CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
SIMON FRASER UNIVERSITY, BURNABY 2, BRITISH COLUMBIA, CANADA

Models for the Interaction of Nitrogen with Transition Metals. I. Crystal and Molecular Structure of Carbonylbis(triphenylphosphine)(1,4-*p*-fluorophenyltetrazene)iridium Tetrafluoroborate

BY F. W. B. EINSTEIN AND D. SUTTON*

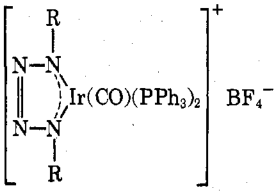
Received May 18, 1972

The reaction of *p*-fluorophenyldiazonium fluoroborate with Vaska's complex *trans*-[IrCl(CO)(PPh$_3$)$_2$] yields the title compound, the crystal and molecular structure of which are reported here. The compound crystallizes in the space group $P\bar{1}$ with two formula units in a unit cell of dimensions a = 13.669 (5) Å, b = 17.423 (7) Å, c = 10.852 (4) Å, α = 104.57 (3)°, β = 98.02 (5)°, γ = 88.43 (3)°. The calculated density is 1.549 g cm^{-3} and measured density 1.53 g cm^{-3}. Full-matrix least-squares refinement of 3252 observed three-dimensional X-ray counter measured intensities led to a final conventional R index of 0.049. The principal feature in the structure of the complex cation is the presence of a five-membered iridium–nitrogen ring, and the cation may alternately be described as the 1-carbonyl-1,1-bis(triphenylphosphino)iridio-2,5-di-*p*-fluorophenyltetrazolium ion. The uncoordinated nitrogen atoms are 1.270 (16) Å apart, and bound to the coordinated nitrogen atoms by essentially single bonds of dimensions 1.400 (16) and 1.350 (16) Å.

Introduction

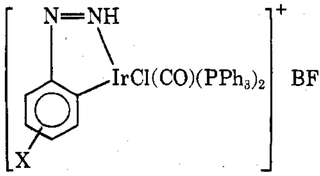
In this series of papers[1–4] we shall report the synthesis and characterization of compounds formed in the reactions of transition metal compounds with ligands which are closely related to dinitrogen. It is anticipated that the results will shed further light upon the unresolved question as to the factors which influence metal–dinitrogen interaction, and in this regard we hope to obtain information pertinent to the problem of the role of the transition metals iron and molybdenum in the nitrogen-fixing enzyme *nitrogenase.* In particular, we shall be concerned with the question of whether, and under what circumstances, facile reduction and eventual fission of the N≡N bond can be achieved by the participation of transition metal intermediates. Thus we hope to provide information as to whether direct coordination of dinitrogen to a transition metal ion is indeed (as presently appears to be the case on circumstantial evidence) a likely factor in the mechanism of dinitrogen reduction by enzyme systems.

For our initial experiments we have chosen to examine the interaction of the aryldiazonium ion with various metals. The significance of this ion as a promising dinitrogen model is suggested by Parshall's demonstration[5] that it will insert into the metal–hydrogen bond in PtHCl(PEt$_3$)$_2$ to produce the substituted diimide complex ArN=NHPtCl(PEt$_3$)$_2^+$. This then undergoes facile reduction to the substituted hydrazine complex ArNH·NH$_2$PtCl(PEt$_3$)$_2^+$ and eventual N–N bond fission to give ArNH$_2$ and NH$_3$ and regenerate PtHCl(PEt$_3$)$_2$. Rather than pursue this type of insertion reaction, we decided to attempt the synthesis of arylazo complexes ArN=NM by straightforward oxidative addition reactions of aryldiazoniun salts to suitable low-oxidation-state metal complexes. In view of the published synthesis and structure[6] of the nitrosyl complex [Ir(NO)(CO)Cl(PPh$_3$)$_2$]BF$_4$ and similarity in the electronic structures of N≡O$^+$ and (ArN≡N)$^+$, the first such reaction attempted was that of para-substituted aryldiazonium salts with Vaska's complex *trans*-[IrCl(CO)(PPh$_3$)$_2$]. To date we have been able to isolate and identify two principal products from these reactions. The first is the compound I, an example of a complex involving the uncommon heterocyclic system of four nitrogen atoms and one metal atom.



I, R=p-XC$_6$H$_4$; X=H, F, Cl, Br, CF$_3$, OCH$_3$

The synthesis and characterization of this compound have been reported briefly[2] and the details of the X-ray crystallographic determination of its crystal and molecular structure are presented here. The second product, II, is a cyclic diimide complex whose crystal structure has also been determined.[3] A full description of this compound and a discussion of the interrelationship of these products and their chemical properties will be presented at a later date.



