Cationic Ruthenium Systems. Part 3.[1] Preparation and Characterization of Cationic Dienehydridotris(phosphine)ruthenium Complexes: The Crystal and Molecular Structure of (η-Buta-1,3-diene)tris(dimethylphenylphosphine)hydridoruthenium(II) Hexafluorophosphate

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The stable salts [RuH(diene)L_3][PF$_6$] {1; diene = cyclo-octa-1,5-diene (cod), hexa-1,3-diene, or buta-1,3-diene, L = PMe$_2$Ph; diene = cod, L = P(OMe)$_3$, P[(OCH$_2$)$_3$CMe], PPh$_2$(OMe), PMe$_3$, or PMePh$_2$} have been prepared from the salt [RuH(cod)(NH$_2$NMe$_2$)$_3$][PF$_6$], and have been characterized by i.r., microanalytical, and ^{1}H n.m.r. measurements. The crystal structure of [RuH(C$_4$H$_6$)(PMe$_2$Ph)$_3$][PF$_6$]·*ca.* 0.5CH$_2$Cl$_2$ has been determined. The yellow crystals are monoclinic, space group $P2_1/n$, a = 17.85, b = 18.96, c = 10.31 Å, β = 106.1°. The structure has been solved by the heavy-atom method and refined by least squares to R 0.070 for 2 429 observed data collected on a diffractometer using graphite-monochromatized Mo-K_α radiation. The ruthenium has a distorted-octahedral co-ordination geometry. It is bonded to all the carbon atoms of the butadiene molecule; Ru–C 2.14—2.38 Å. The phosphine ligands have a *fac* configuration; Ru–P 2.28—2.34 Å, P–Ru–P 94—100°. The butadiene moiety is approximately planar, with bond lengths of 1.48, 1.34, and 1.43 Å (estimated standard deviation 0.03 Å). The position of the hydride ligand is not directly observable but can be inferred from the arrangement of the other ligands in the cation.

ALTHOUGH hydrido-olefin complexes are postulated as the intermediates in hydrogenation,[2] isomerization,[3] and oligomerization[4] reactions, very few have been characterized and only one, [IrH(C$_4$H$_6$)(PPr$^i_3$)$_2$] (C$_4$H$_6$ = buta-1,3-diene), has been elucidated structurally.[5] Previous treatments of hydridoruthenium(II) phosphine complexes with dienes gave[6] only unstable products which could not be fully characterized. Believing this instability to be a consequence of steric repulsions between the bulky PPh$_3$ ligands of the precursors, we undertook the present study to see whether stable dienehydrido-complexes could be prepared by using smaller ligands. We have found that complexes of the type [RuH(diene)L$_3$]$^+$ (L = a tertiary phosphorus donor ligand) can be prepared by a simple, generally applicable, route, provided that the size of the ligand L allows the complex to adopt a *facial* configuration.

RESULTS AND DISCUSSION

Treatment of an argon-saturated solution of [RuH(cod)(NH$_2$NMe$_2$)$_3$][PF$_6$] (1) in methanol at 20 °C with 3.1 mol equivalents of the appropriate ligand L effected precipitation within *ca.* 5 min of the salts [RuH(cod)L$_3$][PF$_6$] {2; L = PMe$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_2$(OMe), P(OMe)$_3$, or P[(OCH$_2$)$_3$CMe]}. The cyclo-octa-1,5-diene (cod) ligand in (2; L = PMe$_2$Ph) was readily replaced and this lability was used to extend the range of dienehydrido-complexes. Thus, (2; L = PMe$_2$Ph) dissolved in refluxing methanol to give a dark red solution which turned yellow on treatment with buta-1,3-diene or hexa-1,3-diene and deposited the salts (2; L = PMe$_2$Ph;

