The Crystal and Molecular Structure
of Iodocarbonylnitrosylbis(triphenylphosphine)iridium Tetrafluoroborate–Benzene, [IrI(CO)(NO)(P(C6H5)3)2][BF4]·C6H6

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The crystal and molecular structure of iodocarbonylnitrosylbis(triphenylphosphine)iridium tetrafluoroborate–benzene, [IrI(CO)(NO)(P(C6H5)3)2][BF4]·C6H6, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group D_{2h}^{15}-Pbca of the orthorhombic system with eight molecules in a cell of dimensions $a = 21.397$ (7), $b = 21.086$ (7), and $c = 18.524$ (6) Å. The observed and calculated densities are 1.71 (1) and 1.704 g cm^{-3}, respectively. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.059 for the 1162 independent reflections having $F^2 > 2\sigma(F^2)$. The crystal structure consists of well-separated monomeric units. The coordination geometry around the Ir is that of a distorted tetragonal pyramid, with CO, I, and *trans*-P atoms in the basal plane and the N of the nitrosyl group at the apex; the Ir lies slightly above the basal plane. The Ir–C bond length of 1.70 (5) Å is short, but the Ir–N bond length of 1.89 (3) Å is long. The Ir–N–O angle is 125 (3)°. The geometry of the cation is very similar to that of the chloro analog, IrCl(CO)(NO)(P(C6H5)3)2$^+$, and lends support to the hypothesis that NO$^+$ is acting as a σ acceptor in these systems.

Introduction

Structural and theoretical investigations of metal nitrosyls have established that the nitrosyl ligand usually acts as a σ donor (Lewis base), giving rise to linear M–N–O linkages with short M–N bonds. We have recently reported the preparation of [IrCl(CO)(NO)-(P(C6H5)3)2][BF4],[1] however, and have shown that this complex contains a distinctly bent M–N–O linkage and a long M–N bond.[1,2] We ascribed this difference in bonding to the amphoteric nature of NO$^+$ and suggested that in this complex the NO$^+$ acts as a σ-acceptor (Lewis acid) ligand. We also suggested that a similar explanation may account for the bent Co–N–O bond in Co(NO)(S2CN(CH3)2)2[3] and that the tetrahedral geometry around sulfur in IrCl(CO)(SO2)(P(C6H5)3)2[4] is the result of SO2 acting as a σ acceptor.

If this explanation were correct, the Ir–N and Ir–S bonds in these systems would be largely σ in character, there being very little π back-bonding from the metal to the ligand. If, however, the bent linkage were the result of some π-type interaction between the metal and the ligand, the Ir–N and Ir–S bonds would have considerable π character. In π-bonded complexes the bonding changes markedly with chemical substitution if the electron density at the central metal atom is changed. Thus, in the molecular oxygen complexes of the type IrX(CO)(O2)(P(C6H5)3)2 the O–O bond length is 1.30 Å when X = Cl[5] and 1.51 Å when X = I.[6] This change is ascribed to the greater electron density at the metal in the iodo complex; the more strongly the O2 group is

bound to the metal, the longer is the O–O bond.[6] If the NO$^+$ ligand were involved in π bonding to the Ir in the complexes IrX(CO)(NO)(P(C6H5)3)2$^+$, one would expect that there would be a large change in the Ir–N–O angle as well as in the N–O bond length on replacing Cl by I. If our explanation were correct, however, and the NO$^+$ ligand is σ bonded in these complexes, then little or no change in the Ir–N–O angle would be anticipated.

In order to test our hypothesis and also to further our studies of closely related five-coordinate transition metal complexes, we have undertaken the preparation and structure determination of IrI(CO)(NO)-(P(C6H5)3)2$^+$.

Collection and Reduction of the X-Ray Data

Violet, well-formed crystals of [IrI(CO)(NO)-(P(C6H5)3)2][BF4]·C6H6 were prepared by the reaction of IrI(CO)(P(C6H5)3)2 with NOBF4 in the manner previously described.[1] The infrared spectrum of the complex (Nujol mull) shows strong, sharp bands at 1720 and 2070 cm^{-1} which we ascribe to N–O and C–O stretches, respectively; these values compare with bands at 1680 and 2050 cm^{-1} found in the chloro complex.[1] *Anal.* Calcd for [IrI(CO)(NO)(P(C6H5)3)2][BF4]·C6H6: C, 48.42; H, 3.40; N, 1.31. Found: C, 48.65; H, 3.36; N, 1.31.

On the basis of optical goniometry and precession photography of the *hk0*, *h0l*, and *0kl* zones using Mo Kα radiation, we established that these crystals belong to the orthorhombic system. The observed extinctions are *0kl* for *k* odd, *h0l* for *l* odd, and *hk0* for *h* odd, which strongly suggests that the space group is D_{2h}^{15}-Pbca. The lattice constants, obtained by the least-squares procedure described below, are $a = 21.397$ (7), $b = 21.086$ (7), and $c = 18.524$ (6) Å. The observations were made at 23° with the wavelength assumed as λ(Mo Kα1) 0.70930 Å. A density of 1.704 g cm^{-3}, calculated for eight molecules in the unit cell, agrees with

(1) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, **90**, 4486 (1968).

(2) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

(3) P. R. H. Alderman and P. G. Owston, *Nature*, **178**, 1071 (1956); P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

(4) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966).

(5) J. A. Ibers and S. J. La Placa, *Science*, **145**, 920 (1964); S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965).

(6) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).

that of 1.71 (1) g cm^{-3} measured by flotation in diiodomethane–bromoethane solution. Hence, no crystallographic symmetry need be imposed on the complex.

