Condensation and degradation products from the thermolysis reactions of the bridged diphenylphosphido derivatives [Ru$_3$(μ_2-PPh$_2$)(μ_2-H)(CO)$_9$], [Ru$_3$(μ_2-PPh$_2$)$_2$(μ_2-H)$_2$(CO)$_8$], [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_7$] and [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_6$(PPh$_2$H)]

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(Received December 22nd, 1989)

Abstract

Thermolysis of [Ru$_3$(μ_2-PPh$_2$)(μ_2-H)(CO)$_9$], [Ru$_3$(μ_2-PPh$_2$)$_2$(μ_2-H)$_2$(CO)$_8$], [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_7$] and [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_6$(PPh$_2$H)] in xylene under reflux gives a wide range of condensation and/or degradation products, including [Ru$_2$(μ-PPh$_2$)$_2$(CO)$_6$], [Ru$_3$(μ_3-PPh)$_2$(CO)$_9$], [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_7$], [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh$_2$)(μ_2-PPh$_2$)$_2$(μ_2-H)(CO)$_6$], [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh)(μ_2-PPh$_2$)(μ_2-H)(CO)$_7$], [Ru$_4$(μ_3-PPh)(CO)$_{13}$], [Ru$_4$(μ_4-PPh)$_2$(μ_2-CO)(CO)$_{10}$], [Ru$_5$(μ_4-PPh)(CO)$_{15}$], [Ru$_5$(μ_4-PPh)(CO)$_{12}$(η^6-C$_6$H$_4$Me$_2$)], [Ru$_6$(μ_4-PPh)$_2$(μ_3-PPh)$_2$(CO)$_{12}$] and [Ru$_7$(μ_4-PPh)$_2$(CO)$_{18}$]. The structures of the unusual trinuclear species [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_7$], [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh$_2$)(μ_2-PPh$_2$)$_2$(μ_2-H)(CO)$_6$] and [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh)(μ_2-PPh$_2$)(μ_2-H)(CO)$_7$] and that of the hexanuclear derivative [Ru$_6$(μ_4-PPh)$_2$(μ_3-PPh)$_2$(CO)$_{12}$] have been established by X-ray crystallography.

Introduction

A method of synthesis of higher nuclearity metal carbonyl clusters involves the thermolysis of low nuclearity derivatives, either in vacuo or in high boiling point solvents, in which the latter undergo fragmentation and decarbonylation to afford unsaturated intermediates, which in turn condense to give the higher nuclearity products. This is well illustrated by the case of trinuclear carbonyl derivatives of the iron triad. Thus pyrolysis of [Os$_3$(CO)$_{12}$] in vacuo at 210–260°C gives a number of higher nuclearity species, including [Os$_5$(CO)$_{16}$], [Os$_6$(CO)$_{18}$], [Os$_7$(CO)$_{21}$], [Os$_8$(CO)$_{23}$], [Os$_5$(C)(CO)$_{15}$], [Os$_8$(C)(CO)$_{21}$] and [Os$_{10}$(C)(CO)$_{24}$]$^{2-}$ [1,2], while thermolysis of the isocyanide derivatives [Os$_3$(CO)$_{12-x}$(CNBu^t)$_x$] (x = 1 or 2) in

octane under reflux gives the series of hexanuclear complexes $[Os_6(CO)_{18-x}$-$(CNBu^t)_x]$ $(x = 1-5)$ [3]. The thermolysis of low nuclearity clusters containing tertiary or ditertiary phosphines can also result in carbon–hydrogen and/or phosphorus–carbon bond cleavage, so that for these compounds a wide range of products is possible in any one reaction. In the case of $[Os_3(CO)_{11}(PPh_2R)]$ (R = Me, Et or Ph) only a single product, viz. the trinuclear benzyne derivative $[Os_3(\mu_3\text{-PR})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9]$, was found to be formed in n-nonane under reflux [4], and similarly, essentially two trinuclear derivatives, $[Ru_3(\mu_3\text{-PPh})(\mu_3\text{-}\eta^2\text{-}CHPPh_2)(CO)_7(\mu\text{-Ph}_2PCH_2PPh_2)]$ and the intermediate in its formation, $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^4\text{-PhPCHPPh}(C_6H_4)\}(CO)_7(\mu\text{-Ph}_2PCH_2PPh_2)]$, were shown to be produced in the controlled thermolysis of $[Ru_3(CO)_8(\mu\text{-Ph}_2PCH_2PPh_2)_2]$ [5]. On the other hand, reaction of $[Ru_3(CO)_{11}(PPh_3)]$ in toluene under reflux has been shown to give condensed as well as trinuclear rearrangement products viz. $[Ru_3(\mu_2\text{-PPh}_2)_2(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_7]$, $[Ru_4(\mu_4\text{-PPh})(\mu_4\text{-}\eta^4\text{-}C_6H_4)(CO)_{11}]$ and $[Ru_5(\mu_4\text{-PPh})(\mu_5\text{-}\eta^6\text{-}C_6H_4)(CO)_{13}]$ [6], while a range of pentanuclear products including $[Os_5\{\mu_4\text{-P(OMe)}\}(CO)_{15}]$ have been isolated from the pyrolysis of $[Os_3(CO)_{11}\{P(OMe)_3\}]$ in vacuo at $210\,^\circ$C, some of these products resulting from carbon–oxygen and/or phosphorus–oxygen bond cleavage [7].

Phosphorus–hydrogen bond cleavage in coordinated secondary or primary phosphines or in coordinated phosphine itself occurs under milder conditions than those used for the bond cleavages described above, and the controlled thermolysis of metal cluster compounds containing these ligands leads to the formation of products containing bridging phosphido ligands, capping phosphinidene groups or encapsulated phosphorus, respectively. Thus ultraviolet irradiation or gentle heating of solutions of $[Ru_3(CO)_{11}(PPh_2H)]$, $[Ru_3(CO)_{10}(PPh_2H)_2]$ or $[Ru_3(CO)_9(PPh_2H)_3]$ gives $[Ru_3(\mu_2\text{-PPh}_2)(\mu_2\text{-}H)(CO)_{10}]$, $[Ru_3(\mu_2\text{-PPh}_2)_2(\mu_2\text{-}H)_2(CO)_8]$ and $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu_2\text{-}H)(CO)_7]$, respectively [8–10], reaction of $[M_3(CO)_{12}]$ (M = Ru or Os) with an equimolar amount of PRH_2 (R = Ph, p-MeOC$_6$H$_4$, p-BrC$_6$H$_4$ or C$_6$H$_{11}$) under mild conditions gives $[M_3(\mu_3\text{-PR})(\mu_2\text{-}H)_2(CO)_9]$ via $[M_3(CO)_{11}(PRH_2)]$ and $[M_3(\mu_2\text{-PRH})(\mu_2\text{-}H)(CO)_{10}]$ as intermediates [11–13], while thermolysis of $[Os_3(\mu_2\text{-}PH_2)(\mu_2\text{-}H)(CO)_{10}]$ in xylene under reflux in the presence of $[Os_3(CO)_{11}(MeCN)]$ gives $[Os_6(\mu_6\text{-P})(\mu\text{-}H)(CO)_{18}]$ [14].

Metal cluster compounds containing coordinated diphenylphosphido or phenylphosphinidene ligands as well as bridging hydride groups readily participate in a further type of reaction involving the loss of benzene and the formation of products containing capping phenylphosphinidene ligands and/or an encapsulated phosphorus [15]. An example of this reaction type is provided by the thermolysis of $[Ru_3(\mu_2\text{-PPh}_2)(\mu_2\text{-}H)(CO)_9]$ (or $[Ru_3(\mu_2\text{-PPh}_2)(\mu_2\text{-}H)(CO)_{10}]$) in heptane at $80\,^\circ$C for 4 h, which affords $[Ru_4(\mu_3\text{-PPh})(CO)_{13}]$ in good yield [16].

As part of a programme aimed at exploring the potential of the diphenylphosphido and phenylphosphinidene ligands, PPh$_2$ and PPh, for stabilizing homo- and hetero-nuclear metal cluster compounds of unusual geometry and stereochemistry, we have carried out a detailed examination of the thermolysis of the diphenylphosphido derivatives $[Ru_3(\mu_2\text{-PPh}_2)(\mu_2\text{-}H)(CO)_9]$, $[Ru_3(\mu_2\text{-PPh}_2)_2(\mu_2\text{-}H)_2(CO)_8]$, $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu_2\text{-}H)(CO)_7]$ and $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$ with the object of developing high yield syntheses of higher nuclearity clusters of ruthenium containing bridging diphenylphosphido and/or capping phenylphosphinidene groups. The results are reported here.

Results and discussion

Thermolysis of [Ru$_3$(μ_2-PPh$_2$)(μ_2-H)(CO)$_9$]

During the various stages of our thermolysis studies, Carty et al. reported the thermolysis of [Ru$_3$(μ_2-PPh$_2$)(μ_2-H)(CO)$_{10}$] (1), and described the products isolated from reactions carried out in both heptane at 80–90°C and in toluene at 120°C in a number of communications [8,16–19]. These products include: (i) [Ru$_3$(μ_2-PPh$_2$)(μ_2-H)(CO)$_9$] (2), in which a P–C(Ph) linkage interacts weakly with an electron deficient ruthenium atom [8,16]; (ii) [Ru$_4$(μ_3-PPh)(CO)$_{13}$] (3), in which a phenylphosphinidene group caps an open face of a butterfly metal atom framework [16]; (iii) [Ru$_5$(μ_4-PPh)(CO)$_{15}$] (4), in which the five ruthenium atoms adopt a square pyramidal geometry with the basal plane being capped by the phenylphosphinidene ligand [20]; (iv) [Ru$_5$(μ_4-PPh)(μ_2-PPh$_2$)(μ-H)(CO)$_{13}$] (5), containing both a capping phenylphosphinidene and a bridging diphenylphosphido ligand and with a structure based on that of [Ru$_5$(μ_4-PPh)(CO)$_{15}$]; (v) [Ru$_5$(μ_5-P)(μ_2-PPh$_2$)(CO)$_{16}$] (6), in which the five ruthenium atoms are situated at the vertices of an open polyhedron, being joined by only five ruthenium–ruthenium bonds and as such partially encapsulate a phosphorus atom [17]; (vi) [Ru$_7$(μ_4-PPh)$_2$(CO)$_{18}$] (7), in which the seven ruthenium atoms define a condensed polyhedron consisting of two square pyramidal Ru$_5$ units sharing a triangular face and with each basal plane being capped by a phenylphosphinidene group [18]; and (vii) [Ru$_8$(μ_6-P)(μ_4-PPh)(μ_2-PPh$_2$)(CO)$_{21}$] (8), in which the metal atom framework can be described in terms of a condensed polyhedron comprising a square pyramidal Ru$_5$ group sharing a common face with an open network of six ruthenium atoms which partially encapsulates a phosphorus atom and in which the basal plane of the square pyramid is capped by a phenylphosphinidene ligand and an edge of the hexaruthenium network is bridged by a diphenylphosphido group [19].

