SYNTHESIS AND STRUCTURES OF FOUR MONO(ORGANO)PHOSPHIDO-BRIDGED PENTARUTHENIUM CARBONYL CLUSTERS, [Ru$_5$(CO)$_{15}$(μ_4-PR)] (R = C$_6$H$_5$, CH$_3$, CH$_2$CH$_3$ AND CH$_2$C$_6$H$_5$)

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Summary

The reactions of [(C$_5$H$_5$)(CO)$_2$MnPRCl$_2$] (R = C$_6$H$_5$, CH$_3$, CH$_2$CH$_3$ and CH$_2$C$_6$H$_5$) with Ru$_3$(CO)$_{12}$ yield clusters of the type [Ru$_5$(CO)$_{15}$PR] in which the phosphorus atom is pentacoordinated and bonded to four ruthenium atoms. The compounds have been studied by ^{31}P NMR spectroscopy and their structures have been determined by X-ray crystallography. The compound [Ru$_5$(CO)$_{15}$PC$_6$H$_5$] crystallises in space group $P\bar{1}$ with a = 9.543(9) Å, b = 9.560(7) Å, c = 29.63(4) Å, β = 89.78(9)° and Z = 4. The structure was solved by direct methods (SHELXTL) and refined by full matrix refinements (Syntex-EXTL System) to a final R value of 0.061 for 2810 independent significant data. The molecular structures of the two independent molecules within the asymmetric unit are nearly identical. The overall molecular geometry is that of a distorted octahedron. The average Ru—Ru, Ru—P and Ru—C distances are 2.852 Å, 2.372 Å and 1.890 Å, respectively. The compound [Ru$_5$(CO)$_{15}$PCH$_2$CH$_3$] crystallises in space group Cc with a = 15.77(2) Å, b = 9.917(6) Å, c = 19.64(2) Å, β = 124.32(6)° and Z = 4. The structure was solved and refined by similar procedures as described for the previous compound to a final R value of 0.046 for 1289 observed data. The overall geometry is that of a distorted octahedron. The average Ru—Ru, Ru—P and Ru—C distances are 2.849 Å, 2.371 Å and 1.885 Å, respectively. The structure of the clusters can be described as square-pyramidal with five ruthenium atoms and the phosphide ligand capping the square face.

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Introduction

Very few clusters are known to possess pentacoordinate phosphorus or arsenic atoms bonded to four metal atoms. They are $[Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2]$ [1], $[Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6]$ [2], $[Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}AsC_6H_5)_2]$ [2] and $[Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_2\text{-}H)(\mu_4\text{-}PC_6H_5)_2]$ monoanion [2]. Though numerous clusters of ruthenium are known, they are all of Ru_3, Ru_4 and Ru_6 type. Only one cluster is known of the Ru_5 type, $[H_2Ru_5(C=CH_2)(CO)_{15}]$ [3], which was obtained as one of the products of the reaction of $NaBH_4$ with $Ru_3(CO)_{12}$. There is one osmium analogue of the title compounds, namely $[Os_5(CO)_{15}POMe]$, which was obtained by the pyrolysis of $[Os_3(CO)_{11}P(OMe)_3]$, and the structure of which was determined [4]. We report here the details of the synthesis of four Ru_5 type carbonyl clusters which contain a pentacoordinated phosphorus atom bonded to four ruthenium atoms. The X-ray crystal structures of $[Ru_5\text{-}(CO)_{15}PR]$ ($R = C_6H_5$ and CH_2CH_3) have been determined. In all these clusters the metal atoms adopt a square-pyramidal geometry with the phosphide ligand capping the square face.

Experimental

Dodecacarbonyltriruthenium was prepared by Bruce and Stone's method [5]. The complexes $[(C_5H_5)(CO)_2MnPRCl_2]$ ($R = C_6H_5$, CH_3, CH_2CH_3, $CH_2C_6H_5$) were prepared photochemically by published procedures [6,7]. The solvents used were dried over sodium benzophenone and distilled under nitrogen. Silica gel (E. Merck) was dried at 25°C under 10^{-2} bar for 30 hours and preserved under nitrogen. All operations were performed under oxygen-free nitrogen or under vacuum.

Microanalyses were done at the Microanalytical Section of our department. ^{31}P NMR spectra were recorded on a Bruker WP-80 FT spectrometer. IR spectra were recorded on a Zeiss Infrarot Spektralphotometer IMR 40. Mass spectra were recorded on a Varian MAT 112. Melting points were determined in open capillaries using Gallenkamp melting point apparatus and are uncorrected.

(1) Preparation of [Ru₅(CO)₁₅(μ₄-PC₆H₅)] (I)

(1) Preparation of $[Ru_5(CO)_{15}(\mu_4\text{-}PC_6H_5)]$ (I)

To a suspension of $Ru_3(CO)_{12}$ (1.59 g, 2.48 mmol) in toluene (80 cm^3) was added $[(C_5H_5)(CO)_2MnPC_6H_5Cl_2]$ (0.88 g, 2.48 mmol), and the mixture was stirred at 100°C (48 h). The resulting dark brown solution was concentrated under vacuum at 25°C 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 silical gel column in pentane at −20°C. The compounds were eluted first with pentane and then with pentane and toluene mixture. The first and second fractions were the starting materials. The third, green fraction, eluted with 4/1 pentane/toluene gave $[Ru_5(CO)_{15}PC_6H_5]$. This was recrystallised from dichloromethane/pentane. Yield 140 mg (5.5% based on $Ru_3(CO)_{12}$). M.p. 185—190°C (dec.). Found: C, 24.49; H, 0.40; P, 3.16. Calcd. for $C_{21}H_5O_{15}Ru_5P$: C, 24.39; H, 0.48; P, 3.00%. Mass spec. *m/e* 1033. The recrystallised compound is stable for weeks in the air and also in solution under nitrogen.

(2) Preparation of $Ru_5(CO)_{15}(\mu_4\text{-}PCH_2CH_3)$ (II)

The compound was prepared as described for I, from $Ru_3(CO)_{12}$ (1.59 g, 2.48 mmol) and $[(C_5H_5)(CO)_2MnPCH_2CH_3Cl_2]$ (0.76 g, 2.48 mmol). The green fraction was eluted with 4/1 pentane/toluene and recrystallised from dichloromethane/pentane. Yield 120 mg (5% based on $Ru_3(CO)_{12}$). M.p. 210—220°C (dec). Found: C, 20.98; H, 0.55; P, 3.59. Calcd. for $C_{17}H_5O_{15}Ru_5P$: C, 20.71; H, 0.50; P, 3.14%. Mass spec. m/e 985. Crystals of II are air stable for weeks, but in solution the compound gives $Ru_3(CO)_{12}$ as one of the decomposition products on long standing.