Diffraction data were collected from a rhombic dipyramidal crystal approximately 0.14 mm on edge. The separation of the (1$\overline{1}\overline{1}$) and ($\overline{1}$11) faces was 0.111 mm, that of the (11$\overline{1}$) and ($\overline{1}\overline{1}$1) 0.149 mm, that of the (111) and ($\overline{1}\overline{1}\overline{1}$) 0.152 mm, and that of the (1$\overline{1}$1) and ($\overline{1}1\overline{1}$) 0.143 mm. The estimated errors in these measurements, namely, ±0.003 mm, result in errors in the absorption corrections which are small compared with those resulting from the numerical approximations involved. The crystal was mounted on a glass fiber normal to the ($\overline{1}$11) face, and in this orientation intensity data were collected at room temperature on a Picker automatic four-circle diffractometer using Mo Kα radiation. The mosaicity of the crystal was examined by means of the narrow-source, open-counter ω-scan technique. The width at half-height for a typical strong reflection was found to be approximately 0.06°, which is acceptably low.[7] Eighteen reflections from the crystal were accurately centered through a narrow vertical slit at a takeoff angle of 0.5°. These observations formed the basis for the least-squares refinement of cell parameters and orientation; the refinement was effected in our program PICK, as previously described.[8]

Intensity data were collected at a takeoff angle of 1.2°; at this angle the peak intensity of a typically strong reflection as a function of takeoff angle is approximately 80% of the maximum value. The receiving aperture size was approximately 4.0 mm × 4.0 mm, and the aperture was placed 29 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 1.0°/min. The scan range for all reflections was 1.5°, from −0.7 to +0.8° from the calculated 2θ value. Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan. The Mo Kα beam was filtered through 3.0-mil Nb foil after diffraction from the crystal. Attenuators were inserted automatically when the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan; the attenuators used were Cu foils, their thicknesses being chosen to give attenuator factors of approximately 2.3. These attenuator factors were determined as previously described.[9] The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak.

A unique data set having 2θ ≤ 30° was gathered; a total of 1703 independent intensities was recorded. The intensities of three standard reflections, measured after every 200 reflections, remained essentially constant throughout the run, showing only the deviations from the mean predicted from counting statistics. Because the crystal was rather small, there were very few reflections above background at values of 2θ > 30°. A more accurate structure determination would have been possible if a larger crystal had been available, but we were unable to grow crystals larger than the one used. Data of somewhat higher quality could have been obtained by using a lower scan rate and longer background counting times, but the signal-to-noise ratio increases rather slowly with time spent on each reflection.

All data processing was carried out as previously described.[8] The value of p in the expression for $\sigma(I)$ was selected as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects and for absorption. The absorption coefficient μ for this compound for Mo Kα radiation is 42.9 cm^{-1}, and for the sample chosen transmission coefficients were found to range from 0.55 to 0.64.[10] Of the 1703 independent intensities, 377 were less than their estimated standard deviations, 541 were less than twice their estimated standard deviations, and 659 were less than three times their estimated standard deviations.

Solution and Refinement

The position of the Ir atom was determined from a three-dimensional Patterson function, and one cycle of least-squares refinement of this position was run. All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c, the atomic scattering factors for Ir and I were taken from Cromer and Waber,[11] and those for hydrogen were taken from Stewart, Davidson, and Simpson;[12] scattering factors for all other atoms were from the tabulation of Ibers.[13] The effects of anomalous dispersion were included in calculations of F_c,[14] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer.[15] In the early stages of the refinement only the 1044 intensities greater than three times their estimated standard deviations were used.

A difference Fourier synthesis based on this first least-squares cycle revealed an approximately square-planar array around the iridium position. The highest peak was *cis* to two peaks which showed evidence of being bonded to other atoms and was *trans* to a peak which showed a tendency to split into two peaks. This highest peak was assigned to the I atom, the two *cis* peaks were assigned to P atoms, and the *trans* peak was assigned to the CO group. Positions for separate C and O atoms could not be deduced from this map but were calculated from a knowledge of the approximate Ir–C and C–O bond lengths. A least-squares refinement of the positions and isotropic thermal parameters of the six atoms was effected; the values of the agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (or weighted R factor) $= (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ were 0.211 and

(7) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(8) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(9) D. J. Hodgson and J. A. Ibers, *Acta Cryst.*, in press.

(10) In addition to various local programs, the programs for the CDC 6400 used in this analysis were local modifications of Hamilton's GONO9 absorption program, Busing and Levy's ORFFE function and error program, Zalkin's FORDAP Fourier program, and Johnson's ORTEP thermal ellipsoid plotting program.

(11) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

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

(13) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, Table 3.3.1A.

(14) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

(15) D. T. Cromer, *ibid.*, **18**, 17 (1965).

TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $[IrI(CO)(NO)(P(C_6H_5)_3)_2][BF_4] \cdot C_6H_6$

Atom	x	y	z	β_{11} or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0.12730 (8)	0.36466 (8)	0.01464 (7)	0.00145 (5)	0.00151 (5)	0.00218 (7)	−0.00024 (6)	0.00001 (6)	−0.00007 (6)
I	0.0503 (1)	0.4429 (1)	0.0845 (2)	0.0021 (1)	0.0028 (1)	0.0042 (1)	0.0000 (1)	0.0003 (1)	−0.0004 (1)
P$_1$	0.0482 (5)	0.2866 (5)	0.0228 (5)	0.0021 (4)	0.0016 (4)	0.0011 (4)	0.0002 (3)	−0.0003 (4)	−0.0005 (3)
P$_2$	0.2044 (5)	0.4426 (5)	0.0326 (5)	0.0017 (4)	0.0016 (4)	0.0018 (5)	0.0003 (3)	−0.0001 (4)	0.0002 (4)
C	0.182 (2)	0.307 (2)	0.004 (2)	6.1 (1.3)					
O$_1$	0.223 (1)	0.268 (1)	0.000 (1)	5.5 (8)					
N	0.109 (2)	0.385 (2)	0.917 (2)	7.0 (1.1)					
O$_2$	0.132 (1)	0.361 (1)	0.867 (2)	7.9 (8)					

