X-Ray Crystal and Molecular Structure of Dichloro-(4-methoxyphenyldi-imide-C^2,N')bis(triphenylphosphine)iridium–Chloroform (1/1)

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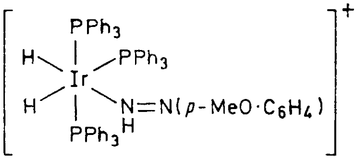
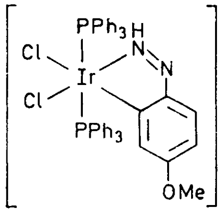
Crystals of the title compound are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell of dimensions: $a = 12{\cdot}55(2)$, $b = 12{\cdot}38(2)$, $c = 15{\cdot}55(2)$ Å, $\alpha = 103{\cdot}07(7)$, $\beta = 91{\cdot}73(7)$, $\gamma = 116{\cdot}28(7)°$. 3699 Independent structure factor moduli were measured by counter methods, and the structure refined by full-matrix least squares to R 0·035. The metal atom, which displays a distorted octahedral co-ordination, is bonded to the terminal nitrogen atom, to C(2) of the aryldi-imide moiety [Ir–N 1·990(7), Ir–C 2·011(8)Å] and to two chloro-ligands [Ir–Cl 2·393(2) and 2·493(2) Å, the bond being *trans* to C(2) of the aryldi-imide group], and to two mutually *trans* phosphine ligands [Ir–P 2·376(2) and 2·364(2) Å]. There is evidence for the protonation of the nitrogen atom bonded to Ir.

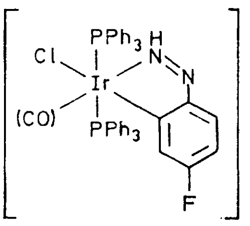
The insertion of aryldiazonium cations into the co-ordination sphere of transition-metal atoms and the reactivity of the resulting complexes are being extensively investigated;[1-6] this chemistry is relevant to current theories on nitrogen fixation.[2,7,8]



(1)



(2)



(3)

The reaction of $IrH_3(PPh_3)_3$ with *p*-substituted aryldiazonium cations has been described.[5,9] When the reaction product, *e.g.* a salt of cation (1), is dissolved in chloroform, or in chloroform–ethanol, and these solutions set aside for several days at room temperature, orange crystals separate, from both systems, which do not display any Ir–H stretching band. Since these species are insoluble in most solvents, no n.m.r. spectra have been recorded.

We report analytical and structural results for the species (2) obtained from solutions of (1) in chloroform. Preliminary determinations on the species obtained similarly from chloroform–ethanol show it to be different from the one described here. We intend to establish the influence of a variety of ligands on the behaviour of the di-imide moiety.

EXPERIMENTAL

Analytical and Spectral Data.—$C_{43}H_{37}Cl_2IrN_2OP_2,CHCl_3$, $M = 1042{\cdot}2$. Calc.: C, 50·6; H, 3·65; Cl, 17·0; N, 2·68; O, 1·53. Found: C, 50·2; H, 3·70; Cl, 16·85; N, 2·65; O, 1·55%. I.r. spectrum (cm^{-1}) recorded on a Perkin-Elmer 621, Nujol mull: ν(N–H) 3350w; other bands 1582s, 1533sh, 1480s, 1432s, 1331w, 1270mw, 1233s, 1183w, 1161w, 1125mw, 1091s, 1060s, 1030mw, 1015w, 881sh, 876s, 843s, 820mw, 760s, 753s, 745s, 726s, 706s, 692sh, and 665w.

Crystal Data.—Orange crystals with oblique habit, $a = 12{\cdot}55(2)$, $b = 12{\cdot}38(2)$, $c = 15{\cdot}55(2)$ Å, $\alpha = 103{\cdot}07(7)$, $\beta = 91{\cdot}73(7)$, $\gamma = 116{\cdot}28(7)°$, $U = 2087$ Å^3, $D_c = 1{\cdot}66$, $Z = 2$, $D_m = 1{\cdot}67$ g cm^{-3} (flotation). Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 38·5 cm^{-1}. Unit cell constants, measured on precession films, were refined on a single-crystal diffractometer with Mo-K_α radiation.

