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R—P AND R—As BRIDGED RUTHENIUM CARBONYL HYDRIDES AND RELATED CLUSTERS. CRYSTAL AND MOLECULAR STRUCTURE OF $[(\mu_2\text{-H})_2Ru_3(CO)_9(\mu_3\text{-P}(p\text{-}CH_3OC_6H_4))]$

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Summary

Reactions of primary phosphines RPH_2 ($R = p\text{-}CH_3OC_6H_4$, $p\text{-}BrC_6H_4$) with $Ru_3(CO)_{12}$ yielded clusters of the type $[(\mu_2\text{-H})_2Ru_3(CO)_9(\mu_3\text{-PR})]$ and $[Ru_3(CO)_9(\mu_3\text{-PR})_2]$. The reaction of $C_6H_5AsH_2$ with $Ru_3(CO)_{12}$ gave $[(\mu_2\text{-H})_2Ru_3(CO)_9(\mu_3\text{-AsC}_6H_5)]$ and $[Ru_2(CO)_6(\mu_2\text{-As}(C_6H_5)H)_2]$. All the compounds have been studied by IR and NMR (^{31}P and ^{1}H) spectroscopy and the structure of $[(\mu_2\text{-H})_2Ru_3(CO)_9(\mu_3\text{-P}(p\text{-}CH_3OC_6H_4))]$ has been determined by single crystal X-ray diffraction ($R = 0.05$). The overall molecular geometry is that of a trigonal pyramid with the phosphorus atom at the apex and two of the three basal Ru—Ru bonds bridged by hydrogens. The average Ru—Ru, Ru—P and Ru—C distances are 2.903 Å, 2.289 Å and 1.941 Å, respectively.

Introduction

Although many clusters with μ_3-P bridging units have been prepared and characterized [1—5], relatively little attention has been given to the μ_3-As bridged clusters. There have been only a few reports of clusters containing μ_3-As bridging units, the first being the preparation and characterization of $[Fe_3(CO)_9(\mu_3\text{-AsC}_6H_5)_2]$ [6]. Other known clusters with μ_3-AsR units are the cubane type $[Fe(CO)_3(AsCH_3)]_4$ [7] and $[Fe(CO)_3(AsC_6H_5)]_4$ [8], the structures of which have been determined crystallographically.

Interest has been mainly focussed towards preparation of μ_3-PR bridged hydrido clusters because of the presence of potentially reactive hydrogens in these systems with an intact metal triangle which facilitate further studies on the reac-

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tivity [8]. With this in mind, we intended to prepare the corresponding μ_3-As bridged hydrido clusters with ruthenium carbonyl and we were able to isolate the the desired $[(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-AsC}_6H_5)]$. In this paper we report the reaction of $C_6H_5AsH_2$ and the reactions of primary phosphines RPH_2 (R = p-$CH_3OC_6H_4$, p-BrC_6H_4) with $Ru_3(CO)_{12}$; the latter reactions were carried out to obtain compounds for structural comparisons *.

Experimental

Dodecacarbonyltriruthenium [9], p-methoxyphenylphosphine [10], p-bromophenylphosphine [11] and phenylarsine [12] were prepared by published methods. Solvents were purified by distillation, dried over sodium/benzophenone, and stored under nitrogen. All the reactions and handling of chemicals were performed under dry nitrogen or under vacuum.

Microanalyses were performed at the Microanalytical section of our department. NMR spectra (^{31}P and ^1H) were recorded on a Bruker WP-80 FT instrument and IR spectra on a Zeiss Infrarot-Spektralphotometer IMR-40. Melting points were determined in open capillaries using a Gallenkamp melting point apparatus, and are uncorrected.