diene = buta-1,3-diene or hexa-1,3-diene) on cooling. It appears that the red species is a solvated cation of the type [RuH(PMe$_2$Ph)$_3$(HOMe)$_x$]$^+$ (x is probably 2). Attempts to isolate a metal complex from the red solution were unsuccessful. However, addition of another mol equivalent of PMe$_2$Ph to the red solution produced a solution, of similar colour, which is believed to contain [RuH(PMe$_2$Ph)$_4$(HOMe)]$^+$ since treatment with H$_2$, CO, or PMe$_2$Ph (1 mol equivalent) gave [RuH$_3$(PMe$_2$Ph)$_4$][PF$_6$],[7] [RuH(CO)(PMe$_2$Ph)$_4$][PF$_6$],[7] and [RuH(PMe$_2$Ph)$_5$][PF$_6$][1] respectively. Although the red species '[RuH(PMe$_2$Ph)$_3$(HOMe)$_x$]$^+$' reacted with H$_2$ and CO, the products were extremely soluble and have not been isolated in the purity required for complete characterization.

Attempts to prepare the complex [RuH(cod){PPh(OMe)$_2$}$_3$][PF$_6$] by similar procedures were unsuccessful; instead only the known salt [RuH{PPh(OMe)$_2$}$_5$][PF$_6$][8] was isolated. In contrast, the corresponding cations [RuHL$_5$]$^+$ {L = P(OMe)$_3$[9] or P[(OCH$_2$)$_3$CMe]} could not be prepared from the appropriate dienehydrido-complexes (2); only starting material was recovered under all the reaction conditions. In view of the similar donor properties of these three ligands, the only plausible reason for this difference is that [RuHL$_5$]$^+$ is thermodynamically more stable than [RuH(cod)L$_3$]$^+$, but a sterically induced labilization of the cod ligand does not occur with the relatively smaller ligands P(OMe)$_3$ and P[(OCH$_2$)$_3$CMe]. A similar situation was found with PMe$_3$ and PMe$_2$Ph; substitution

[1] Part 2, T. V. Ashworth, M. J. Nolte, E. Singleton, and M. Laing, *J.C.S. Dalton*, 1977, 1816.

[2] R. E. Hanson, S. K. Gupta, and D. J. Brown, *Chem. Rev.*, 1973, **73**, 21.

[3] R. F. Heck, 'Organotransition Metal Chemistry,' Academic Press, New York, London, 1974, 76.

[4] M. M. Taqui Khan and A. E. Martell, 'Homogeneous Catalysis by Metal Complexes,' Academic Press, New York, London, 1974, vol. 2, p. 99.

[5] G. Del Piero, G. Perego, and M. Cesari, *Gazzetta*, 1975, **105**, 529.

[6] J. R. Sanders, *J.C.S. Dalton*, 1973, 743; P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 3143.

[7] T. V. Ashworth and E. Singleton, *J.C.S. Chem. Comm.*, 1976, 706.

[8] J. J. Hough and E. Singleton, *J.C.S. Chem. Comm.*, 1972, 371.

[9] D. A. Couch and S. D. Robinson, *Inorg. Chim. Acta*, 1974, **9**, 39.

of the cod ligand in $[RuH(cod)(PMe_3)_3][PF_6]$ by PMe_3 took place only after several hours and even then mixtures of the starting material and the new complex $[RuH(PMe_3)_5][PF_6]$ were obtained. In contrast, a warm solution of $[RuH(cod)(PMe_2Ph)_3][PF_6]$ with excess of PMe_2Ph formed $[RuH(PMe_2Ph)_5][PF_6]$.

A doublet (J 94 Hz) of triplets (J 18 Hz) observed for the hydride resonance in the 100-MHz ^1H n.m.r. spectrum of [2; L = $P(OMe)_3$] is consistent with a *fac* arrangement of phosphite ligands. A ^{31}P nucleus co-ordinated *trans* to a hydride ligand normally gives rise to a P–H coupling constant in the 60—180 Hz region, while the coupling constant when the ^{31}P and hydride nuclei are in mutually *cis* positions is smaller, in the range 5—30 Hz.[10] The hydride pattern recorded at 60 MHz was complex, indicating second-order effects. The signals due to the phosphite methoxy-protons consisted of a doublet (J 5 Hz) at τ 5.68 (9 H), and a 1 : 2 : 1 triplet (J 2 Hz) at τ 5.87 (18 H). Although this pattern normally indicates[11] a *meridional* configuration of phosphorus-donor ligands, and thus conflicts with the evidence of the hydride pattern, it must be assumed that *cis* 'virtual coupling'[12] occurs in this complex. The ^1H n.m.r. spectrum of {2; L = $P[(OCH_2)_3CMe]$} was similar and hence a *fac* arrangement of phosphite ligands was also assigned to this complex. These together with other[12] examples illustrate the danger of using the patterns arising from 'virtually coupled' phosphine systems to assign stereochemistry. In contrast, the ^1H n.m.r. spectrum of (2; L = PMe_3) conformed with that expected for the *fac* isomer; a doublet (J 8.0 Hz) at τ 8.29 (9 H) and a 'filled-in' doublet (J^* 8.0 Hz) at τ 8.58 (18 H) for the methyl protons, and, at high field

