule C	
Ru(1A)–Ru(2A)	2.874(5)	Ru(1B)–Ru(2B)	2.866(5)	Ru(1C)–Ru(2C)	2.853(5)
Ru(1A)–Ru(4A)	2.878(5)	Ru(1B)–Ru(4B)	2.880(5)	Ru(1C)–Ru(4C)	2.910(5)
Ru(2A)–Ru(3A)	2.717(5)	Ru(2B)–Ru(3B)	2.716(5)	Ru(2C)–Ru(3C)	2.714(4)
Ru(3A)–Ru(4A)	2.857(5)	Ru(3B)–Ru(4B)	2.859(5)	Ru(3C)–Ru(4C)	2.836(5)
Ru(1A)–P(1A)	2.39(1)	Ru(1B)–P(1B)	2.39(1)	Ru(1C)–P(1C)	2.39(1)
Ru(2A)–P(1A)	2.48(1)	Ru(2B)–P(1B)	2.50(1)	Ru(2C)–P(1C)	2.50(1)
Ru(3A)–P(1A)	2.45(1)	Ru(3B)–P(1B)	2.47(1)	Ru(3C)–P(1C)	2.49(1)
Ru(4A)–P(1A)	2.42(1)	Ru(4B)–P(1B)	2.37(1)	Ru(4C)–P(1C)	2.40(1)
Ru(1A)–P(2A)	2.39(1)	Ru(1B)–P(2B)	2.38(1)	Ru(1C)–P(2C)	2.39(1)
Ru(2A)–P(2A)	2.46(1)	Ru(2B)–P(2B)	2.49(1)	Ru(2C)–P(2C)	2.47(1)
Ru(3A)–P(2A)	2.52(1)	Ru(3B)–P(2B)	2.49(1)	Ru(3C)–P(2C)	2.52(1)
Ru(4A)–P(2A)	2.38(1)	Ru(4B)–P(2B)	2.38(1)	Ru(4C)–P(2C)	2.39(1)
Ru(2A)–C(6A)	2.09(4)	Ru(2B)–C(6B)	1.96(5)	Ru(2C)–C(6C)	1.98(4)
Ru(3A)–C(6A)	2.01(4)	Ru(3B)–C(6B)	2.14(5)	Ru(3C)–C(6C)	1.96(4)
Ru(1A)–C(3A)	1.90(6)	Ru(1B)–C(3B)	1.92(5)	Ru(1C)–C(3C)	1.90(5)
Ru(2A) ··· C(3A)	2.73(6)	Ru(2B) ··· C(3B)	2.80(5)	Ru(2C) ··· C(3C)	2.69(5)
Ru(3A) ··· C(9A)	2.63(6)	Ru(3B) ··· C(9B)	2.80(7)	Ru(3C) ··· C(9C)	2.61(4)
Ru(4A)–C(9A)	1.74(6)	Ru(4B)–C(9B)	1.82(7)	Ru(4C)–C(9C)	1.92(4)
P(1A) ··· P(2A)	2.76(3)	P(1B) ··· P(2B)	2.76(3)	P(1C) ··· P(2C)	2.80(3)
Ru(2A)–Ru(1A)–Ru(4A)	88.0(1)	Ru(2B)–Ru(1B)–Ru(4B)	88.3(1)	Ru(2C)–Ru(1C)–Ru(4C)	87.5(1)
Ru(1A)–Ru(2A)–Ru(3A)	91.5(1)	Ru(1B)–Ru(2B)–Ru(3B)	91.5(1)	Ru(1C)–Ru(2C)–Ru(3C)	92.1(1)
Ru(2A)–Ru(3A)–Ru(4A)	91.6(1)	Ru(2B)–Ru(3B)–Ru(4B)	91.8(2)	Ru(2C)–Ru(3C)–Ru(4C)	91.8(1)
Ru(3A)–Ru(4A)–Ru(1A)	88.7(1)	Ru(3B)–Ru(4B)–Ru(1B)	88.4(1)	Ru(3C)–Ru(4C)–Ru(1C)	88.5(1)
Ru(2A)–Ru(1A)–C(3A)	66(2)	Ru(2B)–Ru(1B)–C(3B)	68(2)	Ru(2C)–Ru(1C)–C(3C)	66(2)
Ru(3A)–Ru (4A)–C(9A)	65(2)	Ru(3B)–Ru(4B)–C(9B)	69(2)	Ru(3C)–Ru(4C)–C(9C)	63(2)



(**1**)



(**2**)



(**3**)

reaction times. This band, orange in colour and in fact the first to be eluted from the column, gave a crystalline compound, previously reported[1] and characterised as the decacarbonyl $[Ru_3(\mu\text{-}PPhH)(\mu\text{-}H)(CO)_{10}]$ (**2**, R = Ph). The product of the yellow band was similarly found to be the previously reported[1] nonacarbonyl $[Ru_3(\mu_3\text{-}PPh)(\mu\text{-}H)_2(CO)_9]$ (**1**, R = Ph).

Elemental analysis, a molecular mass determination, and a mass spectral measurement revealed that the product of the purple band has the stoicheiometry $[Ru_4(PPh)_2(CO)_{11}]$. Its colour and the presence of a bridging carbonyl stretching band in its i.r. spectrum indicated an unusual stereochemistry and its crystal structure was thus determined.

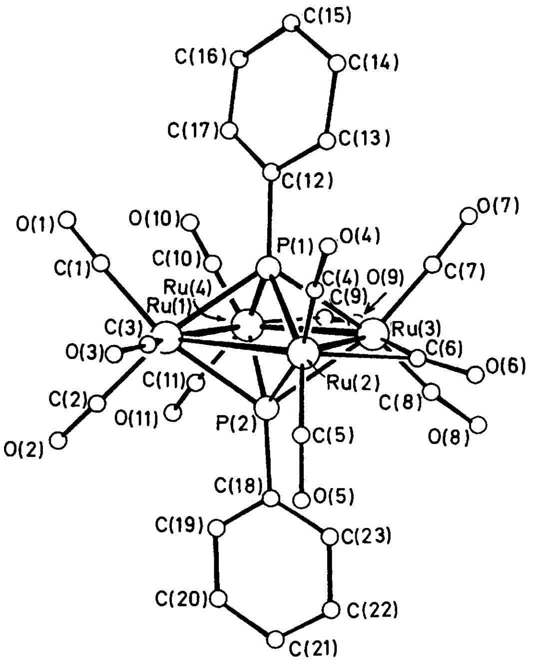
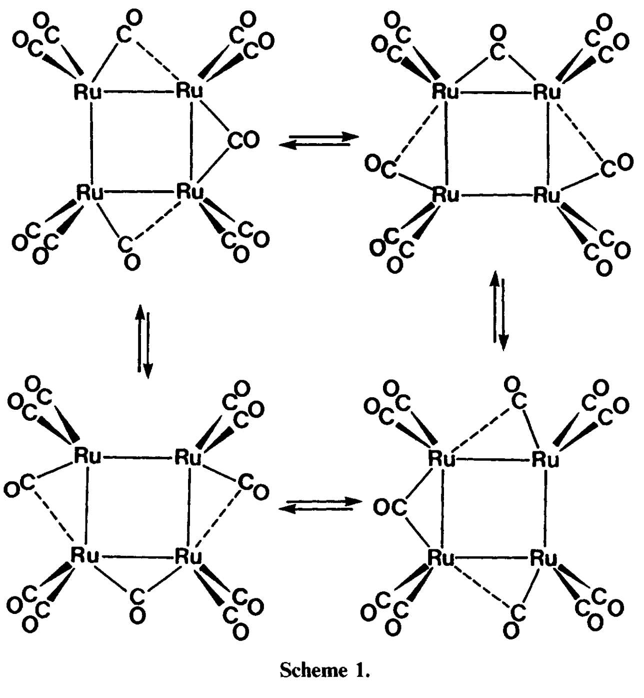


Figure 1. The molecular stereochemistry of $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ (**4**)

The unit cell of this compound, (**4**), was found to contain three molecules per asymmetric unit. The geometries of each of these molecules are very similar and thus the bonding parameters quoted in the following discussion are values averaged over all three molecules. The stereochemistry of each molecule is illustrated in Figure 1 while selected interatomic distances and angles for all three are summarised in Table 1. The compound contains an approximate square planar or, more accurately, trapezoidal array of ruthenium atoms with three of the ruthenium–ruthenium distances being essentially equal with a mean value of 2.868(2) Å and the fourth appreciably shorter, *viz.* 2.716(3) Å. The four ruthenium atoms are capped slightly asymmetrically above and below the metal-atom plane by two phenylphosphinidene ligands such that for each phosphorus atom there is a pair of shorter [mean Ru–P 2.39(1) Å] and a pair of longer [mean Ru-P 2.48(1) Å] ruthenium–phosphorus bonds. The phosphorus–phosphorus separation of 2.77(1) Å is too long to be associated with a phosphorus–phosphorus bond, but molecular orbital calculations on the at present unknown compound $[Fe_4(\mu_4\text{-}PH)_2(CO)_{12}]$ have established that the phosphorus–phosphorus interaction in this species is an attractive one and that the overlap population is +0.501.[7] On this basis it is not unreasonable to assume that the phosphorus–phosphorus interaction in complex (**4**) is also attractive.

Each ruthenium atom is bonded to one terminal carbonyl group above the tetraruthenium plane and to one below the plane. The three remaining carbonyls are coplanar with the ruthenium atoms with one symmetrically bridging the shortest ruthenium–ruthenium edge, Ru(2)–Ru(3). The other two lean towards their adjacent ruthenium atoms, Ru(2) and Ru(3) [Ru(2)–Ru(1)–C(3) 66(2), Ru(3)–Ru(4)–C(9) 65(2)°], and may be considered as semi-bridging on the basis of the ratios of the longer to the shorter ruthenium–carbon distances being considerably less than 1.60, the value taken for practical purposes to be the boundary between terminal and semi-bridging carbonyl groups.[8] The molecular structure described is analogous to those established for $[Fe_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ and $[Fe_2Co_2(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$.[9–11]

The ^{13}C n.m.r. spectrum of a ^{13}CO-enriched sample of (**4**), measured at 32 °C, was found to exhibit a single triplet at 202 p.p.m. corresponding to the carbonyl groups. A decrease in the temperature to −114 °C had no measurable effect on this triplet. These observations can be rationalised in terms of a highly fluxional scrambling process involving the migration of all of the carbonyl groups around the tetraruthenium plane. The mechanism proposed for this process is illustrated in Scheme 1 and involves the intertransformation of carbonyl groups between the bridging and semi-bridging co-ordination modes and the interconversion of out-of-plane terminal and in-plane semi-bridging carbonyl groups in a merry-go-round process.

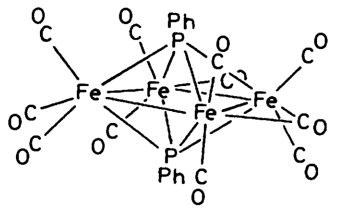


Scheme 1.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (Table 2) of (**4**) contains a single resonance at 168 p.p.m., relative to H_3PO_4, which is upfield of the chemical shifts normally associated with quadruply bridging phenylphosphinidene groups.[12–14] Vahrenkamp and co-workers[13] have noted a similar upfield shift in the ^{31}P n.m.r. spectrum of $[Fe_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ (**5**) with respect to that of $[Fe_4(\mu_4\text{-}PPh)_2(CO)_{12}]$ (**6**) and have explained this shift in terms of compound (**5**) containing an unsaturated tetrairon ring with the effective magnetic field above the centre of the planar tetrairon ring being weakened by a ring current effect.

$[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ (**4**) contains seven skeletal electron pairs and in terms of the polyhedral skeletal electron pair (p.s.e.p.) theory, the $Ru_4(\mu_4\text{-}P)_2$ framework would be predicted to adopt a *closo* octahedral geometry[15] as indeed observed. Compound (**4**) must on this basis be considered a co-ordinatively saturated system. However in the series of structurally characterised clusters containing an $M_4(\mu_4\text{-}E)_2$ (M = metal; E = P, As, or S) square bipyramidal skeletal core,[9–13,16–20] compound (**4**), as well as $[Fe_4(\mu_4\text{-}PC_6H_4Me\text{-}p)_2(\mu\text{-}CO)(CO)_9L]$ [L = CO or $P(OMe)_3$] and $[Rh_4(\mu_4\text{-}PPh)_2(\eta^4\text{-}C_8H_{12})_4]$[9,11,13,16,20] are unusual in that all the other clusters of this series possess eight skeletal electron pairs. Based on molecular orbital calculations for $[Fe_4(\mu_4\text{-}PH)_2(CO)_{12}]$ (see above), Halet *et al.*[7] have provided a rationale for the stabilisation of the eight electron pair systems. The calculations have revealed that for these clusters the eighth skeletal molecular orbital, a metal–metal antibonding orbital, is stabilised by interaction with a 3*d* orbital of each phosphorus atom.[7] Significantly, the downfield shift of the ^{31}P n.m.r. resonances of the eight compared with the seven and six skeletal electron pair systems can also be rationalised in terms of this molecular orbital scheme.

