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# Condensation as well as trinuclear products from the reaction of triruthenium dodecacarbonyl with diphenylphosphine

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## Abstract

The reaction of $[Ru_3(CO)_{12}]$ with $PPh_2H$ in toluene under reflux affords a range of products, the nature and yields of which depend on the reaction times and the molar ratios employed. Compounds isolated include not only the trinuclear species $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$, $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$, $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$, $[Ru_3(\mu_3\text{-}PPh)(\mu\text{-}H)_2(CO)_9]$ and $[Ru_3(\mu\text{-}PPh)(\mu\text{-}PPh_2)_2(CO)_7]$ but also condensation products, such as $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$, $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$, $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$ and $[Ru_7(\mu_4\text{-}PPh)_2(CO)_{18}]$, previously isolated from the reaction of $[Ru_3(CO)_{12}]$ with $PPhH_2$, as well as the highly unusual octaruthenium derivative $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2Ph)(\mu_2\text{-}CO)_2(CO)_{17}]$ and the fragmentation product $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$. The molecular stereochemistries of $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$, $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$, $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$ and $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2Ph)(\mu_2\text{-}CO)_2(CO)_{17}]$ have been established by X-ray crystallography. The eight ruthenium atoms in the latter adopt a square antiprismatic geometry and encapsulate a phosphorus atom derived from the diphenylphosphine. The benzyl group in this compound exhibits an unusual mode of coordination with the benzene ring functioning as a hexahapto ligand towards one of the ruthenium atoms and with the benzylic carbon bonding directly to an adjacent ruthenium atom.

## Introduction

Although there is now substantial evidence that bridging phosphido ligands in di- and poly-nuclear compounds are not necessarily non-labile [1–6], the majority of chemical transformations involving compounds of this type take place without

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cleavage of the formal metal–phosphorus bonds even though the bridging metal–phosphorus–metal configuration may revert from a closed to an open one in the process. As a consequence, phosphido-bridged compounds continue to receive much attention, the object being to produce and investigate new metal cluster compounds which maintain the integrity of their metal atom framework during chemical reaction.

A method of synthesis of phosphido-bridged metal carbonyl derivatives involves the direct reaction of secondary or primary phosphines with metal carbonyls. Thus 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 benzophenone ketyl 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 $[Ru_3(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_{10}]$ in heptane at 60 °C [7]. Significantly, this decacarbonyl derivative has been found to decarbonylate further to the nonacarbonyl $[Ru_3(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_9]$ on reaction with trimethylamine oxide [5b]. Likewise, reaction of $[Ru_3(CO)_{12}]$ with a twice-molar amount of $PPh_2H$ at room temperature in the presence of sodium benzophenone ketyl has been shown to afford the bis-substituted derivative $[Ru_3(CO)_{10}(PPh_2H)_2]$ which produces the phosphido-bridged octacarbonyl derivative $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ together with a minor amount of $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ on thermolysis in toluene at 70 °C [8]. A tris-substituted derivative viz. $[Ru_3(CO)_9(PPh_2H)_3]$ has been isolated in good yield from the reaction of $[Ru_3(CO)_{12}]$ with a three-fold molar amount of $PPh_2H$ in hexane at 45 °C for 12 hours and this has also been shown to rearrange to diphenylphosphido-bridged products under appropriate reaction conditions [9]. In particular, irradiation of a benzene solution of this species with ultraviolet light was found to afford a reaction mixture which could be separated into two fractions; the minor fraction was shown to contain $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ and $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ while the major fraction was found to contain $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_7(PPh_2H)]$ and $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ [9].

We, and a number of other groups, have shown that the reactions of $[Ru_3(CO)_{12}]$ with phenylphosphine affords trinuclear phenylphosphinidene-capped products at temperatures of 80 °C and less [10–12]. However, we also established that the reaction gives higher nuclearity phenylphosphinidene-capped products at higher temperatures [10,13]. As part of a programme of investigation of the chemistry of phosphido-bridged and phosphinidene-capped metal carbonyl clusters, we studied the reaction of $[Ru_3(CO)_{12}]$ with $PPh_2H$ with the object of synthesising higher nuclearity as well as trinuclear diphenylphosphido-bridged clusters of ruthenium. Towards the end of our investigation the synthesis of two of the compounds we isolated, viz. $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu\text{-}H)_2(CO)_8]$ and $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$, was reported, as described above [8,9]. The results of our study are reported here; some of these results have been communicated previously [14,15].

## Results and discussion

### *Reaction of $[Ru_3(CO)_{12}]$ with an equimolar amount of $PPh_2H$*

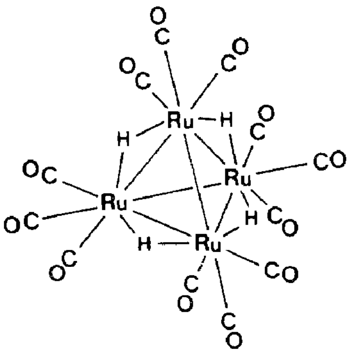
The reaction of equimolar quantities of $[Ru_3(CO)_{12}]$ and $PPh_2H$ in toluene under reflux for 8 to 24 h was found to be highly complex and to produce a product mixture which gave a large number of bands on column chromatographic treatment.

Table 1

Infrared and nuclear magnetic resonance spectroscopic data

| Compound | $\nu$(CO) (cm$^{-1}$) [a] | $^{31}P\{^1H\}$ [c,d] | $^1H$ [c,g] |
|---|---|---|---|
| $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ **(2)** | 2065m, 2035vs, 2005s, 1980s, 1970sh [b] | 110.9(s) [e] | |
| $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ **(4)** | 2075m, 2040vs, 2020vs, 2007s, 1987m, 1970m [b] | 163.0(s) [f] | −16.48(t, Ru−*H*−Ru, *J*(PH) 22.8) [f] |
| $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ **(6)** | 2053ms, 2015s, 1982m, 1952ms [b] | $\nu_A$, 177.7 ($AB_2$ system,<br>$\nu_B$, 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] |
| $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$ **(12)** | 2050s, 2015ms, 1990w, 1970m, 1935m [b] | 179.7(m) [e] | 6.81(d of t, $PPh_2H$, *J*(P′H) 370.6, *J*(P″H) 7.8) |
| | | 162.6(m)<br>36.52(m) | −16.68(d of q, Ru−*H*−Ru, *J*(P′H) 17.3, *J*(P″H) 9.4) [e] |
| $[Ru_3(\mu_3\text{-}PPh)(\mu_2\text{-}H)_2(CO)_9]$ **(9)** | 2100m, 2070s, 2042vs, 2025m, 2012s, 1997m, 1982m [b] | 279.0(s) [e] | −19.12(d, Ru−*H*−Ru, *J*(PH) 15.1) [e] |
| $[Ru_3(\mu_3\text{-}PPh)(\mu_2\text{-}PPh_2)_2(CO)_7]$ **(10)** | 2040m, 2010m, 2000s, 1977m, 1962m, 1927w [b] | $\nu_A$, 236.4 (ABX system,<br>$\nu_B$, 236.2 *J*(AB) 90, *J*(AX) 88.5,<br>$\nu_X$, 124.0 *J*(BX) 88.67) [f] | |
| $[Ru_4(\mu_2\text{-}H)_4(CO)_{12}]$ **(1)** | 2078s, 2063v s, 2028sh, 2024s, 2004w [b] | | −17.78(s, Ru−*H*−Ru) [f] |
| $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ **(5)** | 2070m, 2030vs, 2012s, 1983m, 1965sh, 1833m [b] | 167.8(s) [e] | |
| $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$ **(3)** | 2095w, 2050s, 2027s, 1985m [b] | 434.2(s) [e] | |
| $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$ **(11)** | 2030vs, 2020m, 2002s, 1996w, 1986w, 1963w [b] | 573.8(t, $\mu_4$-*P*, *J*(PP′)46.2) [e]<br>412.4(t, $\mu_3$-*P*, *J*(PP′)46.2) | |
| $[Ru_7(\mu_4\text{-}PPh)_2(CO)_{18}]$ **(7)** | 2090w, 2060vs, 2050s, 2018m, 2005m, 1993w, 1980w, 1945w [b] | 457.0(s) [e] | |
| $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2Ph)(\mu_2\text{-}CO)_2(CO)_{17}]$ **(8)** | 2080m, 2050s, 2035s [b] | | |

[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, q = quartet, m = multiplet. [d] $\delta$ scale in ppm relative to $H_3PO_4$; coupling constants in Hz; measured at 32° C. [e] Measured in $CD_2Cl_2$. [f] Measured in $CDCl_3$. [g] $\delta$ scale in ppm relative to $SiMe_4$; coupling constants in Hz; measured at 32° C.



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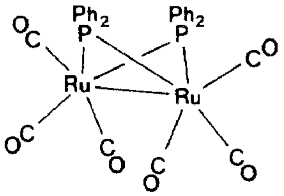


(2)

Fourteen of these (in order of elution: yellow, yellow, white, pink, green, yellow-orange, purple, orange-red, red-brown, green, green, brown, blood-red and blue) were distinct and could be separated although the residues of five of them (pink, red-brown, green (eleventh band), brown and blood-red) could not be obtained in a crystalline form suitable for X-ray diffraction studies and as a consequence could not be fully characterised.

The first band was found to contain minor amounts of the parent species $[Ru_3(CO)_{12}]$ while the product from the second band proved difficult to separate from the parent $[Ru_3(CO)_{12}]$ and was identified spectroscopically (Table 1), as the known tetraruthenium hydride $[Ru_4(\mu_2\text{-}H)_4(CO)_{12}]$ (**1**) [16,17]. The source of the hydride ligand in the formation of this tetrahedral compound was presumably the diphenylphosphine.

A white compound, isolated from the third band, was characterised X-ray crystallographically as well as by elemental analysis and by IR and NMR spectroscopy, as the dinuclear compound $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ (**2**), previously reported as a minor product of the pyrolysis of $[Ru_3(CO)_9(PPh_3)_3]$ [18], as a product of the thermolysis of $[Ru_3(CO)_{10}(PPh_2H)_2]$ in toluene at 70 ° C [8] and as a product of the photolysis of $[Ru_3(CO)_9(PPh_2H)_3]$ in benzene [9] (vide supra). The stereochemistry of this compound is illustrated in Fig. 1. Selected interatomic distances and angles are summarised in Table 2; values quoted in the following discussion are averaged over the two crystallographically independent, but geometrically equivalent, molecules in the asymmetric unit. The two ruthenium atoms are linked not only by a formal metal–metal bond (Ru(1)–Ru(2) 2.820(1) Å) but by two bridging diphenylphosphido groups as well. The $Ru_2P_2$ framework adopts a butterfly structure with the dihedral angle between the two $Ru_2P$ planes being 75.1 °. Overall, the symmetry of the molecule is $C_{2v}$ with two of the three terminal carbonyls on each ruthenium being equivalent. Thus the molecule has the same general structure as its iron analogue [19].

The fourth band (pink) and likewise the twelfth (brown) and thirteenth (blood-red) bands afforded, in very low yield, solid residues, each of which appeared to be mixtures of at least two compounds. Crystalline products could not be isolated from any of these residues and they were thus not investigated further.

The fifth band gave a green product characterised as the phenylphosphinidene-capped pentaruthenium species $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$ (**3**). This compound has been

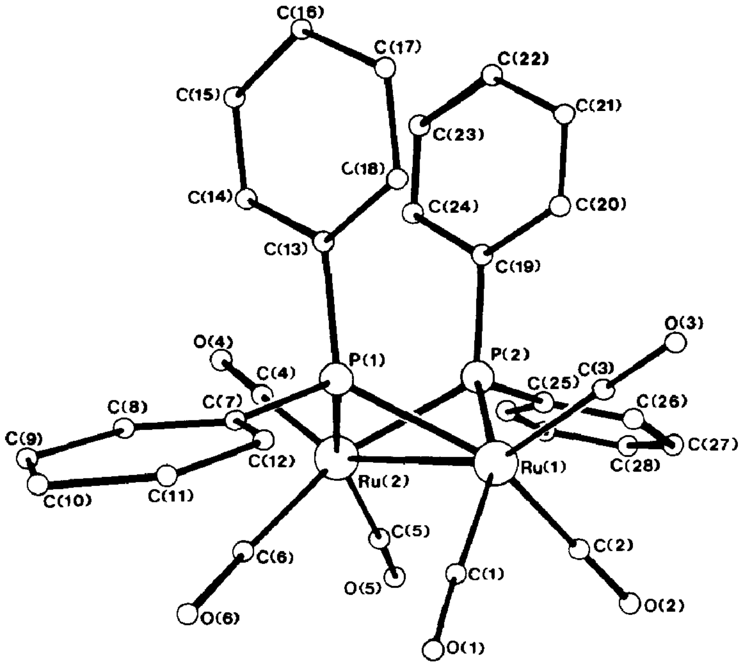


Fig. 1. The molecular stereochemistry of [Ru$_2$($\mu$-PPh$_2$)$_2$(CO)$_6$] (2).

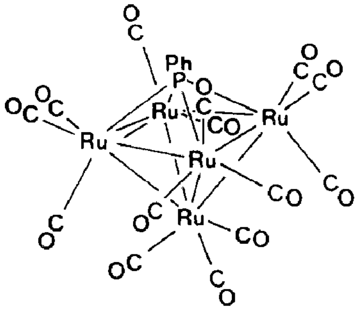
reported previously as a product of the reaction of [Ru$_3$(CO)$_{12}$] with PPhH$_2$ in toluene under reflux [10] as well as from the reaction of [Ru$_3$(CO)$_{12}$] with [Mn($\eta$-C$_5$H$_5$)(CO)$_2$(PPhCl$_2$] [20] and contains the five ruthenium atoms in a square pyramidal geometry with the square basal plane being capped by a phenylphosphinidene ligand.

