Synthesis and Characterisation of Novel Phosphido- and Selenido-substituted Ruthenium Carbonyl Clusters†

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Reaction of the cyclic organophosphorus ligand $P_4Bu^t_4$ **1** with $[Ru_3(CO)_{12}]$ or $[Ru_4H_4(CO)_{12}]$ under forcing conditions yields a number of novel phosphido- and phosphinidene-substituted ruthenium carbonyl clusters. Three products have been structurally characterised in reasonable yield: $[Ru_4(CO)_8(PBu^t)_4]$ **2**, where a square-planar arrangement of four ruthenium atoms is capped above and below the metal-atom plane by two *tert*-butylphosphinidene ligands, and additionally two μ-phosphinidene ligands bridge two Ru–Ru edges; $[Ru_5(CO)_{15}(PBu^t)]$ **3** in which the five ruthenium atoms adopt a square-pyramidal geometry with the square-basal plane capped by a *tert*-butylphosphinidene ligand; and $[Ru_6H_2(CO)_{12}(PBu^t)_3]$ **4**, where the six ruthenium atoms define an octahedron with triply-bridging phosphinidene groups capping three triangular faces. Clusters **2** and **4** were isolated from the thermolysis of compound **1** with the tetraruthenium substrate $[Ru_4H_4(CO)_{12}]$; cluster **3** is a product of the thermolysis of **1** with $[Ru_3(CO)_{12}]$. In addition, the cluster $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ **5** has been isolated by the vacuum pyrolysis of $[Ru_3(CO)_{12}]$ with Ph_2Se_2 at 185 °C. Reaction of this cluster with 1,3-bis(diphenylphosphino)propane (dppp) at room temperature affords the triruthenium phosphine-substituted cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppp)]$ **6**. The structures of clusters **5** and **6** have also been established by single crystal X-ray analysis.

The chemistry of transition-metal main-group clusters has developed extensively over the last decade.[1] The introduction of a main-group element into a transition-metal carbonyl cluster often introduces novel reactivity and frequently stabilises the metal framework with respect to degradation by 'clamping' the metal atoms together. In this context, the stabilising influence of phosphido bridges is well known.[2] A recognised method of preparation of phosphido-bridged or phosphinidene-capped metal carbonyl clusters involves the direct reaction of metal carbonyls with secondary or primary phosphines. Treatment of $[Ru_3(CO)_{12}]$ with an equimolar amount of PPh_2H under mild conditions in the presence of a catalytic amount of sodium diphenylketyl has been observed to lead to the formation of the monosubstituted derivative $[Ru_3(CO)_{11}(PPh_2H)]$, which readily decarbonylates and rearranges to the bridged diphenylphosphido species $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_{10}]$ in heptane at 60 °C.[3] Similarly, reaction of $[Ru_3(CO)_{12}]$ with phenylphosphine has been found to afford trinuclear phenylphosphinidene-capped products at temperatures below 80 °C.[4–6] An increase in the temperature of these reactions results in condensation of the metal atom frameworks, and indeed tetra-, penta-, hexa-, hepta- and octa-nuclear derivatives have been isolated from the reaction of $[Ru_3(CO)_{12}]$ with PPh_2H in toluene under reflux.[7] We have found that direct reaction of the cyclic organophosphorus ligand $P_4Bu^t_4$ with $[Ru_3(CO)_{12}]$ or $[Ru_4H_4(CO)_{12}]$ affords a number of novel phosphido- and phosphinidene-bridged metal carbonyl clusters.[8] The synthesis and characterisation of these clusters is reported herein.

The stabilising influence of μ_3-S and μ_4-S ligands has also been widely exploited in cluster chemistry,[9] and within the last few years μ_3-Te and μ_4-Te ligands have been shown to stabilise triangular and square arrays of metal atoms.[10–12] By comparison, there have been relatively few studies involving the use of selenium as a capping ligand, and until recently,[13] all the structurally characterised examples were of osmium carbonyl clusters.[14] The recent upsurge in the interest of the use of organoselenium compounds in organic and organometallic chemistry[15] prompted us to investigate the reactivity of the reagent Ph_2Se_2 with ruthenium clusters and to extend some of our earlier work on osmium systems.[16] We now report the preparation and full characterisation of the tetraruthenium cluster $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ and its subsequent reaction with 1,3-bis(diphenylphosphino)propane (dppp) to yield the triruthenium phosphine-substituted cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppp)]$. A preliminary account of some of this work has been published.[17]

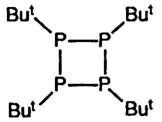

Fig. 1 The structure of the cyclic tetrameric phosphorus ligand $P_4Bu^t_4$ **1**

Results and discussion

(*a*) *Preparation and Characterisation of Compounds* **2–4**.—The reaction of $[Ru_4H_4(CO)_{12}]$ with a two-fold molar amount of $P_4Bu^t_4$ **1** (Fig. 1) in xylene at 140 °C for 12 h afforded a dark brown reaction mixture which gave three distinct bands when subjected to thin layer chromatography (TLC). The major product of this reaction is the novel heptanuclear ruthenium cluster $[Ru_7(CO)_{14}(PBu^t)_4]$.[8] In addition, a blue compound was isolated in 10% yield. Elemental analysis and mass spectroscopic studies implied the identity of this compound was $[Ru_4(CO)_8(PBu^t)_4]$ **2**.‡ The most probable structure of compound **2** is represented schematically in Fig. 2. The residue of the remaining band, present in only 2% yield, could not be

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

‡ The compound contains an approximately square-planar arrangement of ruthenium atoms capped above and below the metal-atom plane by two *tert*-butylphosphinidene ligands. In addition, two μ-phosphinidene ligands bridge the Ru(1)–Ru(4) and Ru(2)–Ru(3) edges.

Table 1 Spectroscopic data for the clusters **2**–**6**

Compound	IR ν(C=O)[a]/cm^{-1}	Mass spectrum m/z[b]	^{31}P NMR (δ)[c]	^{1}H NMR (δ)[d]
2 [$Ru_4(CO)_8(PBu^t)_4$]	2008s, 1993w, 1965m	983 (984)	144.0 (s, 2 P), 127.0 (s, 2 P)	1.35 (m, Bu^t) 1.52 (m, Bu^t)
3 [$Ru_5(CO)_{15}(PBu^t)$]	2054vs, 2030m, 1994w	1016 (1013)	285 (s, 1 P)	1.42 (m, Bu^t)
4 [$Ru_6H_2(CO)_{12}(PBu^t)_3$]	2073w, 2037m, 2021s, 1989m, 1972m	1208 (1207)	433.0 (s, 2 P) 403.0 (s, 1 P)	0.95 (d), 1.96 (d) −9.89 (q), −19.46(m)
5 [$Ru_4Se_2(CO)_{11}$]	2061s, 2029s, 1607m	871 (870)	—	—
6 [$Ru_3Se_2(CO)_7(dppp)$]	2050s, 2018s, 1980m, 1649w, 1638w	1070.4 (1069.6)	−92.13 (s, 2 P)	7.52 (m, 20 H, Ph), 2.81 (m, 6 H)

[a] Recorded in CH_2Cl_2. [b] Negative ion FAB mass spectra: most abundant isotopomer found (simulated). Calculated values in parentheses. [c] Recorded in CD_2Cl_2 at 295 K, $P(OMe)_3$ reference. [d] Recorded in CD_2Cl_2 at 295 K, $SiMe_4$ reference.