The first green compound eluted from the column was characterised as the pentanuclear species $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$ (**7**), previously isolated in low yield from the reaction of $[Ru_3(CO)_{12}]$ with $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(PPhCl_2)]$ in toluene at 100 °C.[14] An *X*-ray crystallographic investigation has revealed that the five ruthenium atoms adopt a square-pyramidal geometry with the square basal plane being capped by the phenylphosphinidene ligand.[14]



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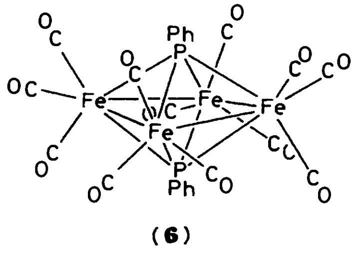


(6)

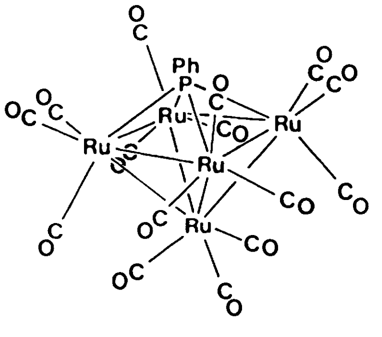
Table 2. Infrared and nuclear magnetic resonance spectroscopic data

	Compound	ν(C–O)/cm^{-1}[a]	^{31}P-{H}[b,c]	^{1}H[b,d]
(2)	$[Ru_3(\mu\text{-}PPhH)(\mu\text{-}H)(CO)_{10}]$	2 098m, 2 060s, 2 050s, 2 024s, 2 011s, 2 000s, 1 990w[e]		7.4 (m, C_6H_5, 5 H)[f] 6.81 (d of d, PH, J_{PH} 388.4, J_{HH} 2.0, 1 H) −16.55 (d of d, RuHRu, J_{PH} 27.2, J_{HH} 2.0, 1 H)
(1)	$[Ru_3(\mu_3\text{-}PPh)(\mu\text{-}H)_2(CO)_9]$	2 105m, 2 073s, 2 045s, 2 030m, 2 018s, 1 998s, 1 985m[e]	279 (s)[g]	7.8 (m, C_6H_5, 5 H)[f] −19.12 (d, RuHRu, J_{PH} 15.1, 2 H)
(3)	$[Ru_3(\mu_3\text{-}PPh)_2(CO)_9]$	2 090w, 2 058s, 2 035s, 2 015s, 2 000s, 1 980m[e]	239 (s)[g]	
(4)	$[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$	2 075m, 2 035s, 2 018s, 1 980s, 1 838m[e] 2 075m, 2 030s, 2 015s, 1 960 (sh), 1 950m, 1 823m, 1 808m[h]	168 (s)[g]	7.1—6.2 (m)[f]
(10)	$[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}PPhH)_2(CO)_8]$	2 013s, 1 992s, 1 967s[e]	379 (t of d, μ_4-P, $J_{PP'}$ 81, $J_{PP''}$ 81)[g,i,j] 161 (d of d, μ-P, $J_{PP''}$ 81, $J_{P'P''}$ 39) −34 (d of t, μ_4-P, $J_{PP'}$ 81, $J_{P'P''}$ 39)	7.4—6.2 (m, C_6H_5, 20 H)[f,k] 6.73 (d of d of d, PH, J_{PH} 379.5, $J_{P'H}$ 18.1, $J_{P''H}$ 14.5, 2 H)
(7)	$[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$	2 090w, 2 050s, 2 030s[e]	434(s)[g]	7.2 (m)[f]
(8)	$[Ru_5(\mu_4\text{-}PPh)\{\mu\text{-}PPh(OPr^n)\}\text{-}(\mu\text{-}H)(CO)_{13}]$	2 083m, 2 048m, 2 030s, 2 022m, 1 993m[e]	439 (d, μ_4-P, J_{PP} 56.2)[g] 273 (d, μ-P, J_{PP} 56.2)	8.0—7.5 (m, C_6H_5)[f] 3.5 (d of t, OCH_2CH$_2$, J_{PH} 8.2, J_{HH} 6.7) 1.5 (OCH$_2$CH_2)[l] 0.8 (t, CH$_2$CH_3, J_{HH} 7.4) −18.67 (d of d, RuHRu, J_{PH} 8.7, $J_{P'H}$ 1.6)
(9)	$[Ru_m(\mu\text{-}PPh)_2(CO)_n]$ (m = 6 or 7, n = 14—18)	2 090w, 2 060s, 2 050s, 2 045 (sh), 2 020s, 2 010m, 1 998w, 1 985w, 1 950w[e]	458 (s)[g]	7.3 (m)[f]
(11)	$[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$	2 030s, 2 020m, 2 007s, 2 000m, 1 990w, 1 983w, 1 958w, 1 950w[e]	578 (t, μ_4-P, $J_{PP'}$ 47.5)[g] 415 (t, μ_3-P, $J_{PP'}$ 47.5)	7.8—7.6 (m)[f]
(12)	$[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]$	2 020s, 1 995w, 1 985w, 1 973w[e]	503 (t of d, μ_4-P, $J_{PP'}$ 44, $J_{PP''}$ 21)[g,i,m] 407 (t of d, μ_3-P, $J_{PP'}$ 44, $J_{P'P''}$ 44) −142 (t of t, μ_4-P, $J_{P'P''}$ 44, $J_{PP''}$ 21)	8.1—7.7 (m)[f]

[a] Abbreviations: s = strong, m = medium, w = weak, sh = shoulder. [b] Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet. [c] δ scale, in p.p.m. relative to H_3PO_4; measured at 32 °C unless otherwise stated. [d] δ scale, relative to $SiMe_4$; measured at 32 °C unless otherwise stated. [e] Measured in cyclohexane. [f] Measured in CD_2Cl_2. [g] Measured in CD_2Cl_2–CH_2Cl_2. [h] Measured in a KBr disc. [i] Measured at −90 °C. [j] Four peaks of triplet of doublets are overlapping producing a quartet; two peaks of doublet of triplets are overlapping producing a five line pattern. [k] Measured at −26 °C. [l] The multiplicity of the set of peaks could not be established because of the presence of an impurity peak. [m] Four peaks of triplet of doublets at 407 are overlapping producing a quartet; four peaks of triplet of triplets are overlapping producing a seven line pattern.

The ^{13}C n.m.r. spectrum of $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$ (7), measured at 25 °C, contains a single broad peak at 196 p.p.m. which can be assigned to the carbon atoms of the carbonyl groups. This resonance is temperature dependent and on cooling to -90 °C, a singlet at 201.1 and a doublet at 194.2 p.p.m. of relative intensity 1:4 are observed; the singlet is assigned to the carbonyls bonded to the apical ruthenium, while the doublet is assigned to the carbonyls bonded to the basal plane ruthenium atoms. These observations are consistent with at least three fluxional processes. First, the presence of a doublet in the low-temperature spectrum can be rationalised in terms of a rapid exchange of the carbonyls co-ordinated to the basal ruthenium atoms such that at -90 °C these carbonyls are equivalent on the n.m.r. time-scale and couple equally with the phosphorus of the phenylphosphinidene ligand. Secondly, the singlet at 201.1 p.p.m. in the spectrum at -90 °C is interpreted in terms of a rapid exchange of the structurally non-equivalent carbonyl ligands of the apical ruthenium at this temperature. The single peak in the spectrum at 25 °C lies at the weighted mean of the two peaks in the low-temperature spectrum which is indicative of a total carbonyl scrambling process over the pentaruthenium core at the higher temperature.

A brown compound, produced in very low yield and only intermittently, and isolated from the first brown band was established by *X*-ray crystallography to be a substituted derivative of $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$ and to have the formula $[Ru_5(\mu_4\text{-}PPh)\{\mu\text{-}PPh(OPr^n)\}(\mu\text{-}H)(CO)_{13}]$ (**8**). The molecular stereochemistry of this compound is illustrated in Figure 2, while selected interatomic distances and angles are given in Table 3. The five ruthenium atoms adopt a square-pyramidal configuration with a basal plane being capped by a quadruply bridging phenylphosphinidene ligand. The ruthenium–ruthenium distances range from 2.778(3) to 2.949(3) Å, typical of formal ruthenium–ruthenium bonds, with the Ru(3)–Ru(4) edge being bridged by a phosphido ligand, PPh(OPr^n). The phosphido bridged ruthenium atoms carry two terminal carbonyls each, with the remaining three rutheniums each carrying three terminal carbonyls. The hydride ligand, evident from the ^1H n.m.r. spectral data, was not located but presumably also bridges Ru(3) and Ru(4).



(**7**)

Table 3. Selected interatomic distances (Å) and angles (°) for $[Ru_5(\mu_4\text{-}PPh)\{\mu\text{-}PPh(OPr^n)\}(\mu\text{-}H)(CO)_{13}]$ (**8**) with estimated standard deviations in parentheses

Ru(1)–Ru(2)	2.879(3)	Ru(1)–Ru(5)	2.836(3)
Ru(2)–Ru(3)	2.939(3)	Ru(2)–Ru(5)	2.949(3)
Ru(3)–Ru(4)	2.778(3)	Ru(3)–Ru(5)	2.891(3)
Ru(4)–Ru(1)	2.936(3)	Ru(4)–Ru(5)	2.899(3)
Ru(1)–P(1)	2.318(7)	Ru(3)–P(1)	2.398(6)
Ru(2)–P(1)	2.360(6)	Ru(4)–P(1)	2.349(7)
Ru(3)–P(2)	2.229(7)	Ru(4)–P(2)	2.232(7)
P(2)–O(14)	1.67(2)	P(2)–C(17)	1.78(2)
Ru(2)–Ru(1)–Ru(4)	89.8(1)	Ru(1)–Ru(4)–Ru(3)	90.2(1)
Ru(2)–Ru(1)–Ru(5)	62.1(1)	Ru(1)–Ru(4)–Ru(5)	58.2(1)
Ru(4)–Ru(1)–Ru(5)	60.3(1)	Ru(3)–Ru(4)–Ru(5)	61.2(1)
Ru(1)–Ru(2)–Ru(3)	88.2(1)	Ru(1)–Ru(5)–Ru(2)	59.6(1)
Ru(1)–Ru(2)–Ru(5)	58.2(1)	Ru(1)–Ru(5)–Ru(3)	90.0(1)
Ru(3)–Ru(2)–Ru(5)	58.8(1)	Ru(1)–Ru(5)–Ru(4)	61.6(1)
Ru(2)–Ru(3)–Ru(4)	91.7(1)	Ru(2)–Ru(5)–Ru(3)	60.4(1)
Ru(2)–Ru(3)–Ru(5)	60.8(1)	Ru(2)–Ru(5)–Ru(4)	89.1(1)
Ru(4)–Ru(3)–Ru(5)	61.5(1)	Ru(3)–Ru(5)–Ru(4)	57.3(1)

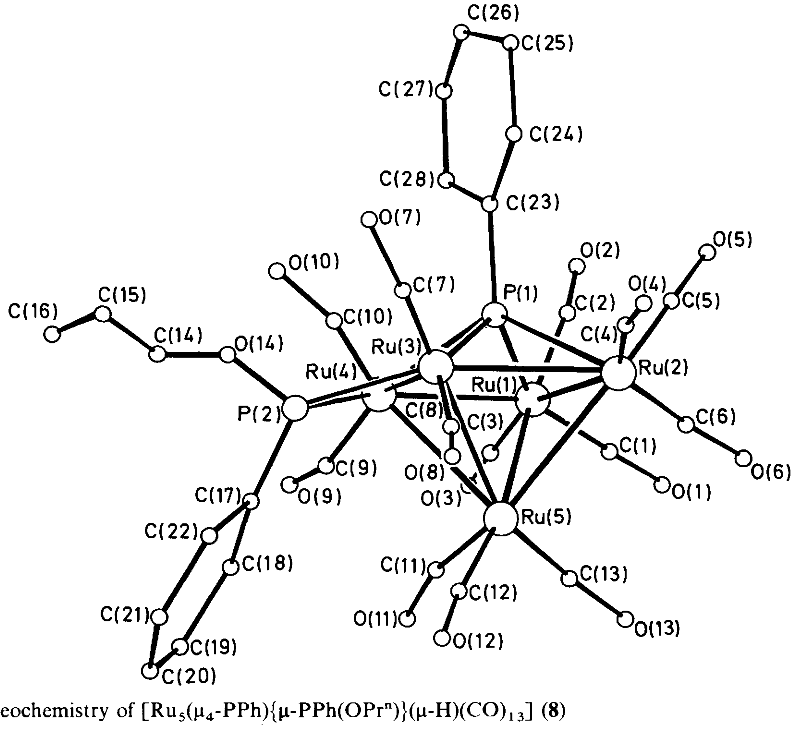


Figure 2. The molecular stereochemistry of $[Ru_5(\mu_4\text{-}PPh)\{\mu\text{-}PPh(OPr^n)\}(\mu\text{-}H)(CO)_{13}]$ (**8**)

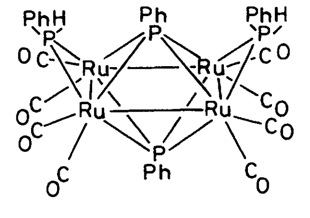
The formation of (**8**) was most unexpected and all possible impurities in phenylphosphine were considered as possible precursors for its formation but none proved likely. However, a reported impurity in toluene is acrolein[21] and insertion of its carbonyl into the P–H bond of unco-ordinated or co-ordinated $PPhH_2$ or PPhH together with hydrogenation of the alkene bond, either prior to or subsequent to the insertion, could well give rise to a $PPh(OPr^n)$ fragment.