Intensity measurements were made on a PAILRED linear diffractometer with a molybdenum tube and a graphite single-crystal monochromator. The crystal was aligned with c parallel to the ω-axis of the instrument and the reflections were collected within the following limiting angles: $3° \leqslant \theta \leqslant 23°$, $0° \leqslant \mu \leqslant 20°$ in 16 different levels ($hk0$—15). Very few significant reflections were present outside these limits. Each measurement was made by an ω-scan (moving crystal, stationary counter) within an angular interval (Δω) varying, as a function of Υ and of μ, between 1·6 and 2·6°, at a scan rate of 1° min^{-1}. Two backgrounds, measured at the extreme points of the scan range, took a time approximately equal to that spent in the ω-scan. Data were corrected for the Lorentz and polarisation effects (the latter including the effect of the monochromator).[10] An absorption correction was made with the method described in refs. 11 and 12. The crystal, having approximate dimensions 0·14 × 0·24 × 0·18 mm, was sampled in 512 points; the resulting transmission factors were in the range 0·51—0·65.

After rejecting the reflections having $\sigma(I)/I \geqslant 0{\cdot}25$ a final set of 3699 structure amplitudes was obtained. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares. The six phenyl rings of the phosphine ligands were treated as rigid bodies of D_{6h} symmetry (C–C 1·392 Å), each carbon atom being given an independent thermal parameter. All

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[1] R. B. King and M. B. Bisnette, *J. Amer. Chem. Soc.*, 1964, **86**, 5694.

[2] G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 2133.

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[4] M. C. Baird and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 865.

[5] J. Toniolo and R. E. Eisenberg, *Chem. Comm.*, 1971, 455.

[6] S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc.* (*A*), 1971, 3441.

[7] F. W. Einstein, A. B. Gilchrist, G. W. Reiner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1971, **93**, 1826.

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[9] M. Angoletta and G. Caglio, *Gazzetta*, 1972, **102**, 462.

[10] W. L. Bond, *Acta Cryst.*, 1959, **12**, 375.

[11] W. R. Levy and H. A. Busing, *Acta Cryst.*, 1957, **10**, 180.

[12] G. Ciani, M. Manassero, and M. Sansoni, *J. Appl. Cryst.*, 1971, **4**, 173.

hydrogen atoms were geometrically placed in the ideal position (C–C–H 120°, C–H 1·08 Å), and never directly refined. Their co-ordinates were recomputed after each cycle of refinement. The thermal parameter assigned to each hydrogen atom was that of the corresponding carbon atom. Observations were weighted according to the formula $w = 1/(A + BF_o + CF_o^2)$, the final values of A, B, and C being 24·6, −0·54, and 0·0042, chosen to give a relatively constant distribution of $w(F_o - |F_c|)^2$ as a function of F_o and sin θ. In the final least-squares cycles all atoms, except carbon atoms of the phosphine groups and the chloroform molecule, were assigned anisotropic thermal parameters. The refinement was terminated when no parameter shift was $>\frac{1}{3}\sigma$. Final R was 0·0353 and R' 0·0436 where $R' = [\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