(1)　　　(2)

(3)　　　(4)

(5)

(6)

(7)

(8)
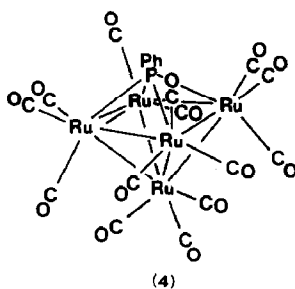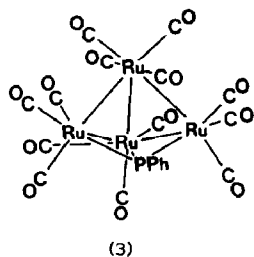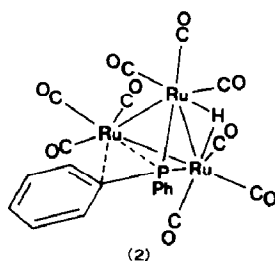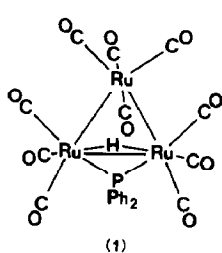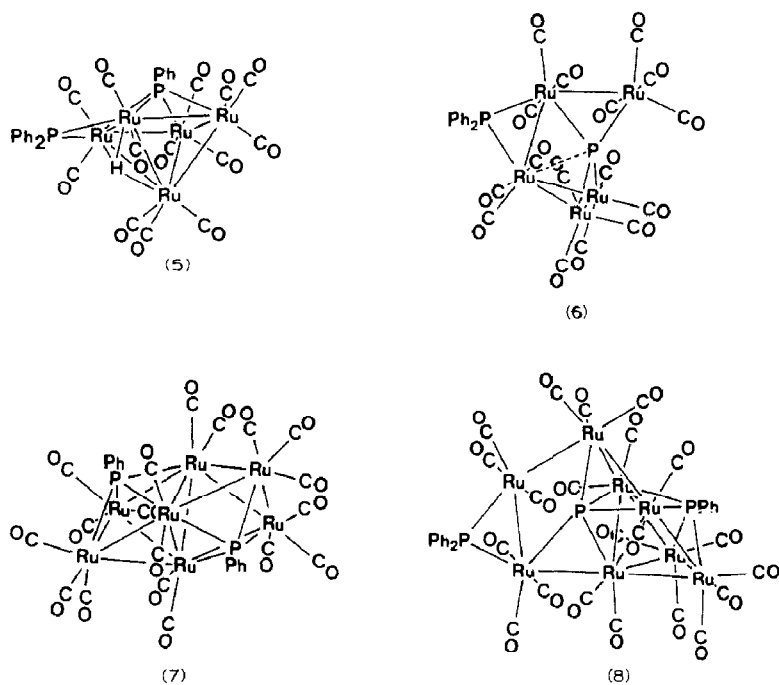
The thermolysis of $[Ru_3(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_9]$ [8] in a solvent with a slightly higher boiling point than that of toluene, viz. xylene, was investigated and it was found that essentially the same compounds (though not all of them) as reported by Carty et al. are formed in this solvent after 30 min under reflux. It was found in particular that eight distinct bands (in order of elution: red-brown, green, orange, yellow, purple/green, green, green and brown) could be separated by thin layer chromatography of the reaction mixture, and the products $[Ru_4(\mu_3\text{-}PPh)(CO)_{13}]$ (3) (band 1), $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$ (4) (band 2), $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ (9) (band 4) and $[Ru_7(\mu_4\text{-}PPh)_2(CO)_{18}]$ (7) (band 6) were isolated and characterised; selected infrared and NMR spectroscopic data for all compounds isolated and characterised are listed in Table 1.

(9)

(10)
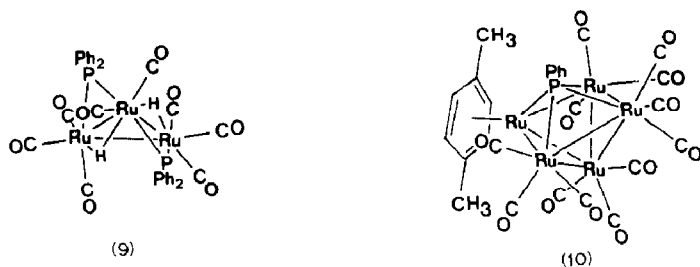
The seventh band afforded a green crystalline product that exhibited a single resonance at 441.4 ppm (relative to H_3PO_4) in its $^{31}P\{^1H\}$ NMR spectrum and whose elemental analysis was consistent with the formulation $[Ru_5(\mu_4\text{-}PPh)(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)]$ (10). Attempts to obtain crystals of this compound suitable for an X-ray diffraction study proved unsuccessful and so the compound could not be fully characterised. However, confirmation of the identity of this compound was obtained by means of a crystal structure determination on a product

isolated from the reaction of $[Ru_3(CO)_{12}]$ with $PPhH_2$ in toluene under reflux. This compound, which has an identical infrared spectrum in the C–O stretching region to that of **10**, as well as also containing a single resonance at 441.6 ppm (relative to H_3PO_4) in its $^{31}P\{^1H\}$ NMR spectrum, was characterised as $[Ru_5(\mu_4\text{-}PPh)(CO)_{12}\text{-}(\eta^6\text{-}C_6H_5Me)]$ [21]. The structure of this compound is based on that of its parent, $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$ (**4**), with the three carbonyl groups of an equatorial ruthenium having been replaced by a π-bonded toluene ligand; it is assumed that compound **10** has a related structure.

The products from the three remaining bands (**3**, **5** and **8**) could not be isolated pure or were formed in very low yield and were not investigated further. Significantly, a reduction in the reaction time was found to lead to an increase in the yield of $[Ru_4(\mu_3\text{-}PPh)(CO)_{13}]$ (**3**) relative to those of the other products.

Thermolysis of $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$

Essentially only three products were found to be formed when a solution of $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ (**9**) [9] in xylene was heated under reflux for 4 h. These were characterised as $[Ru_3(\mu_3\text{-}PPh)_2(CO)_9]$ (**11**), $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ (**12**) and $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$ (**13**), respectively. All three have been reported previously as products of the reaction of $[Ru_3(CO)_{12}]$ with $PPhH_2$ [22]. In compound **11** the three ruthenium atoms adopt an open triangular geometry, while in compound **12** the metal atom framework is approximately square planar. In both cases the ruthenium atoms are capped above and below the metal-atom plane by two phenylphosphinidene ligands.

(11)

(12)

(13)
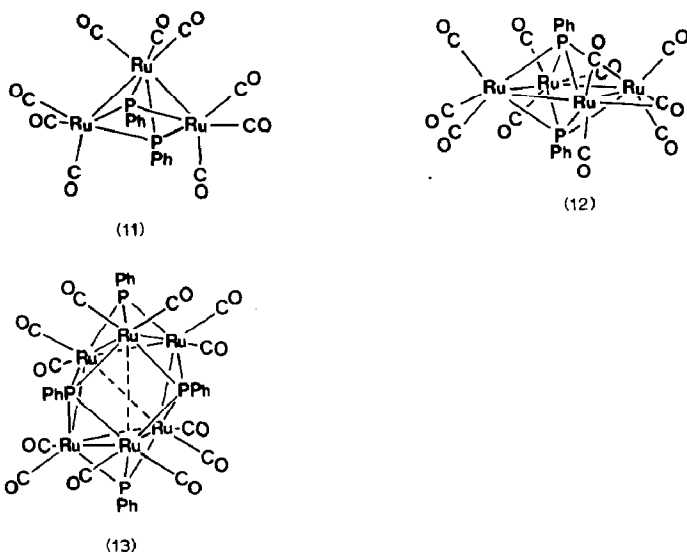
Although the $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$ (**13**) isolated from this reaction exhibited infrared and $^{31}P\{^1H\}$ NMR spectra identical with those of the corresponding product isolated from the reaction of $[Ru_3(CO)_{12}]$ with $PPhH_2$, its single crystals were found to belong to a different space group. As a consequence its structure was determined by X-ray crystallography. The molecular stereochemistry of this complex is illustrated in Fig. 1. As found previously for the $P\bar{1}$ crystal form [22], the geometry of the metal atom framework is a distorted trigonal prism with both triangular and two of the three tetragonal faces being capped by a phenylphos-

Table 1

Infrared and nuclear magnetic resonance spectroscopic data

Compound	ν(CO)(cm^{-1}) [a]	^{31}P{^{1}H} [c,d]	^{1}H [c,g]
[Ru$_2$(μ-PPh$_2$)$_2$(CO)$_6$] (16)	2065m, 2035vs, 2005s, 1980s 1970sh [b]	110.9(s) [e]	—
[Ru$_3$(μ_2-PPh$_2$)(μ_2-H)(CO)$_9$] (2)	2080m, 2055vs, 2030vs, 2010s, 1990m, 1985m [b]	134.5(s) [f]	−16.13(d, Ru–H–Ru, J(PH) 24.4) [f]
[Ru$_3$(μ_3-PPh)$_2$(CO)$_9$] (11)	2090w, 2060s, 2033s, 2012s, 2000s, 1980m [b]	208.4(s) [f]	—
[Ru$_3$(μ_2-PPh$_2$)$_2$(μ_2-H)$_2$(CO)$_8$] (9)	2075m, 2040vs, 2020vs, 2007s, 1987m, 1970m [b]	163.0(s) [f]	−16.48(t, Ru–H–Ru, J(PH) 22.8) [f]
[Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_7$] (14)	2053ms, 2015s, 1982m, 1952ms [b]	$\nu_{\rm A}$, 177.7 (A$_2$B system, $\nu_{\rm B}$, 159.6 J(AB) 120.53) [e]	−17.13(d of t, Ru–H–Ru, J(P'H) 19.7, J(P''H) 15.2) [e]
[Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_7$] (15)	2040m, 2010m, 2000s, 1977m, 1962m, 1927w [b]	$\nu_{\rm A}$, 236.4 (ABX system. $\nu_{\rm B}$, 236.2 J(AB) 90, $\nu_{\rm X}$, 124.0 J(AX) 88.5, $J_{\rm BX}$ 88.67) [f]	—
[Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh)(μ_2-PPh$_2$)(μ_2-H)(CO)$_7$] (19)	2055m, 2015vs, 1990m, 1960m [b]	$\nu_{\rm A}$, 217.0 (AB$_2$ system, $\nu_{\rm B}$, 173.5 J(AB) 119.8) [f]	−17.97(d of t, Ru–H–Ru, J(P'H) 22.0, J(P''H) 15.2)

