

## Cationic Ruthenium Systems. Part 2.<sup>1</sup> Synthesis, Characterization, and X-Ray Structure of Hydridopentakis(dimethylphenylphosphine)-ruthenium(II) Hexafluorophosphate: A Discussion of the Effects of Steric Strains on the Reactivity of the Complex

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The complex  $[\text{RuH}(\text{PMe}_2\text{Ph})_5][\text{PF}_6]$  has been prepared by treatment of a methanolic solution of  $[\text{RuH}(\text{cod})(\text{NH}_2\text{-NMe}_2)_3][\text{PF}_6]$  (cod = cyclo-octa-1,5-diene) with  $\text{PMe}_2\text{Ph}$  under argon and has been characterized by micro-analytical, i.r., and  $^1\text{H}$  n.m.r. data and by a three-dimensional X-ray structure determination. The colourless crystals of  $[\text{RuH}(\text{PMe}_2\text{Ph})_5][\text{PF}_6]$ ,  $M = 938$ , are orthorhombic, space group  $P2_12_12_1$ ,  $a = 21.55(3)$ ,  $b = 19.08(3)$ ,  $c = 10.38(2)$  Å,  $V = 4\,269$  Å<sup>3</sup>,  $D_m = 1.48$ ,  $D_c = 1.46$  g cm<sup>-3</sup>,  $Z = 4$ . The structure has been solved by the heavy-atom method and refined by least squares to  $R$  0.061 for 1 954 observed reflections collected on a diffractometer using graphite-monochromatized Mo- $K_\alpha$  radiation. The co-ordination about the ruthenium is distorted octahedral. The length of the bond to the phosphine *trans* to the hydride ligand (Ru-P 2.48 Å) is significantly longer than those to the other four phosphine ligands (mean Ru-P 2.40 ± 0.01 Å). There is considerable strain within the cation caused by non-bonded repulsions between the methyl and phenyl groups on different phosphine ligands. A discussion of the build-up of steric strain in co-ordination complexes containing  $\text{PMe}_2\text{Ph}$  ligands is presented.

A NUMBER of cationic hydride complexes of the type  $[\text{RuHL}_5]^+$  [1; L = P(OMe)<sub>3</sub>,<sup>2</sup> P(OEt)<sub>3</sub>,<sup>2</sup> PPh(OMe)<sub>2</sub>,<sup>3</sup> and PPh<sub>2</sub>H<sup>4</sup>] have recently been prepared. These species have been shown<sup>2,4</sup> by n.m.r. methods to possess a non-labile octahedral geometry with one unique axial and four equivalent equatorial ligands L. The stability of these complexes in solution seems to preclude their use as intermediates in further substitution or insertion reactions under mild conditions. However, attempts to increase the lability of ligands of (1) in solution by preparing similar complexes of the larger ligands PPh<sub>2</sub>(OMe), PPh<sub>2</sub>(OEt), and PPh(OEt)<sub>2</sub> failed<sup>5</sup> to produce characterizable products. During our investigations of routes to co-ordinatively unsaturated cationic ruthenium(II) hydrides we have prepared a number of complexes containing bulky tertiary phosphine ligands some of which have shown<sup>6</sup> novel reactivity. One of the complexes isolated was of type (1), *viz.*  $[\text{RuH}(\text{PMe}_2\text{Ph})_5][\text{PF}_6]$  (2) and this salt was found to be highly reactive in solution and an ideal precursor to a large range of new ruthenium(II) complexes formed by ready loss of one or more of the phosphine ligands. The structures of several of these derivatives have already been determined:  $[\text{Ru}_2\text{X}_3\text{L}_6][\text{PF}_6]$  (X = Cl<sup>7</sup> or OH<sup>8</sup>),  $[\text{Ru}(\text{O}_2\text{CMe})\text{L}_4][\text{PF}_6]$ ,<sup>9</sup>  $[\text{RuH}(\text{C}_4\text{H}_8)\text{L}_3][\text{PF}_6]$ ,<sup>10</sup>  $[\text{Ru}\{\text{S}_2\text{C}(\text{H})\text{PMe}_2\text{Ph}\}\text{L}_3][\text{PF}_6]$ ,<sup>11</sup> and  $[\text{Ru}(\text{S}_2\text{CH})\text{L}_4][\text{PF}_6]$ <sup>12</sup> (L =  $\text{PMe}_2\text{Ph}$ ). The crystal structure of (2) was determined to discover to what extent steric factors influenced its reactivity, *i.e.* to discover whether the strain energy within the cation provided the driving force for the observed ligand dissociation in solution.

In order to obtain a meaningful estimate of the strain energy in (2) the various structural parameters related to the  $\text{PMe}_2\text{Ph}$  ligand in different environments were compared. The above mentioned structure determinations provided a suitable set for this purpose. In addition, the arrangement of the substituents on the phosphorus atoms was of considerable interest since it would show to what degree the ligands could 'mesh' together, and thus provide a more precise understanding of the build-up of steric strain in co-ordination complexes containing similar ligands. Although the concept<sup>13</sup> of 'cone angle' is frequently used to describe the steric size of tertiary phosphines and phosphites, it assumes conical symmetry about a M-P bond having a length 2.28 Å and therefore predicts that co-ordination of five  $\text{PMe}_2\text{Ph}$  ligands (cone angle of 127°) would not be possible unless significant distortion and meshing of the ligands takes place. Knowledge of the nature of these ligand distortions is of chemical importance since the synthesis of complexes which are highly reactive in solution *via* dissociative processes would be facilitated by choosing the ligands so that distortions within a molecule are at a maximum.

### EXPERIMENTAL

**Synthesis of  $[\text{RuH}(\text{PMe}_2\text{Ph})_5][\text{PF}_6]$ .**—Argon-saturated methanol, which had been dried and distilled over magnesium methoxide, was used as solvent. Dimethylphenylphosphine was obtained commercially and was not further purified. Details of the preparation of  $[\text{RuH}(\text{cod})(\text{NH}_2\text{-NMe}_2)_3][\text{PF}_6]$  (cod = cyclo-octa-1,5-diene) are reported elsewhere.<sup>1</sup> The i.r. spectrum of  $[\text{RuH}(\text{PMe}_2\text{Ph})_5][\text{PF}_6]$

<sup>1</sup> Part 1, T. V. Ashworth, E. Singleton, and J. Hough, *J.C.S. Dalton*, preceding paper.