II, X=H; o-, m-, and p-F, -Cl, -Br, -NO$_2$; p-CF$_3$; m- and p-CH$_3$; m-OCH$_3$

---

[1] For preliminary communications of the results of this study see ref 2–4.

[2] A. B. Gilchrist, F. W. B. Einstein, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, **83**, 1826 (1971).

[3] A. B. Gilchrist, F. W. B. Einstein, G. W. Rayner-Canham, and D. Sutton, *ibid.*, **84**, 645 (1972).

[4] A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *Nature (London)*, **235**, 42 (1972).

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

[6] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968); **8**, 1282 (1969).

Table I

Final Fractional Coordinates and Thermal Parameters[a]

Atom	x	y	z	B, Å^2
Ir	0.1452 (1)	0.1923 (0)	0.2107 (1)	b
P(1)	0.1472 (3)	0.3244 (2)	0.1979 (4)	b
P(2)	0.3115 (3)	0.1540 (2)	0.2632 (4)	b
N(1)	0.1337 (9)	0.1246 (7)	0.0374 (12)	b
N(2)	0.0029 (7)	0.1705 (7)	0.1560 (11)	b
N(3)	0.0401 (9)	0.1010 (7)	−0.0304 (11)	b
N(4)	−0.0288 (10)	0.1294 (7)	0.0345 (13)	b
C(1)	0.1367 (13)	0.2275 (10)	0.3803 (18)	b
O(1)	0.1220 (9)	0.2476 (8)	0.4869 (11)	b
F(1)	0.3718 (8)	−0.0366 (7)	−0.3187 (11)	b
F(2)	−0.3229 (9)	0.2984 (7)	0.3853 (13)	b
F(11)	0.1351 (10)	0.7366 (8)	0.1597 (16)	b
F(12)	0.1701 (14)	0.6131 (8)	0.1476 (16)	b
F(13)	0.2490 (12)	0.7074 (9)	0.3052 (14)	b
F(14)	0.2765 (14)	0.6968 (11)	0.1109 (18)	12.9 (5)
B(1)	0.2043 (22)	0.6863 (17)	0.1884 (28)	6.8 (6)
C(11)	0.2014 (11)	0.0825 (8)	−0.0520 (14)	3.2 (3)
C(12)	0.2017 (12)	0.0008 (9)	−0.0872 (15)	3.9 (3)
C(13)	0.2586 (14)	−0.0414 (11)	−0.1777 (18)	5.3 (4)
C(14)	0.3147 (13)	0.0036 (10)	−0.2259 (16)	4.6 (4)
C(15)	0.3199 (13)	0.0836 (10)	−0.1959 (17)	5.0 (4)
C(16)	0.2605 (13)	0.1242 (10)	−0.1067 (16)	4.2 (4)
C(21)	−0.0838 (13)	0.2039 (10)	0.2136 (17)	4.8 (4)
C(22)	−0.0925 (13)	0.1954 (10)	0.3384 (17)	4.8 (4)
C(23)	−0.1755 (14)	0.2302 (11)	0.3955 (18)	5.5 (4)
C(24)	−0.2448 (15)	0.2652 (11)	0.3228 (19)	5.6 (4)
C(25)	−0.2377 (14)	0.2712 (11)	0.2084 (19)	5.6 (4)
C(26)	−0.1572 (13)	0.2394 (11)	0.1477 (16)	4.6 (4)
C(31)	0.0306 (14)	0.3753 (11)	0.2260 (18)	4.5 (4)
C(32)	0.0045 (14)	0.3899 (11)	0.3481 (17)	4.9 (4)
C(33)	−0.0812 (16)	0.4331 (12)	0.3774 (20)	5.8 (4)
C(34)	−0.1370 (17)	0.4628 (13)	0.2859 (22)	6.5 (5)
C(35)	−0.1108 (16)	0.4481 (13)	0.1666 (22)	6.3 (5)
C(36)	−0.0249 (15)	0.4054 (12)	0.1332 (20)	5.6 (5)
C(41)	0.2302 (11)	0.3972 (9)	0.3092 (15)	3.6 (3)
C(42)	0.2287 (13)	0.4751 (10)	0.3023 (17)	4.8 (4)
C(43)	0.2840 (13)	0.5331 (10)	0.3869 (17)	4.8 (4)
C(44)	0.3500 (14)	0.5139 (11)	0.4835 (18)	5.3 (4)
C(45)	0.3545 (15)	0.4371 (12)	0.4965 (19)	6.0 (5)
C(46)	0.2938 (13)	0.3970 (11)	0.4076 (18)	5.1 (4)
C(51)	0.1649 (11)	0.3288 (8)	0.0389 (14)	2.9 (3)
C(52)	0.2448 (12)	0.3705 (10)	0.0173 (16)	4.2 (4)
C(53)	0.2551 (14)	0.3697 (11)	−0.1112 (18)	4.7 (4)
C(54)	0.1833 (15)	0.3354 (12)	−0.2085 (19)	5.6 (5)
C(55)	0.1065 (14)	0.2958 (11)	−0.1880 (18)	5.4 (4)
C(56)	0.0963 (13)	0.2912 (10)	−0.0674 (16)	4.3 (4)
C(61)	0.3984 (11)	0.1656 (9)	0.1565 (15)	3.3 (3)
C(62)	0.4067 (12)	0.2416 (10)	0.1306 (16)	4.0 (4)
C(63)	0.4738 (13)	0.2550 (10)	0.0558 (17)	4.9 (4)
C(64)	0.5333 (14)	0.1936 (11)	0.0041 (17)	5.3 (4)
C(65)	0.5294 (13)	0.1217 (10)	0.0278 (17)	4.9 (4)
C(66)	0.4626 (12)	0.1070 (9)	0.1048 (15)	4.0 (3)
C(71)	0.3148 (12)	0.0496 (9)	0.2692 (15)	3.4 (3)
C(72)	0.4004 (14)	0.0203 (11)	0.3259 (17)	4.5 (4)
C(73)	0.4033 (15)	−0.0601 (12)	0.3335 (19)	5.1 (4)
C(74)	0.3224 (16)	−0.1074 (12)	0.2801 (19)	5.6 (5)
C(75)	0.2405 (15)	−0.0797 (12)	0.2238 (20)	5.5 (5)
C(76)	0.2347 (14)	−0.0003 (11)	0.2156 (18)	4.5 (4)
C(81)	0.3776 (12)	0.1986 (9)	0.4211 (15)	3.4 (3)
C(82)	0.3427 (14)	0.1947 (11)	0.5319 (18)	4.8 (4)
C(83)	0.3906 (14)	0.2300 (11)	0.6546 (18)	4.8 (4)
C(84)	0.4769 (15)	0.2656 (11)	0.6688 (19)	5.2 (4)
C(85)	0.5200 (14)	0.2675 (11)	0.5623 (19)	5.0 (4)
C(86)	0.4704 (14)	0.2354 (11)	0.4384 (18)	4.6 (4)
C(91)	0.4444 (21)	0.5278 (16)	0.0896 (27)	9.3 (7)
C(92)	0.5230 (24)	0.4819 (18)	0.1183 (29)	10.8 (8)
C(93)	0.5777 (22)	0.4495 (17)	0.0162 (31)	10.3 (8)
C(101)	0.0662 (33)	0.0487 (24)	0.5908 (39)	13.6 (11)
C(102)	−0.0961 (30)	0.0095 (28)	0.5065 (46)	14.5 (12)
C(103)	−0.0329 (38)	0.0617 (24)	0.5976 (40)	14.9 (12)

