

## Preliminary Communication

### High nuclearity ruthenium cluster compounds containing phosphorus ligands; synthesis and crystal structure of $[\text{Ru}_6(\text{CO})_{11}(\text{P}^t\text{Bu})_4]$ , $[\text{Ru}_7(\text{CO})_{14}(\text{P}^t\text{Bu})_4]$ , and $[\text{H}_3\text{Ru}_9(\text{CO})_{20}(\mu_7\text{-P})(\text{P}^t\text{Bu})_3]$

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#### Abstract

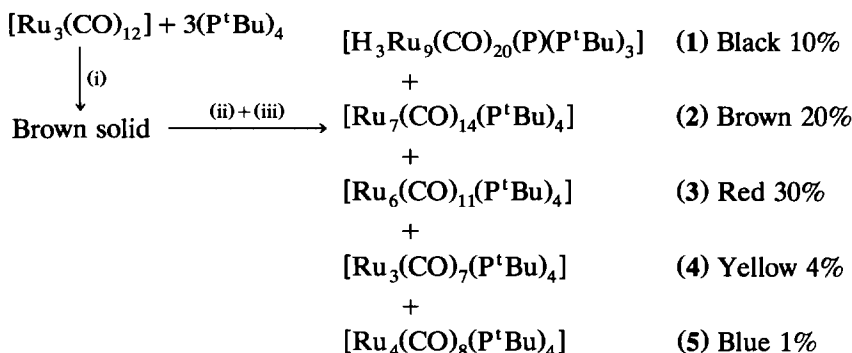
Thermolysis of  $[\text{Ru}_3(\text{CO})_{12}]$  and  $\text{P}_4^t\text{Bu}_4$  (1:3) in xylene followed by separation by TLC has given the four new cluster compounds  $[\text{H}_3\text{Ru}_9(\text{CO})_{20}(\mu_7\text{-P})(\text{P}^t\text{Bu})_3]$  (1),  $[\text{Ru}_7(\text{CO})_{14}(\text{P}^t\text{Bu})_4]$  (2),  $[\text{Ru}_6(\text{CO})_{11}(\text{P}^t\text{Bu})_4]$  (3), and  $[\text{Ru}_3(\text{CO})_7(\text{P}^t\text{Bu})_4]$  (4), which have been characterised by mass spectrometry and IR and <sup>1</sup>H-NMR spectroscopy. The structures of the three largest cluster 1, 2, and 3 were established by an X-ray diffraction study. Complex 1 is a rare

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nonaruthenium cluster, and incorporates the first example of a  $\mu_7\text{-P}$  ligand which is present, semi-encapsulated, within a most unusual type of metal framework.

**Key words:** Ruthenium; Phosphorus; Cluster; Bridging ligand; Crystal structure

There is considerable current interest in the role of phosphorus ligands in stabilising novel polyhedral forms in metal clusters [1]. Triorganophosphines are widely used as traditional two electron donors, but there are also many examples of metal clusters containing diorganophosphido [2] and organophosphidene [3] groups as three and four electron donors respectively, although examples of clusters containing atomic phosphorus as a five electron donor are still relatively rare [4–9]. In the first examples of interstitial phosphorus ligands these ligands were in  $\mu_8$ -sites surrounded by square anti-prismatic arrangements of rhodium atoms [5], and this type of cavity is also present in the octaruthenium cluster  $[\text{Ru}_8(\text{CO})_{21}(\mu_6\text{-P})(\text{PPh})(\text{PPh}_2)]$  [6]. A completely encapsulated  $\mu_6\text{-P}$  atom is found within a trigonal prismatic metal cavity in the monoanion  $[\text{Os}_6(\text{CO})_{18}(\mu_6\text{-P})]^-$  [7], and semi-encapsulated phosphorus ligands have previously been observed in  $\mu_5$ - and  $\mu_6$ -sites [8–10]. We now report the first example of a  $\mu_7\text{-P}$  ligand which is found semi-encapsulated, within



- (i) Xylene, 180°C, 12 h  
(ii)  $\text{CH}_2\text{Cl}_2$  solution  
(iii) TLC on silica; eluant 40/60  $\text{CH}_2\text{Cl}_2$ /hexane

Scheme 1. Reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with  $(\text{P}^t\text{Bu})_4$ .

a most unusual type of metal framework in the rare nonaruthenium cluster  $[\text{H}_3\text{Ru}_9(\text{CO})_{20}(\mu_7\text{-P}(\text{P}^t\text{Bu})_3)]$  (1).

