Synthesis and Structural Studies of New Ruthenium Cluster Carbonyl Derivatives derived from $(PhP)_5$ and $[Ru_3(CO)_{12}]$ and $[Ru_3(CO)_{10}(NCMe)_2]$†

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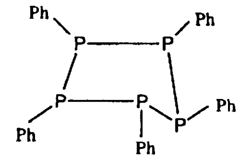
Reaction of the cyclopolyphosphane $(PhP)_5$ with $[Ru_3(CO)_{12}]$ in *p*-xylene at 135 °C for 19 h afforded the new clusters $[Ru_4(CO)_{10}(\mu_3\text{-PPh})_2\{\mu_4\text{-(PPh)}_2\}]$ **1** and $[Ru_4(CO)_8(\mu\text{-PHPh})_2(\mu_4\text{-PPh})\{\mu_4\text{-(PPh)}_2\}]$ **2**. Treatment of $(PhP)_5$ with the activated triruthenium cluster $[Ru_3(CO)_{10}(NCMe)_2]$ at room temperature overnight gave $[Ru_3(CO)_{10}\{(PhP)_5\}]$ **3**. The structures of the three clusters have been established by single-crystal X-ray analysis. In **1** the four ruthenium atoms have a skew, chain structure while in **2** the four ruthenium atoms adopt a rectangular geometry. Novel phosphido or phosphinidene groups are present in both clusters. In the case of **3** the cyclophosphane $(PhP)_5$ remains intact and acts as a bidentate ligand, occupying the equatorial sites of the ruthenium triangular plane, through the two P atoms in the 1,3 positions.

Cyclopolyphosphanes exhibit an interesting and diversified reactivity with transition-metal carbonyls which have been the subject of many articles.[1-5] Thermolysis reactions of the tetramer $(Bu^tP)_4$ with ruthenium carbonyl clusters gave several ruthenium cluster derivatives, each containing one or more phosphido group(s), indicating extensive disruption of the cyclic phosphorus ring.[6,7] On the other hand, we have recently reported that reactions between the pentaphenylcyclopentaphosphane $(PhP)_5$ and activated triosmium carbonyl clusters at room temperature afford several cluster derivatives where the phosphorus ring structure is retained.[8] In addition, some organocyclophosphanes readily reacted with transition-metal carbonyls at higher temperature to give complexes or clusters containing a diphosphene unit due to partial disruption of the cyclic phosphorus ring when the organo groups were CF_3 or C_6F_5.[9-12] However, there is so far no example of degradation of $(PhP)_5$ in which cyclopolyphosphanes serve as stable precursors of phosphido or diphosphene groups.

In this article we report (*i*) the pyrolysis of $[Ru_3(CO)_{12}]$ and $(PhP)_5$ which affords two novel tetramer ruthenium clusters containing the rare $(PhP)_2$ fragment and (*ii*) the reaction between $(PhP)_5$ and the activated cluster $[Ru_3(CO)_{10}(NCMe)_2]$ which gives a cluster derivative where the phosphorus ring structure remains intact.

Results and Discussion

(*a*) *Syntheses and Characterisations of New Clusters.*—The reaction of $[Ru_3(CO)_{12}]$ with an equivalent molar amount of $(PhP)_5$ in *p*-xylene at 135 °C for 19 h yielded a dark brown mixture which afforded three bands when subjected to thin-layer chromatography (TLC). The red crystalline solid $[Ru_4(CO)_{10}(\mu_3\text{-PPh})_2\{\mu_4\text{-(PPh)}_2\}]$ **1** was obtained from a hexane solution of Band 1. The green compound of band 2 decomposed into a brown solid and could not be isolated in crystalline form or fully characterised. The dark red compound $[Ru_4(CO)_8(\mu\text{-PHPh})_2(\mu_4\text{-PPh})\{\mu_4\text{-(PPh)}_2\}]$ **2** was recrystallised from a dichloromethane–hexane mixture of band 3. The ^1H NMR spectra of **1** and **2** show multiplets at δ 7.34 and 7.31 respectively due to the phenyl group. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1** shows two singlets with equal intensity at δ 478.1 due to the phosphinidene, μ_3-PPh, and at δ 202.8 due to the diphosphene, $\mu_4\text{-(PPh)}_2$, respectively. The corresponding spectrum of **2** shows three signals at δ 508.0 (t), 151.4 (d) and 131.4 (s) in the ratio of 1:2:2. The proton-coupled ^{31}P NMR spectrum of **2** shows that the peak at δ 151.4 is split into two with a coupling constant of 350 Hz, owing to protons attached directly to the phosphorus atoms. Therefore, the above three signals are assigned to μ_4-PPh, μ-PHPh and $\mu_4\text{-(PPh)}_2$ respectively. High-field resonances of the ^{31}P nucleus of the $(PhP)_2$ unit relative to free diphosphenes (δ 500–670) indicate that the $(PhP)_2$ units have π-donor property in **1** and **2**.[13] The spectroscopic data for the clusters **1** and **2**, listed in Table 1, are consistent with the solid-state structures.