<sup>2</sup> D. A. Couch and S. D. Robinson, *Inorg. Chim. Acta*, 1974, **9**, 39.

<sup>3</sup> J. J. Hough and E. Singleton, *J.C.S. Chem. Comm.*, 1972, 371.

<sup>4</sup> J. R. Sanders, *J. Chem. Soc. (A)*, 1971, 2991.

<sup>5</sup> D. A. Couch and S. D. Robinson, *Inorg. Chem.*, 1974, **13**, 456.

<sup>6</sup> T. V. Ashworth and E. Singleton, *J.C.S. Chem. Comm.*, 1976, 705.

<sup>7</sup> M. Laing and I. Pope, *Acta Cryst.*, 1976, **B32**, 1547.

<sup>8</sup> T. V. Ashworth, M. J. Nolte, and E. Singleton, in preparation.

<sup>9</sup> T. V. Ashworth, M. J. Nolte, and E. Singleton, *J.C.S. Dalton*, 1976, 2184.

<sup>10</sup> T. V. Ashworth, E. Singleton, and M. Laing, *J. Organometallic Chem.*, 1976, **117**, C113.

<sup>11</sup> T. V. Ashworth, E. Singleton, and M. Laing, *J.C.S. Chem. Comm.*, 1976, 875.

<sup>12</sup> M. Laing, *Acta Cryst.*, in preparation.

<sup>13</sup> C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956; C. A. Tolman, W. C. Seidel, and L. W. Gosser, *ibid.*, 1974, **96**, 53; I. E. Manzer and C. A. Tolman, *ibid.*, 1975, **97**, 1955.

was recorded on a Perkin-Elmer 357 spectrophotometer and the  $^1\text{H}$  n.m.r. spectrum on a Varian A-60A machine.

In a typical synthesis  $[\text{RuH}(\text{cod})(\text{NH}_2\text{NMe}_2)_3][\text{PF}_6]$  (2.0 g, 4 mmol) was dissolved in boiling methanol (100  $\text{cm}^3$ ) under an argon atmosphere and  $\text{PMe}_2\text{Ph}$  (3.2 g, 22.8 mmol)

840s  $\text{cm}^{-1}$   $\nu(\text{P-F})$ ;  $^1\text{H}$  n.m.r. in degassed  $\text{CD}_2\text{Cl}_2$  at  $34^\circ\text{C}$   $\tau$  8.50 (br s, unsymmetrical), at  $-15^\circ\text{C}$ ,  $\tau$  8.10 (br d) 8.50 (br s), and 14.25 (m, hydride; appeared to be two overlapping 1:4:6:4:1 quintets) [ $J(P_{\text{trans.}}-H)$  30,  $J(P_{\text{cis.}}-H)$  10 Hz].

Suitable crystals were obtained by crystallization from  $\text{CH}_2\text{Cl}_2$ -MeOH under an argon atmosphere. One of dimensions  $0.2 \times 0.2 \times 0.3$  mm was used for data collection. Unit-cell constants were determined from least-squares refinement of 25 values of  $2\theta$  measured on a Philips four-circle diffractometer of the N.P.R.L., C.S.I.R.

*Crystal Data.*— $\text{C}_{40}\text{H}_{56}\text{F}_6\text{P}_6\text{Ru}$ ,  $M = 938$ , Orthorhombic, space group  $P2_12_12_1$ ,  $a = 21.55(3)$ ,  $b = 19.08(3)$ ,  $c = 10.38(2)$  Å,  $U = 4.269$  Å $^3$ ,  $D_m = 1.48$  g  $\text{cm}^{-3}$ ,  $Z = 4$ ,  $D_c = 1.46$  g  $\text{cm}^{-3}$ .

Intensities were measured with graphite-monochromatized Mo- $K_\alpha$  radiation ( $\lambda$  0.7107 Å) over the range  $\theta$  3–25°. The  $\omega$ - $2\theta$  scan mode was used; each reflection was scanned for 30 s and the same time was taken to accumulate the background count. Of the 276 intensities measured, 1954 were classified as observed;  $I > 2\sigma(I)$ . Standard reflections [(2 $\bar{2}$ 1), (08 $\bar{6}$ ), and (13 8 $\bar{3}$ )], remeasured every hour, changed respectively by +0.4, +0.4, and -2.0% during data collection (41 h). Lorentz and polarization corrections were applied; corrections for extinction and absorption were considered unnecessary [ $\mu(\text{Mo-}K_\alpha)$  6.40  $\text{cm}^{-1}$ ].

All the calculations were made on an IBM 360/65 computer with programs from the 'X-Ray' system.<sup>14</sup> The positions of the Ru and P atoms were deduced from a Patterson map. A Fourier synthesis, phased on these atoms, revealed the positions of the remaining non-hydrogen atoms. After initial refinement of positional parameters, individual isotropic temperature factors, and one overall scale factor by full-matrix least squares, the Ru, P, and F atoms were made anisotropic and the structure was then refined to convergence:  $R$  0.061 for the observed intensities. Unit weights were used throughout the refinement. The scattering factors were those of Cromer and Mann<sup>15</sup> for neutral atoms corrected only for the real part of the anomalous-dispersion effect. Observed and calculated structure factors and the thermal parameters from the final least-squares cycle are listed in Supplementary Publication No. SUP 22061 (16 pp.).\* Final atomic co-ordinates are listed in Table 1, bond lengths (uncorrected for thermal motion) and angles in Tables 2 and 3, and selected intramolecular non-bonded separations in Table 4. Figure 1 gives the numbering system, Figure 2 the contacts between two of the phenyl rings and the hydrogen atom bonded to the ruthenium, and Figure 3 the projections of groups of facial phosphine ligands on to the plane of the three phosphorus atoms.