Compounds (**7**) and (**8**) are two examples of an expanding series of clusters containing a pseudo-octahedral $M_5(\mu_4\text{-}PR)$ (M = metal; R = alkyl or aryl group, *etc.*) skeletal framework, others being provided by $[Ru_5(\mu_4\text{-}PR)(CO)_{15}]$ (R = Me, Et, or CH_2Ph),[14] $[Ru_5(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)\{\mu_3\text{-}CCH_2(Pr^i)\}(CO)_{12}]$,[22] $[Ru_3Rh_2(\mu_4\text{-}PPh)(CO)_{13}(PEt_3)]$,[23] $[Os_5\{\mu_4\text{-}P(OMe)\}(CO)_{15}]$,[24] and $[M_2Os_3(\mu_4\text{-}PR)(CO)_{15}]$ (M = Os, R = Ph or C_6H_{11}; M = Ru, R = Ph or C_6H_{11}).[25] All of these compounds possess seven skeletal electron pairs, consistent with the p.s.e.p. theory.

The elemental analyses and the molecular mass value, as obtained by vapour-pressure osmometry, of the product isolated from the dark green band eluted from the column were consistent with the stoicheiometry $[Ru_m(PPh)_2(CO)_n]$ (**9**) (*m* = 6 or 7, *n* = 14—18). The presence of a single resonance at δ 458 p.p.m. in the ^{31}P n.m.r. spectrum of this compound is indicative of the phenylphosphinidene ligands being equivalent and co-ordinated to a closed face of the cluster in either the triply or quadruply bridging mode while the dark green colour of the compound is best interpreted in terms of a *closo* structure for the Ru_mP_2 skeletal framework. Numerous attempts to grow crystals of this compound suitable for *X*-ray crystallographic studies proved unsuccessful due to the rapid loss of the solvent of crystallisation. Attempts to establish the molecular ion of this species by electron-impact and field-desorption mass spectrometry also proved unsuccessful.*

Reaction of $[Ru_3(CO)_{12}]$ *with a Three-fold Molar Amount of* $PPhH_2$.—A wide range of products was again found in the reaction of $[Ru_3(CO)_{12}]$ with a three-fold molar amount of $PPhH_2$ in toluene under reflux. Column chromatographic treatment of the reaction mixture led to the separation and isolation of eight distinct bands (in order of elution, yellow, deep yellow, orange, purple, red, magenta, brown, and dull green). The product from the yellow band was shown to be $[Ru_3(\mu_3\text{-}PPh)(\mu\text{-}H)_2(CO)_9]$ (**1**, R = Ph), that from the deep yellow band was characterised as $[Ru_3(\mu_3\text{-}PPh)_2(CO)_9]$ (**3**, R = Ph), previously isolated from the reaction of $[Ru_3(CO)_{12}]$ with an equimolar amount of $PPhH_2$ in toluene at 60 °C[2] (see above), while that from the purple band was also found to be one common to both reactions, *viz.* $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ (**4**).

A red crystalline compound, isolated from the red band, was characterised by means of elemental analysis, mass spectral measurements, and ^1H and ^{31}P n.m.r. spectroscopy as the tetranuclear derivative $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}PPhH)_2(CO)_8]$ (**10**). An *X*-ray crystallographic investigation was carried out on this compound but a suitable solution could not be obtained for the intensity data collected. The Patterson map could be solved in terms of an Ru_4P_2 fragment which defines a square-bipyramidal structure but refinement of this model did not converge. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum at −90 °C (in $CDCl_2\text{–}CH_2Cl_2$) exhibits an overlapping triplet of doublets at 379 p.p.m., a doublet of doublets at 161 p.p.m., and an overlapping doublet of triplets at −34 p.p.m. The set of resonances at 161 p.p.m. occur as a doublet of broad multiplets in the fully coupled ^{31}P n.m.r. spectrum at this temperature with the magnitude of the splitting of the two multiplets, *ca.* 380 Hz, being typical of $^1J_{PH}$. The ^1H n.m.r. spectrum at −26 °C contains, as well as peaks corresponding to phenyl protons, a doublet of doublets of doublets (δ 6.73; J_{PH} 379.5, $J_{P'H}$ 18.1, $J_{P''H}$ 14.5 Hz) readily assigned to a P–H group. On the basis of the crystallographic and spectroscopic results it is proposed that this compound contains an approximate square-planar array of ruthenium atoms capped on both sides of the plane by phenylphosphinidene groups and in which two opposite Ru–Ru edges are bridged by phenylphosphido groups; the latter are *cis* disposed with respect to the tetraruthenium plane as shown below.†



(**10**)

An increase in temperature from −90 °C leads to a shift in the two outer sets of resonances in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**10**) towards each other and subsequently to their collapse such that at room temperature only a doublet of doublets at 162 p.p.m. is observed. Further increases in the temperature up to 120 °C (in $C_6D_5CD_3\text{–}C_6H_5CH_3$) results in only slight changes in the splitting of the set of resonances at 163 p.p.m. and the decomposition of (**10**) prevented the measurement of its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum above 120 °C. The ^1H n.m.r. spectrum of (**10**) also exhibits temperature dependence and the doublet of doublets of doublets at δ 6.73 in the spectrum at −26 °C (in CD_2Cl_2) becomes a doublet of triplets at δ 7.45 at 100 °C (in $C_6D_5CD_3$). It is thus apparent that (**10**) is involved in some fluxional process and the n.m.r. spectroscopic results can be readily rationalised in terms of a 'flapping' motion of the bridging phosphido groups as illustrated in Scheme 2. The ^{31}P n.m.r. spectroscopic data for $[Rh_2(\mu\text{-}PPh_2)_2L_2(\eta^4\text{-}C_8H_{12})]$ (L = PPh_2Me or PEt_3) and $[Fe_2(\mu\text{-}PMe_2)_2(CO)_6]$ have been interpreted in terms of a similar 'flapping' motion.[26,27]

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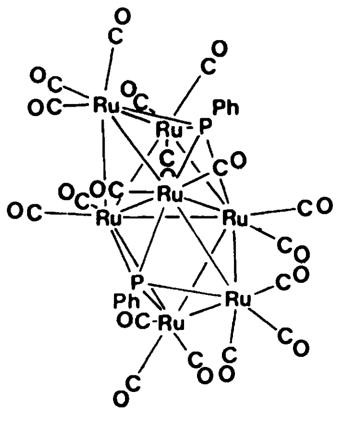
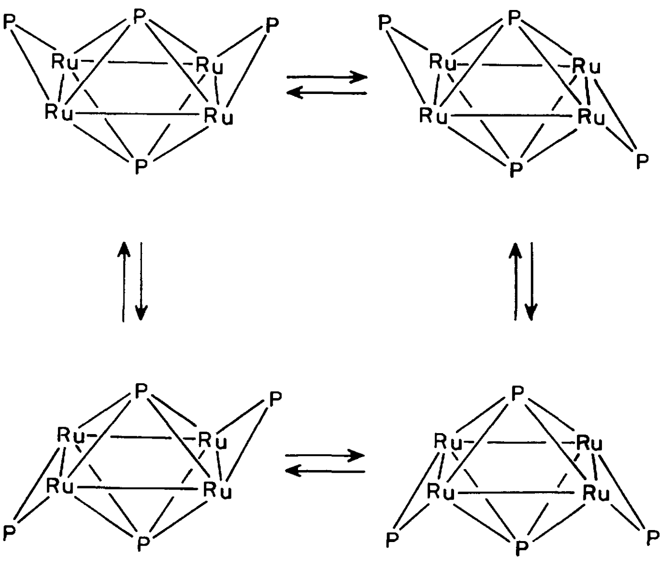
* *Note added in proof.* Subsequent to the submission of this paper the crystal and molecular structure of $[Ru_7(\mu_4\text{-}PPh)_2(CO)_{18}]$ (shown below) has been reported (F. Van Gastel, N. J. Taylor, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1987, 1049). This compound has the same colour, ^{31}P chemical shift, and almost identical C-O stretching frequencies as our compound (**9**) $[Ru_m(PPh)_2(CO)_n]$ (*m* = 6 or 7, *n* = 14 − 18).



† The presence of only four vector lengths of equal height in the Patterson map, corresponding to ruthenium–phosphorus bond distances, is interpreted in terms of the vectors associated with the phenylphosphido groups overlapping with those associated with the phenylphosphinidene groups, consistent with the proposed structure.

Table 4. Selected interatomic distances (Å) and angles (°) for [$Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}$] (**11**) with estimated standard deviations in parentheses

Ru(1A)–Ru(2A)	2.855(2)	Ru(3A)–Ru(4A)	2.838(2)	Ru(1B)–Ru(2B)	2.865(2)	Ru(3B)–Ru(4B)	2.834(2)
Ru(1A)–Ru(3A)	2.852(2)	Ru(3A)–Ru(5A)	3.245(2)	Ru(1B)–Ru(3B)	2.857(2)	Ru(3B)–Ru(5B)	3.220(2)
Ru(1A)–Ru(6A)	3.238(2)	Ru(4A)–Ru(5A)	2.869(2)	Ru(1B)–Ru(6B)	3.258(2)	Ru(4B)–Ru(5B)	2.865(2)
Ru(2A)–Ru(3A)	2.880(2)	Ru(4A)–Ru(6A)	2.859(2)	Ru(2B)–Ru(3B)	2.872(2)	Ru(4B)–Ru(6B)	2.863(2)
Ru(2A)–Ru(5A)	2.818(2)	Ru(5A)–Ru(6A)	2.856(2)	Ru(2B)–Ru(5B)	2.798(2)	Ru(5B)–Ru(6B)	2.857(2)
Ru(1A)–P(1A)	2.288(4)	Ru(2A)–P(3A)	2.321(4)	Ru(1B)–P(1B)	2.276(4)	Ru(2B)–P(3B)	2.320(4)
Ru(2A)–P(1A)	2.198(5)	Ru(5A)–P(3A)	2.329(4)	Ru(2B)–P(1B)	2.183(5)	Ru(5B)–P(3B)	2.343(4)
Ru(3A)–P(1A)	2.281(4)	Ru(6A)–P(3A)	2.432(4)	Ru(3B)–P(1B)	2.294(5)	Ru(6B)–P(3B)	2.436(4)
Ru(4A)–P(2A)	2.194(5)	Ru(1A)–P(4A)	2.432(4)	Ru(4B)–P(2B)	2.199(4)	Ru(1B)–P(4B)	2.432(4)
Ru(5A)–P(2A)	2.288(4)	Ru(3A)–P(4A)	2.320(4)	Ru(5B)–P(2B)	2.295(4)	Ru(3B)–P(4B)	2.338(4)
Ru(6A)–P(2A)	2.290(4)	Ru(4A)–P(4A)	2.318(4)	Ru(6B)–P(2B)	2.272(4)	Ru(4B)–P(4B)	2.334(4)
Ru(1A)–P(3A)	2.391(5)	Ru(6A)–P(4A)	2.391(4)	Ru(1B)–P(3B)	2.382(4)	Ru(6B)–P(4B)	2.378(4)
Ru(2A)–Ru(1A)–Ru(3A)	60.6(1)	Ru(5A)–Ru(4A)–Ru(6A)	59.8(1)	Ru(2B)–Ru(1B)–Ru(3B)	60.3(1)	Ru(5B)–Ru(4B)–Ru(6B)	59.8(1)
Ru(2A)–Ru(1A)–Ru(6A)	90.1(1)	Ru(3A)–Ru(4A)–Ru(5A)	69.3(1)	Ru(2B)–Ru(1B)–Ru(6B)	89.5(1)	Ru(3B)–Ru(4B)–Ru(5B)	68.8(1)
Ru(3A)–Ru(1A)–Ru(6A)	80.6(1)	Ru(3A)–Ru(4A)–Ru(6A)	87.8(1)	Ru(3B)–Ru(1B)–Ru(6B)	80.2(1)	Ru(3B)–Ru(4B)–Ru(6B)	87.8(1)
Ru(1A)–Ru(2A)–Ru(3A)	59.6(1)	Ru(4A)–Ru(5A)–Ru(6A)	59.9(1)	Ru(1B)–Ru(2B)–Ru(3B)	59.7(1)	Ru(4B)–Ru(5B)–Ru(6B)	60.1(1)
Ru(1A)–Ru(2A)–Ru(5A)	87.9(1)	Ru(2A)–Ru(5A)–Ru(4A)	110.1(1)	Ru(1B)–Ru(2B)–Ru(5B)	88.1(1)	Ru(2B)–Ru(5B)–Ru(4B)	110.7(1)
Ru(3A)–Ru(2A)–Ru(5A)	69.4(1)	Ru(2A)–Ru(5A)–Ru(6A)	99.2(1)	Ru(3B)–Ru(2B)–Ru(5B)	69.2(1)	Ru(2B)–Ru(5B)–Ru(6B)	99.7(1)
Ru(1A)–Ru(3A)–Ru(2A)	59.7(1)	Ru(4A)–Ru(6A)–Ru(5A)	60.3(1)	Ru(1B)–Ru(3B)–Ru(2B)	60.0(1)	Ru(4B)–Ru(6B)–Ru(5B)	60.1(1)
Ru(1A)–Ru(3A)–Ru(4A)	98.9(1)	Ru(1A)–Ru(6A)–Ru(4A)	90.1(1)	Ru(1B)–Ru(3B)–Ru(4B)	99.4(1)	Ru(1B)–Ru(6B)–Ru(4B)	90.1(1)
Ru(2A)–Ru(3A)–Ru(4A)	109.2(1)	Ru(1A)–Ru(6A)–Ru(5A)	80.2(1)	Ru(2B)–Ru(3B)–Ru(4B)	109.4(1)	Ru(1B)–Ru(6B)–Ru(5B)	77.9(1)