(3) Preparation of $Ru_5(CO)_{15}(\mu_4\text{-}PCH_3)$ (III)

The compound was prepared by carrying out the reaction as described for I from $Ru_3(CO)_{12}$ (1.59 g, 2.48 mmol) and $[(C_5H_5)(CO)_2MnPCH_3Cl_2]$ (0.73 g, 2.49 mmol). The green fraction was eluted with 4/1 pentane/toluene and recrystallised from dichloromethane/pentane. Yield 200 mg (8% based on $Ru_3(CO)_{12}$). M.p. 135—140°C (dec.). Found: C, 20.20; H, 0.31; P, 3.00. Calcd. for $C_{16}H_3O_{15}Ru_5P$: C, 19.77; H, 0.30; P, 3.19%. Mass spec. m/e 971. Crystals of III are fairly air stable, but a slow decomposition occurs in solution, even under nitrogen, to give $Ru_3(CO)_{12}$.

(4) Preparation of $Ru_5(CO)_{15}(\mu_4\text{-}PCH_2C_6H_5)$ (IV)

The compound was prepared as described for I from $Ru_3(CO)_{12}$ (1.59 g,

TABLE 1

CRYSTAL AND INTENSITY MEASUREMENT PARAMETERS

Parameter or Expt. detail	$Ru_5(CO)_{15}PC_6H_5$	$Ru_5(CO)_{15}PCH_2CH_3$
a (Å)	9.543(9)	15.77(2)
b (Å)	9.560(7)	9.917(6)
c (Å)	29.63(4)	19.64(2)
α (deg)	90.90(9)	90.0
β (deg)	89.78(9)	124.32(6)
γ (deg)	90.33(7)	90.0
mol. wt or formula wt	1033.38	985.32
V (Å^3)	2702.58	2536.93
D_c (g cm^{-3})	2.54	2.58
Z	4	4
$F(000)$	1944	1848
space group	$P\bar{1}$	C_c
μ(Mo-K_α) (cm^{-1})	28	29.7
λ(Mo-K_α) (Å) (graphite monochromator)	0.71069	0.71069
Ω scan $\Delta\omega$	1.0	1.2
background time/peak time	0.4	0.4
reflections measured	h, $\pm k$, $\pm l$	h, k, $\pm l$
$2\theta_{max}$ (deg)	36	42
total number recorded	3331	1331
significance test	$Fo > 4\sigma (Fo)$	$Fo > 3\sigma (Fo)$
reflections remaining	2810	1289
reflections in between ref. reflection	100	100
scan speed (variable) (deg. min^{-1})	1.1—29.3	0.8—29.3

2.48 mmol) and [(C₅H₅)(CO)₂MnPCH₂C₆H₅Cl₂] (0.92 g, 2.49 mmol). The green fraction was eluted with 4/1 pentane/toluene and recrystallised from dichloromethane/pentane. Yield 60 mg (2.5% based on $Ru_3(CO)_{12}$). M.p. 180—190°C (dec.). Found: C, 25.30; H, 0.56; P, 2.68. Calcd. for $C_{22}H_7O_{15}Ru_5P$: C, 25.21; H, 0.66; P, 2.96%. Mass spec. m/e 1047. Crystals of IV are stable for weeks in the air, and solutions are stable under nitrogen.

X-ray crystallography: Data collection and refinement

Suitable crystals for X-ray work, obtained by cooling the solution of the compound in dichloromethane/pentane at −20°C, were mounted in capillaries.

A Syntex-P3 four-circle diffractometer was used. Space groups as determined by diffractometry were checked by examination of precession photographs for systematic absences. Cell parameters (refinement on angular settings for 15 reflections with $2\theta > 14°$) and X-ray diffraction intensities were determined on the same instrument at 223 K (Mo-K_α, λ 0.71069 Å), graphite monochromator, ω-scan, with $1.1 < \omega \leqslant 29.3°$ min⁻¹ and $2 \leqslant 2\theta \leqslant 36°$ for $[Ru_5(CO)_{15}PC_6H_5]$ (I) and $0.8 < \omega \leqslant 29.3°$ min⁻¹, $2 \leqslant 2\theta \leqslant 42°$ for $[Ru_5(CO)_{15}PCH_2CH_3]$ (II). One standard reflection was measured for every 100 reflections during data collection as a check on crystal and instrument stability. A total of 3331 reflections were collected for I of which 2810 having $F_0 > 4\sigma$ were used and a total of 1331 reflections were collected for II of which 1289 having $F_0 > 3\sigma$ were used to solve and refine the structures. The structures were solved by direct methods [8] using Syntex-XTL equipment. The structures were refined using partially anisotropic models with anisotropic thermal parameters for all metal atoms in both cases. A weighting scheme based on counting statistics was used throughout. The refinement converged at $R_1 = 0.061$ and $R_2 = 0.075$ for I and $R_1 = 0.046$ and $R_2 = 0.069$ for II where R_1 and R_2 are given by

$$R_1 = (\Sigma||Fo| - |Fc||)/\Sigma|Fo|$$

$$R_2 = [\Sigma W(|Fo| - |Fc|)^2]^{1/2}/[\Sigma W|Fo|^2]^{1/2}$$

Results and discussion

One of the few routes to trinuclear heterometallic phosphorus-bridged clusters which we have previously developed consists in dehalogenation of dichlorophosphine complexes by metal carbonyls [9—14]. In the present study we tried to extend this method to $Ru_3(CO)_{12}$ as dehalogenating agent. Surprisingly, from the reaction of [C₅H₅(CO)₂MnPRCl₂] with $Ru_3(CO)_{12}$, as in the case of $Fe_3(CO)_{12}$, we did not obtain the expected heteronuclear clusters of the type [RPRu₂Mn(CO)₈(C₅H₅)], but instead isolated manganese-free cluster compounds for the composition [Ru₅(CO)₁₅PR]. These were the only pure complexes which we were able to isolate by chromatography from the reaction mixture other than the starting materials. The fate of the manganese fragment is not clear at present, nor is the role played by manganese in these reactions. Similar experiments with uncomplexed RPCl₂ gave trace amounts of the same compounds [15], whereas preliminary experiments have shown that the penta-

TABLE 2

^{31}P AND IR DATA FOR RUTHENIUM CLUSTERS

No.	Compound	^{31}P NMR ^{a} (ppm)	IR spectra (cm^{-1})	
			Solution in toluene	Solid, in KBr pellets
I	$Ru_5(CO)_{15}PC_6H_5$	434.25	2095w; 2056s; 2030s	2094w; 2047s; 2016s; 2003w; 1992w; 1961w; 1956w
II	$Ru_5(CO)_{15}PCH_2CH_3$	435.44	2091w; 2055s; 2028s; 1995w	2095w; 2048s; 2023w; 1987w; 1955w
III	$Ru_5(CO)_{15}PCH_3$	417.58	2095w; 2055s; 2026s; 1997w	2094w; 2047s; 2030s; 2015s; 1989w; 1965w; 1947w
IV	$Ru_5(CO)_{15}PCH_2C_6H_5$	430.59	2090w; 2052s; 2026s	2090w; 2052s; 2021s; 1999w; 1987w; 1943w; 1923w; 1918w

^{a} δ-value in ppm rel. H_3PO_4 in toluene. s = strong; w = weak.

carbonylchromium moiety [$(CO)_5CrPRCl_2$] may serve the same function as [$C_5H_5(CO)_2MnPRCl_2$] to give [$Ru_5(CO)_{15}PR$] under similar conditions *.