Compound	IR	^{31}P	Hydride
[Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh$_2$)(μ_2-PPh$_2$)$_2$(μ_2-H)(CO)$_6$] (17)	2055w, 2020m, 2005vs, 1993vs, 1962s, 1950s ^{b}	223.7(o, J(PP') 149.4, J(PP'') 74.6, J(PP''') 5.7) ^{f} 178.1(o, J(PP') 149.4, J(P'P'') 102.3, J(P'P''') 17.6, 139.7(o, J(P''P''') 119.6, J(P'P'') 102.3, J(PP'') 74.6, 65.7(o, J(P''P''') 119.6, J(P'P'') 17.6, J(PP''') 5.7)	−18.15(m, Ru—H—Ru)
[Ru$_4$(μ_3-PPh)(CO)$_{13}$] (3)	2093w, 2053vs, 2045vs, 2038s, 2010m, 2003m, 1985m, 1965sh,w ^{b}	407.1(s) ^{f}	—
[Ru$_4$(μ_4-PPh)$_2$(μ_2-CO)(CO)$_{10}$] (12)	2070m, 2030vs, 2012s, 1983m, 1965sh, 1833 ^{b}	167.8(s) ^{e}	—
[Ru$_5$(μ_4-PPh)(CO)$_{15}$] (4)	2095w, 2050s, 2027s, 1985m ^{b}	434.2(s) ^{e}	—
[Ru$_5$(μ_4-PPh)(CO)$_{12}$(η^6-C$_6$H$_4$Me$_2$)] (10)	2065m, 2025vs, 2020s,sh 2005s, 1990w, 1965w ^{b}	441.4(s) ^{f}	—
[Ru$_6$(μ_4-PPh)$_2$(μ_3-PPh$_2$)$_2$(CO)$_{12}$] (13)	2030vs, 2020m, 2002s, 1996w, 1986w, 1963w ^{b}	573.8(t, μ_4-P, J(PP') 46.2) ^{e} 412.4(t, μ_4-P, J(PP') 46.2)	—
[Ru$_7$(μ_4-PPh)$_2$(CO)$_{18}$] (7)	2090w, 2060vs, 2050s, 2018m, 2005m, 1993w, 1980w, 1945w ^{b}	457.0(s) ^{e}	—

^{a} Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. ^{b} Measured in cyclohexane. ^{c} Abbreviations: s, singlet; d, doublet; t, triplet; o, octet; m, multiplet. ^{d} δ scale in ppm relative to H$_3$PO$_4$; coupling constants in Hz; measured at 32°C. ^{e} Measured in CD$_2$Cl$_2$. ^{f} Measured in CDCl$_3$. ^{g} δ scale in ppm relative to SiMe$_4$; coupling constants in Hz; measured at 32°C.
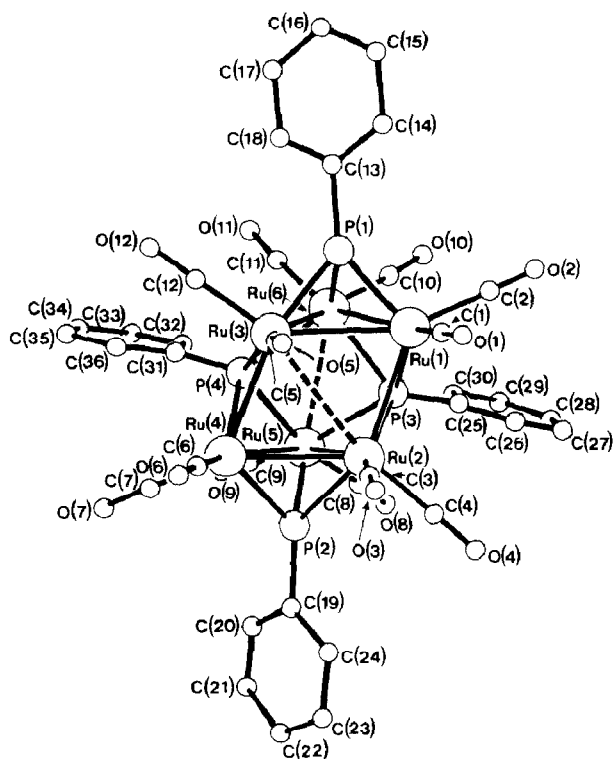
Fig. 1. The molecular stereochemistry of [Ru$_6$(μ_4-PPh)$_2$(μ_3-PPh)$_2$(CO)$_{12}$] (13).

phinidene ligand. It was reported that the distortion could be described in the first instance in terms of a torsional twist of one of the basal planes about the approximate three-fold axis, in this case of a twist of the Ru(1)Ru(3)Ru(6) plane through an angle of 11.6°. The metal atom framework is formally subjected to a further distortion, which results in one interbasal ruthenium–ruthenium distance being significantly greater than the other two (Ru(5)–Ru(6) 3.220(2), Ru(1)–Ru(2) 2.853(1), Ru(3)–Ru(4) 2.794(1) Å) and the two triangular faces not being parallel to each other (dihedral angle 12.6°). An alternative description of the structure of this compound is in terms of either a distorted square antiprismatic or, more appropriately, a dodecadeltahedral Ru$_6$P$_2$ skeletal framework with two diagonally opposite triangular faces being capped by phenylphosphinidene ligands. The major distortion with respect to a square antiprismatic skeletal framework involves an elongation along the Ru(1)–Ru(4) diagonal (Ru(1)–Ru(4) 4.663(2) Å) and a compression along the Ru(2)–Ru(3) diagonal (Ru(2)–Ru(3) 3.211(2) Å). The skeletal framework is subjected to a further perturbation involving a folding of the Ru(1)Ru(2)Ru(4)Ru(3) basal plane about the Ru(1)–Ru(4) and Ru(2)–Ru(3) diagonals through angles of 17.0 and 11.7°, respectively, and by a folding of the Ru(5)P(3)Ru(6)P(4) basal plane about the Ru(5)–Ru(6) and P(3)–P(4) diagonals through angles of 41.3 and 43.1°, respectively. The skeletal framework is also distorted from that for a dodecadeltahedral structure, as reflected by the elongation of the Ru(2)–Ru(3) and Ru(5)–Ru(6) distances (3.211(2) and 3.220(2) Å, respectively) and by the unequal dihedral angles between the Ru(1)Ru(2)Ru(3) and

Table 2

Selected interatomic distances (Å) and angles (°) for [Ru$_6$(μ_4-PPh)$_2$(μ_3-PPh)$_2$(CO)$_{12}$] with estimated standard deviations in parentheses

Ru(1)–Ru(2)	2.854(1)	Ru(1)–Ru(3)	2.836(1)
Ru(1)–Ru(6)	2.863(0)	Ru(2)...Ru(3)	3.211(2)
Ru(2)–Ru(4)	2.879(1)	Ru(2)–Ru(5)	2.852(1)
Ru(3)–Ru(4)	2.794(1)	Ru(3)–Ru(6)	2.868(1)
Ru(4)–Ru(5)	2.866(1)	Ru(5)...Ru(6)	3.220(2)
Ru(1)–P(1)	2.209(2)	Ru(1)–P(3)	2.336(1)
Ru(2)–P(2)	2.290(1)	Ru(2)–P(3)	2.321(1)
Ru(3)–P(1)	2.295(1)	Ru(3)–P(4)	2.349(1)
Ru(4)–P(2)	2.204(2)	Ru(4)–P(4)	2.314(1)
Ru(5)–P(2)	2.298(1)	Ru(5)–P(3)	2.460(1)
Ru(5)–P(4)	2.375(2)	Ru(6)–P(1)	2.276(1)
Ru(6)–P(3)	2.388(1)	Ru(6)–P(4)	2.447(1)
Ru(1)–Ru(2)–Ru(5)	99.2(0)	Ru(1)–Ru(2)–Ru(4)	108.8(0)
Ru(1)–Ru(3)–Ru(6)	60.2(0)	Ru(1)–Ru(6)–Ru(3)	59.3(0)
Ru(2)–Ru(1)–Ru(3)	68.7(0)	Ru(2)–Ru(1)–Ru(6)	87.1(0)
Ru(3)–Ru(1)–Ru(6)	60.4(0)	Ru(4)–Ru(2)–Ru(5)	60.0(0)
Ru(1)–Ru(3)–Ru(4)	111.8(0)	Ru(4)–Ru(3)–Ru(6)	99.4(0)
Ru(2)–Ru(4)–Ru(3)	68.9(0)	Ru(2)–Ru(4)–Ru(5)	59.5(0)
Ru(3)–Ru(4)–Ru(5)	87.7(0)	Ru(2)–Ru(5)–Ru(4)	60.5(0)

Ru(4)Ru(2)Ru(3) and the P(3)Ru(5)Ru(6) and P(4)Ru(5)Ru(6) planes (168.3 and 138.7°, respectively). The number of skeletal electron pairs associated with both a square antiprismatic and a dodecadeltahedral skeletal framework is either nine or eleven [23], but a simple electron count for this compound gives eight skeletal pairs. This deficiency would account for some of the distortion observed for the framework. Selected interatomic distances and angles are presented in Table 2.

It was assumed that the trinuclear species [Ru$_3$(μ_3-PPh)$_2$(CO)$_9$] (11) is an intermediate in the formation of the tetra- and hexa-nuclear products, [Ru$_4$(μ_4-PPh)$_2$(μ_2-CO)(CO)$_{10}$] (12) and [Ru$_6$(μ_4-PPh)$_2$(μ_3-PPh)$_2$(CO)$_{12}$] (13), in the thermolysis of [Ru$_3$(μ_2-PPh$_2$)$_2$(μ_2-H)$_2$(CO)$_8$] (9), and that its relative yield could be increased by reducing the reaction time. However only the two condensation products were observed after 20 min and [Ru$_3$(μ_3-PPh)$_2$(CO)$_9$] (11) was detected in the reaction mixture only after a thermolysis time of 90 min. Furthermore, treatment of [Ru$_3$(μ_2-PPh$_2$)$_2$(μ_2-H)$_2$(CO)$_8$] (9) with CO, even in xylene under reflux for 20 min, did not lead to preferential formation of compound 11. It is thus apparent that the pyrolysis of 9 is complex, and that the formation of [Ru$_3$(μ_3-PPh)$_2$(CO)$_9$] (11) does not involve simple loss of benzene from the octacarbonyl derivative together with the uptake of carbon monoxide but rather some fragmentation and subsequent condensation process.