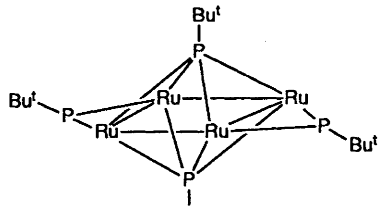

Fig. 2 Schematic representation of the molecular structure of [$Ru_4(CO)_8(PBu^t)_4$] **2**

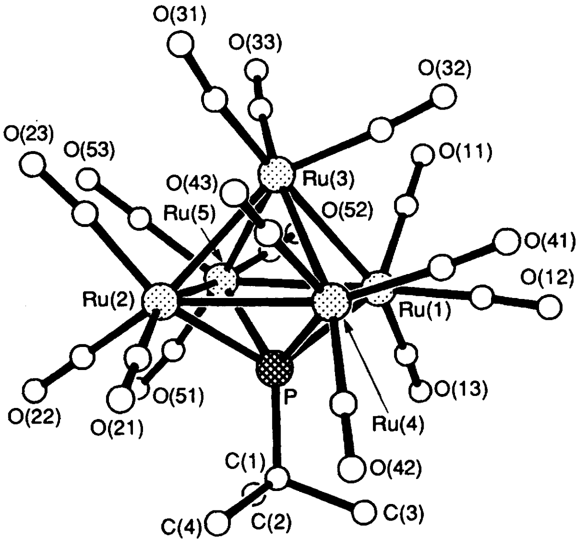

Fig. 3 The molecular structure of [$Ru_5(CO)_{15}(PBu^t)$] **3**

isolated in crystalline form and as a consequence this compound could not be fully characterised. The ^{31}P-{^{1}H} NMR spectrum (Table 1) of compound **2** contains two singlet resonances of equal intensity at δ 127 and 144 relative to trimethyl phosphite. King[18] attributes the μ$_4$-PR phosphinidene clusters chemical-shift values in the range δ 148–253; the singlet at δ 144 in the ^{31}P-{^{1}H} NMR spectrum of compound **2** is therefore attributed to the μ$_4$-P fragment. The ^{1}H NMR spectrum of **2** exhibits two multiplets at δ 1.35 and 1.52 in 1 : 1 ratio relative to tetramethylsilane; these resonances are attributed to the two types of *tert*-butyl group believed to be present in cluster **2**.

Vacuum pyrolysis of [$Ru_3(CO)_{12}$] with an equimolar (1 : 1) amount of $P_4Bu^t_4$ **1** at 180 °C for 17 h affords a black reaction mixture. On work-up by thin layer chromatography, the green pentanuclear species [$Ru_5(CO)_{15}(PBu^t)$] **3** was isolated. An X-ray crystallographic analysis has revealed that the five ruthenium atoms adopt a square-pyramidal geometry, where the square-basal plane is capped by the *tert*-butylphosphinidene ligand (Fig. 3). Compound **3** is isostructural with the set of mono(organo)phosphido-bridged pentaruthenium carbonyl clusters prepared by Huttner and co-workers[19] by reaction of [$MnCl_2(\eta$-$C_5H_5)(CO)_2(PR)$] (R = Ph, Me, CH_2Me or CH_2Ph) with [$Ru_3(CO)_{12}$]. The molecular geometry of **3** may also be described as that of a distorted octahedron with five ruthenium atoms forming a square-based pyramid and one phosphorus atom occupying the sixth octahedral site. Each ruthenium atom has three terminal carbonyl ligands with Ru–C distances 1.84(2)–1.91(2) Å and C–O distances 1.12(3)–1.20(3) Å (Table 2). The Ru–C–O angles range from 170(2) to 179(2)°. Spectroscopic data for compound **3** are fully consistent with the solid-state structure. Mass spectroscopic and analytical data confirm the composition of the cluster as [$Ru_5(CO)_{15}(PBu^t)$]. Fragmentation by successive loss of up to fifteen carbonyls was observed, with [$Ru_5(PBu^t)$]$^+$ as the base peak. The presence of multiply-bridging phosphide ligands was evident from the ^{31}P NMR spectrum, which showed one singlet at δ 285 relative to 85% $P(OMe)_3$ (Table 1). This is in agreement with the chemical shifts observed for similar [$Ru_5(CO)_{15}(PR)$] systems.[19] Low-field shifts of this magnitude are characteristic of multiply-bridging phosphide ligands.[20]

The thermolysis of [$Ru_4H_4(CO)_{12}$] with a three-fold molar amount of $P_4Bu^t_4$ at 140 °C in refluxing xylene for 22 h in an evacuated thick-walled glass Schlenk tube afforded a dark brown residue. TLC on thin silica-coated plates using dichloromethane–hexane (2 : 1) and then pure hexane as eluents afforded five compounds, only one of which was present in sufficiently high yield to allow complete characterisation.