The trinuclear species [Ru$_3$($\mu_2$-PPh$_2$)$_2$($\mu_2$-H)$_2$(CO)$_8$] (4) was isolated from the sixth band. As described above, this compound, which is essentially the major product of this reaction, has also been reported by Carty et al., who established that

Table 2

Selected interatomic distances (Å) and angles (°) for [Ru$_2$($\mu$-PPh$_2$)$_2$(CO)$_6$] with estimated standard deviations in parentheses

| Molecule A | | Molecule B | |
|---|---|---|---|
| Ru(1A)–Ru(2A) | 2.814(1) | Ru(1B)–Ru(2B) | 2.825(3) |
| Ru(1A)–P(1A) | 2.367(3) | Ru(1B)–P(1B) | 2.349(3) |
| Ru(1A)–P(2A) | 2.342(3) | Ru(1B)–P(2B) | 2.353(3) |
| Ru(2A)–P(1A) | 2.346(3) | Ru(2B)–P(1B) | 2.358(3) |
| Ru(2A)–P(2A) | 2.350(3) | Ru(2B)–P(2B) | 2.354(3) |
| P(1A) ··· P(2A) | 2.983(5) | P(1B) ··· P(2B) | 2.983(5) |
| Ru(1A)–P(1A)–Ru(2A) | 73.7(1) | Ru(1B)–P(1B)–Ru(2B) | 73.8(1) |
| Ru(1A)–Ru(2A)–P(1A) | 53.0(1) | Ru(1B)–Ru(2B)–P(1B) | 53.0(1) |
| Ru(2A)–Ru(1A)–P(1A) | 53.3(1) | Ru(2B)–Ru(1B)–P(1B) | 53.3(1) |
| Ru(1A)–P(2A)–Ru(2A) | 73.3(1) | Ru(1B)–P(2B)–Ru(2B) | 73.8(1) |
| P(1A)–Ru(1A)–P(2A) | 78.6(1) | P(1B)–Ru(1B)–P(2B) | 79.0(1) |
| P(1A)–Ru(2A)–P(2A) | 78.9(1) | P(1B)–Ru(2B)–P(2B) | 78.8(1) |



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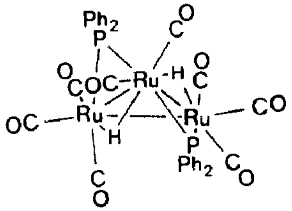
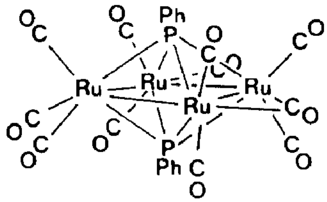


(4)

the hydride ligands bridge the same Ru–Ru edges as each of the diphenylphosphido groups and that the latter are *trans* disposed with respect to the triruthenium plane [8]. The band pattern of the C–O stretching peaks in the solution IR spectrum of this compound is very similar to that for the solid state spectrum indicating that the solid state structure is retained in solution. The presence of a single triplet corresponding to the hydride ligands in the $^1$H NMR spectrum of this compound at both 30 °C and at −90 °C is thus indicative of either of these ligands being involved in a very rapid migratory process on the NMR time-scale or of a non fluxional process and a deceptively simple AA′XX′ pattern.

The purple band (seventh) afforded a product (purple) characterised as the phenylphosphinidene-capped derivative $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ (**5**). This compound, which is obtained in higher yield from the reaction of $[Ru_3(CO)_{12}]$ with phenylphosphine [10], contains an approximate square planar array of ruthenium atoms (the one Ru–Ru distance is actually appreciably shorter than the other three) with the plane being capped on both sides by the phenylphosphinidene ligands and the shorter Ru–Ru distance being bridged by a carbonyl group.



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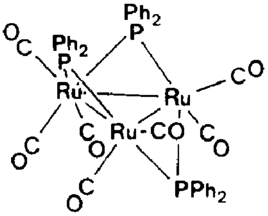


(6)

The product isolated from the eighth band was characterised as the trinuclear heptacarbonyl $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (**6**). An X-ray crystallographic study was carried out on this compound prior to the report by Churchill et al. describing the structure of this species [9] but significantly, their investigation involved a different crystal modification. The structures for the two crystal forms are essentially identical however. The ruthenium atoms adopt an approximately equilateral triangular configuration (Fig. 2) with each edge being bridged by a diphenylphosphido group; one of these groups lies on the opposite side of the triruthenium plane to the other two. The hydride ligand could not be located but presumably bridges

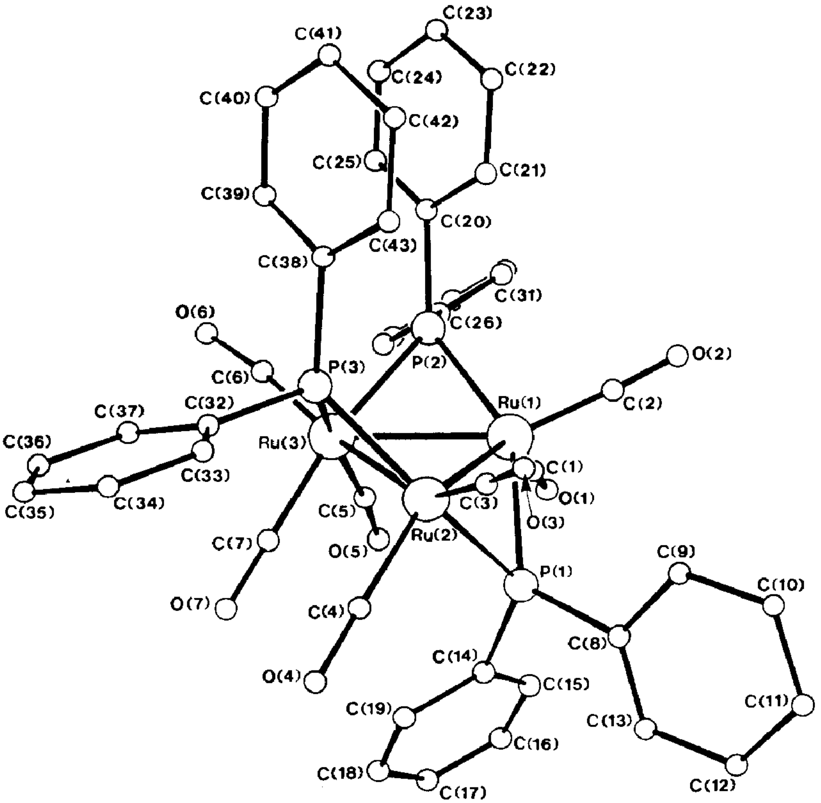


Fig. 2. The molecular stereochemistry of $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (6).

the same Ru–Ru edge as the non-equivalent diphenylphosphido group. The unique Ru atom (the molecule has approximate $C_s$ symmetry) contains three terminal carbonyl groups while the other two contain two each. Selected interatomic distances and angles are given in Table 3.

The band pattern of the C–O stretching bands in the solution IR spectrum of this compound is very similar to that of the solid state spectrum which is indicative of the solid structure being retained in solution. Consistent with this, the $^1H$ NMR spectrum of this compound exhibits a doublet of triplets at −17.10 ppm, readily

Table 3

Selected interatomic distances (Å) and angles (°) for $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.908(2) | Ru(1)–Ru(3) | 2.780(2) |
| Ru(2)–Ru(3) | 2.976(2) | Ru(1)–P(1) | 2.524(4) |
| Ru(2)–P(1) | 2.291(4) | Ru(1)–P(2) | 2.341(4) |
| Ru(3)–P(2) | 2.468(4) | Ru(2)–P(3) | 2.259(4) |
| Ru(3)–P(3) | 2.426(4) | | |
| Ru(3)–Ru(1)–Ru(2) | 63.1(1) | Ru(1)–Ru(2)–Ru(3) | 56.4(1) |
| Ru(1)–Ru(3)–Ru(2) | 60.6(1) | Ru(1)–P(1)–Ru(2) | 74.1(1) |
| Ru(2)–P(2)–Ru(3) | 70.6(1) | Ru(1)–P(3)–Ru(3) | 78.8(1) |

assigned to the hydride ligand while the $^{31}P\{^{1}H\}$ NMR spectrum exhibits a typical eight-line $AB_2$ pattern of resonances.

The red-brown microcrystalline product isolated from the ninth band exhibited a doublet of doublets at $-13.88$ ppm, assigned to a bridging hydride ligand, in its $^{1}H$ NMR spectrum and peaks corresponding to capping phenylphosphinidene and/or bridging diphenylphosphido groups in its $^{31}P\{^{1}H\}$ NMR spectrum. Significantly, the low temperature $^{31}P\{^{1}H\}$ NMR spectrum was found to be considerably more complex than the ambient one indicating either the presence of a second isomer at this temperature or some fluxional process. Attempts to isolate this compound in a crystalline form suitable for an X-ray diffraction study proved unsuccessful however and as a consequence the compound could not be characterised.

The tenth band afforded a green product characterised as the heptaruthenium species $[Ru_7(\mu_4\text{-}PPh)_2(CO)_{18}]$ (**7**). This compound has been reported previously as a product of the reaction of $[Ru_3(CO)_{12}]$ with $PPhH_2$ in toluene under reflux [10] as well as from the pyrolysis of $[Ru_3(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_{10}]$ in toluene at 120 °C [21]. The seven ruthenium atoms in this compound 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 ligand [21].

The green microcrystalline compound isolated from the eleventh band was found to exhibit a singlet at 449 ppm, assigned to a quadruply capping phenylphosphini-

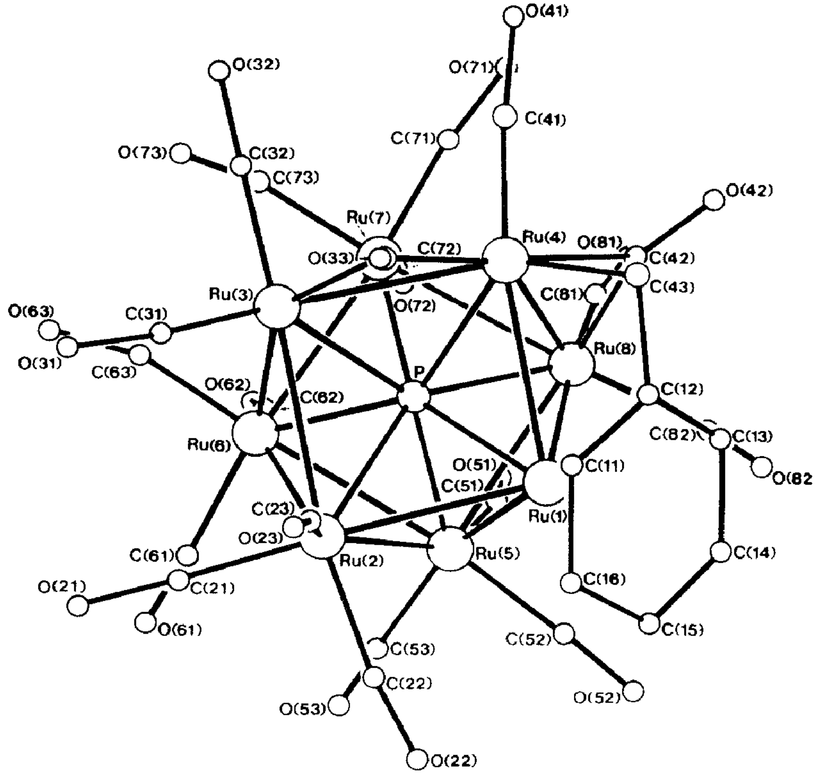
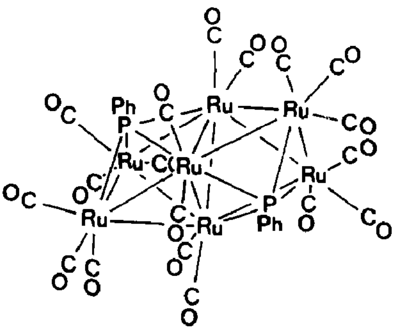


Fig. 3. The molecular stereochemistry of $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2Ph)(\mu_2\text{-}CO)_2(CO)_{17}]$ (**8**).

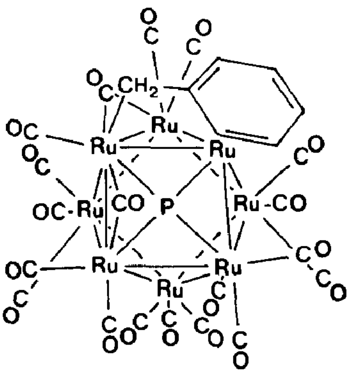
dene ligand, in its $^{31}P\{^1H\}$ NMR spectrum but attempts to isolate single crystals of this species for an X-ray structural investigation proved unsuccessful.

The blue product isolated from the fourteenth band could be obtained only in very low yield, and furthermore it was produced only in isolated reactions. It was characterised by means of X-ray crystallography as the novel octaruthenium species $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2Ph)(\mu_2\text{-}CO)_2(CO)_{17}]$ (**8**). The molecular stereochemistry of this compound is illustrated in Fig. 3. Selected interatomic distances and angles are given in Table 4; values quoted in the following discussion are averaged over the two crystallographically independent, but geometrically equivalent, molecules in the asymmetric unit. The eight ruthenium atoms adopt a square antiprismatic geometry with the Ru–Ru distances ranging from 2.822(5) to 3.007(5) Å. The phosphorus is encapsulated in the center of the metal atom framework, the Ru–P distances being in the range 2.31(1) to 2.43(1) Å. The benzyl group is coordinated to the skeletal framework via two of the ruthenium atoms; the phenyl ring is essentially symmetrically disposed with respect to one of these ruthenium atoms (Ru(1)) (the Ru–C distances are in the range 2.20(3) to 2.29(3) Å) while the benzylic carbon is located at a bonding distance (2.19(4) Å) from the other (Ru(4)). The coordination of the ruthenium atoms is completed by nineteen carbonyl groups with two of these being edge-bridging and the remainder terminal.