Thermolysis of [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_7$]

The number of products formed on heating a xylene solution of [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_7$] (14) (a product of the reaction of [Ru$_3$(CO)$_{12}$] with PPh$_2$H [10,24] under reflux) was found, not surprisingly, to be very dependent on the reaction time. In particular a single product (purple) was found to be present in good yield (ca. 50%) after 20 min, whereas three products (white, purple, and
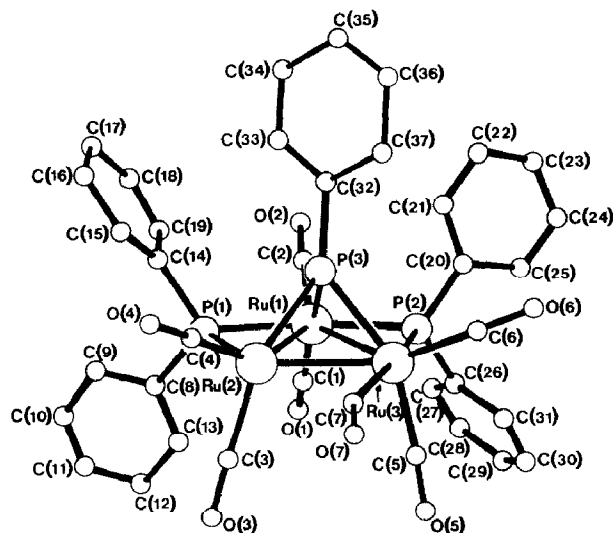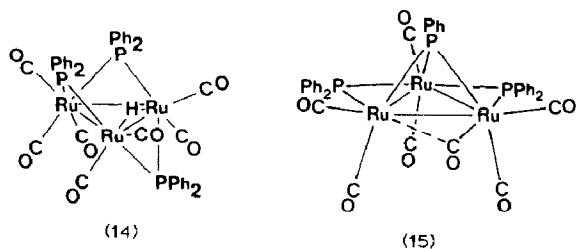
Fig. 2. The molecular stereochemistry of $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7]$ (15).

maroon) were isolated after 45 min. Thin layer chromatography of the reaction mixture after 7 h gave 13 distinct bands, but only two products (orange and maroon) were isolated in sufficient yield for characterization purposes.

(14)

(15)

The purple product isolated from the 20 and 45 min reactions was characterised as $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7]$ (15), resulting from the loss of a benzene molecule from $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu_2\text{-H})(CO)_7]$ in the thermolysis. As shown by X-ray crystallography, the three ruthenium atoms in this compound adopt a triangular configuration, with two of the ruthenium–ruthenium distances essentially equal (Ru(1)–Ru(2) 2.903(1), Ru(1)–Ru(3) 2.890(1) Å) and the third appreciably shorter (Ru(2)–Ru(3) 2.742(1) Å). The ruthenium atoms are capped symmetrically by a phenylphosphinidene ligand (average Ru–P distance 2.332(2) Å) and bridged on two of their edges by two diphenylphosphido groups, as illustrated in Fig. 2; while one of these edges is symmetrically bridged (Ru(1)–P(2) 2.344(2), Ru(3)–P(2) 2.344(2) Å) the other is slightly asymmetrically bridged (Ru(1)–P(1) 2.377(2), Ru(2)–P(1) 2.286(2) Å). From electron-counting considerations it would have been predicted that one of the seven carbonyl groups would have coordinated as a bridging carbonyl, bridging the third ruthenium–ruthenium edge. However, all seven carbonyl ligands are essentially terminal carbonyls, although one of the three coordinated to the Ru(3) atom leans towards the Ru(2) atom and could be classified as semi-bridging on the grounds that the ratio of the Ru(2)–C(7) distance (2.374(8) Å) to the Ru(3)–C(7) distance (2.039(9) Å) viz 1.16, is considerably less than the

ratio 1.6 assumed for practical purposes to represent the boundary between terminal and semi-bridging carbonyl groups [25]. Selected interatomic distances and angles are given in Table 3.

The solution and solid state infrared spectra of this compound were found to exhibit similar peak patterns in the C–O stretching region, except that the peak at 1896 cm^{-1} in the solid state spectrum appears at 1930 cm^{-1} in the solution spectrum. This is interpreted in terms of the retention of the solid state structure in solution except that the semi-bridging carbonyl group reverts to a terminal carbonyl.

The ^{31}P{^{1}H} NMR spectrum of [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_7$] exhibits an ABX pattern of peaks, as expected, but significantly the chemical shift for the phenylphosphinidene phosphorus (124.0 ppm) is considerably upfield of those for the two diphenylphosphido phosphorus atoms (236.2 and 236.4 ppm, measured in CDCl$_3$, relative to H$_3$PO$_4$) contrary to expectation [26].

The white compound isolated from the 45 min thermolysis was characterised as the dinuclear species [Ru$_2$(μ-PPh$_2$)$_2$(CO)$_6$] (16). This compound, which has been reported previously as a minor product of the pyrolysis of [Ru$_3$(CO)$_9$(PPh$_3$)$_3$] [27], as a product of the thermolysis of [Ru$_3$(CO)$_{10}$(PPh$_2$H)$_2$] in toluene at 70°C [9], and as a product of the photolysis of [Ru$_3$(CO)$_9$(PPh$_2$H)$_3$] in benzene [10], has previously been investigated crystallographically [24] and the Ru$_2$P$_2$ framework shown to adopt a butterfly structure, as illustrated.

(16)

(17)

(18)

(19)
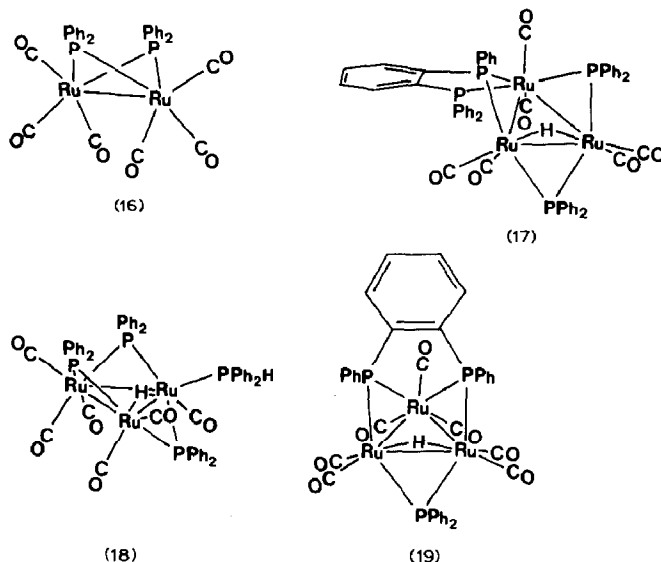
The maroon compound isolated from the 45 min and 7 h reactions was characterised as [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh$_2$)(μ_2-PPh$_2$)$_2$(μ_2-H)(CO)$_6$] (17). It is also a product of the thermolysis of [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_6$(PPh$_2$H)] (18), and is described below.

The orange product of the 17 h reaction was characterised by X-ray crystallography as [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh)(μ_2-PPh$_2$)(μ_2-H)(CO)$_7$] (19). It was obtained in higher yield by thermolysis of its isomer [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_7$] (15) in xylene under reflux, and has a structure related to that of [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_7$] (14) [24]. As illustrated (Fig. 3), the compound contains a triangular array of ruthenium atoms with the one edge slightly shorter than the other two (Ru(2)–Ru(3) 2.782(1), Ru(1)–Ru(2) 2.947(1) and Ru(1)–Ru(3) 2.993(1) Å). The

Table 3

Selected interatomic distances (Å) and angles (°) for [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_7$]·CHCl$_3$ with estimated standard deviations in parentheses

Ru(1)–Ru(2)	2.903(1)	Ru(1)–Ru(3)	2.890(1)
Ru(2)–Ru(3)	2.742(1)	Ru(1)–P(1)	2.377(2)
Ru(1)–P(2)	2.344(2)	Ru(1)–P(3)	2.343(2)
Ru(2)–P(1)	2.286(2)	Ru(2)–P(3)	2.319(2)
Ru(3)–P(2)	2.344(2)	Ru(3)–P(3)	2.333(2)
Ru(2)–C(7)	2.374(8)	Ru(3)–C(7)	2.039(9)
C(7)–O(7)	1.148(12)		
Ru(1)–Ru(2)–Ru(3)	61.5(0)	Ru(1)–Ru(3)–Ru(2)	62.0(0)
Ru(2)–Ru(1)–Ru(3)	56.5(0)	Ru(2)–Ru(3)–C(7)	57.5(2)
Ru(3)–Ru(2)–C(7)	46.3(2)	Ru(1)–P(1)–Ru(2)	77.0(1)
Ru(1)–P(2)–Ru(3)	76.1(1)	Ru(1)–P(3)–Ru(2)	77.0(1)
Ru(1)–P(3)–Ru(3)	76.4(1)	Ru(2)–P(3)–Ru(3)	72.2(1)
Ru(2)–C(7)–O(7)	129.9(5)	Ru(3)–C(7)–O(7)	153.8(5)

PhPC$_6$H$_4$PPh ligand spans the two longer edges, with each phosphorus of this ligand bridging one of these edges; the third ruthenium–ruthenium edge is bridged by a diphenylphosphido group, the latter being on the opposite side of the triruthenium plane to that of the PhPC$_6$H$_4$PPh ligand. The hydride ligand could not be located, but it presumably bridges the same ruthenium–ruthenium edge as the diphenylphosphido group. The unique ruthenium atom bears three terminal carbonyls, while the other two bear two terminal carbonyls each. A salient feature of the structure of this compound compared with that of [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_7$] (14), and arising from the small bite of the PhPC$_6$H$_4$PPh ligand, is the much shorter distance between the phosphorus atoms of this ligand (P(1)...P(2) 3.086 Å) than that between the corresponding phosphorus atoms in compound 14 (P(1)...P(2) 3.691 Å). Selected interatomic distances and angles are given in Table 4.