$(PhP)_5$

The molecular structure of compound **1** was determined by a single-crystal X-ray diffraction study and is shown in Fig. 1 together with the atomic labelling scheme. Selected bond lengths and angles are given in Table 2. The four ruthenium atoms have a skew, chain structure with two μ_3-phosphinidene groups P(5) and P(8) capping Ru(1)–Ru(2)–Ru(3) and Ru(2)–Ru(3)–Ru(4) respectively, and with a μ_4-diphosphene, P(7)–P(6), capping the whole ruthenium chain, each of the two phosphorus atoms being co-ordinated to two of the four ruthenium atoms respectively as a bridging donor. The two Ru–Ru–Ru angles are virtually the same and approximately right angles (average 90.7°). The torsion angle (116.3°) between Ru(1)–Ru(2) and Ru(3)–Ru(4) indicates that the four ruthenium atoms are not on the same plane. The torsion angle (71.6°) between PhP(6) and P(7)Ph indicates that the two phenyl groups are *gauche* in the $(PhP)_2$ unit. A boat conformation, Fig. 2, is formed from the atoms except those of

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

the $(PhP)_2$ unit, consisting of two butterfly units, Ru(1), Ru(2), Ru(3), P(5), and Ru(2), P(8), Ru(4), Ru(3), fused along the common edge Ru(2)–Ru(3). The very small deviations (within ±0.037 Å) from the plane indicate that the bottom atoms are planar. The dihedral angle (90.3°) between the side triangles, Ru(1), Ru(2), P(5), and P(8), Ru(4), Ru(3), indicates that the two planes are perpendicular to each other. Furthermore, the plane of each triangle is tilted at 45° relative to the Ru(3)P(5)P(8)Ru(2) basal plane. The Ru–Ru bond distances (average 2.925 Å) of both ends are longer than that in the middle (2.884 Å) and the average in the parent cluster $[Ru_3(CO)_{12}]$ (2.853 Å).[14] Another unusual feature is the P(6)–P(7) bond distance of 2.163(2) Å which is significantly smaller than the standard value for a P–P single bond (2.22 Å).[15] In comparison with P–P distances in some side-on co-ordinated diphosphene complexes (2.110–2.186 Å),[11,16] the $(PhP)_2$ unit may be considered to contain a P–P double bond.

The molecular structure of compound **2** was determined by a single-crystal X-ray diffraction study and is shown in Fig. 3 together with the atomic labelling scheme. Selected bond lengths and angles are given in Table 3. The four ruthenium atoms adopt a rectangular geometry bicapped by a μ_4-phosphinidene ligand P(1) above and by a μ_4-diphosphene ligand, P(4)–P(5), below. Two shorter edges, Ru(1)–Ru(2) and Ru(3)–Ru(4), of the ruthenium plane are bridged by two phosphido groups, HP(2)Ph and HP(3)Ph, respectively. The hydrogens attached to the phosphorus atoms in the latter groups were located from the difference map in the X-ray analysis, and confirmed by proton-coupled ^{31}P NMR spectroscopy. The torsion angle Ph–P(4)–P(5)–Ph (3.4°) indicates that the two phenyl groups are eclipsed. The P(4)–P(5) distance (2.169 Å), as in **1**, is profoundly shorter than that of a single P–P bond and corresponds to the values found in other complexes with side-on co-ordinated PhP=PPh.

(*b*) *Synthesis and Characterisation of* $[Ru_3(CO)_{10}\{(PhP)_5\}]$ **3**.—Compound **3** was obtained by treatment of $(PhP)_5$ with 1 mol equivalent of $[Ru_3(CO)_{10}(NCMe)_2]$ at room temperature overnight and subsequent purification by TLC using CH_2Cl_2–hexane (25%:75%) as eluent. Dark red crystals were formed upon diffusion of hexane into a dichloromethane solution of **3**.

The molecular structure of $[Ru_3(CO)_{10}\{(PhP)_5\}]$ **3** was established by X-ray crystallography (Fig. 4, Table 4). The ligand, $(PhP)_5$, is bidentate, taking up the equatorial sites of the ruthenium triangular plane and chelating across a Ru–Ru edge, through the two P atoms in the 1,3 positions of the phosphorus ring. The whole five membered phosphorus ring remains intact

Table 1 Infrared absorption bands ($\tilde{\nu}_{CO}/cm^{-1}$)[a] and NMR spectral data[b] for compounds **1**–**3**