(1) Reaction of phenylarsine with $Ru_3(CO)_{12}$

To a suspension of $Ru_3(CO)_{12}$ (640 mg, 1.0 mmol) in toluene (80 cm^3) was added $C_6H_5AsH_2$ (154 mg, 1.0 mmol), and the mixture stirred at 60°C for 12 h. The resulting solution was cooled, the solvent was evaporated under vacuum to small volume (5 cm^3), and silica gel (5 g) was added. The residue was taken to dryness under vacuum and transferred to a silica gel column made up in pentane at −30°C. The products were eluted with pentane, pentane/toluene and toluene/THF mixtures. The first fraction (yellow), eluted with pentane gave unreacted $Ru_3(CO)_{12}$. The second fraction, yellow, was eluted with 10/1 pentane/toluene and gave, after recrystallisation from toluene, 145 mg (20% based on $Ru_3(CO)_{12}$) of $[(\mu_2\text{-H})_2Ru_3(CO)_9(\mu_3\text{-AsC}_6H_5)]$. A third fraction, red, eluted with 5/1 toluene/THF, and gave 250 mg (25% based on $Ru_3(CO)_{12}$) of $[Ru_2(CO)_6(\mu_2\text{-As}(C_6H_5)H)_2]$ after recrystallisation from toluene. For the preparation of $[(\mu_2\text{-H})_2Ru_3(CO)_9(\mu_3\text{-AsC}_6H_5)]$, it is essential to use a 1/1 molar ratio of $Ru_3(CO)_{12}$ and $C_6H_5AsH_2$ because with an excess of $C_6H_5AsH_2$, the only product is $[Ru_2(CO)_6(\mu_2\text{-As}(C_6H_5)H)_2]$. $[(\mu_2\text{-H})_2Ru_3(CO)_9(\mu_3\text{-AsC}_6H_5)]$: M.p. 97°C. Mass spec. m/e 710. Anal. Found: C, 25.55; H, 0.90; As, 10.16. Calcd. for $C_{15}H_7O_9AsRu_3$: C, 25.38; H, 0.98; As, 10.59%. $[Ru_2(CO)_6(\mu_2\text{-As}(C_6H_5)H)_2]$: M.p. >300°C. Anal. Found: C, 31.61; H, 1.87; As, 22.42. Calcd. for $C_{18}H_{12}O_6As_2Ru_2$: C, 31.95; H, 1.77; As, 22.19%.

(2) Reaction of p-$CH_3OC_6H_4PH_2$ with $Ru_3(CO)_{12}$

The reaction was carried out as in (1) with $Ru_3(CO)_{12}$ (640 mg, 1.0 mmol and p-$CH_3OC_6H_4PH_2$ (140 mg, 1.0 mmol) in toluene (80 cm^3). The first (yellow) fraction, eluted with pentane, gave the starting material $Ru_3(CO)_{12}$. The second (yellow) fraction, eluted with 2/1 pentane/toluene, gave $[(\mu_2\text{-H})_2Ru_3(CO)_9(\mu_3\text{-P}(p\text{-CH}_3OC_6H_4))]$ (200 mg, 29% based on $Ru_3(CO)_{12}$) which was recrystallised from toluene. The third (red) fraction, eluted with toluene,

* *Note added in proof.* Similar results for closely related systems have meanwhile been described [16].

gave $[Ru_3(CO)_9(\mu_3\text{-}P(p\text{-}CH_3OC_6H_4))_2]$ (205 mg, 25% based on $Ru_3(CO)_{12}$), which was recrystallised from toluene. $[(\mu_2\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}P(p\text{-}CH_3OC_6H_4))]$: M.p. 129°C. Mass spec. m/e 696. Anal. Found: C, 27.25; H, 1.64; P, 4.89. Calcd. for $C_{16}H_9O_{10}PRu_3$: C, 27.63; H, 1.30; P, 4.45%. $[Ru_3(CO)_9(\mu_3\text{-}P(p\text{-}CH_3OC_6H_4))_2]$: M.p. 151°C. Anal. Found: C, 33.29; H, 1.98; P, 7.81. Calcd. for $C_{23}H_{14}P_2Ru_3$: C, 33.22; H, 1.69; P, 7.45%.