Spectroscopic data

Mass spectroscopic and analytical data indicated that these compounds are of the composition [$Ru_5(CO)_{15}PR$]. The molecular peaks were clearly apparent for the compounds I—IV. Fragmentation by successive loss of up to 15 carbonyl groups was unequivocally demonstrated for each of the compounds, with [Ru_5PR]$^+$ as the base peak.

The presence of multiply-bridging phosphide ligands was evident from the ^{31}P NMR signals with chemical shifts in the region of 430 ppm (Table 2) relative to H_3PO_4. Low field shifts of this unusual magnitude are characteristic of multiply-bridging phosphide ligands [12].

The IR spectra of the clusters gave no indication of the presence of bridging carbonyl groups. Their simple pattern, with only three or four well resolved bands for the solution spectra, indicated a highly symmetrical arrangement of carbonyl groups around the pentametallic framework. The KBr spectra were, as is usual, somewhat more complicated than the solution spectra, the differences being most prominent in the long wavelength region. Of the structures which would be in accord with the above data, there is only one which is also consistent with "electron book keeping rules". These demand the presence of 8 metal—metal bonds within the clusters to give the inert gas configuration. Since the IR spectra indicate highly symmetrical molecules, the most probable structure must contain the ruthenium metal atoms at five positions of an idealised octahedron with the phosphorus atom occupying the sixth position. A structure of this type would be paralleled by that of the isoelectronic cluster

* The reaction product of $Ru_3(CO)_{12}$ and [$(CO)_5CrPCH_2C_6H_5Cl_2$] upon chromatography gave [$Ru_5(CO)_{15}PCH_2C_6H_5$] and the yield was somewhat lower.

[Os$_5$(CO)$_{15}$POMe] [3] and would be consistent with the [Fe$_5$(CO)$_{15}$C] structure [16], where instead of an R—P group a carbon atom acts as the four electron donor. That this model is basically correct has been substantiated by the X-ray structure analyses of clusters I and II.

Structure of Ru$_5$(CO)$_{15}$(μ_4-PC$_6$H$_5$) (I)

This compound was obtained by the reaction of [(C$_5$H$_5$)(CO)$_2$MnPC$_6$H$_5$Cl$_2$] and Ru$_3$(CO)$_{12}$ in toluene at 100°C and is fairly air-stable. The structure of the compound was determined by a single-crystal X-ray study and its molecular structure is shown in Fig. 1. There are two crystallographically-independent molecules within the asymmetric unit. The geometry of these two is so similar, that the following discussion is based on mean values for chemically equivalent distances and angles unless otherwise stated. Correspondingly, Fig. 1. shows the shape of only one molecule. Values for the individual clusters are given in Tables 3—6. The molecule consists of five ruthenium atoms in a square pyramidal arrangement with the phosphide ligand capping the square face. It can also be regarded as a distorted octahedral arrangement with five ruthenium atoms and
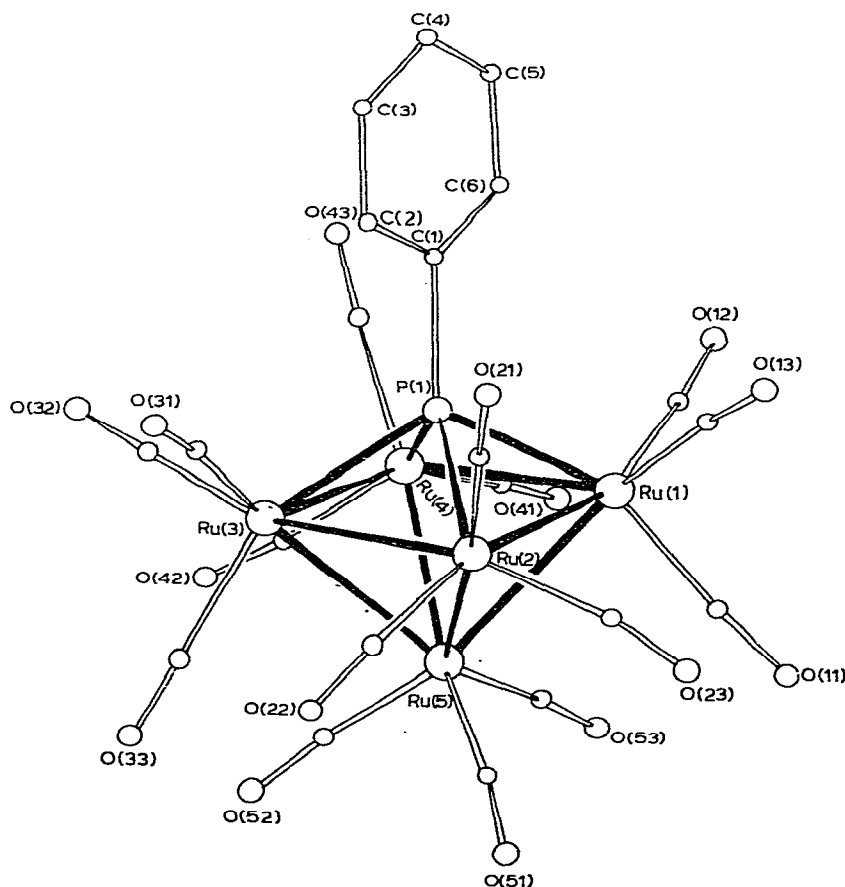

Fig. 1. The molecular structure of [Ru$_5$(CO)$_{15}$PC$_6$H$_5$].

