Models for The Interaction of Nitrogen With Transition Metals. Part II.[1] Crystal and Molecular Structure of Carbonylchloro(4-fluorophenyl-di-imide-2*C*,*N*′)bis(triphenylphosphine)iridium(III) Tetrafluoroborate Acetone Solvate

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The title complex forms yellow orthorhombic crystals space group $P2_12_12_1$, with $Z = 4$ in a unit cell of dimensions: $a = 16{\cdot}008(7)$, $b = 18{\cdot}620(10)$, $c = 14{\cdot}935(7)$ Å. The intensities of 1061 independent reflections were measured by counter methods. The structure was solved by Patterson and Fourier methods and refined by least squares to R 3·2% for 882 observed reflections. The complex cation contains an *ortho*-metallated aryl di-imide moiety, with acetone of crystallisation weakly hydrogen bonded to the hydrogen atom on N(1), the co-ordinated nitrogen atom, of the azo-function.

THE reaction of substituted aryldiazonium ions with Vaska's complex, *trans*-$[IrCl(CO)(PPh_3)_2]$ has been found to yield two principal products: the red, diamagnetic air-stable tetrazene complex (1),[1,2] and the yellow,

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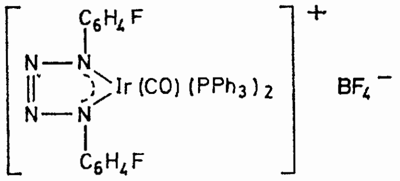
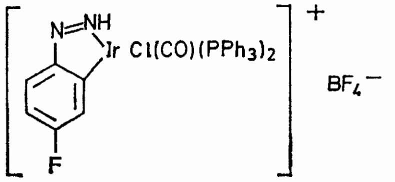
[1] Part I, F. W. B. Einstein and D. Sutton, *Inorg. Chem.*, 1972, **11**, 2827.

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

diamagnetic, air-stable complex (2), obtained[3] as the acetone solvate. We now report the *X*-ray structure determination of (2).



(1)



(2)

EXPERIMENTAL

Synthesis.—IrCl(CO)(PPh$_3$)$_2$ (0·0976 g, 0·125 mmol) dissolved in benzene (15 ml) was treated with *p*-fluorobenzenediazonium fluoroborate (0·0263 g, 0·125 mmol) followed immediately by absolute ethanol (5 ml). The yellow mixture was stirred for 3 h under argon, whereupon the solution gradually became red. Solvent was removed by freeze-drying to leave a dark residue, which was then stirred with benzene (15 ml). The benzene insoluble portion was removed and recrystallised twice from acetone–ether to separate pure yellow crystals of the acetone solvate of (2) (0·015 g) from the red tetrazene complex (1) [Found: C, 52·65; H, 3·90; N, 2·85. Calc. for $C_{43}H_{34}BClF_5IrN_2OP_2,(CH_3)_2CO$: C, 52·70; H, 3·80; N, 2·70%]. Isotopic substitution with ^{15}N at N(1), adjacent to Ir, was achieved by repeating the synthesis with $[p\text{-}BrC_6H_4{}^{14}N{\equiv}{}^{15}N]^+$, prepared by diazotization of *p*-bromoaniline by use of $Na^{15}NO_2$.

Collection of X-*Ray Data.*—A single crystal of maximum dimensions 0·21 × 0·27 × 0·36 mm was cleaved from a larger crystal and used for the entire diffraction results. The space group was determined from precession photographs of the reciprocal lattice layers *h0l*, *0kl*, and *hhl* taken with Cu-K_α radiation (λ = 1·5418 Å), with the crystal mounted about c^*. Cell dimensions were obtained from accurate counter measurements by use of Mo-$K_{\alpha 1}$ radiation of 10 strong reflections in the range 2θ 22—27°.

Crystal Data.—$C_{43}H_{34}BClF_5IrN_2OP_2,(CH_3)_2CO$, Orthorhombic, M = 1047·9, a = 16·008(7), b = 18·620(10), c = 14·935(7) Å, U = 4452 Å^3, D_m = 1·55(1), Z = 4, D_c = 1·563. F(000) = 2080. Space group $P2_12_12_1$. Mo-K_α radiation, λ = 0·70926 Å; μ(Mo-K_α) = 33·6 cm^{-1}.