Group	x_c^b	y_c	z_c	δ	ϵ	η	B, Å^2	α^c
R$_1^d$	0.0860 (5)	0.1479 (8)	0.9683 (8)	2.67 (3)	−2.03 (2)	−2.22 (3)	3.5 (4)	
R$_2$	0.9236 (7)	0.3094 (8)	0.9274 (7)	2.87 (2)	−2.98 (2)	−0.60 (1)	3.9 (5)	
R$_3$	0.0095 (8)	0.2646 (6)	0.1859 (9)	−1.58 (2)	−2.93 (2)	1.41 (1)	4.6 (5)	
R$_4$	0.3412 (8)	0.4087 (6)	0.9724 (9)	2.17 (3)	2.09 (2)	−2.29 (3)	4.6 (5)	
R$_5$	0.1889 (8)	0.5749 (8)	0.9511 (7)	1.85 (2)	2.80 (1)	−0.55 (1)	3.9 (5)	
R$_6$	0.2197 (6)	0.4657 (8)	0.2016 (9)	0.07 (2)	3.00 (2)	1.49 (1)	3.7 (5)	
R$_7$	0.0419 (10)	0.0091 (10)	0.2208 (7)	−3.17 (4)	3.14 (2)	3.15 (2)	9.2 (7)	
BF$_4$(1)	0.240 (1)	0.230 (1)	0.255 (1)	−2.74 (6)	−2.25 (3)	1.20 (5)	9.3 (1.7)	0.49 (5)
BF$_4$(2)	0.246 (2)	0.229 (1)	0.259 (2)	2.04 (4)	−3.00 (4)	2.95 (3)	12.5 (1.8)	0.51 (5)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] x_c, y_c, and z_c are the fractional coordinates of the group centers. The angles δ, ϵ, and η (in radians) have been defined previously.[4,5,16] [c] α is the multiplicity of the two disordered BF$_4^-$ groups, i.e., we have here a 49%–51% disorder. [d] Phenyl rings R$_1$, R$_2$, and R$_3$ are attached to P$_1$; rings R$_4$, R$_5$, and R$_6$ are attached to P$_2$. Ring R$_7$ is the benzene molecule.

0.275, respectively. A difference Fourier map computed at this stage showed five phenyl rings and provided evidence for the NO and BF$_4$ locations. The parameters obtained for these rings were refined by least squares, along with the parameters of the five known atoms. The phenyl rings were treated as rigid groups and restricted to their known geometry (D$_{6h}$ symmetry, C–C = 1.390 Å). The variable parameters for a ring included an over-all isotropic temperature factor, the coordinates of the ring center, and three orientation angles which have been defined previously.[4,5,16] This refinement yielded values of R_1 = 0.141 and R_2 = 0.202. A further difference Fourier synthesis showed the sixth phenyl ring, the BF$_4^-$ group, and the NO group. The probable location of the solvent molecule was also evident, but only three distinct peaks were present. A least-squares calculation including all non-hydrogen atoms except the solvent molecule, with anisotropic thermal parameters assigned to Ir and I, converged to values of R_1 = 0.091 and R_2 = 0.129. A difference Fourier map at this stage clearly revealed the solvent molecule and also indicated that there was disorder in the region of the BF$_4^-$ group. A least-squares calculation which included hydrogen atoms in the positions calculated for D$_{6h}$ symmetry with a C–H distance of 1.08 Å on all seven rings yielded values of R_1 = 0.058 and R_2 = 0.065. In this last calculation the BF$_4^-$ group also was included as a rigid group restricted to its known geometry (T$_d$ symmetry, B–F = 1.43 Å[17–19]). A difference Fourier synthesis at this stage showed evidence of disorder in the region of the BF$_4^-$ group, and another cycle of least squares was run with two BF$_4^-$ groups given multiplicities of α and $(1 - \alpha)$, the parameter α being varied with the appropriate constraints among the derivatives being taken into account.

This least-squares calculation yielded values of R_1 = 0.052 and R_2 = 0.057 and a value of α = 0.51 (4). At this stage we attempted to refine the structure with anisotropic thermal parameters assigned to all the non-group atoms, which gave a total of 137 variable parameters; because of this increase in the number of variables we decided to increase the number of observations by including the 118 reflections which had $2\sigma(F_o^2) < F_o^2 < 3\sigma(F_o^2)$ in the refinement. Unfortunately, the parameters for the carbonyl C atom obtained from this refinement were nonpositive definite by an insignificant amount. It may be that the number and quality of data available is insufficient for the refinement of these 137 parameters. Two final cycles were run, therefore, with the atoms of the carbonyl and nitrosyl groups refined isotropically and the Ir, I, and P atoms refined anisotropically, using the data greater than twice their estimated standard deviations. This yielded final values of R_1 = 0.059 and R_2 = 0.059 and a value of α = 0.49 (5); i.e., we have approximately a 50% disorder in the BF$_4^-$ group. In this final cycle no parameter exhibited a shift of more than 0.2 times its estimated standard deviation. The estimated error in an observation of unit weight is 1.50.