Phosphido ring compounds have been used previously to give unusual cluster compounds, in which they are present as novel multidentate ligands [11]. We have found that the phosphido ring  $\text{P}_4^t\text{Bu}_4$  is a useful source for phosphorus inclusion into metal clusters as monophosphorus ligands, thus vacuum pyrolysis of  $[\text{Ru}_3(\text{CO})_{12}]$  with  $\text{P}_4^t\text{Bu}_4$  (1:1) allows isolation of a pentanuclear cluster  $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-P}^t\text{Bu})]$  [12]. We now report that thermolysis of the same two reactants (1:3) in xylene gives a range of new ruthenium clusters, the largest of which is the trihydrido species 1.

Thermolysis of  $[\text{Ru}_3(\text{CO})_{12}]$  and  $\text{P}_4^t\text{Bu}_4$  (1:3) in xylene (see Scheme 1) gave a brown microcrystalline solid which dissolved in dichloromethane; separation by TLC gave the four new clusters  $[\text{H}_3\text{Ru}_9(\text{CO})_{20}(\mu_7\text{-P}(\text{P}^t\text{Bu})_3)]$  (1),  $[\text{Ru}_7(\text{CO})_{14}(\text{P}^t\text{Bu})_4]$  (2),  $[\text{Ru}_6(\text{CO})_{11}(\text{P}^t\text{Bu})_4]$  (3), and  $[\text{Ru}_3(\text{CO})_7(\text{P}^t\text{Bu})_4]$  (4), which were characterised by IR and  $^1\text{H}$  NMR spectroscopy and FAB mass spectrometry [13\*], together with traces of the known [12] tetranuclear cluster  $[\text{Ru}_4(\text{CO})_8(\text{P}^t\text{Bu})_4]$  (5). X-Ray diffraction study [14\*] of the three largest clusters 1, 2, and 3 established the overall structures illustrated in Figs. 1, 2 and 3, respectively.

The  $\text{Ru}_9\text{P}_4$  framework in 1 [Fig. 1(b)] provides a most unusual illustration of the versatility of phosphorus based ligands in cluster chemistry. It contains a square pyramidal  $\text{Ru}_5$  unit with two opposite triangular faces, Ru(1), Ru(4), Ru(9) and Ru(2), Ru(3), Ru(9), bridged by two  $\mu_3\text{-P}^t\text{Bu}$  ligands. The square base, defined by Ru(1), Ru(2), Ru(3) and Ru(4), is bridged by a naked phosphorus atom which is also bonded to three other ruthenium atoms Ru(5), Ru(6) and Ru(7). These three ruthenium atoms form an arch across the square base, resulting in semi-encapsulation of the  $\mu_7\text{-P}$  ligand; the ends of the arch, Ru(5) and Ru(7), bridge opposite edges of the square base, Ru(3)–Ru(4) and Ru(1)–Ru(1) respectively. The last ruthenium atom Ru(8) is in a more remote site bridging one side of the arch, Ru(6)–Ru(7), the resulting triangle being bridged by the third  $\mu_3\text{-P}^t\text{Bu}$  ligand.

The  $^1\text{H}$  NMR spectrum of 1 at 25°C shows three sets of signals at  $\delta$  –21.71 (dddd)  $\text{H}^a$ , –21.19 (dddd)  $\text{H}^b$ , and –31.26 (dddd)  $\text{H}^c$ , indicating the presence of three bridging hydrido ligands. Decoupling results show that  $\text{H}^a$  couples to  $\text{H}^b$  but that neither of these two H-atoms couple to  $\text{H}^c$ . This is consistent with the results of the X-ray study where bond lengths and