(3) Reaction of p-$BrC_6H_4PH_2$ with $Ru_3(CO)_{12}$

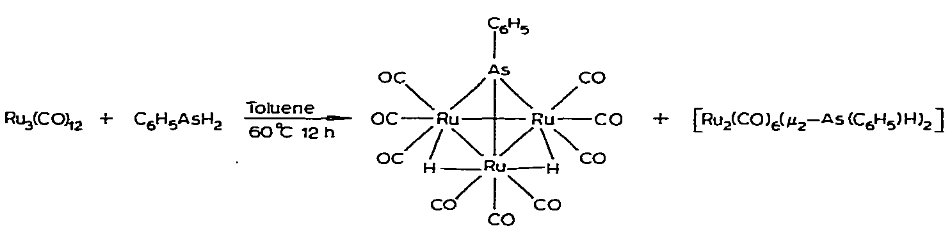
The reaction was carried out as in (1) with $Ru_3(CO)_{12}$ (640 mg, 1.0 mmol) and p-$BrC_6H_4PH_2$ (190 mg, 1.0 mmol) in toluene (80 cm^3). The first (yellow) fraction, eluted with pentane, gave $[(\mu_2\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}P(p\text{-}BrC_6H_4))]$ (180 mg, 24% based on $Ru_3(CO)_{12}$) which was recrystallised from toluene. The second (red) fraction, eluted with 2/1 pentane/toluene, gave $[Ru_3(CO)_9(\mu_3\text{-}P(p\text{-}BrC_6H_4))_2]$ (200 mg, 22% based on $Ru_3(CO)_{12}$), which was recrystallised from toluene. $[(\mu_2\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}P(p\text{-}BrC_6H_4))]$: M.p. 83°C. Mass spec. m/e 746. Anal. Found: C, 24.48; H, 0.68; P, 3.84. Calcd. for $C_{15}H_6O_9BrPRu_3$: C, 24.27; H, 0.53; P, 4.17%. $[Ru_3(CO)_9(\mu_3\text{-}P(p\text{-}BrC_6H_4))_2]$: M.p. >300°C. Anal. Found: C, 27.47; H, 0.92; P, 6.77. Calcd. for $C_{21}H_8O_9Br_2P_2Ru_3$: C, 27.14; H, 0.86; P, 6.66%.

X-Ray crystallography: data collection and refinement

Crystals suitable for the X-ray study were obtained by recrystallisation of $[(\mu_2\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}P(p\text{-}CH_3OC_6H_4))]$ from toluene at −20°C. The compound crystallises in space group $P\bar{1}$ with a = 8.386(9) Å, b = 10.33(1) Å, c = 13.35(3) Å, α = 93.60(13)°, β = 101.83(12)°, γ = 93.75(10)°, D_c = 2.05 g cm^{-3}, μ = 20.6 cm^{-1} and Z = 2. Crystal data were collected using a Syntex-P3 four-circle diffractometer. Cell parameters and diffraction intensities were determined on the same instrument at 233 K (Mo-K_α, λ = 0.71069 Å), graphite monochromator, ω-scan with $1.1 < \dot{\omega} \leqslant 29.3°$ min^{-1} and $2 \leqslant 2\,\theta \leqslant 40°$. One standard reflection was measured for every 100 reflections during data collection as a check on crystal and instrument stability. A total of 2273 reflections were collected, from which 1991 reflections having $I > 3.9\sigma$ were used to solve and refine the structure. The structure was solved by direct methods using a Syntex-EXTL programm system and refined by full matrix least squares. The positions of the bridging hydrides and other hydrogens were found by using difference electron density syntheses, and are not refined. The refinement converged at R_1 = 0.050 and R_2 = 0.067.

Results and discussion

The reaction of $C_6H_5AsH_2$ with $Ru_3(CO)_{12}$ yielded compounds I and II.

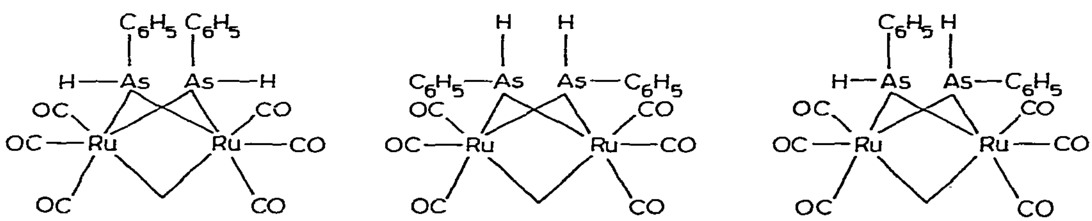


(I) (II)

Compound I is obtained only when the mole ratio of $Ru_3(CO)_{12}$ and $C_6H_5AsH_2$ is close to 1 : 1. With an excess of $C_6H_5AsH_2$, the only pure compound obtained is II.