FIGURE 1

(τ 16.02), a doublet (J 56) of triplets (J 28) due to the hydride ligand which appears as a 1 : 2 : 2 : 2 : 1 quintet

[10] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231.
[11] J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem Soc.* (A), 1966, 1787.

because of coincidental overlap. The labile nature of the other complexes (2) in solution produced broad unresolved resonances without any characteristic ^1H–^{31}P or
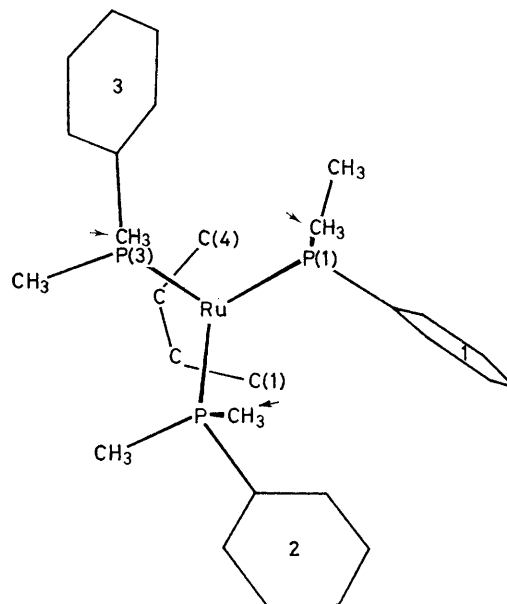

FIGURE 2 Projection of the molecule on to the plane of the three phosphorus atoms. Arrows indicate the three methyl groups which are forced together and for which the Ru–P–C(methyl) angle is 122°

^{31}P–^{31}P coupling, thus making stereochemical assignments from the ^1H n.m.r. impossible.

The presence of a hydride ligand in (2; diene = buta-1,3-diene) could not be detected from either i.r. or ^1H n.m.r. evidence. It was then thought possible that an η-allyl ligand might have been present, since these are known[13] to form on reaction of conjugated dienes with metal hydrides. It was thus decided to determine the structure of this complex by a single-crystal X-ray diffraction study with the aims of discovering (i) the precise formulation of the complex and (ii) the arrangement of the phosphine ligands to see whether the lability in solution was a consequence of interligand contacts.

The overall molecular geometry of the cation is given in Figure 1. The ruthenium atom has a distorted-octahedral co-ordination geometry with the six sites occupied by the three P atoms of the phosphine ligands, the two 'double bonds' of the butadiene molecule, and the hydride ligand. The phosphine ligands are in a *fac* configuration, and the four carbon atoms of the butadiene are all bonded to the ruthenium atom: Ru–C lengths lie between 2.14 and 2.38 Å.