Reflection intensities for the unique set of data in the range $2\theta \leqslant 30°$ were measured with the crystal in a general orientation, using a Picker FACS 1 computer-controlled four-circle automatic diffractometer, fitted with a scintillation detector and pulse-height analyser. Of 1061 independent reflections measured only 882 were considered observed, having $I > 2\sigma$, where σ = (total count + background)$^{\frac{1}{2}}$. Intensities were measured by the θ—2θ technique with a scan of basewidth 1·25° in 2θ (with allowance for dispersion) at a scan rate of 2° min^{-1} in 2θ and a take-off angle of 3°. Background counts of 10 s were taken at either side of the reflection. Two standard reflections, measured at frequent intervals, showed a maximum variation of ±8% over the entire data collection. Lorentz and polarization corrections were applied and structure factors calculated in the usual manner. No absorption correction was made. In an analysis of the variance of the predicted and observed values of R' with sin θ/λ, the light-atom (*e.g.* a carbon atom) contribution was examined as a fraction of the total scattering by use of methods suggested in ref. 4. For the outer-most data the light-atom contribution is only marginally above the noise level. Since the light-atom positions are the features of prime interest we considered that further data collection was therefore not justified.

Solution and Refinement of the Structure.—A three-dimensional Patterson function yielded the positions of the iridium, phosphorus, and chlorine atoms. Structure factors were calculated, based on these atomic co-ordinates, along with suitable scale and isotropic temperature factors. Two consecutive electron-density Fourier syntheses then yielded the positions of thirty-nine non-hydrogen atoms. Two cycles of least-squares refinement varying the positional and isotropic temperature factors for Ir, Cl, P(1), and P(2) but only the positional parameters of the remaining atoms, along with the scale, gave R 15·1%. An electron-density difference map at this stage yielded approximate positions for all the remaining non-hydrogen atoms except those of the acetone of crystallization.

Since the number of atoms now exceeded the dimensions of the structure-factor and least-squares program, further refinement was performed utilizing fixed-atom contributions as input to block full-matrix least-squares refinement of the remaining atom parameters; the fixed atoms were alternated from time to time to ensure refinement of all atoms. Several cycles of refinement, varying the positional parameters of all the atoms and the isotropic temperature factors of Ir, Cl, P(1), and P(2), together with a study of electron-density difference maps at each stage (which allowed inclusion of the acetone molecule) reduced R to 6·2%. Anomalous scattering of the iridium atom had been so far deliberately neglected. In order to determine the correct absolute configuration, refinement of Ir, Cl, P(1), P(2), and ten light atoms was carried out (*a*) in the initial co-ordinates, and (*b*) in the mirror-related positions *x*, *y*, *-z*. The other light atoms were included in the structure-factor calculations but were not refined. The refinement gave R 7·1 and 6·0 respectively indicating the initial arbitrary choice of co-ordinates to be in error. Consequently the *z* co-ordinates of all atoms were changed in sign and in all further refinement the usual anomalous dispersion correction was used for iridium. Anisotropic thermal coefficients were now assigned to iridium and F(12) of the fluoroborate group as a result of inspection of an electron-density difference map. Refinement was continued in stages varying, at each stage, the scale and positional and thermal parameters for Ir, P(1), P(2), and Cl but only positional parameters for the light atoms for the first cycle, all positional and temperature parameters, and the scale being varied in subsequent cycles. This converged at R 3·2% and R' 3·6%.* A difference-Fourier map at this stage showed a clear peak of similar height to those of other

* Weighted index, $R' = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2\}^{\frac{1}{2}}$.

[3] F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1972, **94**, 645.

[4] E. Huber-Buser, *Z. Krist.*, 1971, **133**, 150.

hydrogen atoms [*ca.* 0·2(1) eÅ^{-3}] at the calculated position for a hydrogen atom on N(1), whereas no such peak was observed in the similar position calculated for N(2). In an attempt to clarify the position of this hydrogen atom (whose presence is indicated on chemical and n.m.r. grounds, see later) structure factors were calculated for three possible models: (*a*) no hydrogen atoms present, (*b*) a hydrogen attached to N(1), and (*c*) a hydrogen attached to N(2). Model (*c*) provided a significant worsening of the agreement at the 0·5% confidence level,[5] but no significant difference could be detected between models (*a*) and (*b*). Unobserved reflections were not used in the refinement; observed reflections were given constant weights (σ 3·9), and the final error-of-fit was 0·95. Aromatic hydrogen atoms were excluded from the calculations. Final positional and thermal parameters are listed in Table 1 and selected interatomic distances and angles in Table 2. Atomic scattering factors and anomalous dispersion correction were taken from ref. 6; computer programs used are listed in ref. 1. Final observed and calculated structure factors