Compound	
1	IR 2076w, 2061vs, 2027m, 2017s, 2010m, 1994w, 1972w, 1966w δ_P 478.1 [s, 2 P, P(5) and P(8)], 202.8 [s, 2 P, P(6) and P(7)] δ_H 7.34 (m, 20 H, C_6H_5)
2	IR 2043w, 2017s, 2011s, 1999vw, 1981m, 1973w δ_P 508.0 [t, 1 P, P(1), $J(P^1P^2)$ = 60, $J(P^1P^3)$ = 60), 151.4 [d, 2 P, P(2) and P(3) J(PH) = 350, $J(P^1P^2)$ = 60, $J(P^1P^3)$ = 60], 131.4 [s, 2 P, P(4) and P(5)] δ_H 7.31 (m, 25 H, C_6H_5)
3	IR 2088s, 2068w, 2064w, 2045w, 2036w, 2030m, 2016s (sh), 2013vs, 1988w, 1968m, 1960m δ_P 145.8 (m, 1 P), 6.7 (m, 4 P) δ_H 7.27 (m, 25 H, C_6H_5)

[a] Recorded in cyclohexane. [b] Recorded in $CDCl_3$; ^{31}P NMR reference 85% H_3PO_4 and ^1H NMR reference $SiMe_4$, respectively; J in Hz.

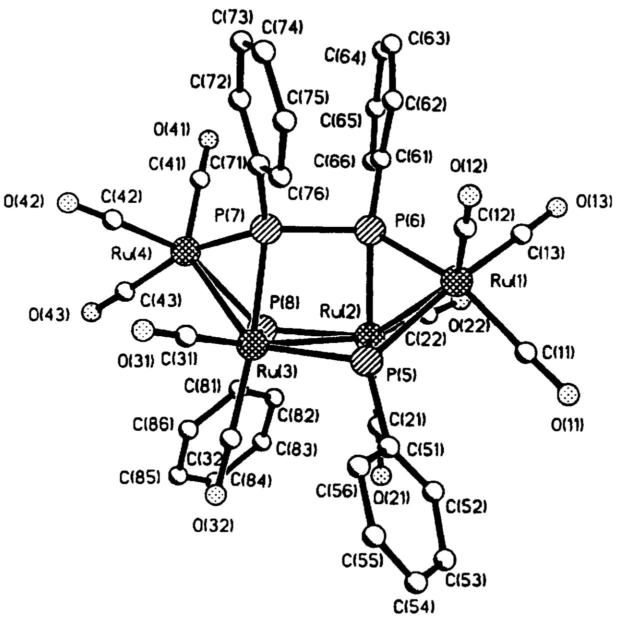

Fig. 1 Molecular structure of $[Ru_4(CO)_{10}(\mu_3\text{-PPh})_2\{\mu_4\text{-(PPh)}_2\}]$ **1**

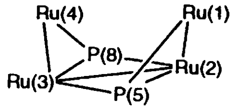

Fig. 2 The boat conformation in cluster **1**

Table 2 Selected bond lengths (Å) and angles (°) of $[Ru_4(CO)_{10}(\mu_3\text{-PPh})_2\{\mu_4\text{-PPh})_2\}]$ **1**

Ru(1)–Ru(2)	2.917(1)	Ru(2)–Ru(3)	2.884(1)	Ru(1)–Ru(3)	2.933(1)
P(6)–P(7)	2.163(2)	P(6)–Ru(1)	2.339(2)	P(6)–Ru(2)	2.347(2)
P(7)–Ru(3)	2.329(2)	P(7)–Ru(4)	2.339(2)	P(5)–Ru(1)	2.336(2)
P(5)–Ru(2)	2.397(2)	P(5)–Ru(3)	2.299(2)	P(8)–Ru(4)	2.339(2)
P(8)–Ru(3)	2.417(2)	P(8)–Ru(2)	2.296(2)		
P–C (mean)	1.819	C–O (mean)	1.135		

Ru(1)–Ru(2)–Ru(3)	90.9(1)	Ru(2)–Ru(3)–Ru(4)	90.5(1)
Ru(3)–P(7)–Ru(4)	77.8(1)	Ru(1)–P(6)–Ru(2)	77.0(1)
Ru(3)–P(7)–P(6)	97.3(1)	Ru(1)–P(6)–P(7)	117.1(1)
Ru(4)–P(7)–P(6)	116.0(1)	Ru(2)–P(6)–P(7)	97.4(1)
C(71)–P(7)–P(6)	108.3(2)	C(61)–P(6)–P(7)	107.1(2)
C(71)–P(7)–Ru(3)	127.4(2)	C(61)–P(6)–Ru(1)	125.1(2)
C(71)–P(7)–Ru(4)	125.0(2)	C(61)–P(6)–Ru(2)	128.7(2)
Ru(1)–P(5)–Ru(2)	76.1(1)	Ru(2)–P(5)–Ru(3)	75.8(1)
Ru(1)–P(5)–Ru(3)	126.2(1)	Ru(2)–P(8)–Ru(3)	75.4(1)
Ru(3)–P(8)–Ru(4)	76.1(1)	Ru(2)–P(8)–Ru(4)	126.0(1)

Table 3 Selected bond lengths (Å) and angles (°) of $[Ru_4(CO)_8(\mu\text{-}PHPh)_2(\mu_4\text{-}PPh)\{\mu_4\text{-}(PPh)_2\}]$ **2**