The mean plane of atoms P(1), P(2), and P(3) is approximately parallel to that defined by C(1), C(2), C(3), and C(4) of the butadiene system. A projection on to the latter plane (Figure 2) shows that the butadiene group is nearly symmetrically placed with P(1) *trans* to the C(2)–C(3) bond, while the projections of Ru–P(2)
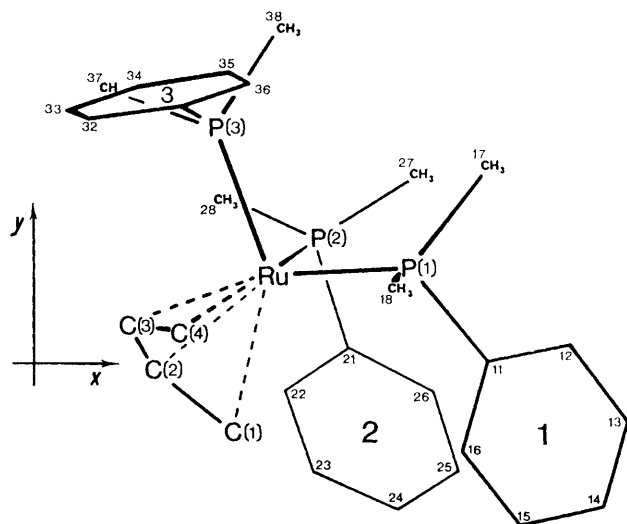
[12] G. M. Bancroft and E. T. Libbey, *Canad. J. Chem.*, 1973, **51**, 1482.
[13] Ref. 3, p. 120.

and Ru–P(3) are approximately perpendicular to bonds C(1)–C(2) and C(3)–C(4) respectively. The hydrogen atom bonded to the ruthenium lies approximately *trans* to P(3) and in the region between C(1) and P(1). This assignment is supported by the small but systematic distortions in the arrangement of the other atoms which are bonded directly to the ruthenium (see Figure 2). Ru–P(3) = 2.28 Å, 0.05 Å shorter than the mean of the other two Ru–P bond lengths. This difference may not be real, because M–P bonds *trans* to hydride tend to be longer rather than shorter.[14]

Unfortunately, the positions of the C atoms of the butadiene group are not as well defined as is desirable. The imprecision is caused by a combination of the disordering in the [PF$_6$]$^-$ anion and the disordered (and

The separations between pairs of C atoms for these methyl groups are considerably smaller than 4 Å (the sum of their usual effective contact radii): C(17)–C(27) 3.71, C(27)–C(38) 3.74, and C(38)–C(17) 3.69 Å. The reasons for these distortions and their effect on the reactivity of the Ru(PMe$_2$Ph)$_x$ system have recently been discussed.[1]

It is evident that the isomer with the *mer* configuration of the phosphine ligands cannot exist because of the excessive strain that would result from the contacts between the butadiene group and the phosphine group which would occupy the site where the hydride ligand is in the *fac* isomer. In fact a *fac* configuration of phosphites was obtained even with the smallest ligand P[(OCH$_2$)$_3$CMe] and hence we assign this stereochemistry

TABLE 1
Analytical and spectroscopic data for the complexes

Complex	Colour	M.p. (θ_c/°C)	Analyses (%) [a]		Infrared (cm^{-1}) ν(RuH)	^{1}H N.m.r. (τ) [b]
			C	H		
[RuH(cod)L$_3$][PF$_6$]						
L = PMe$_2$Ph	Colourless	138	49.6 (49.9)	6.1 (6.0)	2 000w 1 980m	8.30(pt, J^* 8, PMe$_2$), 11.8br (RuH)
PMePh$_2$	Yellow-brown	155	57.6 (59.1)	5.4 (5.5)	2 080w	8.0(br, PMe)
PMe$_3$	Colourless		34.7 (35.0)	6.9 (6.9)	1 985w	6.28br, 6.7 (br, olefinic protons, 4 H) 8.29 (d, J 8.0, PMe$_3$, 9 H), 8.58 (pt, J^* 8.0, PMe$_3$, 18 H), 16.02 [d, (J 56) of t's (J 28)(RuH)]
PPh$_2$(OMe)	Yellow-brown	169	56.0 (56.2)	5.3 (5.2)		6.80 [pt, J^* 11, P(OMe)]
P(OMe)$_3$	Colourless	142	28.0 (28.0)	5.5 (5.5)	1 960s	5.68 d, [J 5, P(OMe)$_3$, 9 H], 5.86 [t, J 2, P(OMe)$_3$, 18 H], 15.9 [d, (J 94) of t's (J 18)(RuH)]
P[(OCH$_2$)$_3$CMe]	Colourless	213	34.7 (34.6)	5.0 (5.0)	1 950s	5.67 [d, J 5, P(OCH$_2$)$_3$, 6 H], 5.85 [t, J 2, P(OCH$_2$)$_3$, 12 H], 9.12 (s, CMe, 3 H), 9.25 (s, CMe, 6 H), 15.7 (m, RuH)
[RuH(C$_4$H$_6$)(PMe$_2$Ph)$_3$][PF$_6$]	Yellow	150	46.2 (46.3)	5.7 (5.6)		4.92 (br, olefinic protons), 8.30 (br, PMe$_2$) [c]
[RuH(C$_6$H$_8$)(PMe$_2$Ph)$_3$][PF$_6$] [d]	Yellow	154—156	48.5 (48.6)	5.8 (5.7)		7.20 (br, CH, 4 H), 8.24 (pt, J^* 5.5), 8.55 (d, J 5, PMe$_2$), 12.5 (br, RuH)