The hexaruthenium species [$Ru_6H_2(CO)_{12}(PBu^t)_3$] **4** was isolated from the residue as a dark brown band at R_f = 0.5 in 15% yield. An X-ray crystallographic study has revealed that the six ruthenium atoms occupy octahedral sites with triply-bridging phosphinidene groups capping the triangular faces Ru(1)–Ru(2)–Ru(2b), Ru(1b)–Ru(2)–Ru(2a) and Ru(1)–Ru(2a)–Ru(2b) (Fig. 4). The molecule possesses crystallographic C_{3v} symmetry. The polyhedral electron count of 86 predicted by the standard electron counting rules for an octahedron is in agreement with the number of cluster valence electrons if all μ$_3$-phosphinidene groups are considered to be four-electron donors. The sites of the two hydrogen ligands could not be deduced directly from the single crystal X-ray study. Each ruthenium atom possesses two terminal carbonyl ligands with Ru–C distances 1.838(17)–1.946(12) Å (Table 3). The Ru–C–O bonds are essentially linear, 177.4(1)–178.9(2)°. An interesting feature of the molecule is the apparent 'openness' of the Ru(1a)–Ru(1b)–Ru(1) plane, illustrated in Fig. 5 by a space-filling model of the cluster. The ^{1}H NMR spectrum of compound **4** shows two doublets at δ 0.95 and 1.96 (J_{PH} = 19.9 Hz) respectively in the ratio 2 : 1 which are attributed to the *tert*-butyl protons. A quartet (ratio 1 : 3 : 3 : 1, J_{PH} = 15.1 Hz) and a poorly resolved multiplet are observed in the hydride region at δ −9.89 and −19.46 at 248 K; these resonances are attributed to two-bond coupling to phosphorus within the molecule. Although no abnormal lengthening of the Ru(1a)–Ru(1b), Ru(1b)–Ru(1) or Ru(1a)–Ru(1) bonds is observed, the

Table 2 Selected bond parameters with estimated standard deviations (e.s.d.s) in parentheses for compound **3**; distances in Å, angles in °

Ru(1)–Ru(3)	2.856(2)	Ru(1)–Ru(4)	2.907(3)	Ru(5)–C(51)	1.86(2)	Ru(5)–C(52)	1.87(2)
Ru(1)–Ru(5)	2.851(3)	Ru(1)–P	2.382(5)	Ru(5)–C(53)	1.84(2)	P–C(1)	1.900(2)
Ru(1)–C(11)	1.84(2)	Ru(1)–C(12)	1.88(2)	C(1)–C(2)	1.50(3)	C(1)–C(3)	1.58(3)
Ru(1)–C(13)	1.91(2)	Ru(2)–Ru(3)	2.909(3)	C(1)–C(4)	1.59(3)	C(11)–O(11)	1.20(3)
Ru(2)–Ru(4)	2.876(3)	Ru(2)–Ru(5)	2.845(3)	C(12)–O(12)	1.16(3)	C(13)–O(13)	1.13(3)
Ru(2)–P	2.380(5)	Ru(2)–C(21)	1.86(2)	C(21)–O(21)	1.18(3)	C(22)–O(22)	1.16(3)
Ru(2)–C(22)	1.87(2)	Ru(2)–C(23)	1.90(2)	C(23)–O(23)	1.15(3)	C(31)–O(31)	1.14(3)
Ru(3)–Ru(4)	2.796(3)	Ru(3)–Ru(5)	2.865(3)	C(32)–O(32)	1.15(3)	C(33)–O(33)	1.12(3)
Ru(3)–C(31)	1.88(2)	Ru(3)–C(32)	1.90(2)	C(41)–O(41)	1.13(3)	C(42)–O(42)	1.16(3)
Ru(3)–C(33)	1.90(2)	Ru(4)–P	2.421(5)	C(43)–O(43)	1.17(3)	C(51)–O(51)	1.19(3)
Ru(4)–C(41)	1.88(3)	Ru(4)–C(42)	1.88(2)	C(52)–O(52)	1.18(3)	C(53)–O(53)	1.19(3)
Ru(4)–C(43)	1.90(1)	Ru(5)–P	2.429(5)				
Ru(4)–Ru(1)–P	53.4(1)	Ru(2)–Ru(5)–P	52.9(1)	Ru(3)–Ru(1)–Ru(4)	58.0(1)	Ru(2)–Ru(4)–Ru(3)	61.7(1)
Ru(3)–Ru(2)–P	76.4(1)	Ru(1)–P–Ru(4)	74.5(1)	Ru(4)–Ru(1)–Ru(5)	89.7(1)	Ru(1)–Ru(5)–Ru(3)	59.9(1)
Ru(5)–Ru(2)–P	54.5(1)	Ru(1)–P–Ru(5)	72.7(1)	Ru(3)–Ru(2)–Ru(5)	59.7(1)	P–Ru(1)–C(12)	118.0(7)
Ru(1)–Ru(4)–P	52.1(1)	Ru(4)–P–Ru(5)	113.7(2)	Ru(4)–Ru(2)–Ru(5)	90.4(1)	Ru(2)–Ru(5)–C(51)	105.2(6)
Ru(3)–Ru(4)–P	78.1(1)			Ru(4)–Ru(3)–Ru(5)	91.7(1)		

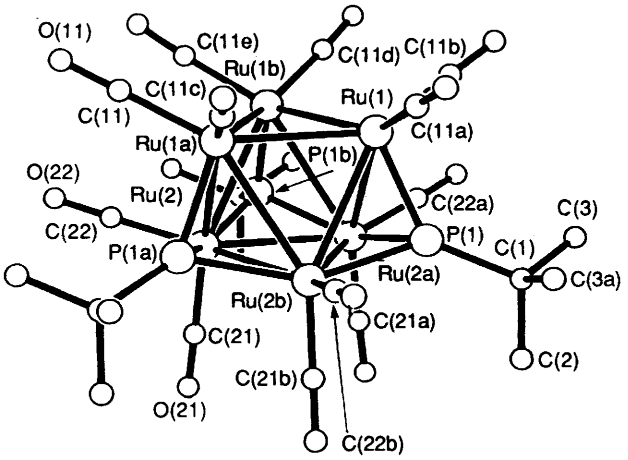

Fig. 4 The molecular structure of $[Ru_6H_2(CO)_{12}(PBu^t)_3]$ **4**; hydrogen atoms were not located

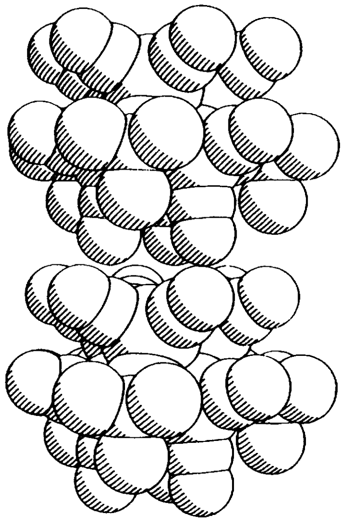

Fig. 5 Space-filling model of $[Ru_6H_2(CO)_{12}(PBu^t)_3]$ **4**

space-filling model of compound **4** (Fig. 5) suggests that one hydrogen atom occupies an edge-bridging position along one edge of the top face of the molecule. The second hydride appears to be located interstitially within the octahedral metal-core framework. The $^{31}P-\{^1H\}$ NMR spectrum of **4** exhibits two singlets in a 2 : 1 ratio at δ 433 and 403 respectively.