Scheme 2.

Table 5. Selected interatomic distances (Å) and angles (°) for [$Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}$] (**12**) with estimated standard deviations in parentheses

Ru(1)–Ru(2)	2.877(3)	Ru(3)–Ru(4)	2.930(3)
Ru(1)–Ru(3)	3.323(3)	Ru(4)–Ru(5)	2.892(3)
Ru(1)–Ru(6)	2.944(3)	Ru(4)–Ru(6)	3.509(3)
Ru(2)–Ru(3)	2.881(3)	Ru(5)–Ru(6)	2.887(3)
Ru(2)–Ru(5)	3.241(3)		
Ru(1)–P(1)	2.365(7)	Ru(3)–P(3)	2.358(7)
Ru(2)–P(1)	2.440(7)	Ru(4)–P(3)	2.345(7)
Ru(5)–P(1)	2.413(6)	Ru(5)–P(3)	2.424(7)
Ru(6)–P(1)	2.315(7)	Ru(4)–P(4)	2.287(7)
Ru(1)–P(2)	2.516(6)	Ru(5)–P(4)	2.303(7)
Ru(3)–P(2)	2.519(8)	Ru(6)–P(4)	2.287(7)
Ru(4)–P(2)	2.466(7)	Ru(1)–P(5)	2.272(7)
Ru(6)–P(2)	2.403(8)	Ru(2)–P(5)	2.280(7)
Ru(2)–P(3)	2.412(6)	Ru(3)–P(5)	2.244(6)
Ru(2)–Ru(1)–Ru(3)	54.8(1)	Ru(3)–Ru(4)–Ru(5)	92.3(1)
Ru(2)–Ru(1)–Ru(6)	93.3(1)	Ru(3)–Ru(4)–Ru(6)	87.7(1)
Ru(3)–Ru(1)–Ru(6)	91.0(1)	Ru(5)–Ru(4)–Ru(6)	52.6(1)
Ru(1)–Ru(2)–Ru(3)	70.5(1)	Ru(2)–Ru(5)–Ru(4)	87.3(1)
Ru(1)–Ru(2)–Ru(5)	86.9(1)	Ru(2)–Ru(5)–Ru(6)	87.1(1)
Ru(3)–Ru(2)–Ru(5)	86.4(1)	Ru(4)–Ru(5)–Ru(6)	74.8(1)
Ru(1)–Ru(3)–Ru(2)	54.7(1)	Ru(1)–Ru(6)–Ru(4)	88.7(1)
Ru(1)–Ru(3)–Ru(4)	92.6(1)	Ru(1)–Ru(6)–Ru(5)	92.6(1)
Ru(2)–Ru(3)–Ru(4)	93.8(1)	Ru(4)–Ru(6)–Ru(5)	52.7(1)

The brown band afforded a hexanuclear product characterised as [$Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}$] (**11**). The molecular stereochemistry of this compound has been determined by *X*-ray crystallography and is illustrated in Figures 3 and 4; these diagrams refer to only one of the two independent molecules in the asymmetric unit. Because of the close similarity in the geometry of these two molecules the following discussion is based on mean values for chemically equivalent distances and angles; selected interatomic distances and angles are summarised in Table 4. The six ruthenium atoms adopt a distorted trigonal-prismatic geometry with both triangular and two of the three 'square' faces being capped by a phenylphosphinidene ligand. The co-ordination to each ruthenium is completed by two terminal carbonyl groups. The distortion in the Ru_6 framework can be described to a first approximation in terms of a torsional twist of the Ru(1)Ru(2)Ru(3) plane through an angle of 12° about the approximate three-fold axis. This twist, away from the eclipsed, trigonal-prismatic geometry towards the staggered octahedral configuration, is manifested by the considerable difference in the lengths of the two diagonals of each quadrilateral face [Ru(1)–Ru(5) 3.938(2) and Ru(2)–Ru(6) 4.321(2), Ru(1)–Ru(4) 4.333(2) and Ru(3)–Ru(6) 3.951(2), Ru(3)–Ru(5) 3.233(2) and Ru(2)–Ru(4) 4.659(2) Å] and by the non-planarity of the quadrilateral faces; the folding about the Ru(3)–Ru(5) diagonal is 12.3°, that about the Ru(2)–Ru(6) diagonal is 18.5°, and that about the Ru(1)–Ru(4) diagonal is 19°. The skeletal framework is subjected to further perturbation as reflected by one interbasal distance being significantly greater than the other two [Ru(1)–Ru(6) 3.248(2), Ru(2)–Ru(5) 2.808(2), and Ru(3)–Ru(4) 2.836(2) Å], resulting in the two triangular faces not being parallel to each other (dihedral angle, 13.1°), and by eight of the ruthenium–ruthenium distances being

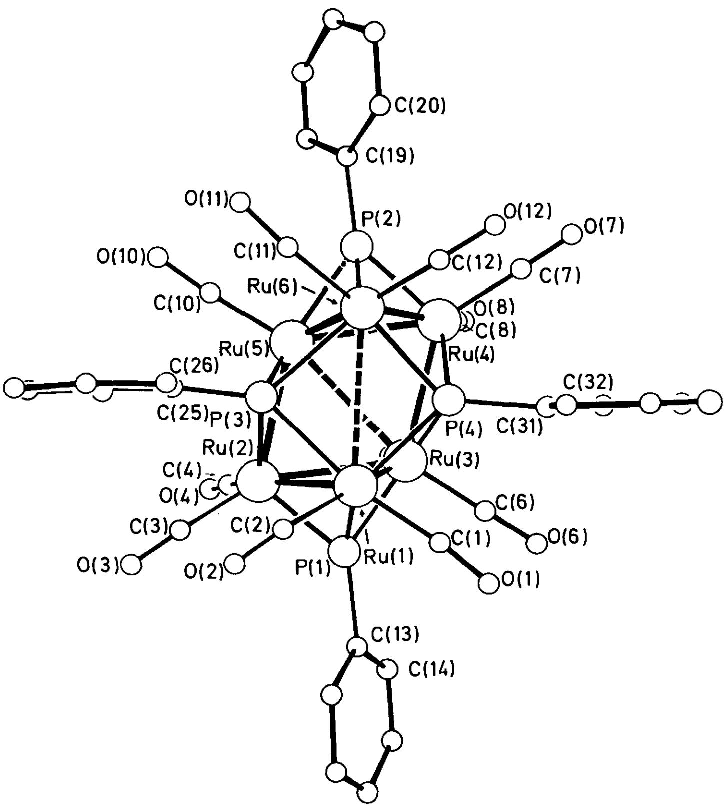


Figure 3. The molecular stereochemistry of $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$ (**11**) [CO(9) is directly behind Ru(5)]

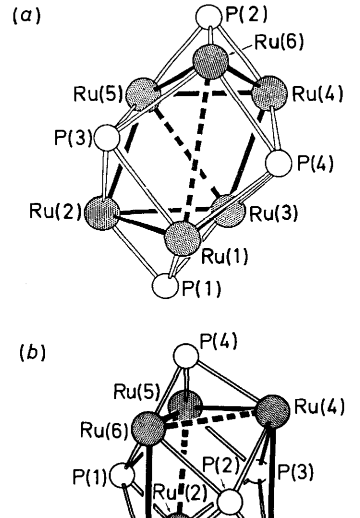


Figure 4. (*a*) The geometry of the Ru_6P_4 framework in $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$ (**11**). (*b*) The geometry of the Ru_6P_5 framework in $[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]$ (**12**)

short [2.808(2)–2.876(2) Å], two being intermediate [3.233(2) and 3.248(2) Å], and five being long [3.938(2)—4.659(2) Å]. A trigonal-prismatic skeletal framework has nine short and six long metal–metal distances while an octahedral framework has twelve short and three long ones.

The product isolated from the green band was also found to be a hexanuclear species, $[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]$ (**12**). The structure of this compound, as established by *X*-ray crystallographically, is illustrated in Figures 4 and 5; interatomic distances and angles are summarised in Table 5. As for compound (**11**), the six ruthenium atoms define a distorted trigonal prism with all faces in this case being capped by a phenylphosphinidene group. Two terminal carbonyl groups are co-ordinated to each ruthenium.

The distortion of the metal-atom framework in (**12**) is different from that in (**11**) in that it can be described in terms of a simple expansion of the skeletal polyhedron. However, this expansion does not correspond to a symmetric elongation along the three-fold axis as observed in $[Pt_6(\mu\text{-}CO)_6(CO)_6]^{2-}$ [28] but to a lengthening of two corresponding basal edges, one to a greater extent than the other [Ru(1)–Ru(3) 3.323(3), Ru(4)–Ru(6) 3.509(3) Å], and to an elongation of the axial edge opposite the two longer basal edges [Ru(2)–Ru(5) 3.241(3) Å]. This distortion results in a lowering of the symmetry of the metal atom framework from D_{3h} to C_{2v}. In contrast to that found in compound (**11**), there is effectively no torsional twist about the three-fold axis.

The low-temperature (−90 °C) ^{31}P n.m.r. spectrum of (**12**) (in CD_2Cl_2—CH_2Cl_2) is consistent with the solid-state structure exhibiting a triplet of doublets at 503 p.p.m., an overlapping triplet of doublets at 407 p.p.m., and an overlapping triplet of triplets at −142 p.p.m. (relative to H_3PO_4) assigned to the two equivalent quadruply capping, to the two equivalent triply capping, and to the unique quadruply capping phenylphosphinidene ligands respectively. Increasing the temperature to 0 °C leads to the collapse of the two outer sets of resonances while a further increase to 133 °C (in $C_6D_5CD_3$–$C_6H_5CH_3$) leads to the formation of a new broad multiplet at 281 p.p.m. (the weighted average); the set of resonances at 407 p.p.m. shifts to 419 p.p.m. in the high-temperature spectrum, and is observed

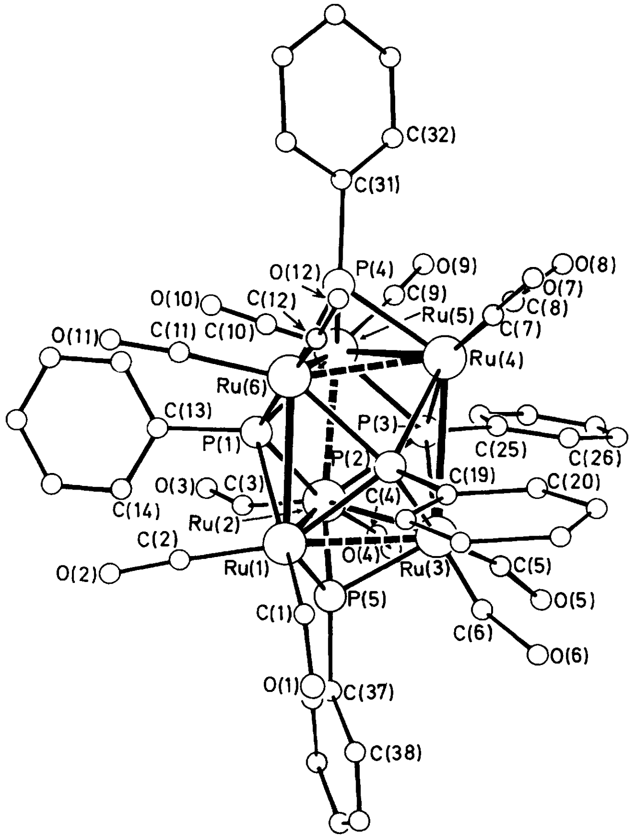
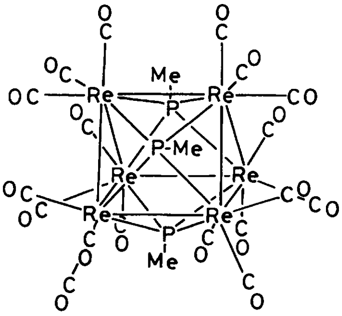