Ru(1)–Ru(2)	2.871(1)	Ru(3)–Ru(4)	2.899(1)	Ru(1)–Ru(3)	3.055(1)
Ru(2)–Ru(4)	3.037(1)	P(4)–P(5)	2.169(3)	P(4)–Ru(1)	2.358(2)
P(4)–Ru(3)	2.343(2)	P(5)–Ru(2)	2.353(2)	P(5)–Ru(4)	2.335(2)
P(2)–Ru(1)	2.291(2)	P(2)–Ru(2)	2.289(2)	P(3)–Ru(3)	2.301(2)
P(3)–Ru(4)	2.290(2)	P(1)–Ru(1)	2.409(2)	P(1)–Ru(2)	2.383(2)
P(1)–Ru(3)	2.395(2)	P(1)–Ru(4)	2.426(2)		
P–C (mean)	1.818	C–O (mean)	1.134		

Ru(2)–Ru(1)–Ru(3)	89.1(1)	Ru(1)–Ru(2)–Ru(4)	90.6(1)
Ru(1)–Ru(3)–Ru(4)	90.1(1)	Ru(2)–Ru(4)–Ru(3)	89.4(1)
Ru(1)–P(1)–Ru(2)	73.6(1)	Ru(3)–P(1)–Ru(4)	73.9(1)
Ru(1)–P(1)–Ru(3)	78.3(1)	Ru(2)–P(1)–Ru(4)	78.3(1)
Ru(1)–P(2)–Ru(2)	77.6(1)	Ru(3)–P(3)–Ru(4)	78.3(1)
Ru(1)–P(4)–Ru(3)	80.4(1)	Ru(2)–P(5)–Ru(4)	80.7(1)
C(41)–P(4)–P(5)	114.1(3)	C(51)–P(5)–P(4)	113.8(3)
C(41)–P(4)–Ru(3)	126.5(3)	C(51)–P(5)–Ru(4)	128.2(2)
C(41)–P(4)–Ru(1)	130.4(2)	C(51)–P(5)–Ru(2)	128.4(3)
Ru(1)–P(4)–P(5)	98.2(1)	Ru(3)–P(4)–P(5)	99.1(1)
Ru(2)–P(5)–P(4)	98.9(1)	Ru(4)–P(5)–P(4)	98.8(1)

Table 4 Selected bond lengths (Å) and angles (°) in $[Ru_3(CO)_{10}\{(PhP)_5\}]$ **3**

Ru(1)–Ru(2)	2.851(1)	Ru(1)–Ru(3)	2.845(1)	Ru(2)–Ru(3)	2.864(1)
P(1)–P(2)	2.257(1)	P(1)–P(5)	2.224(2)	P(2)–P(3)	2.220(2)
P(3)–P(4)	2.263(2)	P(4)–P(5)	2.222(2)	Ru(1)–P(3)	2.337(1)
Ru(3)–P(1)	2.334(1)	P–C (mean)	1.829	C–O (mean)	1.134

Ru(2)–Ru(1)–Ru(3)	60.4(1)	Ru(1)–Ru(2)–Ru(3)	59.7(1)
Ru(1)–Ru(3)–Ru(2)	59.9(1)	P(2)–P(1)–P(5)	85.1(1)
P(1)–P(2)–P(3)	86.7(1)	P(2)–P(3)–P(4)	95.8(1)
P(3)–P(4)–P(5)	100.2(1)	P(1)–P(5)–P(4)	97.5(1)

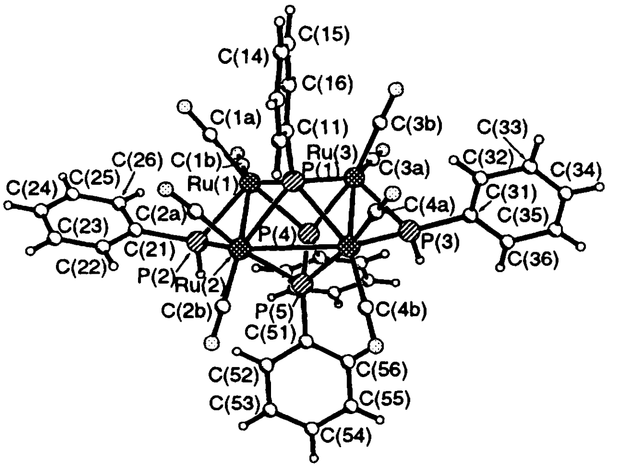

Fig. 3 Molecular structure of $[Ru_4(CO)_8(\mu\text{-}PHPh)_2(\mu_4\text{-}PPh)\{\mu_4\text{-}(PPh)_2\}]$ **2**

but is heavily distorted with respect to the geometry of free $(PhP)_5$. The average P–P–P angle of (93.1°) in the the phosphorus ring in **3** is much smaller than that in $(PhP)_5$ (100.0°).[17] The smallest angle, P(1)–P(2)–P(3), 86.7°, is much smaller than any angle in free $(PhP)_5$ because the two phosphorus atoms at positions 1 and 3 in the phosphorus ring must move closer to fit the short Ru–Ru distance in the triruthenium cluster. Compound **3** is isostructural with one of a pair of inversion isomers with formula $[Os_3(CO)_{10}\{(PhP)_5\}]$.[8] Unfortunately, the corresponding inversion isomer of **3** similar to the osmium system has not yet been obtained.