The value of R_2 obtained from the final cycle of least-squares refinement shows no dependence on $|F_o|$ or sin θ, which indicates that our choice of p = 0.04 is essentially correct. Comparison of the final values of $|F_o|$ and $|F_c|$ suggests to us that no correction for secondary extinction is necessary. A final difference map shows no peak higher than 0.9 e Å^{-3}, the average C atom having an electron density of approximately 4 e Å^{-3}; $\sigma(\Delta\rho)$ for this synthesis is 0.16 e Å^{-3}. Most of the 11 peaks greater than 0.5 e Å^{-3} are in the regions of the rings and the BF$_4^-$ groups and are presumably due to anisotropy of thermal motion of these groups.

The positional, thermal, and group parameters derived

(16) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).
(17) J. L. Hoard and V. Blair, *J. Am. Chem. Soc.*, **57**, 1985 (1935).
(18) D. Pendred and R. E. Richards, *Trans. Faraday Soc.*, **51**, 468 (1955).
(19) D. M. Chackraburtty, *Acta Cryst.*, **10**, 199 (1957).

from the final cycle of least-squares refinement are presented in Table I, along with the associated standard deviations of these parameters as estimated from the inverse matrix. The positional parameters of the ring carbon atoms and of the disordered boron and fluorine atoms which may be derived from the data in Table I are presented in Table II. The final values of $10|F_o|$

and $10|F_o|$ (in electrons) are given in Table III; only the 1162 reflections which were used in the refinement are included in Table III. The reflections for which $F_o^2 \leq 2\sigma(F_o^2)$ all have $|F_c| < 3\sigma(F_o)$.

Description of the Structure

The structure consists of discrete, monomeric ions well separated from the solvent molecule and from each other. The inner coordination geometry is shown in Figure 1, and the whole cation is shown in Figure 2.

TABLE II

Derived Parameters for Group Atoms[a]

Atom	x	y	z
R_1C_1	0.072 (3)	0.208 (1)	−0.005 (1)
R_1C_2	0.090 (2)	0.200 (1)	−0.077 (1)
R_1C_3	0.104 (1)	0.140 (1)	−0.103 (1)
R_1C_4	0.100 (3)	0.088 (1)	−0.058 (1)
R_1C_5	0.082 (2)	0.095 (1)	0.013 (1)
R_1C_6	0.068 (1)	0.155 (1)	0.040 (1)
R_2C_1	0.977 (1)	0.300 (1)	0.969 (1)
R_2C_2	0.965 (1)	0.359 (1)	0.938 (1)
R_2C_3	0.912 (1)	0.368 (1)	0.896 (1)
R_2C_4	0.870 (1)	0.318 (1)	0.886 (1)
R_2C_5	0.882 (1)	0.260 (1)	0.917 (1)
R_2C_6	0.935 (1)	0.251 (1)	0.959 (1)
R_3C_1	0.023 (2)	0.275 (1)	0.113 (1)
R_3C_2	−0.039 (1)	0.270 (1)	0.136 (1)
R_3C_3	−0.052 (1)	0.260 (1)	0.209 (2)
R_3C_4	−0.004 (2)	0.254 (1)	0.258 (1)
R_3C_5	0.058 (1)	0.259 (1)	0.236 (1)
R_3C_6	0.071 (1)	0.270 (1)	0.163 (2)
R_4C_1	0.282 (1)	0.420 (3)	0.001 (1)
R_4C_2	0.335 (1)	0.431 (1)	0.043 (1)
R_4C_3	0.394 (1)	0.419 (2)	0.015 (1)
R_4C_4	0.400 (1)	0.397 (3)	−0.056 (1)
R_4C_5	0.348 (1)	0.387 (1)	−0.098 (1)
R_4C_6	0.288 (1)	0.398 (2)	−0.070 (1)
R_5C_1	0.193 (1)	0.518 (1)	0.988 (1)
R_5C_2	0.242 (1)	0.561 (1)	0.991 (1)
R_5C_3	0.238 (1)	0.618 (1)	0.955 (1)
R_5C_4	0.185 (1)	0.632 (1)	0.914 (1)
R_5C_5	0.136 (1)	0.589 (1)	0.911 (1)
R_5C_6	0.140 (1)	0.531 (1)	0.948 (1)
R_6C_1	0.215 (1)	0.456 (1)	0.128 (1)
R_6C_2	0.222 (1)	0.405 (1)	0.174 (2)
R_6C_3	0.226 (1)	0.414 (1)	0.248 (1)
R_6C_4	0.224 (1)	0.475 (1)	0.276 (1)
R_6C_5	0.218 (1)	0.527 (1)	0.230 (2)
R_6C_6	0.213 (1)	0.517 (1)	0.156 (1)
R_7C_1	−0.023 (1)	0.011 (3)	0.222 (2)
R_7C_2	0.011 (2)	0.067 (2)	0.222 (1)
R_7C_3	0.076 (2)	0.065 (2)	0.221 (1)
R_7C_4	0.107 (1)	0.007 (3)	0.220 (2)
R_7C_5	0.073 (2)	−0.049 (1)	0.220 (1)
R_7C_6	0.008 (2)	−0.047 (1)	0.221 (1)
B(1)	0.240 (1)	0.230 (1)	0.255 (1)
F_1(1)	0.199 (3)	0.266 (4)	0.300 (2)
F_2(1)	0.238 (2)	0.255 (2)	0.183 (2)
F_3(1)	0.220 (5)	0.165 (2)	0.254 (2)
F_4(1)	0.302 (2)	0.234 (4)	0.283 (2)
B(2)	0.246 (2)	0.229 (1)	0.259 (2)
F_1(2)	0.278 (3)	0.171 (2)	0.274 (2)
F_2(2)	0.291 (2)	0.278 (2)	0.244 (3)
F_3(2)	0.210 (3)	0.247 (3)	0.321 (2)
F_4(2)	0.206 (2)	0.222 (3)	0.198 (2)