Figure 5. The molecular stereochemistry of $[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]$ (**12**)

as a quartet. It is thus apparent that at higher temperatures the three quadruply capping phosphinidene ligands are equivalent on the n.m.r. time-scale. This equivalence could result from the migration of these ligands over the surface of the metal-atom framework in a concerted motion, as frequently found for carbon monoxide and hydrogen and recently proposed for the PPh_2 groups in $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(\mu\text{-}CO)_4]$.[29] However, on thermodynamic grounds this migration, which would involve a transformation of the $Ru_6(\mu_4\text{-}PPh)_3$ skeletal framework to a $Ru_6(\mu\text{-}PPh)_3$ skeleton, is considered unlikely. A process involving the contraction and elongation of the ruthenium–ruthenium edges is preferred and proposed. Increasing numbers of examples of metal cluster compounds exhibiting facile rearrangement of their skeletal frameworks have been reported of late but essentially have been limited to rhodium and platinum species and in particular to homo- and hetero-nuclear derivatives containing copper, silver, gold, and mercury.[30–44] Significantly, the fluxional behaviour of those derivatives with trigonal-bipyramidal or capped trigonal-bipyramidal metal core geometries is best interpreted in terms of a restricted Berry pseudo-rotation mechanism.[38–42]

Compound (**11**) contains 88 valence electrons and, on the basis that a capped polyhedral cluster has the same number of bonding skeletal molecular orbitals as the uncapped parent polyhedron, would be expected to adopt a structure based on a *nido* pentagonal-bipyramidal metal-atom core or alternatively based on a metal-atom framework which is intermediate between an octahedron and a trigonal prism.[15,45] As described above, the solid-state structure of this compound is indeed consistent with the latter prediction but only to a first approximation since additional perturbations are also evident. Compound (**12**), on the other hand, contains 92 valence electrons and again on the basis that the capping ligands will not influence the number of bonding skeletal molecular orbitals, would be expected to adopt a structure with a trigonal prismatic Ru_6 core geometry which has been slightly opened up due to the occupancy of an antibonding skeletal orbital by the two electrons in excess of 90. However, Mingos and Forsyth[45] have calculated that capped metal cluster compounds containing a 'substantial' number of capping ligands do not have the same number of bonding skeletal molecular orbitals as their uncapped parent clusters. In any case, this compound contains ten skeletal electron pairs and a regular tricapped trigonal-prismatic geometry would be predicted for the $Ru_6(\mu_4\text{-}P)_3$ core on the basis of the polyhedral skeletal electron pair theory;[15] in other words, a regular bicapped tricapped trigonal-prismatic geometry would be predicted for the $Ru_6(\mu_4\text{-}P)_3(\mu_3\text{-}P)_2$ skeleton and the six ruthenium atoms would as a consequence define a *regular* trigonal prism. This is contrary to that found. It is thus apparent that while current bonding theories can predict the geometries of the metal-atom frameworks of compounds (**11**) and (**12**), they can only do so to a first approximation and cannot account for the various distortions observed. These are considered to be imposed by the capping phenylphosphinidene ligands although whether this imposition is of steric or electronic origin or both cannot be ascertained at this stage. An increase in electron-density donation to the metal core of butterfly complexes has been found to lead to an increase in the dihedral angle and to an unequal lengthening of some of the edges.[46] However, steric effects have also been established to play a very important role in the geometry of clusters.[47–49]



(**13**)

With the object of establishing whether compound (**12**) could be oxidised to the 90-electron species $[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]^{2+}$, which would be predicted to contain a regular trigonal-prismatic metal-atom core, its redox chemistry was investigated by means of cyclic voltammetry. A reversible one-electron oxidation wave at $E_{\frac{1}{2}} = +0.40$ V *vs.* Ag–AgCl (Pt electrode in CH_2Cl_2) was observed. A second oxidation wave was not detected. An irreversible reduction wave at $E_{p,c} = -1.04$ V *vs.* Ag–AgCl was also observed. As a consequence of the results no attempts were made to synthesise $[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]^{2+}$ chemically.

Hexanuclear clusters with trigonal-prismatic geometries have been reported previously, but examples have been limited to $[M_6(\mu_6\text{-}N)(\mu\text{-}CO)_9(CO)_6]^-$ (M = Co or Rh)[50] and $[Rh_6(\mu_6\text{-}C)(\mu\text{-}CO)_9(CO)_6]^{2-}$ [51] containing encapsulated nitrogen or carbon atoms, $[Pt_6(\mu\text{-}CO)_6(CO)_6]^{2-}$ [52] which has four electrons less than the 90 valence electrons normally associated with trigonal-prismatic configurations, and $[Re_6(\mu_4\text{-}PMe)_3(CO)_{18}]$ (**13**)[53] in which each square face of the trigonal prism is capped by a methylphosphinidene group. The latter, with compounds (**11**) and (**12**) are the first and only examples of metal cluster compounds with trigonal-prismatic frameworks in which respectively three, four, and five faces of the cluster have been capped by a phosphinidene group. Clusters with $M_6(\mu_3\text{-}PR)$ and $M_6(\mu_3\text{-}PR)_2$ cores and in which the metal atoms define a trigonal prism have still to be reported, but hypothetical $[Ni_6(\mu_3\text{-PPh})(\mu\text{-CO})_6(CO)_6]^{2-}$ and $[Rh_6(\mu_3\text{-PPh})_2(\mu\text{-H})_3(\mu\text{-CO})_6(CO)_6]^-$ for instance, would be predicted to adopt these skeletal geometries.

The products from the orange and magenta bands could not be isolated in crystalline form and were not characterised.

Experimental

All reactions and manipulations were carried out under an atmosphere of nitrogen, using Schlenk-tube techniques, unless otherwise stated. Solvents were purified and dried using standard procedures. $[Ru_3(CO)_{12}]$ was synthesised from $RuCl_3{\cdot}xH_2O$ by a procedure developed by Mr. P. Loveday of the University of Cambridge while $PPhH_2$ was obtained commercially and used without further purification. Infrared spectra were recorded on Perkin-Elmer 457 and 283 grating spectrophotometers while ^1H and ^{31}P n.m.r. spectra were measured on a Varian FT80A instrument. Mass spectra were obtained on an A.E.I. MS9 spectrometer. Light petroleum with b.p. range 60—80 °C was used throughout.

Synthesis of $[Ru_3(\mu\text{-PPhH})(\mu\text{-H})(CO)_{10}]$ (**2**).—A solution of an equimolar amount of $PPhH_2$ (0.086 g, 0.78 mmol) in toluene (*ca.* 5 cm^3) was added to a stirred suspension of $[Ru_3(CO)_{12}]$ (0.50 g, 0.78 mmol) in toluene (*ca.* 100 cm^3) and the mixture was heated to reflux for 4—6 min. During this time the colour of the solution changed from dark to yellow orange. The solvent was removed under reduced pressure and the orange residue, which consisted largely of unreacted $[Ru_3(CO)_{12}]$, was extracted three times with light petroleum. The extracts were combined and the combined solution was concentrated and stored at 0 °C to afford initially $[Ru_3(CO)_{12}]$ and subsequently orange-red crystals of the title compound. The product was recrystallised from light petroleum by slow cooling. The crystals were washed with cold light petroleum (*ca.* −20 °C) and dried *in vacuo*, yield, 3% (Found: C, 27.5; H, 1.0; P, 4.5. $C_{16}H_7O_{10}PRu_3$ requires C, 27.7; H, 1.0; P, 4.5%; *M*, 693). Mass spectrum: *m/e*, 693; other peaks, $m/e - [x(CO) + y(H)]$ (x = 0—10, y = 0 or 1).

Synthesis of $[Ru_3(\mu_3\text{-PPh})(\mu\text{-H})_2(CO)_9]$ (**1**), $[Ru_4(\mu_4\text{-PPh})_2(\mu\text{-CO})(CO)_{10}]$ (**4**), $[Ru_5(\mu_4\text{-PPh})(CO)_{15}]$ (**7**), $[Ru_5(\mu_4\text{-PPh})\{\mu\text{-PPh(OPr}^n)\}(\mu\text{-H})(CO)_{13}]$ (**8**), *and* $[Ru_m(\mu\text{-PPh})_2(CO)_n]$ (**9**) (m = 6 *or* 7, n = 14—18).—A solution of an equimolar amount of $PPhH_2$ (0.086 g, 0.78 mmol) and $[Ru_3(CO)_{12}]$ (0.50 g, 0.78 mmol) in toluene (*ca.* 100 cm^3) was refluxed for 12—24 h. The solvent was removed under reduced pressure and the dark brown oily residue was extracted with three aliquots of warm (*ca.* 60 °C) light petroleum. The extracts were combined and the combined solution was concentrated and transferred to an alumina column (Merck neutral, activity III). The column was eluted initially with light petroleum and subsequently with light petroleum–dichloromethane mixtures of increasing dichloromethane content.

The first band eluted from the column, yellow in colour, was evaporated to dryness under reduced pressure to afford a residue containing both $[Ru_3(CO)_{12}]$ and $[Ru_3(\mu_3\text{-PPh})(\mu\text{-H})_2(CO)_9]$ (**1**). These were separated by fractional crystallisation, the $[Ru_3(CO)_{12}]$ crystallising from solution first. Recrystallisation of the product was effected from light petroleum. The crystals were isolated as for $[Ru_3(\mu\text{-PPhH})(\mu\text{-H})(CO)_{10}]$; yield: 12 h reaction time, 12—14%; 24 h reaction time, 2—3% (Found: C, 27.1; H, 1.1; P, 4.7. $C_{15}H_7O_9PRu_3$ requires C, 26.8; H, 1.0; P, 4.7%; *M*, 665). Mass spectrum: *m/e*, 665; other peaks, $m/e - [x(CO) + y(H)]$ (x = 0—9, y = 0, 1, or 2).

The second band (green) was concentrated and allowed to stand at 0 °C to produce green crystals of $[Ru_5(\mu_4\text{-PPh})(CO)_{15}]$ (**7**) which were recrystallised by vapour diffusion from dichloromethane–light petroleum. The crystals were isolated as for $[Ru_3(\mu\text{-PPhH})(\mu\text{-H})(CO)_{10}]$; yield: 12 h reaction time 3—6%; 24 h reaction time, 12—15% (Found: C, 24.4; H, 0.5; P, 3.0. $C_{21}H_5O_{15}PRu_5$ requires C, 24.4; H, 0.5; P, 3.0%; *M*, 1 034). Mass spectrum: *m/e*, 1 034; other peaks, $m/e - x(CO)$ (x = 1—15). ^{13}C N.m.r. (measured in CD_2Cl_2 at 25 °C; δ scale relative to $SiMe_4$): 150.1, 131.3, 131.1, 131.0 (all C_6H_5); 196 (br, m, CO); (at −90 °C): 201.1 (s, CO, 3), 194.2 (d, J_{PC} 4, CO, 12).

The solvent from the third band (brown)* was removed under reduced pressure to give a brown residue which was subsequently shown to contain at least two, possibly three, products. Dissolution of the residue in light petroleum followed by concentration of the solution and storage at 0 °C led to the initial separation of brown crystals of $[Ru_5(\mu_4\text{-PPh})\{\mu\text{-PPh(OPr}^n)\}(\mu\text{-H})(CO)_{13}]$ (**8**) and the subsequent separation of a green-brown crystalline material. $[Ru_5(\mu_4\text{-PPh})\{\mu\text{-PPh(OPr}^n)\}(\mu\text{-H})(CO)_{13}]$ was recrystallised by vapour diffusion from dichloromethane–light petroleum and the crystals were isolated as for $[Ru_3(\mu\text{-PPhH})(\mu\text{-H})(CO)_{10}]$; yield: <1%.

Attempts to recrystallise the green-brown material resulted in substantial decomposition and crystals suitable for an *X*-ray determination could not be obtained; yield: <1%; ν(CO): 2 050s, 2 040s, 2 025s, 1 985s, and 1 850m cm^{-1}, in cyclohexane.