## RESULTS AND DISCUSSION

The crystal structure consists of closely packed discrete cations and anions. Apart from four distances in the range 3.18–3.46 Å between F atoms of a hexafluorophosphate anion and C atoms of the neighbouring cations, all the intermolecular distances between non-hydrogen atoms are greater than 3.5 Å. Since these

<sup>14</sup> J. M. Stewart, G. J. Kruger, H. Ammon, C. H. Dickinson, and S. R. Hall, Comput. Sci. Tech. Rep. TR-192, 1972, University of Maryland.

<sup>15</sup> D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

TABLE 1

Final atomic co-ordinates with standard deviations in parentheses

Atom	X	Y	Z
Ru	0.071 1(1)	0.127 4(1)	0.081 5(1)
P(1)	0.004 1(2)	0.026 4(2)	0.083 8(5)
P(2)	0.135 6(2)	0.229 9(2)	0.081 9(5)
P(3)	0.095 8(2)	0.104 4(3)	-0.139 5(5)
P(4)	0.015 3(2)	0.171 4(2)	0.261 6(5)
P(5)	0.156 4(2)	0.062 7(3)	0.188 6(5)
P(6)	0.379 0(3)	0.222 2(3)	0.325 2(6)
F(1)	0.378 2(20)	0.152 2(9)	0.287 2(20)
F(2)	0.322 0(9)	0.240 8(16)	0.271 6(42)
F(3)	0.412 2(14)	0.246 7(12)	0.197 2(20)
F(4)	0.398 1(13)	0.298 2(10)	0.348 8(24)
F(5)	0.438 6(13)	0.209 2(12)	0.399 4(40)
F(6)	0.348 8(13)	0.198 9(22)	0.438 5(23)
C(11)	-0.009 4(9)	-0.015 5(10)	0.246 7(20)
C(12)	0.028 5(9)	-0.055 8(10)	-0.001 1(19)
C(13)	-0.074 9(10)	0.031 0(10)	0.018 8(19)
C(131)	-0.118 3(9)	-0.022 9(11)	0.050 3(20)
C(132)	-0.180 0(11)	-0.020 4(13)	-0.004 0(24)
C(133)	-0.195 6(11)	0.028 9(12)	-0.091 9(27)
C(134)	-0.092 1(8)	0.083 3(9)	-0.070 6(20)
C(135)	-0.153 0(11)	0.079 6(12)	-0.131 6(23)
C(21)	0.161 3(9)	0.271 9(10)	0.240 3(20)
C(22)	0.213 7(9)	0.216 7(9)	0.009 6(20)
C(23)	0.111 2(9)	0.309 8(10)	0.001 1(20)
C(231)	0.048 4(9)	0.320 9(10)	-0.035 6(20)
C(232)	0.033 1(9)	0.388 1(11)	-0.093 9(23)
C(233)	0.074 5(12)	0.438 2(12)	-0.117 1(23)
C(234)	0.141 7(12)	0.427 2(13)	-0.080 8(29)
C(235)	0.156 4(10)	0.363 0(12)	-0.019 8(22)
C(31)	0.150 9(10)	0.032 3(11)	-0.187 0(22)
C(32)	0.030 5(9)	0.079 3(10)	-0.245 6(21)
C(33)	0.125 8(9)	0.176 5(10)	-0.245 5(20)
C(331)	0.083 4(10)	0.230 1(11)	-0.272 0(20)
C(332)	0.103 3(13)	0.286 9(15)	-0.358 9(29)
C(333)	0.165 4(11)	0.279 9(13)	-0.405 7(27)
C(334)	0.201 6(10)	0.230 6(12)	-0.383 5(21)
C(335)	0.185 8(11)	0.171 6(13)	-0.300 5(24)
C(41)	0.006 4(9)	0.267 9(10)	0.276 2(19)
C(42)	0.040 0(8)	0.151 1(10)	0.423 1(22)
C(43)	-0.066 7(8)	0.150 6(8)	0.269 3(17)
C(431)	-0.094 5(10)	0.116 1(12)	0.380 4(21)
C(432)	-0.161 2(11)	0.107 6(12)	0.378 5(23)
C(433)	-0.195 6(11)	0.129 8(14)	0.280 5(25)
C(434)	-0.170 4(11)	0.160 7(12)	0.175 1(24)
C(435)	-0.104 5(8)	0.172 8(10)	0.168 2(19)
C(51)	0.204 3(9)	0.108 9(10)	0.310 6(19)
C(52)	0.222 1(9)	0.031 6(10)	0.088 4(24)
C(53)	0.144 3(8)	-0.019 6(9)	0.280 6(18)
C(531)	0.151 0(9)	-0.085 9(10)	0.220 9(19)
C(532)	0.144 0(9)	-0.147 7(10)	0.290 2(19)
C(533)	0.133 8(9)	-0.143 7(10)	0.423 7(23)
C(534)	0.127 5(9)	-0.078 3(11)	0.483 1(19)
C(535)	0.133 5(8)	-0.017 5(9)	0.411 9(21)

was added. The solution was then heated under reflux for 20 min to give a red solution from which the product  $[\text{RuH}(\text{PMe}_2\text{Ph})_3][\text{PF}_6]$  crystallized as colourless needles on cooling to room temperature. Cooling the solution to  $0^\circ\text{C}$  induced further crystallization. The crystals were collected and washed with cold methanol and then with diethyl ether (yield 2.8 g, 74%), m.p. 90–95  $^\circ\text{C}$  (decomp. in air) (Found: C, 51.6; H, 6.1. Calc. for  $\text{C}_{40}\text{H}_{56}\text{F}_6\text{P}_6\text{Ru}$ : C, 51.2; H, 6.0%): i.r. (Nujol mull) 1900m  $\nu(\text{Ru-H})$ ,

\* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

contact distances are similar to those found in related <sup>7,10,11</sup> relatively unstrained compounds, the large molecular distortions within the cation of (2) (see later)