On the basis of the structural parameters cited, the mode of coordination of the benzyl group is best described as monohapto-hexahapto. Compounds in which the benzyl group functions as a monohapto ligand are numerous. In this coordination mode, the benzyl group coordinates via the benzylic carbon either terminally as in $[Nb(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$ [22] and $[Mo_2(NMe_2)_4(CH_2Ph)_2]$ [23] or as a bridging ligand as in $[Mn_2(\mu\text{-}CH_2Ph)_2(CH_2Ph)_2(PMe_3)_2]$ [24]. Examples of compounds containing the benzyl or related groups functioning as hexahapto ligands i.e. coordinating through the phenyl ring as in $[Cr(\eta^6\text{-}C_6H_5Me)(CO)_2(CNBu^t)]$ [25] are also prolific. However, we have not found any reported examples of compounds in which a benzyl group bridges two metal atoms, formally bonded to each other, in a monohapto–hexahapto coordination mode. An alternative description of the coordination of the benzyl group is one in which it functions as a benzylic system (**I**), bonding to the metal cluster across one of its edges as a heptahapto ligand. The



(**7**)



(**8**)

Table 4

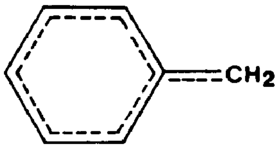
Selected interatomic distances (Å) and angles (°) for $[Ru_8(\mu_8\text{-P})(\mu_2\text{-}\eta^1,\eta^6\text{-CH}_2C_6H_5)(\mu_2\text{-CO})_2(CO)_{17}]$ with estimated standard deviations in parentheses

| Molecule A | | Molecule B | |
|---|---|---|---|
| Ru(1A)–Ru(2A) | 2.839(5) | Ru(1B)–Ru(2B) | 2.839(5) |
| Ru(1A)–Ru(4A) | 2.864(5) | Ru(1B)–Ru(4B) | 2.864(5) |
| Ru(1A)–Ru(5A) | 2.832(5) | Ru(1B)–Ru(5B) | 2.832(5) |
| Ru(1A)–Ru(8A) | 2.822(5) | Ru(1B)–Ru(8B) | 2.822(5) |
| Ru(2A)–Ru(3A) | 2.961(5) | Ru(2B)–Ru(3B) | 2.940(5) |
| Ru(2A)–Ru(5A) | 2.905(5) | Ru(2B)–Ru(5B) | 2.917(5) |
| Ru(2A)–Ru(6A) | 2.867(5) | Ru(2B)–Ru(6B) | 2.862(5) |
| Ru(3A)–Ru(4A) | 2.857(5) | Ru(3B)–Ru(4B) | 2.858(5) |
| Ru(3A)–Ru(6A) | 2.948(5) | Ru(3B)–Ru(6B) | 2.948(5) |
| Ru(3A)–Ru(7A) | 2.919(5) | Ru(3B)–Ru(7B) | 2.905(5) |
| Ru(4A)–Ru(7A) | 3.007(5) | Ru(4B)–Ru(7B) | 3.021(5) |
| Ru(4A)–Ru(8A) | 2.830(5) | Ru(4B)–Ru(8B) | 2.819(5) |
| Ru(5A)–Ru(6A) | 2.956(5) | Ru(5B)–Ru(6B) | 2.957(5) |
| Ru(5A)–Ru(8A) | 2.980(5) | Ru(5B)–Ru(8B) | 2.998(5) |
| Ru(6A)–Ru(7A) | 2.916(5) | Ru(6B)–Ru(7B) | 2.911(5) |
| Ru(7A)–Ru(8A) | 2.931(5) | Ru(7B)–Ru(8B) | 2.946(5) |
| Ru(1A)–P(A) | 2.31(1) | Ru(1B)–P(B) | 2.29(1) |
| Ru(2A)–P(A) | 2.44(1) | Ru(2B)–P(B) | 2.39(1) |
| Ru(3A)–P(A) | 2.38(1) | Ru(3B)–P(B) | 2.38(1) |
| Ru(4A)–P(A) | 2.42(1) | Ru(4B)–P(B) | 2.42(1) |
| Ru(5A)–P(A) | 2.40(1) | Ru(5B)–P(B) | 2.40(1) |
| Ru(6A)–P(A) | 2.43(1) | Ru(6B)–P(B) | 2.43(1) |
| Ru(7A)–P(A) | 2.36(1) | Ru(7B)–P(B) | 2.41(1) |
| Ru(8A)–P(A) | 2.39(1) | Ru(8B)–P(B) | 2.40(1) |
| Ru(1A)–C(11A) | 2.20(3) | Ru(1B)–C(11B) | 2.21(3) |
| Ru(1A)–C(12A) | 2.21(3) | Ru(1B)–C(12B) | 2.20(3) |
| Ru(1A)–C(13A) | 2.25(3) | Ru(1B)–C(13B) | 2.22(3) |
| Ru(1A)–C(14A) | 2.29(3) | Ru(1B)–C(14B) | 2.25(3) |
| Ru(1A)–C(15A) | 2.28(3) | Ru(1B)–C(15B) | 2.26(3) |
| Ru(1A)–C(16A) | 2.24(3) | Ru(1B)–C(16B) | 2.24(3) |
| Ru(4A)–C(43A) | 2.19(4) | Ru(4B)–C(43B) | 2.16(4) |
| C(12A)–C(43A) | 1.48(5) | C(12B)–C(43B) | 1.51(5) |
| Ru(2A)–Ru(1A)–Ru(4A) | 94.0(1) | Ru(2B)–Ru(1B)–Ru(4B) | 92.8(1) |
| Ru(2A)–Ru(1A)–Ru(5A) | 61.6(1) | Ru(2B)–Ru(1B)–Ru(5B) | 61.9(1) |
| Ru(2A)–Ru(1A)–Ru(8A) | 107.0(1) | Ru(2B)–Ru(1B)–Ru(8B) | 106.6(1) |
| Ru(4A)–Ru(1A)–Ru(5A) | 105.6(1) | Ru(4B)–Ru(1B)–Ru(5B) | 105.7(1) |
| Ru(4A)–Ru(1A)–Ru(8A) | 59.7(1) | Ru(4B)–Ru(1B)–Ru(8B) | 59.4(1) |
| Ru(5A)–Ru(1A)–Ru(8A) | 63.6(1) | Ru(5B)–Ru(1B)–Ru(8B) | 64.0(1) |
| Ru(1A)–Ru(2A)–Ru(3A) | 86.5(1) | Ru(1B)–Ru(2B)–Ru(3B) | 87.6(1) |
| Ru(1A)–Ru(2A)–Ru(5A) | 59.1(1) | Ru(1B)–Ru(2B)–Ru(5B) | 58.9(1) |
| Ru(1A)–Ru(2A)–Ru(6A) | 102.0(2) | Ru(1B)–Ru(2B)–Ru(6B) | 102.2(2) |
| Ru(3A)–Ru(2A)–Ru(5A) | 101.2(2) | Ru(3B)–Ru(2B)–Ru(5B) | 101.8(2) |
| Ru(3A)–Ru(2A)–Ru(6A) | 60.8(1) | Ru(3B)–Ru(2B)–Ru(6B) | 61.1(1) |
| Ru(5A)–Ru(2A)–Ru(6A) | 61.6(1) | Ru(5B)–Ru(2B)–Ru(6B) | 61.6(1) |
| Ru(2A)–Ru(3A)–Ru(4A) | 91.5(1) | Ru(2B)–Ru(3B)–Ru(4B) | 90.0(1) |
| Ru(2A)–Ru(3A)–Ru(6A) | 58.0(1) | Ru(2B)–Ru(3B)–Ru(6B) | 58.2(1) |
| Ru(2A)–Ru(3A)–Ru(7A) | 100.6(1) | Ru(2B)–Ru(3B)–Ru(7B) | 100.9(1) |
| Ru(4A)–Ru(3A)–Ru(6A) | 104.5(2) | Ru(4B)–Ru(3B)–Ru(6B) | 104.3(2) |
| Ru(4A)–Ru(3A)–Ru(7A) | 62.7(1) | Ru(4B)–Ru(3B)–Ru(7B) | 63.2(1) |
| Ru(6A)–Ru(3A)–Ru(7A) | 59.6(1) | Ru(6B)–Ru(3B)–Ru(7B) | 59.6(1) |
| Ru(1A)–Ru(4A)–Ru(3A) | 88.0(1) | Ru(1B)–Ru(4B)–Ru(3B) | 88.7(1) |

Table 4 (continued)

| Molecule A | | Molecule B | |
|---|---|---|---|
| Ru(1A)–Ru(4A)–Ru(7A) | 98.2(1) | Ru(1B)–Ru(4B)–Ru(7B) | 98.6(1) |
| Ru(1A)–Ru(4A)–Ru(8A) | 59.4(1) | Ru(1B)–Ru(4B)–Ru(8B) | 59.5(1) |
| Ru(3A)–Ru(4A)–Ru(7A) | 59.6(1) | Ru(3B)–Ru(4B)–Ru(7B) | 59.2(1) |
| Ru(3A)–Ru(4A)–Ru(8A) | 103.5(1) | Ru(3B)–Ru(4B)–Ru(8B) | 103.6(1) |
| Ru(7A)–Ru(4A)–Ru(8A) | 60.2(1) | Ru(7B)–Ru(4B)–Ru(8B) | 60.5(1) |
| Ru(1A)–Ru(5A)–Ru(2A) | 59.3(1) | Ru(1B)–Ru(5B)–Ru(2B) | 59.2(1) |
| Ru(1A)–Ru(5A)–Ru(6A) | 99.9(1) | Ru(1B)–Ru(5B)–Ru(6B) | 100.0(1) |
| Ru(1A)–Ru(5A)–Ru(8A) | 58.0(1) | Ru(1B)–Ru(5B)–Ru(8B) | 57.8(1) |
| Ru(2A)–Ru(5A)–Ru(6A) | 58.6(1) | Ru(2B)–Ru(5B)–Ru(6B) | 58.3(1) |
| Ru(2A)–Ru(5A)–Ru(8A) | 101.3(1) | Ru(2B)–Ru(5B)–Ru(8B) | 102.2(1) |
| Ru(6A)–Ru(5A)–Ru(8A) | 91.7(1) | Ru(6B)–Ru(5B)–Ru(8B) | 91.1(1) |
| Ru(2A)–Ru(6A)–Ru(3A) | 61.2(1) | Ru(2B)–Ru(6B)–Ru(3B) | 60.8(1) |
| Ru(2A)–Ru(6A)–Ru(5A) | 59.8(1) | Ru(2B)–Ru(6B)–Ru(5B) | 60.1(1) |
| Ru(2A)–Ru(6A)–Ru(7A) | 102.9(1) | Ru(2B)–Ru(6B)–Ru(7B) | 102.7(1) |
| Ru(3A)–Ru(6A)–Ru(5A) | 100.3(1) | Ru(3B)–Ru(6B)–Ru(5B) | 100.7(1) |
| Ru(3A)–Ru(6A)–Ru(7A) | 59.7(1) | Ru(3B)–Ru(6B)–Ru(7B) | 59.5(1) |
| Ru(5A)–Ru(6A)–Ru(7A) | 87.6(1) | Ru(5B)–Ru(6B)–Ru(7B) | 88.5(1) |
| Ru(3A)–Ru(7A)–Ru(4A) | 57.6(1) | Ru(3B)–Ru(7B)–Ru(4B) | 57.6(1) |
| Ru(3A)–Ru(7A)–Ru(6A) | 60.7(1) | Ru(3B)–Ru(7B)–Ru(6B) | 60.9(1) |
| Ru(3A)–Ru(7A)–Ru(8A) | 99.5(1) | Ru(3B)–Ru(7B)–Ru(8B) | 99.3(1) |
| Ru(4A)–Ru(7A)–Ru(6A) | 101.6(1) | Ru(4B)–Ru(7B)–Ru(6B) | 101.2(1) |
| Ru(4A)–Ru(7A)–Ru(8A) | 56.9(1) | Ru(4B)–Ru(7B)–Ru(8B) | 56.4(1) |
| Ru(6A)–Ru(7A)–Ru(8A) | 93.5(1) | Ru(6B)–Ru(7B)–Ru(8B) | 93.0(1) |
| Ru(1A)–Ru(8A)–Ru(4A) | 60.9(1) | Ru(1B)–Ru(8B)–Ru(4B) | 61.0(1) |
| Ru(1A)–Ru(8A)–Ru(5A) | 58.4(1) | Ru(1B)–Ru(8B)–Ru(5B) | 58.1(1) |
| Ru(1A)–Ru(8A)–Ru(7A) | 101.0(1) | Ru(1B)–Ru(8B)–Ru(7B) | 101.4(1) |
| Ru(4A)–Ru(8A)–Ru(5A) | 107.2(1) | Ru(4B)–Ru(8B)–Ru(5B) | 102.6(2) |
| Ru(4A)–Ru(8A)–Ru(7A) | 62.9(1) | Ru(4B)–Ru(8B)–Ru(7B) | 63.2(1) |
| Ru(5A)–Ru(8A)–Ru(7A) | 86.9(1) | Ru(5B)–Ru(8B)–Ru(7B) | 87.1(1) |

interatomic distances and angles associated with the benzylic carbon are no different from those normally observed for the benzyl group coordinated in the monohapto mode however [26] and on this basis this model can be eliminated.



(I)

A square anti-prism is the geometry predicted for eight metal atom frameworks with nine skeletal electron pairs [26b]. A simple electron count leads to this number of skeletal electron pairs for this compound if one allows for the benzyl group functioning as a seven electron donor ligand. The geometry of compound 8 is thus consistent with the benzyl group co-ordinating in the monohapto-hexahapto coordination mode. Square anti-prismatic coordination of interstitial main group elements in metal cluster compounds is unusual [27–29] but has been observed previously in $[Co_8(\mu_8\text{-}C)(\mu_2\text{-}CO)_{10}(CO)_8]^{2-}$ [30], $[Rh_9(\mu_8\text{-}P)(\mu_2\text{-}CO)_{12}(CO)_9]^{2-}$ [31] and $[Rh_{10}(\mu_8\text{-}P)(\mu_2\text{-}CO)_{12}(CO)_{10}]^{3-}$ [32]. One of the square faces of the anti-prism is capped by a rhodium atom in the nonarhodium derivative while both square faces are capped by rhodium atoms in the decarhodium compound.