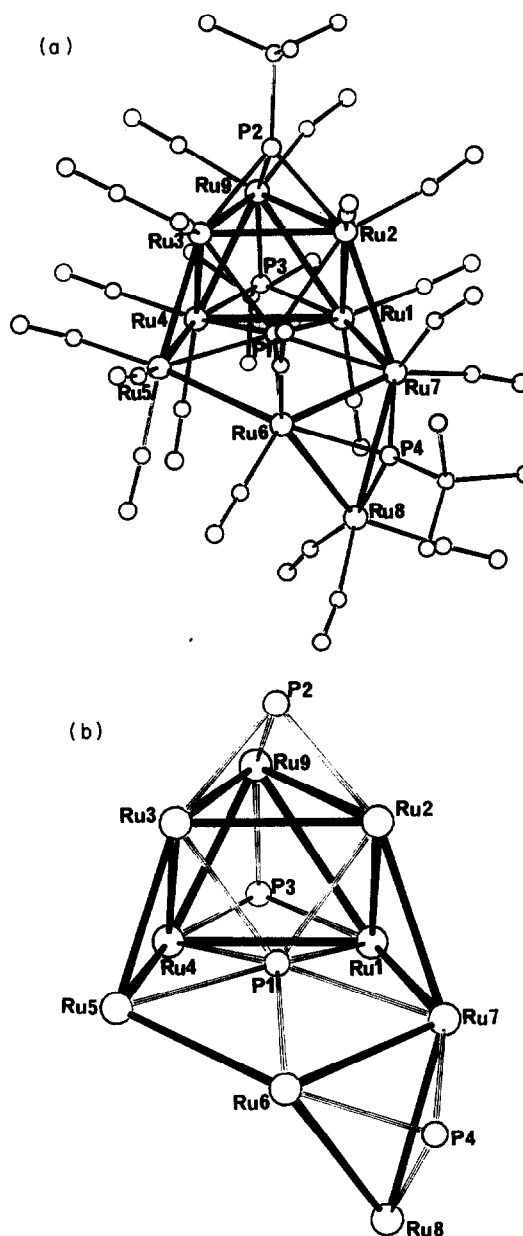


Fig. 1. The molecular structure of  $[\text{H}_3\text{Ru}_9(\text{CO})_{20}(\mu_7\text{-P}(\text{P}^t\text{Bu})_3)]$  (1). (a) The overall structure with H-atom omitted. (b) The  $\text{Ru}_9\text{P}_4$  framework. Principal bond distances ( $\text{\AA}$ ): Ru(1)–Ru(2) 3.005; Ru(1)–Ru(4) 2.917; Ru(1)–Ru(7) 2.916; Ru(1)–Ru(9) 3.040; Ru(2)–Ru(3) 2.894; Ru(2)–Ru(7) 3.001; Ru(2)–Ru(9) 3.111; Ru(3)–Ru(4) 2.747; Ru(3)–Ru(5) 2.829; Ru(3)–Ru(9) 2.819; Ru(4)–Ru(5) 2.851; Ru(4)–Ru(9) 2.826; Ru(5)–Ru(6) 2.897; Ru(6)–Ru(7) 2.885; Ru(6)–Ru(8) 2.960; Ru(7)–Ru(8) 3.009; P(1)–Ru(1) 2.591; P(1)–Ru(2) 2.504; P(1)–Ru(3) 2.506; P(1)–Ru(4) 2.470; P(1)–Ru(5) 2.488; P(1)–Ru(6) 2.530; P(1)–Ru(7) 2.541; P(2)–Ru(2) 2.259; P(2)–Ru(3) 2.246; P(2)–Ru(9) 2.318; P(3)–Ru(1) 2.251; P(3)–Ru(4) 2.249; P(3)–Ru(9) 2.310; P(4)–Ru(6) 2.254; P(4)–Ru(7) 2.266; P(4)–Ru(8) 2.313. (Maximum estimated standard deviation for Ru–Ru and P–Ru bond distances is 0.003 and 0.007  $\text{\AA}$  respectively.)

\* References number with asterisk indicates a note in the list of references.

potential energy minimisation calculations [15] indicate that two of the H-ligands bridge adjacent edges, Ru(6)–Ru(8) 2.954 and Ru(7)–Ru(8) 3.009 Å, and that the third adopts a  $\mu_3$ -site on the Ru(1), Ru(2), Ru(9) face [Ru(1)–Ru(2) 3.005(3), Ru(1)–Ru(9) 3.042, Ru(2)–Ru(9) 3.112 Å]. The cluster has a total of 132 valence electrons, two more than the 130e predicted by either by the Effective Atomic Number Rule or the Polyhedral Fusion approach [16].