[a] Esd's in the least significant figures are given in parentheses in this and subsequent tables. [b] Anisotropic thermal coefficients U_{ij} are given in Table II.

Collection of X-Ray Data

A single crystal in the form of a thin wedge of maximum dimensions 0.04 × 0.18 × 0.34 mm, with the direction of greatest elongation along c, was used for the entire diffraction results. Weissenberg photographs of the zones $hk0$–$hk5$ using Cu Kα radiation and precession photographs of the zones $h0l$ and $0kl$ using Mo Kα and Cu Kα radiation showed the crystal to belong to the triclinic space groups $P1$ or $P\bar{1}$. Cell dimensions were obtained from accurate counter measurements (using Mo Kα_1) of thirty of the strongest reflections in the region 2θ 40–45° at 22°. Crystal data: $[Ir\{N_4(FC_6H_4)_2\}CO(PPh_3)_2]BF_4\cdot C_6H_6$; $M = 1156$, $P\bar{1}$, $a = 13.669$ (5) Å, $b = 17.423$ (7) Å, $c = 10.852$ (4) Å, $\alpha = 104.57$ (3)°, $\beta = 98.02$ (5)°, $\gamma = 88.43$ (3)°, $U = 2477$ Å^3, $d_{measd} = 1.53$ (3), $Z = 2$, d_{calcd} 1.549 g cm^{-3}, λ 0.70926 Å, μ(Mo Kα) = 29.9 cm^{-1}, $F(000) = 1152$.

