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THE CRYSTAL STRUCTURE OF TETRAKIS(METHYLDIPHENYLPHOSPHINE)IRIDIUM(I) TETRAFLUOROBORATE WITH CYCLOHEXANE OF SOLVATION: $Ir[P(C_6H_5)_2CH_3]_4BF_4 \cdot C_6H_{12}$

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Summary

The crystal structure of tetrakis(methyldiphenylphosphine)iridium(I) tetrafluoroborate with cyclohexane of solvation, $[Ir(PPh_2Me)_4]BF_4 \cdot C_6H_{12}$, has been determined from a three-dimensional X-ray analysis. The compound has been analysed in space group $C2/c$ of the monoclinic system. There are twelve molecules (i.e. 1.5 molecules per asymmetric unit) in a cell of dimensions a = 36.804(8), b = 22.93(2), c = 21.676(4)Å, β = 121.41(1)°. Block-diagonal least-squares refinement has given a final R-factor of 0.060 for 7905 reflections having $I > 3\sigma(I)$.

The structure consists of two crystallographically distinct, but structurally similar molecules, one on a general position and one on a crystallographic two-fold axis. The phosphine ligands around the iridium atoms are in a very distorted square-planar arrangement. The reactions of the cation are discussed in terms of this structure.

Introduction

During recent years it has been established that four-coordinate d^8 complexes of some Group VIII metals react with molecular oxygen to form 1/1 adducts. The first of these, $IrCl(CO)(O_2)(PPh_3)_2$, was reported by Vaska [1] in 1963, a crystal structure determination [2, 3] subsequently verifying that the oxygen atoms occupy adjacent positions of a distorted coordination octahedron. Since then a number of other dioxygen adducts have been prepared [4-12] and these have served as model systems for the more complicated biological oxygen carriers.

When $[Ir(CO)(PPh_2Me)_3]^+$ is treated with excess phosphine in refluxing ethanol the carbon monoxide moiety is replaced to give the deep-red cation

$[\mathrm{Ir(PPh_2Me)_4}]^+$, which can be isolated as a salt with a variety of anions [13]. Surprisingly, this compound fails to coordinate dioxygen, or to even react with it in ethanol solution at 393 K, although a number of very similar complexes form stable 1/1 adducts. For example, the cation $[\mathrm{Ir(Ph_2PCH_2CH_2PPh_2)_2}]^+$, whicl differs from $[\mathrm{Ir(PPh_2Me)_4}]^+$ only in the linking of the methyl carbon atoms into an ethylene bridge, coordinates molecular oxygen strongly [9]. In addition, $[\mathrm{Ir(Ph_2PCH_2CH_2PPh_2)_2}]^+$ adds CO reversibly to form a five coordinate species, but $[\mathrm{Ir(PPh_2Me)_4}]^+$ fails to undergo such a reaction. Despite these anomalies $[\mathrm{Ir(PPh_2Me)_4}]^+$ does undergo the normal reversible addition of hydrogen halides and other strong acids to give a six coordinate product [14].

To investigate the extent of steric influences in accounting for this anomalo reactivity we have determined the crystal structure of the tetrafluoroborate salt of $[\mathrm{Ir(PPh_2Me)_4}]^+$.

Experimental

The complex $[\mathrm{Ir(PPh_2Me)_4}]\mathrm{BF_4}$ was prepared by Reed and Roper, red crystals being obtained by recrystallisation from dichloromethane/ethanol/cyclohexane solution [13]. From NMR spectroscopy and molecular weight determinations it was concluded that ca. one molecule of cyclohexane per molecule of complex was present in the crystal.

A crystal, approximately cubic in shape, was mounted along a face diagonal, this direction being subsequently established as that of the unique axis of the monoclinic system. Systematic absences were consistent with the space groups *Cc* or *C2/c*. Cell constants and their standard deviations were accurately determined from a least-squares refinement of four-circle diffractometer settings for twelve high-angle reflections [15] (θ = 16-18° for Mo-K_α radiation). The density was measured by flotation in potassium iodide solution to be 1.49 g $\mathrm{cm^{-3}}$. The calculated density based on the stoichiometric formula $[\mathrm{Ir(PPh_2Me)_4}]\mathrm{BF_4}\cdot\mathrm{C_6H_{12}}$ is 1.498 $\mathrm{cm^{-3}}$ for $Z = 12$. Thus the asymmetric volume was presumed to contain the equivalent of 1.5 formula units.

The crystal data are: a = 36.805(8), b = 22.93(2), c = 21.676(4)Å, β = 121.41(1)°, Z = 12, U = 15615 Å^3. Molecular formula = $[\mathrm{Ir(PPh_2Me)_4}]\mathrm{BF_4}\cdot\mathrm{C_6H_{12}}$; mol. wt. 1746. Linear absorption coefficient μ(Mo-K_α) = 31.29 $\mathrm{cm^{-1}}$.

Mo-K_α radiation (λ = 0.71069 Å with primary beam filter) was employed in the collection of the data set with a $2\theta/\omega$ technique using a 1.20° scan at a rate of 0.02° $\mathrm{sec^{-1}}$. The background was counted in stationary mode for 15 seconds at the beginning and end of each track. The diameter of the primary beam collimator was 0.4 mm and that of the counter collimator 3.5 mm. Intensity data were collected for hkl and $\bar{h}kl$ reflections for which $\theta \leqslant 25°$. Since the intensity of any reflection did not exceed 10^4 counts $\mathrm{sec^{-1}}$ no attenuation of the beam proved necessary. The intensities of three standard reflections ($\bar{1}404$, 604, $\bar{1}35$) were checked after each one hundred measurements. These showed a variation of less than 3% from their means. The data were corrected for Lorentz and polarisation effects and for absorption. Of the 13.566 reflections examined 7905 independent reflections were found to have intensities greater than three times their standard deviations, σ, (55.4% of 1/4 of the copper sphere) where $\sigma = [(I + t/(t_1 + t_2))^2(B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$. ($I$ = total counts in time t, B_1 and B_2 are background counts in times t_1 and t_2, $p = 0.05$ [16].

Structure determination and refinement

A 'sharpened' Patterson function was computed and the positions of the six largest maxima were found to be consistent with one iridium atom on a general position (molecule A) and one on a crystallographic two-fold axis in space group $C2/c$ (molecule B). A structure factor calculation based on these two atoms gave an R-factor of 0.284 both atoms being arbitrarily assigned an isotropic thermal parameter of 2.0 Å^2. From the subsequent electron density synthesis which retained $C2/c$ symmetry the positions of the six phosphorus atoms of the asymmetric unit were located. These were included in a second structure factor calculation before computation of a second electron density synthesis revealed the positions of all the carbon atoms of the ligands and a cyclohexane molecule. A structure factor calculation including these atoms returned an R-factor of 0.19 and from a further electron density map the BF_4^- anion in the general position was located. A number of other peaks were also observed but none could be fitted to the BF_4^- ion or to the cyclohexane molecule supposedly associated with the cation on the special position. A structure factor calculation based on all atoms located at this point returned an R of 0.17, all light atoms being assigned isotropic temperature factors of 3.0 Å^2.

The scattering factors assigned to the C, O, B, and F atoms were those tabulated in the International Tables [17] but literature values were used for neutral iridium and phosphorus [18]. Corrections were made for anomalous dispersion effects [19].

Refinement was undertaken by a block-diagonal least-squares method with a weighting scheme of the form $w = 4F^2/\sigma^2(F^2)$. The symmetry of space group $C2/c$ was retained, but even then the size of the structure and the small storage capacity of the computer (IBM 1130 with 16K fast core) allowed only the positional and thermal parameters of the heavy (iridium and phosphorus) atoms to be refined in the initial stages. After five cycles of isotropic refinement the value of R dropped to 0.119 and R' to 0.158 (where $R' = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$. A "difference" synthesis then computed did not reveal satisfactory positions for the missing BF_4^- and cyclohexane groups.