The ^{1}H NMR spectrum of this compound exhibits a doublet of triplets at −17.97 ppm, consistent with the retention of the solid state structure in solution and with the hydride ligand bridging the two equivalent ruthenium atoms, while the ^{31}P{^{1}H}

Table 4

Selected interatomic distances (Å) and angles (°) for [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh)(μ_2-PPh$_2$)(μ_2-H)(CO)$_7$] with estimated standard deviations in parentheses

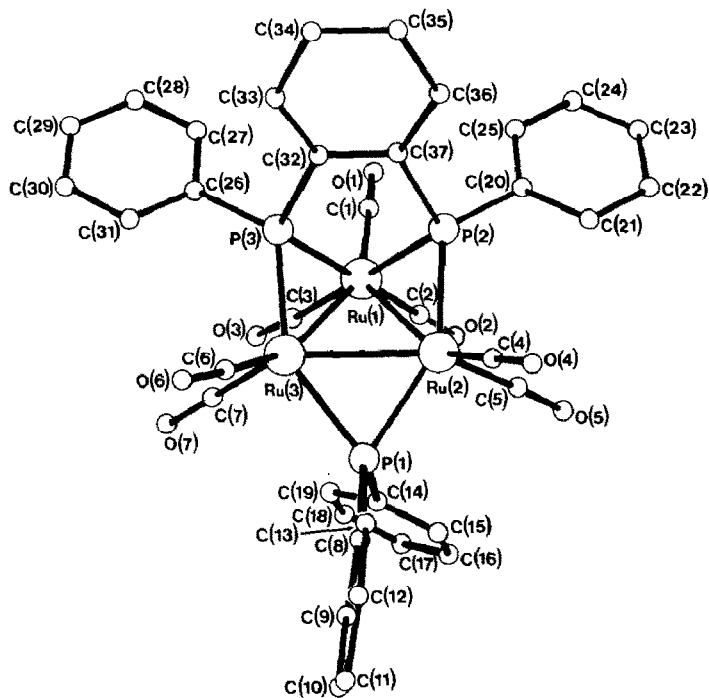| Ru(1)–Ru(2)	2.947(1)	Ru(1)–Ru(3)	2.993(1)
Ru(2)–Ru(3)	2.782(1)	Ru(1)–P(2)	2.362(2)
Ru(1)–P(3)	2.378(2)	Ru(2)–P(1)	2.338(2)
Ru(2)–P(2)	2.316(2)	Ru(3)–P(1)	2.347(2)
Ru(3)–P(3)	2.318(2)	P(2)–C(37)	1.825(8)
P(3)–C(32)	1.823(8)		
Ru(1)–Ru(2)–Ru(3)	62.9(0)	Ru(1)–Ru(3)–Ru(2)	61.2(0)
Ru(2)–Ru(1)–Ru(3)	55.8(0)	Ru(1)–P(2)–Ru(2)	78.1(1)
Ru(1)–P(3)–Ru(3)	79.2(1)	Ru(2)–P(1)–Ru(3)	72.9(1)
Ru(1)–P(2)–C(37)	108.9(3)	Ru(2)–P(2)–C(37)	118.5(3)
Ru(1)–P(3)–C(32)	108.5(2)	Ru(3)–P(3)–C(32)	117.1(2)

Fig. 3. The molecular stereochemistry of $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhPC_6H_4PPh)(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_7]$ (19).

NMR spectrum exhibits a typical eight-line AB_2 pattern of resonances, again consistent with the solid state structure.

Compound **19** is presumably derived from $[Ru_3(\mu_3\text{-}PPh)(\mu_2\text{-}PPh_2)_2(CO)_7]$ (**15**) by metal-assisted cleavage of an *ortho* carbon–hydrogen bond of one of the diphenylphosphido groups followed by coupling of the C_6H_4PPh to the coordinated phenylphosphinidene through the formation of a carbon–phosphorus bond. The compound represents a rare example of a compound containing a linked bis(μ-phosphido) ligand, and in particular of one in which a ligand of this type caps three metal atoms. In fact the first example of this type of ligand with this mode of coordination was communicated only recently [28].

Thermolysis of $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$

The thermolysis of $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$ (**18**) in xylene under reflux for 30 min was found to afford primarily two products, $[Ru_3(\mu_3\text{-}PPh)(\mu_2\text{-}PPh_2)_2(CO)_7]$ (**15**) and the maroon species described above. Thin layer chromatography of the reaction mixture also gave a brown band, but this was found to contain a mixture of products which could not be effectively separated.

Many more products were formed when the thermolysis of compound **18** was carried out under the above reaction conditions for 7 h, and 9 distinct bands were separated by thin layer chromatography treatment. Most of the compounds were produced in low yield, however. The major species was the maroon product, while $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhPC_6H_4PPh)(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_7]$ (**19**) and $[Ru_3(\mu_3\text{-}PPh)(\mu_2\text{-}PPh_2)_2(CO)_7]$ (**15**) were formed in sufficient yield for characterization purposes. Other products identified were $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ (**12**) and $[Ru_7(\mu_4\text{-}PPh)_2(CO)_{18}]$ (**7**).
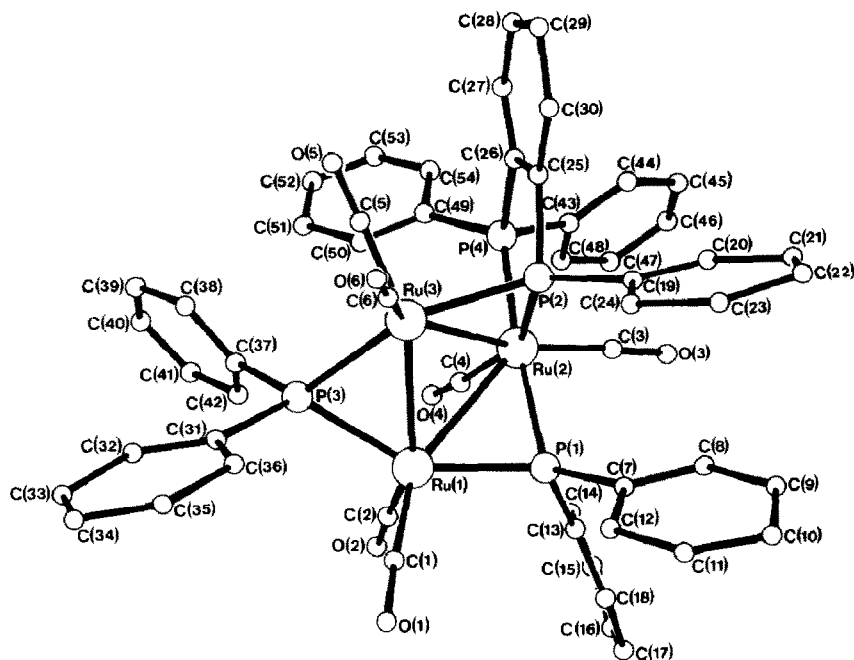
Fig. 4. The molecular stereochemistry of $[Ru_3(\mu_3\text{-}\eta^2\text{-PhPC}_6H_4PPh_2)(\mu_2\text{-PPh}_2)_2(\mu_2\text{-H})(CO)_6]$ (17).

The maroon compound was characterised by conventional methods and by X-ray crystallography as $[Ru_3(\mu_3\text{-}\eta^2\text{-PhPC}_6H_4PPh_2)(\mu_2\text{-PPh}_2)_2(\mu_2\text{-H})(CO)_6]$ (17). The molecular stereochemistry of this species is illustrated in Fig. 4, and selected interatomic distances and angles are given in Table 5. This compound also contains a triangular array of ruthenium atoms, with one ruthenium–ruthenium distance appreciably shorter than the other two (Ru(1)–Ru(3) 2.779(1), Ru(1)–Ru(2) 3.097(1), Ru(2)–Ru(3) 3.091 Å). The three ruthenium–ruthenium edges are bridged in turn by the secondary phosphorus of a novel phosphido-phosphine ligand $PhPC_6H_4PPh_2$ and by two diphenylphosphido groups, with the latter is an *anti* disposition with

Table 5

Selected interatomic distances (Å) and angles (°) for $[Ru_3(\mu_3\text{-}\eta^2\text{-PhPC}_6H_4PPh_2)(\mu_2\text{-PPh}_2)_2(\mu_2\text{-}$ H)(CO)$_6$]·2CHCl$_3$ with estimated standard deviations in parentheses

Ru(1)–Ru(2)	3.097(1)	Ru(1)–Ru(3)	2.779(1)
Ru(2)–Ru(3)	3.091(1)	Ru(1)–P(1)	2.307(3)
Ru(1)–P(3)	2.340(3)	Ru(2)–P(1)	2.377(3)
Ru(2)–P(2)	2.334(3)	Ru(2)–P(4)	2.349(3)
Ru(3)–P(2)	2.323(3)	Ru(3)–P(3)	2.349(3)
P(2)–C(25)	1.833(11)	P(4)–C(26)	1.819(13)
Ru(1)–Ru(2)–Ru(3)	53.4(0)	Ru(1)–Ru(3)–Ru(2)	63.4(0)
Ru(2)–Ru(1)–Ru(3)	63.2(0)	Ru(1)–P(1)–Ru(2)	82.8(1)
Ru(2)–P(2)–Ru(3)	83.2(1)	Ru(1)–P(3)–Ru(3)	72.7(1)
Ru(1)–Ru(2)–P(4)	136.2(1)	Ru(3)–Ru(2)–P(4)	94.6(1)
Ru(2)–P(2)–C(25)	110.2(4)	Ru(3)–P(2)–C(25)	109.7(3)
Ru(2)–P(4)–C(26)	111.5(4)		

respect to the triruthenium plane. The tertiary phosphorus of the $PhPC_6H_4PPh_2$ ligand is coordinated to one of the two ruthenium atoms bridged by the secondary phosphorus of this ligand, and in particular to that opposite the short Ru–Ru edge viz. Ru(2). Again the hydride ligand could not be located, but it presumably bridges the edge analogous to the hydride-bridged ones in $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (14) and $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhPC_6H_4PPh)(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_7]$ (19), i.e. the short Ru(1)–Ru(3) edge. The structure is completed by two terminal carbonyl groups per ruthenium atom.

The band pattern of the C–O stretching peaks in the solution infrared spectrum of this compound is very similar to that in the corresponding solid state spectrum, while the compound's $^{31}P\{^1H\}$ NMR spectrum exhibits four sets of octets of a pattern consistent with the spectrum being of first order and resulting from an AMXZ system. This evidence, together with the presence of a multiplet at -18.15 ppm in the ^1H NMR spectrum, is interpreted in terms of the retention of the solid state structure in solution.

Compounds containing the o-phenylene linked phosphido-phosphine ligand $PhPC_6H_4PPh_2$ do not appear to have been reported previously although several derivatives containing the related ligand $PhPCH_2PPh_2$ are known. Thus thermolysis of $[Ru_3(CO)_{10}(\mu\text{-}Ph_2PCH_2PPh_2)]$ and $[Ru_3(CO)_8(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ in the presence of hydrogen has been found to produce $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhPCH_2PPh_2)(\mu_2\text{-}H)(CO)_9]$ and $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhPCH_2PPh_2)_2(\mu_2\text{-}H)_2(CO)_6]$, respectively [29–31], and similarly the direct thermolysis of $[Ru_4(\mu_2\text{-}H)_4(CO)_{10}(\mu\text{-}Ph_2PCH_2PPh_2)]$ in toluene at 90°C has been shown to afford $[Ru_4(\mu_3\text{-}\eta^2\text{-}PhPCH_2PPh_2)(\mu_2\text{-}H)_3(CO)_{10}]$ [6]. The $PhPCH_2PPh_2$ group in these compounds functions as a capping ligand, however, in contrast to the $PhPC_6H_4PPh_2$ ligand in compound 17, which bridges one of the edges of the triruthenium triangle.