The IR spectrum of I shows a pattern of $\nu(CO)$ bands (Table 1) which is very similar to that observed for $[H_2Fe_3(CO)_9(PR)]$ and $[H_2Ru_3(CO)_9(PR)]$ [4,5], indicating structural similarity. Its ^1H NMR spectrum (Table 1) shows a singlet at −19.46 ppm, which indicates chemically equivalent bridging hydrides. The phenyl protons give rise to a multiplet around 7.64 ppm. All the data are in accordance with the structure proposed for I. It should be noted that this is the first reported hydrido ruthenium cluster containing a μ_3-AsR bridging unit.

The pattern of $\nu(CO)$ bands observed in the IR spectrum of II is closely similar to that observed for the analogous compounds $[Fe_2(CO)_6(PRH)_2]$ (R = C_6H_5, CH_3) [1], $[Fe_2(CO)_6(AsMe_2)_2]$ [13] and $[Ru_2(CO)_6(AsMe_2)_2]$ [14]. This indicates that the framework geometry of II is similar to that found for the related compounds with a nonplanar Ru_2As_2 cycle. For a static molecule of this type, three isomeric forms might be expected.



(C_{2v}) (C_{2v}) (C_s)

It is known that complexes with this framework geometry often rapidly isomerise by a formal rotation of the M—As—M planes around the M—M axis [1,13,14]. By such a process the two isomers with C_{2v} symmetry are intercon-

TABLE 1

SPECTROSCOPIC DATA FOR RUTHENIUM CLUSTER COMPOUNDS I—IV

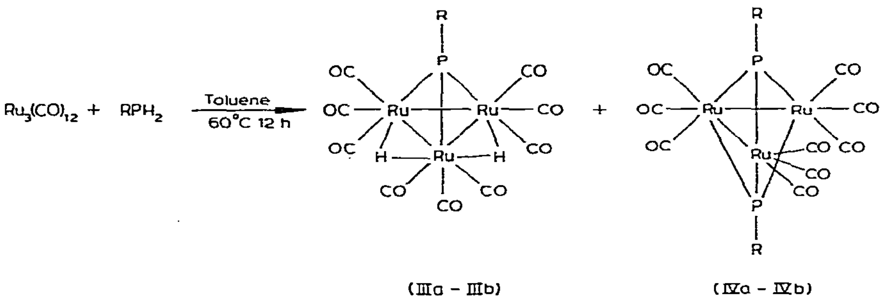
Compound	^1H NMR [a]		^{31}P NMR [b]	IR [c]
I	i) C_6H_5:	7.64(m)	—	2106s, 2074s, 2060s, 2048s
	ii) RuHRu:	−19.46(s)		2030s, 2012s, 1984s
II	i) C_6H_5:	7.2(m)	—	2089w, 2051s, 1992w, 1937w
	ii) AsH:	4.23(s)		
IIIa	i) C_6H_4:	7.12(m)	281.1	2106s, 2073s, 2045s, 2024w
	ii) CH_3:	3.84(s)		2014s, 1996s, 1981s
	iii) RuHRu:	−19.06(d)		
	(J(PH) = 15 Hz)			
IIIb	i) C_6H_4:	7.2(m)	274.6	2109s, 2077s, 2062s, 2059s
	ii) RuHRu:	−19.16(d)		2028w, 2016s, 2001w
	(J(PH) = 15.4 Hz)			
IVa	i) C_6H_4:	7.4(m)	330.2	2076s, 2066s, 2035s, 1984w
	ii) CH_3:	3.74(s)		
IVb	i) C_6H_4:	7.2(m)	330.9	2080w, 2063w, 2040s, 2006w

[a] δ value in ppm relative to external reference TMS (in acetone-d_6) (s = singlet, d = doublet, m = multiplet) at 0°C. [b] δ value in ppm relative to H_3PO_4 in toluene at 0°C. [c] cm^{-1} in toluene (s = strong, w = weak).

verted, whereas the isomer with C_s symmetry regenerates itself. Hence, even if this kind of isomerisation operated for II as a process rapid on the NMR time scale, two H_{As} signals should be observed if all the isomers were present. Only one H_{As} signal is found for II, at 4.23 ppm. If the very unlikely coincidence of the signals belonging to the different isomers is excluded, this means that isomers with exclusively C_s or C_{2v} symmetry must be present in II, assuming that no rapid process is available for interconversion of the species with different symmetries.