Experimental

The reactions described were carried out under nitrogen in evacuated reaction tubes using vacuum-line techniques. All solvents were dried over appropriate drying agents[18] and distilled prior to use. The compounds $(PhP)_5$,[19] $[Ru_3(CO)_{12}]$[20] and $[Ru_3(CO)_{10}(NCMe)_2]$[21] were prepared by the literature methods. The products of the reactions were separated by thin-layer chromatography on 20 × 20 cm glass plates coated with 0.3 mm of Merck Kieselgel $60GF_{254}$, using mixtures of dichloromethane and hexane in various proportions as eluents. Infrared spectra were recorded as solutions in 0.5 mm KBr cells on a Perkin-Elmer model 983G spectrometer, ^1H and ^{31}P NMR spectra on a Bruker 300 FT spectrometer using $SiMe_4$ (^1H) or H_3PO_4 (^{31}P) as references.

Syntheses.—$[Ru_4(CO)_{10}(\mu_3\text{-}PPh)_2\{\mu_4\text{-}(PPh)_2\}]$ **1** *and* $[Ru_4(CO)_8(\mu\text{-}PHPh)_2(\mu_4\text{-}PPh)\{\mu_4\text{-}(PPh)_2\}]$ **2**. The compounds $[Ru_3(CO)_{12}]$ (0.200 g, 0.313 mmol), $(PhP)_5$ (0.169 g, 0.313 mmol) and *p*-xylene (5 cm^3) were added in a Carius tube and degassed *in vacuo*. The mixture was heated in an oven at 135 °C for 19 h. The excess of solvent was removed under vacuum. The residue was dissolved in dichoromethane (3 cm^3) and subjected to TLC on silica using dichloromethane–hexane (30% : 70%) as eluent. Red crystalline $[Ru_4(CO)_{10}(\mu_3\text{-}PPh)_2\{\mu_4\text{-}(PPh)_2\}]\cdot 0.5C_6H_{14}$ **1** was extracted from band 1 and recrystallised from hexane at low temperature. Yield 7 mg (Found: C, 39.3; H, 2.80; P, 10.45. Calc. for $C_{37}H_{27}O_{10}P_4Ru_4$: C, 38.3; H, 2.35; P, 10.7%). The dark red crystals of $[Ru_4(CO)_8(\mu\text{-}PHPh)_2(\mu_4\text{-}PPh)\{\mu_4\text{-}(PPh)_2\}]$ **2** extracted from band 3 were obtained from a mixture of dichoromethane and hexane at low temperature. Yield 15 mg (Found: C, 39.2; H, 2.20; P, 13.3. Calc. for $C_{38}H_{27}O_{18}P_5Ru_4$: C, 38.95; H, 2.30; P, 13.25%).