Table 3 Selected bond parameters with e.s.d.s in parentheses for compound **4**; distances in Å, angles in °

Ru(1)–P(1)	2.187(4)	Ru(1)–Ru(1a)	2.838(2)
Ru(1)–Ru(1b)	2.838(2)	Ru(1)–Ru(2a)	2.973(2)
Ru(1)–Ru(2b)	2.973(2)	Ru(1)–C(11a)	1.946(7)
Ru(1)–C(11b)	1.946(2)	Ru(2)–C(21)	1.838(17)
Ru(2)–C(22)	1.875(1)	Ru(2)–Ru(1a)	2.973(2)
Ru(2)–Ru(1b)	2.973(2)	Ru(2)–Ru(2a)	2.806(2)
Ru(2)–Ru(2b)	2.806(2)	Ru(2)–P(1a)	2.312(5)
Ru(2)–P(1b)	2.312(2)	P(1)–C(1)	1.826(15)
P(1)–Ru(2a)	2.312(3)	P(1)–Ru(2b)	2.312(3)
C(11)–O(11)	1.11(2)	C(11)–Ru(1a)	1.946(1)
C(21)–O(21)	1.17(2)	C(22)–O(22)	1.15(2)
C(1)–C(2)	1.52(3)	C(1)–C(3)	1.55(2)
C(1)–C(3a)	1.55(2)		
P(1)–Ru(1)–Ru(1a)	111.8(1)	Ru(1a)–Ru(1)–Ru(2b)	61.5(1)
Ru(1a)–Ru(1)–Ru(1b)	60.0(1)	Ru(1a)–Ru(1)–C(11a)	97.2(5)
Ru(1a)–Ru(1)–Ru(2a)	89.7(1)	Ru(2b)–Ru(1)–C(11b)	150.5(4)
P(1)–Ru(1)–Ru(2b)	50.5(1)	Ru(1)–P(1)–C(1)	134.5(6)
Ru(1b)–Ru(1)–C(11a)	145.2(4)	C(1)–P(1)–Ru(2a)	130.5(3)
Ru(2b)–Ru(1)–C(11a)	102.3(4)	Ru(2)–C(21)–O(21)	177.4(1)
P(1)–C(1)–C(2)	110.7(1)		

(*b*) *Preparation and Characterisation of Compounds* **5** *and* **6**.—The vacuum pyrolysis of $[Ru_3(CO)_{12}]$ with Ph_2Se_2 at 185 °C affords the cluster $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ **5** as the only isolable product (40% yield). Complex **5** has been characterised by mass and IR spectroscopy (Table 1) and the crystal and molecular structure established by X-ray crystallography. The molecular structure is shown in Fig. 6 with selected bond parameters in Table 4. The molecule lies on a crystallographic two-fold axis which passes through the carbonyl C(21)O(21) and the mid-points of the Ru(1)–Ru(1a) and Ru(2)–Ru(2a) edges. It consists of a trapizoidal array of four ruthenium atoms which is asymmetrically bridged on each side by a μ_4-Se ligand. The three shorter Ru–Ru edges are bridged by carbonyl ligands; the Ru(2)–Ru(2a) edge is symmetrically bridged [Ru(2)–C(21) 2.073(18) and Ru(2a)–C(21) 2.073(18) Å, Ru(2)–C(21)–Ru(2a) 84.2(9)°] while the carbonyl along the Ru(1)–Ru(2) edge (and its symmetry equivalent) shows considerable asymmetry [Ru(1)–C(13) 1.919(18) and Ru(2)–C(13) 2.520(18) Å, Ru(1)–C(13)–Ru(2) 76.8(6)°] and the bridge may be described as incipient. Each ruthenium atom is also bonded to two terminal carbonyl groups which lie on either side of the Ru_4 plane. Complex **5** is isomorphous and isostructural with the tellurium-capped analogues $[Ru_4(\mu_4\text{-}Te)_2(CO)_{11}]$[11] and $[Fe_2Ru_2(\mu_4\text{-}Te)_2(CO)_{11}]$,[12] and with the iron–sulfur cluster $[Fe_4(\mu_4\text{-}S)_2(CO)_{11}]$.[21] The bond parameters in **5** follow the same

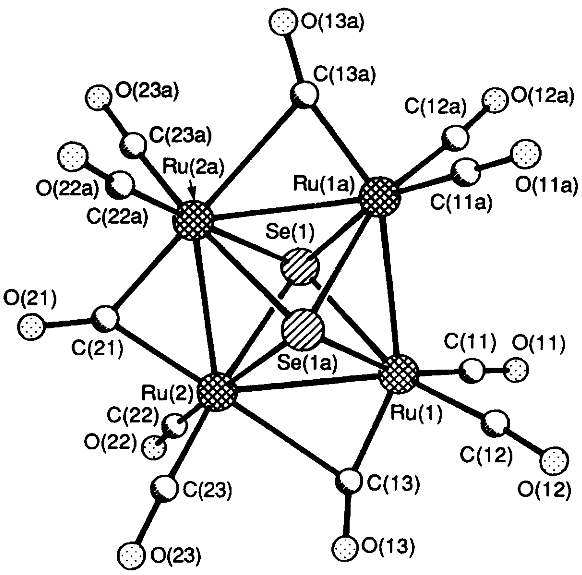

Fig. 6 The molecular structure of $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ **5**

Table 4 Selected bond parameters with e.s.d.s in parentheses for compound **5**; distances in Å, angles in °

Ru(1)–Ru(2)	2.796(2)	Ru(2)–Ru(2a)	2.778(3)
Ru(1)–Ru(1a)	2.845(3)	Se(1)–Ru(1)	2.565(2)
Se(1)–Ru(2)	2.605(2)	Se(1)–Ru(1a)	2.556(2)
Se(1)–Ru(2a)	2.610(2)		
Ru(2)–Ru(1)–Se(1)	58.0(1)	Ru(1)–Ru(2)–Se(1)	56.6(1)
Ru(2)–Ru(1)–Ru(1a)	89.3(1)	Se(1)–Ru(2)–Ru(2a)	57.9(1)
Ru(2)–Ru(1)–Se(1a)	58.2(1)	Se(1)–Ru(2)–Se(1a)	78.9(1)
Ru(1a)–Ru(1)–Se(1a)	56.4(1)	Ru(1)–Se(1)–Ru(1a)	67.5(1)
Ru(1)–Ru(2)–Ru(2a)	90.7(1)	Ru(1)–Se(1)–Ru(2a)	100.0(1)
Ru(1)–Ru(2)–Se(1a)	56.3(1)	Ru(1a)–Se(1)–Ru(2a)	65.5(1)
Ru(2a)–Ru(2)–Se(1a)	57.7(1)	Ru(1)–Se(1)–Ru(2)	65.5(1)
Se(1)–Ru(1)–Ru(1a)	56.1(1)	Ru(2)–Se(1)–Ru(1a)	100.4(1)
Se(1)–Ru(1)–Se(1a)	80.6(1)	Ru(2)–Se(1)–Ru(2a)	64.4(1)