Table 1

Positional and thermal parameters (all $\times 10^9$) of non-group atoms

Atom	x	y	z	B/Å^2 or β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Ir	3965(0)	4461(0)	2223(0)	33(0)	31(0)	7(0)	40(0)	12(0)	27(0)
Cl(1)	5185(1)	4818(1)	3573(1)	49(1)	52(2)	−7(2)	68(1)	13(2)	33(1)
Cl(2)	5653(1)	5160(2)	1340(1)	58(1)	62(2)	34(2)	71(1)	34(2)	42(1)
Cl(3) *	9084(4)	6874(4)	899(3)	159(3)	224(5)	41(5)	388(4)	422(4)	202(2)
Cl(4) *	9628(3)	4976(4)	1150(3)	162(3)	129(5)	77(5)	153(3)	2(6)	129(3)
Cl(5) *	9326(4)	6513(5)	2617(3)	308(5)	428(7)	8(6)	367(6)	−35(6)	61(2)
P(1)	4164(1)	6507(1)	2756(1)	49(1)	45(2)	9(2)	48(1)	10(2)	30(1)
P(2)	3730(1)	2403(1)	1786(1)	41(1)	38(2)	11(2)	41(1)	14(2)	31(1)
N(1)	2761(5)	4084(5)	1192(4)	51(4)	56(6)	5(6)	63(4)	25(6)	32(3)
N(2)	1644(5)	3630(5)	1244(4)	56(4)	46(7)	−11(6)	55(4)	10(6)	30(3)
C(1)	1439(6)	3497(6)	2087(5)	40(5)	42(7)	−4(7)	50(5)	4(7)	33(4)
C(2)	2415(6)	3807(6)	2731(5)	46(5)	36(7)	1(7)	31(5)	0(7)	33(4)
C(3)	2207(6)	3641(7)	3577(6)	49(5)	46(8)	13(8)	58(6)	7(8)	37(4)
C(4)	1039(7)	3145(7)	3760(6)	62(6)	48(9)	37(8)	50(6)	13(8)	46(4)
C(5)	54(7)	2843(8)	3123(7)	38(5)	33(9)	21(9)	67(7)	14(10)	63(5)
C(6)	240(6)	3001(7)	2295(6)	40(5)	60(8)	9(8)	80(6)	14(9)	43(4)
O	732(5)	2920(6)	4562(4)	76(4)	81(8)	72(6)	123(6)	63(7)	56(3)
C(7)	1700(10)	3181(11)	5236(8)	135(10)	174(15)	62(12)	200(11)	120(12)	54(5)
C(8) *	8846(10)	5833(10)	1506(8)	5·6(2)					

Numbers in parentheses here and in subsequent Tables are the estimated standard deviations on least significant digits. The form of anisotropic temperature factors is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

* These atoms belong to the chloroform molecule.

Table 2

Rigid-group parameters * of phenyl rings bonded to phosphorus

Group	10^4X	10^4Y	10^4Z	α/°	β/°	γ/°
P(1)R(1)	3194(4)	7396(4)	1243(3)	72·5(3)	−41·0(2)	160·6(3)
P(1)R(2)	6777(4)	8877(4)	3495(4)	−159·8(3)	10·0(3)	−34·4(2)
P(1)R(3)	2710(4)	6510(4)	4424(3)	−102·1(3)	37·3(2)	−173·5(3)
P(2)R(1)	6024(4)	1891(4)	1743(3)	−2·0(3)	−33·6(3)	77·4(2)
P(2)R(2)	2402(4)	762(4)	3131(3)	−43·6(3)	−23·1(2)	1·2(3)
P(2)R(3)	2301(4)	994(4)	−214(3)	79·1(3)	−16·6(2)	−113·0(3)

* X, Y, Z, α, β, and γ Are defined in Figure 1 of V. G. Albano, P. L. Bellon, and M. Sansoni, *J. Chem. Soc.* (*A*), 1971, 2420.

Both the real and imaginary parts of the anomalous dispersion were taken into account for iridium, chlorine, and phosphorus, according to the values of ref. 13. Atomic scattering factors for non-hydrogen atoms were taken from ref. 14, and for hydrogen atoms from ref. 15.

The largest peak in the final difference Fourier synthesis (2·1 eÅ^{-3}) is associated with the Ir atom (see later).

Table 1 gives fractional co-ordinates and thermal parameters for all non-group atoms; the group parameters for the phenyl rings of the phosphine ligands are listed in Table 2, and the derived parameters of group carbon atoms, together with their individually refined temperature factors, in Table 3. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20863 (4 pp., 1 microfiche).*

RESULTS AND DISCUSSION

The crystal consists of discrete monomeric molecules IrCl$_2$(*p*-MeO·C$_6$H$_3$·N:NH)(PPh$_3$)$_2$,CHCl$_3$ (1/1). The two molecular species pack together as required by space group $P\bar{1}$ (Figure 1).

All non-bonding intra- and inter-molecular interactions were computed. Most of the closer contacts are between hydrogen atoms of the phenyl rings, at distances of 2·35 Å or more. A few H · · · H contacts, however, are in the range 2·1—2·3 Å. These short interactions are, very probably, a consequence of the assumptions concerning the symmetry and the dimensions of the C$_6$ groups and of the C–C–H angles, introduced in the rigid-body treatment of the phenyl rings during the refinement.

The most significant results of the structural analysis show that: (i) cation (1) has reacted with the solvent in such a way that two hydrido-ligands have been replaced by two chloride ions originating from chloroform (or from some decomposition product of this solvent); and (ii) there is an accompanying metallation of the

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

[13] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[14] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[15] J. B. Forsyth and M. Wells, *Acta Cryst.*, 1959, **12**, 412.