The sixth band (purple) was concentrated and allowed to stand at 0 °C to afford purple crystals of $[Ru_4(\mu_4\text{-PPh})_2(\mu\text{-CO})(CO)_{10}]$ (**4**) which were recrystallised by vapour diffusion from dichloromethane(chloroform)–light petroleum. The crystals were isolated as for $[Ru_3(\mu\text{-PPhH})(\mu\text{-H})(CO)_{10}]$; yield: 12 or 24 h reaction time, 6—9% [Found: C, 29.5; H, 1.0; Cl, 0.7; P, 6.4%. *M* (vapour-pressure osmometry), 920. $C_{23}H_{10}O_{11}P_2Ru_4{\cdot}0.6CHCl_3$ requires C, 29.6; H, 1.1; Cl, 0.7; P, 6.6%; *M* 929]. Mass spectrum: *m/e* 929; other peaks, $m/e - x(CO)$ (x = 1—11). ^{13}C N.m.r. (measured in CD_2Cl_2 at 32 °C; δ scale relative to $SiMe_4$): 132.3, 131.1, 131.0, 130.8, 130.4, 129.0, 128.7 (all C_6H_5); 202 (t, J_{PC} 10.3, CO); (at −114 °C): 202 (t, J_{PC} 10.6, CO).

The seventh band (green) was similarly concentrated and allowed to stand at 0 °C to produce dark green crystals of $[Ru_m(\mu\text{-PPh})_2(CO)_n]$ (**9**) [m = 6 or 7, n = 14—18]. The compound was recrystallised as for $[Ru_4(\mu_4\text{-PPh})_2(\mu\text{-CO})(CO)_{10}]$ but crystals suitable for a single-crystal *X*-ray diffraction study could not be obtained; yield: 12—24 h reaction time, 2—4% [Found: C, 24.0; H, 1.0; P, 5.0%; *M* (vapour-pressure osmometry in benzene), 1 310].

The last band, the eighth [brown (iii)] was concentrated and on cooling afforded a dull brown powder which was not investigated further.

Synthesis of $[Ru_3(\mu_3\text{-PPh})(\mu\text{-H})_2(CO)_9]$ (**1**), $[Ru_3(\mu_3\text{-PPh})_2(CO)_9]$ (**3**), $[Ru_4(\mu_4\text{-PPh})_2(\mu\text{-CO})(CO)_{10}]$ (**4**), $[Ru_4(\mu_4\text{-PPh})_2(\mu\text{-PPhH})_2(CO)_8]$ (**10**), $[Ru_6(\mu_4\text{-PPh})_2(\mu_3\text{-PPh})_2(CO)_{12}]$ (**11**), *and* $[Ru_6(\mu_4\text{-PPh})_3(\mu_3\text{-PPh})_2(CO)_{12}]$ (**12**).—A solution of a three-fold molar amount of $PPhH_2$ (0.26 g, 2.35 mmol) and $[Ru_3(CO)_{12}]$ (0.50 g, 0.78 mmol) in toluene (*ca.* 100 cm^3) was refluxed for 8 h. The solvent was removed under reduced pressure and the dark brown oily residue was extracted with three aliquots of warm (*ca.* 60 °C) light petroleum. The extracts were combined and the combined solution was concentrated and transferred to a silica column. The column was eluted initially with light petroleum and subsequently with light petroleum–dichloromethane mixtures of increasing dichloromethane content, up to a 1:1 mixture.

The first band eluted from the column, yellow in colour, was

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* This band appeared to comprise three poorly separated bands, brown (i), green-brown, and brown (ii).

Table 6. Fractional atomic co-ordinates (× 10^4 for Ru and P; × 10^3 for other atoms) for $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]\cdot0.14CHCl_3$ (**4**) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ru(1A)	1 334(1)	3 104(2)	977(1)	C(4A)	141(2)	401(3)	210(2)
Ru(2A)	1 549(1)	3 091(2)	1 847(1)	C(5A)	111(2)	261(4)	205(2)
Ru(3A)	2 389(1)	2 612(2)	1 863(1)	C(6A)	208(2)	276(3)	232(2)
Ru(4A)	2 212(1)	2 536(2)	1 001(1)	C(7A)	289(2)	316(3)	208(2)
P(1A)	2 010(4)	3 573(6)	1 388(4)	C(8A)	265(2)	179(3)	211(2)
P(2A)	1 706(3)	2 104(6)	1 389(3)	C(9A)	275(2)	229(4)	125(2)
O(1A)	131(1)	432(2)	33(1)	C(10A)	242(2)	308(3)	61(2)
O(2A)	75(1)	206(2)	35(1)	C(11A)	205(2)	176(3)	59(2)
O(3A)	52(1)	369(2)	125(1)	C(12A)	220(1)	454(2)	140(1)
O(4A)	133(1)	453(2)	225(1)	C(13A)	228(1)	492(2)	177(1)
O(5A)	84(1)	224(2)	215(1)	C(14A)	246(1)	565(2)	180(1)
O(6A)	213(1)	271(2)	268(1)	C(15A)	255(1)	600(2)	146(1)
O(7A)	319(1)	356(2)	224(1)	C(16A)	247(1)	562(2)	109(1)
O(8A)	284(1)	127(2)	232(1)	C(17A)	229(1)	489(2)	106(1)
O(9A)	314(1)	194(2)	134(1)	C(18A)	153(1)	114(2)	145(1)
O(10A)	256(1)	349(2)	38(1)	C(19A)	132(1)	74(2)	111(1)
O(11A)	196(1)	132(2)	37(1)	C(20A)	115(1)	2(2)	115(1)
C(1A)	132(2)	389(3)	57(2)	C(21A)	119(1)	−30(2)	153(1)
C(2A)	97(2)	244(3)	59(2)	C(22A)	140(1)	10(2)	187(1)
C(3A)	88(2)	349(3)	121(2)	C(23A)	157(1)	82(2)	184(1)
Ru(1B)	4 019(1)	4 854(2)	1 554(1)	C(4B)	324(2)	507(3)	45(2)
Ru(2B)	3 818(1)	4 866(2)	686(1)	C(5B)	376(2)	390(3)	48(2)
Ru(3B)	4 495(1)	5 840(2)	675(1)	C(6B)	404(2)	523(3)	22(2)
Ru(4B)	4 737(1)	5 887(2)	1 539(1)	C(7B)	442(2)	687(4)	43(2)
P(1B)	3 999(4)	5 972(6)	1 153(3)	C(8B)	495(2)	572(3)	45(2)
P(2B)	4 563(3)	4 756(5)	1 154(3)	C(9B)	514(2)	640(4)	132(2)
O(1B)	362(1)	563(2)	216(1)	C(10B)	470(2)	671(3)	191(2)
O(2B)	448(1)	365(2)	216(1)	C(11B)	519(2)	545(3)	197(2)
O(3B)	323(1)	385(2)	125(1)	C(12B)	361(1)	674(1)	112(1)
O(4B)	286(1)	514(2)	28(1)	C(13B)	341(1)	700(1)	739(1)
O(5B)	371(1)	329(2)	37(1)	C(14B)	311(1)	760(1)	70(1)
O(6B)	385(1)	532(2)	−13(1)	C(15B)	302(1)	795(1)	104(1)
O(7B)	444(1)	740(2)	28(1)	C(16B)	322(1)	769(1)	142(1)
O(8B)	526(1)	557(2)	28(1)	C(17B)	352(1)	709(1)	147(1)
O(9B)	540(1)	684(2)	121(1)	C(18B)	491(1)	400(2)	108(1)
O(10B)	461(1)	717(2)	211(1)	C(19B)	492(1)	376(2)	70(1)
O(11B)	543(1)	513(2)	220(1)	C(20B)	518(1)	314(2)	64(1)
C(1B)	375(2)	523(3)	191(2)	C(21B)	543(1)	275(2)	98(1)
C(2B)	428(2)	410(3)	193(2)	C(22B)	541(1)	299(2)	137(1)
C(3B)	349(2)	428(3)	134(2)	C(23B)	515(1)	361(2)	142(1)
Ru(1C)	783(1)	4 572(2)	4 162(1)	C(4C)	0(2)	405(3)	307(2)
Ru(2C)	548(1)	4 603(2)	3 299(1)	C(5C)	87(2)	384(3)	306(2)
Ru(3C)	635(1)	6 129(2)	3 281(1)	C(6C)	52(2)	535(3)	286(2)
Ru(4C)	900(1)	6 202(2)	4 137(1)	C(7C)	17(2)	673(3)	305(2)
P(1C)	283(4)	5 469(6)	3 778(4)	C(8C)	101(2)	655(3)	302(2)
P(2C)	1 172(3)	5 269(6)	1 154(3)	C(9C)	82(2)	715(3)	385(2)
O(1C)	22(2)	429(3)	475(2)	C(10C)	62(2)	649(3)	454(2)
O(2C)	162(1)	426(3)	475(1)	C(11C)	146(2)	646(3)	443(2)
O(3C)	62(1)	296(2)	387(1)	C(12C)	−28(7)	561(2)	382(1)
O(4C)	−30(1)	371(2)	289(1)	C(13C)	−41(7)	561(2)	419(1)
O(5C)	103(1)	347(2)	288(1)	C(14C)	−86(1)	570(2)	419(1)
O(6C)	48(1)	535(2)	249(1)	C(15C)	−117(1)	580(2)	383(1)
O(7C)	−13(1)	713(2)	290(1)	C(16C)	−103(1)	580(2)	346(1)
O(8C)	123(1)	705(2)	284(1)	C(17C)	−59(1)	571(2)	346(1)
O(9C)	86(1)	777(2)	381(1)	C(18C)	174(1)	510(2)	370(1)
O(10C)	43(1)	663(2)	482(1)	C(19C)	182(1)	495(2)	331(1)
O(11C)	180(1)	667(2)	466(1)	C(20C)	225(1)	480(2)	327(1)
C(1C)	45(2)	443(3)	455(2)	C(21C)	260(1)	481(2)	361(1)
C(2C)	128(2)	435(3)	452(2)	C(22C)	252(1)	496(2)	399(1)
C(3C)	65(2)	361(3)	392(2)	C(23C)	209(1)	511(2)	404(1)
Cl(1)	321	285	383	Cl(3)	328	203	451
Cl(2)	306	352	461	C	336	292	423

Table 7. Fractional atomic co-ordinates ($\times 10^4$ for Ru and P; $\times 10^3$ for other atoms) for $[Ru_5(\mu_4\text{-}PPh)\{\mu\text{-}PPh(OPr^n)\}(\mu\text{-}H)(CO)_{13}]$ (**8**) with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Ru(1)	6 420(1)	2 909(1)	4 528(1)
Ru(2)	4 842(1)	1 976(1)	4 604(1)
Ru(3)	4 841(1)	1 810(1)	3 592(1)
Ru(4)	6 327(1)	2 770(1)	3 517(1)
Ru(5)	6 332(1)	1 278(1)	4 108(1)
P(1)	5 229(4)	3 017(4)	4 054(2)
P(2)	5 729(5)	1 916(4)	2 992(2)
O(1)	696(2)	213(2)	545(1)
O(2)	609(1)	465(1)	495(1)
O(3)	824(1)	333(2)	427(1)
O(4)	312(1)	122(1)	443(1)
O(5)	409(1)	338(2)	520(1)
O(6)	520(1)	83(1)	544(1)
O(7)	337(1)	260(1)	310(1)
O(8)	43(2)	9(2)	345(1)
O(9)	812(2)	294(2)	318(5)
O(10)	595(1)	435(1)	296(1)
O(11)	697(2)	31(2)	493(1)
O(12)	815(1)	136(1)	377(1)
O(13)	605(2)	40(2)	360(1)
O(14)	526(2)	239(1)	254(1)
C(1)	671(2)	241(2)	509(1)
C(2)	624(2)	399(2)	480(1)
C(3)	750(2)	317(2)	433(1)
C(4)	377(2)	149(2)	448(1)
C(5)	440(2)	288(2)	498(1)
C(6)	504(2)	127(2)	513(1)
C(7)	395(2)	230(2)	329(1)
C(8)	434(2)	76(2)	353(1)
C(9)	746(2)	287(2)	330(1)
C(10)	611(2)	380(2)	321(1)
C(11)	743(2)	138(2)	388(1)
C(12)	671(2)	71(2)	462(1)
C(13)	613(2)	25(2)	377(1)
C(14)	520(4)	221(3)	208(2)
C(14′)	616(5)	259(5)	217(3)
C(15)	518(4)	277(4)	171(2)
C(15′)	575(6)	294(5)	189(3)
C(16)	577(4)	292(3)	138(2)
C(16′)	630(5)	293(5)	162(3)
C(17)	458(1)	399(1)	401(1)
C(18)	369(1)	395(1)	403(1)
C(19)	321(1)	469(1)	397(1)
C(20)	362(1)	547(1)	391(1)
C(21)	451(1)	551(1)	390(1)
C(22)	450(1)	477(1)	395(1)
C(23)	624(2)	103(1)	272(1)
C(24)	713(2)	101(1)	268(1)
C(25)	753(2)	32(1)	246(1)
C(26)	704(2)	−36(1)	230(1)
C(27)	615(2)	−35(1)	235(1)
C(28)	575(2)	34(1)	256(1)

found to contain unreacted $[Ru_3(CO)_{12}]$ and $[Ru_3(\mu_3\text{-}PPh)(\mu\text{-}H)_2(CO)_9]$ (**1**). These were separated and purified as described above; yield of (**1**), 1%.