TABLE 3

FRACTIONAL COORDINATES (WITH e.s.d.'s) AND ISOTROPIC THERMAL PARAMETERS FOR [Ru$_5$(CO)$_{15}$PC$_6$H$_5$] [a]

Atom	x	y	z	B
Ru(1)	0.3910(2)	0.6021(2)	0.0998(1)	
Ru(2)	0.2633(2)	0.6777(2)	0.1832(1)	
Ru(3)	0.1056(2)	0.8904(2) ·	0.1416(1)	
Ru(4)	0.2192(2)	0.8070(2)	0.0551(1)	
Ru(5)	0.0924(2)	0.6054(2)	0.1080(1)	
P(1)	0.3414(7)	0.8301(7)	0.1257(2)	0.8(1)
C(11)	0.3612(25)	0.4025(24)	0.1003(8)	1.0(5)
O(11)	0.3535(19)	0.2843(18)	0.0963(6)	2.4(4)
C(12)	0.4992(27)	0.6179(26)	0.0486(8)	1.8(6)
O(12)	0.5675(19)	0.6371(19)	0.0166(6)	2.6(4)
C(13)	0.5559(25)	0.5770(24)	0.1353(8)	1.1(5)
O(13)	0.6451(18)	0.5555(17)	0.1572(5)	1.9(4)
C(21)	0.3851(29)	0.7546(27)	0.2243(9)	2.0(6)
O(21)	0.4684(25)	0.8046(24)	0.2496(8)	5.7(6)
C(22)	0.1182(28)	0.6884(28)	0.2226(9)	2.0(6)
O(22)	0.0241(24)	0.6913(23)	0.2499(7)	5.0(5)
C(23)	0.3223(30)	0.4967(29)	0.1968(9)	2.4(6)
O(23)	0.3436(21)	0.3841(20)	0.2082(6)	3.6(5)
C(31)	0.1442(29)	1.0121(28)	0.1924(9)	2.4(6)
O(31)	0.1538(20)	1.0726(19)	0.2252(6)	3.0(4)
C(32)	0.0543(30)	1.0497(29)	0.1081(9)	2.3(6)
O(32)	0.0281(18)	1.1504(17)	0.0909(5)	2.0(4)
C(33)	−0.0874(29)	0.8453(28)	0.1602(9)	2.2(6)
O(33)	−0.1940(19)	0.8241(19)	0.1744(6)	2.7(4)
C(41)	0.2473(31)	0.7004(30)	0.0013(9)	2.6(6)
O(41)	0.2607(17)	0.6382(17)	−0.0315(5)	1.8(4)
C(42)	0.0370(26)	0.8530(25)	−0.0354(8)	1.2(5)
O(42)	−0.0698(19)	0.8864(19)	0.0240(6)	2.7(4)
C(43)	0.3086(29)	0.9745(28)	0.0304(9)	1.8(6)
O(43)	0.3630(18)	1.0667(17)	0.0158(6)	2.0(4)
C(51)	0.0442(30)	0.4697(29)	0.1515(9)	2.8(6)
O(51)	−0.0018(19)	0.3872(18)	0.1743(6)	2.5(4)
C(52)	−0.0864(27)	0.6484(26)	0.0919(8)	1.5(5)
O(52)	−0.2055(19)	0.6643(19)	0.0782(6)	2.9(4)
C(53)	0.1070(30)	0.4846(29)	0.0585(9)	2.6(6)
O(53)	0.1057(17)	0.4068(17)	0.0265(5)	1.9(4)
C(1)	0.4867(27)	0.9655(26)	0.1301(8)	1.7(6)
C(2)	0.4870(26)	1.0568(25)	0.1658(8)	1.2(5)
C(3)	0.5945(28)	1.1583(27)	0.1678(8)	1.8(6)
C(4)	0.6930(26)	1.1590(25)	0.1331(8)	1.2(5)
C(5)	0.6904(25)	1.0689(25)	0.0995(8)	1.1(5)
C(6)	0.5901(28)	0.9663(27)	0.0981(9)	1.8(6)
Ru(6)	−0.3774(2)	1.1011(2)	0.3573(1)	
Ru(7)	−0.1588(2)	1.2604(2)	0.3168(1)	
Ru(8)	−0.0924(2)	1.3885(2)	0.4010(1)	
Ru(9)	−0.3032(2)	1.2175(2)	0.4445(1)	
Ru(10)	−0.0960(2)	1.0911(2)	0.3921(1)	
P(2)	−0.3174(7)	1.3365(6)	0.3744(2)	0.5(1)
C(61)	−0.5406(24)	1.0576(23)	0.3921(7)	0.6(5)
O(61)	−0.6408(19)	1.0241(18)	0.4091(6)	2.5(4)
C(62)	−0.4895(26)	1.1312(26)	0.3073(8)	1.4(5)
O(62)	−0.5487(20)	1.1536(20)	0.2754(6)	3.4(4)
C(63)	−0.3353(30)	0.9183(29)	0.3366(9)	2.5(6)
O(63)	−0.3141(18)	0.8070(17)	0.3214(6)	2.0(4)
C(71)	−0.2347(27)	1.3899(26)	0.2753(8)	1.7(6)
O(71)	−0.2741(24)	1.4697(23)	0.2496(7)	5.2(5)
C(72)	−0.1688(29)	1.1127(29)	0.2770(9)	2.4(6)

TABLE 3 (continued)

Atom	x	y	z	B
O(72)	−0.1679(21)	1.0184(20)	0.2499(6)	3.8(5)
C(73)	0.0169(31)	1.3104(30)	0.3032(10)	3.2(7)
O(73)	0.1373(20)	1.3354(19)	0.2933(6)	2.9(4)
C(81)	0.0968(27)	1.3606(27)	0.4079(8)	1.8(6)
O(81)	0.2227(18)	1.3500(18)	0.4089(6)	2.3(4)
C(82)	−0.0621(26)	1.5538(26)	0.3665(8)	1.5(5)
O(82)	0.0417(19)	1.6440(18)	0.3440(6)	2.6(4)
C(83)	−0.1168(28)	1.4955(27)	0.4555(8)	2.0(6)
O(83)	−0.1312(16)	1.5681(15)	0.4843(5)	0.9(3)
C(91)	−0.4665(24)	1.3084(24)	0.4699(7)	0.6(5)
O(91)	−0.5677(17)	1.3609(17)	0.4812(5)	1.8(4)
C(92)	−0.1932(26)	1.2494(26)	0.4990(8)	1.3(5)
O(92)	−0.1394(18)	1.2601(18)	0.5318(6)	2.2(4)
C(93)	−0.3557(29)	1.0337(29)	0.4634(9)	2.4(6)
O(93)	−0.3839(20)	0.9315(19)	0.4769(6)	3.0(4)
C(101)	0.0443(27)	1.0343(26)	0.3507(8)	1.5(6)
O(101)	0.1259(22)	0.9790(22)	0.3260(7)	4.2(5)
C(102)	−0.1430(26)	0.9075(26)	0.4096(8)	1.6(6)
O(102)	−0.1703(18)	0.7938(17)	0.4199(6)	2.3(4)
C(103)	0.0287(26)	1.1015(26)	0.4418(8)	1.4(5)
O(103)	0.1007(19)	1.1017(18)	0.4725(6)	2.6(4)
CX(1)	−0.4543(28)	1.4794(28)	0.3649(9)	2.0(6)
CX(2)	−0.4565(26)	1.5840(25)	0.4009(8)	1.3(5)
CX(3)	−0.5588(25)	1.6808(24)	0.4005(8)	0.9(5)
CX(4)	−0.6499(28)	1.6816(27)	0.3663(8)	1.9(6)
CX(5)	−0.6466(27)	1.5916(26)	0.3305(8)	1.5(6)
CX(6)	−0.5497(26)	1.4835(25)	0.3327(8)	1.3(5)
H(2)	0.4061	1.0515	0.1891	5.0
H(3)	0.5991	1.2395	0.1932	5.0
H(4)	0.7655	1.2254	0.1331	5.0
H(5)	0.7677	1.0712	0.0761	5.0
H(6)	0.5891	0.8947	0.0733	5.0
HX(2)	−0.3793	1.5863	0.4227	5.0
HX(3)	−0.5583	1.7562	0.4253	5.0
HX(4)	−0.7372	1.7477	0.3690	5.0
HX(5)	−0.7032	1.6108	0.3030	5.0
HX(6)	−0.5479	1.4145	0.3057	5.0

