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The Structures of the *fac* and *mer* Isomers of Trichlorotris[dimethyl(phenyl)phosphine]iridium(III)

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Abstract

The structure of the *facial* isomer of trichlorotris[dimethyl(phenyl)phosphine]iridium(III) has been determined, and that of the *meridional* isomer has been redetermined. *fac*-$[Ir^{III}Cl_3(PMe_2Ph)_3]$ (1) crystallizes in space group *Ia* with $a = 16{\cdot}198$ (2), $b = 14{\cdot}923$ (2), $c = 22{\cdot}024$ (2) Å, $\beta = 96{\cdot}37$ (2)°, $Z = 8$. *mer*-$[Ir^{III}Cl_3(PMe_2Ph)_3]$ (2) crystallizes in space group $P2_1/n$ with $a = 10{\cdot}814$ (1), $b = 38{\cdot}894$ (3), $c = 13{\cdot}663$ (1) Å, $\beta = 107{\cdot}15$ (1)°, $Z = 8$. The structures were refined to $R = 0{\cdot}025$ [(1), 5471 independent reflections] and 0·031 [(2), 12 556 independent reflections]. Metal–ligand distances in (1) are Ir–Cl 2·456 (2)–2·468 (2) Å (*trans* to P) and Ir–P 2·285 (2)–2·295 (2) Å (*trans* to Cl). Metal–ligand distances in (2) do not differ significantly from those reported earlier but are more precise and reveal the existence of small differences between chemically equivalent bonds due to inequivalence of intramolecular non-bonding interactions. Values from this experiment are: Ir–Cl 2·434 (1)–2·439 (1) Å (*trans* to P) and 2·359 (1)–2·368 (1) Å (*trans* to Cl), Ir–P 2·278 (1)–2·282 (1) Å (*trans* to Cl) and 2·363 (1)–2·384 (1) Å (*trans* to P).

Introduction

Recently, we have carried out a series of X-ray analyses (and in some cases neutron analyses) on the series of complexes $L_3H_{(3-n)}Cl_nIr^{III}$ (L = PMe_2Ph, $n = 0,1,2,3$). Clearly, metal–ligand bond lengths in such a series are not only a function of the primary ligand type (Cl, H, L). Other determinants include the isomeric arrangement of the ligands (*cis*, *trans*, *mer*, *fac*), the differing steric requirements of differing substituents (Cl or H), and differing bond compression and angle deformations due to changes in non-bonding interactions to the methyl and phenyl substituents of the phosphine ligands (as the PMe_2Ph configurations alter). The present series of experiments are intended to

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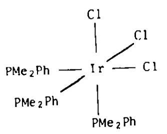
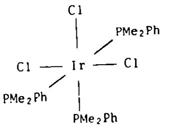
provide a more detailed insight into the relative importance of such effects on molecular stereochemistry.

Complexes (1) to (7) are relatively stable isolable solids (Jenkins & Shaw, 1965, 1966; Brookes, Masters & Shaw, 1971) whereas the remaining three (possible) members of the series appear to be unstable with respect to their other isomer(s). An X-ray diffraction study of (7) has been carried out by Bau (1978) and some details of the structure of (2) have been communicated (Aslanov, Mason, Wheeler & Whimp, 1970). In this paper we report the structures of both *fac*-[Ir^{III}Cl$_3$(PMe$_2$Ph)$_3$] (1) and *mer*-[Ir^{III}Cl$_3$(PMe$_2$Ph)$_3$] (2).


(1)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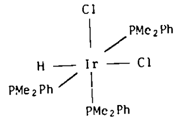
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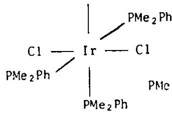
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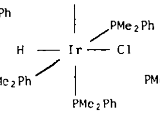
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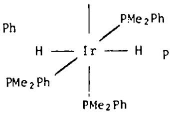
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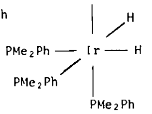
(7)

Experimental

mer-[Ir^{III}Cl$_3$(PMe$_2$Ph)$_3$] (2) was prepared according to literature methods and satisfactory single crystals were grown from benzene/methanol solutions. Although the *fac* isomer (1) may be prepared by the photoisomerization of (2) in benzene solution, it is insoluble in all common solvents and could not be recrystallized. However, good-quality single crystals of (1) could be obtained by allowing a solution of (4) in chloroform to stand for a few days.

Collection and reduction of X-ray intensities

Approximate cell dimensions were obtained, for crystals of each complex, from Weissenberg and precession photographs. Photographs of (1) exhibit $2/m$ diffraction symmetry and systematic absences (hkl, $h + k + l = 2n + 1$; $h0l$, $h = 2n + 1$, $l = 2n + 1$) consistent with either of the non-standard monoclinic space groups Ia or $I2/a$. Subsequent solution and refinement of the structure confirmed the noncentrosymmetric alternative Ia. For (2) the diffraction symmetry ($2/m$) and systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) uniquely define the monoclinic space group $P2_1/n$. In both instances densities (measured by flotation) were consistent with $Z = 8$.

Intensities were collected on a Picker FACS-1 diffractometer with crystal-monochromated Mo $K\bar{\alpha}$ radiation. Crystals were mounted with Araldite on quartz fibers. Cell dimensions and crystal-orientation matrices were determined by least-squares analysis of the setting angles, 2θ, ω, χ and φ, for twelve centered high-angle reflections [$2\theta > 50°$, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}70926$ Å]. E.s.d.'s in the cell dimensions derive directly from the least-squares analyses.

Crystal data

(1) *fac*-[Ir{P(CH$_3$)$_2$(C$_6$H$_5$)}$_3$Cl$_3$], $M_r = 713{\cdot}03$, monoclinic, space group Ia (non-standard setting of Cc); $a = 16{\cdot}198$ (2), $b = 14{\cdot}923$ (2), $c = 22{\cdot}024$ (2) Å, $\beta = 96{\cdot}37$ (2)°, $V_c = 5290{\cdot}8$ Å^3, $\rho_o = 1{\cdot}79$ (1), $\rho_c = 1{\cdot}79$ Mg m^{-3}, $Z = 8$, $F(000) = 2800$, $\mu(\text{Mo } K\alpha) = 5{\cdot}53$ mm^{-1}, graphite monochromator, $\bar{\lambda} = 0{\cdot}7107$ Å, $T = 294{\cdot}7 \pm 1$K.