TABLE 2

Bond lengths (Å) with probable errors in parentheses

Ru-P(1)	2.41(1)	Ru-P(2)	2.40(1)
Ru-P(3)	2.40(1)	Ru-P(4)	2.38(1)
Ru-P(5)	2.48(1)		

P(1)-C(11)	1.89(2)	P(1)-C(12)	1.87(2)
P(2)-C(21)	1.91(2)	P(2)-C(22)	1.86(2)
P(3)-C(31)	1.88(2)	P(3)-C(32)	1.85(2)
P(4)-C(41)	1.86(2)	P(4)-C(42)	1.80(2)
P(5)-C(51)	1.86(2)	P(5)-C(52)	1.85(2)

Mean P-C(alkyl) 1.86 (range  $\pm 0.05$  Å)

P(1)-C(13)	1.83(2)	P(2)-C(23)	1.82(2)
P(3)-C(33)	1.88(2)	P(4)-C(43)	1.81(2)
P(5)-C(53)	1.86(2)		

Mean P-C(phenyl) 1.84 (range  $\pm 0.034$  Å)

Mean phenyl C-C distances for individual rings to:

P(1) 1.42(3); P(2) 1.43(3); P(3) 1.40(3)	
P(4) 1.41(3); P(5) 1.39(3) (range within each ring $\pm 0.06$ Å)	
P(6)-F(1) 1.39(2)	P(6)-F(2) 1.39(3)
P(6)-F(3) 1.58(2)	P(6)-F(4) 1.53(2)
P(6)-F(5) 1.52(3)	P(6)-F(6) 1.42(3)

Mean P-F 1.47 (range  $\pm 0.10$  Å)

cannot be due to lattice forces. In addition, it has previously been shown,\* from the crystal structures of two different salts of the same cation, that packing factors have a negligible effect on the conformations of co-ordinated tertiary phosphorus groups.

The co-ordination geometry of the cation is distorted

TABLE 3

Bond angles ( $^\circ$ ) with probable errors in parentheses

P(1)-Ru-P(2)	178(1)	P(2)-Ru-P(4)	90(1)
P(1)-Ru-P(3)	90(1)	P(2)-Ru-P(5)	89(1)
P(1)-Ru-P(4)	88(1)	P(3)-Ru-P(4)	159(1)
P(1)-Ru-P(5)	92(1)	P(3)-Ru-P(5)	100(1)
P(2)-Ru-P(3)	91(1)	P(4)-Ru-P(5)	101(1)
Ru-P(1)-C(11)	116(1)	Ru-P(2)-C(21)	121(1)
Ru-P(1)-C(12)	120(1)	Ru-P(2)-C(22)	114(1)
Ru-P(1)-C(13)	121(1)	Ru-P(2)-C(23)	121(1)
Ru-P(3)-C(31)	122(1)	Ru-P(4)-C(41)	118(1)
Ru-P(3)-C(32)	117(1)	Ru-P(4)-C(42)	121(1)
Ru-P(3)-C(33)	120(1)	Ru-P(4)-C(43)	117(1)
Ru-P(5)-C(51)	119(1)	Ru-P(5)-C(53)	123(1)
Ru-P(5)-C(52)	118(1)		

Mean Ru-P-C 119(1)

C(11)-P(1)-C(12)	96(1)	C(21)-P(2)-C(22)	98(1)
C(11)-P(1)-C(13)	102(1)	C(21)-P(2)-C(23)	98(1)
C(12)-P(1)-C(13)	97(1)	C(23)-P(2)-C(22)	101(1)
C(31)-P(3)-C(32)	98(1)	C(41)-P(4)-C(42)	100(1)
C(31)-P(3)-C(33)	99(1)	C(41)-P(4)-C(43)	96(1)
C(32)-P(3)-C(33)	96(1)	C(42)-P(4)-C(43)	102(1)
C(51)-P(5)-C(52)	96(1)	C(51)-P(5)-C(53)	97(1)
C(52)-P(5)-C(53)	97(1)		

Mean C-P-C 98(1)

octahedral with two pairs of *trans*-phosphines and a unique phosphine which is *trans* to the 'vacant' position occupied by the hydride ligand.

The mean Ru-P bond length (2.40 Å) for the two pairs of *trans*-phosphine ligands falls in the upper end of the

\* M. Nolte, E. Singleton, and M. Laing, *J.C.S. Dalton*, 1976, 1979.

<sup>16</sup> L. J. Guggenberger, *Inorg. Chem.*, 1973, **12**, 1317.

range of observed values in ruthenium(II) complexes (see Table 6) but is similar to those found<sup>9</sup> for the pair of *trans*-phosphine groups in  $[\text{Ru}(\text{O}_2\text{CMe})(\text{PMe}_2\text{-Ph})_4]^+$  (mean Ru-P 2.425 Å). The Ru-P bond length (2.48 Å) to the remaining phosphine ligand is the longest yet observed in this class of complex, and although it is shorter than the 2.54 Å estimated by Guggenberger<sup>16</sup> it is longer than the 2.43 Å for a single bond estimated

TABLE 4

Selected non-bonded interatomic distances (Å)

C(13) $\cdots$ C(43)	3.47	C(13) $\cdots$ C(435)	3.18
C(11) $\cdots$ C(43)	3.41	C(11) $\cdots$ C(53)	3.33
C(11) $\cdots$ C(431)	3.41	C(134) $\cdots$ C(32)	3.21
C(134) $\cdots$ C(434)	3.40	C(134) $\cdots$ C(435)	3.02
C(21) $\cdots$ C(51)	3.33	C(21) $\cdots$ C(41)	3.36
C(23) $\cdots$ C(331)	3.27	C(22) $\cdots$ C(33)	3.35
C(22) $\cdots$ C(325)	3.39	C(31) $\cdots$ C(52)	3.25

from Pauling's covalent radii. The shortening of metal-phosphorus distances below that obtained from Pauling's covalent radii has often been cited as evidence for M-P  $\pi$  bonding, even when the ligands are relatively strong  $\sigma$  donors such as  $\text{PMe}_2\text{Ph}$ . It appears, therefore, that  $\pi$  bonding contributes very little to the bond between ruthenium and the unique phosphine in the present case.