[a] P(1), Ru(1)...Ru(5), C(11)...C(53), O(11)...O(53), C(1)...C(6), H(2)...H(6) for the first molecule; P2, Ru(6)...Ru(10), C(61)...C(103), O(61)...O(103), CX(1)...CX(6), HX(2)...HX(6) for the second molecule. Numbering of carbonyl groups, C(11)...C(13), O(11)...O(13) bonded to Ru(1) ..., C(101)...C(103), O(101)...O(103) bonded to Ru(10). Hydrogen positions as calculated from sp^2 geometry of carbon atoms. H(i) bonded to C(i) for the first molecule and HX(i) to CX(i) for the second molecule.

TABLE 4

ANISOTROPIC THERMAL PARAMETERS FOR $[Ru_5(CO)_{15}PC_6H_5]$ [a, b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru(1)	0.87(10)	1.19(10)	0.76(9)	−0.20(8)	−0.06(8)	0.19(8)
Ru(2)	1.55(11)	1.66(11)	0.56(9)	−0.41(9)	−0.09(8)	0.60(8)
Ru(3)	0.90(10)	1.36(10)	1.09(10)	−0.11(8)	0.05(8)	−0.01(8)
Ru(4)	0.78(10)	1.17(10)	0.92(10)	−0.03(8)	0.03(8)	0.24(8)
Ru(5)	0.49(10)	1.29(10)	1.10(10)	−0.40(8)	−0.15(8)	0.28(8)
Ru(6)	1.03(10)	1.12(10)	1.22(10)	−0.15(8)	−0.24(8)	0.28(8)
Ru(7)	1.37(11)	1.59(10)	0.58(9)	0.03(9)	0.15(8)	0.32(8)
Ru(8)	0.85(10)	1.01(10)	0.78(9)	−0.24(8)	−0.03(8)	0.39(8)
Ru(9)	1.03(10)	1.00(10)	0.81(9)	−0.20(8)	0.11(8)	0.51(8)
Ru(10)	0.98(10)	1.06(10)	1.21(10)	0.24(8)	−0.02(8)	0.19(8)

[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.

TABLE 5

BOND LENGTHS WITH e.s.d's (Å) FOR [Ru$_5$(CO)$_{15}$PC$_6$H$_5$]

Molecule 1		Molecule 2	
Atoms	Length	Atoms	Length
(a) Ruthenium—ruthenium bonds			
Ru(1)—Ru(2)	2.837(3)	Ru(6)—Ru(7)	2.848(3)
Ru(1)—Ru(4)	2.900(3)	Ru(6)—Ru(9)	2.886(3)
Ru(1)—Ru(5)	2.859(3)	Ru(6)—Ru(10)	2.883(5)
Ru(2)—Ru(3)	2.838(3)	Ru(7)—Ru(8)	2.835(3)
Ru(2)—Ru(5)	2.840(3)	Ru(7)—Ru(10)	2.845(3)
Ru(3)—Ru(4)	2.882(3)	Ru(8)—Ru(9)	2.896(3)
Ru(3)—Ru(5)	2.887(3)	Ru(8)—Ru(10)	2.851(3)
Ru(4)—Ru(5)	2.774(3)	Ru(9)—Ru(10)	2.780(3)
(b) Ruthenium—phosphorus distances			
Ru(1)—P(1)	2.350(7)	Ru(6)—P(2)	2.366(6)
Ru(2)—P(1)	2.375(7)	Ru(7)—P(2)	2.384(6)
Ru(3)—P(1)	2.370(7)	Ru(8)—P(2)	2.339(6)
Ru(4)—P(1)	2.407(7)	Ru(9)—P(2)	2.391(6)
(c) Ruthenium—carbon distances			
Ru(1)—C(11)	1.929(23)	Ru(6)—C(61)	1.912(23)
Ru(1)—C(12)	1.840(25)	Ru(6)—C(62)	1.858(24)
Ru(1)—C(13)	1.915(26)	Ru(6)—C(63)	1.889(28)
Ru(2)—C(21)	1.829(26)	Ru(7)—C(71)	1.907(25)
Ru(2)—C(22)	1.810(26)	Ru(7)—C(72)	1.827(27)
Ru(2)—C(23)	1.872(28)	Ru(7)—C(73)	1.787(30)
Ru(3)—C(31)	1.924(27)	Ru(8)—C(81)	1.839(26)
Ru(3)—C(32)	1.897(27)	Ru(8)—C(82)	1.916(24)
Ru(3)—C(33)	1.968(27)	Ru(8)—C(83)	1.912(25)
Ru(4)—C(41)	1.897(28)	Ru(9)—C(91)	1.932(23)
Ru(4)—C(42)	1.892(25)	Ru(9)—C(92)	1.947(24)
Ru(4)—C(43)	1.960(27)	Ru(9)—C(93)	1.916(28)
Ru(5)—C(51)	1.896(28)	Ru(10)—C(101)	1.888(25)
Ru(5)—C(52)	1.824(25)	Ru(10)—C(102)	1.888(25)
Ru(5)—C(53)	1.859(27)	Ru(10)—C(103)	1.898(24)
(d) Phosphorus—carbon distances			
P(1)—C(1)	1.895(26)	P(2)—CX(1)	1.920(27)
(e) Carbon—oxygen distances			
C(11)—O(11)	1.136(29)	C(61)—O(61)·	1.125(29)
C(12)—O(12)	1.164(31)	C(62)—O(62)	1.127(30)
C(13)—O(13)	1.094(29)	C(63)—O(63)	1.168(32)
C(21)—O(21)	1.188(35)	C(71)—O(71)	1.152(33)
C(22)—O(22)	1.205(35)	C(72)—O(72)	1.199(33)
C(23)—O(23)	1.152(34)	C(73)—O(73)	1.208(35)
C(31)—O(31)	1.126(32)	C(81)—O(81)	1.207(31)
C(32)—O(32)	1.127(32)	C(82)—O(82)	1.114(30)
C(33)—O(33)	1.118(33)	C(83)—O(83)	1.099(29)
C(41)—O(41)	1.138(32)	C(91)—O(91)	1.137(28)
C(42)—O(42)	1.125(31)	C(92)—O(92)	1.105(29)
C(43)—O(43)	1.113(31)	C(93)—O(93)	1.093(33)
C(51)—O(51)	1.132(33)	C(101)—O(101)	1.187(32)
C(52)—O(52)	1.220(31)	C(102)—O(102)	1.162(30)
C(53)—O(53)	1.195(32)	C(103)—O(103)	1.141(30)