[a] C_1 is attached to P; other C atoms are numbered in succession so that C_4 is *para* to C_1.
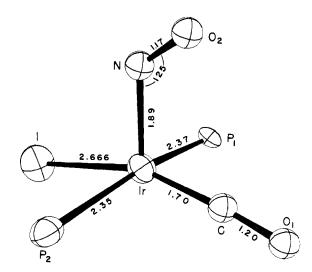

Figure 1.—Inner coordination sphere around Ir in the $IrI(CO)(NO)(P(C_6H_5)_3)_2^+$ cation.
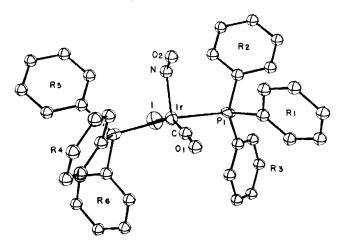

Figure 2.—View of the $IrI(CO)(NO)(P(C_6H_5)_3)_2^+$ cation. Phenyl hydrogen atoms are not shown. Phenyl carbon atoms are shown with $B = 2.5 \text{ Å}^2$.

The coordination polyhedron about the Ir is a distorted tetragonal pyramid, with *trans* P, I, and CO in the base and the N of NO at the apex. The Ir atom lies above the basal plane, the N–Ir–I, N–Ir–P₁, N–Ir–P₂, and N–Ir–C angles being 101 (1), 94 (1), 97 (1), and 101 (2)°, respectively. If the best weighted least-squares plane is determined using the coordinates of I, P₁, P₂, and C, then I, P₁, and P₂ do not deviate significantly from this plane, C lies 0.28 (4) Å below the plane, and Ir is 0.23 Å above the plane. The BF_4^- group occupies roughly the sixth coordination site, the closest Ir–B approach being 5.72 Å while the shortest Ir–F separa-

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) IN ELECTRONS FOR $[IrI(CO)(NO)(P(C_6H_5)_3)_2][BF_4] \cdot C_6H_6$