It is assumed that the formation of $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhPC_6H_4PPh_2)(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)(CO)_6]$ (17) proceeds through a pathway analogous to that for $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhPC_6H_4PPh)(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_7]$ (19), involving a metal-assisted cleavage of an ortho carbon–hydrogen bond of one of the diphenylphosphido groups followed by coupling of the C_6H_4PPh to an adjacent coordinated diphenylphosphido ligand through the formation of a carbon-phosphorus bond.

Experimental

All reactions and manipulations were carried out under nitrogen by Schlenk tube techniques. Solvents were purified and dried by standard procedures. $[Ru_3(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_9]$, $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$, $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ and $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$ were synthesised by published methods [8,9,24]. Chromatographic separations were carried out on preparative thin layer plates (Kieselgel 60 PF_{254}) with chloroform/light petroleum mixtures as eluents. Infrared spectra were recorded on Perkin Elmer 457 and 283 grating spectrometers, and ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian FT80A instrument. Light petroleum with a b.pt. range 60–80°C was used throughout.

Thermolysis of $[Ru_3(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_9]$

A solution of $[Ru_3(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_9]$ (0.52 g, 0.7 mmol) in xylene (ca. 100 cm^3) was refluxed for 20 or 30 min. The solvent was removed under reduced

Table 6

Fractional atomic coordinates $(\times 10^4)$ for $[Ru_6(\mu_4\text{-PPh})_2(\mu_3\text{-PPh})_2(CO)_{12}]$ with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Ru(1)	1297(1)	7042(1)	4208(1)	C(8)	2531(3)	6536(6)	6857(3)
Ru(2)	2029(1)	5024(1)	5106(1)	C(9)	3761(3)	7051(6)	6852(3)
Ru(3)	2667(1)	6846(1)	4239(1)	C(10)	1673(3)	33(6)	5135(3)
Ru(4)	3462(1)	5216(1)	5281(1)	C(11)	2897(3)	300(6)	5065(3)
Ru(5)	2923(1)	6606(1)	6161(1)	C(12)	3267(3)	7515(6)	3826(3)
Ru(6)	2315(1)	8821(1)	5024(1)	C(13)	1757(3)	−204(5)	3264(3)
P(1)	1890(1)	8525(1)	3885(1)	C(14)	1134(3)	−55(7)	2759(3)
P(2)	2993(1)	4401(1)	5981(1)	C(15)	1047(4)	953(8)	2274(4)
P(3)	1754(1)	7093(1)	5387(1)	C(16)	1585(4)	1796(7)	2332(4)
P(4)	3348(1)	7461(1)	5341(1)	C(17)	2219(3)	1641(6)	2843(3)
O(1)	625(2)	5109(5)	3082(2)	C(18)	2305(3)	627(6)	3313(3)
O(2)	−43(2)	8396(6)	4015(3)	C(19)	3215(3)	3105(5)	6590(3)
O(3)	1686(3)	2937(5)	4015(2)	C(20)	3815(4)	3198(7)	7166(4)
O(4)	1112(2)	3619(5)	5719(2)	C(21)	4017(4)	2166(8)	7619(4)
O(5)	2207(3)	4862(5)	3104(2)	C(22)	3610(3)	1029(7)	7509(4)
O(6)	3467(3)	3339(5)	4164(3)	C(23)	3018(3)	968(7)	6963(3)
O(7)	4972(2)	4824(7)	6067(4)	C(24)	2810(3)	2017(6)	6504(3)
O(8)	2340(3)	6540(7)	7292(3)	C(25)	1146(3)	7441(5)	5805(3)
O(9)	4252(3)	7292(6)	7287(2)	C(26)	528(3)	6731(6)	5620(3)
O(10)	1290(3)	786(5)	5171(3)	C(27)	56(4)	6968(7)	5948(4)
O(11)	3200(3)	1214(4)	5071(3)	C(28)	202(4)	7946(8)	6429(4)
O(12)	3601(3)	7826(6)	3535(3)	C(29)	795(4)	8664(8)	6614(4)
C(1)	872(3)	5820(5)	3512(3)	C(30)	1277(3)	8428(6)	6290(3)
C(2)	455(3)	7880(6)	4083(3)	C(31)	4157(3)	8362(6)	5594(3)
C(3)	1826(3)	3748(6)	4412(3)	C(32)	4288(3)	9322(7)	6089(3)
C(4)	1454(3)	4173(5)	5490(3)	C(33)	4968(5)	9959(9)	6301(5)
C(5)	2382(3)	5579(6)	3549(3)	C(34)	5408(5)	9582(10)	5983(5)
C(6)	3473(3)	4063(6)	4585(3)	C(35)	5288(5)	8689(9)	5516(5)
C(7)	4401(3)	4970(7)	5761(3)	C(36)	4636(4)	8009(8)	5286(4)

pressure and the residue was dissolved in a minimum of chloroform and transferred to thin layer plates. Eight distinct bands were obtained on elution with chloroform/ light petroleum (1/5). The products isolated from these bands, in order of their elution, were as follows:

Band 1; red-brown; $[Ru_4(\mu_3\text{-PPh})(CO)_{13}]$ (3). This compound was crystallised from light petroleum and identified by spectroscopic means; yield: 20 min reaction time, ca. 20%; 30 min reaction time, ca. 12%.

Band 2; green; $[Ru_5(\mu_4\text{-PPh})(CO)_{15}]$ (4). This compound was crystallised by vapour diffusion from dichloromethane/light petroleum; yield: ca. 15%. (Found: C, 24.5; H, 0.5. $C_{21}H_5O_{15}PRu_5$ calcd.: C, 24.4; H, 0.5%).

Band 3; orange. This product was isolated in very low yield and was not investigated further.

Band 4; yellow; $[Ru_3(\mu_2\text{-PPh}_2)_2(\mu_2\text{-H})_2(CO)_8]$ (9). This compound was crystallised by vapour diffusion from chloroform/light petroleum; yield: ca. 3%. (Found: C, 42.3; H, 2.2. $C_{32}H_{22}O_8P_2Ru_3$ calcd.: C, 42.7; H, 2.4%).

Band 5; purple/green and Band 8; brown. It was apparent that these bands

contained at least two products each, and because of their low yields they were not investigated further.

Band 6; green; [Ru$_7$(μ_4-PPh)$_2$(CO)$_{18}$] (7). This compound was crystallised by vapour diffusion from dichloromethane/light petroleum; yield: ca. 8%. (Found C, 25.6; H, 1.0. C$_{30}$H$_{10}$O$_{18}$P$_2$Ru$_7$ calcd.: C, 25.2; H, 0.7%).

Band 7; green; [Ru$_5$(μ_4-PPh)(CO)$_{12}$(η^6-C$_6$H$_4$Me$_2$)] (10). This compound was crystallised from chloroform/light petroleum; yield: ca. 3%. (Found C, 29.8; H, 1.7. C$_{26}$H$_{15}$O$_{12}$PRu$_5$ calcd.: C, 29.6; H, 1.4%).

Thermolysis of [Ru$_3$(μ_2-PPh$_2$)$_2$(μ_2-H)$_2$(CO)$_8$]

A solution of [Ru$_3$(μ_2-PPh$_2$)$_2$(μ_2-H)$_2$(CO)$_8$] (0.54 g, 0.6 mmol) in xylene (ca. 100 cm^3) was refluxed for periods of 20 min to 4 h. The solvent was removed under reduced pressure and the residue dissolved in a minimum of chloroform and transferred to thin layer plates. A maximum of three bands was obtained on elution with chloroform/light petroleum (1/5). The products isolated from these bands, in order of their elution, were as follows:

Band 1; yellow; [Ru$_3$(μ_3-PPh)$_2$(CO)$_9$] (11). This compound was crystallised from light petroleum at 0°C; yield: 20 min reaction time, not detected; 2 h reaction time, ca. 20%; 4 h reaction time, ca. 10%. (Found: C, 32.7; H, 1.4. C$_{33}$H$_{20}$O$_9$P$_2$Ru$_3$ calcd.: C, 32.7; H, 1.3%). Mass spectrum: m/e, 773; other peaks, m/e $- x$(CO) ($x = 1-9$).

Band 2; purple; [Ru$_4$(μ_4-PPh)$_2$(μ_2-CO)(CO)$_{10}$] (12). This compound was crystallised by vapour diffusion from chloroform/light petroleum; yield: 20 min reaction time, ca. 5%; 2 h reaction time, ca. 10%; 4 h reaction time, ca. 10%. (Found: C, 29.6; H, 1.3. C$_{23}$H$_{10}$O$_{11}$P$_2$Ru$_4$ calcd.: C, 29.7; H, 1.1%).

Band 3; brown; [Ru$_6$(μ_4-PPh)$_2$(μ_3-PPh)$_2$(CO)$_{12}$] (13). This compound was crystallised from chloroform/light petroleum; yield: 20 min reaction time, ca. 5%; 2 h reaction time, ca. 15%; 4 h. reaction time, ca. 22%. (Found: C, 31.2; H, 1.9. C$_{36}$H$_2$O$_{12}$P$_4$Ru$_6$ calcd.: C, 31.4; H, 1.4%).

Thermolysis of [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_7$]

A solution of [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_7$] (0.53 g, 0.5 mmol) in xylene (ca. 100 cm^3) was refluxed for 25–45 min. The solvent was removed under reduced pressure and the residue dissolved in a minimum of chloroform and transferred to thin layer plates. A maximum of four bands was obtained on elution with chloroform/light petroleum (1/5). The products isolated from these bands, in order of their elution, were as follows:

Band 1; white; [Ru$_2$(μ-PPh$_2$)$_2$(CO)$_6$] (16). This compound was crystallised from chloroform/light petroleum; yield: 25 min reaction time, not detected; 45 min reaction time, ca. 12%.

Band 2; purple; [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_7$] (15). This compound was crystallised by vapour diffusion from dichloromethane/light petroleum; yield: 25 min reaction time, ca. 50%; 45 min reaction time, ca. 25%. (Found: C, 45.1; H, 3.1. C$_{37}$H$_{25}$O$_7$P$_3$Ru$_3$ calcd.: C, 45.4; H, 2.6%). Mass spectrum: m/e 977.