Reflection intensities for the unique set of data were collected with the crystal mounted with a general orientation with the plane 402 approximately parallel to the Φ axis of a Picker FACS-1 computer-controlled four-circle diffractometer using niobium-filtered Mo Kα radiation and a scintillation detector with pulse height analysis. The data were collected in two stages. First, 1992 reflections having $0° < 2\theta < 30°$ were measured using a symmetrical θ–2θ scan of base width 1.5° (with allowance for dispersion) at a scan rate of 1°/min and a takeoff angle of 1.4°. Background counts of 20-sec duration were taken at either side of the reflection. The remaining reflections out to $2\theta = 45°$ were then measured by the stationary-crystal, stationary-counter technique using a takeoff angle of 2.3°. Each reflection peak was counted for 20 sec and 10 sec background counts were taken on either side of the reflection offset by 0.75° plus the correction for dispersion. Two standard reflections were measured at frequent intervals and were used to scale the two sets of data. Reflections (3252) having intensities greater than 2σ (where $\sigma = (\text{total count} + \text{background})^{1/2}$) were counted as observed; of these, the 1396 reflections in the range $0° < 2\theta < 30°$ were used for the initial solution of the structure. Lorentz and polarization factors were applied and the structure factors were calculated in the usual manner. No absorption correction was made; examination of the (402) reflection at $\chi = 90°$ as a function of Φ showed an extreme variation of less than 8% in intensity with only a 10° range of Φ affected.

Solution and Refinement of the Structure

A three-dimensional Patterson function based upon the 1396 observed inner reflections yielded the positions of the iridium and phosphorus atoms along with the positions of two probable light atoms, later identified as N(1) and C(31). The positions and temperature factors of these atoms together with a scale factor were varied through two cycles of least-squares refinement to $R = 22.3\%$, where $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. A further 43 atoms were located from the first electron-density difference synthesis, including six phenyl rings, F(1), O(1), and BF_4^-. A further two cycles of least-squares refinement varying the positions of all atoms, but only temperature factors of iridium and phosphorus, decreased R to 15.3%. At this stage the remainder of the structure of the complex cation was revealed in an electron density difference map, the only doubt being the number of atoms and dimensions of the iridium–nitrogen ring. The ring appeared to consist of an iridium and three nitrogen atoms; however, the apparent N–N distances of ~1.8 Å and interatomic angles (~90°), together with the presence of neighboring peaks in a subsequent difference map computed from this model, indicated that this ring was not yet correctly described. Nevertheless, this model refined to $R = 9.2\%$. Additional peaks distributed around the special positions $^1/_2$, $^1/_2$, 0 and 0, 0, $^1/_2$ were interpreted as benzene molecules of crystallization.

A proper description of the iridium–nitrogen ring was obtained by refining the atomic coordinates and temperature factors of all atoms, excluding the "nitrogen atoms" and solvent benzene from the structure factor calculations, whereupon the electron density difference map revealed four clear peaks corresponding to the four nitrogen atoms of the tetrazene moiety at sensible bond distances. Two cycles of refinement of this model lowered R to 7.2% which decreased further to 4.6% upon inclusion of the solvent benzene atoms. Fixed atom contributions were taken 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. Refine-

TABLE II

FINAL ANISOTROPIC THERMAL COEFFICIENTS[a] ($\times 10^3$ Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir[b]	359 (5)	338 (4)	332 (4)	−13 (2)	68 (2)	13 (3)
P(1)	46 (3)	41 (2)	41 (3)	2 (2)	12 (2)	4 (2)
P(2)	49 (3)	37 (2)	40 (3)	1 (2)	12 (2)	5 (2)
N(1)	40 (8)	52 (9)	52 (9)	−8 (7)	−2 (7)	22 (7)
N(2)	3 (6)	60 (8)	52 (8)	0 (6)	5 (6)	5 (7)
N(3)	53 (9)	45 (8)	37 (8)	−1 (7)	4 (7)	−3 (6)
N(4)	64 (9)	36 (8)	55 (9)	−15 (7)	7 (8)	−7 (7)
C(1)	51 (12)	51 (11)	68 (12)	−17 (9)	2 (9)	−19 (9)
O(1)	72 (9)	89 (9)	52 (8)	1 (7)	14 (7)	−7 (7)
F(1)	88 (8)	101 (9)	94 (9)	4 (7)	58 (7)	−23 (7)
F(2)	79 (9)	102 (9)	136 (11)	−2 (7)	58 (8)	−36 (8)
F(11)	88 (9)	109 (11)	195 (16)	−5 (8)	−11 (10)	59 (11)
F(12)	218 (18)	85 (10)	146 (14)	−64 (11)	−66 (12)	40 (9)
F(13)	153 (14)	147 (13)	118 (20)	−54 (11)	−72 (10)	51 (10)