Coordinated triphenylphosphine is known to readily lose a phenyl group under appropriate reaction conditions to give rise to products containing a bridging diphenylphosphido ligand [33]. The latter can, in turn, be dephenylated to give compounds containing a phenylphosphinidene group and/or an encapsulated phosphorus. Examples of this type of rearrangement are provided by the thermolysis of $[RhH(CO)(PPh_3)_3]$ which produces either $[Rh_3(\mu_2\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$ or $[Rh_4(\mu_2\text{-}PPh_2)_4(\mu_2\text{-}CO)_2(CO)_4]$ depending on the reaction conditions [34,35], the reaction of $[RuHCl(CO)(PPh_3)_3]$ with $Na[Co(CO)_4]$ at 40 °C which yields $[CoRu(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2]$ as well as $[RuHCl(CO)_2(PPh_3)_2]$ and $[Ru(CO)_3(PPh_3)_2]$ [36], the reaction of $[Fe_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ with CO at room temperature which gives $[Fe_3(\mu_3\text{-}PPh)_2(CO)_9]$ [8,37] and the reaction of $[Rh(CO)_2(acetylacetone)]$ with $PPh_3$ in the presence of caesium benzoate in tetraethylene glycol dimethyl ether at a temperature of 140–160 °C and a 300 atmosphere pressure of $CO/H_2$ which selectively produces $[Rh_9(\mu_8\text{-}P)(\mu_2\text{-}CO)_{12}(CO)_9]^{2-}$ [31]. Compounds **3**, **5** and **7** are not only condensation products but also result from the dephenylation of a phosphorus ligand with $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2Ph)(\mu_2\text{-}CO)_2(CO)_{17}]$ (**8**) representing an isolated example of a compound containing an encapsulated phosphorus derived by a dephenylation process *.

### *Reaction of $[Ru_3(CO)_{12}]$ with a twice molar amount of $PPh_2H$*

The reaction of $[Ru_3(CO)_{12}]$ with a two molar proportion of $PPh_2H$ in toluene under reflux for two to eight hours was found to also give a large number of products, and of the very large number of bands observed on thin layer chromatographic treatment of the product mixture nine were distinct and could be separated. With one exception, the products isolated were found to be similar to those formed in the 1/1 reaction except that their relative yields were different. The yields of these products were also found to depend on the reaction time, with the relative yields of those products resulting from fragmentation and/or condensation increasing for longer reaction times but with the overall total yield of the isolatable products decreasing with increase in the duration of the reaction. Products isolated and identified include $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ (**2**), $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ (**4**), $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (**6**), $[Ru_3(\mu_3\text{-}PPh)(\mu_2\text{-}H)_2(CO)_9]$ (**9**), $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ (**5**) $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$ (**3**) and $[Ru_7(\mu_4\text{-}PPh)_2(CO)_{18}]$ (**7**). $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ and $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ (**4**) could not be separated chromatographically by preparative thin layer chromatography but were readily separated by fractional crystallisation. The yield of the dinuclear species relative to that of the trinuclear species was small for the short duration reactions and yields of $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ (**4**) of up to 25% could be obtained. This compares favourably with previously reported yields of ca. 12% for this species [8,9].

The only product of this reaction which was not detected in the 1/1 reaction, was characterised as $[Ru_3(\mu_3\text{-}PPh)(\mu_2\text{-}H)_2(CO)_9]$ (**9**). This compound, which was eluted ahead of all of the other products, has been reported previously as a product of the

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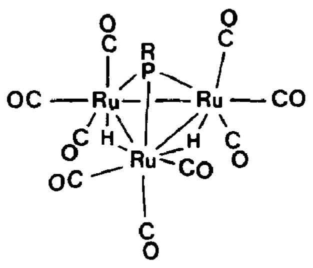
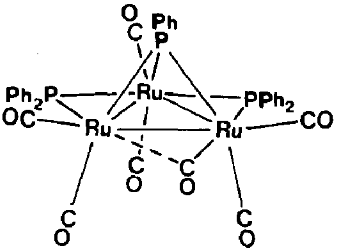
* At the time of the preparation of this paper, a note describing the formation of the partially interstitial phosphide derivative $[Ru_8(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu_2\text{-}PPh_2)(CO)_{21}]$ by thermolysis of $[Ru_3(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(CO)_{10}]$ in toluene under reflux, appeared in print [38].



(9)



(10)

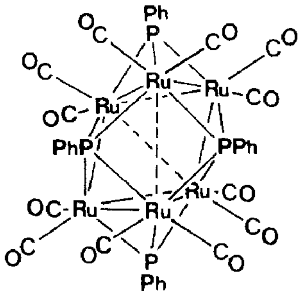
reaction of $[Ru_3(CO)_{12}]$ with phenylphosphine [10–12] and contains a triangular array of ruthenium atoms capped by a phenylphosphinidene group and bridged over two edges by hydride ligands [11,12].

*Reaction of* $[Ru_3(CO)_{12}]$ *with a three-fold molar amount of* $PPh_2H$

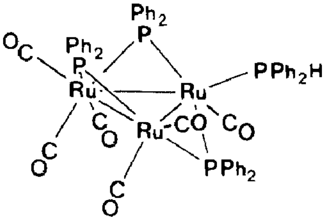
The products, and their relative yields, of the reaction of $[Ru_3(CO)_{12}]$ with a three-fold molar amount of $PPh_2H$ in toluene under reflux were found to be very dependent on the length of the reaction. For a 2 h reaction time essentially three products were found to be formed viz. $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ (**2**), $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ (**4**) and $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (**6**) with the latter being obtained in yields of ca. 75%. As before, $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ (**2**) and $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ (**4**) could not be separated by thin layer chromatography and were thus identified by means of IR and $^{31}P\{^1H\}$ NMR spectroscopy only. With an eight hour reaction time the reaction was considerably more complex, however, and at least fourteen bands could be observed on thin layer chromatographic treatment of the product mixture. Not all of these bands were distinct, but six products could be isolated and identified or characterised. Four of these products correspond with those formed in the 1/1 and 1/2 reactions viz. $[Ru_2(\mu\text{-}PPh_2)(CO)_6]$ (**2**), $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ (**4**), $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (**6**) and $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ (**5**), with compound (**6**) being the major product (yield ca. 20%), but two of them had not been detected in either the 1/1 or the 1/2 reaction.

One of these products was isolated from a purple band which was eluted immediately behind a purple band containing $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ (**5**) and was characterised as the phenylphosphinidene-capped derivative $[Ru_3(\mu_3\text{-}PPh)(\mu_2\text{-}PPh_2)_2(CO)_7]$ (**10**). This compound has been shown to be the major product of the pyrolysis of $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (**6**) and to adopt a structure comprising a near-equilateral triangle of ruthenium atoms capped by a phenylphosphinidene ligand and bridged over two edges by diphenylphosphido groups [39].

The other product of this reaction which was not detected in the 1/1 or the 1/2 reaction was characterised as the hexanuclear species $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$ (**11**). This compound which is obtained in higher yield from the reaction of $[Ru_3(CO)_{12}]$ with phenylphosphine contains an approximate trigonal prismatic array of ruthenium atoms with both triangular faces and two of the square faces being capped by phenylphosphinidene ligands [10,13].



(11)



(12)

The reaction was even more complex for a 22 hour reaction time such that separation of the large number of products formed, particularly in view of their low yields, was virtually impossible. The only compounds that could be separated and identified were $[Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}]$ **(5)**, $[Ru_3(\mu_3\text{-}PPh)(\mu_2\text{-}PPh_2)_2(CO)_7]$ **(10)**, $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$ **(11)** and $[Ru_3(\mu_3\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ **(6)**.

### *Reaction of $[Ru_3(CO)_{12}]$ with a four-fold molar amount of $PPh_2H$*

The reaction mixture obtained by treatment of $[Ru_3(CO)_{12}[$ with a four-fold molar amount of $PPh_2H$ in toluene under reflux for two hours was found to afford essentially three bands, all orange-red in colour, on thin-layer chromatographic treatment using chloroform/light petroleum as the eluting mixture. The first band gave a single product identified as the trinuclear heptacarbonyl species $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ **(6)**.

The second band contained two products, **A** and **B**, which were separated by thin layer chromatography with benzene/light petroleum instead of chloroform/light petroleum as the eluting mixture. The higher yield product **A** was characterised by X-ray crystallography, as well as by conventional methods, as the diphenylphosphine-substituted derivative $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$ **(12)**. The molecular stereochemistry of this species is illustrated in Fig. 4 and selected interatomic distances and angles are given in Table 5. The structure is closely related to that of the parent $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ **(6)**, with a carbonyl from one of the two ruthenium atoms bridged by the hydride ligand having been replaced by the diphenylphosphine. Two features of this structure warrant comment. Firstly, the Ru–Ru distances are overall longer than those for $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ **(6)** and secondly, the Ru–Ru edge bridged by the hydride ligand is shorter than the other two (Ru(1)–Ru(2) 2.793(1); Ru(1)–Ru(3) 3.020(1); Ru(2)–Ru(3) 3.057(1) Å).

The band patterns of the C–O stretching peaks in the solid state and solution IR spectra of product **A** are very similar which is indicative of the solid state structure being retained in solution. However, the $^1H$ NMR spectrum exhibits an apparent doublet of quartets at −16.68 ppm ($J(P'\text{-}H)$ 17.3; $J(P''\text{-}H)$ 9.4 Hz) assigned to the bridging hydride ligand and a doublet of triplets at 6.81 ppm ($J(P'\text{-}H)$ 370.6; $J(P''\text{-}H)$ 7.8 Hz) assigned to the phosphine hydrogen of the coordinated diphenylphosphine, which is more consistent with two of the phosphorus atoms being effectively equivalent. The $^{31}P\{^1H\}$ NMR spectrum measured at 32°C is also

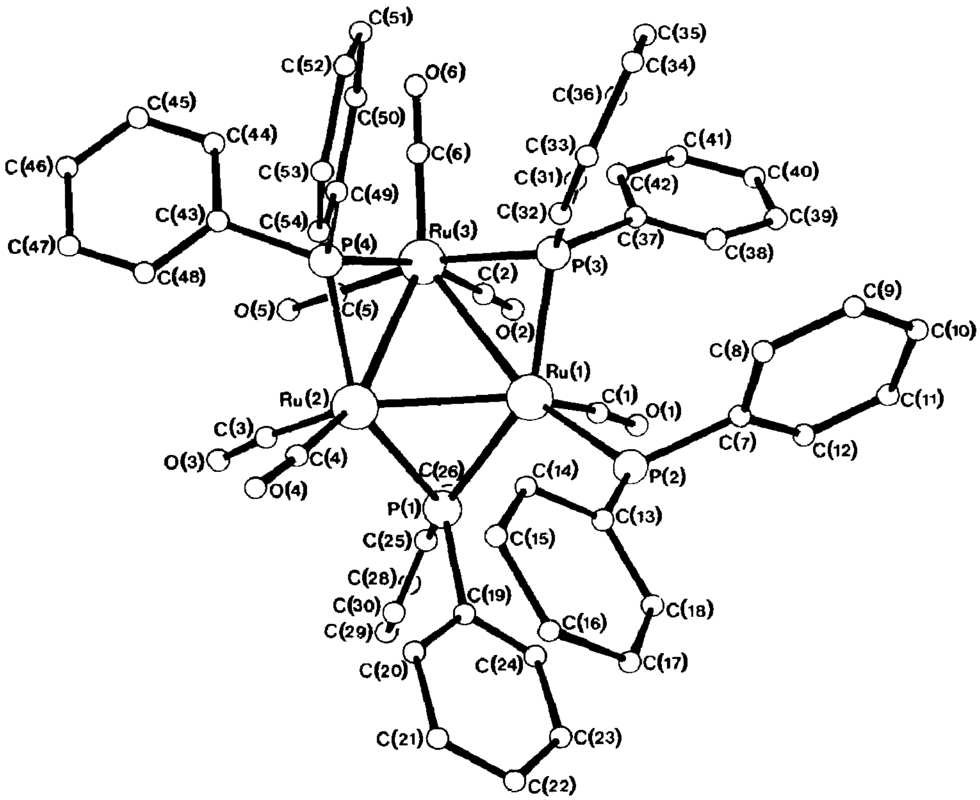


Fig. 4. The molecular stereochemistry of [Ru$_3$($\mu_2$-PPh$_2$)$_3$($\mu_2$-H)(CO)$_6$(PPh$_2$H)] (12).