Three full-matrix refinement cycles were then computed on an IBM 360/44 computer. All atoms were refined isotropically, but with the phenyl rings being kept as rigid groups, and the R-factor fell to 0.085. A "difference" synthesis was again computed and it was now seen that the BF_4^- ion was disordered about a crystallographic two-fold axis passing through one fluorine atom F(11). It was approximately equidistant from the fluorine atoms F(12) and F(13). The cyclohexane molecule was also disordered about a two-fold axis passing close to atoms C(7) and C(10).

This disorder makes it likely that the space group is correctly Cc but since the remainder of the cell contents had refined smoothly in the centrosymmetric space group and would not therefore "break" this symmetry, and since the atoms already being handled taxed the available computing services to the limit, relaxation of the spatial requirements and doubling of parameters to be refined was not contemplated. As noted later there is no evidence that the final results are in any way suspect at the level of accuracy claimed. Refinement had to be continued on the smaller 1130 computer. All atoms, except the boron atom of the BF_4^- ion in the special position and the half-weighted cyclohexane group for which positional parameters were fixed were included. Due to the very large number of atoms in the asymmetric unit, refinement was divided into two blocks of atoms. The cyclohexane and tetrafluoroborate residues and the atoms of the cation on the special position were included in one block together with all the heavy atoms, the remaining carbon atoms being included in the other. The iridium and phosphorus atoms were assigned anisotropic temperature factors and after three cycles for each block of atoms the values of R and R' were 0.060 and 0.067 respectively. At this stage the fall in R-factors was insignificant and the parameter shifts were less than one third their estimated standard deviations. There was no evidence from the thermal parameters or the bond lengths and angles that the cation on the special position, which has imposed two-fold symmetry, had an "averaged" geometry so retention of the space group was justified. Nor was it considered that further anisotropic refinement, which would require vast and expensive amounts of computing time even in $C2/c$ would add useful additional information.

An agreement and error analysis of the data showed that $<w\Delta^2>$ was approximately constant over all ranges of $|F_o|$ justifying the application of the weighting scheme and the selection of 0.05 for the 'p' factor. The final atomic coordinates and temperature factors, together with their estimated standard deviations, are listed in Tables 1 and 2. The atomic numbering scheme for molecules A and B are shown in Figs. 1 and 2 respectively.

Root mean square amplitudes of vibration along the principal axes of the thermal ellipsoids are recorded in Table 3. Bond lengths and angles are tabulated in Tables 4 and 5. Diagrammatical representation of bond lengths and angles for molecule A are displayed in Figs. 3 and 4 respectively. For molecule B selected bond lengths and angles are shown in Fig. 5. Tables of observed and calculated structure factors may be obtained on request from the authors.

(continued on p. 386)

TABLE 1

POSITIONAL PARAMETERS, ISOTROPIC THERMAL PARAMETERS AND STANDARD DEVIATIONS FOR $[Ir(PPh_2Me)_4]BF_4 \cdot C_6H_{12}$

Atom	*x/a*	*y/b*	*z/c*	*B*
Ir(1)	0.35694(1)	0.10693(2)	0.46389(2)	
Ir(2)	0.0	−0.03611(3)	0.25	
P(1)	0.39481(9)	0.06559(16)	0.41643(15)	
P(2)	0.29372(8)	0.12255(15)	0.46049(15)	
P(3)	0.35756(9)	0.19969(16)	0.42121(16)	
P(4)	0.38155(9)	0.03982(17)	0.55691(16)	
P(5)	0.06792(9)	−0.01068(16)	0.34171(16)	
P(6)	−0.02211(9)	−0.06173(16)	0.32902(15)	
C(101)	0.4520(4)	0.0791(6)	0.4511(6)	3.8(3)
C(111)	0.3696(3)	0.0836(6)	0.3201(6)	3.1(2)
C(112)	0.3931(4)	0.1050(7)	0.2903(6)	3.8(3)
C(113)	0.3720(4)	0.1194(7)	0.2161(8)	5.1(3)
C(114)	0.3282(4)	0.1120(8)	0.1720(8)	5.7(4)
C(115)	0.3045(4)	0.0892(7)	0.2004(7)	4.9(3)

(to be continued)

TABLE 1 (continued)

Atom	x/a	y/b	z/c	B
C(116)	0.3257(4)	0.0763(6)	0.2757(6)	3.9(3)
C(121)	0.3924(4)	−0.0144(6)	0.4166(6)	3.3(3)
C(122)	0.3522(4)	−0.0428(7)	0.3782(7)	4.4(3)
C(123)	0.3504(4)	−0.1046(8)	0.3831(7)	5.2(3)
C(124)	0.3862(5)	−0.1363(8)	0.4250(8)	5.9(4)
C(125)	0.4252(5)	−0.1097(9)	0.4617(8)	6.3(4)
C(126)	0.4289(4)	−0.0482(7)	0.4591(7)	4.7(3)
C(201)	0.2889(4)	0.1617(6)	0.5297(7)	4.0(3)
C(211)	0.2671(4)	0.0525(6)	0.4534(6)	3.5(3)
C(212)	0.2626(4)	0.0112(6)	0.4017(6)	3.7(3)
C(213)	0.2423(4)	−0.0425(7)	0.3943(7)	5.0(3)
C(214)	0.2277(5)	−0.0562(8)	0.4411(8)	5.3(4)
C(215)	0.2319(4)	−0.0149(7)	0.4923(7)	4.7(3)
C(216)	0.2510(4)	0.0392(7)	0.4983(6)	3.9(3)
C(221)	0.2545(4)	0.1619(6)	0.3774(6)	3.5(3)
C(222)	0.2411(4)	0.1369(6)	0.3088(6)	4.2(3)
C(223)	0.2140(4)	0.1685(7)	0.2462(7)	4.7(3)
C(224)	0.2016(5)	0.2252(8)	0.2517(8)	5.8(4)
C(225)	0.2137(5)	0.2496(9)	0.3174(8)	5.9(4)
C(226)	0.2405(4)	0.2184(7)	0.3801(7)	4.6(3)
C(301)	0.3247(4)	0.2220(6)	0.3273(6)	3.7(3)
C(311)	0.3485(3)	0.2577(6)	0.4701(6)	3.2(2)
C(312)	0.3273(4)	0.3098(7)	0.4358(7)	4.0(3)
C(313)	0.3215(4)	0.3530(8)	0.4770(8)	5.2(4)
C(314)	0.3376(4)	0.3454(7)	0.5500(7)	5.0(3)
C(315)	0.3585(5)	0.2942(8)	0.5849(8)	5.5(4)
C(316)	0.3633(4)	0.2498(7)	0.5437(7)	4.4(3)
C(321)	0.4111(4)	0.2174(6)	0.4431(6)	3.5(3)
C(322)	0.4441(4)	0.2191(6)	0.5175(7)	3.9(3)
C(323)	0.4860(4)	0.2287(7)	0.5362(7)	5.2(3)
C(324)	0.4961(4)	0.2390(8)	0.4831(7)	5.3(4)
C(325)	0.4644(4)	0.2392(8)	0.4113(8)	5.5(4)
C(326)	0.4211(4)	0.2287(7)	0.3887(7)	4.5(3)
C(401)	0.3614(4)	−0.0352(6)	0.5470(6)	3.8(3)
C(411)	0.3756(3)	0.0692(6)	0.6296(6)	3.5(3)
C(412)	0.3489(4)	0.0422(7)	0.6501(7)	4.3(3)
C(413)	0.3434(5)	0.0689(8)	0.7039(8)	5.4(4)
C(414)	0.3634(5)	0.1210(8)	0.7349(8)	5.5(4)
C(415)	0.3901(5)	0.1475(8)	0.7154(8)	5.4(4)
C(416)	0.3967(4)	0.1211(6)	0.6623(7)	4.1(3)
C(421)	0.4394(3)	0.0304(6)	0.6061(6)	3.3(2)
C(422)	0.4587(4)	−0.0237(7)	0.6352(7)	4.6(3)
C(423)	0.5040(4)	−0.0277(8)	0.6745(7)	5.2(3)
C(424)	0.5286(5)	0.0212(8)	0.6839(8)	5.4(4)
C(425)	0.5098(5)	0.0740(8)	0.6529(8)	5.5(4)
C(426)	0.4645(4)	0.0787(7)	0.6137(7)	4.2(3)
C(501)	0.1099(4)	−0.0631(6)	0.3962(6)	3.7(3)
C(511)	0.0923(3)	0.0372(6)	0.3068(6)	3.3(2)
C(512)	0.1295(4)	0.0208(7)	0.3068(7)	4.7(3)
C(513)	0.1462(5)	0.0580(8)	0.2750(8)	5.3(4)
C(514)	0.1250(4)	0.1097(8)	0.2420(7)	5.1(3)
C(515)	0.0884(5)	0.1265(8)	0.2423(8)	5.4(4)
C(516)	0.0726(4)	0.0902(6)	0.2743(7)	4.2(3)
C(521)	0.0681(3)	0.0378(6)	0.4094(6)	3.2(2)
C(522)	0.0351(4)	0.0782(7)	0.3879(7)	4.2(3)
C(523)	0.0342(4)	0.1192(7)	0.4359(7)	5.1(3)
C(524)	0.0664(4)	0.1164(7)	0.5083(7)	5.2(3)
C(525)	0.0991(4)	0.0758(8)	0.5331(8)	5.1(3)
C(526)	0.0998(4)	0.0361(7)	0.4825(7)	4.7(3)