TABLE 1

Final fractional co-ordinates and thermal parameters [a]

Atom	*x*	*y*	*z*	*B*/Å^2
Ir	0·1856(1)	0·0506(1)	−0·0446(1)	*b*
P(1)	0·2765(5)	0·1530(4)	−0·0444(7)	3·6(2)
P(2)	0·0966(4)	−0·0514(5)	−0·0442(7)	3·8(2)
Cl	0·2587(6)	0·0043(5)	0·0870(6)	5·5(3)
F(11)	−0·3075(22)	−0·0062(15)	−0·1264(22)	14·5(9)
F(12)	−0·3366(18)	−0·0568(17)	0·0010(27)	*b*
F(13)	−0·2195(13)	−0·0882(11)	−0·0654(16)	10·1(7)
F(14)	−0·2421(17)	0·0205(15)	−0·0060(18)	14·8(10)
B	−0·2811(55)	−0·0378(50)	−0·0532(62)	15·2(25)
C(1)	0·2533(21)	0·0082(16)	−0·1332(24)	3·4(8)
O(1)	0·2877(13)	−0·0167(11)	−0·1895(15)	5·5(7)
N(1)	0·1012(15)	0·1039(12)	0·0331(19)	4·3(6)
N(2)	0·0444(18)	0·1427(14)	−0·0025(17)	4·1(8)
C(11)	0·0523(26)	0·1422(20)	−0·0951(25)	4·9(10)
C(12)	0·1140(18)	0·1015(15)	−0·1350(20)	2·0(7)
C(13)	0·1176(22)	0·0997(19)	−0·2301(23)	5·3(9)
C(14)	0·0560(26)	0·1433(21)	−0·2687(26)	5·9(10)
C(15)	−0·0039(24)	0·1840(19)	−0·2332(26)	5·4(9)
C(16)	−0·0108(21)	0·1881(18)	−0·1410(26)	6·0(10)
F(1)	0·0590(12)	0·1412(10)	−0·3639(15)	7·7(6)
C(21)	0·3902(16)	0·1328(15)	−0·0480(22)	2·9(7)
C(22)	0·4462(18)	0·1912(14)	−0·0576(20)	3·1(7)
C(23)	0·5280(19)	0·1766(15)	−0·0598(23)	4·3(8)
C(24)	0·5613(17)	0·1093(17)	−0·0496(25)	4·4(8)
C(25)	0·5082(19)	0·0502(19)	−0·0380(27)	6·0(8)
C(26)	0·4174(16)	0·0610(17)	−0·0356(22)	3·6(7)
C(31)	0·2618(18)	0·2048(16)	−0·1481(20)	3·6(8)
C(32)	0·2011(20)	0·2585(16)	−0·1496(20)	4·3(8)
C(33)	0·1843(24)	0·2951(16)	−0·2296(23)	6·1(9)
C(34)	0·2312(21)	0·2729(19)	−0·3079(23)	5·8(10)
C(35)	0·2882(19)	0·2167(17)	−0·3080(21)	4·4(8)
C(36)	0·3062(21)	0·1855(15)	−0·2253(21)	4·3(8)
C(41)	0·2661(16)	0·2151(15)	0·0505(24)	3·2(7)
C(42)	0·2491(24)	0·1810(20)	0·1345(30)	5·4(10)
C(43)	0·2469(29)	0·2253(25)	0·2142(30)	7·4(12)
C(44)	0·2585(23)	0·2989(21)	0·1990(26)	6·2(10)
C(45)	0·2727(19)	0·3310(17)	0·1183(27)	5·2(9)
C(46)	0·2770(18)	0·2918(18)	0·0353(28)	5·3(9)
C(51)	0·1473(23)	−0·1381(19)	−0·0491(33)	5·2(9)
C(52)	0·0940(20)	−0·1986(19)	−0·0517(29)	6·2(9)
C(53)	0·1317(22)	−0·2673(18)	−0·0527(30)	7·9(9)
C(54)	0·2190(22)	−0·2254(17)	−0·0463(30)	5·8(9)
C(55)	0·2724(19)	−0·2161(19)	−0·0381(32)	5·4(9)
C(56)	0·2333(22)	−0·1431(19)	−0·0351(32)	4·2(9)
C(61)	0·0301(17)	−0·0594(17)	0·0504(28)	4·0(7)
C(62)	−0·0535(23)	−0·0811(17)	0·0404(32)	7·7(10)
C(63)	−0·1019(23)	−0·0903(20)	0·1242(29)	7·9(11)
C(64)	−0·0664(27)	−0·0816(21)	0·2108(29)	8·3(12)
C(65)	0·0164(26)	−0·0574(25)	0·2179(28)	6·5(11)
C(66)	0·0621(18)	−0·0475(20)	0·1354(25)	4·8(8)
C(71)	0·0293(18)	−0·0526(19)	−0·1426(22)	3·0(8)
C(72)	0·0612(21)	−0·0868(16)	−0·2218(24)	4·8(9)
C(73)	0·0177(25)	−0·0762(20)	−0·3044(26)	5·9(11)
C(74)	−0·0597(20)	−0·0363(18)	−0·3024(20)	4·6(8)
C(75)	−0·0914(21)	−0·0049(18)	−0·2250(24)	5·3(9)
C(76)	−0·0444(21)	−0·0136(16)	−0·1427(23)	4·6(9)
O(2)	0·0637(21)	0·1271(16)	0·2214(20)	8·8(9)
C(81)	−0·0060(34)	0·1382(23)	0·2413(33)	8·9(13)
C(82)	−0·0857(30)	0·1189(24)	0·1993(30)	10·6(14)
C(83)	−0·0088(36)	0·1618(30)	0·3447(40)	15·6(20)