(2) *mer*-[Ir{P(CH$_3$)$_2$(C$_6$H$_5$)}$_3$Cl$_3$], $M_r = 713{\cdot}03$, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$); $a = 10{\cdot}814$ (1), $b = 38{\cdot}894$ (3), $c = 13{\cdot}663$ (1) Å, $\beta = 107{\cdot}15$ (1)°, $V_c = 5491{\cdot}1$ Å^3, $\rho_o = 1{\cdot}72$ (1), $\rho_c = 1{\cdot}72$ Mg m^{-3}, $Z = 8$, $F(000) = 2800$, $\mu(\text{Mo } K\alpha) = 5{\cdot}35$ mm^{-1}, graphite monochromator, $\bar{\lambda} = 0{\cdot}7107$ Å, $T = 294{\cdot}7 \pm 1$K.

Data-recording procedures and algorithms used to reduce reflection intensities to $|F_o|$ and $\sigma(F_o)$ have been described (Ferguson, Mau & Whimp, 1979). Relevant details have been tabulated and included in the supplementary material.*

During data collection, the intensities of three standard reflections were monitored at regular intervals; for (1) a moderate (<9%), time-dependent, isotropic loss of intensity was observed and the intensities were corrected accordingly. Data for both complexes were corrected for absorption (de Meulenaer & Tompa, 1965). Data with $I < 3\sigma(I)$, and with uneven backgrounds ($\Delta B > 10\sigma$), were discarded and equivalent reflections averaged. Statistical R factors [$R_s = \sum\sigma_s(F_o)/\sum|F_o|$, where $\sigma_s(F_o) = \sigma(I)\,(\text{Lp})^{-1}/2|F_o|$ is the error contribution to $|F_o|$ from counting statistics alone] for the terminal data sets are 0·014 [(1), 5471 unique reflections] and 0·019 [(2), 12 556 unique reflections].

Solution and refinement of the structures

Both structures were solved by Patterson and Fourier syntheses and refined initially by block-diagonal, and ultimately by full-matrix least-squares analysis. Atom parameters, unit-cell dimensions, and

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* Supplementary crystal data and data-collection details for (1) and (2), anisotropic thermal parameters, bond lengths and bond angles in the phenyl groups, atom deviations from selected best planes and observed and calculated structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35741 (68 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

reflection indices quoted throughout this paper refer everywhere to the non-standard settings. Equipoints for *Ia* are x, y, z; $x, -y, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$; and for $P2_1/n$ are x, y, z; $-x, -y, -z$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ and the transformation matrices relating *Ia* and $P2_1/n$ coordinates to those in the corresponding standard settings, *Cc* and $P2_1/c$, are $\mathbf{x}_{Cc} = \mathbf{M}\mathbf{x}_{Ia}$ (where $m_{11} = -1$, $m_{12} = 0$, $m_{13} = 0$, $m_{21} = 0$, $m_{22} = -1$, $m_{23} = 0$, $m_{31} = -1$, $m_{32} = 0$ and $m_{33} = 1$) and $\mathbf{x}_{P2_1/c} = \mathbf{M}\mathbf{x}_{P2_1/n}$ (where $m_{11} = -1$, $m_{12} = 0$, $m_{13} = 1$, $m_{21} = 0$, $m_{22} = -1$, $m_{23} = 0$, $m_{31} = 0$, $m_{32} = 0$ and $m_{33} = 1$). For $Z = 8$, crystals of each isomer contain two crystallographically independent molecules per asymmetric unit.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and for Ir, P and Cl both real and imaginary anomalous-scattering contributions were included in the scattering model. Difference syntheses, calculated after block-diagonal least-squares refinement of positional and anisotropic thermal parameters (and scale factor) for all non-hydrogen atoms, exhibited a series of maxima at sites where H atoms might be expected. H atom contributions were therefore included at positions computed from the molecular geometry and with isotropic thermal parameters equal to (the isotropic equivalent of) those of the atoms to which they were bound. A C—H length of 0·95 Å was assumed. The methyl H positions were optimized to be 120° apart on the basal circumference of a cone of semi-angle 70°33′. H atom parameters were not refined but were recomputed every other cycle. On the final full-matrix refinement cycle for each complex, calculated parameter shifts were uniformly < 0·4 of the corresponding e.s.d. For both complexes an extinction parameter was refined with Zachariasen's (1967) approximation. Terminal values were 0·40 (6) × 10^{-5} for (1) and 0·120 (7) × 10^{-6} for (2). No serious dependence of $w(|F_o|-|F_c|)^2$ on $|F_o|$ or on $\sin\theta/\lambda$ was observed for either structure. The final $R = 0{\cdot}025$, $R_w\{=[\sum w(|F_o| - |F_c|)^2/\sum |F_o|^2]^{1/2}\} = 0{\cdot}034$ for (1) (5471 reflections) and $R = 0{\cdot}031$, $R_w = 0{\cdot}045$ for (2) (12 556 reflections). *R* values for the enantiomer of (1) were $R = 0{\cdot}029$, $R_w = 0{\cdot}045$ (*cf.* 0·025 and 0·034 for the present model). The *R*-factor ratio is significant at the 99·5% confidence level (Hamilton, 1965).

For both complexes, final difference syntheses show several peaks and troughs with absolute values in the range 0·8 to 1·1 e $Å^{-3}$ and within 1·1 Å of the metal atom. Comparison of their spatial distribution about the two independent metal atoms in each complex confirms that they are essentially random features and do not reflect a systematic non-spherical deformation of the metal-atom valence-shell electron density. Terminal values of the standard error estimates for observations of unit weight {defined as $[\sum w(|F_o|-|F_c|)^2/(m-n)]^{\frac{1}{2}}$ with *m* the number of observations and *n* the number of

Table 1. *Final atomic coordinates, with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters* ($Å^2$) *for* (1)