general trends as in the isostructural complexes. The Ru–Se distances are *ca.* 0.1 Å longer than the Ru–Se distances in $[Ru_4(\mu_3\text{-}Se)(\mu\text{-}C_4H_4)(CO)_{11}]$,[13] consistent with the increase in the co-ordination number of the Se atoms in complex **5**. The carbonyl-bridged Ru–Ru edges in **5** are similar in length to the Ru–Ru carbonyl-bridged edge in $[Fe_2Ru_2(\mu_4\text{-}Te)_2(CO)_{11}]$ [2.795(3) Å],[12] and are significantly shorter than the Ru–Ru bond length of 2.854(4) Å in the parent binary carbonyl $[Ru_3(CO)_{12}]$.[22] The unbridged Ru(1)–Ru(1a) edge length is similar to that found in $[Ru_3(CO)_{12}]$,[22] whereas, in $[Ru_4(\mu_4\text{-}Te)_2(CO)_{11}]$, presumably with the influence of the larger capping Te atoms, the equivalent Ru–Ru edge that is not bridged by a carbonyl is lengthened to 2.945(1) Å.[11] Complex **5** is a 62 electron system if both μ_4-Se atoms are considered to act as four-electron donors. This count is consistent with the presence of seven bonding electron pairs required by the polyhedral skeletal electron-pair theory[23] for the *pseudo* octahedral Ru_4Se_2 core observed.

It is of interest to contrast the formation of complex **5** with that of $[Os_3(\mu\text{-}SePh)_2(CO)_{10}]$, which is obtained by the room temperature reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with Ph_2Se_2.[16,24] By using the activated cluster $[Os_3(CO)_{10}(MeCN)_2]$ the reaction can proceed under mild conditions, and apparently only the Se–Se bond of Ph_2Se_2 is cleaved in the process. Deeming and co-workers[24] have shown that three isomers of $[Os_3(\mu\text{-}SePh)_2(CO)_{10}]$ are formed, which differ in the co-ordination positions of the μ-SePh groups, although in the case of one isomer a Se–Se bond may still be present. In the reaction reported herein, in which the kinetically more labile carbonyl $[Ru_3(CO)_{12}]$ {compared to $[Os_3(CO)_{12}]$} was used under forcing pyrolysis conditions, Se–Se and Se–C bond rupture has occurred and the carbonyl cluster has fragmented, so that the isolation of the tetraruthenium cluster $[Ru_4(\mu_4\text{-}Se)_2(CO)_{11}]$ **5** from the mixture as the major component suggests that this may be the thermodynamically-favoured product. It was therefore of interest to investigate the reactivity of complex **5** to establish whether the *pseudo* octahedral core was a stable unit or whether the reaction chemistry would show a change in nuclearity of the product molecules.

Table 5 Selected bond parameters with e.s.d.s in parentheses for compound **6**; distances in Å, angles in °

Ru(1)–Ru(3)	2.836(3)	Ru(1)–Se(1)	2.499(3)
Ru(1)–Se(2)	2.516(3)	Ru(1)–P(1)	2.297(6)
Ru(2)–Ru(3)	2.815(3)	Ru(2)–Se(1)	2.507(3)
Ru(2)–Se(2)	2.520(3)	Ru(2)–P(2)	2.320(7)
Ru(3)–Se(1)	2.539(3)	Ru(3)–Se(2)	2.539(4)
Ru(3)–Ru(1)–Se(1)	56.4(1)	Ru(3)–Ru(1)–Se(2)	56.3(1)
Se(1)–Ru(1)–Se(2)	79.9(1)	Ru(3)–Ru(2)–Se(1)	56.6(1)
Ru(3)–Ru(2)–Se(2)	56.5(1)	Se(1)–Ru(2)–Se(2)	79.7(1)
Ru(1)–Ru(3)–Ru(2)	85.8(1)	Ru(1)–Ru(3)–Se(1)	55.1(1)
Ru(2)–Ru(3)–Se(1)	55.5(1)	Ru(1)–Ru(3)–Se(2)	55.5(1)
Ru(2)–Ru(3)–Se(2)	55.9(1)	Se(1)–Ru(3)–Se(2)	78.7(1)
Ru(1)–Se(1)–Ru(2)	100.4(1)	Ru(1)–Se(1)–Ru(3)	68.5(1)
Ru(2)–Se(1)–Ru(3)	67.8(1)	Ru(1)–Se(2)–Ru(2)	99.6(1)
Ru(1)–Se(2)–Ru(3)	68.3(1)	Ru(2)–Se(2)–Ru(3)	67.6(1)

The room-temperature reaction of complex **5** with the bidentate phosphine 1,3-bis(diphenylphosphino)propane (dppe) in dichloromethane solution, affords the orange triruthenium cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppp)]$ **6** in 70% yield. The only other product isolated from the reaction was $[Ru_3(CO)_{12}]$, which may be formed by the condensation of '$Ru(CO)_4$' fragments lost from complex **5** during the formation of the cluster. Complex **6** was initially characterised by mass, IR and both ^1H and ^{31}P NMR spectroscopy (Table 1). The spectroscopic data suggested the presence of only one isomer and the ^{31}P NMR data indicated that the two phosphorus nuclei are in equivalent environments. The molecular structure of complex **6** was established by X-ray crystallography and is depicted in Fig. 7. Selected bond parameters are listed in Table 5. The three ruthenium atoms define an isosceles triangle, the long edge of which is sufficiently lengthened [3.846(3) Å] to indicate no direct metal–metal interaction. The two selenium atoms μ_3-cap above and below the Ru_3 plane. The bidentate phosphine spans the long Ru(1)–Ru(2) edge, with the two phosphorus atoms occupying equatorial sites on the two metal atoms. The atoms Ru(1) and Ru(2) are also co-ordinated to two terminal carbonyl ligands, and Ru(3) is co-ordinated to three. Complex **6** is a 50 electron system, consistent with the presence of only two 'formal' Ru–Ru bonds, and the geometry of the Ru_3Se_2 core is similar to that observed in $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$[25] and its many Group 8 chalcogenide analogues and their derivatives.[9,15] The Ru–Se distances in **6** are *ca.* 0.06 Å longer than the average value of 2.45 Å for the Ru–(μ_3-Se) distance in $[Ru_4(\mu_3\text{-}Se)(\mu\text{-}C_4H_4)(CO)_{11}]$,[13] while the bonded Ru–Ru distances are similar to the values of 2.814(1) and 2.835(1) Å for two of the edges of the selenium-capped triangle in $[Ru_4(\mu_3\text{-}Se)(\mu\text{-}C_4H_4)(CO)_{11}]$.[13] The Ru–P distances in **6** (average 2.31 Å) lie in the range found for similar bonds in other ruthenium clusters with edges spanned by bidentate phosphine ligands.[26]

Experimental

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques.