The P-Ru-P angles for the two pairs of *trans* ligands differ considerably [P(1)-Ru-P(2) 178 and P(3)-Ru-P(4)

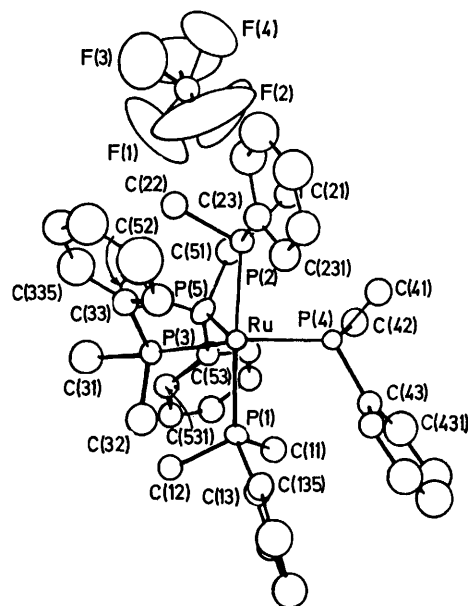


FIGURE 1 The numbering system of  $[\text{RuH}(\text{PMe}_2\text{Ph})_3][\text{PF}_6]$

159 $^\circ$ ]. P-M-P angles similar in size to the latter have been observed in other hydridophosphine complexes of transition metals<sup>17</sup> and have been attributed<sup>17</sup> to the small van der Waals radius of the hydrogen atom. The effect is well illustrated<sup>18</sup> by the three meridional triphenylphosphine groups in  $[\text{OsBrH}(\text{CO})(\text{PPh}_3)_3]$  where the P-Os-P angle for the *trans* pair of P atoms is 158 $^\circ$ . The repulsions between the phenyl rings on the different

<sup>17</sup> H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231, 279.

<sup>18</sup> P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 1962, 333.

phosphine ligands is relieved by the *trans* pair folding towards the hydrido-atom. However, the overcrowding is so severe in  $[\text{RuH}(\text{PMe}_2\text{Ph})_5]^+$  that the strains cannot be relieved by a simultaneous reduction of the P-Ru-P angle of both *trans* pairs of P atoms. The P(1) and P(2) atoms are prevented from bending away from P(5) [as do P(3) and P(4)] because the *ortho*-H atoms of C(135) and C(231) are in contact with the hydrido-atom on the ruthenium (see Figure 2) and cannot be further compressed.\* The resulting strain is reflected in the Ru-P-C(phenyl) angles being opened up to  $121^\circ$  in these two  $\text{PMe}_2\text{Ph}$  groups.

The high reactivity of  $[\text{RuH}(\text{PMe}_2\text{Ph})_5][\text{PF}_6]$  is apparently caused by the large compression strains which

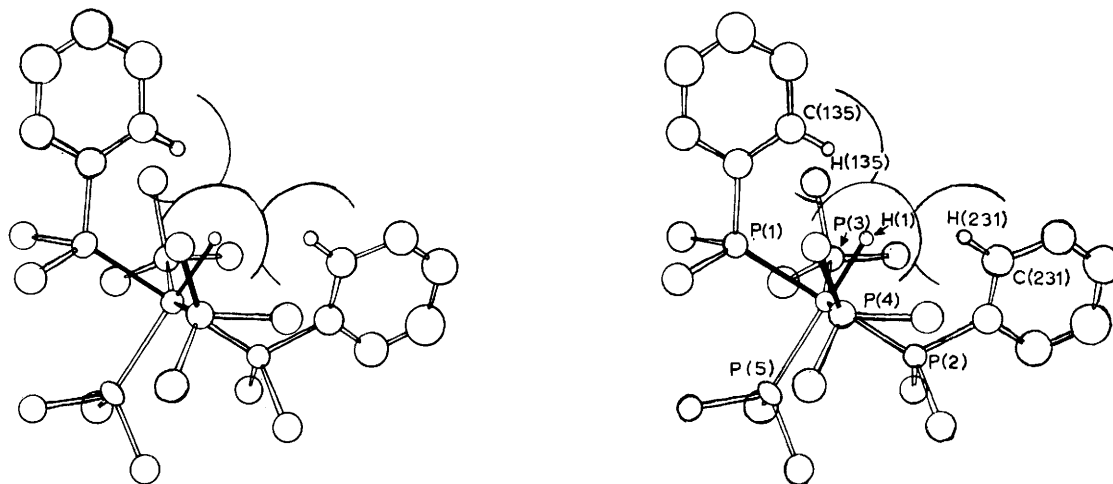


FIGURE 2 Stereoscopic projection of  $[\text{RuH}(\text{PMe}_2\text{Ph})_5][\text{PF}_6]$  on to the plane of H(1), H(231), and H(135) to illustrate the contacts between these hydrogen atoms. Some atoms have been omitted for clarity

result from the short interligand separations. In order to obtain some estimate of the energy associated with these interactions the angular distortions and C...C contact distances within the ligands were compared with those found in the related complexes containing three and four  $\text{PMe}_2\text{Ph}$  ligands. These parameters are listed in Table 5. (The structural changes which lead to the relief of steric strain have been discussed in the reports of several crystal structures containing phosphine ligands in *trans*,<sup>19</sup> *mer*,<sup>20</sup> and square-planar<sup>21</sup> arrangements.)

In the related complexes<sup>7,10,11</sup> containing three  $\text{PMe}_2\text{Ph}$  ligands arranged facially, one Ru-P-C(Me) angle always exceeds  $120^\circ$ . The methyl groups involved have an identical steric environment in each case [see Figure 3(a)]. The P-C bonds to these methyl groups are approximately parallel to each other and are perpendicular to the plane of the three *facial* P atoms. The Me...Me separations lie between 3.5 and 3.8 Å, significantly less than 4.0 Å which is twice the usual effective van der Waals radius of a methyl group. In

\* The hydride-atom position H(1) was calculated using a distance of 1.7 Å to the metal and assuming that it was symmetrically placed with respect to the four *cis*-phosphorus atoms. Although the van der Waals radii (1.2 Å) of H(1) overlaps those of H(135) and H(231) respectively, the respective contact distances of 2.14 and 2.16 Å are acceptable; see, for example, G. R. Clark, B. W. Skelton, and T. N. Waters, *Inorg. Chim. Acta*, 1975, **12**, 235.