	x	*y*	*z*	B_{eq}†
Ir(1)	0·00323 (13)	0·0	−0·00065 (9)	1·94
Ir(2)	0·50201 (13)	0·00000 (10)	0·24996 (9)	1·80
Cl(1)	0·15011 (15)	0·03371 (15)	0·03144 (12)	3·46
Cl(2)	0·02734 (15)	0·08902 (13)	−0·09147 (11)	3·38
Cl(3)	0·06116 (16)	−0·12273 (13)	−0·05770 (11)	3·53
Cl(4)	0·65048 (15)	−0·02089 (15)	0·28349 (12)	3·22
Cl(5)	0·53208 (15)	−0·09781 (13)	0·16487 (11)	3·12
Cl(6)	0·55263 (17)	0·11833 (12)	0·18550 (11)	3·31
P(1)	−0·12594 (15)	−0·02137 (11)	−0·05288 (11)	2·11
P(2)	0·00141 (15)	−0·10589 (11)	0·07421 (10)	2·15
P(3)	−0·02032 (14)	0·12706 (11)	0·05268 (11)	2·11
P(4)	0·37223 (16)	0·00627 (10)	0·19668 (12)	2·23
P(5)	0·48681 (15)	−0·12136 (11)	0·31106 (11)	2·38
P(6)	0·49357 (16)	0·11484 (11)	0·31765 (11)	2·28
C(1)	−0·2121 (4)	−0·0676 (4)	−0·0164 (3)	2·18
C(2)	−0·2331 (4)	−0·1576 (4)	−0·0225 (3)	2·76
C(3)	−0·2979 (4)	−0·1923 (4)	0·0075 (3)	3·38
C(4)	−0·3409 (4)	−0·1381 (5)	0·0417 (3)	3·76
C(5)	−0·3232 (4)	−0·0484 (5)	0·0471 (3)	3·36
C(6)	−0·2589 (4)	−0·0130 (4)	0·0175 (3)	3·06
C(7)	−0·1739 (4)	0·0786 (4)	−0·0878 (3)	3·11
C(8)	−0·1238 (4)	−0·0935 (4)	−0·1187 (3)	3·47
C(9)	−0·0554 (4)	−0·0892 (4)	0·1403 (2)	2·12
C(10)	−0·1408 (4)	−0·1059 (4)	0·1367 (3)	2·79
C(11)	−0·1837 (4)	−0·0924 (5)	0·1861 (3)	3·56
C(12)	−0·1447 (5)	−0·0611 (5)	0·2402 (3)	3·43
C(13)	−0·0579 (5)	−0·0456 (4)	0·2459 (3)	2·89
C(14)	−0·0145 (4)	−0·0600 (4)	0·1969 (3)	3·44
C(15)	−0·0381 (4)	−0·2145 (4)	0·0481 (3)	3·09
C(16)	0·1038 (4)	−0·1351 (5)	0·1102 (3)	3·22
C(17)	−0·1230 (3)	0·1566 (3)	0·0720 (3)	2·16
C(18)	−0·1728 (4)	0·2180 (4)	0·0380 (3)	2·61
C(19)	−0·2516 (4)	0·2385 (4)	0·0530 (3)	3·35
C(20)	−0·2815 (4)	0·1977 (4)	0·1022 (3)	3·49
C(21)	−0·2321 (4)	0·1379 (4)	0·1376 (3)	3·16
C(22)	−0·1531 (4)	0·1192 (4)	0·1232 (3)	2·73
C(23)	0·0090 (4)	0·2286 (4)	0·0158 (4)	3·66
C(24)	0·0398 (4)	0·1359 (4)	0·1266 (3)	3·06
C(25)	0·2834 (3)	0·0491 (4)	0·2306 (3)	2·37
C(26)	0·2547 (4)	0·1369 (4)	0·2196 (3)	3·07
C(27)	0·1865 (5)	0·1686 (5)	0·2478 (3)	3·90
C(28)	0·1470 (4)	0·1154 (5)	0·2844 (3)	3·94
C(29)	0·1716 (4)	0·0268 (6)	0·2946 (3)	3·55
C(30)	0·2392 (4)	−0·0050 (4)	0·2665 (3)	2·87
C(31)	0·3699 (4)	0·0718 (5)	0·1270 (3)	3·66
C(32)	0·3317 (4)	−0·1016 (4)	0·1675 (3)	3·48
C(33)	0·3861 (3)	−0·1533 (4)	0·3343 (3)	2·37
C(34)	0·3557 (4)	−0·1118 (4)	0·3825 (3)	3·06
C(35)	0·2774 (4)	−0·1350 (4)	0·3993 (3)	3·49
C(36)	0·2315 (4)	−0·2006 (5)	0·3687 (4)	3·78
C(37)	0·2626 (4)	−0·2448 (4)	0·3218 (4)	3·63
C(38)	0·3386 (4)	−0·2224 (4)	0·3044 (3)	3·20
C(39)	0·5496 (4)	−0·1162 (5)	0·3852 (3)	3·66
C(40)	0·5222 (4)	−0·2250 (4)	0·2803 (3)	3·37
C(41)	0·4358 (4)	0·1035 (4)	0·3837 (2)	2·50
C(42)	0·3515 (4)	0·1155 (4)	0·3784 (3)	3·05
C(43)	0·3064 (4)	0·1054 (4)	0·4286 (3)	3·51
C(44)	0·3474 (5)	0·0840 (5)	0·4853 (3)	3·94
C(45)	0·4326 (5)	0·0745 (5)	0·4916 (3)	3·87
C(46)	0·4772 (4)	0·0841 (4)	0·4415 (3)	3·08
C(47)	0·4489 (4)	0·2176 (4)	0·2839 (3)	3·51
C(48)	0·5939 (4)	0·1524 (4)	0·3508 (3)	3·53

† $B_{eq} = \frac{1}{3}\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

Table 2. *Final atomic coordinates, with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters* (Å^2) *for* (2)