(to be continued)

TABLE 1 (continued)

Atom	*x/a*	*y/b*	*z/c*	*B*
C(601)	−0.0397(4)	−0.0098(6)	0.3731(6)	3.5(3)
C(611)	0.0194(3)	−0.1027(6)	0.4072(6)	3.4(2)
C(612)	0.0387(4)	−0.0801(7)	0.4769(7)	4.9(3)
C(613)	0.0726(5)	−0.1113(8)	0.5341(8)	5.9(4)
C(614)	0.0866(5)	−0.1625(9)	0.5212(9)	6.3(4)
C(615)	0.0678(4)	−0.1861(8)	0.4537(8)	5.3(4)
C(616)	0.0344(4)	−0.1561(7)	0.3953(7)	4.3(3)
C(621)	−0.0668(3)	−0.1131(6)	0.2858(6)	3.3(2)
C(622)	−0.0634(4)	−0.1611(6)	0.2481(6)	3.9(3)
C(623)	−0.0959(4)	−0.2029(7)	0.2157(7)	4.9(3)
C(624)	−0.1334(5)	−0.1944(8)	0.2159(8)	5.6(4)
C(625)	−0.1372(4)	−0.1473(7)	0.2522(7)	4.4(3)
C(626)	−0.1038(4)	−0.1058(7)	0.2581(6)	4.1(3)
B(1)	0.2240(13)	−0.041(2)	0.192(2)	14.7(14)
F(11)	0.2171(6)	−0.0238(10)	0.1281(10)	16.8(7)
F(12)	0.1916(6)	−0.0657(9)	0.1907(10)	16.0(6)
F(13)	0.2449(6)	0.0005(9)	0.2428(10)	14.7(5)
F(14)	0.2505(7)	−0.0805(11)	0.2182(11)	18.5(7)
B(2)	0.494	0.190	0.227	12.0(18)
F(21)	0.5	0.2442(14)	0.25	14.8(8)
F(22)	0.4682(12)	0.160(2)	0.243(2)	15.4(13)
F(23)	0.4747(13)	0.200(2)	0.159(2)	16.5(15)
F(24)	0.5317(12)	0.160(2)	0.256(2)	15.4(13)
C(1)	0.2029(6)	0.3138(10)	0.0259(10)	7.8(5)
C(2)	0.1666(5)	0.2729(9)	−0.0188(9)	6.5(4)
C(3)	0.1806(5)	0.2086(9)	−0.0179(9)	6.5(4)
C(4)	0.2065(5)	0.1878(9)	0.0592(9)	6.9(5)
C(5)	0.2459(5)	0.2282(9)	0.1108(9)	7.2(5)
C(6)	0.2300(6)	0.2900(9)	0.1059(10)	7.1(5)
C(7)	−0.015	0.205	0.254	10.9(9)
C(8)	−0.025	0.230	0.184	10.9(10)
C(9)	−0.031	0.294	0.185	13.6(10)
C(10)	0.007	0.325	0.244	14.6(9)
C(11)	0.013	0.291	0.311	13.3(10)
C(12)	0.025	0.231	0.310	9.2(10)

TABLE 2

ANISOTROPIC TEMPERATURE FACTORS[a] WITH STANDARD DEVIATIONS (X 10^5) FOR $[Ir(PPh_2Me)_4]BF_4 \cdot C_6H_{12}$

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ir(1)	58(1)	115(1)	176(1)	7(1)	119(1)	17(2)
Ir(2)	55(1)	125(1)	160(1)	0	104(1)	0
P(1)	71(2)	144(7)	218(7)	16(7)	154(5)	10(12)
P(2)	63(2)	140(7)	212(7)	6(6)	135(5)	3(12)
P(3)	76(2)	131(7)	224(7)	− 2(7)	145(5)	21(12)
P(4)	78(2)	147(7)	191(7)	16(7)	127(5)	24(13)
P(5)	64(2)	152(7)	197(7)	−21(7)	102(6)	−19(13)
P(6)	68(2)	149(7)	212(6)	− 7(7)	149(5)	− 3(12)

[a] The scattering factor is of the form: $f = f_o \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

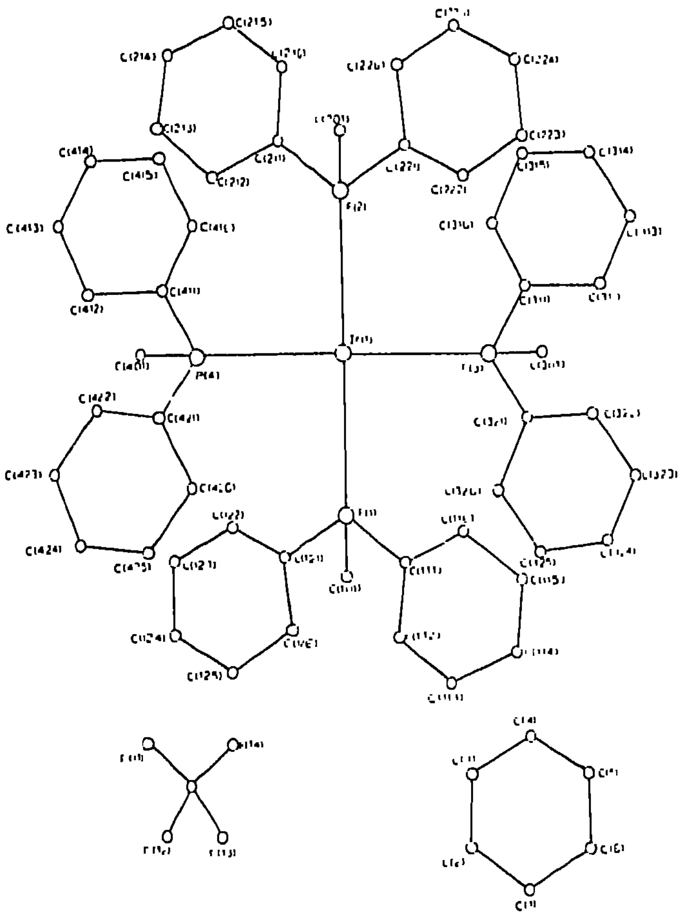

Fig. 1. Atomic numbering scheme for molecule A.