$[Ru_3(CO)_{10}\{(PhP)_5\}]$ **3**. The compound $(PhP)_5$ (0.132 g,

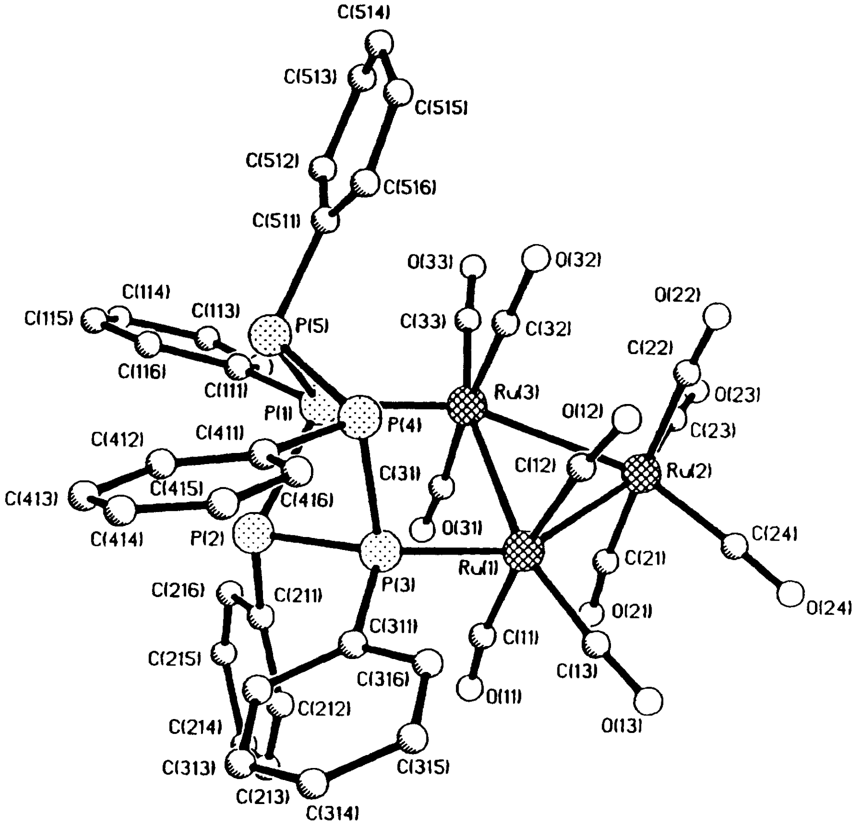

Fig. 4 Molecular structure of $[Ru_3(CO)_{10}\{(PhP)_5\}]$ **3**

Table 5 Crystal data and data collection parameters for compounds **1**–**3**

Compound	**1**	**2**	**3**
Formula	$C_{37}H_{27}O_{10}P_4Ru_4$	$C_{38}H_{27}O_8P_5Ru_4$	$C_{40}H_{25}O_{10}P_5Ru_3$
M	1159.7	1170.7	1123.7
Colour, habit	Reddish prism	Dark orange prisms	Dark red block
Crystal size/mm	0.20 × 0.30 × 0.40	0.30 × 0.30 × 0.25	0.35 × 0.35 × 0.40
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	11.948(2)	18.260(4)	10.629(3)
b/Å	20.983(4)	11.964(2)	38.909(7)
c/Å	17.206(3)	20.995(4)	10.895(3)
β°	90.93(3)	110.00(3)	108.88(2)
U/Å^3	4313(2)	4310(2)	4263(2)
Z	4	4	4
F(000)	2260	2280	2208
D_c/g cm^{-3}	1.786	1.804	1.292
μ(Mo-Kα)/cm^{-1}	15.74	16.08	12.92
2θ range/°	3.5–50	3.5–45.0	3.5–50
Scan speed/° min^{-1}	2.49–19.53	2.00–29.30	3.00–18.03
Scan range/°	1.20	1.20	1.30
Total reflections	7950	7022	7809
Unique reflections	7572	6784	7401
Observed reflections	5533 $[F > 4.0\sigma(F)]$	4526 $[F > 4.0\sigma(F)]$	4947 $[F > 6.0\sigma(F)]$
k, In weighting scheme $w^{-1} = \sigma^2(F) + kF^2$	0.0005	0.001	0.0006
R (observed data)	0.0378	0.0386	0.0255
R′ (observed data)	0.0486	0.0480	0.0323
Goodness of fit	1.38	0.99	0.92

0.243 mmol) was added to a solution of $[Ru_3(CO)_{10}(NCMe)_2]$ (0.162 g, 0.243 mmol) in acetonitrile–dichloromethane (1 : 1 v/v, 10 cm^3). The mixture was allowed to stir at room temperature overnight, during which time it changed from brown to dark red. The solvent was removed under vacuum and TLC of the residue using CH_2Cl_2–hexane (25%: 75%) as eluent afforded $[Ru_3(CO)_{10}\{(PhP)_5\}]$ (76 mg) (Found: C, 42.95; H, 2.15; P, 13.65. Calc. for $C_{40}H_{25}O_{10}P_5Ru_3$: C, 42.75; H, 2.25; P, 13.8%).

Crystal Structure Determinations.—Crystal data and details of measurements for clusters **1**–**3** are reported in Table 5, atomic coordinates in Tables 6–8. Diffraction intensities were collected at 298 K on a Siemens R3m/V diffractometer, using the ω–2θ