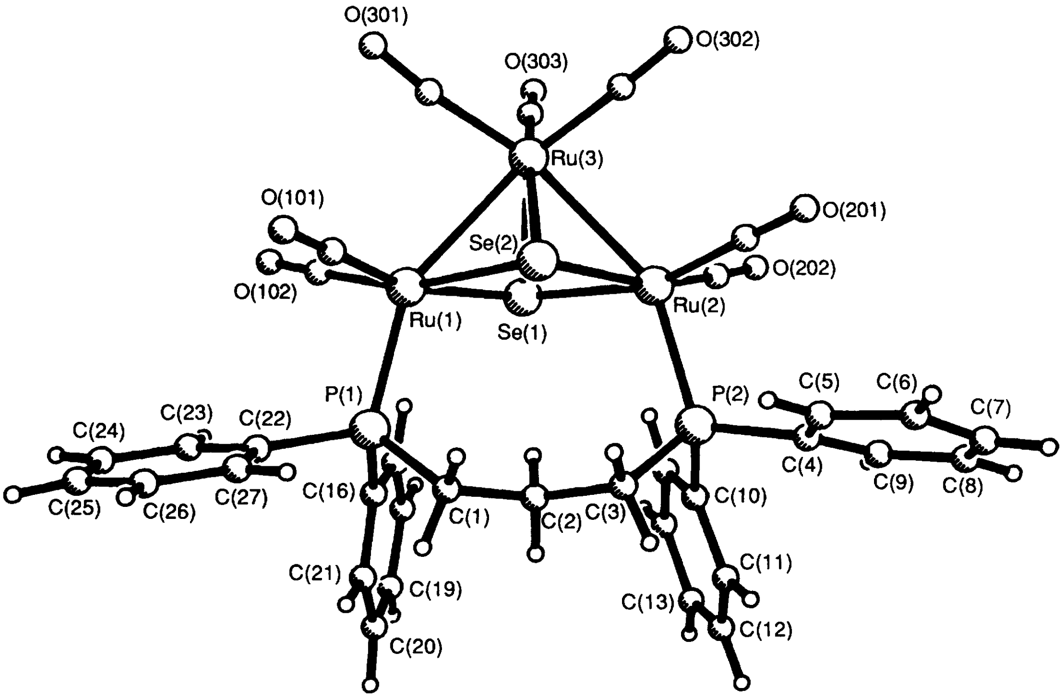

Fig. 7 The molecular structure of $[Ru_3Se_2(CO)_7(dppp)]$ **6**

Table 6 Crystal and X-ray structure analysis data for the clusters **3**–**6** *

Compound	**3**	**4**	**5**	**6**
Empirical formula	$C_{19}H_9O_{15}PRu_5$	$C_{24}H_{27}O_{12}P_3Ru_6$	$C_{11}O_{11}Ru_4Se_2$	$C_{34}H_{26}O_7P_2Ru_3Se_2$
M_r	1013.6	1206.8	870.3	1069.6
Crystal size/mm	0.05 × 0.22 × 0.34	0.14 × 0.22 × 0.45	0.30 × 0.35 × 0.32	0.20 × 0.10 × 0.32
Crystal system	Monoclinic	Trigonal	Orthorhombic	Triclinic
Space group	$P2_1/n$	$R3m$	$Pccn$	$P\bar{1}$
a/Å	9.517(3)	18.633(5)	6.624(2)	11.505(5)
b/Å	17.537(9)		16.138(3)	12.263(5)
c/Å	16.807(9)	9.169(4)	18.036(4)	14.426(9)
α/°				97.04(5)
β/°	97.00(4)			112.62(4)
γ/°				91.47(4)
U/Å^3	2784(2)	2756.9(16)	1928.1(7)	1858.7(15)
Z	4	3	4	2
D_c/Mg m^{-3}	2.418	2.181	2.998	1.911
μ(Mo-Kα)/cm^{-1}	2.776	2.540	6.901	3.292
F(000)	1912	1728	1592	1032
T/K	288	288	291	291
Scan speed/° min^{-1}	2.93–29.30	3.08–29.30	3.00–14.65	3.00–19.53
Scan range/°	$1.40 + 0.34 \tan\theta$	$1.20 + 0.34 \tan\theta$	$1.60 + 0.34 \tan\theta$	$1.40 + 0.34 \tan\theta$
Reflections measured	4209	8093	1563	5019
Unique reflections	3658	506	1272	4590
Observed reflections $[F_o > 3\sigma(F_o)]$	2608	502	962	3036
g	0.0020	0.0014	0.0030	0.0020
R	0.0613	0.0305	0.0490	0.0579
R'	0.0807	0.0502	0.0838	0.0949

* 2θ Range = 5–45°; weighting scheme $w = [\sigma^2F + gF^2]^{-1}$.

The solvents were distilled prior to use under a nitrogen atmosphere, over the appropriate drying agent. Routine separation of products was performed by thin layer chromatography, using commercially prepared glass plates, pre-coated to 0.25 mm thickness, or laboratory prepared glass plates coated to 1 mm thickness, with Merck-Kieselgel $60F_{254}$. Infrared spectra were recorded as solutions in 0.5 mm CaF_2 cells on a Perkin Elmer 983 spectrometer with carbon monoxide as calibrant. Fast atom bombardment (FAB) mass spectra were obtained on Kratos MS50 or MS890 spectrometers using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Proton NMR spectra were recorded on a Bruker WM250 spectrometer using CD_2Cl_2 as solvent and ^{31}P NMR spectra on a Bruker AM-400 spectrometer using CD_2Cl_2 as solvent and $P(OMe)_3$ as reference. Microanalyses were performed by members of the Department of Chemistry, University of Cambridge. The compounds $[Ru_3(CO)_{12}]$,[26] $[Ru_4H_4(CO)_{12}]$[27] and $P_4Bu^t{}_4$[28] were prepared by literature methods. Other chemicals were used as obtained from Aldrich.