Band 3; orange; [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_7$].

Band 4; maroon; [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh$_2$)(μ_2-PPh$_2$)$_2$(μ_2-H)(CO)$_6$] (17). This compound was crystallised by vapour diffusion from chloroform/light petroleum; yield: 25 min reaction time, not detected; 45 min reaction time, ca. 18%. (Found: C, 53.6; H, 3.3. C$_{54}$H$_{40}$O$_6$P$_4$Ru$_3$ calcd.: C, 53.5; H, 3.3%).

Table 7

Fractional atomic coordinates ($\times 10^4$) for $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7]\cdot CHCl_3$ with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Ru(1)	3732(1)	4958(1)	6667(1)	C(22)	2444(10)	8652(9)	8133(7)
Ru(2)	2739(1)	2808(1)	7179(1)	C(23)	3249(10)	9790(8)	8621(7)
Ru(3)	4026(1)	5078(1)	8423(1)	C(24)	4497(14)	10023(11)	8895(15)
P(1)	2579(2)	2843(2)	5821(1)	C(25)	4968(10)	9095(9)	8707(11)
P(2)	4756(2)	6708(2)	7896(1)	C(26)	6502(6)	7579(6)	8175(4)
P(3)	2121(2)	4451(2)	7408(1)	C(27)	7109(7)	7868(7)	7542(5)
C(1)	5245(6)	5096(6)	6239(4)	C(28)	8455(8)	8512(9)	7753(6)
C(2)	3064(7)	5649(7)	5974(4)	C(29)	9158(8)	8856(8)	8567(7)
C(3)	3879(9)	1971(8)	7151(5)	C(30)	8566(8)	8546(8)	9205(6)
C(4)	1284(8)	1459(7)	7100(5)	C(31)	7194(7)	7905(6)	9003(4)
C(5)	5740(7)	5143(7)	8763(5)	C(32)	646(6)	4678(6)	7410(4)
C(6)	3854(8)	6066(7)	9443(5)	C(33)	−247(7)	4304(8)	6657(5)
C(7)	3392(7)	3481(7)	8687(5)	C(34)	−1353(9)	4550(10)	6662(6)
C(8)	3321(7)	2005(6)	5127(4)	C(35)	−1577(10)	5137(10)	7433(7)
C(9)	2591(10)	1114(8)	4337(5)	C(36)	−676(11)	5510(12)	8171(7)
C(10)	3237(14)	460(10)	3858(6)	C(37)	448(8)	5276(10)	8184(5)
C(11)	4451(14)	654(11)	4106(8)	C(38)	1295(22)	8298(20)	11054(11)
C(12)	5191(11)	1555(10)	4877(8)	O(1)	6104(5)	5223(5)	5946(4)
C(13)	4607(9)	2249(8)	5412(6)	O(2)	2611(7)	6089(6)	5571(4)
C(14)	992(7)	2400(6)	5132(4)	O(3)	4531(8)	1449(8)	7153(5)
C(15)	−99(7)	1554(7)	5205(5)	O(4)	432(7)	631(6)	7101(5)
C(16)	−1294(8)	1218(8)	4684(6)	O(5)	6730(5)	5130(6)	8947(4)
C(17)	−1415(8)	1794(8)	4102(6)	O(6)	3742(7)	6688(6)	10044(4)
C(18)	−265(8)	2687(8)	4014(6)	O(7)	3296(6)	2916(5)	9135(3)
C(19)	915(8)	2966(7)	4533(5)	Cl(1)	1743(3)	8288(3)	10183(3)
C(20)	4185(7)	7943(6)	8189(4)	Cl(2)	2235(6)	7750(6)	11722(3)
C(21)	2913(9)	7704(8)	7898(7)	Cl(3)	−358(5)	7082(8)	10786(4)

The thermolysis was also effected for 7 h. 13 distinct bands (in order of elution: orange, purple, brown, orange, green, purple, green, maroon, green/brown, blue/green, brown, green and brown) were obtained on elution of the product mixture as described above but only two afforded products in sufficient yield for characterisation purposes. The products isolated from these bands were as follows: Band 1; orange; $[Ru_3(\mu_3\text{-}\eta^2\text{-PhPC}_6H_4PPh)(\mu_2\text{-PPh}_2)(\mu_2\text{-H})(CO)_7]$ (19). This compound was crystallised by liquid diffusion from chloroform/light petroleum; yield: ca. 12%. (Found: C, 45.7; H, 2.6. $C_{37}H_{25}O_7P_3Ru_3$ calcd.: C, 45.4; H, 2.6%). Mass spectrum: m/e 977.

Band 8; maroon; $[Ru_3(\mu_3\text{-}\eta^2\text{-PhPC}_6H_4PPh_2)(\mu_2\text{-PPh}_2)_2(\mu_2\text{-H})(CO)_6]$ (17); yield: ca. 5%.

Thermolysis of $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu_2\text{-H})(CO)_6(PPh_2H)]$

A solution of $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu_2\text{-H})(CO)_6(PPh_2H)]$ (0.61 g, 0.5 mmol) in xylene (ca. 100 cm³) was refluxed for either 30 min or 7 h. The solvent was removed under reduced pressure and the residue dissolved in a minimum of chloroform and transferred to thin layer plates. Three and nine distinct bands respectively were obtained on elution with chloroform/light petroleum (1/5). The products isolated from these bands, in order of their elution, were as follows:

Band 1; orange; [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh)(μ_2-PPh$_2$)(μ_2-H)(CO)$_7$] (**17**); yield: 30 min. reaction time, not detected; 7 h reaction time, ca. 8%.

Band 2; purple; [Ru$_4$(μ_4-PPh)$_2$(μ_2-CO)(CO)$_{10}$] (**12**); yield: 30 min reaction time, not detected; 7 h reaction time, < 2%.

Band 3; purple; [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_7$] (**15**); yield: 30 min reaction time, not detected; 7 h reaction time, ca. 4%.

Band 4; orange; [Ru$_3$(μ_2-PPh$_2$)$_3$(μ_2-H)(CO)$_6$(PPh$_2$H)].

Band 5; green; [Ru$_7$(μ_4-PPh)$_2$(CO)$_{18}$] (**7**); yield; 30 min reaction time, not detected; 7 h reaction time, ca. 5%.

Band 6, Band 8 and Band 9; all yellow. These compounds were isolated in very low yield and were not investigated further.

Band 7; maroon; [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh$_2$)(μ_2-PPh$_2$)$_2$(μ_2-H)(CO)$_6$] (**17**); yield: 30 min. reaction time, ca. 20%; 7 h reaction time, ca. 7%.

Crystal Structure Determinations

(i) *[Ru$_6$(μ_4-PPh)$_2$(μ_3-PPh)$_2$(CO)$_{12}$]* *(13)*.   Crystal data. C$_{36}$H$_{20}$O$_{12}$P$_4$Ru$_6$, M = 1374.82, brown crystal of dimensions 0.32 × 0.61 × 0.43 mm grown by liquid diffusion from chloroform/light petroleum, monoclinic, space group $P2_1/c$, a 20.817(4), b 10.219(2), c 21.165(2) Å, β 110.62(2)°, U 4213.7 Å^3, $Z = 4$, D_c 2.168 g cm^{-3}, μ(Mo-K_α) 10.40 cm^{-1}, $F(000) = 2624$.

Unit-cell parameters and intensity data were obtained by previously described procedures [32] using a Nonius CAD-4 diffractometer operating in the ω–2θ scan mode, with graphite monochromated Mo-K_α radiation. A total of 9672 unique reflections were collected in the range $2 \le \theta \le 23°$ and of these 8750 with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. The reflection intensities were corrected for absorption by the azimuthal-scan method [33].

The six ruthenium atoms in the asymmetric unit were located from a Patterson map calculated using the program SHELX-76. [34] All the remaining non-hydrogen atoms were located from a Fourier synthesis phased on the Ru atoms. The Ru, P and O atoms were assigned anisotropic temperature factors and the C atoms isotropic temperature factors. The hydrogen atoms were not located. A final full-matrix least-squares refinement (343 variables) using the weighting scheme $w = K/[\sigma^2(F) + 0.019F^2]$ ($\sigma(F)$ from counting statistics; $K = 1.69$) converged at $R = 0.037$, $R_w = 0.048$ (maximum shift/e.s.d. in the last cycle = 0.37). A final difference Fourier calculated at this stage was featureless.

(ii) *[Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_7$] · CHCl$_3$* *(15)*. Crystal data. C$_{38}$H$_{26}$Cl$_3$O$_7$P$_3$Ru$_3$, M = 977.74, purple crystal of dimensions 0.38 × 0.23 × 0.15 mm grown by vapour diffusion from chloroform/light petroleum, triclinic, space group $P\bar{1}$, a 11.406(2), b 12.321(2), c 16.828(3) Å, α 106.04(1), β 96.90(2), γ 110.54(2)°, U 2067.0 Å^3, $Z = 2$, D_c 1.762 g cm^{-3}, μ(Mo-K_α) 8.82 cm^{-1}, $F(000) = 1062$.

Unit-cell parameters and intensity data were obtained by previously described procedures [32] using a Nonius CAD-4 diffractometer operating in the ω–2θ scan mode, with graphite monochromated Mo-K_α radiation. A total of 5454 unique reflections were collected in the range $2 \le \theta \le 23°$, and of these 5166 with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. The reflection intensities were corrected for absorption using the azimuthal-scan method [33].