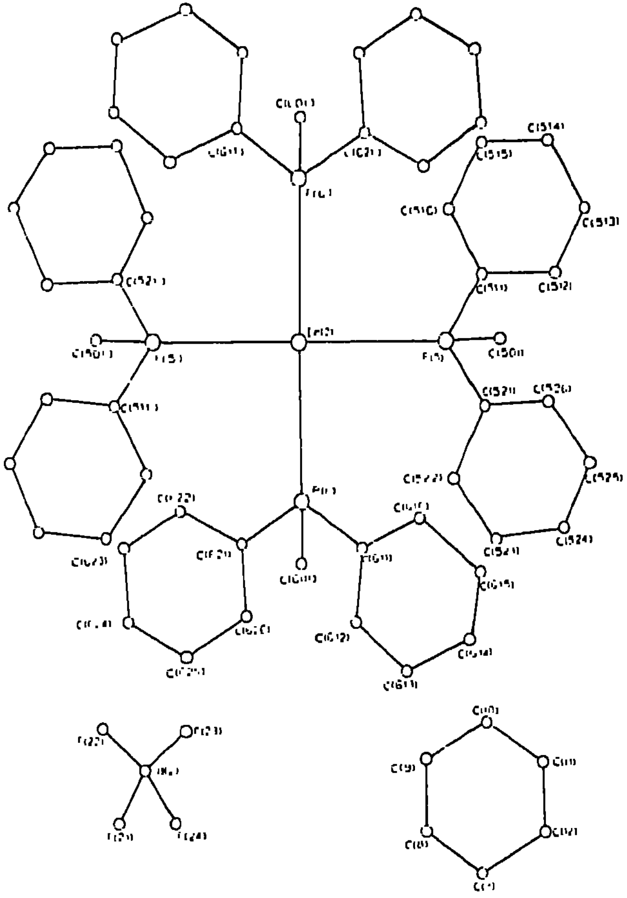

Fig. 2. Atomic numbering scheme for molecule B.

TABLE 3

ROOT MEAN SQUARE AMPLITUDES OF VIBRATION FOR $[Ir(PPh_2Me)_4]BF_4 \cdot C_6H_{12}$

Atom	Minor axis	Medium axis	Major axis
Ir(1)	0.157Å	0.176Å	0.210Å
Ir(2)	0.152	0.182	0.204
P(1)	0.170	0.197	0.243
P(2)	0.166	0.193	0.233
P(3)	0.179	0.187	0.240
P(4)	0.169	0.200	0.237
P(5)	0.161	0.203	0.231
P(6)	0.174	0.218	0.226

TABLE 4

BOND LENGTHS AND STANDARD DEVIATIONS FOR $[Ir(PPh_2Me)_4]BF_4 \cdot C_6H_{12}$

Ir(1)—P(1)	2.322(4)Å	C(121)—C(126)	1.40(2)
Ir(1)—P(2)	2.317(5)	C(122)—C(123)	1.42(2)
Ir(1)—P(3)	2.324(4)	C(123)—C(124)	1.35(3)
Ir(1)—P(4)	2.313(4)	C(124)—C(125)	1.37(3)
Ir(2)—P(5)	2.315(4)	C(125)—C(126)	1.42(3)
Ir(2)—P(6)	2.322(4)	C(211)—C(212)	1.41(2)
P(1)—C(101)	1.856(14)	C(211)—C(216)	1.41(2)
P(1)—C(111)	1.837(13)	C(212)—C(213)	1.40(2)
P(1)—C(121)	1.835(14)	C(213)—C(214)	1.40(3)
P(2)—C(201)	1.834(14)	C(214)—C(215)	1.40(2)
P(2)—C(211)	1.846(13)	C(215)—C(216)	1.39(2)
P(2)—C(221)	1.852(13)	C(221)—C(222)	1.42(2)
P(3)—C(301)	1.817(14)	C(221)—C(226)	1.40(2)
P(3)—C(311)	1.835(12)	C(222)—C(223)	1.39(2)
P(3)—C(321)	1.816(14)	C(223)—C(224)	1.40(3)
P(4)—C(401)	1.840(14)	C(224)—C(225)	1.37(3)
P(4)—C(411)	1.829(13)	C(225)—C(226)	1.39(2)
P(4)—C(421)	1.830(12)	C(311)—C(312)	1.41(2)
P(5)—C(501)	1.823(14)	C(311)—C(316)	1.40(2)
P(5)—C(511)	1.814(13)	C(312)—C(313)	1.42(2)
P(5)—C(521)	1.838(12)	C(313)—C(314)	1.38(2)
P(6)—C(601)	1.841(14)	C(314)—C(315)	1.39(2)
P(6)—C(611)	1.841(13)	C(315)—C(316)	1.42(2)
P(6)—C(621)	1.833(13)	C(321)—C(322)	1.42(2)
C(111)—C(112)	1.41(2)	C(321)—C(326)	1.43(2)
C(111)—C(116)	1.39(2)	C(322)—C(323)	1.39(3)
C(112)—C(113)	1.41(2)	C(323)—C(324)	1.40(3)
C(113)—C(114)	1.39(3)	C(324)—C(325)	1.37(2)
C(114)—C(115)	1.40(3)	C(325)—C(326)	1.42(3)
C(115)—C(116)	1.42(2)	C(411)—C(412)	1.41(2)
C(121)—C(122)	1.42(2)	C(411)—C(416)	1.39(2)
C(412)—C(413)	1.42(3)	C(615)—C(616)	1.40(2)
C(413)—C(414)	1.38(3)	C(621)—C(622)	1.41(2)
C(414)—C(415)	1.39(3)	C(621)—C(626)	1.40(2)
C(415)—C(416)	1.43(3)	C(622)—C(623)	1.40(2)
C(421)—C(422)	1.40(2)	C(623)—C(624)	1.39(3)
C(421)—C(426)	1.39(2)	C(624)—C(625)	1.38(2)
C(422)—C(423)	1.42(3)	C(625)—C(626)	1.42(2)
C(423)—C(424)	1.39(3)	C(1)—C(2)	1.50(3)
C(424)—C(425)	1.38(3)	C(1)—C(6)	1.58(3)
C(425)—C(426)	1.42(3)	C(2)—C(3)	1.56(3)

(to be continued)

TABLE 4 (continued)

C(511)—C(512)	1.42(3)	C(3)—C(4)	1.50(3)
C(511)—C(516)	1.40(2)	C(4)—C(5)	1.58(3)
C(512)—C(513)	1.42(3)	C(5)—C(6)	1.51(3)
C(513)—C(514)	1.39(3)	B(1)—F(11)	1.33(6)
C(514)—C(515)	1.40(3)	B(1)—F(12)	1.30(6)
C(515)—C(516)	1.39(3)	B(1)—F(13)	1.35(5)
C(521)—C(522)	1.40(2)	B(1)—F(14)	1.23(6)
C(521)—C(526)	1.39(2)	C(7)—C(8)	1.48
C(522)—C(523)	1.41(2)	C(7)—C(12)	1.46
C(523)—C(524)	1.39(2)	C(8)—C(9)	1.49
C(524)—C(525)	1.39(2)	C(9)—C(10)	1.50
C(525)—C(526)	1.43(2)	C(10)—C(11)	1.56
C(611)—C(612)	1.39(2)	C(11)—C(12)	1.45
C(611)—C(616)	1.42(2)	B(2)—F(21)	1.31
C(612)—C(613)	1.41(3)	B(2)—F(22)	1.35
C(613)—C(614)	1.37(3)	B(2)—F(23)	1.27
C(614)—C(615)	1.36(3)	B(2)—F(24)	1.37