H	K	FO	FC
***** L = 0 *****			
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2	2	997	945
2	3	3821	3767
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2	5	3266	3203
2	6	1219	1485
2	8	1818	1774
2	9	3866	3917
2	10	1063	1151
2	11	717	590
2	12	1041	849
2	13	5767	5666
2	14	1000	948
4	0	1915	1994
4	1	1982	1870
4	2	624	789
4	3	3426	3407
4	4	8569	8571
4	5	2150	2368
4	6	3585	3508
4	7	1757	1780
4	8	4895	4959
4	9	1250	1242
4	10	921	1027
4	12	2306	2209
4	13	1637	1492
4	14	2086	2236
6	0	4628	4545
6	1	1164	1197
6	3	1344	1010
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6	6	2041	2070
6	7	3034	3147
6	9	5014	5273
6	11	2075	2097
6	13	1088	1213
8	0	1434	1444
8	1	933	984
8	2	1133	1026
8	3	1255	1088
8	4	6155	6178
8	6	2857	2939
8	8	5426	5621
8	12	1432	1294
8	13	1159	1127
10	0	1487	1488
10	1	2774	2882
10	3	2492	2605
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10	9	4323	4114
10	10	1980	1763
12	0	7457	7207
12	1	1646	1618
12	3	830	794
12	4	2200	2295
12	8	1396	1425
14	0	972	1236
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14	2	710	102
14	3	3759	3667
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1	4	1033	1045
1	6	2062	2094
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1	10	1599	1548
1	11	5299	5271
1	12	3208	3092
1	14	2161	2198
1	15	2925	2902
2	1	1449	1364
2	2	502	440
2	3	791	670
2	4	813	481
2	6	2278	2325
2	7	628	490
2	11	872	778
2	12	878	1042
3	1	2603	2252
3	2	4054	3811
3	3	3234	3106
3	4	1778	1639
3	5	912	1003
3	6	2103	1829
3	7	5363	5525
3	8	2008	1965
3	9	817	755
3	10	2208	2290
3	11	2179	2193
3	12	2559	2530
3	14	2566	2518
3	15	1592	1717
4	3	942	614
4	4	1030	910
4	7	746	815
4	8	752	448
4	9	737	598
4	11	880	865
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5	3	2470	2567
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5	10	2745	2735
5	11	2028	2116
6	1	3154	3291
6	3	2457	2475
6	4	616	614
6	7	1327	1096
6	9	773	700
6	13	734	33
7	2	836	892
7	3	4981	5022
7	4	2692	2837
7	5	1551	1513
7	6	5398	5456
7	7	4251	4479
7	8	1511	1407
7	9	1723	1726
7	10	2551	2651
7	11	801	984
8	1	614	549
8	2	706	597
8	6	1491	1579
8	9	766	467
8	12	1012	709
9	2	3667	3796
9	3	2706	2769
9	4	1346	1350
9	5	1017	992
9	6	3055	3010
9	7	3846	3932
9	8	1360	1439
9	9	1399	1582
9	10	2642	2651
9	11	1288	1349
9	12	2006	1963
10	1	1027	1410
10	2	953	816
10	4	1108	1249
10	6	1049	1140
11	1	4874	4859
11	2	2685	2627
11	3	2204	2251
11	5	1441	1302
11	6	2251	2329
11	9	801	439
11	10	1513	1341
12	1	1528	1064
12	2	1417	849
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13	2	4674	4618
13	3	1504	1601
13	6	1044	1098
13	8	1363	1229
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15	1	2225	2367
15	2	2472	2531
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1	2	1306	1216
1	3	2568	2435
1	4	1750	1703
1	5	3519	3639
1	7	754	760
1	8	1494	1633
1	10	1615	1516
1	11	1242	1103
1	13	1871	1743
1	15	889	561
2	0	1558	1579
2	1	5205	4848
2	2	2562	2239
2	3	2963	2833
2	5	3997	4129
2	6	735	619
2	9	3456	3502
2	10	751	664
2	13	4693	4678
3	0	3389	3038
3	1	1072	976
3	3	976	708
3	5	2447	2535
3	7	1080	1092
3	8	998	1206
3	10	2131	2036
3	11	894	1076
3	14	833	752
4	0	8373	8013
4	1	1477	1311
4	2	1035	871
4	3	2006	1950
4	4	4408	4545
4	5	1191	1361
4	6	1255	1257
4	8	4579	4704
4	9	830	793
4	10	1890	1971
4	12	1394	1534
4	14	1516	1684
5	0	4309	4459
5	1	1643	1612
5	2	2496	2615
5	3	728	551
5	6	1775	1821
5	8	1969	2071
5	10	1616	1676
6	0	712	781
6	1	2400	2419
6	3	2308	2276
6	5	6665	6770
6	6	1197	1371
6	7	3058	3165
6	9	3896	3901
6	13	1440	1571
7	0	2611	2690
7	1	1057	1127
7	2	1873	2023
7	3	1018	1158
7	5	2128	1962
7	6	1212	1156
7	7	918	872
7	8	2261	2364
7	10	871	801
7	11	1126	1177
7	13	802	647
8	0	2146	2156
8	1	806	739
8	2	1313	1470
8	3	800	658
8	4	4399	4582
8	6	1188	1514
8	8	4577	4611
8	9	743	233
8	10	1558	1576
8	12	1591	1649
9	0	1060	967
9	1	1454	1503
9	2	877	869
9	3	999	1066
9	5	1871	2050
9	7	1176	986
9	9	671	98
9	11	987	813
10	0	2067	2153
10	1	2573	2480
10	3	1420	1490
10	4	624	484
10	5	2743	2854
10	7	1250	1262
10	9	4061	4031
10	10	969	1014
11	1	1792	1761
11	2	676	168
11	3	2080	2109
11	5	1704	1729
11	6	854	573
11	10	996	252
12	0	4935	4840
12	4	2850	2860
12	6	726	452
12	8	1768	1646
13	0	2322	2478
13	2	1210	1143
13	3	1049	684
13	5	1135	886
13	7	909	639
13	8	1102	923
14	1	3050	3148
14	3	2776	2931
14	5	1571	1625
15	0	1204	1329
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0	12	3012	3149
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1	2	4446	4064
1	3	1961	1987
1	4	877	869
1	6	1751	1712
1	7	3025	3143
1	8	1040	1085
1	10	1944	1999
1	11	3048	2935
1	12	2330	2132
1	14	1542	1388
2	1	4205	3773
2	2	602	596
2	3	1275	1114
2	4	2648	2774
2	5	680	525
2	6	2068	2216
2	7	904	915
2	8	1153	979
2	9	1268	1113
2	10	725	835
2	11	1987	2051
2	12	1154	843
3	1	2013	1884
3	2	3586	3434
3	3	2778	2868
3	4	826	901
3	5	756	725
3	6	3502	3574
3	7	3055	3047
3	8	1151	1055
3	10	1934	2027
3	11	3208	3257
3	12	1440	1416
3	13	742	298
3	14	1481	1441