$[\text{Ru}(\text{O}_2\text{CMe})(\text{PMe}_2\text{Ph})_4]^+$  [Figure 3(b)] there are two sets of phosphine ligands with *facial* geometry,<sup>9</sup> both of which exhibit enlarged Ru-P-C angles. One set [A in Figure 3(b)] has the same arrangement of methyl groups as was found in the three-ligand cases, while the second set (B) is different. In set B, only the *trans*-axial phosphine ligand, P(1), is sterically similar to the phosphines described above. Atom P(4) of the *cis*-equatorial pair has its phenyl ring pointing parallel to the methyl group on P(1), which has the largest Ru-P-C angle ( $126^\circ$ ), with the result that the Ru-P(4)-C(phenyl) angle is also enlarged ( $121^\circ$ ). Atom P(3) of the equatorial pair has both its methyl groups involved in close contacts, a different methyl in each *facial* arrangement,

hence the Ru-P-C angle of each of the methyl groups on P(3) exceeds  $120^\circ$ . The Ru-P-C angle to the phenyl ring, which is not involved in short C...C contacts, is only  $108^\circ$ . The Me...C(phenyl) and Me...Me separations (*ca.* 3.4 Å) for this *facial* set of ligands are shorter than those of the other set. Quite clearly there is an increased compression strain in this arrangement of two adjacent *facial* sets of  $\text{PMe}_2\text{Ph}$  ligands. It is evident that this type of internal compression strain drives the dissociation and rearrangement of *cis*- $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]$  to form the triply bridged dimer  $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$ .<sup>22</sup> Two sets of highly strained adjacent *facial* arrangements are thus eliminated and simultaneously replaced by two well separated relatively unstrained arrangements. The rearrangement of the orange dithioformato-complex  $[\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_4]^+$  to the purple isomer<sup>11</sup>  $[\text{Ru}(\text{S}_2\text{C}(\text{H})\text{PMe}_2\text{Ph})(\text{PMe}_2\text{Ph})_3]^+$  is also caused by relief of these interligand strains.

The four *facial* sets in  $[\text{RuH}(\text{PMe}_2\text{Ph})_5]^+$  [Figure 3(c)] all differ in varying degrees from the simple arrange-

<sup>19</sup> B. J. Davis and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 578.

<sup>20</sup> L. Manojlović-Muir, *J. Chem. Soc. (A)*, 1971, 2796.

<sup>21</sup> (a) N. W. Alcock and P. G. Leviston, *J.C.S. Dalton*, 1974, 1834; (b) G. R. Clark, B. W. Skelton, and T. N. Waters, *J. Organometallic Chem.*, 1975, **85**, 375.

<sup>22</sup> P. W. Armit, A. S. F. Boyd, and T. A. Stephenson, *J.C.S. Dalton*, 1975, 1663.

ment found in the three-ligand complexes. In all sets, relatively large Ru-P-C angles are observed (see Table

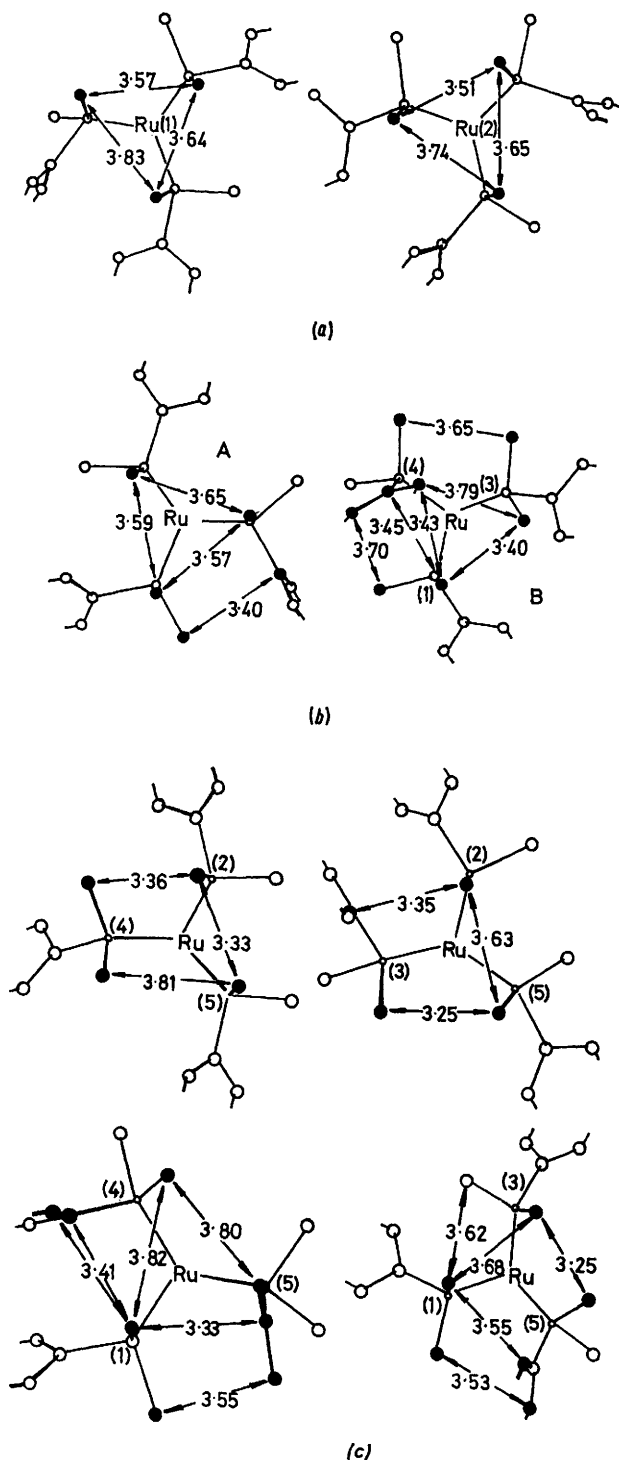


FIGURE 3 (a) Projections of the two sets of *facial* phosphine ligands in  $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6][\text{PF}_6]$ . (b) Projections of the two adjacent sets of *facial* phosphine ligands in  $[\text{Ru}(\text{O}_2\text{CMe})(\text{PMe}_2\text{Ph})_4][\text{PF}_6]$ . (c) Projections of the four adjacent sets of *facial* phosphine ligands in  $[\text{RuH}(\text{PMe}_2\text{Ph})_5][\text{PF}_6]$