TABLE 5

BOND ANGLES AND STANDARD DEVIATIONS FOR [Ir(PPh$_2$Me)$_4$] · C$_6$H$_{12}$

P(1)—Ir(1)—P(2)	150.9(1)[c]
P(1)—Ir(1)—P(3)	93.7(1)
P(1)—Ir(1)—P(4)	93.6(1)
P(2)—Ir(1)—P(3)	93.7(1)
P(2)—Ir(1)—P(4)	93.5(1)
P(3)—Ir(1)—P(4)	151.1(1)
P(5)—Ir(2)—P(5')	150.8(1)
P(5)—Ir(2)—P(6)	93.8(1)
P(5)—Ir(2)—P(6')	93.5(1)
P(6)—Ir(2)—P(6')	150.7(1)
Ir(1)—P(1)—C(101)	124.7(6)
Ir(1)—P(1)—C(111)	110.3(6)
Ir(1)—P(1)—C(121)	111.5(6)
Ir(1)—P(2)—C(201)	124.9(7)
Ir(1)—P(2)—C(211)	110.4(6)
Ir(1)—P(2)—C(221)	111.6(6)
Ir(1)—P(3)—C(301)	124.4(7)
Ir(1)—P(3)—C(311)	113.0(6)
Ir(1)—P(3)—C(321)	109.6(6)
Ir(1)—P(4)—C(401)	124.7(7)
Ir(1)—P(4)—C(411)	109.8(6)
Ir(1)—P(4)—C(421)	113.2(6)
Ir(2)—P(5)—C(501)	124.2(7)
Ir(2)—P(5)—C(511)	110.0(6)
Ir(2)—P(5)—C(521)	113.0(6)
Ir(2)—P(6)—C(601)	124.9(7)
Ir(2)—P(6)—C(611)	111.5(6)
Ir(2)—P(6)—C(621)	110.5(6)
C(111)—P(1)—C(121)	103.3(8)
C(101)—P(1)—C(121)	102.1(6)
C(101)—P(1)—C(111)	102.6(7)
C(211)—P(2)—C(221)	103.4(8)
C(201)—P(2)—C(221)	101.4(7)
C(201)—P(2)—C(211)	102.7(7)

(to be continued)

TABLE 5 (continued)

C(311)—P(3)—C(321)	100.6(8)
C(301)—P(3)—C(311)	103.1(7)
C(301)—P(3)—C(321)	103.1(8)
C(411)—P(4)—C(421)	99.6(8)
C(401)—P(4)—C(411)	102.9(8)
C(401)—P(4)—C(421)	103.5(8)
C(511)—P(5)—C(521)	99.8(8)
C(501)—P(5)—C(511)	103.4(7)
C(501)—P(5)—C(521)	103.5(7)
C(611)—P(6)—C(621)	103.6(8)
C(601)—P(6)—C(611)	101.5(7)
C(601)—P(6)—C(621)	102.5(8)
P(1)—C(111)—C(112)	122.1(12)
P(1)—C(111)—C(116)	118.3(12)
C(112)—C(111)—C(116)	119.6(14)
C(111)—C(112)—C(113)	119.9(14)
C(112)—C(113)—C(114)	120.5(17)
C(113)—C(114)—C(115)	120.3(18)
C(114)—C(115)—C(116)	119.0(16)
C(115)—C(116)—C(111)	120.7(15)
P(1)—C(121)—C(122)	119.5(12)
P(1)—C(121)—C(126)	121.6(13)
C(126)—C(121)—C(122)	118.7(14)
C(121)—C(122)—C(123)	119.1(15)
C(122)—C(123)—C(124)	121.2(17)
C(123)—C(124)—C(125)	120.4(19)
C(124)—C(125)—C(126)	120.8(19)
C(125)—C(126)—C(121)	119.8(16)
P(2)—C(211)—C(212)	119.2(12)
P(2)—C(211)—C(216)	121.7(12)
C(216)—C(211)—C(212)	119.1(14)
C(211)—C(212)—C(213)	120.9(14)
C(212)—C(213)—C(214)	119.5(16)
C(213)—C(214)—C(215)	119.6(17)
C(214)—C(215)—C(216)	121.0(16)
C(215)—C(216)—C(211)	119.9(15)
P(2)—C(221)—C(222)	119.4(12)
P(2)—C(221)—C(226)	121.7(13)
C(226)—C(221)—C(222)	118.6(14)
C(221)—C(222)—C(223)	119.3(15)
C(222)—C(223)—C(224)	119.9(16)
C(223)—C(224)—C(225)	121.5(18)
C(224)—C(225)—C(226)	119.1(18)
C(225)—C(226)—C(221)	121.5(16)
P(3)—C(311)—C(312)	121.8(12)
P(3)—C(311)—C(316)	118.9(13)
C(316)—C(311)—C(312)	119.3(14)
C(311)—C(312)—C(313)	118.8(15)
C(312)—C(313)—C(314)	121.1(17)
C(313)—C(314)—C(315)	120.9(17)
C(314)—C(315)—C(316)	118.5(17)
C(315)—C(316)—C(311)	121.3(15)
P(3)—C(321)—C(322)	118.1(12)
P(3)—C(321)—C(326)	122.4(14)
C(326)—C(321)—C(322)	119.5(14)
C(321)—C(322)—C(323)	119.7(15)
C(322)—C(323)—C(324)	121.0(17)
C(323)—C(324)—C(325)	119.8(17)
C(324)—C(325)—C(326)	121.9(17)
C(325)—C(326)—C(321)	118.0(15)

(to be continued)

TABLE 5 (continued)

P(4)—C(411)—C(412)	121.6(12)
P(4)—C(411)—C(416)	117.8(12)
C(416)—C(411)—C(412)	120.5(14)
C(411)—C(412)—C(413)	119.3(15)
C(412)—C(413)—C(414)	120.1(17)
C(413)—C(414)—C(415)	120.8(18)
C(414)—C(415)—C(416)	120.0(17)
C(415)—C(416)—C(411)	119.2(15)
P(4)—C(421)—C(422)	121.9(12)
P(4)—C(421)—C(426)	118.1(12)
C(426)—C(421)—C(422)	120.0(14)
C(421)—C(422)—C(423)	119.1(15)
C(422)—C(423)—C(424)	120.4(17)
C(423)—C(424)—C(425)	120.7(18)
C(424)—C(425)—C(426)	119.5(17)
C(425)—C(426)—C(421)	120.3(15)
P(5)—C(511)—C(512)	121.8(12)
P(5)—C(512)—C(516)	119.7(12)
C(516)—C(511)—C(512)	118.4(14)
C(511)—C(512)—C(513)	120.0(16)
C(512)—C(513)—C(514)	119.6(17)
C(513)—C(514)—C(515)	120.7(17)
C(514)—C(515)—C(516)	119.4(17)
C(515)—C(516)—C(511)	121.9(15)
P(5)—C(521)—C(522)	119.6(12)
P(5)—C(521)—C(526)	122.8(12)
C(526)—C(521)—C(522)	117.6(14)
C(521)—C(522)—C(523)	122.9(15)
C(522)—C(523)—C(524)	117.8(16)
C(523)—C(524)—C(525)	121.6(17)
C(524)—C(525)—C(526)	119.1(17)
C(525)—C(526)—C(521)	120.8(16)
P(6)—C(611)—C(612)	120.1(12)
P(6)—C(611)—C(616)	119.2(12)
C(616)—C(611)—C(612)	119.4(14)
C(611)—C(612)—C(613)	118.8(16)
C(612)—C(613)—C(614)	120.6(18)
C(613)—C(614)—C(615)	121.8(19)
C(614)—C(615)—C(616)	119.3(18)
C(615)—C(616)—C(611)	120.0(15)
P(6)—C(621)—C(622)	118.1(12)
P(6)—C(621)—C(626)	122.4(12)
C(626)—C(621)—C(622)	119.5(14)
C(621)—C(622)—C(623)	120.9(15)
C(622)—C(623)—C(624)	119.2(17)
C(623)—C(624)—C(625)	120.3(17)
C(624)—C(625)—C(626)	121.2(16)
C(625)—C(626)—C(621)	118.6(14)
C(1)—C(2)—C(3)	113.9(18)
C(2)—C(3)—C(4)	109.1(18)
C(3)—C(4)—C(5)	114.6(18)
C(4)—C(5)—C(6)	108.6(18)
C(5)—C(6)—C(1)	113.5(19)
C(6)—C(1)—C(2)	109.5(19)
F(11)—B(1)—F(12)	115(4)
F(11)—B(1)—F(13)	111(4)
F(11)—B(1)—F(14)	112(4)
F(12)—B(1)—F(13)	116(5)
F(12)—B(1)—F(14)	101(3)
F(13)—B(1)—F(14)	100(3)

(to be continued)

TABLE 5 (continued)

C(7)—C(8)—C(9)	109
C(8)—C(9)—C(10)	113
C(9)—C(10)—C(11)	102
C(10)—C(11)—C(12)	111
C(11)—C(12)—C(7)	103
C(18)—C(7)—C(12)	107
F(21)—B(2)—F(22)	113
F(21)—B(2)—F(23)	101
F(21)—B(2)—F(24)	111
F(22)—B(2)—F(23)	109
F(22)—B(2)—F(24)	108
F(23)—B(2)—F(24)	115

Description of the structure

The crystal structure contains two sets of crystallographically independent molecules, one on general positions (molecule A) and the other in special positions (molecule B), the cation of the latter being such that a two-fold axis passes through the iridium atom perpendicular to the coordination plane. The cations are four-coordinate, the phosphine ligands being in a very distorted square-planar arrangement around each iridium atom as seen in Fig. 6.