	x	y	z	B_{eq}†
Ir(1)	0·256952 (15)	0·295597 (4)	0·259530 (12)	2·51
Ir(2)	0·317109 (16)	0·010566 (4)	0·214529 (11)	2·42
Cl(1)	0·38676 (14)	0·24542 (3)	0·28942 (11)	4·55
Cl(2)	0·11673 (11)	0·34359 (3)	0·23005 (9)	3·44
Cl(3)	0·07635 (13)	0·25702 (4)	0·18362 (11)	4·70
Cl(4)	0·34132 (14)	0·00836 (3)	0·39173 (8)	3·88
Cl(5)	0·28753 (16)	0·00869 (4)	0·03611 (8)	4·59
Cl(6)	0·14181 (13)	−0·03096 (4)	0·18673 (11)	4·53
P(1)	0·26494 (13)	0·30130 (4)	0·08935 (9)	3·45
P(2)	0·19793 (12)	0·28616 (3)	0·41173 (9)	3·16
P(3)	0·43809 (10)	0·32707 (3)	0·33341 (8)	2·81
P(4)	0·15394 (12)	0·05256 (3)	0·19929 (9)	3·30
P(5)	0·44365 (13)	−0·04061 (3)	0·23602 (8)	2·98
P(6)	0·48158 (12)	0·04898 (3)	0·23139 (9)	3·00
C(1)	0·3444 (5)	0·3376 (1)	0·0516 (3)	3·65
C(2)	0·4361 (5)	0·3346 (2)	−0·0013 (4)	4·91
C(3)	0·4853 (7)	0·3640 (3)	−0·0341 (5)	6·72
C(4)	0·4446 (7)	0·3962 (2)	−0·0157 (5)	6·86
C(5)	0·3548 (6)	0·3994 (2)	0·0354 (5)	5·53
C(6)	0·3048 (5)	0·3708 (2)	0·0680 (4)	4·25
C(7)	0·3283 (7)	0·2636 (2)	0·0431 (5)	6·27
C(8)	0·1062 (6)	0·3059 (2)	−0·0017 (4)	5·15
C(9)	0·2067 (5)	0·3485 (1)	0·5097 (4)	3·91
C(10)	0·2389 (7)	0·3719 (2)	0·5912 (5)	5·19
C(11)	0·3124 (7)	0·3606 (2)	0·6851 (5)	5·73
C(12)	0·3553 (7)	0·3270 (2)	0·6986 (4)	5·56
C(13)	0·3236 (5)	0·3044 (1)	0·6172 (4)	4·34
C(14)	0·2482 (4)	0·3150 (1)	0·5206 (3)	3·31
C(15)	0·0245 (5)	0·2877 (2)	0·3887 (4)	4·92
C(16)	0·2375 (6)	0·2441 (1)	0·4650 (4)	5·06
C(17)	0·5638 (4)	0·3288 (1)	0·2684 (3)	3·50
C(18)	0·6085 (5)	0·3594 (2)	0·2416 (4)	4·33
C(19)	0·7104 (6)	0·3599 (2)	0·1983 (4)	6·01
C(20)	0·7681 (6)	0·3288 (3)	0·1833 (5)	7·24
C(21)	0·7221 (6)	0·2993 (2)	0·2083 (5)	6·08
C(22)	0·6223 (5)	0·2987 (2)	0·2510 (4)	4·52
C(23)	0·4124 (5)	0·3716 (1)	0·3596 (4)	4·13
C(24)	0·5334 (5)	0·3106 (2)	0·4580 (4)	4·34
C(25)	0·2003 (5)	0·0941 (1)	0·2620 (4)	3·69
C(26)	0·2687 (5)	0·0947 (1)	0·3651 (4)	4·06
C(27)	0·3058 (6)	0·1256 (2)	0·4143 (5)	5·47
C(28)	0·2761 (7)	0·1559 (2)	0·3635 (7)	6·63
C(29)	0·2047 (7)	0·1556 (2)	0·2607 (6)	6·00
C(30)	0·1661 (6)	0·1247 (2)	0·2104 (5)	4·83
C(31)	0·0584 (6)	0·0615 (2)	0·0688 (5)	5·75
C(32)	0·0312 (6)	0·0394 (2)	0·2583 (5)	5·17
C(33)	0·6193 (5)	−0·0399 (1)	0·2707 (3)	3·19
C(34)	0·6895 (6)	−0·0316 (2)	0·3706 (4)	4·34
C(35)	0·8234 (6)	−0·0303 (2)	0·3972 (5)	5·53
C(36)	0·8882 (6)	−0·0367 (2)	0·3268 (6)	5·43
C(37)	0·8191 (6)	−0·0445 (2)	0·2283 (5)	5·08
C(38)	0·6869 (6)	−0·0466 (1)	0·1998 (4)	4·04
C(39)	0·3962 (6)	−0·0680 (1)	0·1238 (4)	4·90
C(40)	0·4175 (6)	−0·0675 (1)	0·3356 (4)	4·44
C(41)	0·4426 (5)	0·0919 (1)	0·1740 (4)	3·47
C(42)	0·4837 (6)	0·1217 (1)	0·2276 (5)	4·50
C(43)	0·4635 (7)	0·1539 (2)	0·1814 (6)	5·77
C(44)	0·3990 (7)	0·1556 (2)	0·0789 (7)	6·52
C(45)	0·3569 (7)	0·1259 (2)	0·0216 (5)	5·87
C(46)	0·3802 (6)	0·0944 (1)	0·0706 (4)	4·59
C(47)	0·5776 (6)	0·0575 (2)	0·3627 (4)	5·10
C(48)	0·6037 (6)	0·0367 (1)	0·1701 (5)	4·85

† $B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

parameters} were 1·47 for (1) and 1·49 for (2) respectively.

Table 1 lists final atomic coordinates for (1), whilst those for (2) are listed in Table 2. H atom coordinates and anisotropic thermal parameters for the non-hydrogen atoms are contained in the supplementary material.*

Computer programs are part of the *ANUCRYS* package implemented on the Univac 1100/42 computer of the Australian National University Computer Services Centre by Drs P. O. Whimp and D. Taylor (Ferguson *et al.*, 1979). The molecular diagrams were produced with *ORTEP* (Johnson, 1965).

Results and description of the structures

For each complex, the asymmetric unit contains two discrete molecules separated by normal van der Waals contacts. For (1), the two independent molecules are nearly identical. Each molecule exhibits approximate C_3 symmetry, the principal deviations from exact C_3 symmetry resulting from differing relative orientations of the methyl groups about the P—C bonds. The stereochemistry and atom nomenclature is shown in Fig. 1(*a*) and the approximate C_3 symmetry is illustrated more clearly in Fig. 1(*b*). For (2), the two

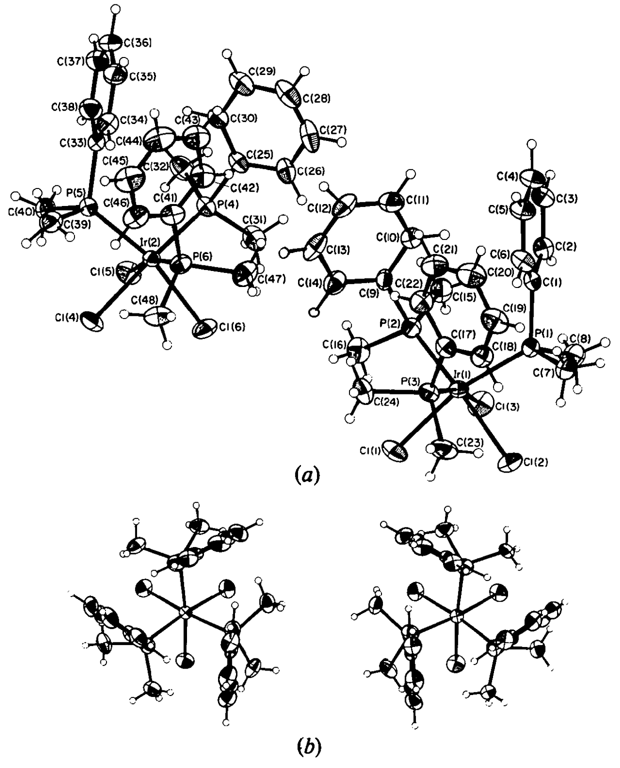

Fig. 1. (*a*) Molecular geometry and atom numbering in the two independently determined molecules of (1). Thermal ellipsoids are scaled to 50% probability. (*b*) View along the approximate C_3 axis of each molecule.

