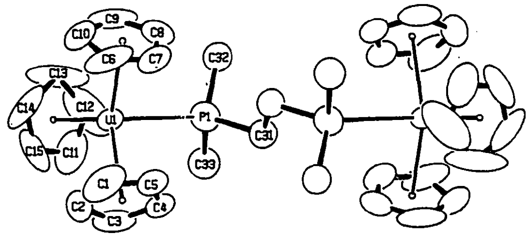

Fig. 1. *ORTEP* (Johnson, 1965) drawing of molecule 1; 50% probability ellipsoids.

The geometry of the complex is unusual since $(CH_3)_2PCH_2CH_2P(CH_3)_2$ usually acts as a bidentate ligand towards a given metal center, rather than as a bridging ligand as found in the title compound. The reason for this structural change presumably is steric, since in a hypothetical molecule, $(C_5H_5)_3U.(CH_3)_2PCH_2CH_2P(CH_3)_2$ in which the phosphine acts as a bidentate ligand, the coordination number of the U is one greater than found in the title compound. Inspection of the *ORTEP* diagram in Fig. 1 clearly shows that the molecule is economically arranged and that increasing the coordination number by one would require a substantial reorganization of the coordination sphere about U so that the intramolecular ligand–ligand repulsions are minimized. The coordination geometry about each uranium atom is similar to that found in $(CH_3C_5H_4)_3U.P(CH_3)_3$ (Brennan & Zalkin, 1985), in which the U—P distance is 2·972 (6) Å. In the title compound the averaged U—P distance is 3·022 (2) Å; the other bond lengths in these two molecules are also similar. The averaged U—C($CH_3C_5H_4$) distance in $(CH_3C_5H_4)_3U.P(CH_3)_3$ is 2·79 (4) Å and the U–(ring centroid) distance is 2·52 (1) Å, the (ring centroid)—U–(ring centroid) angle is 112 (7)° and the (ring centroid)—U—P angle is 106 (9)°. In the title complex, the averaged U—C(C_5H_5) distance is 2·77 (3) Å, the U–(ring centroid) distance is 2·52 (1) Å, the (ring centroid)—U–(ring centroid) angle is 118 (1)° and the (ring centroid)—U—P angle is 98 (1)°. Given the large uncertainty in the bond parameters and the range in individual parameters, the coordination geometries about the trivalent U atoms in the title compound and in $(CH_3C_5H_4)_3U.P(CH_3)_3$ are essentially the same.

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Structure of Tetrakis(methyldiphenylphosphine)iridium(I) Tetrafluoroborate with Cyclohexane of Solvation: a Reappraisal

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Abstract. $[Ir\{P(C_6H_5)_2CH_3\}_4]BF_4.\frac{2}{3}C_6H_{12}$, $M_r =$ 1135·95, rhombohedral, $R\bar{3}c$, $a = 22{\cdot}895\,(4)$, $c = 51{\cdot}535\,(5)$ Å, $U = 23394$ Å^3, $Z = 18$, $D_m = 1{\cdot}49$, $D_x = 1{\cdot}45$ Mg m^{-3}, $F(000) = 10\,332$. This structure has been reported [Clark, Skelton & Waters (1975). *J. Organomet. Chem.* **85**, 375–394] as monoclinic, space group *C*2/*c*. The original *C*2/*c* reflexion data (7905 reflexions) have been transformed to a rhombohedral

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setting and the structure has been successfully refined in the true space group $R\bar{3}c$ ($R = 0{\cdot}065$, $R' = 0{\cdot}065$). Apparent disorder of the BF_4^- and cyclohexane solvent of crystallization in the $C2/c$ refinement has been eliminated by the $R\bar{3}c$ refinement. Bond lengths and angles in the rhombohedral structure do not differ significantly from those reported earlier for the $C2/c$ structure.

Introduction. The X-ray structure of the title compound was reported by Clark, Skelton & Waters (1975) as monoclinic, space group $C2/c$, $a = 36{\cdot}805$, $b = 22{\cdot}93$, $c = 21{\cdot}676$ Å, $\beta = 121{\cdot}41°$, $Z = 12$. However, the $[10\bar{1}]$ zone axis of the $C2/c$ cell coincides with the unique c axis of a trigonal cell with $a = 22{\cdot}895$, $c = 51{\cdot}535$ Å. The Laue symmetry and systematic absences are consistent with the space group $R\bar{3}c$. The original reflexion data were transformed to $R\bar{3}c$ (hexagonal axes) setting and equivalents were averaged to give 3086 unique reflexions with $I > 3\sigma(I)$ using the transformation where hkl are $R\bar{3}c$ indices and $h'k'l'$ are $C2/c$ indices.

$$\begin{pmatrix} h \\ k \\ l \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -\frac{1}{2} & \frac{1}{2} & 1 \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} h' \\ k' \\ l' \end{pmatrix}$$