Table 5

Selected interatomic distances (Å) and angles (°) for [Ru$_3$($\mu_3$-PPh$_2$)$_3$($\mu_2$-H)(CO)$_6$(PPh$_2$H)] with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.793(1) | Ru(1)–Ru(3) | 3.020(1) |
| Ru(2)–Ru(3) | 3.057(1) | Ru(1)–P(1) | 2.315(2) |
| Ru(1)–P(2) | 2.249(2) | Ru(1)–P(3) | 2.327(2) |
| Ru(2)–P(1) | 2.338(2) | Ru(2)–P(4) | 2.322(2) |
| Ru(3)–P(3) | 2.416(2) | Ru(3)–P(4) | 2.385(2) |
| Ru(3)–Ru(1)–Ru(2) | 63.3(1) | P(1)–Ru(1)–Ru(2) | 53.5(1) |
| P(2)–Ru(1)–Ru(2) | 120.5(1) | P(2)–Ru(1)–Ru(3) | 159.0(1) |
| P(2)–Ru(1)–P(1) | 96.1(1) | P(3)–Ru(1)–Ru(2) | 101.5(1) |
| P(3)–Ru(1)–Ru(3) | 51.8(1) | P(3)–Ru(1)–P(1) | 152.0(1) |
| P(3)–Ru(1)–P(2) | 109.0(1) | Ru(3)–Ru(1)–P(1) | 101.2(1) |
| P(1)–Ru(2)–Ru(1) | 52.7(1) | Ru(3)–Ru(2)–Ru(1) | 62.0(1) |
| Ru(3)–Ru(2)–P(1) | 99.6(1) | P(4)–Ru(2)–Ru(1) | 98.6(1) |
| P(4)–Ru(2)–Ru(3) | 50.4(1) | Ru(3)–Ru(2)–P(4) | 50.4(1) |
| P(3)–Ru(3)–Ru(1) | 49.2(1) | P(1)–Ru(2)–P(4) | 148.6(1) |
| Ru(2)–Ru(3)–P(3) | 92.4(1) | Ru(2)–Ru(3)–Ru(1) | 54.7(1) |
| Ru(2)–Ru(3)–P(4) | 48.6(1) | P(4)–Ru(3)–Ru(1) | 91.3(1) |
| Ru(2)–P(1)–Ru(1) | 73.8(1) | P(3)–Ru(3)–P(4) | 97.3(1) |
| Ru(3)–P(4)–Ru(2) | 81.0(1) | Ru(3)–P(3)–Ru(1) | 79.1(1) |

deceptively simple containing two sets of peaks centered at 179.7 and 162.6 ppm respectively corresponding to the bridging diphenylphosphido groups and a set of peaks at 36.52 ppm corresponding to the diphenylphosphine ligand; the latter is split into two broad doublets separated by 366.4 Hz in the coupled spectrum. The set of resonances at 36.52 ppm occurs as a sextet with an apparent symmetrical pattern and with a separation between the two outer peaks of 19 Hz. However, a close examination of these peaks revealed that they are not in fact symmetrically disposed while furthermore, whereas the separation between the outer peaks remains unchanged on lowering the temperature to −90 °C, the frequency values of the other peaks are temperature dependent. A similar temperature dependence was observed for the set of seven peaks at 179.7 ppm and for the set of eight peaks at 162.6 ppm. This $^{31}P\{^1H\}$ NMR spectral evidence is interpreted in terms of product **A** occurring in two closely related isomeric or conformational forms in solution.

The $^{31}P\{^1H\}$ NMR spectrum of product **B** is somewhat more complex and exhibits two, more intense sets of peaks at 157.4 and 12.4 ppm and two, less intense sets of peaks at 21.0 and 16.5 ppm with each of the three sets of peaks at higher field being split into broad doublets in the coupled spectrum. Attempts to isolate crystals of product **B** suitable for an X-ray crystal structure determination proved unsuccessful. In fact, crystallisation of this species always led to a microcrystalline mixture of **A** and **B** or solely crystals of **A** depending on the rate of crystallisation. Furthermore, it was found that both product **B** and product **A** afforded a mixture of each other on dissolution, as established by monitoring by means of $^{31}P\{^1H\}$ NMR spectroscopy. On the basis of this solution behaviour, it is concluded that product **B** is either an isomer of **A** or that the two species are readily interconvertible. The $^{31}P$ NMR spectroscopic data cannot be reconciled in terms of product **B** being a diphenylphosphine-substituted derivative of $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (**6**) however, unless more than one isomer is present in solution.

The third band separated chromatographically gave, in low yield, an oil which could not be crystallised and, as a consequence, could not be characterised.

## Experimental

All reactions and manipulations were carried out under nitrogen by Schlenk tube techniques. Solvents were purified and dried by standard procedures. $[Ru_3(CO)_{12}]$ was synthesised from $RuCl_3 \cdot xH_2O$ by a procedure developed by Mr P. Loveday of the University of Cambridge, while $PPh_2H$ was obtained commercially and used without further purification. Infrared spectra were recorded on Perkin–Elmer 457 and 283 grating spectrometers while $^1H$ and $^{31}P$ NMR spectra were measured on a Varian FT 80A instrument. Light petroleum with a b.p. range of 60–80 °C was used throughout.

### *Reaction of $[Ru_3(CO)_{12}]$ with an equimolar amount of $PPh_2H$*

A solution of $[Ru_3(CO)_{12}]$ (0.52 g, 0.81 mmol) and $PPh_2H$ (0.16 g, 0.86 mmol) in toluene (ca. 50 $cm^3$) was refluxed for 8 to 24 h. The solvent was removed under reduced pressure, the residue dissolved in a minimum of chloroform, and the solution transferred to an alumina column. The column was eluted initially with light petroleum and subsequently with chloroform/light petroleum mixtures of increasing chloroform content *.

The first band eluted from the column, yellow in colour, was shown to contain solely $[Ru_3(CO)_{12}]$. The second band, also yellow in colour, was evaporated to dryness to afford a residue containing $[Ru_4(\mu_2\text{-}H)_4(CO)_{12}]$ (**1**) together with a little $[Ru_3(CO)_{12}]$. The former was separated from the latter by repeated fractional crystallisation from dichloromethane/light petroleum; yield: 8 h reaction time, 4%; 24 h reaction time, < 1%. (Found: C, 19.4; H, 0.8. $C_{12}H_4O_{12}Ru_4$ calcd.: C, 19.4; H, 0.5%).

The solvent from the third band was removed under reduced pressure to give $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ (**2**) as a white microcrystalline solid, which was recrystallised from chloroform/light petroleum; yield: 8 h reaction time, 3%; 24 h reaction time, 4%. (Found: C, 48.1; H, 2.8. $C_{30}H_{20}O_6P_2Ru_2$ calcd.: C, 48.6; H, 2.7%).

The fourth band (pink) and similarly the twelfth (brown) and thirteenth (blood-red) bands afforded residues, each of which appeared to be mixtures of at least two products on removal of the solvent under reduced pressure. The products could not be isolated from any of these residues.

The solution of the fifth band (green) was concentrated and allowed to stand at 0 °C to produce green crystals of $[Ru_5(\mu_4\text{-}PPh)(CO)_{15}]$ (**3**) which were recrystallised by vapour diffusion from dichloromethane/light petroleum; yield: 8 h reaction time, 15%; 24 h reaction time, 12%. (Found: C, 24.5; H, 0.5. $C_{21}H_5O_{15}PRu_5$ calcd.: C, 24.4; H, 0.5%).

The sixth band (yellow-orange) was similarly concentrated and allowed to stand at 0 °C to afford yellow crystals of $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ (**4**) which were recrystallised by vapour diffusion from chloroform/light petroleum; yield: 8 h reaction time, 20%; 24 h reaction time, 8%. (Found: C, 42.3; H, 2.2. $C_{32}H_{22}O_8P_2Ru_3$ calcd.: C, 42.7; H, 2.4%).

The seventh band (purple) was also concentrated and allowed to stand at 0 °C. The purple crystals of $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ (**5**) which separated were recrystallized by vapour diffusion from dichloromethane/light petroleum; yield: 8 h reaction time, 8%; 24 h reaction time, 7%. (Found: C, 29.6; H, 1.3. $C_{23}H_{10}O_{11}P_2Ru_4$ calcd.: C, 29.7; H, 1.1%).

The solvent from the eighth band (orange-red) was removed under reduced pressure to afford $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (**6**) as a deep red microcrystalline solid. The compound was recrystallised from chloroform/light petroleum; yield: 8 h reaction time, 20%; 24 h reaction time, 10%. (Found: C, 48.3; H, 3.0. $C_{43}H_{31}O_7P_3Ru_3$ calcd.: C, 48.9; H, 2.9%).

The solution of the ninth band was evaporated to dryness to afford a residue which on crystallisation from dichloromethane/light petroleum gave red-brown microcrystalline material. Attempts to isolate this species as crystals for an X-ray crystal structure determination were unsuccessful. $\nu$(CO): 2070m, 2050w, 2038s, 2020vs, 2008m and 1980m $cm^{-1}$, in light petroleum. $^1H$ NMR (measured in $CD_2Cl_2$

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* A better separation was achieved by first extracting the residue with light petroleum, transferring this solution to an alumina column and eluting the column as above. The residue remaining after the light petroleum extraction was extracted in turn with chloroform, this extract transferred to a second alumina column and the column again eluted as above. The order of elution of the products was the same.

at 32°C; $\delta$ scale relative to $SiMe_4$): 7.36 (m, $C_6H_5$), −13.88 ppm (d of d, Ru–H–Ru). $^{31}P\{^1H\}$ NMR (measured in $CD_2Cl_2$ at 32°C; $\delta$ scale relative to $H_3PO_4$): 214.0d, 168.3s, 59.2m ppm.

The solvent from the tenth band (green) was removed under reduced pressure to give $[Ru_7(\mu_4\text{-PPh})_2(CO)_{18}]$ (7) as a microcrystalline solid which was recrystallised by vapour diffusion from dichloromethane/light petroleum; yield: 8 h reaction time, 3%; 24 h reaction time, 5%. (Found: C, 25.6; H, 1.0. $C_{30}H_{10}O_{18}P_2Ru_7$ calcd.: C, 25.2; H, 0.7%).

The eleventh band was evaporated to dryness to afford a green microcrystalline solid. This was recrystallised from chloroform/light petroleum. These crystals were unsuitable for X-ray diffraction studies and no suitable ones could be obtained. $\nu$(CO): 2070m, 2028vs, 2023sh, 2008s, 1982w, 1958m cm$^{-1}$, in cyclohexane. $^1H$ NMR (measured in $CD_2Cl_2$ at 32°C; $\delta$ scale relative to $SiMe_4$): 7.2 ppm (m, $C_6H_5$). $^{31}P\{^1H\}$ NMR (measured in $CD_2Cl_2$ at 32°C; $\delta$ scale relative to $H_3PO_4$): 448.9s ppm.

The fourteenth band (blue), which was observed intermittently, was evaporated to dryness to give a residue which afforded blue crystals of $[Ru_8(\mu_8\text{-P})(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2Ph)(\mu_2\text{-CO})_2(CO)_{17}]$ (**8**) on crystallisation from dichloromethane/light petroleum; yield: 8 h reaction time, not detected; 24 h reaction time, < 2%.

### *Reaction of $[Ru_3(CO)_{12}]$ with a twice molar amount of $PPh_2H$*

A solution of $[Ru_3(CO)_{12}]$ (1.0 g, 1.56 mmol) and $PPh_2H$ (0.60 g, 3.2 mmol) in toluene (ca. 100 cm$^3$) was refluxed for 2 to 8 h. The solvent was removed under reduced pressure and the residue dissolved in a minimum of chloroform and transferred to thin layer plates (silica). Nine distinct bands were obtained on elution with chloroform/light petroleum (1/5). The products isolated from these bands in order of their elution, and their relative yields were as follows:

Band 1; yellow; $[Ru_3(CO)_{12}]$.

Band 2; yellow; $[Ru_3(\mu_3\text{-PPh})(\mu\text{-H})_2(CO)_9]$ (**9**). This compound which was not detected in the 1/1 reaction, was crystallised from light petroleum: yield: 2 h reaction time, 2%; 8 h reaction time, < 1%. (Found: C, 26.8; H, 1.02. $C_{15}H_7O_9PRu_3$ calcd.: C, 27.1; H, 1.05%)

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

Band 4; $[Ru_5(\mu_4\text{-PPh})(CO)_{15}]$ (**3**); yield: 2 h reaction time, 15%; 8 h reaction time, 5%.

Band 5; yellow-orange; $[Ru_2(\mu\text{-PPh}_2)_2(CO)_6]$ (**2**)/$[Ru_3(\mu_2\text{-PPh}_2)_2(\mu_2\text{-H})_2(CO)_8]$ (**4**). These two compounds could be separated by fractional crystallisation from chloroform/light petroleum; yield, $[Ru_2(\mu\text{-PPh}_2)_2(CO)_6]$: 2 h reaction time ca. 5%; 8 h reaction time, ca. 10%; $[Ru_3(\mu_2\text{-PPh}_2)_2(\mu_2\text{-H})_2(CO)_8]$: 2 h reaction time, ca. 25%; 8 h reaction time, ca. 5%.

Band 6; purple; $[Ru_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(CO)_{10}]$ (**5**); yield: 2 h reaction time, 8%; 8 h reaction time, 5%.

Band 7; green; $[Ru_7(\mu_4\text{-PPh})_2(CO)_{18}]$ (**7**); yield: 2 h reaction time, 2%; 8 h reaction time 2%.

Band 8; orange-red; $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu_2\text{-H})(CO)_7]$ (**6**); yield: 2 h reaction time, 20%; 8 h reaction time, 10%.

Band 9; brown-purple. It was apparent that this band contained at least two products and because of their low yields they were not investigated further.

*Reaction of $[Ru_3(CO)_{12}]$ with a three-fold molar amount of $PPh_2H$*

A solution of $[Ru_3(CO)_{12}]$ (0.82 g, 1.28 mmol) and $PPh_2H$ (0.74 g, 4.0 mmol) in toluene (ca. 100 $cm^3$) was refluxed for 2 to 8 h. The solvent was removed under reduced pressure and the residue dissolved in a minimum of chloroform and transferred to thin layer plates (silica). At least fourteen bands were produced on elution with chloroform/light petroleum (1/5), but only 8 of these were distinct and could be separated. The products isolated from these bands, in order of their elution, and their relative yields were as follows:

Band 1; yellow; $[Ru_3(CO)_{12}]$.

Band 2; yellow-orange; $[Ru(\mu_2\text{-}PPh_2)_2(CO)_6]$ (**2**)/$[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ (**4**); yield, $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$: 2 h reaction time, ca. 3%; 8 h reaction time, ca. 8%; $[Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$: 2 h reaction time, ca. 15%; 8 h reaction time, ca. 2%.

Band 3; purple; $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ (**5**); yield: 2 h reaction time, not detected; 8 h reaction time, 5%.