The reaction of primary phosphines RPH_2 with $Ru_3(CO)_{12}$ to give μ_3-PR bridged clusters $[(\mu_2\text{-H})_2Ru_3(CO)_9(\mu_3\text{-PR})]$ has already been described [5] for R = C_6H_5 and C_6H_{11}, and the structure of the C_6H_{11} derivative had been determined.

We prepared complexes III in order to obtain suitable crystals for an X-ray study of an aryl substituted cluster of this type, and at the same time we isolated compounds IV from these reactions.



The IR spectra of IIIa and IIIb show bands in the ν(CO) region (Table 1) which are very similar to those observed for $[H_2Ru_3(CO)_9(PR)]$ [5], which clearly indicates their structural similarity. In the ^{31}P NMR spectra of compounds III there is a singlet in the region of 270—280 ppm (Table 1) indicative of a μ_3-PR bridiging unit. The two chemically equivalent hydrides give a doublet around —19 ppm (Table 1) in the ^{1}H NMR spectra of these compounds. Other signals due to R groups appear as expected. The crystal structure of $(\mu_2H)_2Ru_3(CO)_9(\mu_3\text{-P}(p\text{-}CH_3OC_6H_4))$ was determined by X-ray crystallography.

Compounds IVa and IVb show bands in the IR spectra which are very much consistent with those observed for $[Fe_3(CO)_9(PR)_2]$ and $[Fe_3(CO)_9\text{-}(AsC_6H_5)_2]$ [1,8,17]. In the ^{31}P NMR spectra signals around 330 ppm indicate the presence of μ_3-PR bridging ligands, which is very close to the value observed for the iron analogues [17]. The ^{1}H NMR spectra show the expected signals for the aryl and alkyl groups.

Structure of $[(\mu_2\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}P(p\text{-}CH_3OC_6H_4))]$

The molecular structure of the cluster is shown in Fig. 1 and the structural parameters are given in Tables 2—4.

The overal molecular geometry is that of a trigonal pyramid with a ruthenium trianlge at the base and the phosphorus atom at the apex. Two of the three

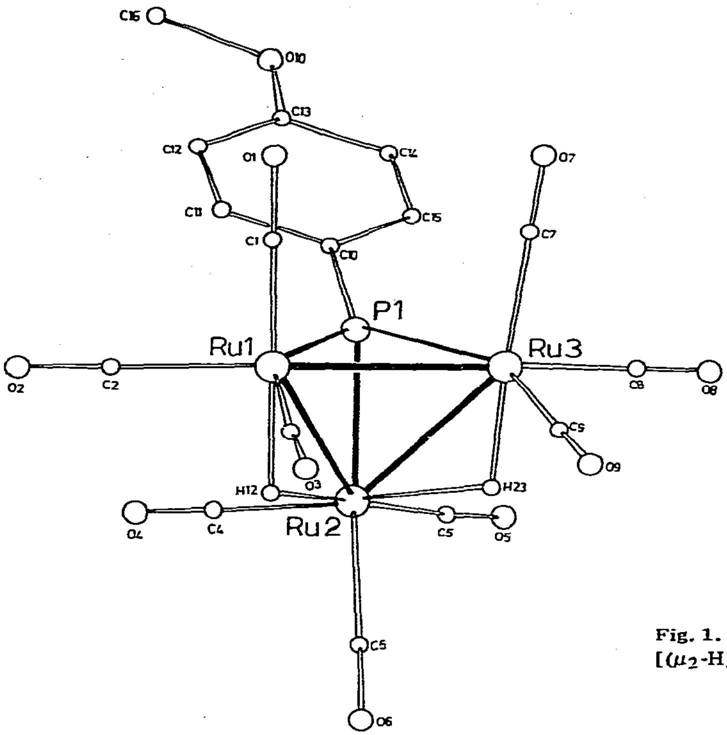


Fig. 1. Molecular structure of $[(\mu_2\text{-H})_2Ru_3(CO)_9(\mu_3\text{-}P(p\text{-}CH_3OC_6H_4))]$.