3) indicating that strain energy is being taken up in angular distortions (see Tables 3–6). Figure 1 shows

that to a fair approximation the set of four ligands, P(1)–P(4), has two-fold symmetry. The phenyl rings on P(3) and P(4) twist about the P–C bonds in the same sense until they make contact with the phenyl rings on P(2) and P(1) respectively. This configuration, together with the distortions arising from the close contacts between the two *o*-hydrogen atoms and the hydride ligand (described above), determine the arrangement of the substituents attached to the phosphorus atoms in the cation. One of the *facial* projections of  $\text{PMe}_2\text{Ph}$  ligands in (2), that involving P(2), P(4), and P(5), is similar to the arrangement found in the simplest cases: parallel P–Me bonds, close Me...Me contacts, and large Ru–P–C(methyl) angles. The other three arrangements have phenyl rings parallel to the P–Me bonds; these involve large numbers of short C...C separations, and the Me groups involved in the close contacts generally have large Ru–P–C angles. So as to achieve the minimum repulsion energy, one of the *facial* sets adopts the preferred arrangement (with one P–Me bond on each group standing approximately parallel to the plane of the P atoms) and then the fourth and fifth  $\text{PMe}_2\text{Ph}$  ligands each adjust their orientation so that their Me and Ph groups mesh with the groups on the first *facial* set to give the most energetically favourable compromise.

It is not possible to compare directly this structure with one containing a *meridional* configuration of  $\text{PMe}_2\text{Ph}$  ligands about a ruthenium atom because no crystal structure of this type has as yet been reported. However, the structure of the anion  $\text{mer-}[\text{RuCl}_3(\text{PEt}_2\text{Ph})_3]^-$  is known<sup>23</sup> and its geometry can be usefully compared with those of  $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]^+$ ,  $[\text{Ru}(\text{O}_2\text{CMe})(\text{PMe}_2\text{Ph})_4]^+$ , and  $[\text{RuH}(\text{PMe}_2\text{Ph})_5]^+$ . The arrangement of the groups attached to the P atoms differs completely from that found in the *facial* complexes. It is now the phenyl groups that stand approximately parallel to each other, and the large Ru–P–C bond angles are those involving the phenyl C atoms (119, 121, and 122°). This is clearly seen in Figure 3 of ref. 23. The shortest contacts are between the C atoms of the phenyl ring on P(7) and the methylene C atoms on P(8) (3.29, 3.43, and 3.48 Å) and between the phenyl rings on P(8) and P(9) (3.26, 3.40, and 3.42 Å). There are no methylene–methylene contacts. It is clear that the internal stresses in the *mer* case are small, with the energy being absorbed both in the angle strains associated with the phenyl groups and in the P–Ru–P angle of 168°.

In order to estimate the angular-strain energy in the ligands of  $[\text{RuH}(\text{PMe}_2\text{Ph})_5]^+$ , the relevant angles in the  $\text{PMe}_2\text{Ph}$  ligands of  $\text{trans-}[\text{Pt}(\text{CH}=\text{CHCH}_2\text{OMe})_2(\text{PMe}_2\text{Ph})_2]$ <sup>24</sup> were used as typical of a co-ordinated  $\text{PMe}_2\text{Ph}$  ligand suffering negligible angular distortions. The angles are M–P–C (methyl) 117 and 116°, M–P–C (phenyl) 113°, and the mean Ru–P–C angle is 115°. If a 5° deviation from this mean value requires<sup>25</sup> ca.

<sup>23</sup> K. A. Raspin, *J. Chem. Soc. (A)*, 1969, 461.

<sup>24</sup> K. H. P. O'Flynn and W. S. McDonald, *Acta Cryst.*, 1976, **B32**, 1596.

<sup>25</sup> A. I. Kitaigorodsky, 'Molecular Crystals and Molecules,' Academic Press, New York, 1973, p. 188.

0.2 kcal mol<sup>-1</sup> (greater than 0.1, less than 0.4) then the strain energy may be calculated. The sum of the Ru-P-C angular deviations in (2) is 55°, equivalent to *ca.* 2.2 kcal mol<sup>-1</sup>.\*

It is evident from the range of M-P-C and C-P-C

substituents attached to the phosphorus atom in ligands such as PEt<sub>3</sub> and P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub> apparently<sup>21a</sup> cannot 'fold back' to relieve interligand close contacts because of the intraligand repulsions. Thus PMe<sub>2</sub>Ph groups offer considerably less steric repulsion than PEt<sub>3</sub> in a complex

TABLE 5  
Structural parameters \* related to PMe<sub>2</sub>Ph ligands in different steric environments  
Complex (L = PMe<sub>2</sub>Ph, L' = PEt<sub>2</sub>Ph)