[a] Calculated values are given in parentheses. [b] J values in Hz. [c] Hydride resonance not observed. [d] C$_6$H$_8$ = Cyclohexa-1,3-diene.

non-stoicheiometric) solvent molecule. The y co-ordinates of the C atoms of the butadiene molecule are close to those of the C and Cl atoms of the solvent molecule and thus are adversely affected by the disordering. In spite of the imprecision, the trend of long–short–long C–C bonds does seem to be real. This effect has been seen before [15] and, in addition, the systematic alternation of the C atoms above and below their mean plane (see Table 3) was also observed. The reduction of the C–C–C angles to 118 and 119° is normal, and has been observed [15] in other butadienemetal complexes.

The Ru–P–C angles in each of the phosphine ligands show the same distortion that was observed [16] in the [Ru$_2$Cl$_3$(PMe$_2$Ph)$_6$]$^+$ cation: one Ru–P–CH$_3$ angle is close to 122°, while the other is far smaller, *ca.* 114°. The three methyl groups indicated by arrows in Figure 2 are those associated with Ru–P–C angles of *ca.* 122°.

to all the other dienehydrides prepared here. It is interesting to note that for larger ligands the interligand repulsions would prevent the formation of even the *fac* isomer and this probably accounts for the inability to characterize dienehydridoruthenium(II) complexes with such ligands as PPh$_3$.[6] We have recently found that the salt [RuH(C$_4$H$_6$)(PMe$_2$Ph)$_3$][PF$_6$] may also be obtained by reaction of [RuH(PMe$_2$Ph)$_5$][PF$_6$] with buta-1,3-diene. A possible reason for the failure to isolate an η-allyl derivative from this reaction is that the ligands in the likely product, [Ru(η^3-C$_4$H$_7$)(PMe$_2$Ph)$_4$]$^+$, would be too crowded and, thus, the dienehydrido-structure with three PMe$_2$Ph ligands is sterically more favoured. Steric hindrance in the possible 1—3-η-allyl complex has been invoked [17] previously to explain the preferential formation of [CoH(C$_4$H$_4$Me$_2$)(PPh$_3$)$_2$] (C$_4$H$_4$Me$_2$ = 2,3-dimethylbuta-1,3-diene), despite the existence of the corresponding 1—3-η-allyl complexes [Co(C$_6$H$_{11}$)(CO)$_3$] and [Co(C$_6$H$_{11}$)(PF$_3$)$_3$].

[14] A. Immirzi and A. Succarelli, *Cryst. Struct. Comm.*, 1972, **1**, 317.
[15] G. Huttner, D. Neugebauer, and A. Razavi, *Angew. Chem. Internat. Edn.*, 1975, **14**, 352.

[16] M. Laing and L. Pope, *Acta Cryst.*, 1976, **B32**, 1547.
[17] P. V. Rinze, *Angew. Chem. Internat. Edn.*, 1974, **13**, 336.