The heptametal cluster  $[\text{Ru}_7(\text{CO})_{14}(\text{P}^t\text{Bu}_4)]$  (**2**) has the 100 cluster valence electrons expected [16] for the observed metal core of two square pyramidal units fused through a triangular face Ru(2), Ru(3) and Ru(5) (Fig. 2), geometry previously reported for the phenylphosphinidene cluster  $[\text{Ru}_7(\text{CO})_{18}(\text{PPh}_2)_2]$  [17], one of the first heptaruthenium clusters to be isolated. In both these clusters the square faces are stabilised by  $\mu_4$ -organophosphinidene ligands; in **2** P(1) bridges the four atoms Ru(3), Ru(5), Ru(6) and Ru(7), and P(4)

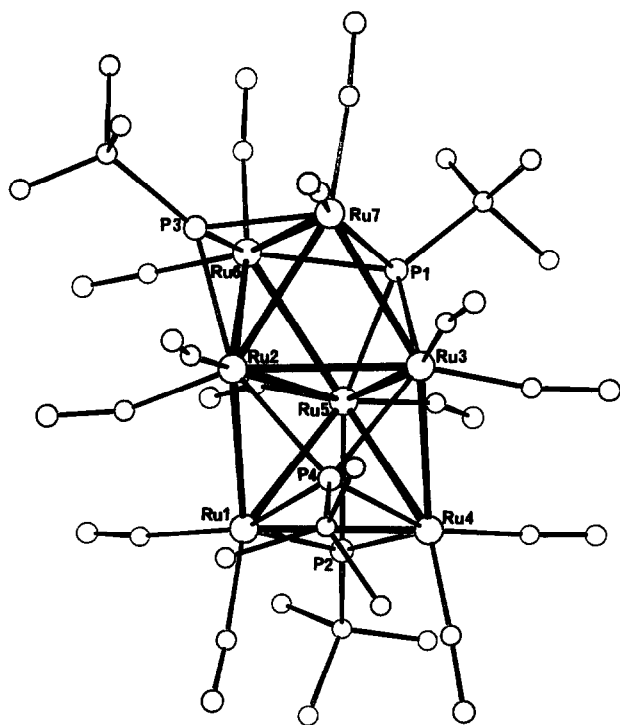


Fig. 2. The molecular structure of  $[\text{Ru}_7(\text{CO})_{14}(\text{P}^t\text{Bu}_4)]$  (**2**). Principle bond distances (Å): Ru(1)–Ru(2) 2.808; Ru(1)–Ru(4) 2.907; Ru(1)–Ru(5) 2.934; Ru(2)–Ru(3) 2.951; Ru(2)–Ru(5) 3.209; Ru(2)–Ru(6) 2.959; Ru(2)–Ru(7) 2.899; Ru(3)–Ru(4) 2.799; Ru(3)–Ru(5) 2.966; Ru(3)–Ru(7) 2.813; Ru(4)–Ru(5) 2.918; Ru(5)–Ru(6) 2.816; Ru(6)–Ru(7) 2.903; P(1)–Ru(3) 2.351; P(1)–Ru(5) 2.409; P(1)–Ru(6) 2.418; P(1)–Ru(7) 2.395; P(2)–Ru(1) 2.202; P(2)–Ru(4) 2.203; P(2)–Ru(5) 2.369; P(3)–Ru(2) 2.330; P(3)–Ru(6) 2.210; P(3)–Ru(7) 2.182; P(4)–Ru(1) 2.409; P(4)–Ru(2) 2.403; P(4)–Ru(3) 2.358; P(4)–Ru(4) 2.421. (Maximum estimated standard deviation for Ru–Ru and P–Ru bond distances is 0.004 and 0.009 Å respectively.)