Although crystallographically different the two cations are very similar in geometry, the similarities extending to the periphery of the ions. The two tetrafluoroborate anions are also crystallographically different. That one associated with the cation on the special position is "disordered" about a two-fold axis

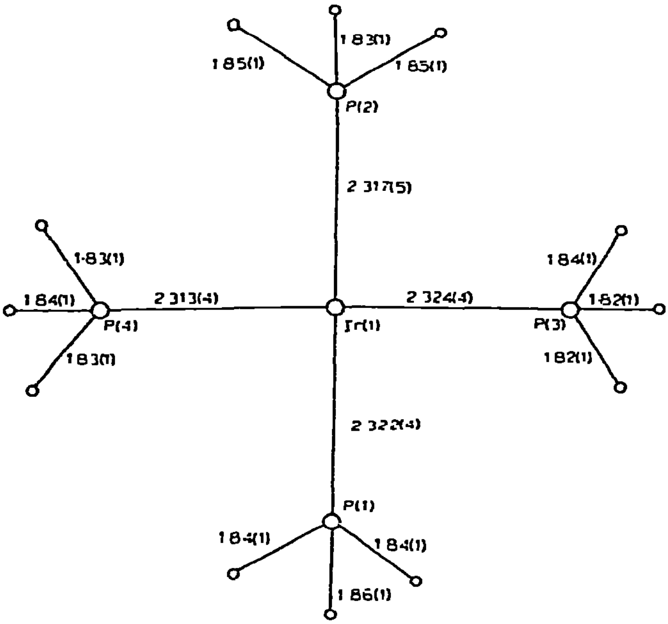

Fig. 3. Selected bond lengths (Å) for cation A.

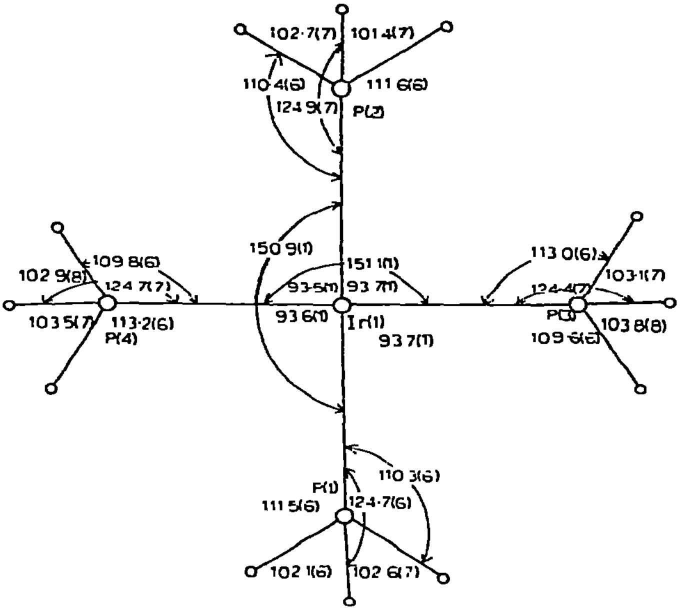

Fig. 4. Selected bond angles (degrees) for cation A.

which passes through fluorine atom F(21) undoubtedly as a consequence of the choice of space group. One cyclohexane solvent molecule is also "disordered" for the same reason. The other cyclohexane solvent molecule has no such complications imposed on it and adopts the chair conformation.

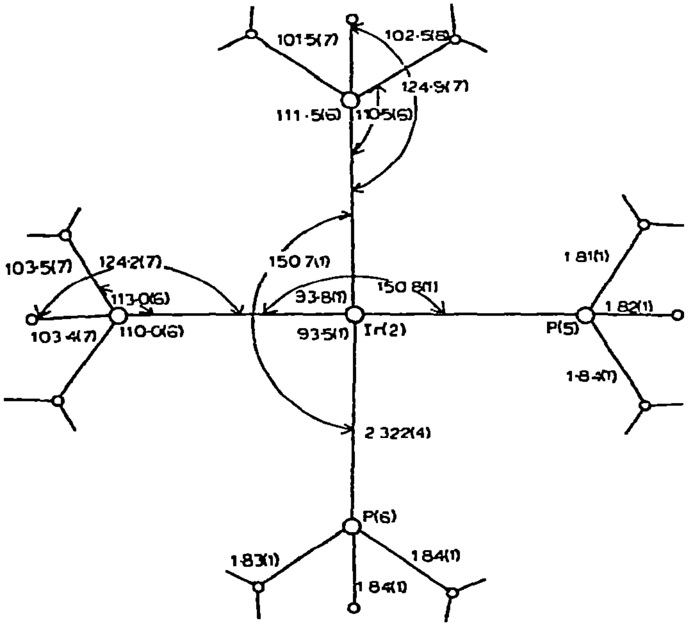

Fig. 5. Selected bond lengths (Å) and bond angles (degrees) for cation B.

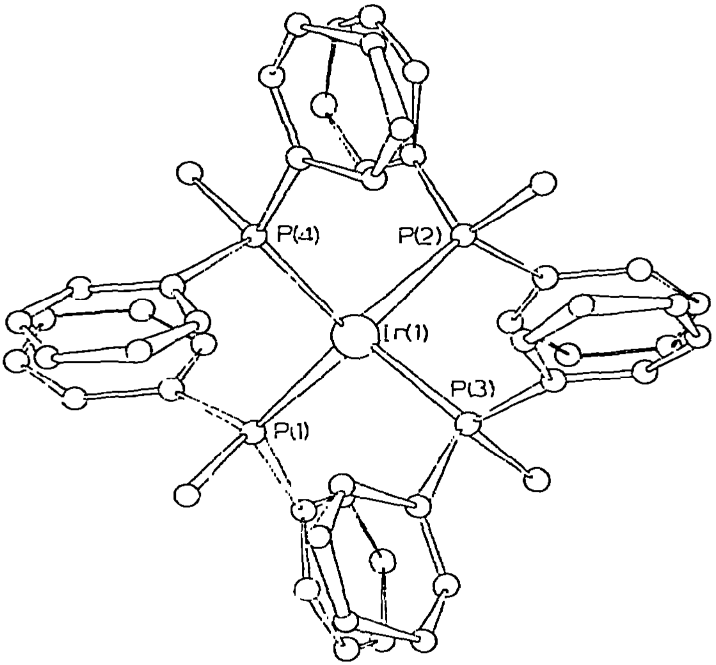

Fig. 6. A perspective view of cation A.

An examination of the bond lengths and angles for the phenyl rings in Tables 4 and 5 reveal no unusual C—C distances or C—C—C angles, no value differing by more than three times the standard deviations from the mean. The average C—C bond lengths of 1.398 Å and angle of 119.9° are in good agreement with the expected values. Standard deviations calculated over the spread of values are 0.02 Å and 1.1°, in reasonable agreement with those obtained from the least squares calculations (0.02 Å and 1.6°). The average P—C—C angle is 120.4° and the standard deviation calculated over the spread of values, 1.7°, can be compared with 1.3° obtained from the least-squares procedure. No P—C—C angle varies from the expected 120° by more than three times its standard deviation. The Ir—P bond lengths do not differ significantly from their mean (2.314 Å) and similarly the P—C bond lengths (1.81-1.85 Å) do not differ by more than 3σ from the mean.