[a] For the expression $\exp(-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23}))$. [b] Iridium value is $\times 10^4$ Å^2.

ment of the iridium atom and atoms F(11), F(12), and F(13) (but not F(14)) using anisotropic thermal parameters was justified by the appearance of the difference map at this stage and by the subsequent improvement in agreement to $R = 4.0\%$. The positions of the 44 aromatic hydrogen atoms were now calculated using a C–H bond distance[7] of 0.97 Å; about half of these could be clearly distinguished as separate peaks in the difference map at $\rho > 0.24$ (9) e/Å^3. Inclusion of these hydrogen atoms caused a significant improvement in the agreement ($R = 3.8\%$), and some alteration in the positions of the aromatic carbon atoms which were therefore refined further to a final $R = 3.6\%$ for the inner set of data. Examination of the carbon and hydrogen positions showed that the change this introduced in the C–H bond lengths was insufficient to warrant any further refinement using recalculated hydrogen atom positions. At this point there were no difference Fourier peaks or troughs greater than $\rho = 0.44$ (8) e/Å^3, the most prominent features being associated with the iridium and phosphorus atoms.

Structure factors were now calculated for the full 3252 observed reflections, the model yielding $R = 5.4\%$. Further refinement of two scale factors, atomic positions, and temperature factors with atoms Ir, P(1), P(2), F(1), F(2), C(1), O(1), F(11)–F(13), and N(1)–N(4) being treated anisotropically gave a final agreement factor $R = 4.9\%$ and a weighted R index of 5.8% ($wR = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$). The inclusion of anisotropic temperature factors was justified by the improved agreement in each case, and for all but one of these atoms the values of the appropriate tensor are physically sensible. The exception is N(2), for which U_{11} is close to zero (Table II) and the thermal ellipsoid shows extreme atomic motion perpendicular to the ring. The major features in the final electron-density difference map based upon the final structure parameters given in Table I were peaks and troughs up to 0.9 (1) e/Å^3 in the vicinity of Ir.

The weighting scheme used was $w = 1/A$ for $B \leq F_o \leq C$, $w = F_o/AB$ for $B > F_o$ and $w = C/AF_o$ for $C < F_o$, where A is a constant which reduces to unity the error in an observation of unit weight. Unobserved reflections were not used in the refinement. Final values were $A = 15$, $B = 55$, $C = 80$, and the error of fit was 0.975. This scheme gave constant $\Sigma w(|F_o| - |F_c|)^2/n$ for ranges of F_o and $\sin\theta$. Scattering factors for the neutral atoms and anomalous dispersion corrections for iridium were obtained from ref 8 with the exception of hydrogen which was taken from ref 7.

All calculations were performed on an IBM 360/50 computer. Programs used were FORDAP, crystallographic Fourier summation with optional numeric and alphanumeric plotting and peak searching (A. Zalkin), BUCILS, crystallographic structure factors and full-matrix least squares (University of Canterbury), ORFFE, a Fortran crystallographic function and error program (W. R. Busing, K. O. Martin, and H. A. Levy), ORTEP, a Fortran thermal-ellipsoid plot program for crystal structure illustrations (C. K. Johnson), and MEANPLANE, calculation of weighted mean planes through atom groups with esd's (M. E. Pippy and F. R. Ahmed).

Final fractional atomic coordinates and thermal parameters with esd's are listed in Tables I and II, selected interatomic distances and angles in Table III, and the equations for calculated mean planes in Table IV.[9]

Description and Discussion of the Structure

The structure consists of discrete pentacoordinate iridium complex cations and tetrafluoroborate anions together with benzene molecules of crystallization. The molecular configuration of the cation is shown in Figure 1. The environment of Ir is quite irregular but is closer to square-pyramidal geometry with P(1) as apex, and basal atoms N(1), N(2), C(1), and P(2); these four atoms are not, however, coplanar. In addition, the hydrogen atom bound to C(76) (an ortho position of a P(2) phenyl group) is located trans to P(1) at Ir···H 2.9 Å, with an angle H–Ir–P(1) 161°, probably blocking the sixth position of an octahedron.[10] The iridium atom is located 0.42 Å toward P(1) out of the best plane through N(1), N(2), C(1), and P(2).