Band 4; purple. The residue isolated from this band was crystallised from chloroform/light petroleum to afford purple crystals of $[Ru_3(\mu_3\text{-}PPh)(\mu_2\text{-}PPh_2)_2(CO)_7]$; yield: 2 h reaction time, not detected; 8 h reaction time, 8%. (Found: C, 45.1; H, 3.1. $C_{37}H_{25}O_7P_3Ru_3$ calcd.: C, 45.4; H, 2.6%).

Band 5; brown. This band overlapped to a small extent with band 6 and was purified by means of thin layer chromatography using benzene/light petroleum (1/5) as the eluent. The product isolated from the purified band was crystallised from chloroform/light petroleum to give brown crystals of $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh_2)_2(CO)_{12}]$ (**11**); yield: 2 h reaction time, not detected; 8 h reaction time, < 1%. (Found: C, 31.2; H, 1.9. $C_{36}H_{20}O_{12}P_4Ru_6$ calcd.: C, 31.4; H, 1.4%).

Band 6; red-orange; $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (**6**); yield: 2 hour reaction time, 75%; 8 hour reaction time, 20%.

Band 7; brown and Band 8; red. Both of these bands contained at least two products and because of their low yields they were not investigated further.

*Reaction of $[Ru_3(CO)_{12}]$ with a four-fold molar amount of $PPh_2H$*

A solution of $[Ru_3(CO)_{12}]$ (0.50 g, 0.78 mmol) and $PPh_2H$ (0.59 g, 3.2 mmol) in toluene (ca. 50 $cm^3$) was refluxed for 2 h. The solvent was removed under reduced pressure and the residue dissolved in a minimum of chloroform and transferred to thin layer plates (silica). Three bands were produced on elution with chloroform/light petroleum (1/5).

Band 1; The product isolated from this band was identified as $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (**6**); yield: 45%.

Band 2; The residue isolated from this band was redissolved in a minimum of chloroform and transferred to thin layer plates (silica). Elution with benzene/light petroleum (1/2) gave two bands, both red-orange in colour. The residue from the first band A was crystallised from chloroform/light petroleum to give red-orange crystals of a compound characterised as $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$ (**12**); yield: 20%. (Found: C, 54.6; H, 3.8. $C_{54}H_{42}O_6P_4Ru_3$ calcd.: C, 53.4; H, 3.5%). The solvent from the second band was removed under reduced pressure to afford a microcrystalline solid which is proposed to be an isomer of $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$; yield: 10%. (Found: C, 51.4; H, 4.7). $\nu(CO)$: 2050w, 2025m, 2015s, 1997m, 1977w, 1957m, 1942w $cm^{-1}$, in cyclohexane. $^1H$ NMR (measured in $CD_2Cl_2$ at 32°C; $\delta$ scale relative to $SiMe_4$): 7.71 (d of t of d, $PPh_2H$, $J(P'\text{-}H)$ 351.7, $J(P''\text{-}H)$ 7.8, $J(P'''\text{-}H)$ ca. 2 Hz), 7.09 (m, $C_6H_5$), −16.79 pm (q of d, Ru–$H$–Ru, $J(P'\text{-}H)$ 16.3, $J(P''\text{-}H)$ 1.9 Hz). $^{31}P\{^1H\}$ NMR (measured in $CD_2Cl_2$ at 32°C $\delta$ scale relative to $H_3PO_4$): 157.4 (m), 21.0 (m), 16.5 (m), 12.4 ppm (m). Band 3; Removal of the solvent of this band under reduced pressure gave an oil which could not be crystallised.

### *Crystal structure determinations* *

*(i) $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ (2).* Crystal data. $C_{30}H_{20}O_6P_2Ru_2$, $M = 740.57$, colourless crystal of dimensions $0.05 \times 0.50 \times 0.37$ mm grown from chloroform/light petroleum, triclinic, space group $P\bar{1}$, $a$ 10.200(2), $b$ 16.217(3), $c$ 21.682(4) Å, $\alpha$ 88.48(4), $\beta$ 77.54(4), $\gamma$ 80.34(4)°, $U$ 3452.2 $Å^3$, $Z = 4$, $D_c$ 1.425 g $cm^{-3}$, $\mu(Mo\text{-}K_\alpha)$ 9.84 $cm^{-1}$, $F(000) = 1464$.

Intensity data were collected on a Nonius CAD-4 diffractometer using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda$ 0.71069 Å). A least-squares fit of high-angle reflections ($\theta > 12°$) was used to obtain accurate cell constants. Diffraction intensities were measured in the range $3 \leq 2\theta \leq 50°$ using the $\omega\text{-}2\theta$ scan technique, with background counts made for half the total scan time on each side of the peak. Three standard reflections, measured every hour, showed no decrease in intensity during data collection. Lorentz and polarisation as well as empirical absorption corrections were made. Of the 11329 unique reflections measured, 9753 were classed as observed ($I > 3\sigma(I)$) and these were used for the solution and refinement of the structure.

The four ruthenium atoms in the asymmetric unit were located from a Patterson map calculated using the program SHELX [40]. 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, the carbonyl carbon and oxygen atoms individual isotropic temperature factors and the phenyl carbon atoms a single averaged (but variable) isotropic temperature factor. The phenyl rings were defined as rigid groups with idealised geometry (C–C–C angles = 120°; C–C distances = 1.395 Å). A final full-matrix least-squares refinement (225 variables) using weights $\omega = 1/[\sigma^2(F) + 0.04F^2]$ ($\sigma(F)$ from counting statistics) converged at $R = 0.098$, $R_\omega = 0.119$. Hydrogen atoms were not located. There were no significant features in the final difference Fourier. Fractional atomic coordinates are listed in Table 6.

*(ii) $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7]$ (6).* Crystal data. $C_{43}H_{31}O_7P_3Ru_3$, $M = 1055.80$, yellow-green crystal of dimensions $0.20 \times 0.30 \times 0.60$ mm grown by vapour diffusion from chloroform/light petroleum solution, monoclinic, space group $P2_1/c$, $a$ 21.580(10), $b$ 11.947(8), $c$ 20.102(10) Å, $\beta$ 112.8(2)°, $U$ 4776.6 $Å^3$, $D_c$ 1.468 g $cm^{-3}$, $Z = 4$, $\mu(Mo\text{-}K_\alpha)$ 10.6 $cm^{-1}$ $F(000) = 522$.

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* For all structures, complete tables of temperature factors and interatomic distances and angles as well as lists of observed and calculated structure factors are available from the authors.

Table 6

Fractional atomic coordinates ($\times 10^4$) for $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ with estimated standard deviations in parentheses

| Molecule A | | | | Molecule B | | | |
|---|---|---|---|---|---|---|---|
| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
| Ru(1A) | 7365(1) | 1846(1) | 7364(0) | Ru(1B) | 7749(1) | 3116(1) | 2085(0) |
| Ru(2A) | 6669(1) | 3461(1) | 7906(0) | Ru(2B) | 8026(1) | 1429(0) | 2467(0) |
| P(1A) | 6346(3) | 3073(2) | 6921(1) | P(1B) | 8261(3) | 2591(2) | 3041(1) |
| P(2A) | 5510(3) | 2325(2) | 8187(1) | P(2B) | 9596(3) | 2045(2) | 1715(1) |
| O(1A) | 82(12) | 1923(7) | 6469(6) | O(1B) | 4819(12) | 3826(7) | 2759(6) |
| O(2A) | 8943(11) | 824(7) | 8242(5) | O(2B) | 6731(11) | 3144(7) | 859(5) |
| O(3A) | 6503(13) | 389(8) | 6854(6) | O(3B) | 8929(11) | 4721(7) | 1926(5) |
| O(4A) | 4529(12) | 4970(8) | 8366(6) | O(4B) | 9678(13) | 15(8) | 3040(6) |
| O(5A) | 7844(12) | 3283(8) | 9104(6) | O(5B) | 7248(12) | 487(7) | 1425(6) |
| O(6A) | 9040(12) | 4333(7) | 7251(6) | O(6B) | 5197(13) | 1348(8) | 3295(6) |
| C(1A) | 9073(14) | 1901(8) | 6799(7) | C(1B) | 5892(14) | 3598(9) | 2509(7) |
| C(2A) | 8314(12) | 1232(8) | 7945(6) | C(2B) | 7181(13) | 3096(8) | 1275(6) |
| C(3A) | 6825(14) | 938(9) | 7037(7) | C(3B) | 8471(13) | 4105(8) | 1977(6) |
| C(4A) | 5355(12) | 4395(8) | 8164(6) | C(4B) | 9012(11) | 546(7) | 2816(5) |
| C(5A) | 7468(12) | 3288(7) | 8627(6) | C(5B) | 7542(12) | 814(8) | 1777(6) |
| C(6A) | 8128(13) | 4022(8) | 7485(6) | C(6B) | 6243(12) | 1385(7) | 2988(6) |
| C(7A) | 7300(10) | 3501(5) | 6208(3) | C(7B) | 7044(9) | 2917(5) | 3751(4) |
| C(8A) | 7994(10) | 2975(5) | 5701(3) | C(8B) | 6547(9) | 3770(5) | 3847(4) |
| C(9A) | 8658(10) | 3312(5) | 5145(3) | C(9B) | 5561(9) | 4046(5) | 4386(4) |
| C(10A) | 8627(10) | 4174(5) | 5095(3) | C(10B) | 5071(9) | 3470(5) | 4828(4) |
| C(11A) | 7933(10) | 4700(5) | 5602(3) | C(11B) | 5569(9) | 2618(5) | 4733(4) |
| C(12A) | 7269(10) | 4364(5) | 6158(3) | C(12B) | 6555(9) | 2341(5) | 4194(4) |
| C(13A) | 4670(7) | 3198(5) | 6725(4) | C(13B) | −193(8) | 2714(6) | 3323(5) |
| C(14A) | 4279(7) | 2522(5) | 6467(4) | C(14B) | 262(8) | 3483(6) | 3263(5) |
| C(15A) | 3032(7) | 2620(5) | 6285(4) | C(15B) | 1436(8) | 3576(6) | 3468(5) |
| C(16A) | 2175(7) | 3394(5) | 6361(4) | C(16B) | 2155(8) | 2900(6) | 3732(5) |
| C(17A) | 2565(7) | 4069(5) | 6619(4) | C(17B) | 1700(8) | 2131(6) | 3791(5) |
| C(18A) | 3812(7) | 3971(5) | 6801(4) | C(18B) | 526(8) | 2038(6) | 3587(5) |
| C(19A) | 3766(6) | 2327(5) | 8090(5) | C(19B) | 1310(7) | 2061(6) | 1799(5) |
| C(20A) | 2822(6) | 3066(5) | 8197(5) | C(20B) | 1871(7) | 2790(6) | 1666(5) |
| C(21A) | 1488(6) | 3073(5) | 8134(5) | C(21B) | 3223(7) | 2792(6) | 1697(5) |
| C(22A) | 1096(6) | 2342(5) | 7965(5) | C(22B) | 4013(7) | 2066(6) | 1861(5) |
| C(23A) | 2039(6) | 1603(5) | 7858(5) | C(23B) | 3452(7) | 1337(6) | 1993(5) |
| C(24A) | 3374(6) | 1596(5) | 7921(5) | C(24B) | 2100(7) | 1334(6) | 1962(5) |
| C(25A) | 5379(19) | 1881(12) | 8949(6) | C(25B) | 60(13) | 1754(8) | 926(4) |
| C(26A) | 4930(19) | 2422(12) | 9496(6) | C(26B) | 28(13) | 2361(8) | 458(4) |
| C(27A) | 4870(19) | 2110(12) | 79(6) | C(27B) | 428(13) | 2126(8) | −177(4) |
| C(28A) | 5260(19) | 1256(12) | 168(6) | C(28B) | 860(13) | 1284(8) | −346(4) |
| C(29A) | 5709(19) | 715(12) | 9648(6) | C(29B) | 891(13) | 677(8) | 121(4) |
| C(30A) | 5769(19) | 1027(12) | 9039(6) | C(30B) | 491(13) | 913(8) | 757(4) |

Intensity data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ 0.71069 Å). A least-squares fit of high angle reflections ($\theta > 12°$) was used to obtain accurate cell constants. Diffraction intensities were measured in the range $6 \leq 2\theta \leq 46°$ using the $\omega$–$2\theta$ scan technique, with background counts made for half the total scan time on each side of the peak. Three standard reflections, measured every hour, showed no