Table 7 Atomic coordinates (× 10^4) for compound **3**

Atom	x	y	z
Ru(1)	−1 218(2)	7 512(1)	2 638(1)
Ru(2)	1 648(2)	9 225(1)	2 670(1)
Ru(3)	1 437(2)	7 821(1)	3 568(1)
Ru(4)	−702(2)	8 916(1)	3 547(1)
Ru(5)	1 218(2)	7 808(1)	1 853(1)
P	−586(5)	8 716(3)	2 131(3)
C(1)	−1 812(2)	9 233(1)	1 330(1)
C(2)	−1 684(2)	8 920(1)	514(2)
C(3)	−3 397(2)	9 165(1)	1 505(1)
C(4)	−1 430(2)	10 114(1)	1 381(1)
C(11)	−696(2)	6 533(1)	2 932(1)
O(11)	−358(2)	5 886(1)	3 098(1)
C(12)	−2 765(2)	7 474(1)	3 229(1)
O(12)	−3 781(2)	7 446(1)	3 543(1)
C(13)	−2 401(2)	7 195(1)	1 699(1)
O(13)	−3 087(2)	7 013(9)	1 135(9)
C(21)	1 256(2)	10 215(1)	2 970(1)
O(21)	1 004(2)	10 847(1)	3 145(1)
C(22)	2 247(2)	9 519(1)	1 698(1)
O(22)	2 626(2)	9 721(1)	1 103(1)
C(23)	3 540(2)	9 227(1)	3 178(1)
O(23)	4 724(2)	9 251(1)	3 413(1)
C(31)	2 945(2)	8 159(1)	4 311(1)
O(31)	3 864(2)	8 281(1)	4 797(1)
C(32)	429(2)	7 378(1)	4 365(1)
O(32)	−93(2)	7 085(9)	4 864(1)
C(33)	2 515(2)	6 933(1)	3 415(12)
O(33)	3 100(2)	6 381(1)	3 372(1)
C(41)	−1 793(2)	8 618(1)	4 357(1)
O(41)	−2 354(2)	8 463(1)	4 886(1)
C(42)	−1 839(2)	9 794(1)	3 419(1)
O(42)	−2 536(2)	10 340(9)	3 360(9)
C(43)	753(2)	9 324(1)	4 305(1)
O(43)	1 482(2)	9 632(9)	4 813(9)
C(51)	1 216(2)	8 041(1)	773(1)
O(51)	1 364(2)	8 197(1)	101(1)
C(52)	909(2)	6 786(1)	1 571(1)
O(52)	768(2)	6 142(1)	1 386(1)
C(53)	3 160(2)	7 758(1)	1 963(1)
O(53)	4 412(2)	7 717(9)	2 023(1)

Table 8 Atomic coordinates (× 10^4) for compound **4**

Atom	x	y	z
Ru(1)	3841(1)	7682(1)	0
Ru(2)	2831(1)	5663(1)	2712(1)
P(1)	4131(1)	8263(2)	2155(4)
C(11)	1658(9)	5103(8)	−989(1)
O(11)	1262(7)	4492(6)	−1506(1)
C(21)	2766(4)	5533(8)	4703(2)
O(21)	2708(5)	5416(9)	5964(1)
C(22)	2264(4)	4529(9)	2267(2)
O(22)	1919(4)	3837(8)	1971(2)
C(1)	4666(4)	9332(9)	2806(2)
C(2)	4679(6)	9359(1)	4466(2)
C(3)	5574(7)	9792(8)	2262(2)

Table 9 Atomic coordinates (× 10^4) for compound **5**

Atom	x	y	z
Ru(1)	1705(2)	1681(1)	1892(1)
Ru(2)	1710(2)	1703(1)	3442(1)
Se(1)	181(2)	2884(1)	2633(1)
C(11)	−443(3)	1670(1)	1226(1)
O(11)	−1744(2)	1650(9)	798(1)
C(12)	3277(3)	1100(1)	1180(1)
O(12)	4192(2)	703(9)	776(8)
C(13)	842(3)	707(1)	2414(1)
O(13)	278(3)	48(1)	2511(8)
C(21)	2500	2500	4295(1)
O(21)	2500	2500	4924(1)
C(22)	−692(3)	1449(1)	3920(1)
O(22)	−2262(2)	1261(1)	4188(8)
C(23)	2955(2)	835(1)	3923(1)
O(23)	3726(3)	256(9)	4215(8)

Preparations.—$[Ru_4(CO)_8(PBu^t)_4]$ **2**. A xylene solution of $[Ru_4H_4(CO)_{12}]$ (0.4040 g, 0.5420 mmol) and $P_4Bu^t_4$ (0.3924 g, 1.0860 mmol) was refluxed at 140 °C for 12 h under reduced pressure in a thick-walled glass Schlenk tube. Excess solvent was removed *in vacuo*; the residue was dissolved in dichloromethane (5 cm^3) and subjected to TLC on thin silica-coated plates using pure hexane as eluent. A blue band of $[Ru_4(CO)_8(PBu^t)_4]$ **2** (R_f = 0.4) was extracted in 10% yield. Turquoise-blue crystals of compound **2** were obtained by solvent vapour diffusion from acetonitrile to a solution of compound **2** in dichloromethane–hexane. Yield 50 mg (Found: C, 28.90; H, 3.50; P, 12.40. Calc. for $C_{24}H_{36}O_8P_4Ru_4$: C, 29.30; H, 3.65; P. 12.60%).

$[Ru_5(CO)_{15}(PBu^t)]$ **3**. A 180 cm^3 Carius tube was filled with a suspension of $[Ru_3(CO)_{12}]$ (0.8072 g, 1.251 mmol) and $P_4Bu^t_4$ (0.440 g, 1.251 mmol) in dichloromethane (20–30 cm^3). The solvent was then removed *in vacuo* at room temperature and the solid starting material evenly distributed over the interior surface of the tube. After sealing the tube under vacuum, the precursor compounds were pyrolysed at 180 °C for 17 h to yield a black residue. Separation of the reaction mixture by TLC on thin silica-coated plates using dichloromethane–hexane (1 : 1) afforded six distinct products in low yield. A dark green band (R_f = 0.74) of $[Ru_5(CO)_{15}(PBu^t)]$ **3** was noted. Green crystals of compound **3** suitable for single crystal X-ray diffraction were obtained by solvent vapour diffusion from acetonitrile to a solution of compound **3** in dichloromethane–hexane. Yield 5 mg (Found: C, 22.35; H, 0.80; P, 3.00. Calc. for $C_{19}H_9O_{15}PRu_5$: C, 22.50; H, 0.90; P, 3.05%).