The significant feature of the complex cation is the presence of the five-membered iridium–nitrogen heterocycle. The four nitrogen atoms are coplanar ($\chi^2 = 7.57$, $\chi^2 = 2.87$ before inclusion of the outer data) and the iridium atom is displaced only 0.095 Å out of this plane toward P(1). The N(3)–N(4) bond is significantly shorter than both N(1)–N(3) and N(2)–N(4), but the apparent difference between the latter two bond lengths is within experimental error, and could be accounted for by an error in one nitrogen atom position. In the structure[11] of 1,4-bis(*N*-ethyl-1,2-dihydrobenzthiazol-2-ylidene)tetrazene, $(C_9H_9N_3S)_2$, where the tetrazene moiety adopts a trans configuration the central N═N bond length is 1.26 Å and the adjacent N—N bonds 1.40 Å, in good agreement with those reported here.

---

[7] R. F. Stewart, E. F. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[8] "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

[9] A table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2827. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[10] M. A. Bennett, G. B. Robertson, R. Watt, and P. O. Whimp, *Chem. Commun.*, 762 (1971); N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, *ibid.*, 237 (1965).

[11] R. Allmann, *Acta Crystallogr.*, **22**, 246 (1967); *Angew. Chem., Int. Ed. Engl.*, **5**, 133 (1966).

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)

(a) Intramolecular Bonded Contacts

Ir–P(1)	2.340 (4)	C(11)–C(12)	1.379 (20)
Ir–P(2)	2.383 (4)	C(12)–C(13)	1.389 (22)
Ir–C(1)	1.806 (18)	C(13)–C(14)	1.352 (23)
Ir–N(1)	1.941 (13)	C(14)–C(15)	1.352 (23)
Ir–N(2)	1.971 (10)	C(15)–C(16)	1.393 (22)
P(1)–C(31)	1.829 (16)	C(16)–C(11)	1.384 (21)
P(1)–C(41)	1.811 (16)	C(21)–C(22)	1.421 (23)
P(1)–C(51)	1.796 (16)	C(22)–C(23)	1.418 (24)
P(2)–C(61)	1.820 (16)	C(23)–C(24)	1.375 (25)
P(2)–C(71)	1.834 (16)	C(24)–C(25)	1.289 (24)
P(2)–C(81)	1.815 (16)	C(25)–C(26)	1.393 (24)
C(1)–O(1)	1.166 (19)	C(26)–C(21)	1.374 (22)
N(1)–N(3)	1.400 (16)	Av C–C (phenyl groups[a])	1.382 (4)[c]
N(1)–C(11)	1.481 (18)		
N(2)–N(4)	1.350 (16)	Av C–C (benzene)	1.368 (14)[c]
N(2)–C(21)	1.456 (18)		
N(3)–N(4)	1.270 (16)		
F(1)–C(14)	1.397 (19)		
F(2)–C(24)	1.381 (21)		
B(1)–F(11)	1.330 (30)[b]		
B(1)–F(12)	1.317 (29)[b]		
B(1)–F(13)	1.295 (20)[b]		
B(1)–F(14)	1.426 (29)		

(b) Interatomic Angles (Excluding Those within Benzene and Triphenylphosphine Groups)