[a] Estimated standard deviations are given in parentheses in this and subsequent Tables. [b] Anisotropic thermal parameters, U_{ij}, for the expression: $\exp[-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23}$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir (× 10^4)	393(8)	423(9)	313(9)	40(9)	37(10)	−5(10)
F(12) (× 10^2)	17(3)	19(3)	49(7)	11(2)	21(4)	15(4)

TABLE 2

Selected interatomic distances (Å) and angles (°)

(*a*) Intramolecular bonded contacts

Ir–P(1)	2·399(8)	B–F(11)	1·32(8)
Ir–P(2)	2·373(9)	B–F(12) [a]	1·26(7)
Ir–Cl	2·444(9)	B–F(13)	1·37(8)
Ir–C(1)	1·88(4)	B–F(14)	1·44(8)
Ir–N(1)	2·04(3)		
Ir–C(12)	2·01(3)		
P(1)–C(21)	1·86(3)	C(11)–C(12)	1·38(4)
P(1)–C(31)	1·84(3)	C(12)–C(13)	1·42(4)
P(1)–C(41)	1·84(3)	C(13)–C(14)	1·40(4)
P(2)–C(51)	1·81(3)	C(14)–C(15)	1·33(4)
P(2)–C(61)	1·78(4)	C(15)–C(16)	1·38(4)
P(2)–C(71)	1·82(3)	C(16)–C(11)	1·49(4)
C(1)–O(1)	1·11(3)	C(81)–C(82)	1·47(5)
N(1)–N(2)	1·28(3)	C(81)–C(83)	1·61(7)
N(2)–C(11)	1·39(3)	C(81)–O(2)	1·17(5)
F(1)–C(14)	1·42(4)	Mean C–C(Ph)	1·416(15) [b]

(*b*) Interatomic angles (excluding PPh$_3$ groups)