TABLE 3

Derived positional parameters and individual thermal factors (all × 10^4) for group carbon atoms *

Atom	x	y	z	B/Å^2
C(111)	3603(8)	7031(8)	1912(3)	2·8(1)
C(112)	2939(5)	7683(5)	2105(3)	3·6(2)
C(113)	2529(7)	8047(7)	1435(4)	4·1(2)
C(114)	2784(8)	7760(8)	573(3)	4·4(2)
C(115)	3448(5)	7108(5)	380(3)	4·1(2)
C(116)	3859(7)	6744(7)	1049(4)	3·2(1)
C(121)	5664(4)	7831(5)	3178(5)	3·0(1)
C(122)	6708(6)	7697(4)	3196(5)	3·5(2)
C(123)	7821(5)	8743(6)	3513(6)	4·5(2)
C(124)	7890(4)	9922(5)	3812(5)	5·1(2)
C(125)	6845(6)	10 057(4)	3793(5)	5·9(3)
C(126)	5732(5)	9011(6)	3476(6)	5·1(2)
C(131)	3341(5)	6583(8)	3700(3)	2·6(1)
C(132)	2125(5)	6267(6)	3574(3)	3·3(1)
C(133)	1494(4)	6193(8)	4298(4)	4·3(2)
C(134)	2077(5)	6436(9)	5146(3)	5·0(2)
C(135)	3294(5)	6753(6)	5272(3)	4·6(2)
C(136)	3926(4)	6825(8)	4549(4)	3·7(2)
C(211)	5071(4)	2178(5)	1715(4)	2·0(1)
C(212)	6197(5)	3082(4)	2175(4)	2·8(1)
C(213)	7150(4)	2795(5)	2202(4)	3·5(2)
C(214)	6976(4)	1602(5)	1770(4)	4·0(2)
C(215)	5850(5)	698(4)	1311(4)	4·0(2)
C(216)	4897(4)	986(5)	1283(4)	3·3(1)
C(221)	2966(6)	1455(7)	2541(4)	2·5(1)
C(222)	3640(4)	1247(7)	3152(5)	3·9(2)
C(223)	3075(6)	555(6)	3742(4)	5·5(2)
C(224)	1837(6)	68(7)	3720(4)	6·0(3)
C(225)	1163(4)	276(7)	3109(5)	5·2(2)
C(226)	1728(6)	969(6)	2520(4)	3·4(2)
C(231)	2892(5)	1553(5)	660(3)	2·6(1)
C(232)	1865(5)	402(5)	453(3)	3·3(2)
C(233)	1273(5)	−156(4)	−420(4)	4·1(2)
C(234)	1710(5)	435(5)	−1088(3)	4·3(2)
C(235)	2737(5)	1586(5)	−881(3)	3·7(2)
C(236)	3328(5)	2145(4)	−7(4)	3·5(2)

* C(*ij*1), bonded to P(*i*), belongs to ring R(*j*) and is *para* to C(*ij*4).

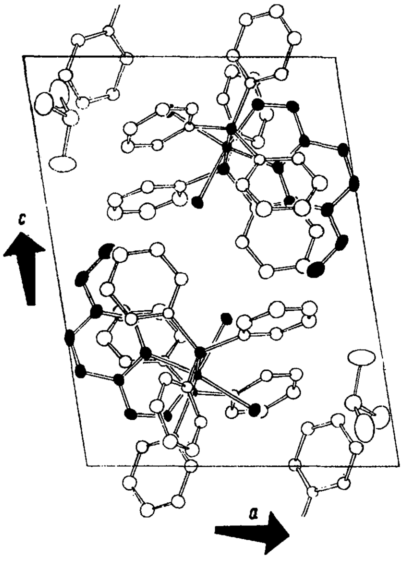

FIGURE 1 ORTEP view of the molecular packing projected along *b* (positive direction of *b* downward). Carbon atoms of the triphenylphosphine groups are shown in open circles

di-imide ligand at carbon-2 of the aromatic ring. The latter phenomenon is not new since an equivalent metallation has been reported,[8] but the chlorination of cation (1) is a novel and unexpected result. The series of reactions which lead to the final product are still unknown; probably, in the initial steps, the replacement of a hydrido- by a chloro-ligand takes place in the position *trans* to that which will subsequently support the metallation of the aromatic ring.