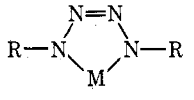
P(1)–Ir–P(2)	108.0 (1)	N(1)–N(3)–N(4)	112.2 (12)
P(1)–Ir–C(1)	88.8 (6)	N(3)–N(4)–N(2)	114.2 (12)
P(1)–Ir–N(1)	108.2 (4)	Ir–C(1)–O(1)	173.5 (15)
P(1)–Ir–N(2)	98.4 (4)		
P(2)–Ir–C(1)	89.2 (6)	F(11)–B(1)–F(12)	109.9 (24)
P(2)–Ir–N(1)	93.0 (4)	F(11)–B(1)–F(13)	114.0 (24)
P(2)–Ir–N(2)	153.2 (4)	F(11)–B(1)–F(14)	101.0 (22)
C(1)–Ir–N(1)	161.2 (6)	F(12)–B(1)–F(13)	117.0 (25)
C(1)–Ir–N(2)	96.0 (6)	F(12)–B(1)–F(14)	108.7 (23)
N(1)–Ir–N(2)	74.0 (5)	F(13)–B(1)–F(14)	104.6 (23)
C(31)–P(1)–Ir	113.1 (5)	N(1)–C(11)–C(12)	119.8 (13)
C(31)–P(1)–C(41)	98.5 (7)	N(1)–C(11)–C(16)	120.8 (13)
C(31)–P(1)–C(51)	105.1 (7)	C(12)–C(11)–C(16)	119.4 (14)
C(41)–P(1)–Ir	121.6 (5)	C(11)–C(12)–C(13)	122.0 (15)
C(41)–P(1)–C(51)	106.8 (7)	C(12)–C(13)–C(14)	115.0 (16)
C(51)–P(1)–Ir	110.2 (5)	C(13)–C(14)–C(15)	127.0 (17)
		F(1)–C(14)–C(13)	116.7 (16)
C(61)–P(2)–Ir	116.6 (5)	F(1)–C(14)–C(15)	116.3 (16)
C(61)–P(2)–C(71)	107.2 (7)	C(14)–C(15)–C(16)	116.6 (16)
C(61)–P(2)–C(81)	102.6 (7)	C(15)–C(16)–C(11)	120.1 (15)
C(71)–P(2)–Ir	109.9 (5)		
C(71)–P(2)–C(81)	99.6 (7)	N(2)–C(21)–C(22)	117.8 (15)
C(81)–P(2)–Ir	119.1 (5)	N(2)–C(21)–C(26)	121.4 (15)
Ir–N(1)–N(3)	119.7 (9)	C(22)–C(21)–C(26)	120.7 (17)
Ir–N(1)–C(11)	137.1 (9)	C(21)–C(22)–C(23)	117.5 (17)
N(3)—N(1)–C(11)	103.1 (10)	C(22)–C(23)–C(24)	117.6 (18)
		C(23)–C(24)–C(25)	124.6 (20)
Ir–N(2)–N(4)	119.6 (9)	F(2)–C(24)–C(23)	114.2 (18)
Ir–N(2)–C(21)	131.8 (10)	F(2)–C(24)–C(25)	121.1 (19)
N(4)–N(2)–C(21)	107.3 (11)	C(24)–C(25)–C(26)	120.6 (19)
		C(25)–C(26)–C(21)	118.8 (17)

(c) Selected Nonbonded Contacts (Å)

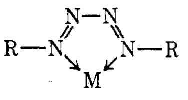
Ir···N(3)	2.90	N(1)···N(2)	2.35
Ir···N(4)	2.89	N(1)···N(4)	2.22
		N(2)···N(3)	2.20

[a] Triphenylphosphine groups. [b] Uncorrected for riding motion; corrected values are 1.380 (F(11)), 1.406 (F(12)), and 1.396 (F(13)). [c] Errors calculated form the formula $1/\sigma^2_{av} = \Sigma_{i=1}^{n} 1/\sigma_i^2$.

The short N(3)–N(4) bond indicates a formal valence structure III rather than the tetraazadiene ligand[12] formalism IV which was suggested in the case[13] of the iron complex $(Me_2N_4)Fe(CO)_3$. This is further supported by the fact that the aromatic rings are not coplanar with each other nor with the four nitrogen atoms whereas the conjugated π system in IV (R =



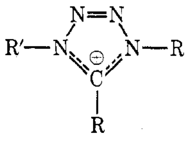
III



IV

FC_6H_4) would be expected to produce a near planar configuration. Instead the N(1), N(3), N(4) plane makes dihedral angles of 66 and 131° with the planes of phenyl rings C(1X) and C(2X), respectively, and these rings have a common dihedral angle of 65°.

Although the atoms C(11), N(1), N(2), N(3), N(4), and C(21) are not strictly coplanar, the departure from coplanarity is clearly quite small and certainly is much less than would be expected if the N(1) and N(2) lone pairs of electrons are localized. Indeed N(1) is closely coplanar with its three neighboring atoms. Delocalization of these electron pairs must be considered important, and in this regard we are struck by the similarity between this heterocyclic ring and the corresponding ring in tetrazolium salts[14] V. The N(1)–N(3) and N(2)–N(4) bond lengths of 1.40 and 1.35 Å indicate essentially single bonds, whereas the Ir–N bond lengths of 1.94 and 1.97 Å represent the lower extreme of the range (1.95–2.15 Å) suggested by Ibers and coworkers for M–N single bonds.[15] The overall geometry of the structure is therefore quite indicative of a representation of this complex ion as an iridio-2,5-di-*p*-fluorophenyltetrazolium ion I.