Parameter	<i>mer</i> -[RuCl <sub>3</sub> L' <sub>3</sub> ] <sup>-</sup>	<i>fac</i> -[Ru <sub>2</sub> Cl <sub>3</sub> L <sub>6</sub> ] <sup>+</sup>	[Ru(O <sub>2</sub> CMe)L <sub>4</sub> ] <sup>+</sup>	[RuHL <sub>5</sub> ] <sup>+</sup>
P-M-P angle (°)	95, 96 168	93, 94, 94, 95 98, 98	91, 91, 97, 99 166	90(6), 100(2) 159, 178
M-P-C angle (°)	112, 113, 119 114, 117, 121 111, 118, 122	112, 113(3), 114(3) 116, 117(2), 118 119, 122(5), 124	(113, 113, 126)(2) (108, 122, 122)(2)	114, 116(3), 117, 118(2) 119, 120(4), 121(2), 123
C-P-C angles (°)	97, 101, 102 100, 103, 101 97, 102, 103 Mean 101	97, 99(5), 100(5), 101(4), 102(3) Mean 100	97, 101, 105(2) 100, 100, 103(2) Mean 101	95, 96(3), 97(5), 98, 99(2) 101(2), 102 Mean 98
M-P distances (Å)	2.26, 2.36 2.39	2.28(2) 2.29(2) 2.30(2)	2.30(2) 2.42(2)	2.38, 2.40(2), 2.41 2.48
C...C non-bonded contacts	3.3—3.8	3.5—3.8	3.4(3) 3.5	3.0, 3.1, 3.2(3), 3.3(5), 3.4(4)

\* Numbers in parentheses refer to the number of similar sets of parameters. It should be noted that as M-P-C angles open, compressions increase (see P-M-P and C-P-C angles) and separations become smaller across the Table.

angles (see Table 5) that a PMe<sub>2</sub>Ph ligand can suffer considerable angular distortions. In addition, groups of these ligands can 'mesh' together as shown by the short interligand contact distances (Table 4) and the projections in Figure 3(c). These properties cause the

in spite of the cone angles proposed for PMe<sub>2</sub>Ph (127°) and PEt<sub>3</sub> (130°) which suggest similar steric effects for these two ligands.

A final point to be considered is whether the long bond to P(5) in [RuH(PMe<sub>2</sub>Ph)<sub>5</sub>][PF<sub>6</sub>] is due to the structural

TABLE 6  
Ruthenium-phosphorus bond lengths (Å) for linear groups with the X-Ru-P angle ≥ 155°

Complex	X	Ru-P	Ref.
[Ru <sub>2</sub> Cl <sub>3</sub> (PMe <sub>2</sub> Ph) <sub>6</sub> ] <sup>+</sup>	Cl	2.28—2.30	7
[Ru <sub>2</sub> (OH) <sub>3</sub> (PMe <sub>2</sub> Ph) <sub>6</sub> ] <sup>+</sup>	OH	2.27—2.30	8
[RuH(C <sub>4</sub> H <sub>9</sub> )(PMe <sub>2</sub> Ph) <sub>3</sub> ] <sup>+</sup>	C	2.32, 2.34	10
	H	2.28	
[Ru{S <sub>2</sub> C(H)PMe <sub>2</sub> Ph}(PMe <sub>2</sub> Ph) <sub>3</sub> ] <sup>+</sup>	S	2.28, 2.31 2.20	11
[Ru(O <sub>2</sub> CMe)(PMe <sub>2</sub> Ph) <sub>4</sub> ] <sup>+</sup>	P	2.42, 2.43	8
	O	2.30, 2.31	
[RuH(O <sub>2</sub> CMe)(PPh <sub>3</sub> ) <sub>3</sub> ]	P	2.35, 2.36 2.23	<i>a</i>
[RuH(PMe <sub>2</sub> Ph) <sub>5</sub> ] <sup>+</sup>	P	2.38—2.41	
	H	2.48	
[RuH(C <sub>10</sub> H <sub>7</sub> )(dmpe) <sub>2</sub> ] <sup>b</sup>	H	2.33	27
	(σ-C <sub>10</sub> H <sub>7</sub> )	2.30	
	P	2.28, 2.30	
[{RuH(dmpe)[Me <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PMe(σ-CH <sub>2</sub> )] <sub>2</sub> ] <sup>b</sup>	H	2.31	28
	σ-CH <sub>2</sub>	2.27	
	P	2.29, 2.32	

<sup>a</sup> A. C. Skapski and F. A. Stephens, *J.C.S. Dalton*, 1974, 390. <sup>b</sup> dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>.

effective size of the ligand to be smaller than would be associated with its 'cone angle'. It would be expected that similar distortions could occur in other co-ordinated PR<sub>2</sub>Ph ligands (R = Et, Pr<sup>n</sup>, Bu<sup>n</sup>, etc.) and that the interligand repulsions caused by increasing the bulk of the alkyl groups would determine the stability of complexes containing these ligands. In contrast, the alkyl

*trans* influence of the hydrido-ligand. Lengthening of the metal-phosphorus bond *trans* to a hydrido-ligand has been observed in [OsBrH(CO)(PPh<sub>3</sub>)<sub>3</sub>]<sup>18</sup> and [IrH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>][SiF<sub>5</sub>]<sup>26</sup>. Three structures of ruthenium(II) complexes of this type have been determined<sup>10,27,28</sup> and have Ru-P distances in the 2.28—

\* Throughout this paper: 1 cal = 4.184 J.

<sup>26</sup> P. Bird, J. F. Harrod, and K. A. Than, *J. Amer. Chem. Soc.*, 1974, **96**, 1222.

<sup>27</sup> S. D. Ibekwe, B. T. Kilbourn, U. A. Raeburn, and D. R. Russell, *Chem. Comm.*, 1969, 433.

<sup>28</sup> F. A. Cotton, D. L. Hunter, and B. A. Frenz, *Inorg. Chim. Acta*, 1975, **15**, 155.

2.33 Å region for the bond *trans* to the hydrido-ligand. All three have relatively unstrained ligand environments. These limited data suggest that the Ru-P distance of the bond *trans* to a hydride ligand would be in the region of 2.30 Å, *i.e.* similar to that of the bond *trans* to Cl<sup>-</sup> in complexes with little steric crowding. Ru-P lengths of bonds *trans* to a variety of ligands are given in Table 6.

Thus it appears that the lengthening of the Ru-P(5) bond in [RuH(PMe<sub>2</sub>Ph)<sub>5</sub>]<sup>+</sup> is a steric effect caused by the many and large repulsions between the methyl and phenyl groups on this and the other ligands, and is not caused by any electronic effects of the hydride ligand.

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