P(1)–Ir–P(2)	179·5(10)	C(61)–P(2)–C(71)	107(1)
P(1)–Ir–Cl	89·3(3)	C(71)–P(2)–Ir	111(1)
P(1)–Ir–N(1)	90·8(6)		
P(1)–Ir–C(1)	89·1(9)	Ir–N(1)–N(2)	120(2)
P(1)–Ir–C(12)	88·4(8)	N(1)–N(2)–C(11)	110(3)
P(2)–Ir–Cl	90·2(3)	Ir–C(1)–O(1)	175(3)
P(2)–Ir–N(1)	89·5(6)	N(2)–C(11)–C(12)	120(4)
P(2)–Ir–C(1)	90·7(9)	C(12)–C(11)–C(16)	127(3)
P(2)–Ir–C(12)	92·1(8)	Ir–C(12)–C(11)	112(2)
Cl–Ir–N(1)	91·8(8)	C(11)–C(12)–C(13)	118(3)
Cl–Ir–C(1)	98·2(9)	C(12)–C(13)–C(14)	112(3)
Cl–Ir–C(12)	168·6(9)	C(13)–C(14)–C(15)	132(4)
N(1)–Ir–C(1)	170·0(12)	F(1)–C(14)–C(13)	112(4)
N(1)–Ir–C(12)	77·0(10)	F(1)–C(14)–C(15)	116(4)
C(1)–Ir–C(12)	93·0(12)	C(14)–C(15)–C(16)	119(4)
		C(11)–C(16)–C(15)	112(3)
C(21)–P(1)–Ir	116(1)	F(11)–B–F(12)	116(7)
C(21)–P(1)–C(31)	102(1)	F(11)–B–F(13)	116(7)
C(21)–P(1)–C(41)	104(1)	F(11)–B–F(14)	102(6)
C(31)–P(1)–Ir	110(1)	F(12)–B–F(13)	114(7)
C(31)–P(1)–C(41)	108(1)	F(12)–B–F(14)	101(6)
C(41)–P(1)–Ir	117(1)	F(13)–B–F(14)	106(6)
C(51)–P(2)–Ir	116(1)	C(82)–C(81)–O(2)	133(5)
C(51)–P(2)–C(61)	103(1)	C(82)–C(81)–C(83)	117(5)
C(51)–P(2)–C(71)	103(1)	C(83)–C(81)–O(2)	109(5)
C(61)–P(2)–Ir	115(1)		

(*c*) Distances (Å) and angles (°) for selected long contacts

N(1) · · · O(2)	2·91	N(1)–H(1) · · · O(2)	149
H(1) · · · O(2)	1·99	H(1) · · · O(2)–C(81)	127

[a] Uncorrected for riding motion; corrected value 1·41Å.

[b] PPh$_3$ groups. Error calculated according to: $1/\sigma_{av}{}^2 = \sum_{i=1}^{n} 1/\sigma_i{}^2$.

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[5] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

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

are listed in Supplementary Publication No. SUP 20592 (3 pp.).[*]

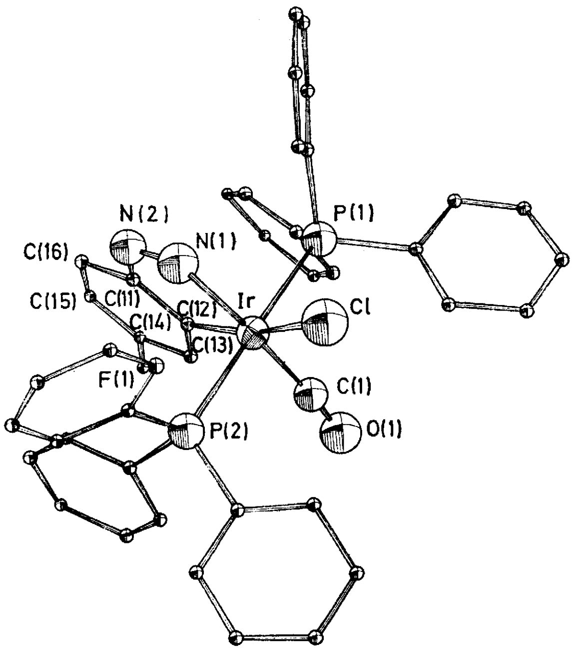

FIGURE 1 The molecular configuration of the complex cation

DISCUSSION

The structure consists of an array of discrete six-co-ordinate iridium(III) complex cations and tetrafluoroborate anions together with acetone molecules of crystallization. A view of the complex cation is shown in Figure 1. The octahedral co-ordination environment of iridium is distorted from regularity by the presence of the five-membered ring which imposes an angle of 77° at the iridium. The C(1)–Ir–Cl angle adjusts to 98° as compensation; the C(1)–Ir–C(12) and Cl–Ir–N(1) angles are only slightly greater than 90°. Apart from the apical triphenylphosphine groups, the remaining 'equatorial' atoms of the complex cation are very nearly coplanar [Table 3, plane (4)] and certain groups of these atoms are accurately planar [planes (1)—(3)]. The iridium–phosphorus vectors are normal to the ligand-atom equatorial plane (3). The phosphine groups are *trans* and the Ir–P bond lengths are almost identical with the longer of the two distinctly different Ir–P bond lengths in the five-co-ordinate tetrazene complex,[1,2] where the phosphines are *cis*.