Table 7. Fractional atomic coordinates ($\times 10^4$) for [$Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7$] with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ru(1) | 2686(1) | 2634(1) | −204(1) |
| Ru(2) | 1638(1) | 1424(1) | 67(1) |
| Ru(3) | 2833(1) | 2427(1) | 1228(1) |
| P(1) | 1443(2) | 3020(3) | −616(2) |
| P(2) | 3704(2) | 2153(3) | 731(2) |
| P(3) | 2381(2) | 542(3) | 1046(2) |
| O(1) | 3193(7) | 4974(12) | −293(7) |
| O(2) | 3019(7) | 2092(13) | −1403(8) |
| O(3) | 922(7) | −456(13) | −865(8) |
| O(4) | 306(7) | 1588(12) | 392(7) |
| O(5) | 2893(7) | 4986(12) | 1049(7) |
| O(6) | 3972(7) | 2141(11) | 2635(7) |
| O(7) | 1564(7) | 3005(12) | 1627(8) |
| C(1) | 2995(8) | 4068(13) | −260(8) |
| C(2) | 2872(9) | 2327(16) | −940(10) |
| C(3) | 1188(8) | 309(14) | −519(9) |
| C(4) | 820(8) | 1512(13) | 269(8) |
| C(5) | 2907(9) | 4013(15) | 1105(9) |
| C(6) | 3522(8) | 2255(15) | 2106(9) |
| C(7) | 2033(9) | 2744(14) | 1458(9) |
| C(8) | 876(5) | 2952(10) | −1474(5) |
| C(9) | 991(5) | 2069(10) | −1865(5) |
| C(10) | 560(5) | 1900(10) | −2583(5) |
| C(11) | 15(5) | 2614(10) | −2909(5) |
| C(12) | −101(5) | 3497(10) | −2518(5) |
| C(13) | 330(5) | 3666(10) | −1800(5) |
| C(14) | 1236(6) | 4390(8) | −348(6) |
| C(15) | 1409(6) | 5349(8) | −633(6) |
| C(16) | 1310(6) | 6405(8) | −395(6) |
| C(17) | 1038(6) | 6502(8) | 128(6) |
| C(18) | 865(6) | 5543(8) | 414(6) |
| C(19) | 964(6) | 4487(8) | 176(6) |
| C(20) | 4271(5) | 874(8) | 870(6) |
| C(21) | 4082(5) | 77(8) | 319(6) |
| C(22) | 4494(5) | −844(8) | 368(6) |
| C(23) | 5096(5) | −969(8) | 967(6) |
| C(24) | 5285(5) | −173(8) | 1518(6) |
| C(25) | 4873(5) | 749(8) | 1469(6) |
| C(26) | 4455(5) | 3210(8) | 946(6) |
| C(27) | 4600(5) | 3977(8) | 1509(6) |
| C(28) | 5116(5) | 4755(8) | 1639(6) |
| C(29) | 5487(5) | 4765(8) | 1205(6) |
| C(30) | 5343(5) | 3998(8) | 642(6) |
| C(31) | 4827(5) | 3220(8) | 512(6) |
| C(32) | 1896(6) | 60(10) | 1570(6) |
| C(33) | 1329(6) | −625(10) | 1301(6) |
| C(34) | 990(6) | −923(10) | 1740(6) |
| C(35) | 1218(6) | −536(10) | 2450(6) |
| C(36) | 1785(6) | 149(10) | 2720(6) |
| C(37) | 2124(6) | 447(10) | 2280(6) |
| C(38) | 2932(5) | −696(8) | 1093(6) |
| C(39) | 2719(5) | −1447(8) | 517(6) |
| C(40) | 3085(5) | −2422(8) | 549(6) |
| C(41) | 3665(5) | −2645(8) | 1158(6) |
| C(42) | 3879(5) | −1893(8) | 1734(6) |
| C(43) | 3512(5) | −919(8) | 1702(6) |

decrease in intensity during data collection. Lorentz and polarisation, but no absorption corrections, were made. Of the 8289 unique reflections measured, 6941 were classed as observed ($I > 3\sigma(I)$) and these were used for the solution and refinement of the structure.

The three ruthenium atoms were located from a Patterson map calculated using the program SHELX [40]. All the remaining non-hydrogen atoms were located from a Fourier synthesis phased on the ruthenium atoms. A full-matrix least-squares refinement was performed with anisotropic ruthenium and phosphorus atoms and isotropic carbon and oxygen atoms, the phenyl rings being treated as rigid groups with idealised geometry (see (i) above). Using unit weights convergence was reached at a final conventional $R$ factor of 0.102. There were no significant features in the final difference Fourier and the H atoms were not located. Fractional atomic coordinates are listed in Table 7.

*(iii)* $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2Ph)(\mu_2\text{-}CO)_2(CO)_{17}] \cdot CH_2Cl_2$ *(8)*. Crystal data. $C_{26}H_7O_{19}PRu_8 \cdot CH_2Cl_2$, blue crystals of dimensions 0.07 × 0.12 × 0.25 mm grown from dichloromethane/light petroleum, $M = 1547.81$, orthorhombic, space group $Pca2_1$, $a$ 23.234(4), $b$ 10.515(2), $c$ 31.144(5) Å, $U = 7608.6$ Å$^3$, $D_c$ 2.702 g cm$^{-3}$, $Z = 8$, $\mu$(Mo-$K_\alpha$) 32.6 cm$^{-1}$, $F(000) = 5792$.

Intensity data were collected as described in (i) above. Lorentz and polarisation as well as empirical absorption corrections were made. Of the 6822 unique reflections measured, 4391 were classed as observed ($I > 1.5\sigma(I)$) and these were used for the solution and refinement of the structure. The structure was solved by direct methods (SHELX-86 [41]) and refined by full-matrix least-squares methods (554 variables, using SHELXTL [42]) to $R = 0.091$ and $R_\omega = 0.082$. The weighting scheme was $\omega = 1/[\sigma^2(F) + 0.001F^2]$ ($\sigma(F)$ from counting statistics). The ruthenium, phosphorus and solvent carbon and chlorine atoms were assigned anisotropic temperature factors, and the remaining carbon and oxygen atoms individual isotropic temperature factors. The hydrogen atoms were not located. The Rogers $\eta$-parameter refined to zero with a large e.s.d., indicating racemic twinning such that the determination of the absolute configuration was not possible. There were no significant features in the final difference Fourier. Fractional atomic coordinates are listed in Table 8.

*(iv)* $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$ *(12)*. Crystal data. $C_{54}H_{42}O_6P_4Ru_3$, $M = 1213.97$, triclinic, space group $P\bar{1}$, $a$ 12.228(2), $b$ 13.608(2), $c$ 15.377(3) Å, $\alpha$ 87.4(2), $\beta$ 89.1(2), $\gamma$ 86.2(2)°, $U$ 2550.2 Å$^3$, $D_c$ 1.581 g cm$^{-3}$, $Z = 2$, $\mu$(Mo-$K_\alpha$) 10.3 cm$^{-1}$, $F(000) = 1212$.

Intensity data were collected as described in (i) above. Lorentz and polarisation as well as empirical absorption corrections were made. Of the 8280 unique reflections measured 7062 were classed as observed ($I > 3\sigma(I)$) and these were used for the solution and refinement of the structure. Solution of the Patterson function and subsequent Fourier syntheses allowed the location of all the non-hydrogen atoms. With anisotropic temperature factors for the ruthenium and phosphorus atoms, isotropic temperature factors for the carbonyl atoms, and averaged (but variable) isotropic temperature factors for the carbon atoms of each phenyl ring, a full-matrix least-squares refinement (169 variables, using SHELX [40]) converged at $R = 0.066$ and $R_w = 0.079$. The weighting scheme was $3.12/[\sigma^2(F) + 0.0007F^2]$ ($\sigma(F)$ from counting statistics). The hydrogen atoms were not located. There were no significant features in the final difference Fourier. Fractional atomic coordinates are listed in Table 9.

Table 8

Fractional atomic coordinates for $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2Ph)(\mu_2\text{-}CO)_2(CO)_{17}]\cdot CH_2Cl_2$ with estimated standard deviations in parentheses

| Molecule **A** | | | | Molecule **B** | | | |
|---|---|---|---|---|---|---|---|
| Atom | *x/a* | *y/b* | *z/c* | Atom | *x/a* | *y/b* | *z/c* |
| Ru(1A) | 0.1576(2) | 0.9517(3) | 0.4632(1) | Ru(1B) | 0.5839(2) | 0.4307(3) | 0.1946(1) |
| Ru(2A) | 0.2309(2) | 1.0604(3) | 0.5262(1) | Ru(2B) | 0.5027(2) | 0.5302(3) | 0.1353(1) |
| Ru(3A) | 0.3279(2) | 0.9554(4) | 0.4757(2) | Ru(3B) | 0.4118(2) | 0.4278(4) | 0.1911(2) |
| Ru(4A) | 0.2502(2) | 0.8478(3) | 0.4142(2) | Ru(4B) | 0.4960(2) | 0.3263(3) | 0.2486(1) |
| Ru(5A) | 0.1744(2) | 1.2185(3) | 0.4624(2) | Ru(5B) | 0.8649(2) | 0.6958(3) | 0.1941(2) |
| Ru(6A) | 0.3003(2) | 1.2291(3) | 0.4758(2) | Ru(6B) | 0.4379(2) | 0.7019(4) | 0.1877(2) |
| Ru(7A) | 0.3128(2) | 1.0921(3) | 0.3949(1) | Ru(7B) | 0.4328(2) | 0.5695(3) | 0.2697(1) |
| Ru(8A) | 0.1884(2) | 1.0606(3) | 0.3837(1) | Ru(8B) | 0.8588(2) | 0.5422(3) | 0.2748(1) |
| P(A) | 0.2433(5) | 1.0536(10) | 0.4485(4) | P(B) | 0.4991(5) | 0.5292(8) | 0.2119(4) |
| C(11A) | 0.1550(10) | 0.7606(24) | 0.4919(9) | C(11B) | 0.5844(12) | 0.2352(28) | 0.1686(10) |
| C(12A) | 0.1480(10) | 0.7480(24) | 0.4476(9) | C(12B) | 0.5954(12) | 0.2303(28) | 0.2126(10) |
| C(13A) | 0.1031(10) | 0.8112(24) | 0.4269(9) | C(13B) | 0.6413(12) | 0.2985(28) | 0.2299(10) |
| C(14A) | 0.0652(10) | 0.8870(24) | 0.4504(9) | C(14B) | 0.6763(12) | 0.3718(28) | 0.2032(10) |
| C(15A) | 0.0722(10) | 0.8994(24) | 0.4947(9) | C(15B) | 0.6654(12) | 0.3767(28) | 0.1592(10) |
| C(16A) | 0.1171(10) | 0.8363(24) | 0.5155(9) | C(16B) | 0.6195(12) | 0.3085(28) | 0.1419(10) |
| C(21A) | 0.2737(25) | 1.1230(55) | 0.5695(19) | C(21B) | 0.4507(20) | 0.5844(43) | 0.0936(15) |
| O(21A) | 0.3043(16) | 1.1660(37) | 0.5993(13) | O(21B) | 0.4114(16) | 0.6205(36) | 0.0697(12) |
| C(22A) | 0.1620(17) | 1.1100(38) | 0.5516(13) | C(22B) | 0.5019(23) | 0.3752(47) | 0.1067(17) |
| O(22A) | 0.1180(16) | 1.1252(35) | 0.5653(12) | O(22B) | 0.4963(17) | 0.2768(35) | 0.0897(13) |
| C(23A) | 0.2374(17) | 0.9055(38) | 0.5515(14) | C(23B) | 0.5667(22) | 0.5883(45) | 0.0987(16) |
| O(23A) | 0.2399(16) | 0.8139(33) | 0.5749(12) | O(23B) | 0.6091(20) | 0.6160(41) | 0.0845(15) |
| C(31A) | 0.3578(26) | 0.9075(58) | 0.5278(21) | C(31B) | 0.3720(18) | 0.4002(41) | 0.1381(18) |
| O(31A) | 0.3862(16) | 0.8945(35) | 0.5605(12) | O(31B) | 0.3441(17) | 0.3748(38) | 0.1120(14) |
| C(32A) | 0.3905(19) | 0.8970(40) | 0.4460(14) | C(32B) | 0.3483(25) | 0.3635(51) | 0.2236(19) |
| O(32A) | 0.4318(15) | 0.8485(35) | 0.4279(12) | O(32B) | 0.3108(21) | 0.3177(47) | 0.2450(18) |
| C(33A) | 0.2955(13) | 0.7693(28) | 0.4675(10) | C(33B) | 0.4522(15) | 0.2563(32) | 0.1987(12) |
| O(33A) | 0.2924(15) | 0.6827(33) | 0.4885(12) | O(33B) | 0.4507(14) | 0.1509(33) | 0.1761(11) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(41A) | 0.2990(22) | 0.7447(48) | 0.3833(18) | C(41B) | 0.4513(27) | 0.2102(57) | 0.2837(20) |
| O(41A) | 0.3278(15) | 0.6758(34) | 0.3610(12) | O(41B) | 0.4257(18) | 0.1590(39) | 0.3060(14) |
| C(42A) | 0.1995(20) | 0.8796(42) | 0.3031(15) | C(42B) | 0.5486(16) | 0.3601(35) | 0.3020(12) |
| O(42A) | 0.1859(14) | 0.8298(30) | 0.3284(11) | O(42B) | 0.5682(14) | 0.3070(31) | 0.3286(12) |
| C(43A) | 0.1916(19) | 0.6865(42) | 0.4202(15) | C(43B) | 0.5507(19) | 0.1622(41) | 0.2394(15) |
| C(51A) | 0.1696(21) | 1.3048(45) | 0.4116(17) | C(51B) | 0.5652(17) | 0.8435(37) | 0.1595(14) |
| O(51A) | 0.1756(16) | 1.3853(36) | 0.3837(13) | O(51B) | 0.5703(17) | 0.9266(38) | 0.1359(14) |
| C(52A) | 0.0940(15) | 0.1892(33) | 0.4657(13) | C(52B) | 0.6485(17) | 0.6685(39) | 0.1915(15) |
| O(52A) | 0.0448(15) | 1.1827(33) | 0.4676(13) | O(52B) | 0.6952(13) | 0.6691(28) | 0.1875(10) |
| C(53A) | 0.1690(19) | 1.3670(41) | 0.4957(15) | C(53B) | 0.5675(22) | 0.7940(46) | 0.2436(19) |
| O(53A) | 0.1647(14) | 1.4585(32) | 0.5147(11) | O(53B) | 0.5735(13) | 0.8665(29) | 0.2698(11) |
| C(61A) | 0.2875(19) | 1.3562(42) | 0.5201(15) | C(61B) | 0.4437(18) | 0.0864(42) | 0.1415(15) |
| O(61A) | 0.2817(18) | 1.4278(40) | 0.5468(14) | O(61B) | 0.4454(14) | 0.8899(29) | 0.1131(11) |
| C(62A) | 0.3156(18) | 0.3682(38) | 0.4392(14) | C(62B) | 0.4294(24) | 0.8521(48) | 0.2218(18) |
| O(62A) | 0.3279(16) | 1.4610(35) | 0.4228(12) | O(62B) | 0.4206(17) | 0.9392(35) | 0.2406(13) |
| C(63A) | 0.3777(17) | 1.1832(37) | 0.4894(13) | C(63B) | 0.3525(40) | 0.6787(93) | 0.1676(33) |
| O(63A) | 0.4248(16) | 1.1966(35) | 0.5046(13) | O(63B) | 0.3106(16) | 0.6720(37) | 0.1721(13) |
| C(71A) | 0.3256(20) | 0.9883(41) | 0.3482(15) | C(71B) | 0.4311(19) | 0.4719(39) | 0.3189(15) |
| O(71A) | 0.3270(17) | 0.9387(37) | 0.3101(14) | O(71B) | 0.4292(13) | 0.4200(29) | 0.3513(11) |
| C(72A) | 0.3052(16) | 1.2338(35) | 0.3606(13) | C(72B) | 0.3511(24) | 0.5968(51) | 0.2662(19) |
| O(72A) | 0.3002(15) | 1.3281(34) | 0.3419(12) | O(72B) | 0.3028(13) | 0.6165(29) | 0.2703(11) |
| C(73A) | 0.3942(19) | 1.1209(42) | 0.3961(16) | C(73B) | 0.4435(16) | 0.7077(35) | 0.3007(13) |
| O(73A) | 0.4419(13) | 1.1544(30) | 0.4022(10) | O(73B) | 0.4475(14) | 0.8036(30) | 0.3228(11) |
| C(81A) | 0.2028(17) | 1.1267(36) | 0.3298(13) | C(81B) | 0.5511(19) | 0.6193(41) | 0.3276(15) |
| O(81A) | 0.2044(14) | 1.1574(31) | 0.2932(11) | O(81B) | 0.5418(20) | 0.6549(45) | 0.3661(16) |
| C(82A) | 0.1039(28) | 1.0462(60) | 0.3708(22) | C(82B) | 0.6393(15) | 0.5399(34) | 0.2847(12) |
| O(82A) | 0.0596(19) | 1.0452(40) | 0.3669(15) | O(82B) | 0.6880(17) | 0.5412(38) | 0.2920(13) |
| Occluded solvent | | | | | | | |
| Cl(1A) | 0.1868(7) | 1.0340(20) | 0.6628(7) | Cl(1B) | 0.0676(12) | 0.5684(22) | −0.0029(8) |
| Cl(2A) | 0.2975(11) | 0.9815(28) | 0.6895(11) | Cl(2B) | −0.0294(13) | 0.4581(22) | −0.0388(14) |
| C(1A) | 0.2268(24) | 1.0013(69) | 0.7072(19) | C(1B) | 0.0200(27) | 0.5359(76) | −0.0512(26) |