The second band, also yellow but darker than the first, was concentrated and allowed to stand at 0 °C to produce yellow crystals of $[Ru_3(\mu_3\text{-}PPh)_2(CO)_9]$ (**3**). These were recrystallised from light petroleum by slow cooling; yield, 3—5% (Found: C, 32.9; H, 1.4; P, 8.2. $C_{21}H_{10}O_9P_2Ru_3$ requires C, 32.7; H, 1.3; P, 8.0%). Mass spectrum: *m*/*e*, 772; other peaks, *m*/*e* − *x*(CO) (*x* = 1—9).

The third band was orange in colour but afforded a white precipitate on removal of the solvent under reduced pressure; dissolution of this precipitate in dichloromethane produced a colourless solution. Attempts to obtain this compound in crystalline and purified form proved unsuccessful; yield, 3%; ν(CO): 2 080m, 2 010s, and 1 975m cm^{-1}, in cyclohexane.

The fourth band (purple) was shown to contain $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ (**4**) which was isolated and purified as described above; yield, 1%.

The fifth and sixth bands which, in general, tended to overlap, were collected together, concentrated and allowed to stand at 0 °C. A red crystalline product (**10**) separated from solution leaving a magenta mother-liquor. The red crystalline material was recrystallised by vapour diffusion from dichloromethane–light petroleum; yield, 5% (Found: C, 36.6; H, 2.3; P, 11.5. $C_{32}H_{22}O_8P_4Ru_4$ requires C, 36.2; H, 2.1; P, 11.7%). Mass spectrum: *m*/*e*, 1 063; other peaks, *m*/*e* − [*x*(CO) + *y*(H)] (*x* = 0—8, *y* = 0, 1, or 2).

Attempts were made to recrystallise the material isolated from the magenta solution, but it was found to decompose rapidly in solution; yield, < 1%; ν(CO): 2 045w, 2 010s, and 1 980m cm^{-1}, in cyclohexane. ^1H N.m.r. (measured in CD_2Cl_2 at 20 °C; δ scale relative to $SiMe_4$): 7.4 (m, C_6H_5), −16.3 (6 lines, Ru-*H*-Ru).

The solvent from the seventh band (brown) was removed under reduced pressure to afford a brown residue which was crystallised by vapour-diffusion techniques from benzene–light petroleum to give (**11**); yield: 5—8% [Found: C, 31.3; H, 1.4; P, 10.3. $C_{36}H_{20}O_{12}P_4Ru_6$ requires C, 31.5; H, 1.5; P, 9.0% (calculations based on 0.5 C_6H_6 being occluded)].

The residue obtained by removal of the solvent from the eighth band (green) was crystallised by vapour-diffusion techniques from benzene–light petroleum to give (**12**); yield: 15—18% [Found: C, 39.9; H, 2.5; *M* (vapour-pressure osmometry in benzene), 1550. $C_{42}H_{25}O_{12}P_5Ru_6$ requires C, 40.8; H, 2.4%; *M*, 148.3 (C, H calculations based on 2.5 C_6H_6 being occluded)].

Synthesis of ^{13}CO-*Enriched* $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ (**4**).—A solution of $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ (0.1 g) in toluene (*ca.* 25 cm^3) was stirred under an atmosphere of ^{13}CO at room temperature in the absence of light for 6 h. During this period a colour change from purple to yellow occurred. The yellow solution was placed in direct sunlight for 6 h which resulted in the solution reverting to purple. The solvent was removed under reduced pressure and the purple residue crystallised from dichloromethane–light petroleum using vapour-diffusion techniques.

Crystal Structure Determinations.—(*i*) $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]\cdot 0.14CHCl_3$. *Crystal data.* $C_{23}H_{10}O_{11}P_2Ru_4\cdot 0.14CHCl_3$, *M* = 945.24, purple crystal of dimensions 0.31 × 0.33 × 0.16 mm grown from chloroform–light petroleum, monoclinic, space group *C*2/*c*, *a* = 30.87(4), *b* = 17.69(2), *c* = 33.87(4) Å, β = 102.8(1)°, *U* = 18 039.5 $Å^3$, D_m = 2.09 g cm^{-3}, *Z* = 24, D_c = 2.13 g cm^{-3}, μ(Mo-K_α) = 16.4 cm^{-1}, *F*(000) = 10 784.

Intensity data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). A least-squares fit of high-angle reflections (θ > 12°) was used to obtain accurate cell constants. Because of the unusually large cell dimensions it was not possible to

Table 8. Fractional atomic co-ordinates (× 10^4) for [$Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}$] (**11**) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ru(1A)	2 111(1)	1 805(1)	137(1)	C(8A)	3 747(9)	2 757(9)	5 975(20)
Ru(2A)	1 417(1)	2 063(1)	−2 147(1)	C(9A)	2 262(9)	3 057(9)	5 695(20)
Ru(3A)	2 634(1)	1 717(1)	−2 468(1)	C(10A)	1 905(9)	3 866(9)	7 529(19)
Ru(4A)	3 523(1)	2 845(1)	−2 262(1)	C(11A)	2 620(9)	3 902(9)	1 035(19)
Ru(5A)	2 298(1)	3 162(1)	−2 446(1)	C(12A)	3 582(9)	3 361(9)	1 279(19)
Ru(6A)	2 909(1)	3 225(1)	103(1)	C(13A)	1 394(5)	337(4)	829(12)
P(1A)	1 742(2)	1 161(2)	8 304(4)	C(14A)	1 483(5)	−90(4)	7 212(12)
P(2A)	3 212(2)	3 768(2)	8 235(4)	C(15A)	1 192(5)	−725(4)	7 200(12)
P(3A)	1 837(2)	2 806(2)	9 532(4)	C(16A)	813(5)	−933(4)	8 260(12)
P(4A)	3 159(2)	2 191(2)	9 443(4)	C(17A)	725(5)	−506(4)	9 332(12)
O(1A)	2 582(7)	750(8)	1 606(17)	C(18A)	1 016(5)	129(4)	9 345(12)
O(2A)	1 025(5)	1 664(6)	2 027(12)	C(19A)	3 542(5)	4 596(4)	8 157(12)
O(3A)	162(8)	1 809(8)	9 014(17)	C(20A)	3 969(5)	4 885(4)	9 129(12)
O(4A)	925(7)	2 038(8)	5 012(17)	C(21A)	4 241(5)	5 522(4)	9 034(12)
O(5A)	3 238(7)	524(8)	7 490(16)	C(22A)	4 086(5)	5 869(4)	7 965(12)
O(6A)	2 597(7)	1 663(8)	4 469(17)	C(23A)	3 659(5)	5 579(4)	6 992(12)
O(7A)	4 838(8)	3 162(8)	8 737(17)	C(24A)	3 387(5)	4 943(4)	7 088(12)
O(8A)	3 888(7)	2 719(8)	4 845(17)	C(25A)	1 272(5)	3 171(6)	482(11)
O(9A)	2 243(7)	3 027(8)	4 510(17)	C(26A)	1 295(5)	3 214(6)	1 882(11)
O(10A)	1 673(7)	4 342(8)	7 472(16)	C(27A)	816(5)	3 433(6)	2 603(11)
O(11A)	2 479(7)	4 357(8)	1 619(17)	C(28A)	314(5)	3 607(6)	1 924(11)
O(12A)	4 039(7)	3 462(8)	1 969(17)	C(29A)	290(5)	3 563(6)	524(11)
C(1A)	2 435(9)	1 160(9)	1 051(19)	C(30A)	769(5)	3 345(6)	−197(11)
C(2A)	1 463(9)	1 753(9)	1 345(19)	C(31A)	3 770(5)	1 867(6)	313(11)
C(3A)	640(9)	1 915(9)	8 538(19)	C(32A)	3 813(5)	1 894(6)	1 711(11)
C(4A)	1 145(9)	2 053(9)	6 101(20)	C(33A)	4 322(5)	1 706(6)	2 340(11)
C(5A)	3 008(9)	994(9)	7 483(19)	C(34A)	4 789(5)	1 491(6)	1 572(11)
C(6A)	2 626(9)	1 706(9)	5 665(20)	C(35A)	4 746(5)	1 464(6)	174(11)
C(7A)	4 337(9)	3 025(9)	8 335(19)	C(36A)	4 237(5)	1 652(6)	−456(11)
Ru(1B)	6 965(1)	2 941(1)	8 451(1)	C(8B)	8 788(10)	2 678(11)	4 407(24)
Ru(2B)	6 413(1)	2 264(1)	6 077(1)	C(9B)	7 480(10)	1 661(11)	3 938(24)
Ru(3B)	7 511(1)	3 188(1)	5 900(1)	C(10B)	7 223(10)	783(11)	5 670(23)
Ru(4B)	8 566(1)	2 570(1)	6 155(1)	C(11B)	7 841(10)	1 212(11)	9 336(23)
Ru(5B)	7 461(1)	1 655(1)	5 835(1)	C(12B)	8 652(10)	2 222(11)	−301(23)
Ru(6B)	7 997(1)	1 979(1)	8 445(1)	C(13B)	8 864(6)	902(5)	6 552(14)
P(1B)	6 533(2)	3 291(2)	6 604(4)	C(14B)	9 503(6)	1 020(5)	6 392(14)
P(2B)	8 428(2)	1 552(2)	6 607(4)	C(15B)	9 848(6)	516(5)	6 417(14)
P(3B)	6 909(2)	1 833(2)	7 792(4)	C(16B)	9 554(6)	−105(5)	6 602(14)
P(4B)	8 053(2)	3 063(2)	7 869(4)	C(17B)	8 914(6)	−223(5)	6 763(14)
O(1B)	5 911(7)	2 650(7)	376(15)	C(18B)	8 569(6)	280(5)	6 738(14)
O(2B)	7 207(7)	4 239(7)	−20(15)	C(19B)	6 030(5)	3 879(6)	6 504(14)
O(3B)	6 146(7)	2 064(7)	3 071(16)	C(20B)	6 190(5)	4 501(6)	7 067(14)
O(4B)	5 100(7)	1 883(7)	6 852(15)	C(21B)	5 766(5)	4 933(6)	7 048(14)
O(5B)	7 834(7)	4 618(8)	5 776(15)	C(22B)	5 182(5)	4 742(6)	6 466(14)
O(6B)	7 512(7)	3 111(7)	2 834(16)	C(23B)	5 022(5)	4 119(6)	5 903(14)
O(7B)	8 911(7)	2 753(7)	3 264(16)	C(24B)	5 446(5)	3 688(6)	5 922(14)
O(8B)	−120(7)	3 005(7)	7 067(15)	C(25B)	8 512(6)	3 708(5)	8 878(12)
O(9B)	7 077(7)	220(8)	5 538(15)	C(26B)	8 860(6)	4 214(5)	8 251(12)
O(10B)	7 501(7)	1 663(7)	2 782(16)	C(27B)	9 178(6)	4 732(5)	9 021(12)
O(11B)	9 072(7)	2 353(7)	392(15)	C(28B)	9 147(6)	4 744(5)	10 419(12)
O(12B)	7 781(7)	727(7)	9 871(15)	C(29B)	8 799(6)	4 238(5)	11 045(12)
C(1B)	7 130(10)	3 743(11)	9 396(23)	C(30B)	8 481(6)	3 720(5)	10 275(12)
C(2B)	6 304(11)	2 747(11)	9 639(23)	C(31B)	6 450(6)	1 219(5)	8 725(12)
C(3B)	5 624(11)	2 014(11)	6 555(23)	C(32B)	6 099(6)	693(5)	8 040(12)
C(4B)	6 246(10)	2 125(11)	4 223(24)	C(33B)	5 797(6)	190(5)	8 752(12)
C(5B)	7 731(10)	4 066(11)	5 859(23)	C(34B)	5 845(6)	213(5)	10 149(12)
C(6B)	7 537(10)	3 140(11)	4 009(24)	C(35B)	6 196(6)	739(5)	10 834(12)
C(7B)	9 359(11)	2 842(11)	679(23)	C(36B)	6 498(6)	1 242(5)	10 122(12)
C(1S)	5 539(12)	128(13)	4 365(27)	C(4S)	9 409(12)	4 975(13)	4 533(27)
C(2S)	4 577(12)	445(13)	5 189(27)	C(5S)	10 198(12)	4 454(13)	5 428(27)
C(3S)	5 172(12)	593(13)	4 508(27)	C(6S)	9 608(12)	4 430(13)	4 966(27)

measure reflection intensities using normal scan techniques; rather a peak-top counting method was employed, with backgrounds estimated from a background count *versus* θ curve, generated by measuring intensities along lines of systematic absences. Thus the quality of the intensity data was not good. Three standard reflections, measured every hour, showed no decrease in intensity during data collection. Lack of facilities precluded the application of empirical absorption corrections to the measured intensities, and an ill-defined crystal shape prevented the successful application of analytical absorption