Table 6 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Ru(1)	4 762(1)	382(1)	1 889(1)
Ru(2)	3 329(1)	1 463(1)	2 254(1)
Ru(3)	3 718(1)	1 269(1)	3 896(1)
Ru(4)	4 820(1)	2 515(1)	4 015(1)
P(5)	3 602(1)	489(1)	2 960(1)
P(6)	5 290(2)	1 404(1)	2 292(1)
P(7)	5 517(1)	1 556(1)	3 528(1)
P(8)	3 320(1)	2 242(1)	3 191(1)
O(11)	3 211(6)	−675(3)	1 258(3)
O(12)	6 660(6)	−478(3)	2 413(4)
O(13)	5 548(7)	745(3)	268(4)
O(21)	788(5)	1 346(3)	2 174(4)
O(22)	3 353(6)	1 975(4)	602(3)
O(31)	4 617(5)	793(3)	5 447(3)
O(32)	1 361(4)	1 069(3)	4 504(3)
O(41)	6 406(6)	3 397(3)	3 196(4)
O(42)	6 109(6)	2 286(3)	5 548(4)
O(43)	3 381(6)	3 550(3)	4 752(4)
C(11)	3 784(7)	−290(4)	1 502(4)
C(12)	5 958(7)	−148(4)	2 204(5)
C(13)	5 253(8)	598(4)	868(5)
C(21)	1 733(7)	1 368(3)	2 205(4)
C(31)	4 275(5)	973(3)	4 861(4)
C(32)	2 232(6)	1 161(3)	4 253(4)
C(41)	5 820(7)	3 081(4)	3 502(5)
C(42)	5 652(7)	2 379(4)	4 985(5)
C(43)	3 890(7)	3 160(3)	4 488(4)
C(51)	2 523(6)	−111(3)	3 101(4)
C(52)	1 634(7)	−189(4)	2 587(6)
C(53)	815(9)	−636(6)	2 766(9)
C(54)	945(12)	−1 029(5)	3 412(10)
C(55)	1 839(12)	−966(5)	3 741(5)
C(61)	6 294(6)	1 907(3)	1 807(4)
C(62)	7 391(7)	1 727(4)	1 779(5)
C(63)	8 192(7)	2 162(5)	1 496(5)
C(64)	7 902(9)	2 729(5)	1 226(5)
C(65)	6 801(10)	2 900(4)	1 198(6)
C(66)	5 984(3)	2 494(2)	1 509(3)
C(71)	6 827	1 188	3 831
C(72)	7 800	1 547	3 833
C(73)	8 816(7)	1 261(4)	3 974(6)
C(74)	8 848(8)	604(5)	4 103(7)
C(75)	7 904(7)	243(4)	4 091(5)
C(76)	6 886(6)	547(3)	3 962(4)
C(81)	1 976(6)	2 650(3)	3 287(4)
C(82)	1 480(6)	2 921(3)	2 636(4)
C(83)	443(8)	3 194(4)	2 661(7)
C(84)	−140(8)	3 174(4)	3 350(8)
C(85)	339(8)	2 931(4)	3 989(6)
C(86)	1 401(7)	2 663(3)	3 971(5)
C(1s)	2 126(1)	548(1)	9 768(1)
C(2s)	1 286(1)	126(1)	9 479(1)
C(3s)	490	198	10 105

Table 7 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Ru(1)	9 057(1)	2 055(1)	1 997(1)
Ru(2)	9 475(1)	2 080(1)	797(1)
Ru(3)	7 694(1)	3 595(1)	1 310(1)
Ru(4)	8 093(1)	3 577(1)	87(1)
P(1)	8 981(1)	3 614(2)	1 250(1)
P(2)	6 898(1)	3 802(2)	199(1)
P(4)	7 819(1)	1 663(2)	1 196(1)
P(5)	8 142(1)	1 656(2)	293(1)
C(1a)	10 001(5)	2 639(7)	2 650(4)
C(1b)	8 817(5)	1 364(7)	2 704(4)
C(2a)	10 504(5)	2 689(7)	1 193(4)
C(2b)	9 698(4)	1 527(7)	52(4)
C(3a)	7 030(4)	3 322(7)	1 808(4)
C(3b)	7 814(4)	5 147(7)	1 580(4)
C(4a)	8 313(5)	5 114(7)	−48(4)
C(4b)	7 836(5)	3 265(7)	−850(4)
O(1a)	10 553(4)	2 925(6)	3 047(4)
O(1b)	8 689(4)	968(6)	3 150(3)
O(2a)	11 125(3)	3 003(6)	1 442(4)
O(2b)	9 846(4)	1 207(6)	−410(3)
O(3a)	6 628(4)	3 132(5)	2 102(3)
O(3b)	7 862(4)	6 042(5)	1 747(4)
O(4a)	8 435(4)	5 996(5)	−163(4)
O(4b)	7 676(4)	3 054(6)	−1 411(3)
C(11)	9 597(4)	4 854(7)	1 554(4)
C(12)	9 986(5)	5 290(7)	1 145(4)
C(13)	10 414(6)	6 269(8)	1 356(5)
C(14)	10 442(6)	6 768(9)	1 931(5)
C(15)	10 069(5)	6 356(8)	2 344(5)
C(16)	9 640(5)	5 347(7)	2 152(4)
C(21)	10 592(4)	128(6)	2 093(4)
C(22)	11 196(5)	34(7)	1 853(5)
C(23)	11 917(6)	−407(8)	2 249(5)
C(24)	12 027(6)	−738(8)	2 900(5)
C(25)	11 457(5)	−651(7)	3 155(5)
C(26)	10 726(5)	−217(7)	2 749(4)
C(31)	6 284(4)	5 019(7)	−122(4)
C(32)	6 576(5)	6 069(7)	42(4)
C(33)	6 105(6)	7 013(9)	−222(5)
C(34)	5 357(6)	6 841(9)	−645(5)
C(35)	5 053(6)	5 843(8)	−810(5)
C(36)	5 516(5)	4 883(7)	−559(4)
C(41)	7 116(4)	611(6)	1 198(4)
C(42)	7 351(5)	−462(7)	1 426(4)
C(43)	6 806(6)	−1 287(9)	1 413(5)
C(44)	6 038(6)	−1 040(8)	1 177(5)
C(45)	5 778(7)	3(9)	949(5)
C(46)	6 335(6)	825(9)	958(5)
C(51)	7 695(4)	540(6)	−294(4)
C(52)	8 073(5)	−460(7)	−268(4)
C(53)	7 723(5)	−1 323(8)	−726(5)
C(54)	7 007(6)	−1 163(8)	−1 191(5)
C(55)	6 616(6)	−173(9)	−1 229(5)
C(56)	6 976(5)	694(8)	−779(5)