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* See deposition footnote.

independent molecules again exhibit quite similar stereochemical arrangements of the ligands, but the match is poorer than for (1). Neither molecule possesses virtual symmetry in excess of C_1 and there is a difference of some few degrees in the angular orientation of those phosphine ligands which are not involved in the face-to-face phenyl contacts. The relationship is illustrated in Fig. 2. The packing is illustrated in the stereopairs of Figs. 3 (1) and 4 (2), and important bond lengths and angles are listed in Tables 3 (1) and 4 (2). Bond lengths and angles in the phenyl groups of the phosphine ligands are contained in the supplementary material.* The e.s.d.'s given in parentheses in Tables 1 to 4 derive in the usual way from inversion of the least-squares matrix and might be expected to be underestimates. Comparison of the experimental e.s.d.'s of formally equivalent bonds in the phenyl groups in each structure (C_{2v} symmetry assumed) with the theoretical estimate suggests that the latter is underestimated by a factor of 1·5 to 2. When discussing possible differences in bond lengths and angles, and for the purposes of applying one-parameter significance tests, the e.s.d.'s in Tables 3 and 4 are assumed to be underestimated by a factor of two. Standard error estimates quoted together with mean values refer throughout to the sampling estimate of the standard error of the mean ($\sigma(\bar{x}) = \{\sum (x - \bar{x})^2/[n(n-1)]\}^{1/2}$).

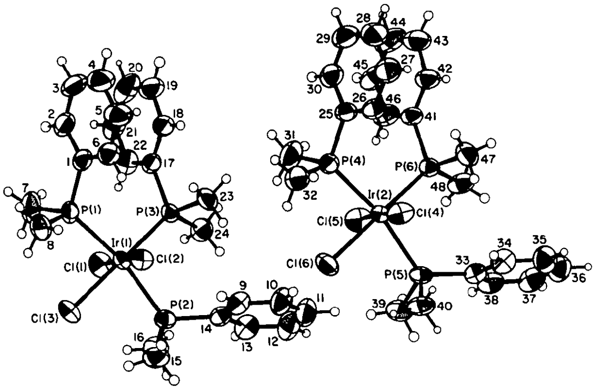

Fig. 2. Molecular geometry and atom numbering in the two independently determined molecules of (2). Thermal ellipsoids are scaled to 50% probability.

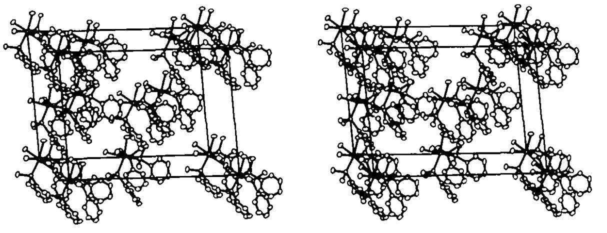

Fig. 3. Unit-cell packing for (1) viewed approximately along *b*.

Table 3. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses for* (1)

Ir(1)–Cl(1)	2·458 (2)	Ir(2)–Cl(6)	2·463 (2)
Ir(1)–Cl(2)	2·468 (2)	Ir(2)–Cl(4)	2·456 (2)
Ir(1)–Cl(3)	2·465 (2)	Ir(2)–Cl(5)	2·466 (2)
Ir(1)–P(1)	2·295 (2)	Ir(2)–P(5)	2·286 (2)
Ir(1)–P(2)	2·286 (2)	Ir(2)–P(4)	2·293 (2)
Ir(1)–P(3)	2·285 (2)	Ir(2)–P(6)	2·286 (2)
P(1)–C(1)	1·821 (6)	P(5)–C(33)	1·826 (6)
P(2)–C(9)	1·824 (6)	P(4)–C(25)	1·811 (6)
P(3)–C(17)	1·816 (6)	P(6)–C(41)	1·823 (6)
P(1)–C(7)	1·814 (6)	P(5)–C(39)	1·826 (7)
P(1)–C(8)	1·809 (6)	P(5)–C(40)	1·808 (6)
P(2)–C(15)	1·812 (6)	P(4)–C(32)	1·828 (6)
P(2)–C(16)	1·810 (6)	P(4)–C(31)	1·815 (6)
P(3)–C(23)	1·808 (6)	P(6)–C(48)	1·796 (6)
P(3)–C(24)	1·806 (6)	P(6)–C(47)	1·819 (6)
Cl(1)–Ir(1)–Cl(2)	83·55 (7)	Cl(6)–Ir(2)–Cl(4)	83·50 (7)
Cl(1)–Ir(1)–Cl(3)	83·54 (7)	Cl(6)–Ir(2)–Cl(5)	83·09 (7)
Cl(1)–Ir(1)–P(1)	166·43 (7)	Cl(6)–Ir(2)–P(5)	166·42 (8)
Cl(1)–Ir(1)–P(2)	91·35 (7)	Cl(6)–Ir(2)–P(4)	91·18 (7)
Cl(1)–Ir(1)–P(3)	83·90 (7)	Cl(6)–Ir(2)–P(6)	83·47 (6)
Cl(2)–Ir(1)–Cl(3)	83·30 (7)	Cl(4)–Ir(2)–Cl(5)	83·34 (7)
Cl(2)–Ir(1)–P(1)	83·46 (7)	Cl(4)–Ir(2)–P(5)	83·59 (7)
Cl(2)–Ir(1)–P(2)	166·48 (7)	Cl(4)–Ir(2)–P(4)	166·07 (7)
Cl(2)–Ir(1)–P(3)	91·17 (7)	Cl(4)–Ir(2)–P(6)	91·52 (8)
Cl(3)–Ir(1)–P(1)	91·08 (7)	Cl(5)–Ir(2)–P(5)	91·25 (7)
Cl(3)–Ir(1)–P(2)	83·69 (7)	Cl(5)–Ir(2)–P(4)	83·25 (7)
Cl(3)–Ir(1)–P(3)	166·77 (7)	Cl(5)–Ir(2)–P(6)	166·07 (6)
P(1)–Ir(1)–P(2)	100·45 (6)	P(5)–Ir(2)–P(4)	100·43 (6)
P(1)–Ir(1)–P(3)	100·26 (6)	P(5)–Ir(2)–P(6)	101·07 (8)
P(2)–Ir(1)–P(3)	100·75 (7)	P(4)–Ir(2)–P(6)	100·69 (6)
Ir(1)–P(1)–C(1)	122·1 (2)	Ir(2)–P(5)–C(33)	122·0 (2)
Ir(1)–P(2)–C(9)	121·9 (2)	Ir(2)–P(4)–C(25)	121·9 (2)
Ir(1)–P(3)–C(17)	122·1 (2)	Ir(2)–P(6)–C(41)	121·6 (2)
Ir(1)–P(1)–C(7)	115·0 (2)	Ir(2)–P(5)–C(39)	114·0 (2)
Ir(1)–P(1)–C(8)	112·7 (2)	Ir(2)–P(5)–C(40)	113·5 (2)
Ir(1)–P(2)–C(15)	115·0 (2)	Ir(2)–P(4)–C(32)	114·6 (2)
Ir(1)–P(2)–C(16)	113·4 (2)	Ir(2)–P(4)–C(31)	112·7 (2)
Ir(1)–P(3)–C(23)	113·4 (3)	Ir(2)–P(6)–C(48)	112·5 (2)
Ir(1)–P(3)–C(24)	114·8 (2)	Ir(2)–P(6)–C(47)	114·5 (2)
C(1)–P(1)–C(7)	100·7 (3)	C(33)–P(5)–C(39)	100·8 (3)
C(1)–P(1)–C(8)	102·3 (3)	C(33)–P(5)–C(40)	102·3 (3)
C(7)–P(1)–C(8)	101·3 (3)	C(39)–P(5)–C(40)	101·7 (3)
C(9)–P(2)–C(15)	100·6 (3)	C(25)–P(4)–C(32)	100·7 (3)
C(9)–P(2)–C(16)	101·7 (3)	C(25)–P(4)–C(31)	102·5 (3)
C(15)–P(2)–C(16)	101·4 (3)	C(32)–P(4)–C(31)	101·8 (3)
C(17)–P(3)–C(23)	101·3 (3)	C(41)–P(6)–C(48)	103·0 (3)
C(17)–P(3)–C(24)	100·8 (3)	C(41)–P(6)–C(47)	100·9 (3)
C(23)–P(3)–C(24)	101·6 (3)	C(48)–P(6)–C(47)	101·7 (3)
P(1)–C(1)–C(2)	121·0 (4)	P(5)–C(33)–C(38)	121·4 (5)
P(1)–C(1)–C(6)	120·4 (4)	P(5)–C(33)–C(34)	120·6 (5)
P(2)–C(9)–C(10)	120·9 (4)	P(4)–C(25)–C(30)	121·0 (4)
P(2)–C(9)–C(14)	121·1 (4)	P(4)–C(25)–C(26)	121·4 (5)
P(3)–C(17)–C(18)	121·8 (4)	P(6)–C(41)–C(46)	120·5 (5)
P(3)–C(17)–C(22)	120·3 (4)	P(6)–C(41)–C(42)	120·9 (5)