The three ruthenium atoms in the asymmetric unit were located from a Patterson map calculated using the program SHELX-86. [35] All the remaining non-hydrogen

Table 8

Fractional atomic coordinates ($\times 10^4$) for $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhPC_6H_4PPh)(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_7]$ with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Ru(1)	1776(1)	1651(1)	−44(1)	C(13)	3905(5)	−621(7)	−113(4)
Ru(2)	3246(1)	2620(1)	−501(1)	C(14)	4113(5)	1108(7)	−1725(4)
Ru(3)	1978(1)	1568(1)	−1456(1)	C(15)	4007(6)	2026(8)	−2180(4)
P(1)	3408(1)	992(2)	−1144(1)	C(16)	4548(6)	2196(8)	−2609(5)
P(2)	2279(1)	3587(2)	−9(1)	C(17)	5228(6)	1424(8)	−2587(5)
P(3)	873(1)	2353(2)	−1039(1)	C(18)	5342(6)	496(8)	−2148(5)
O(1)	435(5)	1758(7)	780(4)	C(19)	4780(5)	334(7)	−1714(4)
O(2)	3115(5)	1057(7)	1199(4)	C(20)	2622(5)	4442(6)	745(3)
O(3)	1518(5)	−925(7)	−393(4)	C(21)	3448(5)	4855(7)	911(4)
O(4)	4593(4)	2276(6)	755(3)	C(22)	3705(6)	5580(8)	1463(5)
O(5)	4331(5)	4428(7)	−951(4)	C(23)	3123(6)	5858(9)	1852(5)
O(6)	1211(5)	−753(6)	−1952(3)	C(24)	2310(7)	5447(9)	1694(5)
O(7)	1718(5)	2489(7)	−2845(4)	C(25)	2034(6)	4724(8)	1134(5)
C(1)	928(6)	1755(8)	452(4)	C(26)	−233(5)	1903(7)	−1296(4)
C(2)	2648(6)	1271(8)	712(4)	C(27)	−807(6)	2182(9)	−922(5)
C(3)	1602(6)	50(8)	−283(4)	C(28)	−1678(8)	1825(10)	−1125(6)
C(4)	4079(5)	2397(7)	268(4)	C(29)	−1912(9)	1195(12)	−1681(7)
C(5)	3919(6)	3720(8)	−777(4)	C(30)	−1352(10)	882(14)	−2076(8)
C(6)	1499(5)	144(8)	−1759(4)	C(31)	−463(9)	1269(12)	−1871(7)
C(7)	1805(5)	2098(8)	−2310(4)	C(32)	822(5)	3935(7)	−991(4)
C(8)	3575(5)	−475(7)	−796(4)	C(33)	217(6)	4588(8)	−1434(4)
C(9)	3297(6)	−1419(8)	−1197(4)	C(34)	261(6)	5788(9)	−1416(5)
C(10)	3344(6)	−2539(9)	−930(5)	C(35)	917(6)	6347(8)	−962(5)
C(11)	3652(7)	−2695(9)	−243(5)	C(36)	1522(5)	5692(8)	−520(4)
C(12)	3925(7)	−1755(9)	160(5)	C(37)	1470(5)	4492(7)	−533(4)

atoms were located from a Fourier synthesis phased on the Ru atoms. All these atoms were assigned anisotropic temperature factors. A final full-matrix least-squares refinement (487 variables) using the weighting scheme $w = K/[\sigma^2(F) + 0.001F^2]$ ($\sigma(F)$ from counting statistics; $K = 2.61$) converged at $R = 0.036$, $R_w = 0.042$. Hydrogen atoms were not located. A final difference Fourier calculated at this stage was featureless.

(iii) *$[Ru_3(\mu_3\text{-}\eta^2\text{-}PhPC_6H_4PPh)(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_7]$* *(19)*. Crystal data. C_{37}-$H_{25}O_7P_3Ru_3$, $M = 977.66$, orange crystal of dimensions $0.12 \times 0.46 \times 0.17$ mm grown by liquid diffusion from chloroform/light petroleum, monoclinic, space group $P2_1/c$, a 16.091(3), b 11.489(2), c 20.572(4) Å, β 102.57(2)°, U 3711.9 Å^3, $Z = 4$, D_c 1.750 g cm^{-3}, μ(Mo-K_α) 7.74 cm^{-1}, $F(000) = 1920$.

Unit-cell parameters and intensity data were obtained by previously described procedures [32] using a Nonius CAD-4 diffractometer operating in the ω–2θ scan mode, with graphite monochromated Mo-K_α radiation. A total of 6880 unique reflections were collected in the range $2 \leq \theta \leq 23°$, and of these 5898 with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. The reflection intensities were corrected for absorption using the azimuthal-scan method [33].

The three ruthenium atoms in the asymmetric unit were located from a Patterson map calculated using the program SHELX-76. [34] All the remaining non-hydrogen atoms were located from a Fourier synthesis phased on the Ru atoms. The

ruthenium and phosphorus atoms were assigned anisotropic temperature factors and the remaining carbon and oxygen atoms individual isotropic temperature factors. The hydrogen atoms were not located. A final full-matrix least-squares refinement (231 variables) using the weighting scheme $w = K/[\sigma^2(F) + 0.001F^2]$ ($\sigma(F)$ from counting statistics; $K = 1.62$) converged at $R = 0.050$, $R_w = 0.055$ (maximum shift/e.s.d. in the last cycle = 0.03). A final difference Fourier calculated at this stage was featureless.

(iv) *[Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh$_2$)(μ_2-PPh$_2$)$_2$(μ_2-H)(CO)$_6$] · 2CHCl$_3$ (17).* Crystal data. C$_{56}$H$_{42}$Cl$_6$O$_6$P$_4$Ru$_3$, $M = 1450.71$, maroon crystal of dimensions 0.23 × 0.31 × 0.65 mm grown by liquid diffusion from chloroform/light petroleum, mono-

Table 9

Fractional atomic coordinates ($\times 10^4$) for [Ru$_3$(μ_3-η^2-PhPC$_6$H$_4$PPh$_2$)(μ_2-PPh$_2$)$_2$(μ_2-H)(CO)$_6$]·2CHCl$_3$ with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Ru(1)	4730(1)	7279(1)	6768(1)	C(26)	5510(6)	7996(5)	4712(4)
Ru(2)	4595(1)	7261(1)	5543(1)	C(27)	5707(6)	8409(6)	4358(5)
Ru(3)	5720(1)	7739(1)	6284(1)	C(28)	6319(8)	8425(7)	4249(5)
P(1)	4499(2)	6496(1)	6183(1)	C(29)	6765(8)	8004(7)	4513(6)
P(2)	5667(1)	7153(1)	5523(1)	C(30)	6553(7)	7614(6)	4885(5)
P(3)	5218(1)	8209(1)	6947(1)	C(31)	5646(6)	8284(5)	7610(4)
P(4)	4709(1)	7961(1)	4867(1)	C(32)	5536(7)	8770(6)	7942(5)
O(1)	4980(6)	6641(5)	7791(4)	C(33)	5834(10)	8793(8)	8457(6)
O(2)	3396(6)	7506(6)	6991(5)	C(34)	6299(9)	8362(9)	8621(5)
O(3)	4063(5)	6341(4)	4740(4)	C(35)	6410(9)	7910(8)	8283(6)
O(4)	3432(5)	7969(5)	5752(5)	C(36)	6078(7)	7861(6)	7794(5)
O(5)	6135(5)	8864(4)	5755(4)	C(37)	4871(6)	8963(5)	6858(5)
O(6)	7043(5)	7539(5)	6739(5)	C(38)	5258(7)	9442(5)	6832(5)
C(1)	4874(7)	6895(6)	7413(5)	C(39)	5005(11)	10051(6)	6820(6)
C(2)	3897(8)	7447(6)	6901(5)	C(40)	4389(10)	10144(7)	6818(6)
C(3)	4272(6)	6704(5)	5026(5)	C(41)	3999(8)	9641(10)	6837(7)
C(4)	3870(7)	7691(5)	5706(5)	C(42)	4237(7)	9046(5)	6853(6)
C(5)	5960(6)	8443(5)	5948(5)	C(43)	4265(6)	7709(4)	4252(5)
C(6)	6544(7)	7618(5)	6570(5)	C(44)	4562(7)	7436(6)	3851(5)
C(7)	4976(6)	5823(4)	6197(4)	C(45)	4169(11)	7171(7)	3421(7)
C(8)	4937(8)	5439(6)	5772(5)	C(46)	3510(13)	7210(9)	3395(8)
C(9)	5259(9)	4895(6)	5792(6)	C(47)	3240(8)	7489(8)	3797(7)
C(10)	5653(8)	4734(6)	6248(6)	C(48)	3617(7)	7753(6)	4226(6)
C(11)	5716(11)	5136(8)	6663(9)	C(49)	4466(6)	8755(5)	4907(4)
C(12)	5373(8)	5668(5)	6635(5)	C(50)	4514(6)	9022(5)	5392(5)
C(13)	3742(7)	6144(6)	6174(5)	C(51)	4353(7)	9642(5)	5441(6)
C(14)	3205(8)	6348(7)	5895(7)	C(52)	4165(7)	9968(5)	4982(6)
C(15)	2600(9)	6037(14)	5940(11)	C(53)	4139(7)	9685(5)	4489(6)
C(16)	2606(16)	5575(11)	6274(13)	C(54)	4293(6)	9077(5)	4445(5)
C(17)	3100(11)	5332(12)	6527(13)	Cl(1)	2521(6)	956(6)	3339(4)
C(18)	3673(9)	5622(8)	6471(9)	Cl(2)	1655(5)	1307(5)	2628(6)
C(19)	6083(6)	6455(5)	5434(5)	Cl(3)	2492(14)	867(8)	2166(7)
C(20)	5939(7)	6140(5)	4977(5)	Cl(4)	7625(6)	1009(6)	3574(5)
C(21)	6268(8)	5595(6)	4879(6)	Cl(5)	8621(6)	1133(9)	2896(6)
C(22)	6758(9)	5415(7)	5252(7)	Cl(6)	7289(7)	1072(7)	2441(5)
C(23)	6875(10)	5713(9)	5738(9)	C(55)	2369(12)	1259(12)	2627(9)
C(24)	6526(8)	6250(6)	5827(6)	C(56)	7568(23)	1465(16)	2785(17)
C(25)	5924(5)	7596(5)	4980(4)				

clinic, space group $I2/a$ (No. 15), a 21.599(4), b 22.202(4), c 25.429(5) Å, β 96.39(2)°, U 12118.5 Å^3, $Z = 8$, D_c 1.590 g cm^{-3}, μ(Mo-K_α) 8.16 cm^{-1}, $F(000) =$ 5680.

Unit-cell parameters and intensity data were obtained by previously described procedures [32] using a Nonius CAD-4 diffractometer operating in the ω–2θ scan mode, with graphite monochromated Mo-K_α radiation. A total of 15766 unique reflections were collected in the range $2 \le \theta \le 23°$, and of these 13955 with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. The reflection intensities were corrected for absorption using the azimuthal-scan method [33].

The three ruthenium atoms in the asymmetric unit were located from a Patterson map calculated using the program SHELX-86. [35] All the remaining non-hydrogen atoms were located from a Fourier synthesis phased on the Ru atoms. All these atoms were assigned anisotropic temperature factors. A final full-matrix least-squares refinement (676 variables) using the weighting scheme $w = K/[\sigma^2(F) + 0.002F^2]$ ($\sigma(F)$ from counting statistics; $K = 5.65$) converged at $R = 0.082$, $R_w = 0.092$ (maximum shift/e.s.d. in the last cycle = 0.40). The hydrogen atoms were not located. A final difference Fourier calculated at this stage was featureless.

For all four complexes, complete tables of bond lengths and angles and thermal parameters and lists of observed and calculated structure factors are available from the authors.

Acknowledgements

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