The structure was re-solved in space group $R\bar{3}c$, and refined by full-matrix least squares, with neutral-atom scattering factors, unit weights, and anisotropic thermal parameters for the iridium and phosphorus atoms. Disorder in the BF_4^- and cyclohexane groups previously encountered in the $C2/c$ refinement was eliminated in the $R\bar{3}c$ refinement, and it is now established that the unit cell contains two-thirds of a molecule of cyclohexane of solvation for every ion pair of the complex. Final coordinates are in Table 1; all calculations performed with *SHELX*76 (Sheldrick, 1976).*

Discussion. The structure of the cation is illustrated in Fig. 1, together with the atomic numbering scheme. There are no significant differences between bond lengths and angles in the $R\bar{3}c$ and $C2/c$ structures. It should be borne in mind that the model refined in $C2/c$ contained two crystallographically independent cations, one of which occupied a general position, whereas the other occupied a special position straddling a twofold axis. In the $R\bar{3}c$ structure all cations are equivalent, and exhibit crystallographically imposed twofold symmetry.

Table 1. *Atomic coordinates*

	x	*y*	*z*
Ir	0·28609 (3)	0·0	0·25
P(1)	0·2074 (2)	−0·1065 (2)	0·2353 (1)
P(2)	0·3307 (2)	0·0379 (2)	0·2089 (1)
C(1)	0·2278 (7)	−0·1715 (7)	0·2254 (3)
C(2)	0·1367 (7)	−0·1514 (7)	0·2577 (2)
C(3)	0·1146 (8)	−0·1150 (8)	0·2720 (3)
C(4)	0·0588 (9)	−0·1463 (9)	0·2886 (3)
C(5)	0·0263 (9)	−0·2172 (9)	0·2916 (3)
C(6)	0·0472 (8)	−0·2551 (9)	0·2778 (3)
C(7)	0·1030 (8)	−0·2223 (8)	0·2606 (3)
C(8)	0·1633 (7)	−0·0996 (7)	0·2069 (3)
C(9)	0·1667 (8)	−0·1258 (8)	0·1824 (3)
C(10)	0·1352 (9)	−0·1142 (9)	0·1611 (3)
C(11)	0·1008 (9)	−0·0796 (9)	0·1644 (3)
C(12)	0·0968 (9)	−0·0554 (9)	0·1877 (3)
C(13)	0·1278 (8)	−0·0651 (8)	0·2095 (3)
C(14)	0·2874 (7)	0·0550 (7)	0·1825 (3)
C(15)	0·3535 (7)	−0·0203 (6)	0·1933 (2)
C(16)	0·3341 (9)	−0·0435 (8)	0·1680 (3)
C(17)	0·3506 (8)	−0·0908 (8)	0·1576 (3)
C(18)	0·3884 (9)	−0·1120 (9)	0·1720 (3)
C(19)	0·4088 (9)	−0·0878 (9)	0·1972 (3)
C(20)	0·3902 (8)	−0·0428 (8)	0·2079 (3)
C(21)	0·4108 (7)	0·1173 (7)	0·2104 (3)
C(22)	0·4186 (9)	0·1779 (9)	0·2000 (3)
C(23)	0·4786 (10)	0·2386 (10)	0·2034 (3)
C(24)	0·5320 (10)	0·2400 (10)	0·2168 (4)
C(25)	0·5274 (9)	0·1810 (9)	0·2274 (3)
C(26)	0·4659 (8)	0·1198 (8)	0·2247 (3)
C(27)	0·4022 (11)	0·6772 (11)	0·1170 (4)
C(28)	0·3456 (11)	0·6084 (11)	0·1268 (4)
B	0·4354	0·4354	0·25
F(1)	0·3976	0·4210	0·2299
F(2)	0·4622	0·5005	0·2581

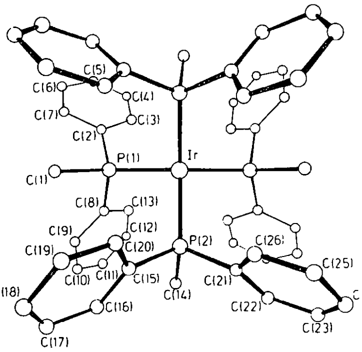

Fig. 1. The geometry of the $Ir[P(C_6H_5)_2CH_3]_4^+$ cation. A crystallographic twofold axis passes through the iridium atom and is perpendicular to the page.

The Ir—P bond distances are 2·318 and 2·321 (3) Å. At first sight the diagram might suggest a square-planar coordination geometry, but in fact the donor atoms are appreciably twisted (by about 40°) towards a tetrahedral arrangement. As a consequence, the P—Ir—P angles are P(1)—Ir—P(2) 93·5 (1), P(1)—Ir—P(2)′ 93·8 (1), P(1)—Ir—P(1)′ 150·9 (1) and P(2)—Ir—P(2)′ 150·7 (1)°. The Ir—P—Me angles (average 124·6°) and Ir—P—Ph angles (average 111·2°) are significantly different, presumably because of a need to minimize interligand steric interactions.

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* Lists of structure factors, atomic thermal parameters, bond lengths and angles, and a diagram showing the weighted *hk*3 reciprocal-lattice section have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44010 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.