scan mode with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). All computations were carried out on a Micro VAX 2000 computer using the SHELXTL PLUS program package.[22] The structures were solved by direct methods for the ruthenium atoms and Fourier-difference techniques for the remaining non-hydrogen atoms. Full-matrix least-squares refinement was performed with all non-hydrogen atoms anisotropic. An empirical (ψ-scan) absorption correction was applied in each case.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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Table 8 Atomic coordinates (× 10^4) for $[Ru_3(CO)_{10}\{(PhP)_5\}]$ **3**

Atom	*x*	*y*	*z*
Ru(1)	6 251(1)	3 899(1)	6 783(1)
Ru(2)	8 774(1)	4 185(1)	8 194(1)
Ru(3)	6 908(1)	4 015(1)	9 496(1)
P(1)	4 832(1)	3 847(1)	9 589(1)
P(2)	3 012(1)	3 885(1)	7 809(1)
P(3)	4 236(1)	3 648(1)	6 726(1)
P(4)	4 529(1)	3 138(1)	7 783(1)
P(5)	4 253(1)	3 300(1)	9 636(1)
C(11)	5 530(5)	4 358(1)	6 388(4)
C(12)	7 195(5)	3 472(1)	7 117(5)
C(13)	6 307(5)	3 876(1)	5 070(5)
C(21)	7 987(5)	4 634(2)	7 628(5)
C(22)	9 625(5)	3 750(1)	8 816(5)
C(23)	10 103(6)	4 431(1)	9 502(6)
C(24)	9 294(5)	4 157(2)	6 680(6)
C(31)	6 326(5)	4 485(1)	9 128(4)
C(32)	7 640(5)	3 555(1)	9 801(5)
C(33)	7 893(5)	4 122(1)	11 248(5)
O(11)	5 137(4)	3 215(1)	7 177(4)
O(13)	6 418(5)	3 859(1)	4 073(3)
O(21)	7 732(4)	4 907(1)	7 315(4)
O(22)	10 250(4)	3 510(1)	9 170(4)
O(23)	10 844(5)	4 597(1)	10 237(5)
O(24)	9 545(4)	4 132(1)	5 745(4)
O(31)	6 005(4)	4 764(1)	9 036(3)
O(32)	8 092(4)	3 289(1)	10 081(4)
O(33)	8 514(5)	4 176(1)	12 284(4)
C(111)	4 242(4)	4 035(1)	10 855(4)
C(112)	4 861(5)	4 327(1)	11 500(4)
C(113)	4 449(6)	4 476(1)	12 464(4)
C(114)	3 416(6)	4 329(2)	12 775(5)
C(115)	2 778(6)	4 047(1)	12 140(5)
C(116)	3 180(5)	3 894(1)	11 171(4)
C(211)	2 788(4)	4 336(1)	7 305(4)
C(212)	2 379(5)	4 418(1)	6 009(5)
C(213)	1 959(6)	4 749(2)	5 603(6)
C(214)	1 953(6)	4 999(1)	6 463(6)
C(215)	2 336(6)	4 920(1)	7 757(6)
C(216)	2 762(5)	4 592(1)	8 179(5)
C(311)	3 076(4)	3 504(1)	5 173(4)
C(312)	1 709(5)	3 539(1)	4 826(4)
C(313)	892(6)	3 402(2)	3 664(5)
C(314)	1 430(7)	3 229(2)	2 877(5)
C(315)	2 779(7)	3 187(2)	3 197(5)
C(316)	3 610(5)	3 329(1)	4 344(4)
C(411)	2 961(4)	2 911(1)	7 040(4)
C(412)	1 760(5)	2 972(1)	7 253(5)
C(413)	646(6)	2 780(2)	6 635(6)
C(414)	702(7)	2 527(2)	5 784(6)
C(415)	1 860(8)	2 463(2)	5 544(6)
C(416)	2 985(5)	2 652(1)	6 175(5)
C(511)	5 644(5)	3 092(1)	10 839(4)
C(512)	6 176(6)	3 228(2)	12 058(5)
C(513)	7 127(8)	3 050(2)	13 006(7)
C(514)	7 526(8)	2 735(3)	12 777(9)
C(515)	7 030(7)	2 596(2)	11 565(8)
C(516)	6 088(5)	2 766(1)	10 612(6)

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