one phosphorus atom taking the sixth position of the octahedron. The overall geometry is similar to that of [Os$_5$(CO)$_{15}$POMe] [3], which contains a penta-coordinated phosphorus atom. The average Ru—Ru distance in [Ru$_5$(CO)$_{15}$-PC$_6$H$_5$] (I) is 2.852 Å as compared to the Ru—Ru distances in other organo-

metallic species (2.848 Å for [Ru$_3$(CO)$_{12}$] [17], 2.840—3.034 Å for [Ru$_6$-(CO)$_{17}$C] [18], 2.853—2.956 Å for [Ru$_6$(CO)$_{14}$(mesitylene)) [19] and 2.954 Å for [H$_2$Ru$_6$(CO)$_{18}$] [20]). No significant difference is observed for the chemically different bonds between ruthenium atoms in the equatorial plane (mean 2.864 Å) and those radiating from the apical ruthenium atoms Ru(5), even though one of these 'apical' bonds appears to be significantly shorter than the mean (2.840 Å) for both the molecules. The mean Ru—P distance is 2.375 Å, which is almost the same as that observed for the very similar osmium analogue [Os$_5$-(CO)$_{15}$POMe] [3], in which the average Os—P distance is 2.362 Å. There is also not much difference between the observed Ru—P distance and that between ruthenium and a terminally bonded phosphine in [Ru$_3$(CO)$_{11}$PPh$_3$] (2.308 Å) [21].

Every one of the five ruthenium atoms has three terminal carbonyl ligands with Ru—C distances ranging from 1.808 Å to 1.971 Å (average 1.888 Å) and C—O distances ranging from 1.096 to 1.223 Å, the average being 1.148 Å. The Ru—C—O angles range from 169.9(2.4)° to 178.2(2.4)°. Even though the individual deviation from linearity for most of the MCO fragments are not very significant, in the light of the reported standard deviations, bending might be expected on the basis of simple symmetry arguments [22,23].

The four basal ruthenium atoms are coplanar (maximum deviation 0.16 Å) and the fifth ruthenium atom lies 1.990 Å below this plane for the first molecule. Almost exactly the same distance (1.989 Å) is observed for the second independent molecule within the unit cell. The phosphorus atom of the phosphide ligand bonds to four basal ruthenium atoms, lying 1.241 Å above the equatorial Ru$_4$ plane with the equivalent value for the second molecule (1.228 Å) being almost the same within the limits of error (average 1.235 Å). Ruthenium atoms 2 and 4 are almost equidistant from the diagonal plane passing through the phosphorus atom and ruthenium atoms 1 and 3 (Ru(2) and Ru(4)) lie 1.979 and 2.057 Å, respectively, out of this plane). The distance of Ru(5) from this plane when extended down, is 0.114 Å, indicating a rather small deviation from C_4 symmetry for the cluster framework. The deviation is also apparent from one relatively short apical Ru—Ru distance (see above). The same kind of distortion is observed for [Os$_5$(CO)$_{15}$POMe] [3], where one apical Os—Os bond (2.803 Å) is significantly shorter than the mean Os—Os distance (2.851 Å), and is also found in [Ru$_5$(CO)$_{15}$PCH$_2$CH$_3$] (II) (Table 9).

The carbonyl ligands bonded to the equatorial ruthenium atoms roughly fall into two classes: those on the side of the phosphorus atom and those pointing to the side of the apical ruthenium atoms. Adjacent Ru(CO)$_3$ groups have one or two CO groups pointing alternately up or down, so that the Ru(CO)$_3$ groups on opposite corners of the equatorial plane have very similar surroundings. This same type of alternating behaviour is present in both independent molecules of I, and also observed for [Ru$_5$(CO)$_{15}$PCH$_2$CH$_3$] (II). Obviously it is not a consequence of steric influences of the organic groups (R) bonded to the phosphorus atoms, since their orientation, while being the same for the two independent molecules of I (R = C$_6$H$_5$), is different for II (R = CH$_2$CH$_3$); the ring plane is parallel to the Ru(1)—Ru(2) axis in I, whereas for II the CH$_3$ group is almost staggered with respect to Ru(4).
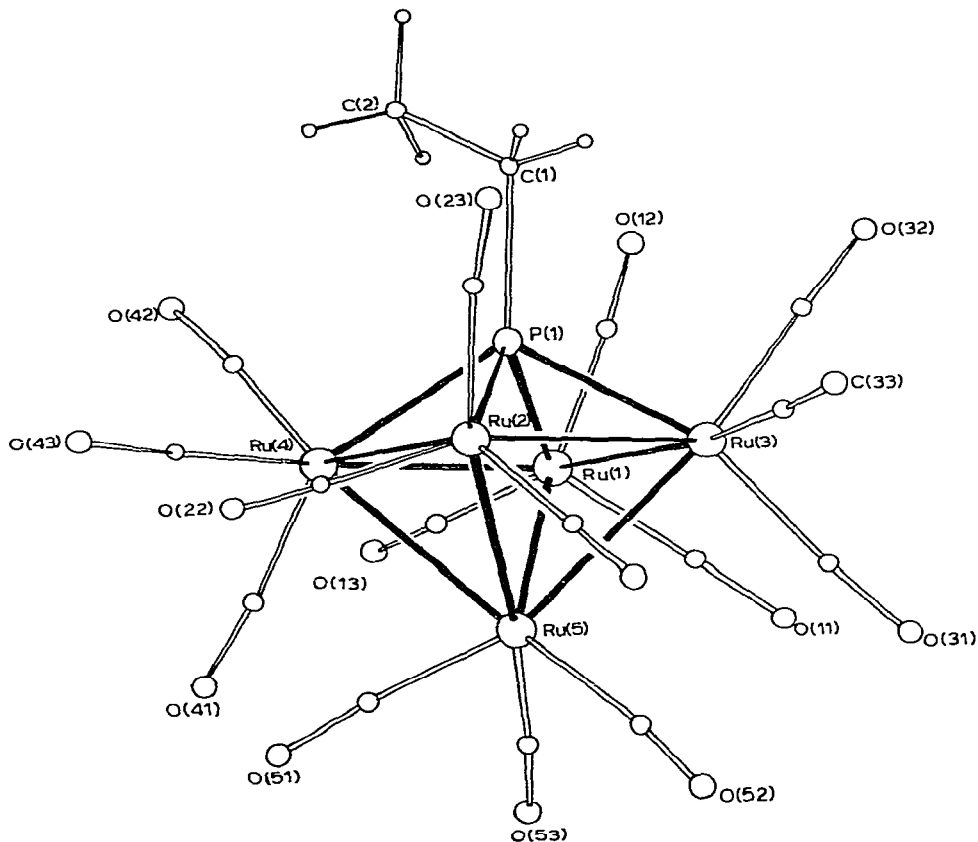
Fig. 2. The molecular structure of [Ru$_5$(CO)$_{15}$PCH$_2$CH$_3$].