4	1	4323	4438
4	3	1006	1089
4	6	1680	1608
4	7	2230	2355
4	9	1458	1700
4	10	682	687
4	11	1504	1544
5	1	873	789
5	2	4429	4406
5	3	1484	1511
5	4	717	631
5	5	1833	1807
5	6	3481	3495
5	7	3689	3866
5	8	1904	1787
5	9	667	410
5	11	1984	1908
5	12	1641	1595
5	14	1574	1507
6	1	2065	2141
6	3	2183	2228
6	6	1115	1006
6	7	3925	3990
6	9	2532	2560
6	11	1002	885
7	1	2973	2933
7	2	2305	2276
7	3	2856	2773
7	5	2070	2081
7	6	3110	3263
7	7	3284	3218
7	8	1863	1822
7	9	977	817
7	10	1733	1799
7	11	1877	1875
7	12	1040	839
8	1	703	932
8	4	2320	2275
8	6	2865	2938
8	7	796	666
8	9	808	722
8	10	1324	1339
9	1	1519	1455
9	2	2504	2478
9	3	1984	1910
9	4	1585	1504
9	5	936	844
9	6	2567	2641
9	7	1980	2140
9	8	1180	1042
9	10	2265	2150
9	11	2462	2393
9	12	1457	1388
10	1	638	405
10	2	1604	1414
10	3	1560	1566
10	4	1885	2158
10	6	1691	1590
10	11	1212	1128
11	1	1913	1873
11	2	3043	2978
11	3	2872	2842
11	5	1065	1103
11	6	1546	1506
11	7	1995	2099
11	8	835	737
11	9	929	867
11	10	1276	1321
12	2	1951	2051
12	4	1619	1717
12	6	883	784
12	8	1187	976
12	9	797	837
13	1	1738	1710
13	2	2854	2863
13	3	1810	1748
13	6	1520	1468
13	7	1406	1185
14	1	2267	2227
14	3	779	524
15	1	1877	1835
15	2	1798	1796
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0	12	1559	1577
0	14	2486	2479
1	0	1257	1050
1	1	678	727
1	2	922	859
1	3	3943	4078
1	3	3814	4076
1	5	875	1027
1	7	1689	1735
1	9	829	816
1	10	2389	2574
1	12	758	646
1	13	2344	2275
1	14	1225	1167
2	0	2498	2452
2	1	4643	4607
2	2	924	939
2	3	1201	1362
2	5	4659	4958
2	6	890	907
2	7	1941	1844
2	8	928	1208
2	9	3005	3098
2	10	1446	1415
2	11	1001	1007
2	13	2767	2638
3	0	3702	3791
3	1	1026	1011
3	4	1056	997
3	5	2252	2381
3	6	608	425
3	7	1181	1057
3	9	1848	1757
3	10	1976	1980
3	11	747	895
3	12	1028	938
3	14	1135	937
4	0	832	1058
4	2	693	760
4	3	1676	1809
4	4	3930	4051
4	5	1128	969
4	6	1672	1761
4	8	2957	2889
4	10	2011	1908
4	11	1116	1300
4	12	2127	2167
4	13	1162	808
4	14	2007	2153
5	0	2166	2329
5	1	653	540
5	2	1614	1796
5	4	1977	1824
5	5	2167	2078
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5	8	2461	2543
5	10	890	919
5	13	735	528
6	0	630	535
6	1	2706	2825
6	2	607	523
6	3	3749	3733
6	5	2461	2407
6	6	786	621
6	9	3221	3314
6	13	2770	2604
7	0	3381	3506
7	2	1337	1320
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7	4	1379	1306
7	5	2310	2440
7	6	2018	1947
7	7	1774	1654
7	8	2102	2185
7	9	869	1066
7	11	771	497
8	0	3483	3684
8	2	1372	1377
8	4	3942	3891
8	5	1390	1263
8	6	701	825
8	8	2200	2325
8	10	2793	2707
8	12	2110	1955
9	0	2222	2169
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9	4	951	1023
9	5	1455	1604
9	7	1261	1216
9	9	1197	1326
10	1	2231	2323
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10	3	1557	1441
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10	7	1098	1088
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11	2	920	884
11	3	2547	2504
11	5	797	830
11	7	998	932
11	9	880	556
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12	2	933	1194
12	3	833	743
12	4	2662	2812
12	5	837	996
12	6	1452	1540
12	8	2872	2941
13	0	2845	2932
13	1	917	895
13	3	1159	956
13	5	983	565
13	6	750	463
14	0	1118	1367
14	1	2397	2330
14	5	2833	2762
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1	3	4166	4300
1	4	2581	2583
1	6	2907	3020
1	7	4074	4207
1	9	2465	2595
1	10	1527	1435
1	11	1389	1328
1	12	1718	1880
1	14	1043	865
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2	3	2232	2212
2	5	1146	1138
2	6	891	1097
2	7	837	799
2	11	2097	2129
3	1	4299	4278
3	2	1863	1865
3	3	1010	995
3	4	2660	2834
3	5	1646	1813
3	6	3314	3439
3	7	1627	1795
3	8	1287	1309
3	9	962	877
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4	2	2721	2623
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4	6	1786	1928
4	7	665	979
4	8	912	1066
4	10	975	1080
4	12	761	728
5	1	835	746
5	2	4842	4955
5	3	2233	2369
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5	5	1021	767
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6	9	1236	1149
7	1	2880	3029
7	2	3541	3537
7	3	2014	1971
7	4	942	1038
7	5	2030	1953
7	6	871	959
7	7	2010	2108
7	8	1296	1222
7	10	900	881
7	11	2699	2710
7	12	2167	2061
8	2	1516	1446
8	4	1022	1240
8	5	731	558
8	6	3144	3106
8	8	961	937
8	10	999	1238
8	11	1030	820
9	1	2872	2926
9	2	2021	2018
9	3	696	728
9	4	1417	1352
9	5	1756	1768
9	6	2686	2621
9	7	1023	845
9	8	969	975
9	9	1532	1411
9	10	1876	1969
9	11	2669	2505
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10	3	1670	1565
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10	5	1077	820
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11	2	2783	2926
11	3	3185	3158
11	6	1066	1295
11	7	3161	2922
11	9	2312	2205
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1	10	1365	1378
1	12	825	952
1	13	1283	1319
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2	2	2471	2453
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2	5	4628	4598
2	6	1614	1709
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2	8	1277	1310