Table 9

Fractional atomic coordinates ($\times 10^4$) for $[Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_6(PPh_2H)]$ with estimated standard deviations in parentheses

| Atom | x/a | y/b | z/c |
|---|---|---|---|
| Ru(1) | 3086(0) | 2111(0) | 2211(0) |
| Ru(2) | 3369(1) | 4019(0) | 1536(0) |
| Ru(3) | 3687(1) | 3602(1) | 3488(0) |
| P(1) | 4153(2) | 2541(2) | 1015(1) |
| P(2) | 2049(2) | 1102(2) | 1512(1) |
| P(3) | 2290(2) | 2425(2) | 3563(1) |
| P(4) | 2657(2) | 4891(2) | 2702(1) |
| O(1) | 4412(6) | 2841(5) | 2785(5) |
| O(2) | 5382(7) | 1947(6) | 3992(5) |
| O(3) | 5346(7) | 5120(6) | 1014(5) |
| O(4) | 2089(7) | 5009(6) | 63(5) |
| O(5) | 5710(8) | 4653(7) | 3102(6) |
| O(6) | 3148(8) | 4325(7) | 5277(7) |
| C(1) | 3885(7) | 992(6) | 2584(5) |
| C(2) | 2595(8) | 4622(7) | 624(6) |
| C(3) | 4571(8) | 4729(7) | 1231(6) |
| C(4) | 4700(8) | 2535(7) | 3787(6) |
| C(5) | 4916(9) | 4338(8) | 3215(7) |
| C(6) | 3380(9) | 4045(8) | 4594(8) |
| C(7) | 1202(5) | 267(5) | 2133(4) |
| C(8) | 164(5) | 581(5) | 2443(4) |
| C(9) | −445(5) | −64(5) | 2953(4) |
| C(10) | −16(5) | −1022(5) | 3154(4) |
| C(11) | 1021(5) | −1355(5) | 2844(4) |
| C(12) | 1630(5) | −691(5) | 2334(4) |
| C(13) | 1191(5) | 1604(4) | 623(3) |
| C(14) | 789(5) | 2589(4) | 576(3) |
| C(15) | 166(5) | 2952(4) | −135(3) |
| C(16) | −55(5) | 2330(4) | −798(3) |
| C(17) | 347(5) | 1346(4) | −751(3) |
| C(18) | 970(5) | 983(4) | −40(3) |
| C(19) | 3821(5) | 2100(4) | −56(3) |
| C(20) | 3291(5) | 2706(4) | −697(3) |
| C(21) | 2998(5) | 2315(4) | −1477(3) |
| C(22) | 3235(5) | 1317(4) | −1615(3) |
| C(23) | 3765(5) | 710(4) | −975(3) |
| C(24) | 4058(5) | 1102(4) | −195(3) |
| C(25) | 5634(4) | 2299(6) | 997(5) |
| C(26) | 6188(4) | 2011(6) | 1763(5) |
| C(27) | 7317(4) | 1784(6) | 1740(5) |
| C(28) | 7893(4) | 1846(6) | 951(5) |
| C(29) | 7338(8) | 2134(6) | 185(5) |
| C(30) | 6209(4) | 2360(6) | 209(5) |
| C(31) | 822(4) | 2757(5) | 3749(4) |
| C(32) | 160(4) | 3034(5) | 3036(4) |
| C(33) | −969(4) | 3203(5) | 3153(4) |
| C(34) | −1437(4) | 3095(5) | 3982(4) |
| C(35) | −775(4) | 2817(5) | 4694(4) |
| C(36) | 354(4) | 2648(5) | 4578(4) |
| C(37) | 2524(7) | 1462(5) | 4439(5) |
| C(38) | 2072(7) | 564(5) | 4321(5) |
| C(39) | 2251(7) | −216(5) | 4934(5) |

Table 9 (continued)

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| C(40) | 2882(7) | −97(5) | 5665(5) |
| C(41) | 3334(7) | 801(5) | 5784(5) |
| C(42) | 3155(7) | 1581(5) | 5171(5) |
| C(43) | 3161(6) | 6115(4) | 2888(5) |
| C(44) | 3220(6) | 6426(4) | 3737(5) |
| C(45) | 3671(6) | 7316(4) | 3892(5) |
| C(46) | 4063(6) | 7894(4) | 3199(5) |
| C(47) | 4005(6) | 7583(4) | 2350(5) |
| C(48) | 3554(6) | 6693(4) | 2194(5) |
| C(49) | 1185(4) | 5177(5) | 2858(4) |
| C(50) | 738(4) | 5301(5) | 3688(4) |
| C(51) | −377(4) | 5567(5) | 3790(4) |
| C(52) | −1044(4) | 5710(5) | 3061(4) |
| C(53) | −596(4) | 5586(5) | 2230(4) |
| C(54) | 518(4) | 5320(5) | 2129(4) |

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## References

1 Y.-F. Yu, J. Galluci and A. Wojcicki, J. Am. Chem. Soc., 105 (1983) 4826; A. Wojcicki, Inorg. Chim. Acta, 100 (1985) 125; Y.-F. Yu, C.-N. Chau and A. Wojcicki, Inorg. Chem., 25 (1986) 4098.

2 W.F. Smith, N.J. Taylor and A.J. Carty, Chem. Commun., (1976) 896; R. Regragui, P. Dixneuf, N.J. Taylor and A.J. Carty, Organometallics, 3 (1984) 814.

3 G.L. Geoffroy, S. Rosenberg, P.M. Shulman and R.R. Whittle, J. Am. Chem. Soc., 106 (1984) 1519; M.J. Breen, P.M. Shulman, G.L. Geoffroy, A.L. Rheingold and W.C. Fultz, Organometallics, 3 (1984) 782; S. Rosenberg, R.R. Whittle and G.L. Geoffroy, J. Am. Chem. Soc., 106 (1980) 5934.

4 K. Henrick, J.A. Iggo, M.J. Mays and P.R. Raithby, Chem. Commun., (1984) 209; A.D. Horton, M.J. Mays and P.R. Raithby, Chem. Commun., (1985) 247.

5 (a) A.J. Carty, Pure App. Chem., 54 (1982) 113; (b) S.A. MacLaughlin, A.J. Carty and N.J. Taylor, Can. J. Chem., 60 (1982) 87.

6 B. Klingert and H. Werner, J. Organomet. Chem., 252 (1983) C47; R. Zolk and H. Werner, ibid., 252 (1983) C53; R. Zolk and H. Werner, ibid., 303 (1986) 233; R. Zolk and H. Werner, ibid., 331 (1987) 95; H. Werner and R. Zolk, Chem. Ber., 120 (1987) 1003.

7 S.A. MacLaughlin, N.J. Taylor and A.J. Carty, Organometallics, 3 (1984) 392.

8 V.D. Patel, A.A. Cherkas, D. Nucciarone, N.J. Taylor and A.J. Carty, Organometallics, 4 (1985) 1792.

9 R.P. Rosen, G.L. Geoffroy, C. Bueno, M.R. Churchill and R.B. Ortega, J. Organomet. Chem., 254 (1983) 89.

10 (a) J.S. Field, R.J. Haines and D.N. Smit, J. Organomet. Chem., 224 (1988) C49; (b) J.S. Field, R.J. Haines and D.N. Smit, J. Chem. Soc., Dalton Trans., (1988) 1315.

11 F. Iwasaki, M.J. Mays, P.R. Raithby, P.L. Taylor and P.J. Wheatley, J. Organomet. Chem., 213 (1981) 185.

12 K. Natarajan, O. Scheidsteger and G. Huttner, J. Organomet. Chem., 221 (1981) 301.

13 J.S. Field, R.J. Haines and D.N. Smit, J. Organomet. Chem., 304 (1986) C17.

14 J.S. Field, R.J. Haines, M.H. Moore, D.N. Smit and L.M. Steer, S. Afr. J. Chem., 37 (1984) 138.

15 L.M. Bullock, J.S. Field, R.J. Haines, E. Minshall, D.N. Smit and G.M. Sheldrick, J. Organomet. Chem., 310 (1986) C47.

16 B.F.G. Johnson, R.D. Johnston, J. Lewis, B.H. Robinson and G. Wilkinson, J. Chem. Soc., A, (1968) 2856.

17 A.A. Bhattacharyya, C.N. Nagel and S.G. Shore, Organometallics, 2 (1983) 1187.

18 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1972) 2094.

19 J.N. Gerlach, S.L. Mc Mullin and P.C. Ellgen, Inorg. Chem., 15 (1976) 1232; J.P. Collman, R.K. Rothrock, R.G. Finke and F. Rose-Munch, J. Am. Chem. Soc., 99 (1977) 7381.

20 K. Natarajan, L. Zsolnai and G. Huttner, J. Organomet. Chem., 209 (1981) 85.

21 F. van Gastel, N.J. Taylor and A.J. Carty, J. Chem. Soc., Chem Commun., (1987) 1049.

22 P.B. Hitchcock, M.F. Lappert and C.R.C. Milne, J. Chem. Soc., Dalton Trans., (1981) 180.

23 M.J. Chetcuti, M.H. Chisholm, K. Folting, D.A. Haitko, J.C. Huffmann and J. Janos, J. Am. Chem. Soc., 105 (1983) 1163.

24 C.G. Howard, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1983) 2025.

25 G.W. Harris, M.O. Albers, J.C.A. Boeyens and N.J. Coville, Organometallics, 2 (1983) 609.

26 (a) See references 22–24; (b) B.K. Teo, Inorg. Chem., 23 (1984) 1251; B.K. Teo, G. Zongoni and F.R.K. Chung, ibid, 23 (1984) 1257.

27 V.G. Albano and S. Martinengo, Nach. Chem. Tech. Lab., 28 (1980) 654.

28 M. Tachikawa and E.L. Muetterties, Prog. Inorg. Chem., 28 (1981) 203.

29 J.S. Bradley, Adv. Organomet. Chem., 22 (1983) 1.

30 V.G. Albano, P. Chini, G. Ciani, S. Martinengo and M. Sansoni, J. Chem. Soc., Dalton Trans., (1978) 463.

31 J.L. Vidal, W.E. Walker, R.L. Pruett and R.C. Schoening, Inorg. Chem., 18 (1979) 129.

32 J.L. Vidal, W.E. Walker and R.C. Schoening, Inorg. Chem., 20 (1981) 238.

33 P.E. Garrou, Chem. Rev., 85 (1985) 171.

34 E.D. Billig, J.D. Jamerson and R.L. Pruett, J. Organomet. Chem., 192 (1980) C49.

35 J.D. Jamerson, R.L. Pruett, E. Billig and F.A. Fiato, J. Organomet. Chem., 193 (1980) C43.

36 H.C. Foley, W.C. Finch, C.G. Pierpont and G.L. Geoffroy, Organometallics, 1 (1982) 1379.

37 V.D. Patel, N.J. Taylor and A.J. Carty, J. Chem. Soc., Chem. Commun., (1984) 99.

38 F. van Gastel, N.J. Taylor and A.J. Carty, Inorg. Chem., 28 (1989) 384.

39 F. Mulla, unpublished results.

40 G.M. Sheldrick, SHELX-76, Program for crystal structure determination and refinement, University of Cambridge, 1976.

41 G.M. Sheldrick, SHELXS-86, Program for crystal structure determination, University of Göttingen, 1986.

42 G.M. Sheldrick, SHELXTL, an integrated system for solving, refining and displaying crystal structures from diffraction data, Nicolet XRD Corporation, Madison, Wisconsin, 1983.