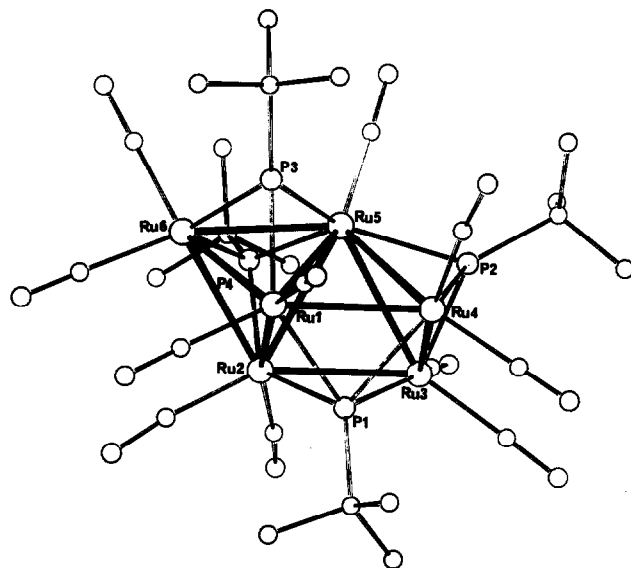


Fig. 3. The molecular structure of  $[\text{Ru}_6(\text{CO})_{11}(\text{P}^t\text{Bu}_4)]$  (**3**). Principle bond distances (Å): Ru(1)–Ru(2) 2.909; Ru(1)–Ru(4) 2.789; Ru(1)–Ru(5) 2.929; Ru(1)–Ru(6) 2.825; Ru(2)–Ru(3) 2.782; Ru(2)–Ru(5) 2.919; Ru(2)–Ru(6) 2.869; Ru(3)–Ru(4) 2.852; Ru(3)–Ru(5) 2.989; Ru(4)–Ru(5) 2.984; Ru(5)–Ru(6) 2.786; P(1)–Ru(1) 2.371; P(1)–Ru(2) 2.386; P(1)–Ru(3) 2.427; P(1)–Ru(4) 2.406; P(2)–Ru(3) 2.214; P(2)–Ru(4) 2.204; P(2)–Ru(5) 2.318; P(3)–Ru(1) 2.259; P(3)–Ru(5) 2.242; P(3)–Ru(6) 2.262; P(4)–Ru(2) 2.252; P(4)–Ru(5) 2.276; P(4)–Ru(6) 2.239. (Maximum estimated standard deviation for Ru–Ru and P–Ru bond distances is 0.003 and 0.007 Å respectively.)

bridges Ru(1), Ru(2), Ru(3) and Ru(4). The remaining two P<sup>t</sup>Bu ligands in the new cluster **2** cap two triangular faces with P(2) and P(3) bonded in  $\mu_3$ -mode to Ru(1), Ru(4), Ru(5) and Ru(2), Ru(6), Ru(7), respectively. Overall the cluster has virtual  $C_2$  symmetry with the two fold axis passing through Ru(3) and the midpoint of Ru(2)–Ru(5).

The hexaruthenium cluster **3** has a capped-square pyramidal metal framework (Fig. 3) which is a rare alternative to the octahedron for clusters with 86 electrons [18]. As in the structure of **2**, the open square face of the metal core is stabilised by one P<sup>t</sup>Bu ligand, bonded in a  $\mu_4$ -mode, and the remaining three are symmetrically distributed in  $\mu_3$ -sites. The unique triangular face Ru(3), Ru(4), Ru(5) of the square pyramid is bridged by P(2), and P(3) and P(4) bridge two equivalent triangles of the capping  $\text{Ru}_4$  tetrahedron, Ru(1), Ru(5), Ru(6) and Ru(2), Ru(5), Ru(6) respectively, so that these two phosphinidene groups are related by the overall virtual  $C_2$  symmetry of the cluster.

An interesting feature this study of the use of  $\text{P}_4^t\text{Bu}_4$  in cluster build-up is the presence of four phosphorus atoms in each of the five clusters isolated, which seems to indicate an important role for an intact phosphinidene tetramer in the initial stages of cluster assembly. This observation is supported by analogous

synthetic studies using the hexameric phosphinidene  $P_6Ph_6$  where both of the two clusters isolated both also contain six phosphorus atoms [19].