fac-[$Ir^{III}Cl_3(PMe_2Ph)_3$] (1)

On the above criteria, none of the six independently determined Ir–Cl distances differs significantly from the mean and, indeed, would not be expected to do so for approximately identical molecules with approximate C_3 symmetry. The mean Ir–Cl distance is

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* See deposition footnote.

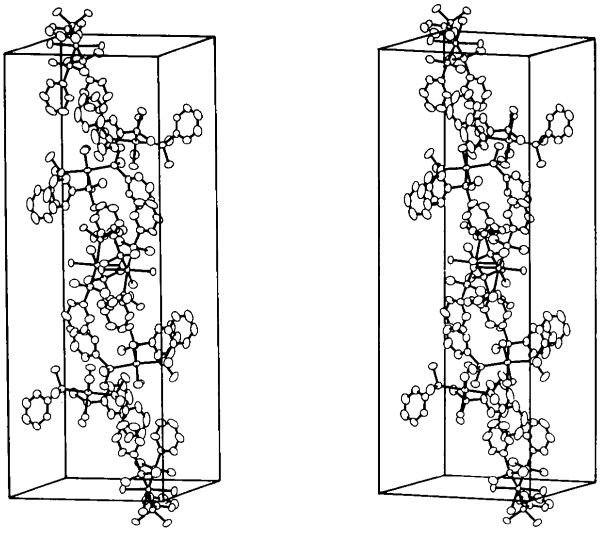

Fig. 4. Unit-cell packing for (2) viewed approximately along *a*.

Table 4. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses for* (2)

Ir(1)–Cl(1)	2·368 (1)	Ir(2)–Cl(5)	2·364 (1)
Ir(1)–Cl(2)	2·363 (1)	Ir(2)–Cl(4)	2·359 (1)
Ir(1)–Cl(3)	2·439 (1)	Ir(2)–Cl(6)	2·434 (1)
Ir(1)–P(1)	2·363 (1)	Ir(2)–P(4)	2·368 (1)
Ir(1)–P(2)	2·377 (1)	Ir(2)–P(5)	2·384 (1)
Ir(1)–P(3)	2·278 (1)	Ir(2)–P(6)	2·282 (1)
P(1)–C(1)	1·806 (5)	P(4)–C(25)	1·828 (5)
P(2)–C(14)	1·812 (5)	P(5)–C(33)	1·817 (5)
P(3)–C(17)	1·832 (5)	P(6)–C(41)	1·841 (5)
P(1)–C(7)	1·809 (7)	P(4)–C(31)	1·811 (6)
P(1)–C(8)	1·808 (6)	P(4)–C(32)	1·818 (6)
P(2)–C(15)	1·809 (6)	P(5)–C(40)	1·804 (5)
P(2)–C(16)	1·792 (6)	P(5)–C(39)	1·813 (5)
P(3)–C(23)	1·805 (5)	P(6)–C(47)	1·818 (6)
P(3)–C(24)	1·827 (5)	P(6)–C(48)	1·824 (6)