TABLE 6

BOND ANGLES (deg) WITHIN THE [Ru$_5$(CO)$_{15}$PC$_6$H$_5$] CLUSTERS

Molecule 1		Molecule 2	
Atoms	Angle	Atoms	Angle
Ru—Ru—Ru angles			
Apical angles at Ru(5)		Apical angles at Ru(10)	
Ru(2)—Ru(5)—Ru(1)	59.7(1)	Ru(7)—Ru(10)—Ru(6)	59.6(1)
Ru(3)—Ru(5)—Ru(1)	90.0(1)	Ru(8)—Ru(10)—Ru(6)	90.0(1)
Ru(3)—Ru(5)—Ru(2)	59.4(1)	Ru(8)—Ru(10)—Ru(7)	59.7(1)
Ru(4)—Ru(5)—Ru(1)	62.0(1)	Ru(9)—Ru(10)—Ru(6)	61.2(1)
Ru(4)—Ru(5)—Ru(2)	91.9(1)	Ru(9)—Ru(10)—Ru(7)	92.1(1)
Ru(4)—Ru(5)—Ru(3)	61.2(1)	Ru(9)—Ru(10)—Ru(8)	61.9(1)
Angles at equatorial Ru(1)...Ru(4)		Angles at equatorial Ru(6)...Ru(9)	
Range 57.5(1)°—61.4(1)° and		Range 57.6(1)°—61.1(1)° and	
89.4(1)°—91.4(1)°, respectively		89.1(1)°—91.0(1)°, respectively	
P—Ru—Ru angles			
P(1)—Ru(1)—Ru(5)	76.0(2)	P(2)—Ru(6)—Ru(10)	74.9(2)
P(1)—Ru(2)—Ru(5)	76.0(2)	P(2)—Ru(7)—Ru(10)	75.4(2)
P(1)—Ru(3)—Ru(5)	75.2(2)	P(2)—Ru(8)—Ru(10)	75.9(2)
P(1)—Ru(4)—Ru(5)	76.9(2)	P(2)—Ru(9)—Ru(10)	76.6(2)
Terminal atoms P(1), Ru(1)...Ru(4)		Terminal atoms P(2), Ru(6)...Ru(9)	
Range 52.3(2)°—53.5(2)°		Range 51.4(2)°—53.8(2)°	
C—Ru—C angles			
Range 88.8(1.2)°—100.3(1.1)°		Range 88.3(1.1)°—98.2(1.1)°	
Ru—C—O angles			
Range 170.4(2.4)°—178.0(2.4)°		Range 170.2(2.2)°—179.0(2.1)°	

Structure of $Ru_5(CO)_{15}(\mu_4\text{-}PCH_2CH_3)$ (II)

This compound was obtained by treating $[(C_5H_5)(CO)_2MnPC_2H_5Cl_2]$ with $Ru_3(CO)_{12}$ in toluene at 100°C. It is air-stable but dilute solutions in dichloromethane decompose to give $Ru_3(CO)_{12}$ and other, unidentified, products. In order to confirm the crystallographic results obtained for I, the structure of II, which gave good crystals from dichloromethane/pentane, was determined by

TABLE 7

FRACTIONAL COORDINATES (with e.s.d.'s) AND ISOTROPIC THERMAL PARAMETERS FOR $[Ru_5(CO)_{15}PCH_2CH_3]$ [a]

Atom	x	y	z	B
Ru(1)	0.4722	0.4845	0.0999	
Ru(2)	0.4729(2)	0.4679(2)	0.3067(1)	
Ru(3)	0.5134(2)	0.6745(2)	0.2262(1)	
Ru(4)	0.4289(2)	0.2811(2)	0.1763(1)	
Ru(5)	0.6170(2)	0.4215(2)	0.2697(2)	
P(1)	0.3815(5)	0.5115(5)	0.1628(4)	
C(1)	0.2431(20)	0.5725(23)	0.1039(16)	2.5(4)
C(2)	0.1652(22)	0.4745(29)	0.0490(17)	3.1(5)
C(11)	0.5727(23)	0.5823(28)	0.0973(18)	2.8(5)
O(11)	0.6357(18)	0.6430(23)	0.0941(13)	5.2(5)
C(12)	0.3637(18)	0.5730(25)	0.0042(15)	1.4(5)
O(12)	0.2948(17)	0.6192(22)	−0.0543(13)	3.5(4)
C(13)	0.4738(23)	0.3361(29)	0.0401(18)	2.7(6)
O(13)	0.4712(18)	0.2545(23)	−0.0018(14)	3.6(5)
C(21)	0.5796(18)	0.5526(23)	0.4004(14)	1.8(4)
O(21)	0.6447(16)	0.6035(21)	0.4621(13)	4.9(4)
C(22)	0.4847(22)	0.3220(27)	0.3726(17)	2.5(5)
O(22)	0.4908(16)	0.2364(22)	0.4151(13)	4.6(4)
C(23)	0.3629(20)	0.5377(26)	0.3117(16)	3.1(5)
O(23)	0.3044(16)	0.5901(18)	0.3182(12)	3.0(4)
C(31)	0.6372(23)	0.7451(29)	0.2462(17)	2.2(6)
O(31)	0.7095(17)	0.7968(22)	0.2558(13)	4.1(4)
C(32)	0.4249(20)	0.8043(27)	0.1485(16)	2.6(5)
O(32)	0.3726(17)	0.8864(24)	0.1000(13)	4.6(5)
C(33)	0.5263(20)	0.7825(26)	0.3093(15)	2.0(5)
O(33)	0.5288(17)	0.8546(22)	0.3571(14)	4.8(4)
C(41)	0.5153(19)	0.1597(24)	0.1721(15)	1.9(5)
O(41)	0.5649(16)	0.0739(19)	0.1669(13)	3.4(4)
C(42)	0.3145(16)	0.2190(22)	0.0764(13)	1.1(4)
O(42)	0.2489(15)	0.1679(19)	0.0173(12)	2.3(4)
C(43)	0.3990(19)	0.1603(24)	0.2314(15)	2.7(4)
O(43)	0.3731(16)	0.0796(19)	0.2609(13)	3.5(4)
C(51)	0.6485(19)	0.2634(25)	0.3342(15)	1.6(5)
O(51)	0.6714(13)	0.1652(17)	0.3717(11)	2.9(3)
C(52)	0.7327(20)	0.5211(26)	0.3558(16)	2.4(5)
O(52)	0.8031(17)	0.5672(20)	0.4074(13)	4.3(4)
C(53)	0.6935(22)	0.3746(29)	0.2238(17)	1.9(5)
O(53)	0.7373(15)	0.3397(18)	0.1990(11)	3.4(4)
H(1)	0.2359	0.6466	0.0650	5.0
H(2)	0.2279	0.6047	0.1414	5.0
H(3)	0.1988	0.4718	0.0137	5.0
H(4)	0.1649	0.3888	0.0759	5.0
H(5)	0.0911	0.5118	0.0176	5.0

[a] Numbering of carbonyl groups, C(11)...C(13), O(11)...O(13) bonded to Ru(1) ..., H(1) and H(2) bonded to C(1) and H(3)...H(5) bonded to C(2). Hydrogen positions as indicated by difference Fourier methods.