The metal atom, formally Ir^{III}, displays a distorted octahedral co-ordination with the two bulky phosphine groups occupying mutually-*trans* positions. A list of bonding parameters, and some relevant non-bonding interactions, is given in Table 4.

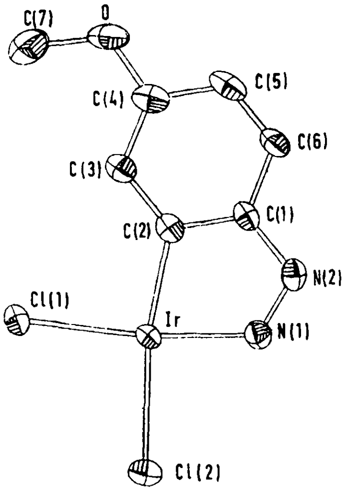

FIGURE 2 ORTEP view of the planar $IrCl_2(p\text{-}MeO\cdot C_6H_3\cdot N{:}NH)$ moiety

The planarity of the $IrCl_2(p\text{-}MeO\cdot C_6H_3\cdot N{:}NH)$ moiety can be appreciated from Figure 2 and the data of Table 5. Most of the atoms do not depart significantly from the ' best ' planes[16] defined in section (*a*) of the Table. Some significant deviations, however, are N(2) and O, mutually *para*, which depart from the plane of the aromatic ring which is strictly planar.

In Table 6 the most significant interactions in the present structure are compared with values reported[8] for cation (3). There is, in general, good agreement between the two sets of data although, in our case, the larger number of experimentally measured intensities, probably resulting from a better crystal sample, has allowed a higher precision to be obtained.

A comparison of the lengths of the Ir–Cl interactions *trans* to the aromatic carbon atom in the two structures shows that in (2) the bond is longer [2·493(2) *vs.* 2·444(9) Å] and the difference is statistically significant. The *trans*-influence of the carbon atom is somehow limited, in cation (3), by the presence of the positive charge. (A comparison of the lengths of the two Ir–Cl bonds in the neutral species clearly shows the extent of this *trans*-influence; see Table 4.)

In cation (3), the interactions Ir–N and Ir–C(aromatic) are not statistically different, in view of their relatively large estimated standard deviations; on the other hand,

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[16] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

previous results on similar complexes containing *ortho*-metallated rings [17,18] indicate that these two bonds have the same length. We confirm this fact at a high confidence level: in the present molecule the bonds are 1·996(8) and 2·011(9) Å, respectively. The N–N distance found in cation (3), is also confirmed here at a more significant level. Its length, ' indicating a conventional double bond ' [8] is, incidentally, almost exactly the same as that of the C=N bond found in $Mn(CO)_4$-(C_6H_4CHNPh),[18] *i.e.* 1·288(9) Å.