The principal feature established by this structure determination is the internal metallation of the arylazo-ligand at atom C(12) to give a five-membered heterocyclic ring. Recently, *ortho*-metallation has been recognized as being an important substitution reaction of aromatic compounds possessing a donor atom, and numerous examples have appeared since the subject was reviewed.[7] The phenomenon is well established on chemical evidence but only a few crystal structure determinations have been completed,[8-11] and none has been reported in detail. The five-membered ring in the present structure is closely similar in dimensions to the corresponding ring in acetatobis-[(2-phenylazo)phenyl]-rhodium.[9] The Ir–C(12) and Ir–N(1) bonds in the chelate ring are not, in view of the rather large standard errors, significantly different in our structure. Since no

TABLE 3

(*a*) Equations of mean planes through selected atoms, in the form $AX + BY + CZ + D = 0$

Plane	Atoms in plane	A	B	C	D	χ^2
(1)	Ir, N(1), N(2), C(11), C(12)	−0·612	−0·790	−0·0386	2·54	0·13
(2)	C(11)—(16)	−0·627	−0·779	−0·015	2·58	0·29
(3)	Cl, N(1), C(1), C(12)	−0·596	−0·803	−0·013	2·55	3·47
(4)	Ir, Cl, N(1), N(2), C(1), C(11)—(16)	−0·613	−0·790	−0·001	2·57	48·5 †
(5)	P(1), P(2), N(1), C(1)	−0·491	0·371	−0·788	0·58	60·3 †
(6)	P(1), P(2), Cl, C(12)	0·631	−0·478	−0·611	−1·81	156·9 †
(7)	O(2), C(81)—(83)	−0·007	0·939	−0·344	−1·10	4·74
(8)	O(2), C(81)—(83), H(1)	−0·022	0·950	−0·311	−1·24	6·9

(*b*) Deviations (Å) of atoms from the planes

Plane (1): Ir 0·000(2), N(1) 0·00(2), N(2) 0·00(3), C(11) −0·01(4), C(12) 0·00(3)

Plane (2): C(11) 0·02(4), C(12) −0·01(3), C(13) 0·00(4), Cl −0·121(9), C(14) 0·00(4), C(15) 0·00(4), C(16) −0·01(3), Ir −0·007(2), F(1) 0·02(2), N(1) 0·05(2), N(2) 0·07(2), C(1) −0·05(3), O(1) −0·03(2)

Plane (3): Cl −0·002(9), N(1) 0·02(2), C(1) 0·03(3), C(12) −0·03(3), Ir 0·029(2), N(2) −0·01(3), O(1) 0·09(2), C(11) −0·06(4)

Plane (4): Ir 0·002(2), Cl −0·037(9), N(1) 0·05(2), N(2) 0·03(3), C(1) −0·04(3), C(11) −0·04(4), C(12) −0·04(3), C(13) −0·05(4), C(14) −0·09(4), C(15) −0·10(4), C(16) −0·09(3), O(1) −0·01(2), F(1) −0·08(2)

Plane (5): P(1) −0·014(10), P(2) −0·015(10), N(1) 0·11(3), C(1) 0·21(3), Ir −0·005(2), O(1) 0·43(2)

Plane (6): P(1) 0·028(9), P(2) 0·028(9), Cl −0·028(9), C(12) −0·33(3), Ir 0·022(1)

Plane (7): O(2) −0·01(3), C(81) 0·09(4), C(82) −0·03(4), C(83) −0·03(6)

Plane (8): O(2) −0·04(3), C(81) 0·09(4) C(82) −0·03(4), C(83) 0·02(6), H(1) 0·01

† These group of atoms are not coplanar.

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[*] For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[7] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[8] J. M. Guss and R. Mason, *Chem. Comm.*, 1971, 58.

[9] A. R. M. Craik, G. R. Knox, P. L. Pauson, R. J. Hoare, and O. S. Mills, *Chem. Comm.*, 1971, 168.

[10] G. Bourbieri, L. Caglioti, L. Cattalini, E. Forsellini, F. Gasparrini, R. Graziani, and P. A. Vigato, *Chem. Comm.*, 1971, 1415.