TABLE 8

ANISOTROPIC THERMAL PARAMETERS FOR $[Ru_5(CO)_{15}PCH_2CH_3]$ [a, b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru(1)	2.23(9)	1.88(9)	1.56(8)	−0.38(7)	0.94(8)	−0.05(7)
Ru(2)	1.54(8)	1.93(9)	1.31(7)	0.19(7)	0.61(7)	0.10(6)
Ru(3)	1.72(9)	1.22(8)	1.80(9)	−0.21(6)	0.55(7)	−0.07(6)
Ru(4)	1.57(8)	1.35(8)	1.56(8)	−0.10(6)	0.58(6)	0.12(6)
Ru(5)	1.49(7)	1.47(7)	1.53(8)	0.14(6)	0.69(6)	0.00(6)
P(1)	1.56(25)	0.62(23)	1.04(24)	0.26(20)	0.50(22)	−0.34(19)

[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.

X-ray methods. Its molecular structure is shown in Fig. 2.

As illustrated, this cluster also involves a square-pyramidal arrangement of five ruthenium atoms with the phosphorus atom capping the square face. The geometry is very similar to that of I, even quantitatively. In the following discussion, wherever appropriate, corresponding values for compound I are given in square brackets. The average Ru—Ru distance in $[Ru_5(CO)_{15}PCH_2CH_3]$ is 2.849 Å [2.852 Å] and the average Ru—P distance of 2.371 Å [2.375 Å] is also in agreement within the range of experimental error.

TABLE 9

BOND LENGTHS WITH e.s.d.'s (Å) FOR $[Ru_5(CO)_{15}PCH_2CH_3]$

Atoms	Length	Atoms	Length
(a) Ruthenium—ruthenium bonds			
Ru(1)—Ru(3)	2.882(2)	Ru(2)—Ru(4)	2.910(3)
Ru(1)—Ru(4)	2.817(2)	Ru(2)—Ru(5)	2.788(5)
Ru(1)—Ru(5)	2.852(2)	Ru(3)—Ru(5)	2.850(3)
Ru(2)—Ru(3)	2.873(3)	Ru(4)—Ru(5)	2.822(4)
(b) Ruthenium—phosphorus distances			
Ru(1)—P(1)	2.373(8)	Ru(3)—P(1)	2.360(7)
Ru(2)—P(1)	2.380(6)	Ru(4)—P(1)	2.372(6)
(c) Phosphorus—carbon and carbon—carbon distances			
P(1)—C(1)	1.903(33)	C(1)—C(2)	1.457(40)
(d) Ruthenium—carbon distances			
Ru(1)—C(11)	1.883(38)	Ru(3)—C(33)	1.864(27)
Ru(1)—C(12)	1.898(25)	Ru(4)—C(41)	1.854(30)
Ru(1)—C(13)	1.892(31)	Ru(4)—C(42)	1.870(22)
Ru(2)—C(21)	1.852(25)	Ru(4)—C(43)	1.846(28)
Ru(2)—C(22)	1.878(28)	Ru(5)—C(51)	1.897(25)
Ru(2)—C(23)	1.920(35)	Ru(5)—C(52)	1.921(28)
Ru(3)—C(31)	1.895(39)	Ru(5)—C(53)	1.926(37)
Ru(3)—C(32)	1.879(27)		
(e) Carbon—oxygen distances			
C(11)—O(11)	1.194(49)	C(33)—O(33)	1.163(36)
C(12)—O(12)	1.141(34)	C(41)—O(41)	1.198(38)
C(13)—O(13)	1.139(39)	C(42)—O(42)	1.149(30)
C(21)—O(21)	1.172(33)	C(43)—O(43)	1.186(37)
C(22)—O(22)	1.157(36)	C(51)—O(51)	1.150(30)
C(23)—O(23)	1.128(43)	C(52)—O(52)	1.095(37)
C(31)—O(31)	1.165(48)	C(53)—O(53)	1.101(45)
C(32)—O(32)	1.168(36)		

TABLE 10

BOND ANGLES (deg) WITHIN THE [Ru$_5$(CO)$_{15}$PCH$_2$CH$_3$] CLUSTER

Atoms	Angle	Atoms	Angle
Ru—Ru—Ru angles			
Apical angles at Ru(5)			
Ru(2)—Ru(5)—Ru(1)	92.0(1)	Ru(4)—Ru(5)—Ru(1)	59.5(1)
Ru(3)—Ru(5)—Ru(1)	60.7(1)	Ru(4)—Ru(5)—Ru(2)	62.5(1)
Ru(3)—Ru(5)—Ru(2)	61.2(1)	Ru(4)—Ru(5)—Ru(3)	91.4(1)
Angles at equatorial Ru(1)...Ru(4) range 58.2(1)°—60.8(1)° and 89.2(1)°—90.9(1)° respectively.			
P—Ru—Ru angles			
P(1)—Ru(1)—Ru(5)	74.8(2)	P(1)—Ru(3)—Ru(5)	75.0(2)
P(1)—Ru(2)—Ru(5)	75.9(2)	P(1)—Ru(4)—Ru(5)	75.4(2)
Terminal atoms P(1), Ru(1)...Ru(4) range 45.5(1)°—53.6(2)°			
C—Ru—C angles			
Range 88.9(1.3)°—97.3(1.2)°			
Ru—C—O angles			
Range 172.9(2.2)°—178.6(2.0)°			

As in compound I, each of the five ruthenium atoms has three terminal carbonyl ligands in compound II. Ruthenium—carbonyl linkages are quite normal, with Ru—C distances ranging from 1.852 to 1.926 Å (average 1.885 Å) [1.808 to 1.971 Å (average 1.888 Å)] and C—O distances ranging from 1.095 to 1.198 Å, the average being 1.153 Å [1.096 to 1.223 Å (average 1.148 Å)]. The Ru—C—O angles range from 172.9(2.2) to 178.6(2.0)° [169.9(2.4) to 178.2-(2.4)°]. The four basal ruthenium atoms are coplanar and the fifth ruthenium atom lies 1.969 Å [1.990 Å] below this plane, with the phosphorus atom lying 1.226 Å [1.241 Å] above it.

Acknowledgements

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