V

The apical iridium–phosphorus bond Ir–P(1) is significantly shorter than the equatorial bond Ir–P(2) by 0.043 Å, a difference which reflects the absence of a

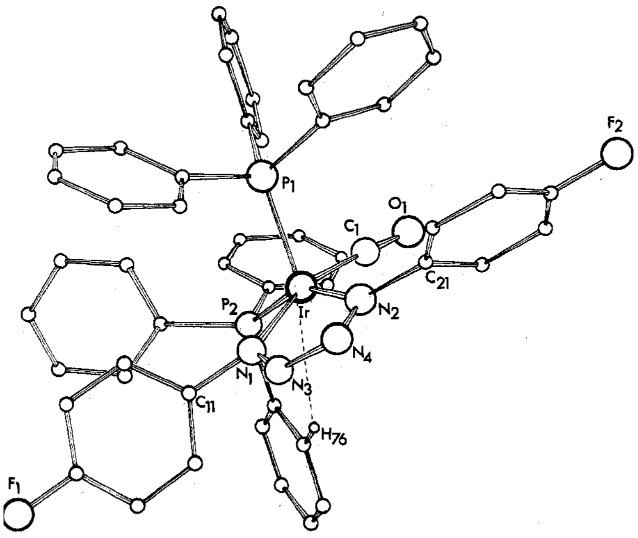


Figure 1.—A general view of the molecular configuration of the complex cation.

---

[12] R. J. Doedens, *Chem. Commun.*, 1271 (1968).

[13] M. Dekker and G. R. Knox, *ibid.*, 1243 (1967).

[14] L. A. Lee and J. W. Wheeler, *J. Org. Chem.*, **37**, 348 (1972).

[15] B. R. Davis, N. C. Payne, and J. A. Ibers, *Inorg. Chem.*, **8**, 2719 (1969).

TABLE IV

EQUATIONS FOR MEAN PLANES THROUGH SELECTED ATOMS, OF THE FORM $AX + BY + CZ + D = 0$

Plane	Atoms in plane	A	B	C	D	χ^2
1	N(1), N(2), N(3), N(4)	0.0376	0.9446	−0.3259	−1.8857	7.58
2	N(1), N(2), C(1), P(2)	0.2046	0.9604	−0.1872	−2.2021	184.8[a]
3	Ir, N(1), N(3), C(11)	0.0691	0.9243	−0.3754	−1.8708	4.03
4	Ir, N(2), N(4), C(21)	0.0340	0.9278	−0.3715	−1.8271	47.4[a]
5	N(1), N(2), N(3), N(4), C(11), C(21)	0.0648	0.9370	−0.3433	−1.8753	46.12[a]
6	C(11), C(12), C(13), C(14), C(15), C(16)	−0.6476	0.2000	−0.7353	1.1475	0.61
7	C(21), C(22), C(23), C(24), C(25), C(26)	−0.4602	−0.8029	−0.3789	2.5808	3.35

Deviations from the Planes (Å)

Plane 1: N(1), 0.011; N(2), −0.010; N(3), −0.020; N(4), 0.025; Ir, 0.095; C(11), −0.111; C(21), 0.150
Plane 2: N(1), 0.090, N(2), −0.080; C(1), 0.170; P(2), −0.007; Ir, 0.423; N(3), −0.242; N(4), −0.273
Plane 3: Ir, 0.000; N(1), 0.022; N(3), −0.007; C(11), −0.115
Plane 4: Ir, 0.000; N(2), −0.068; N(4), 0.032; C(21), 0.062
Plane 5: N(1), 0.049; N(2), −0.050; N(3), 0.001; N(4), 0.002; C(11), −0.026; C(21), 0.062; Ir, 0.094

[a] As noted in the text, these atoms are not coplanar.

ligand trans to P(1). A study of the electron-density difference map and the lack of further significant improvement upon refinement justifies the assignment of anisotropic motion to only three of the fluorine atoms of the BF_4^-. A correction for riding motion of these atoms yields values in good agreement with the B–F(14) length of 1.43 Å. There seems to be no clear explanation for the isotropic character of F(14); certainly there exist no nonbonded contacts which obviously restrain its movement.

The structure contains benzene molecules of crystallization located about the special positions $^1/_2, ^1/_2$, 0 and 0, 0, $^1/_2$. The isotropic temperature factors for the atoms in these molecules are rather high (~10 and ~14 Å^2, respectively). We experienced difficulty in obtaining acceptably close elemental analyses for this compound, and tentatively explain this as due to a small percentage of absences in the occupancy of these special positions by benzene.

An examination of the intra- and intermolecular contacts reveals nothing particularly noteworthy. The shortest H---H intramolecular contact involving nonadjacent aromatic hydrogen atoms is 2.1 Å between H(15) and H(83), and the majority are 2.3 Å or greater. There is no indication of hydrogen bonding to the fluorine, oxygen, or nitrogen atoms.

Acknowledgments.—We thank the National Research Council (Canada) for generous support of this work through operating grants, and Dr. D. G. Tuck for preliminary discussions leading to the commencement of this study.