TABLE 4

Selected intramolecular interactions

Atoms	Dist./Å	Atoms	Angle/°
(*a*) Within the co-ordination sphere			
Ir–P(1)	2·376(2)	P(1)–Ir–P(2)	176·2(1)
Ir–P(2)	2·364(2)	P(1)–Ir–Cl(1)	88·6(1)
Ir–Cl(1)	2·393(2)	P(1)–Ir–Cl(2)	93·0(1)
Ir–Cl(2)	2·493(2)	P(1)–Ir–N(1)	91·1(2)
Ir–N(1)	1·990(7)	P(1)–Ir–C(2)	88·5(2)
Ir–C(2)	2·011(8)	P(2)–Ir–Cl(1)	88·9(1)
P(1) ··· Cl(1)	3·333(4)	P(2)–Ir–Cl(2)	90·2(1)
P(1) ··· Cl(2)	3·532(4)	P(2)–Ir–N(1)	91·0(2)
P(1) ··· N(1)	3·128(6)	P(2)–Ir–C(2)	88·8(2)
P(1) ··· C(2)	3·072(7)	Cl(1)–Ir–Cl(2)	95·8(1)
P(2) ··· Cl(1)	3·332(3)	Cl(1)–Ir–N(1)	172·2(2)
P(2) ··· Cl(2)	3·441(3)	Cl(1)–Ir–C(2)	94·2(3)
P(2) ··· N(1)	3·115(9)	Cl(2)–Ir–N(1)	92·0(2)
P(2) ··· C(2)	3·072(9)	Cl(2)–Ir–C(2)	169·9(2)
Cl(1) ··· Cl(2)	3·626(4)	N(1)–Ir–C(2)	77·9(3)
Cl(1) ··· C(2)	3·238(8)		
Cl(2) ··· N(1)	3·244(7)		
(*b*) Within the arylazo-moiety			
N(1)–N(2)	1·272(9)	Ir–N(1)–N(2)	121·6(6)
N(2)–C(1)	1·376(12)	Ir–C(2)–C(1)	110·4(6)
C(1)–C(2)	1·409(12)	N(1)–N(2)–C(1)	110·7(7)
C(2)–C(3)	1·392(13)	N(2)–C(1)–C(2)	119·3(7)
C(3)–C(4)	1·382(12)	N(2)–C(1)–C(6)	120·1(8)
C(4)–C(5)	1·413(14)	C(1)–C(2)–C(3)	119·5(7)
C(5)–C(6)	1·358(16)	C(2)–C(3)–C(4)	119·1(8)
C(6)–C(1)	1·430(11)	C(3)–C(4)–C(5)	122·0(9)
C(4)–O	1·369(13)	C(4)–C(5)–C(6)	119·8(8)
O–C(7)	1·450(15)	C(5)–C(6)–C(1)	119·2(8)
N(1) ··· C(2)	2·516(12)	C(6)–C(1)–C(2)	120·5(8)
N(1) ··· C(1)	2·179(11)	C(3)–C(4)–O	123·8(9)
N(2) ··· C(2)	2·404(12)	C(5)–C(4)–O	114·2(8)
		C(4)–O–C(7)	116·9(8)
(*c*) Within the phosphine ligands			
P(1)–C(111)	1·836(10)	Ir–P(1)–C(111)	113·7(3)
P(1)–C(121)	1·835(5)	Ir–P(1)–C(121)	119·4(3)
P(1)–C(131)	1·829(7)	Ir–P(1)–C(131)	110·2(4)
P(2)–C(211)	1·826(8)	Ir–P(2)–C(211)	118·8(2)
P(2)–C(221)	1·836(8)	Ir–P(2)–C(221)	113·5(3)
P(2)–C(231)	1·831(5)	Ir–P(2)–C(231)	112·5(3)
(*d*) Within the chloroform molecule			
Cl–C(8) *	1·72(1)	Cl(3)–C(8)–Cl(4)	109·8(8)
Cl ··· Cl *	2·81(1)	Cl(3)–C(8)–Cl(5)	113·4(7)
		Cl(4)–C(8)–Cl(5)	106·8(8)

* Mean of three values.

One problem, with cation (3) and with the present complex, is to establish which of the two nitrogen atoms, the one attached to the metal atom, N(1), or the other, N(2), has been protonated. Sutton [8] assigned the proton to N(1) for the following reasons: the proton peak is split into a doublet when the cation is labelled with ^{15}N at N(1); the acetone molecule solvating the BF_4^- salt of (3) seems to interact with N(1) *via* a weak hydrogen bond. This model is confirmed by structure-factor computations and Fourier analysis.[8]

Since the present complex is sparingly soluble in most solvents, no n.m.r. spectra could be obtained. The structural analysis, however, yields good evidence for a proton bonded to N(1), in agreement with Sutton's model. A general difference synthesis ($\sin^2 \theta/\lambda^2 \leqslant 0·30$, 3699 reflections) shows one peak of 2·10(8) $e\text{Å}^{-3}$ in the position occupied by the metal atom, and one peak of 0·42(8) $e\text{Å}^{-3}$ in a position which correctly defines an N(1) ··· H vector 1·0 Å long. The possibility of determining the positions of light atoms in the presence of heavy ones has been thoroughly discussed.[19,20] If a signal in the difference Fourier map is an artifact, then it should markedly reduce its height or disappear completely when the number of terms in the series is varied. In our

TABLE 5

Best planes within the $IrCl_2(p\text{-}MeO{\cdot}C_6H_3{\cdot}N{:}NH)$ moiety

(*a*) Equation of best planes through specified atoms in the form $Ax + By + Cz + D = 0$