Cl(1)–Ir(1)–Cl(2)	176·55 (5)	Cl(5)–Ir(2)–Cl(4)	175·92 (5)
Cl(1)–Ir(1)–Cl(3)	85·75 (5)	Cl(5)–Ir(2)–Cl(6)	87·49 (5)
Cl(1)–Ir(1)–P(1)	93·17 (5)	Cl(5)–Ir(2)–P(4)	93·43 (5)
Cl(1)–Ir(1)–P(2)	91·16 (5)	Cl(5)–Ir(2)–P(5)	89·97 (5)
Cl(1)–Ir(1)–P(3)	88·74 (5)	Cl(5)–Ir(2)–P(6)	89·36 (5)
Cl(2)–Ir(1)–Cl(3)	91·17 (5)	Cl(4)–Ir(2)–Cl(6)	88·95 (5)
Cl(2)–Ir(1)–P(1)	88·05 (4)	Cl(4)–Ir(2)–P(4)	88·26 (4)
Cl(2)–Ir(1)–P(2)	86·95 (4)	Cl(4)–Ir(2)–P(5)	87·55 (4)
Cl(2)–Ir(1)–P(3)	94·34 (4)	Cl(4)–Ir(2)–P(6)	94·18 (5)
Cl(3)–Ir(1)–P(1)	84·04 (5)	Cl(6)–Ir(2)–P(4)	85·31 (5)
Cl(3)–Ir(1)–P(2)	83·63 (5)	Cl(6)–Ir(2)–P(5)	81·80 (5)
Cl(3)–Ir(1)–P(3)	174·49 (5)	Cl(6)–Ir(2)–P(6)	176·79 (4)
P(1)–Ir(1)–P(2)	166·59 (4)	P(4)–Ir(2)–P(5)	166·51 (4)
P(1)–Ir(1)–P(3)	96·29 (4)	P(4)–Ir(2)–P(6)	95·48 (5)
P(2)–Ir(1)–P(3)	96·49 (4)	P(5)–Ir(2)–P(6)	97·60 (5)
Ir(1)–P(1)–C(1)	120·9 (2)	Ir(2)–P(4)–C(25)	118·3 (2)
Ir(1)–P(2)–C(14)	122·0 (2)	Ir(2)–P(5)–C(33)	122·4 (2)
Ir(1)–P(3)–C(17)	117·9 (2)	Ir(2)–P(6)–C(41)	118·5 (2)
Ir(1)–P(1)–C(7)	113·3 (2)	Ir(2)–P(4)–C(31)	114·4 (2)
Ir(1)–P(1)–C(8)	112·6 (2)	Ir(2)–P(4)–C(32)	112·9 (2)
Ir(1)–P(2)–C(15)	112·0 (2)	Ir(2)–P(5)–C(40)	111·4 (2)
Ir(1)–P(2)–C(16)	113·8 (2)	Ir(2)–P(5)–C(39)	112·2 (2)
Ir(1)–P(3)–C(23)	116·2 (2)	Ir(2)–P(6)–C(47)	114·9 (2)
Ir(1)–P(3)–C(24)	113·5 (2)	Ir(2)–P(6)–C(48)	115·5 (2)
C(1)–P(1)–C(7)	105·8 (3)	C(25)–P(4)–C(31)	106·9 (3)
C(1)–P(1)–C(8)	99·3 (3)	C(25)–P(4)–C(32)	100·2 (3)
C(7)–P(1)–C(8)	102·7 (3)	C(31)–P(4)–C(32)	102·2 (3)
C(14)–P(2)–C(15)	99·6 (3)	C(33)–P(5)–C(40)	101·4 (2)
C(14)–P(2)–C(16)	104·7 (2)	C(33)–P(5)–C(39)	104·1 (3)
C(15)–P(2)–C(16)	102·2 (3)	C(40)–P(5)–C(39)	103·2 (3)
C(17)–P(3)–C(23)	104·0 (3)	C(41)–P(6)–C(47)	104·3 (3)
C(17)–P(3)–C(24)	99·7 (2)	C(41)–P(6)–C(48)	98·5 (2)
C(23)–P(3)–C(24)	103·2 (3)	C(47)–P(6)–C(48)	102·7 (3)
P(1)–C(1)–C(2)	123·6 (5)	P(4)–C(25)–C(30)	121·9 (4)
P(1)–C(1)–C(6)	118·9 (4)	P(4)–C(25)–C(26)	118·9 (4)
P(2)–C(14)–C(9)	119·3 (4)	P(5)–C(33)–C(34)	119·1 (4)
P(2)–C(14)–C(13)	123·1 (4)	P(5)–C(33)–C(38)	122·4 (4)
P(3)–C(17)–C(18)	122·0 (4)	P(6)–C(41)–C(42)	122·7 (4)
P(3)–C(17)–C(22)	119·7 (4)	P(6)–C(41)–C(46)	118·8 (4)

2·463 (2) Å. Correction for riding motion (Cl on Ir) increases this to 2·474 (2) Å. There is also evidence of some libration shortening towards the extremities of the phenyl groups, but distances and angles quoted in the tables have not been corrected for thermal motion. The mean Ir–P length is 2·289 (2) Å. There is no experimentally verifiable difference between the P–C(phenyl) and P–C(methyl) distances and the mean P–C length is 1·815 (2) Å. The agreement between equivalent quantities (not involving H atoms) in the two independent molecules is excellent. Mean Cl–Ir–Cl and P–Ir–P angles are 83·4 (1) and 100·6 (1)° respectively, the difference representing the greater steric bulk of the phosphine *vis à vis* the Cl ligands. The P–Ir–Cl angles fall into three groups: (i) where P is *trans* to Cl [166·4 (1)°]; (ii) where the two methyl groups of the phosphine are staggered with respect to the Cl atom [83·6 (1)°]; and (iii) where one methyl eclipses the Cl [91·3 (1)°] (Fig. 1*a*).

The Ir–P–C(phenyl) angles [mean 121·9 (1)°] are larger than the Ir–P–C(methyl) angles. The phenyl groups, all pointing towards the viewer in Fig. 1(*b*), approach each other fairly closely, the distance between the plane of one phenyl group and the closest H atom of a second group lying in the range 2·47 – 2·49 Å. The mean intermethyl angle at the P atoms is 101·6 (1)°. The Ir–P–C(methyl) and C(phenyl)–P–C(methyl) angles each fall into two (correlated) groups: large Ir–P–C [114·6 (1)°] and small C–P–C [100·7 (1)°] or small Ir–P–C [113·0 (2)°] and large C–P–C [102·2 (2)°]. The differences are small but significant at a 99% confidence limit. The reason is presumably because the phenyl group is more nearly eclipsed with respect to one of the two methyl groups (Fig. 1*b*). The phenyl groups are planar to within experimental error with the attached P atom within 0·07 Å from the plane. Results of best-plane calculations for the phenyl groups and other relevant molecular fragments are included in the supplementary material.*

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* See deposition footnote.

mer-[$Ir^{III}Cl_3(PMe_2Ph)_3$] (2)

Chemically equivalent Ir—Cl distances in the two molecules do not differ significantly from their mean values [2·366 (2) Å *trans* to Cl; 2·437 (2) Å *trans* to P]. The two Ir—P distances *trans* to Cl are also equivalent within experimental error [mean 2·280 (2) Å]. In contrast, the four chemically equivalent Ir—P (*trans* to PMe_2Ph) distances are geometrically equivalent only in pairs. The reason is clearly related to the intramolecular packing of the phosphine ligands. Substituents on the chemically unique P(3)/P(6) (Fig. 2) interact differently with those on P(1)/P(4) and on P(2)/P(5). The result is to differentiate between the metal—ligand distances Ir—P(1)/P(4) [mean 2·366 (2) Å] and Ir—P(2)/P(5) [mean 2·381 (3) Å].

The conformational difference between the two (independent) molecules, though larger than for (1), is nevertheless small, being restricted largely to relatively small differences in the P(2) and P(5) phosphine-group orientations. Seemingly the conformational difference results from small differences in the intermolecular non-bonded interactions to the two molecules. Although no resultant bond-length inequivalences can be identified, there are several highly significant differences [between molecules (I) and (II)] in the bond angles at the metal and at the P atoms. The angular differences at the metals are also reflected by the fact that the IrPPPCl coordination plane in (I) is slightly more tetrahedrally distorted than in (II) [best planes are tabulated in the supplementary material* but typically the atoms lie *ca* 0·10 Å from the best plane in (I) compared with *ca* 0·07 Å in (II)].