$[Ru_6H_2(CO)_{12}(PBu^t)_3]$ **4**. A xylene solution of $[Ru_4H_4(CO)_{12}]$ (0.4056 g, 0.5430 mmol) and $P_4Bu^t_4$ (0.5886 g, 1.6300 mmol) was refluxed at 140 °C for 22 h under reduced pressure in a thick-walled glass Schlenk tube. Excess solvent was removed *in vacuo*; the residue was dissolved in dichloromethane and subjected to TLC on thin silica-coated plates using dichloromethane–hexane (2 : 1) and hexane as eluents. Five bands were isolated in low yield including a dark brown band of $[Ru_6H_2(CO)_{12}(PBu^t)_3]$ **4** at R_f = 0.5. Brown crystals of compound **4** suitable for X-ray analysis were obtained by solvent vapour diffusion from acetonitrile to a solution of compound **4** in dichloromethane–hexane. Yield 10 mg (Found: C, 23.90; H, 2.20; P, 7.90. Calc. for $C_{24}H_{27}O_{12}P_3Ru_6$: C, 23.85; H, 2.25; P, 7.70%).

$[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ **5**. A 180 cm^3 Carius tube was filled with a suspension of $[Ru_3(CO)_{12}]$ (0.2144 g, 0.3350 mmol) and Ph_2Se_2 (0.1212 g, 0.3880 mmol) in dichloromethane (20–30 cm^3). The solvent was then removed *in vacuo* at room temperature and the solid starting material distributed evenly over the interior surface of the tube. After sealing the tube under vacuum, the precursor compounds were pyrolysed at 185 °C for 19 h to yield red crystalline $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ **5** (90 mg, 40%) in a form suitable for X-ray diffraction studies as the only isolable product (Found: C, 15.25; O, 20.15. Calc. for $C_{11}O_{11}Ru_4Se_2$: C, 15.15; O, 20.20%).

$[Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppp)]$ **6**. To a stirring solution of $[Ru_4Se_2(CO)_{11}]$ (0.0271 g, 0.0312 mmol) in freshly distilled dichloromethane (20 cm^3) dppp (0.020 g, 0.0485 mmol) was added. The mixture was stirred for 2 h at room temperature until the reaction was complete, as judged by IR spectroscopy. The solution was concentrated *in vacuo* and then subjected to

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

Atom	x	y	z
Ru(1)	258(2)	4520(1)	2382(1)
Ru(2)	2373(2)	2157(1)	3247(1)
Ru(3)	2829(2)	4231(1)	2751(1)
Se(1)	987(2)	2850(2)	1652(2)
Se(2)	1802(2)	3933(2)	3984(1)
P(1)	−1698(5)	3879(4)	2255(4)
P(2)	1105(5)	908(4)	3601(4)
C(101)	22(5)	5840(2)	3200(2)
O(101)	187(2)	6648(1)	3732(1)
C(102)	−462(2)	5149(2)	1152(2)
O(102)	−860(2)	5526(2)	424(1)
C(201)	3745(2)	2055(2)	4464(2)
O(201)	4582(2)	1982(2)	5223(1)
C(202)	2975(2)	1129(2)	2506(2)
O(202)	3410(2)	497(2)	2069(2)
C(301)	2784(2)	5795(2)	2825(2)
O(301)	2872(2)	6731(2)	2921(2)
C(302)	4472(3)	4078(2)	3678(3)
O(302)	5487(2)	4030(2)	4275(2)
C(303)	3323(2)	4089(2)	1627(2)
O(303)	3622(2)	3976(2)	983(1)
C(1)	−1574(2)	3084(2)	3286(2)
C(2)	−1062(2)	1973(2)	3084(2)
C(3)	−83(2)	1526(2)	3995(1)
C(5)	2401(2)	726(2)	5643(2)
C(6)	3187(2)	167(3)	6438(2)
C(7)	3436(2)	−873(3)	6256(2)
C(8)	3040(2)	−1416(2)	5300(2)
C(9)	2336(2)	−898(2)	4485(2)
C(10)	107(2)	−138(2)	2570(2)
C(11)	−583(2)	−957(2)	2766(2)
C(12)	−1385(2)	−1741(2)	1945(2)
C(13)	−1480(3)	−1726(2)	1007(2)
C(14)	−785(4)	−930(2)	816(2)
C(15)	37(3)	−138(2)	1591(2)
C(16)	−2687(2)	2930(2)	1147(2)
C(17)	−2338(2)	2578(2)	348(2)
C(18)	−3042(3)	1808	−447(2)
C(19)	−4142(3)	1344(3)	−507(2)
C(20)	−4525(2)	1596(2)	296(2)
C(21)	−3781(2)	2438(2)	1101(2)
C(22)	−2753(2)	4956(2)	2262(1)
C(23)	−3470(2)	5381(2)	1389(2)
C(24)	−4244(2)	6212(2)	1408(2)
C(25)	−4361(2)	6577(2)	2284(2)
C(26)	−3660(3)	6175(2)	3162(2)
C(27)	−2870(2)	5349(2)	3159(2)

TLC on thin silica-coated plates using dichloromethane–hexane (2:3) as eluent. A bright orange band of [$Ru_3(\mu_3$-$Se)_2(CO)_7$(dppp)] **6** was extracted in 70% yield. A further yellow band of [$Ru_3(CO)_{12}$] (R_f = 0.92) was also isolated in low yield (30%). Orange crystals of compound **6** suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane–hexane solution. Yield 19 mg (Found: C, 38.25; H, 2.35; P, 5.80. Calc. for $C_{34}H_{26}O_7P_2Ru_3Se_2$: C, 38.15; H, 2.45; P, 5.80%).

Crystal Structure Analyses of Compounds **3**–**6**.—Intensity data were collected on a Nicolet R3m/V four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The unit-cell parameters were refined by a least-squares procedure. Three check reflections were monitored periodically throughout the data collection and showed no significant variation in all cases. All intensity data were corrected for Lorentz polarisation effects and absorption corrections by the ψ-scan method were applied for all compounds. Crystal data and a summary of data collection and structure parameters are given in Table 6. The structures were solved by a combination of direct methods and Fourier difference techniques and refined on F by full-matrix least-squares analysis using the SHELXTL PLUS[29] program installed on a MicroVax II computer. An attempt was made to resolve the polar direction for compound **4**, which crystallised in the space group $R3m$, but refinements with a change in handedness were inconclusive. For complex **3** the ruthenium and phosphorus atoms were refined with anisotropic thermal parameters; for the other three structures all non-hydrogen atoms were treated anisotropically. Hydrogen atoms in compounds **4** and **6** were generated in the ideal positions (C–H 0.96 Å). Final atomic coordinates for the four structures are presented in Tables 7–10.

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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