Table 9. Fractional atomic co-ordinates (× 10^4) for $[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]$ (**12**) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	1 957(1)	377(1)	3 975(1)
Ru(2)	3 111(1)	5(1)	4 489(1)
Ru(3)	2 819(1)	965(1)	5 133(1)
Ru(4)	2 361(1)	245(1)	5 940(1)
Ru(5)	2 550(1)	−792(1)	5 340(1)
Ru(6)	1 440(1)	−372(1)	4 722(1)
P(1)	2 225(3)	−556(3)	4 324(3)
P(2)	1 812(3)	571(3)	4 981(3)
P(3)	3 143(3)	61(3)	5 516(2)
P(4)	1 765(3)	−527(3)	5 698(3)
P(5)	2 786(3)	894(3)	4 178(3)
O(1)	897(11)	1 067(11)	3 453(10)
O(2)	1 989(10)	43(10)	2 748(10)
O(3)	3 400(9)	−518(10)	3 448(9)
O(4)	4 384(10)	285(10)	4 736(10)
O(5)	3 984(9)	1 470(9)	5 470(9)
O(6)	2 424(12)	2 081(13)	5 507(12)
O(7)	1 834(10)	1 188(11)	6 548(10)
O(8)	3 088(11)	−110(12)	7 127(12)
O(9)	3 363(12)	−1 359(12)	6 375(12)
O(10)	2 169(9)	−2 006(10)	5 055(9)
O(11)	914(10)	−1 529(10)	4 320(9)
O(12)	222(11)	132(11)	4 377(10)
C(1)	1 324(13)	834(13)	3 715(13)
C(2)	1 962(12)	153(12)	3 213(12)
C(3)	3 268(12)	−304(12)	3 833(12)
C(4)	3 891(12)	153(12)	4 655(11)
C(5)	3 542(13)	1 271(13)	5 354(12)
C(6)	2 521(14)	1 655(14)	5 304(13)
C(7)	2 011(11)	831(11)	6 335(11)
C(8)	2 792(13)	18(13)	6 714(13)
C(9)	3 054(13)	−1 119(14)	5 971(13)
C(10)	2 336(12)	−1 525(12)	5 116(12)
C(11)	1 143(12)	−1 102(13)	4 491(12)
C(12)	670(14)	−51(13)	4 515(13)
C(13)	2 182(10)	−1 148(8)	3 808(9)
C(14)	1 714(10)	−1 195(8)	3 334(9)
C(15)	1 679(10)	−1 656(8)	2 951(9)
C(16)	2 113(10)	−2 068(8)	3 043(9)
C(17)	2 582(10)	−2 021(8)	3 517(9)
C(18)	2 616(10)	−1 516(8)	3 899(9)
C(19)	1 275(9)	1 094(9)	5 032(10)
C(20)	869(9)	993(9)	5 363(10)
C(21)	443(9)	1 398(9)	5 379(10)
C(22)	423(9)	1 905(9)	5 062(10)
C(23)	829(9)	2 006(9)	4 731(10)
C(24)	1 255(9)	1 600(9)	4 716(10)
C(25)	3 846(7)	−12(10)	5 984(9)
C(26)	4 031(7)	406(10)	6 406(9)
C(27)	4 594(7)	394(10)	6 742(9)
C(28)	4 971(7)	−36(10)	6 656(9)
C(29)	4 786(7)	−455(10)	6 233(9)
C(30)	4 224(7)	−443(10)	5 897(9)
C(31)	1 444(9)	−963(9)	6 160(9)
C(32)	1 760(9)	−1 184(9)	6 685(9)
C(33)	1 486(9)	−1 515(9)	7 034(9)
C(34)	897(9)	−1 625(9)	6 859(9)
C(35)	581(9)	−1 404(9)	6 355(9)
C(36)	855(9)	−1 073(9)	5 985(9)
C(37)	3 125(9)	1 334(9)	3 712(9)
C(38)	3 218(9)	1 147(9)	3 180(9)
C(39)	3 521(9)	1 492(9)	2 869(9)
C(40)	3 731(9)	2 023(9)	3 090(9)
C(41)	3 637(9)	2 210(9)	3 623(9)
C(42)	3 334(9)	1 865(9)	3 934(9)

corrections. Lorentz and polarisation corrections were applied yielding 13 165 unique reflections; 8 426 of these were classed as observed [$I > 4\sigma(I)$] and were used in the solution and refinement of the structure.

The 12 Ru atoms in the asymmetric unit were located from an *E* map calculated using phases generated by the automatic direct methods routine for centrosymmetric crystal structures in the program SHELX.[54] A Fourier synthesis phased on the Ru atoms revealed the remaining non-hydrogen atoms. Full-matrix least-squares techniques were used to refine the structure with anisotropic thermal parameters for the Ru and P atoms and individual isotropic thermal parameters for the remaining non-hydrogen atoms excluding the phenyl C atoms, which were assigned a single (but variable) isotropic thermal parameter. Phenyl rings were treated as rigid groups with idealised geometry. The site occupation factors of the C and Cl atoms in the chloroform molecule were tied together and refined [final value 0.42(2)] while fixing their isotropic thermal parameter at 0.07 Å^2. Hydrogen atoms were not located. Convergence was reached at a final conventional *R* of 0.14 using unit weights. The high *R* factor is a consequence of the poor quality data (see above). Thus, although the structure is qualitatively correct, the standard deviations in bond lengths and angles should be treated with some caution, as they derive from the least-squares analysis and take no account of systematic errors, which undoubtedly exist because no absorption corrections were applied (see above). A final difference map was featureless. Fractional atomic co-ordinates are listed in Table 6.

(*ii*) $[Ru_5(\mu_4\text{-}PPh)\{\mu\text{-}PPh(OPr^n)\}(\mu\text{-}H)(CO)_{13}]$. *Crystal data.* $C_{28}H_{18}O_{14}P_2Ru_5$, *M* = 1 144.71, brown crystal of dimensions 0.40 × 0.40 × 0.05 mm grown from chloroform–light petroleum, orthorhombic, space group *Pbca*, *a* = 15.635(2), *b* = 15.698, *c* = 28.917(3) Å, *U* = 7 097.3 Å^3, D_m = 2.33 g cm^{-3}, *Z* = 8, D_c = 2.13 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 21.6 cm^{-1}, *F*(000) = 4 704.

Intensity data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). A least-squares fit of high-angle reflections ($\theta > 12°$) was used to obtain accurate cell constants. Diffraction intensities were measured in the range $3 \leqslant 2\theta \leqslant 46°$ using the ω–2θ scan technique, with background counts made for half the total scan time on each side of the peak. Three standard reflections, measured every hour, showed no decrease in intensity during data collection. Lorentz and polarisation, but no absorption corrections were made. Of the 4 567 unique reflections measured, 3 022 were classed as observed [$I > 3\sigma(I)$] and these were used for the solution and refinement of the structure.

The five Ru atoms were located from an *E* map calculated using phases generated by the automatic direct methods routine for centrosymmetric crystal structures in the program SHELX.[54] A Fourier synthesis phased on the Ru atoms revealed the remaining non-hydrogen atoms except for those of the propyl group. A unit weights refinement of the atoms so far located, with anisotropic thermal parameters for the Ru and P atoms, individual isotropic thermal factors for the O and carbonyl C atoms, and averaged (but variable) isotropic thermal factors for the C atoms in each phenyl ring (phenyl rings were refined as rigid groups with idealised geometry), gave *R* = 0.088. A difference Fourier calculated at this stage showed that the propyl group was disordered between two alternative positions. The C atoms in each of these positions were assigned averaged (but variable) site occupation factors which were constrained to add up to one; at the same time all the propyl C atoms were assigned a fixed isotropic thermal factor of 0.08 Å^2. A final full-matrix least-squares refinement (205 variables) using weights $w = K/[\sigma^2(F) + 0.003F^2]$ [$\sigma(F)$ from counting statistics; $K = 6.81$] converged at $R = 0.0824$ ($R' = 0.0805$; final value for the refined site occupation factor = 0.60). Hydrogen atoms were not located. There were no significant features in the final difference Fourier. Fractional atomic co-ordinates are listed in Table 7.

(*iii*) $[Ru_6(\mu_4\text{-PPh})_2(\mu_3\text{-PPh})_2(CO)_{12}]\cdot 0.5C_6H_6$. *Crystal data.* $C_{39}H_{23}O_{12}P_4Ru_6$, $M = 1\,413.87$, brown crystal of dimensions 0.31 × 0.30 × 0.22 mm grown from benzene–light petroleum, triclinic, space group $P\bar{1}$, $a = 21.88(3)$, $b = 21.13(3)$, $c = 9.98(1)$ Å, $\alpha = 93.1(1)$, $\beta = 90.3(1)$, $\gamma = 98.6(1)°$, $U = 4\,552.8$ Å^3, $D_m = 1.98$ g cm^{-3}, $Z = 4$, $D_c = 2.02$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 20.9$ cm^{-1}, $F(000) = 2\,842$.

Data were collected and accurate cell constants obtained as decribed in (*ii*) above. From a total of 12 923 reflections measured in the range $3 \leqslant 2\theta \leqslant 46°$, 10 078 with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. No crystal or instrumental instability was detected during the measurements. The data were corrected for Lorentz and polarisation effects but not for absorption.

The 12 Ru atoms in the asymmetric unit were located from an *E* map calculated using phases generated by the automatic direct methods routine for centrosymmetric crystal structures in the program SHELX.[54] A Fourier synthesis phased on the Ru atoms revealed the remaining non-hydrogen atoms. Full-matrix least-squares techniques were used to refine the structure with anisotropic thermal parameters for the Ru and P atoms, and averaged isotropic thermal parameters for the carbonyl C atoms, the carbonyl O atoms, the C atoms of each phenyl ring and the C atoms of each benzene solvent molecule (phenyl rings were refined as rigid hexagons). Hydrogen atoms were not located. Convergence was reached at a final conventional *R* of 0.067 using unit weights. A final difference map calculated at this stage was featureless. Fractional atomic co-ordinates are listed in Table 8.

(*iv*) $[Ru_6(\mu_4\text{-PPh})_3(\mu_3\text{-PPh})_2(CO)_{12}]$. *Crystal data.* $C_{42}H_{25}O_{12}P_5Ru_6$, $M = 1\,482.89$, two green crystals of dimensions 0.55 × 0.21 × 0.15 and 0.40 × 0.15 × 0.11 mm grown from dichloromethane–light petroleum, monoclinic, space group $C2/c$ (previously reported[6] incorrectly as Cc), $a = 23.82(3)$, $b = 23.36(3)$, $c = 23.60(3)$ Å, $\beta = 103.0(1)°$, $U = 12\,802.05$ Å^3, $D_c = 1.54$ g cm^{-3}, $Z = 8$, $\mu(\text{Mo-}K_\alpha) = 14.8$ cm^{-1}, $F(000) = 5\,119$.

Data were collected and accurate cell constants obtained as in (*ii*) above but two crystals were needed to complete the intensity data collection. Based on the measurement of three reference reflections every hour neither crystal lost more than 5% of its scattering power. The two sets of data were brought onto the same scale and combined to give a total of 9 317 unique reflections measured in the range $3 \leqslant 2\theta \leqslant 46°$, 7 446 of which with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. The data were corrected for Lorentz and polarisation effects but not for absorption.

The structure was initially solved in the space group Cc[6] using the TANG routine of the program SHELX;[54] subsequent consideration of the atomic co-ordinates revealed the presence of a crystallographic centre of symmetry and indicated the true space group to be $C2/c$. Weighted full-matrix least-squares refinement in $C2/c$, with anisotropic thermal parameters for the Ru and P atoms, individual isotropic thermal parameters for the carbonyl groups atoms, and a single averaged isotropic thermal parameter for the phenyl C atoms (the phenyl groups were refined as rigid hexagons) converged at $R = 0.123$ and $R' = 0.134$. A final difference Fourier calculated at this stage was featureless. Hydrogen atoms were not located. Fractional atomic co-ordinates are listed in Table 9. Additional material available from the Cambridge Crystallographic Data Centre comprise the thermal parameters and remaining bond lengths and angles.

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