TABLE 2

FRACTIONAL COORDINATES (with e.s.d.'s) AND ISOTROPIC THERMAL PARAMETERS FOR $[H_2Ru_3(CO)_9(P(p\text{-}CH_3OC_6H_4))]$

Atom	X	Y	Z	B
Ru(1)	−0.0415(1)	0.7108(1)	0.3771(1)	
Ru(2)	0.1479(1)	0.5535(1)	0.2603(1)	
Ru(3)	0.2422(1)	0.8290(1)	0.3236(1)	
P(1)	0.0095(5)	0.7363(4)	0.2182(3)	
C(1)	−0.1403(19)	0.8675(16)	0.3934(11)	2.2(3)
O(1)	−0.1993(14)	0.9641(11)	0.4020(9)	
C(2)	−0.2467(23)	0.6046(16)	0.3596(12)	2.8(3)
O(2)	−0.3655(15)	0.5433(12)	0.3452(11)	
C(3)	0.0584(18)	0.7059(14)	0.5223(12)	1.8(3)
O(3)	0.1200(14)	0.7057(10)	0.6038(8)	
C(4)	−0.0310(22)	0.4307(17)	0.1903(12)	2.9(3)
O(4)	−0.1355(16)	0.3636(13)	0.1490(10)	
C(5)	0.2577(21)	0.5498(16)	0.1477(13)	3.1(4)
O(5)	0.3205(18)	0.5551(12)	0.0822(10)	
C(6)	0.2836(20)	0.4290(16)	0.3494(12)	2.5(3)
O(6)	0.3511(15)	0.3669(11)	0.4001(10)	
C(7)	0.1724(19)	0.1000(16)	0.3335(11)	2.0(3)
O(7)	0.1290(14)	1.1019(10)	0.3386(9)	
C(8)	0.3951(23)	0.8713(17)	0.2390(13)	3.3(4)
O(8)	0.4838(19)	0.8914(13)	0.1877(12)	
C(9)	0.3836(20)	0.8456(14)	0.4611(12)	2.3(3)
O(9)	0.4635(14)	0.8564(10)	0.5385(8)	
C(10)	−0.1101(17)	0.7659(13)	0.0964(10)	1.6(3)
C(11)	−0.2774(19)	0.7334(15)	0.0733(11)	2.5(3)
C(12)	−0.3723(19)	0.7540(15)	−0.0211(11)	2.4(3)
C(13)	−0.3007(18)	0.8061(13)	−0.0935(10)	1.7(3)
C(14)	−0.1348(21)	0.8413(16)	−0.0711(12)	3.4(4)
C(15)	−0.0417(20)	0.8191(15)	0.0230(11)	2.8(3)
O(10)	−0.3768(13)	0.8283(11)	−0.1884(8)	
C(16)	−0.5559(23)	0.7953(18)	−0.2171(13)	4.5(4)
H(12)	0.058	0.562	0.378	6.0
H(23)	0.321	0.679	0.321	6.0

TABLE 3

ANISOTROPIC THERMAL PARAMETERS FOR $[H_2Ru_3(CO)_9(P(p\text{-}CH_3OC_6H_4))]$ [a, b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru(1)	1.16(6)	1.68(6)	2.39(6)	0.33(5)	0.40(4)	0.03(4)
Ru(2)	1.58(6)	1.19(6)	3.22(6)	0.29(5)	0.72(5)	—0.15(5)
Ru(3)	1.30(6)	1.14(6)	2.68(6)	0.15(4)	0.34(4)	0.01(4)
P(1)	1.3(2)	1.3(2)	2.0(2)	0.3(1)	0.2(1)	—0.1(1)
O(1)	3.4(6)	3.8(6)	5.9(6)	1.9(5)	1.4(5)	0.1(5)
O(2)	2.0(6)	4.5(7)	9.6(9(	—1.1(6)	1.2(6)	—0.5(6)
O(3)	4.4(6)	3.3(6)	2.8(6)	0.3(5)	—0.1(5)	0.7(4)
O(4)	3.5(7)	5.3(8)	6.0(7)	—3.0(6)	0.3(6)	—2.2(6)
O(5)	7.6(9)	4.6(7)	5.8(7)	—0.1(6)	4.9(7)	—0.1(6)
O(6)	4.3(7)	2.8(6)	5.6(7)	2.0(5)	—0.1(5)	2.7(5)
O(7)	3.6(6)	1.0(5)	5.6(6)	0.8(5)	1.7(5)	0.9(4)
O(8)	7.5(9)	3.8(7)	9.4(9)	0.1(7)	7.0(8)	0.3(7)
O(9)	3.4(6)	2.9(6)	3.3(6)	0.8(5)	—1.0(5)	0.4(4)
O(10)	1.5(5)	5.4(6)	2.8(5)	—1.0(5)	—0.8(4)	1.2(4)