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- IR [ $\nu(\text{CO})$ ,  $\text{CH}_2\text{Cl}_2/\text{cm}^{-1}$ ]; 1 2103(m), 2069(m), 2053(m), 2044(vs), 2036(s), 2020(s), 2003(w), 1985(w), 1970(w), 1943(w); 2 2052(w), 2020(vs), 2002(s), 1989(s), 1972(s), 1938(w); 3 2046(m), 2017(vs), 2005(vs), 1991(m), 1985(w), 1972(m), 1963(w), 1953(m), 1948(w); 4 2053(m), 2016(s), 1993(m), 1961(m); FAB MS ( $m/z$ ): 1 1764; 2 1458; 3 1272; 4 854; 5 984.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\text{SiMe}_4$  reference): 1  $\delta$  -31.26 (dddd), -2.19 (dddd), -21.71 (dddd), 1.60 (d  $J_{\text{P-H}}$  18.3 Hz, 9H), 1.86 (d  $J_{\text{P-H}}$  20.1 Hz, 9H), 2.28 (d  $J_{\text{P-H}}$  19.4 Hz, 9H); 2  $\delta$  1.90 (d  $J_{\text{P-H}}$  19.5 Hz, 18H), 0.93 (d  $J_{\text{P-H}}$  19.8 Hz, 18H); 3 1.57 (d  $J_{\text{P-H}}$  19.3 Hz, 9H), 1.56 (d  $J_{\text{P-H}}$  18.7 Hz, 18H), 0.95 (d  $J_{\text{P-H}}$  19.2 Hz, 9H); 4  $\delta$  1.05-1.10.
- Crystal data for 1, 2, and 3: all the crystals are monoclinic.  $[\text{H}_3\text{Ru}_9(\text{CO})_{20}(\text{P}^t\text{Bu})_3] \cdot (0.5\text{C}_6\text{H}_{14})$  1:  $\text{C}_{35}\text{H}_{37}\text{O}_{20}\text{P}_4\text{Ru}_9$ ,  $M = 1811.19$ , space group  $P2_1/n$ ,  $a = 11.699(2)$ ,  $b = 44.001(9)$ ,  $c = 11.263(2)$  Å,  $\beta = 110.02(2)^\circ$ ,  $V = 5547.48$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 2.208$  cm<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 24.0$  cm<sup>-1</sup>,  $F(000) = 3452$ ,  $R = 0.0563$ ,  $R_w = 0.0562$  for 3278 data.  $[\text{Ru}_7(\text{CO})_{14}(\text{P}^t\text{Bu})_4]$  2:  $\text{C}_{30}\text{H}_{36}\text{O}_{14}\text{P}_4\text{Ru}_7$ ,  $M = 1451.99$ , space group  $P2_1/n$ ,  $a = 18.428(4)$ ,  $b = 23.507(5)$ ,  $c = 11.115(2)$  Å,  $\beta = 96.49(2)^\circ$ ,  $V = 4783.98$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 2.016$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 21.5$  cm<sup>-1</sup>,  $F(000) = 2784$ ,  $R = 0.0599$ ,  $R_w = 0.0570$  for 2274 data.  $[\text{Ru}_6(\text{CO})_{11}(\text{P}^t\text{Bu})_4]$  3:  $\text{C}_{27}\text{H}_{36}\text{O}_{11}\text{P}_4\text{Ru}_6$ ,  $M = 1266.89$ , space group  $P2_1/c$ ,  $a = 20.216(4)$ ,  $b = 10.693(2)$ ,  $c = 21.040(4)$  Å,  $\beta = 116.05(2)^\circ$ ,  $V = 4086.06$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 2.059$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 21.8$  cm<sup>-1</sup>,  $F(000) = 2440$ ,  $R = 0.0551$ ,  $R_w = 0.0567$  for 2985 data. Absorption corrected data with  $I/\sigma(I) \geq 3.0$  collected on a Philips PW1100 diffractometer in the  $\theta$ -range 3-25° were used in all determinations. The structures were solved by a combination of direct methods and difference-Fourier techniques and refinement was by the full-matrix least-squares method with anisotropic thermal parameters assigned to the ruthenium and phosphorus atoms.
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