EXPERIMENTAL

The salt [RuH(cod)(NH$_2$NMe$_2$)$_3$][PF$_6$] was prepared as described previously.[18] All the other reagents were obtained commercially and were not further purified. All the operations were performed in an argon atmosphere with dry argon-saturated solvents. Melting points were determined on a Kofler hot-stage apparatus and were corrected. Infrared spectra were recorded on a Perkin-Elmer model 457 grating spectrophotometer and ^{1}H n.m.r. spectra with Varian A-60A and HA-100 instruments. Elemental analyses were carried out in the N.C.R.L. laboratory. Physical and spectroscopic data for all the new complexes are presented in Table 1.

Preparations.—(η-*Cyclo-octa*-1,5-*diene*)*tris*(*dimethylphenylphosphine*)*hydridoruthenium hexafluorophosphate.* Dimethylphenylphosphine (0.42 g, 3.1 mmol) was added to a stirred solution of [RuH(cod)(NH$_2$NMe$_2$)$_3$][PF$_6$] (0.5 g, 1 mmol) in methanol at 20 °C. Within *ca.* 2 min a colourless precipitate formed which was filtered off and recrystallized from CH$_2$Cl$_2$–EtOH at 0 °C to give the required product as colourless *prisms* (0.6 g, yield 78%).

Similarly prepared were: [RuH(cod)(PMe$_3$)$_3$][PF$_6$] as a colourless *powder* (0.33 g, 58%), [RuH(cod)(PMePh$_2$)$_3$][PF$_6$] as a pale brown *powder* (0.8 g, 84%), [RuH(cod){PPh$_2$-(OMe)}$_3$][PF$_6$] as a yellow *powder* (0.8 g, 80%), [RuH(cod)-{P(OMe)$_3$}$_3$][PF$_6$] as colourless *prisms* (0.5 g, 67%), and [RuH(cod){P[(OCH$_2$)$_3$CMe]}$_3$][PF$_6$] as colourless *prisms* (0.5 g, 65%).

Reaction of [RuH(cod)(NH$_2$NMe$_2$)$_3$][PF$_6$] *with Excess of* P(OMe)$_3$.—Trimethyl phosphite (0.75 g, 6.1 mmol) was added to a refluxing solution of [RuH(cod)(NH$_2$NMe$_2$)$_3$]-[PF$_6$] (0.5 g, 1 mmol). After 1 h the solvent was evaporated off under reduced pressure and addition of methanol gave a colourless precipitate of [RuH(cod){P(OMe)$_3$}$_3$][PF$_6$]. Under similar conditions P[(OCH$_2$)$_3$CMe] gave [RuH(cod)-{P[(OCH$_2$)$_3$CMe]}$_3$][PF$_6$].

(η-*Buta*-1,3-*diene*)*tris*(*dimethylphenylphosphine*)*hydridoruthenium Hexafluorophosphate.*—On passing a stream of buta-1,3-diene through a suspension of [RuH(cod)-(PMe$_2$Ph)$_3$][PF$_6$] (0.38 g, 0.5 mmol) in warm methanol a yellow precipitate was obtained which was recrystallized from CH$_2$Cl$_2$–MeOH mixtures to give the required product as yellow *prisms* (0.6 g, yield 81%). The corresponding cyclohexa-1,3-diene complex was similarly prepared using an excess of cyclohexa-1,3-diene and was obtained as yellow prisms (0.6 g, yield 80%).

Crystal-structure Determination of [RuH(C$_4$H$_6$)(PMe$_2$Ph)$_3$]-[PF$_6$].—Recrystallization of the complex from CH$_2$Cl$_2$–MeOH gave well shaped, yellow, monoclinic crystals.

Crystal data. C$_{28}$H$_{40}$F$_6$P$_4$Ru, M = 715, Monoclinic, space group $P2_1/n$, a = 17.85(2), b = 18.96(2), c = 10.31(1) Å, β = 106.1(1)°, U = 3 305 Å^3, D_m = 1.48 g cm^{-3}, Z = 4, D_c = 1.44 g cm^{-3}.