Again, no significant differences between P—C(methyl) and P—C(phenyl) distances can be identified [mean 1·815 (3) Å]. In contrast to what is observed for (1), the P—C—C(phenyl) angles are significantly deformed. The deformations arise because the phenyl group of each phosphine ligand is approximately eclipsed by a methyl group on that ligand. The larger angle is always to the eclipsed phenyl C atom and has a mean of 122·6 (3)°; the smaller angle, to the staggered phenyl C atom, averages 119·1 (2)°. The C(methyl)—P—C(phenyl) angles are similarly affected with a mean of 105·0 (5)° to the eclipsed methyls and 99·8 (4)° to the *gauche* groups. The C(methyl)—P—C(methyl) angle is 102·7 (2)°. As in (1) the Ir—P—C(phenyl) angles are uniformly greater (by *ca* 5–6°) than the Ir—P—C(methyl) angles, but the angular spread within each group is itself substantial (*ca* 4°). The phenyl groups are each planar to within experimental error and attached P atoms are all within 0·14 Å of the best planes. Plane equations and atom deviations are included in the supplementary material.*

Discussion

For both (1) and (2) the two independently determined molecules each occupy sites, and hence experience intermolecular (packing) force fields, of C_1 symmetry. The force field is not only asymmetric at each molecular site but also differs in magnitude. Thus in (1) the two independent molecules exhibit near C_3 symmetry, suggesting that there is a virtually indistinguishable, stable, free-molecule configuration possessing exact C_3 symmetry, and that the deformations observed in the crystal reflect the asymmetry of the packing forces. The deviations from C_3 symmetry and inequivalences between molecules, both, are restricted largely to small differences in the relative orientations of the methyl groups. There are no significant differences between bond lengths and angles not involving H atoms in the two molecules. In this instance, therefore, it is clear that the non-hydrogen skeleton is not easily deformed and, in consequence, that its geometry approximates closely to that of the free molecule in its ground state.

For (2) the situation is rather different. Again, the two molecules have quite similar conformations, but here the inequivalence of the packing forces (which they experience) serves to generate small differences in the orientation of one phosphine ligand. Once more, there are no large differences between equivalent (non-hydrogen) bond lengths; however, in this instance there are highly significant differences in equivalent bond angles between the two molecules. This invites the inference that where the ligand configuration is suitably open, and hence deformable, asymmetric intermolecular (packing) forces will generally result in distributed angular strain (*vis à vis* the free molecule) but that bond-length compression is likely to be about or below the detectable limit. In contrast, at least in the present instance, asymmetry of the intramolecular (as distinct from the intermolecular) forces results in both bond-angle *and* bond-length deformations. Thus, the chemically equivalent, mutually *trans* Ir—P distances in molecules of (2) differ by *ca* 0·015 Å ($\Delta/\sigma \simeq 5$) because of the differing intramolecular non-bonded contacts experienced by the phosphine ligands in the solid state. [Note, however, that NMR spectra indicate the phosphine to be equivalent in solution (Jenkins & Shaw, 1966).]

The metal—ligand bond distances in (2) are within experimental error of those reported by Aslanov *et al.* (1970), and are compatible with those in (1) in the sense that they reflect, at least qualitatively, the larger *trans* influence of the phosphine ligand *vis à vis* Cl. However, there is a substantial difference between the Ir—Cl (*trans* to PMe_2Ph) bond lengths (*ca* 0·026 Å, Δ/σ ~9) in (1) and (2). There is also a much smaller but apparently significant difference between the Ir—P (*trans* to Cl) distances (*ca* 0·009 Å, Δ/σ ~4). We

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* See deposition footnote.

suggest that these differences [*between* (1) and (2)] are of similar origin to the Ir—P (*trans* to P) differences in (2), *viz* asymmetric intramolecular non-bonding interactions.

In view of these observations a wider comparison of Ir—P (or Ir—Cl) lengths, with those in other Ir^{III} complexes containing different phosphine ligands, seems of doubtful value. However, we note that in seven structures completed to date, in the series $(PMe_2Ph)_3H_{(3-n)}Cl_nIr^{III}$, the Ir—P (*trans* to P) distances vary by up to about 0·1 Å and the Ir—Cl (*trans* to Cl) distances vary by about half that amount. For triphenylphosphine–Ir^{III} complexes, the range of Ir—P (*trans* to P) is a little larger, *ca* 2·29 to 2·42 Å. For example: 2·286 in *mer*-$[Ir(PPh_3)_3H_3]$ (Clark, Skelton & Waters, 1975), 2·40 in $[Ir(PPh_3)_3(CO)H_2]^+$ (Bird, Harrod & Than, 1974), 2·340 in $[Ir(PPh_3)_2$(phenylazophenyl-2-C,N′)HCl] (van Baar, Meij & Olie, 1974), 2·35 in $[Ir(PPh_3)_2(NO_3)_2]$ (Cash, Harris, Nyburg & Pickard, 1975), 2·37 in $[Ir(PPh_3)_2(\sigma\text{-}N_2C_6H_4NO_2)(CO)Cl_2]$ (Cobbledick, Einstein, Farrell, Gilchrist & Sutton, 1977), 2·370 in $[Ir(PPh_3)_2(NH{:}NC_6H_3OMe)Cl_2]$ (Bellon, Caglio, Manassero & Sansoni, 1974), 2·379 in $[Ir(PPh_3)_2(C{\equiv}CR)(CH{=}CHR)(CO)Cl]$ ($R = B_{10}C_2H_{11}$, Callahan, Strouse, Layten & Hawthorne, 1973), 2·38 in $[Ir(PPh_3)_2(NH{:}NC_6H_3CF_3)(CO)F]^+$ (Carroll, Cobbledick, Einstein, Farrell, Sutton & Vogel, 1977), 2·386 in $[Ir(PPh_3)_2(NH{:}NC_6H_3F)(CO)Cl]^+$ (Einstein & Sutton, 1973), 2·392 in $[Ir(PPh_3)_2(NH{:}NC_6H_3F)(CO)F]^+$ (Angoletta, Bellon, Manassero & Sansoni, 1977), 2·40 in $[Ir(PPh_3)_2(CO)ClBr(HgBr)]_2$ and 2·383 in $[Ir(PPh_3)_2(CO)Cl_2(HgCl)]_2$ (Brotherton, Raston, White & Wild, 1976), 2·412 in $[Ir(PPh_3)_2(CO)(CHF_2)(OCOCF_2Cl)Cl]$ (Schultz, Khare, Meyer & Eisenberg, 1974), 2·418 in $[Ir(PPh_3)_2(CO)(CN)(NCS)Cl]$ (Ibers, Hamilton & Baddley, 1973) and 2·420 Å in $[Ir(PPh_3)_2(CHF_2)(CO)Cl_2]$ (Schultz, McArdle, Khare & Eisenberg, 1974).

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