The Ir—P bond lengths [average 2.314(4) Å] are slightly lower than most of those found for other iridium phosphine complexes but are still within the range of values observed (see Table 6). However, the different geometries of the complexes and the considerable steric strain imposed on the phosphine ligands preclude any deductions on the relative strengths of these bonds. The P—C(phenyl) bond lengths [average 1.83(1) Å] are also similar to those found in other structural analyses [16, 21-28]. The P—C(methyl) bond lengths [average 1.83(1) Å] are lower than those found for other structures containing P—C(methyl) bonds, but are only slightly lower than that observed for the only other complex containing the methyldiphenylphosphine ligand (1.853(7) Å [29]). There is significant departure from the expected planarity of the coordinating phosphorus

TABLE 6

IRIDIUM—PHOSPHORUS BOND LENGTHS

Compound[a]	Geometry[b]	Ir—P (Å)	Ref.
$Ir(NO)(PPh_3)_3$	TET	2.321(6)-2.298(10)	20
$[IrH(CO)_2(PPh_3)_2]$	TBP	2.372	21
$[Ir(DPPE)_2O_2]PF_6$	O	2.283(7)-2.452(9)	22
$[IrCl(SO_2)CO(PPh_3)_2]$	TP	2.359(9)-2.328(8)	23
$[Ir(DPPE)_2CO]Cl$	TBP	2.37(2)	24
$[IrCl_2(NO)(PPh_3)_2]$	TP	2.367(2)	25
$[C_3(C_6H_5)_3IrCl(CO)(PMe_3)_2]$	O	2.369(5)	26
$[IrO_2Cl(CO)(PPh_3)_2]$	TBP	2.38-2.76(1)	27
$[Ir(CO)_3(PMe_2Ph)_2]ClO_4$	TBP	2.34(2), 2.29(2)	28

[a] DPPE = $Ph_2PCH_2CH_2PPh_2$. [b] TP = tetragonal pyramidal, O = octahedral, TET = tetrahedral, TBP = trigonal bipyramidal.

atoms around the iridium as shown by the 'least-squares' planes of best fit in Table 7. These show that in both cations opposite donor atoms are on the same side of the mean plane and are displayed from it by 0.4 to 0.7 Å. The angles subtended by the phosphorus atom at the metal centre deviate considerably from the expected values of 90° and 180° for planar coordination, the P—Ir—P angles averaging 93.7° and 150.5°. Thus there is considerable distortion towards a tetrahedral arrangement and this is similar in both cations. The amount of tetrahedral distortion is measured by the angles between opposite planes containing the iridium atom and two *cis* phosphorus atoms. For perfect square planar coordination this is 0° and for a tetrahedral arrangement the angle is 90°. These angles are 40° for both cations and thus the distortion towards a tetrahedral geometry is considerable. This is an unusual result since all structural studies of

TABLE 7

PLANES OF 'BEST FIT' THROUGH THE COORDINATED ATOMS[a]

(1). Coordination plane for cation A. Ir(1), P(1), P(2), P(3), P(4).

$0.363X + 0.488Y + 0.794Z - 10.851 = 0$

Ir(1)	0.0016	P(3)	0.595
P(1)	−0.457	P(4)	0.563
P(2)	−0.702		

(2). Coordination plane for cation B. Ir(2), P(5), P(5'), P(6), P(6').

$Y - 0.828 = 0$

Ir(2)	0.0017	P(5')	0.583
P(5)	0.583	P(6')	−0.584
P(6)	−0.584		

[a] The equations of the planes of best fit are referred to an orthogonal set of axes and are given in the cosine form, $AX + BY + CZ - D = 0$, where A, B, and C are the direction cosines. The relationship between the orthogonal and crystallographic axes are $X = x + z\cos\beta$, $Y = y$, $Z = z\sin\beta$. The displacements of the atoms are given in Å.

four-coordinate iridium(I) complexes have shown them to be square planar or very nearly so.

Phosphine groups in *trans* positions have their methyl groups on the same side of the mean coordination plane (see Fig. 6) but opposite to those of adjacent groups.

From studies of models it is estimated that in a strictly square planar arrangement (assuming similar bond lengths and angles for the phosphine ligands) the distances between phenyl rings of adjacent phosphine ligands would be ca. 2.8 Å compared with the van der Waals distance of ca. 3.4 Å and the observed distance of 3.8 Å. The hydrogen atoms of methyl and phenyl groups would be as close to one another as 1.8 Å, which is much less than the van der Waals sum of 2.4 Å. Again, the observed figures of 2.4-2.6 Å for the H(phenyl)—H(phenyl) distances and 3.1-3.2 Å for C(methyl)—H(phenyl) distances indicate that the distortion towards a tetrahedral geometry results, at least in part, from the need to reduce these interactions. In addition to these effects there are two other observations which are undoubtedly a result of steric factors. The angles around the phosphorus atoms are unusual; the average Ir—P—C(methyl) angle of 125.0(8)° is markedly different from the expected tetrahedral angle of 109°. Other instances in which the M—P—C(methyl) angle is large have been found in sterically crowded complexes and are listed in Table 8. These are however, less than those found in the present structure.

In addition to this distortion there is also, within each ligand, a slight but significant shift of the phenyl and methyl groups towards each other. The Ir—P—C(phenyl) angles average 111°, which is only slightly greater than tetrahedral, but the C(phenyl)—P—C(phenyl) (average 102°) and C(methyl)—P—C(phenyl) angles (average 103°) are less than tetrahedral. It is probable that this particular geometry of the methyldiphenylphosphine ligand is due to intra-ligand crowding.

The average B—F bond length of the two BF_4^- ions are 1.30(4) Å and 1.33(4) Å and the average F—B—F angles are 109(4)°, the value in parenthesis being the rms value. These distances seem short when compared with the reported values of 1.40 and 1.43 Å [34, 35] but such lengths have been observed previously and were attributed to the thermal motion [36]. It seems probable that this is occuring in the present analysis since high isotropic thermal parameters were observed for atoms of both anions.

The majority of the shortest non-bonded inter-molecular approaches are between phenyl rings and fluorine atoms or cyclohexane solvent molecules.

TABLE 8

METAL—P—C(METHYL) BOND ANGLES

Compound	M—P—C(methyl)	Ref.
$[ReN_2Cl(PPhMe_2)_4]$	116(1)°	30
$[Pd(PhCH_3P(CH_2)_2PCH_3Ph)_2Cl_2]$	113.5-122.4	31
$Os[RuH(C_{10}H_{18})(DMPE)_2]^a$	118°-121°	32
$[Ni(CN)_2(PPhMe_2)_3]$	115°-118°	33

[a] $C_{10}H_{18}$ = naphthyl. DMPE = $(CH_3)_2PCH_2CH_2P(CH_3)_2$.

Interactions between phenyl rings of different molecules are few and thus the cyclohexane solvent molecule appears to fill a gap in the structure. The O—F distances are not less than 3.16 Å and the C—C distances (not less than 3.2 Å) are not unusual.

Discussion

The cation, $[\mathrm{Ir(PPh_2Me)_4}]^+$, does not form adducts with molecular oxygen or carbon monoxide, a rather surprising result in view of the ease with which similar compounds form stable adducts with these ligands. It does, however, undergo oxidative addition reactions with HCl, H_2, and Cl_2. To explain these apparent anomalies three arguments can be put forward.

Firstly, a result of the tetrahedral distortion is to bring the phenyl groups of *trans* phosphine ligands closer together thereby shielding the central iridium atom from attack by reactants such as O_2. The geometry of the cations can be compared with that of the square planar ion $[\mathrm{Rh(Ph_2PCH_2CH_2PPh_2)_2}]^+$ [37] ($\mathrm{Ph_2PCH_2CH_2PPh_2}$ = DPPE) which is assumed to be isostructural with its iridium analogue.

The hydrogen positions of the cations, $[\mathrm{Ir(PPh_2Me)_4}]^+$ and $[\mathrm{Rh(DPPE)_2}]^+$ have been calculated and their positions relative to the central metal atom compared. The relative distances are given in Tables 9 and 10. The numbering system for the hydrogen atom being the same as those of the carbon atoms to which they are bound for both cations. The numbering system for $[\mathrm{Rh(DPPE)_2}]^+$ is that of ref. 37.