Structure solution and refinement. Intensity data were collected on a Philips four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ 0.710 7 Å) for θ between 3 and 20°. The ω—2θ scan technique was used; the scan width was 1°, the scan time was 33 s, and the background was counted for 33 s. Of the 3 232 reflections measured, 2 429 were classed as observed, $I > 1.65\sigma(I)$. Three reflections were used as standards and were remeasured after every 60 reflections; no crystal decom-

position was observed. Intensities were corrected for Lorentz and polarization effects only; μ(Mo-K_α) is 7.4 cm^{-1}. The RuP$_3$ moiety was located from a Patterson map, and all the remaining atoms were found in the subsequent Fourier maps. The structure was refined by the block-diagonal least-squares method with Ru, four P, and six F atoms anisotropic and the Cl and all the C atoms isotropic. Weighting was proportional to 1/F for F > 50 and to F for R < 50 with a proportionality constant that gave a weighting of 1.0 for F = 50 (F_o ranged from *ca.* 10 to 250). About half a molecule of CH$_2$Cl$_2$ solvent was found to be disordered about the inversion centre at 0,0,½; thus, in the structure-factor calculations the Cl atom was given the weighting 0.50 while that for C (of solvent) was 0.25. Scattering factors for neutral atoms were used (' International Tables for *X*-Ray Crystallography,' 1962); that of the Ru atom was corrected for anomalous dispersion.

The refinement converged at R 0.070 for the 2 429 observed data. Observed and calculated structure factors and the thermal parameters are listed in Supplementary

TABLE 2

Fractional atomic co-ordinates for [RuH(C$_4$H$_6$)(PMe$_2$Ph)$_3$]-[PF$_6$]

Atom	x/a	y/b	z/c
Ru	0.207 70(6)	0.068 10(6)	0.148 00(10)
P(1)	0.304 9(2)	0.075 5(2)	0.036 3(3)
P(2)	0.281 2(2)	0.093 0(2)	0.366 3(3)
P(3)	0.161 8(2)	0.180 7(2)	0.107 5(4)
P(4)	0.355 6(3)	0.310 7(2)	0.716 7(5)
F(1)	0.323 4(9)	0.387 8(6)	0.710 2(14)
F(2)	0.375 5(13)	0.234 4(8)	0.717 4(17)
F(3)	0.338 1(11)	0.307 5(9)	0.857 5(16)
F(4)	0.380 4(12)	0.321 3(11)	0.595 6(16)
F(5)	0.435 8(8)	0.319 6(14)	0.804 2(18)
F(6)	0.275 1(9)	0.294 2(11)	0.643 9(27)
C(1)	0.191 2(10)	−0.052 1(9)	0.203 3(17)
C(2)	0.128 5(10)	−0.001 2(9)	0.207 7(17)
C(3)	0.088 4(10)	0.030 1(9)	0.093 3(17)
C(4)	0.114 0(10)	0.020 6(9)	−0.025 0(17)
C(11)	0.376 6(7)	0.002 2(7)	0.080 6(12)
C(12)	0.454 6(8)	0.015 9(7)	0.149 6(14)
C(13)	0.504 7(9)	−0.043 8(8)	0.188 2(16)
C(14)	0.478 3(9)	−0.109 6(9)	0.157 1(16)
C(15)	0.402 1(10)	−0.123 0(9)	0.086 8(18)
C(16)	0.348 1(8)	−0.065 7(8)	0.044 7(14)
C(17)	0.367 8(8)	0.153 0(8)	0.040 5(14)
C(18)	0.268 2(8)	0.061 9(8)	−0.146 9(14)
C(21)	0.322 9(7)	0.012 5(7)	0.459 7(13)
C(22)	0.287 9(8)	−0.019 4(8)	0.553 4(14)
C(23)	0.323 5(9)	−0.081 7(9)	0.621 4(16)
C(24)	0.389 5(9)	−0.109 2(8)	0.597 8(16)
C(25)	0.421 4(8)	−0.079 8(8)	0.501 3(15)
C(26)	0.388 1(8)	−0.018 1(7)	0.434 8(14)
C(27)	0.369 3(9)	0.147 9(8)	0.401 5(15)
C(28)	0.230 9(9)	0.133 4(9)	0.480 0(14)
C(31)	0.106 6(8)	0.197 0(7)	−0.069 5(14)
C(32)	0.025 7(10)	0.185 9(9)	−0.107 7(18)
C(33)	−0.015 0(11)	0.193 8(10)	−0.251 2(19)
C(34)	0.025 3(10)	0.210 3(10)	−0.337 1(18)
C(35)	0.104 5(10)	0.222 8(9)	−0.298 8(18)
C(36)	0.146 7(8)	0.214 3(8)	−0.161 2(14)
C(37)	0.089 7(11)	0.207 1(10)	0.201 5(19)
C(38)	0.227 7(9)	6.257 7(9)	0.145 3(17)
Cl	0.063 9(13)	0.025 3(12)	0.561 5(24)
C(s)	−0.007(11)	−0.018(10)	0.547(16)