	A	*B*	*C*	*D*
Plane (1): Ir, Cl(1), Cl(2), N(1), C(2)	−4·437	11·801	0·886	−3·703
Plane (2): Ir, N(1), N(2), C(1), C(2)	−4·609	11·793	1·008	−3·658
Plane (3): N(1), N(2), C(1)—(6), O	−4·598	11·741	1·227	−3·680
Plane (4): C(1)—(6)	−4·612	11·724	1·302	−3·708

(*b*) Distances (Å × 10^3) of all atoms of the $IrCl_2(p\text{-}MeO{\cdot}$-$C_6H_3{\cdot}N{:}NH)$ moiety from best planes

Plane	(1)	(2)	(3)	(4)
Atom				
Ir	0(0)	0(0)	8(0)	−16(0)
Cl(1)	−1(2)	−6(2)	31(2)	1(2)
Cl(2)	−3(2)	−44(2)	−57(2)	−91(2)
N(1)	−3(7)	5(7)	−9(7)	−38(7)
N(2)	−38(7)	−10(7)	−21(7)	−49(7)
C(1)	−30(8)	13(8)	20(8)	0(8)
C(2)	−40(8)	−6(8)	15(8)	−3(8)
C(3)	−68(9)	−21(9)	19(9)	8(9)
C(4)	−119(9)	−49(9)	−3(9)	−10(9)
C(5)	−95(10)	−15(10)	17(10)	7(10)
C(6)	−65(10)	2(9)	15(9)	−1(10)
O	−177(8)	−92(8)	−28(8)	−2(8)
C(7)	−239(14)	−163(14)	−85(14)	−81(14)

TABLE 6

Comparison of the most relevant intramolecular interactions (bond lengths in Å, angles in °) in (*a*) species (2) and (*b*) cation (3)

	(*a*)	(*b*)
Ir–P(1)	2·376(2)	2·399(8)
Ir–P(2)	2·364(2)	2·373(9)
Ir–Cl(1)	2·493(2)	2·444(9)
Ir–N(1)	1·990(7)	2·04(3)
Ir–C(2)	2·011(8)	2·01(3)
N(1)–N(2)	1·272(9)	1·28(3)
N(2)–C(1)	1·376(12)	1·39(3)
C(1)–C(2)	1·409(12)	1·38(4)
P(1)–Ir–P(2)	176·2(1)	179·5(10)
N(1)–Ir–C(2)	77·9(3)	77·0(10)
Cl(2)–Ir–N(1)	92·0(2)	91·8(8)
Cl(2)–Ir–C(2)	169·9(2)	168·6(9)

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case, the signal associated with the metal atom reduces to 1/5 of the original value, 0·42(5) $e\text{Å}^{-3}$, in a difference map computed with terms having $\sin^2\theta/\lambda^2 \leqslant 0{\cdot}10$ (848 reflections). In the latter map the peak height due to the hydrogen atom is 0·23(5) $e\text{Å}^{-3}$. The signal-to-noise ratio in both maps is *ca.* 5 for the hydrogen peak and the position (at 0·300, 0·425, 0·060) does not significantly shift when the number of terms is varied. The peak-height in the former map is appropriate for a hydrogen atom having a thermal parameter of *ca.* 6·5 Å^2 (see, *e.g.* ref. 20); in the latter map this peak has 3/4 of the height predicted.

Structure-factor computations are also consistent with a hydrogen atom being bonded to N(1). For all reflections, the final *R* computed without this atom is 0·0353. This value remains constant if the contribution of a hydrogen atom bonded to N(2) is included, but becomes 0·0351 if the hydrogen is bonded to N(1). Therefore, the absence of any proton or the N(2)H model can be rejected at a 0·5% confidence level. For structure factors restricted to $\sin^2\theta/\lambda^2 \leqslant 0{\cdot}1$ more definite results are obtained: *R* is 0·0293 without that hydrogen, 0·0295 for the N(2)H, and 0·0288 for the N(1)H model. With respect to a non-protonated model, the N(2)H model can be rejected, and the former can be rejected with respect to the N(1)H model; in both cases the confidence level is <0·5%.[21]

We are confident that a thorough structural investigation of the species obtained from solutions of (1) in chloroform–ethanol will eventually confirm the present results.

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