As can be seen from Table 10, the Ir—H distances [average 3.2(1) Å] are only slightly shorter than the corresponding Rh—H distances in $[\mathrm{Rh(DPPE)_2}]^+$. However the H—H interactions for the iridium complex are significantly shorter so that the approach of a ligand must be significantly more hindered in $[\mathrm{Ir(PPh_2Me)_4}]^+$ than in $[\mathrm{Ir(DPPE)_2}]^+$. However, in spite of the plausibility of this argument it must be noted that $[\mathrm{Ir(PPh_2Me)_4}]^+$ is oxidised rapidly by hydrogen, hydrogen chloride and chlorine to give six-coordinate products *cis*-$[\mathrm{IrH_2(PPh_2Me)_4}]^+$, *trans*-$[\mathrm{IrHCl(PPh_2Me)_4}]^+$ and *trans*-$[\mathrm{IrCl_2(PPh_2Me)_4}]^+$ [13]

TABLE 9

INTRA-MOLECULAR APPROACHES FOR $[\mathrm{Ir(PPh_2Me)_4}]\mathrm{BF_4} \cdot \mathrm{C_6H_{12}}$

Ir(1)—H(116)	3.26 Å	H(126)—H(422)	3.49
Ir(1)—H(212)	3.31	H(216)—H(412)	2.94
Ir(1)—H(316)	3.13	H(226)—H(312)	3.54
Ir(1)—H(426)	3.10	H(315)—H(415)	3.05
Ir(2)—H(522)	3.12	H(316)—H(426)	2.31
Ir(2)—H(622)	3.26	H(322)—H(416)	3.03
C(101)—H(426)	3.19	H(323)—H(425)	3.06
C(201)—H(316)	3.16	H(512)—H(626′)	2.95
C(601)—H(522)	3.16	H(515)—H(523′)	3.03
H(115)—H(223)	3.31	H(516)—H(516′)	3.04
H(116)—H(212)	2.71	H(522)—H(522′)	2.31
H(116)—H(222)	2.42	H(526)—H(612)	3.51
H(122)—H(212)	2.40	H(615)—H(623′)	3.30
H(123)—H(213)	3.33	H(616)—H(622′)	2.37
		H(622)—H(622′)	2.67

TABLE 10

HYDROGEN INTERACTIONS (Å) FOR CATIONS

$[Rh(DPPE)_2]^+$			$[Ir(PPh_2Me)_4]^+$	
M-H	Rh—H(6)	3.04	Ir(1)—H	3.10-3.31
	Rh—H(14)	3.20	Ir(2)—H	3.12-3.26
	Rh—H(48)	3.24		
	Rh—H(26)	2.94		
'cis' H H	H(6)—H(36)	2.50	H(116)—H(222)	2.42
	H(6)—H(48)	3.03	H(122)—H(212)	2.48
	H(8)—H(26)	2.67	H(316)—H(416)	2.31
	H(12)—H(32)	3.22	H(322)—H(426)	2.31
	H(14)—H(26)	2.58	H(516)—H(522')	2.31
	H(14)—H(38)	2.63	H(616)—H(622')	2.37
'trans' H-H	H(6)—H(24)	4.49	H(116)—H(212)	2.71
	H(8)—H(14)	4.24	H(122)—H(222)	3.62
	H(26)—H(38)	4.01	H(316)—H(426)	3.30
	H(36)—H(48)	4.59	H(322)—H(416)	3.03
			H(516)—H(516')	3.04
			H(522)—H(522')	3.37
			H(616)—H(616')	3.61
			H(622)—H(622')	2.67

and it seems unlikely that the approach of these ligands would be any less hindered than that of molecular oxygen or carbon monoxide. Thus in spite of its simplicity the explanation that the reactivity of this cation is purely steric in origin does have difficulties.

Another consideration is that the theoretical adduct with oxygen, $[IrO_2(PPh_2Me)_4]^+$, may be so sterically strained as to favour elimination of the oxygen molecule. The crystal structure of $[Ir(O_2)(DPPE)_2]PF_6$ shows that these ligands can be associated in an approximately octahedral geometry with little apparent strain. It is possible, however, especially in view of the crowding effects found in the compound, that four methyldiphenylphosphine ligands cannot occupy four adjacent positions of an octahedron (assuming the oxygen would occupy two *cis* sites.) The only known complex having this geometry [14] is *cis*-$[IrH_2(PPh_2Me)_4]^+$ but here the two additional ligands are very small and may allow the phosphine ligands to occupy more space than would oxygen and thus decrease the non-bonding contacts. However, since the hydrogen is bonded as individual hydrogen atoms with a minimum separation of approximately 1.9 Å whereas oxygen coordinates as dioxygen, the separation of the latter atoms would probably be much less at about 1.5 Å. Thus the volume occupied by molecular oxygen would probably not be much more than that of two individual hydride atoms. Also pertinent to this argument is the observation that $[Ir(PPh_2Me)_4]^+$ does not add carbon monoxide. Here the product would presumably be the five coordinate cation $[Ir(CO)(PPh_2Me)_4]^+$ analogous to $[Ir(CO)(DPPE)_2]^+$ [38] and $[Ir(CO)(PPhMe_2)_4]^+$ [39]. It thus seems unlikely that a purely steric argument could account for this difference since the $[Ir(PPh_2Me)_4]^+$ forms stable addition products with HCl and Cl_2, ligands of approximately the same size as carbon monoxide.

A third and perhaps more plausible argument lies in the observation that the two ligands which do not form adducts with $[Ir(PPh_2Me)_4]^+$, namely O_2 and CO, both require considerable π-bonding with the iridium atom. The dihedral angles between planes containing the iridium atom and two *cis* phosphorus atoms are 40°, showing that the stereochemistry of the phosphorus arrangement around the iridium is almost as tetrahedral as it is planar. In this very distorted state the appropriate *d*-orbitals which are necessary for back-bonding to carbon monoxide and molecular oxygen may not be available for this purpose, since they are now just the orbitals required for bonding to these tetrahedrally disposed donors.

As a result of the tetrahedral distortion the *ortho*-hydrogens of the phenyl groups have been brought closer to the iridium than they would otherwise be (see Table 9). It is thus possible that they are interacting with the metal atom and also competing with the incoming ligands in the formation of π-bonds. These iridium-to-hydrogen distances range from 3.1-3.3 Å (approximately the sum of the van der Waals radii), however, so it is not obvious that the hydrogen atoms would offer serious impediment to carbon monoxide or molecular oxygen. We incline to the view, therefore, that the steric factors in the cation which account for the partially tetrahedral stereochemistry about the iridium atom have the chemical consequence of interfering with the ability of the metal to bind ligands such as O_2 and CO. A composite steric and electronic argument is thus needed to explain the reaction anomalies associated with $[Ir(PPh_2Me)_4]^+$.

Finally we note that the NMR spectrum [14] of $[Ir(PPh_2Me)_4]^+$ shows that the methyl protons are shifted to a value of τ 9.67, considerably higher than in $[Ir(CO)(PPh_2Me)_3]^+$ (τ 8.1 ppm) and that the possible reasons for this, namely: *(1)*, that there is excellent back-bonding between the iridium and phosphorus atoms; *(2)*, that rapid reversible proton transfer is taking place and *(3)*, that the methyl group may be close to the plane of a phenyl ring, can now be assessed in the light of the structural data. Thus the last reason now seems improbable since the crystal structure clearly shows that the methyl carbon atoms are far removed from the plane of phenyl groups. Proton transfer also seems unlikely since the methyl carbon atoms are similarly far removed from the iridium atom, the distortion of the complex shifting the methyl groups from the metal centre. It is not so easy to judge the remaining possibility, namely the extent of Ir—P double-bonding, because of their unusual geometry. However, they do seem to be significantly shorter than the majority of those found in other complexes (see Table 6) and this explanation is therefore likely to be the correct one and, incidentally, to be in line with our main conclusion concerning the reaction anomalies.

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