[11] M. I. Bruce, B. L. Goodall, M. Z. Iqbal, F. G. A. Stone, R. J. Doedens, and R. G. Little, *Chem. Comm.*, 1971, 1595.

errors are reported in ref. 9, it is not possible to decide whether the corresponding distances are different in the rhodium compound either;[9] however, the closely related *ortho*-metallated phenyl ring in a manganese–benzilidene-aniline[11] complex is bound to manganese with identical Mn–C and Mn–N distances. The N(1)–N(2) bond length (1·28 Å) indicates this to be a conventional double-bond, again as in the related compounds.[9,11]

The presence of an N–H bond has been established by i.r. and n.m.r. spectroscopy, and by deprotonation with base.[3] Isotopic substitution with ^{15}N at N(1) further establishes the existence of an N(1)–H bond since the weak n.m.r. signal at τ 3·61 is split into a doublet having J (^{15}N–H) 29 Hz. The structure-factor calculations, whilst not sufficient to confirm unambiguously the presence of N(1)–H nevertheless are more consistent with the site of protonation being N(1) than N(2) and this is chemically sensible insofar as the hydrogen atom then has the position occupied by the phenyl group in the acetatobis-[(2-phenylazo)phenyl]rhodium complex.[9] In addition N(1) shows a relatively short contact with the oxygen O(2) of the acetone molecule (2·91 Å), consistent with the existence of weak hydrogen bonding (Figure 2).

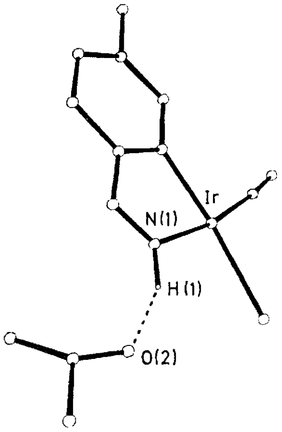

FIGURE 2 Location of acetone of crystallization showing the proximity to the proton H(1) on N(1) of the azo-group

The computed angles based upon the calculated position of H(1) are given in Table 2(*c*), and it can be seen from Table 3 that H(1) is approximately coplanar with the acetone molecule. Similar calculations based upon the expected position of a hydrogen atom on N(2) show a much longer contact with O(2) and angles irreconcilable with hydrogen bonding. Protonation of the co-ordinating nitrogen atom of an arylazo-group has been observed previously. The insertion of $[FC_6H_4N_2]^+$ into a Pt–H bond gave[12] $[Pt\{N(H){:}NC_6H_4F\}Cl(PEt_3)_2]BF_4$ and $[IrH_2(NH{:}NC_6H_4NO_2)(PPh_3)_3]BF_4$ was obtained similarly.[13] We therefore feel quite confident that the position of protonation in our compound is correctly established.

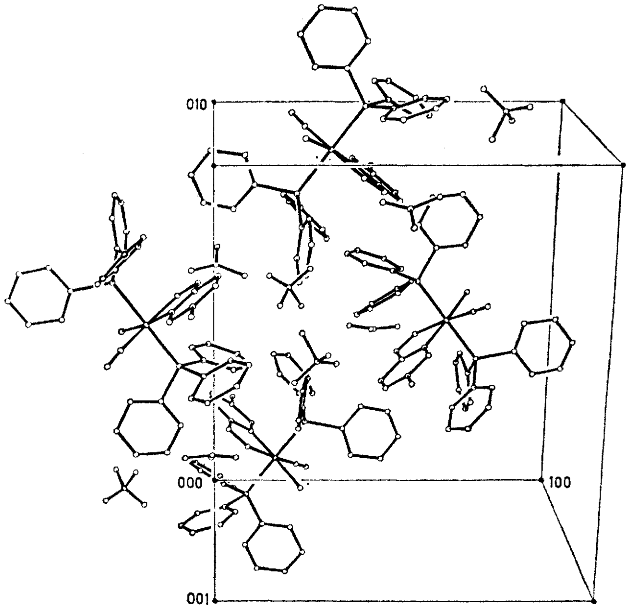

FIGURE 3 The molecular packing

Figure 3 shows the molecular packing. There are no notable short contacts other than that already described.

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[12] G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 2133; 1967, **89**, 1822.

[13] L. Toniolo and R. Eisenberg, *Chem. Comm.*, 1971, 455.