[a] The anisotropic thermal parameter (T) is defined as $T = \exp[-1/4(B_{11}h^2a^{*2} + ... + 2B_{23}klb^*c^*)]$. B_{ij} in Å^2. [b] E.s.d.'s are shown in parentheses.

Ru—Ru bonds are bridged by hydrogens, and the Ru—Ru distances which are bridged by hydrogens are longer (average 2.932 Å) than the unbridged one (2.844 Å). This feature is also seen in Ru—P distances where two are equal (average 2.274 Å) and the third one involving Ru(2), which bears two bridging hydrogens, is slightly longer (2.320 Å). The average Ru(1)—C_{CO} distance (1.927 Å) and Ru(3)—C_{CO} distance (1.928 Å) are equal, whereas a slightly longer Ru(2)—C_{CO} distance (average 1.968 Å) is observed. The axial CO groups

TABLE 4

BOND DISTANCES AND BOND ANGLES FOR $[H_2Ru_3(CO)_9(P(p\text{-}CH_3OC_6H_4))]$

(A) Bond distances (Å)			
Ru(1)—Ru(2)	2.937(2)	Ru(2)—C(6)	2.05(2)
Ru(1)—Ru(3)	2.844(2)	Ru(3)—C(7)	1.90(2)
Ru(2)—Ru(3)	2.928(2)	Ru(3)—C(8)	1.92(2)
Ru(1)—P(1)	2.275(4)	Ru(3)—C(9)	1.96(2)
Ru(2)—P(1)	2.320(4)	Ru(1)—H(12)	1.8
Ru(3)—P(1)	2.273(4)	Ru(2)—H(12)	1.9
Ru(1)—C(1)	1.89(2)	Ru(2)—H(23)	1.9
Ru(1)—C(2)	1.94(2)	Ru(3)—H(23)	1.7
Ru(1)—C(3)	1.95(2)	C(10)—P(1)	1.78(1)
Ru(2)—C(4)	1.94(2)	C(13)—O(10)	1.34(2)
Ru(2)—C(5)	1.92(2)	C(16)—O(10)	1.48(2)
The C—O distances range from 1.07(2) to 1.15(2)			
The C—C distances in the phenyl group range from 1.36(2) to 1.39(2)			
(B) Bond angles (deg)			
Ru(1)—Ru(3)—Ru(2)	61.2	Ru(3)—P(1)—Ru(2)	79.2(1)
Ru(2)—Ru(1)—Ru(3)	60.9	Ru(1)—P(1)—C(10)	135.3(5)
Ru(3)—Ru(2)—Ru(1)	58.0	Ru(2)—P(1)—C(10)	127.2(5)
Ru(2)—P(1)—Ru(1)	79.5(1)	Ru(3)—P(1)—C(10)	136.1(5)
Ru(3)—P(1)—Ru(1)	77.4(1)	C(16)—O(10)—C(13)	117.4(12)
The Ru—C—O angles range from 176.0(16) to 179.2(14)			

appear to form slightly longer Ru—C bonds than the equatorial ones. The framework geometry corresponds to an idealized C_S symmetry for the $Ru_3(CO)_9PH_2$ unit.

The phosphorus atom lies 1.559 Å below the plane of the three ruthenium atoms and the hydride ligands lie 0.88 Å (H(12)) and 0.78 Å (H(23) above the plane.

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