* Weighting for Cl was 0.5 and for C(s) was 0.25.

Publication No. SUP 22267 (17 pp.).* The final difference-Fourier map showed that the [PF$_6$]$^-$ ion was disordered

* For details see Notices to Authors No. 7, *J.C.S. Dalton,* 1977, Index issue.

[18] T. V. Ashworth, E. Singleton, and J. J. Hough, *J.C.S. Dalton,* 1977, 1809.

TABLE 3

Bond lengths (Å) and angles (°). Estimated standard deviations: Ru–P 0.01; P–C and Ru–C 0.02; C–C 0.03 Å; of bond angles ±1°

P(1)–C(11)	1.86	Ru–P(1)	2.34
P(1)–C(17)	1.84	Ru–P(2)	2.32
P(1)–C(18)	1.84	Ru–P(3)	2.28
P(2)–C(21)	1.85	Ru–C(1)	2.38
P(2)–C(27)	1.84	Ru–C(2)	2.14
P(2)–C(28)	1.83	Ru–C(3)	2.17
P(3)–C(31)	1.84	Ru–C(4)	2.26
P(3)–C(37)	1.88	C(1)–C(2)	1.48
P(3)–C(38)	1.85	C(2)–C(3)	1.34
		C(3)–C(4)	1.43

Mean (Ph)C–C(Ph) 1.39 ±0.07

P(1)–Ru–P(2)	100	C(1)–C(2)–C(3)	119
P(2)–Ru–P(3)	94	C(2)–C(3)–C(4)	118
P(1)–Ru–P(3)	98		
Ru–P(1)–C(11)	113	C(11)–P(1)–C(17)	103
Ru–P(1)–C(17)	124	C(17)–P(1)–C(18)	100
Ru–P(1)–C(18)	113	C(11)–P(1)–C(18)	100
Ru–P(2)–C(21)	112	C(21)–P(2)–C(27)	100
Ru–P(2)–C(27)	122	C(27)–P(2)–C(28)	101
Ru–P(2)–C(28)	117	C(21)–P(2)–C(28)	102
Ru–P(3)–C(31)	114	C(31)–P(3)–C(37)	102
Ru–P(3)–C(37)	115	C(37)–P(3)–C(38)	101
Ru–P(3)–C(38)	122	C(31)–P(3)–C(38)	102

about the F(1)–P(4)–F(2) axis and that the anisotropic thermal parameters derived for the F atoms were inadequate to describe the disorder. Final positional parameters are given in Table 2, bond lengths and angles in Table 3. The numbering system within the cation is shown in Figure 1.

Description of the hexafluorophosphate anion. The disorder of the $[PF_6]^-$ anion is non-random. F(1) is well defined while the thermal ellipsoids of P(4) and F(2) correspond to a pendulum-like motion. Superimposed on this there is a large amplitude of oscillation (or disordering between two orientations) for the four F atoms in the

TABLE 4

Plane of butadiene moiety

Direction cosines relative to:

x	y	z
0.605	0.755	0.253

Deviations (Å) from the plane:

C(1) −0.02, C(2) 0.04, C(3) −0.04, C(4) 0.02

equatorial plane. Disordering of a $[PF_6]^-$ anion is not unusual, but in this case the distinctly smaller motion of F(1) can be rationalized. It lies below Ru, in contact with phenyl rings 1 and 2, and with carbons C(1) and C(4) of the butadiene group; one is even tempted to ask the question ' Is there a Ru–H $\cdots$ F hydrogen bond? ' The Ru $\cdots$ F separation is 4.96 Å.