2	9	3382	3386
2	10	2372	2364
2	11	1292	1194
2	13	2040	1983
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3	1	2431	2364
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3	3	1157	1155
3	4	1517	1563
3	5	1525	1483
3	6	831	849
3	8	1775	1828
3	9	1711	1752
3	10	934	978
3	12	1086	1021
3	13	1319	1373
4	0	3428	3424
4	1	1808	1962
4	3	2458	2359
4	4	3689	3790
4	5	2252	2403
4	6	1540	1594
4	8	2054	2120
4	10	2470	2452
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4	12	1951	1913
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5	0	1192	1256
5	1	1862	1727
5	2	937	786
5	4	2725	2705
5	5	2045	2255
5	6	696	756
5	8	1527	1724
5	9	2020	1989
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5	12	821	621
6	1	2527	2564
6	2	856	689
6	3	4372	4431
6	5	1135	1096
6	9	2790	2880
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7	5	1653	1682
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7	7	715	132
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7	10	880	782
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8	2	1298	1426
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9	2	906	1019
9	3	1623	1591
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9	5	1345	1265
9	6	778	584
9	8	1516	1728
9	9	782	873
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10	2	2486	2417
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10	4	748	640
10	5	2285	2324
10	6	1013	1166
10	7	971	1044
10	8	2100	1981
10	9	2962	2837
11	0	1016	1031
11	1	1682	1661
11	4	1335	1224
11	5	1183	1125
12	0	1677	1792
12	2	1612	1495
12	4	2552	2457
12	5	1239	1216
12	6	1648	1523
12	7	925	721
13	0	1940	1739
13	1	847	913
13	3	785	452
13	4	1201	1329
13	5	814	190
***** L = 7 *****			
0	2	3127	3175
0	4	1367	1367
0	6	2256	2556
0	8	678	714
0	10	2066	2165
0	12	1094	905
1	1	1314	1043
1	2	2974	2894
1	3	2811	2932
1	4	1191	1469
1	6	2137	2194
1	7	2702	2752
1	8	876	893
1	9	2046	2095
1	10	2255	2243
1	11	1033	1052
1	12	1187	1349
2	1	934	838
2	2	1730	1985
2	3	2643	2733
2	4	1395	1560
2	5	829	864
2	6	857	773
2	7	1986	2107
2	8	699	641
2	9	1368	1334
2	10	867	685
2	11	1799	1813
3	1	3201	3158
3	2	1666	1449
3	3	2005	2014
3	4	2622	2629
3	5	1080	948
3	6	3129	3085
3	7	1849	1666
3	8	696	588
3	10	1799	1726
3	11	2261	2419
4	1	1393	1590
4	2	2929	2870
4	5	1027	984
4	6	1738	1777
4	8	1162	1156
4	9	1763	1780
4	10	1606	1580
4	11	957	767
4	12	1367	1266
5	2	3636	3929
5	3	2203	2060
5	4	1583	1675
5	5	1560	1613
5	6	715	854
5	7	2448	2483
5	8	1717	1802
5	10	904	746
5	11	1580	1428
5	12	2211	2163
6	1	2197	2211
6	3	829	882
6	4	757	944
6	5	1933	2045
6	7	2228	2093
6	8	860	713
6	11	1846	1720
7	1	2161	2061
7	2	2697	2817
7	3	1849	1703
7	4	1499	1379
7	5	1639	1729
7	7	1651	1784
7	8	1261	1246
7	9	989	667
7	11	2258	2103
8	2	2768	2987
8	3	1133	1064
8	6	2068	2078
8	7	1081	900
8	8	1513	1620
8	9	807	728
8	10	1013	1061
9	1	3104	3204
9	2	2148	2151
9	4	749	978
9	6	2754	2734
9	9	1100	806
10	1	1689	1660
10	3	1914	1946
10	4	1825	1942
10	5	1171	1155
10	6	869	885
10	7	1714	1733
11	2	2178	2100
11	3	2754	2767
11	7	2779	2817
12	1	948	781
12	2	1764	1758
13	2	1655	1483
13	3	1642	1449
***** L = 8 *****			
0	0	4078	3863
0	2	1839	1823
0	4	2330	2264
0	6	1585	1767
0	8	2423	2396
0	12	1324	1400
1	0	3305	3424
1	1	1384	1436
1	2	863	772
1	3	1009	906
1	4	2379	2301
1	5	3423	3557
1	7	1407	1151
1	8	1691	1637
1	9	2035	2004
1	11	1479	1440
1	12	1058	928
2	0	1915	1383
2	1	2758	2713
2	2	1643	1630
2	3	1205	1103
2	5	3138	3202
2	7	1587	1498
2	8	1090	1130
2	9	2856	2890
3	0	655	308
3	1	2042	1996
3	2	2968	2653
3	3	2326	2365
3	4	1998	1992
3	6	1303	1299
3	7	757	571
3	8	3068	3014
3	9	1735	1750
3	10	848	787
4	0	2458	2427
4	3	1704	1608
4	4	3845	3941
4	6	1703	1607
4	7	823	639
4	8	2423	2347
4	10	1561	1558
5	0	3056	3120
5	1	1876	1999
5	2	2043	2216
5	4	2713	2602
5	5	2570	2667
5	7	840	1039
5	8	699	164
5	9	1421	1541
5	10	2407	2367
6	1	1958	1947
6	3	2451	2499
6	5	1223	1388
6	7	744	262
6	9	2860	2754
7	0	2080	2010
7	1	1045	1229
7	2	1136	1172
7	3	710	841
7	4	1679	1669
7	5	946	967
7	9	1673	1815
7	10	1468	1662
8	0	3414	3424
8	4	2655	2643
8	8	1586	1573
9	0	770	721
9	1	1967	1985
9	3	2983	2845
9	4	1935	1807
9	6	1517	1244
9	8	1871	1880
10	1	1979	1904
10	2	1265	1090
10	3	1291	1356
10	5	2495	2315
11	0	2208	2104
11	1	1058	1007
11	2	1016	988
11	4	1376	1344
11	5	2435	2415
12	0	1518	1849
12	2	822	792
***** L = 9 *****			
0	2	2009	2205
0	4	1900	2042
0	6	2962	2950
0	10	2816	2922
1	2	1789	1851
1	3	2235	2313
1	4	995	1062
1	5	870	848
1	6	1603	1604
1	7	1259	1283
1	8	935	599
1	10	1237	1266
1	11	1140	1235
2	1	854	847
2	2	1558	1633
2	3	2665	2766
2	4	2849	2823
2	5	803	658
2	6	1267	1305
2	7	2742	2699
2	8	946	792
2	9	1260	1389
2	10	1377	1223
2	11	1724	1820
3	1	1635	1641
3	2	1725	1662
3	3	1661	1734
3	5	885	829
3	6	1301	1134
3	7	1691	1775
3	8	970	1134
3	10	974	859
3	11	1309	1237
4	1	2685	2707
4	2	2675	2601
4	3	1243	1245
4	5	955	1148
4	6	2167	2194
4	7	976	872
4	8	1478	1499
4	9	2423	2482
4	10	1542	1562
5	1	1551	1519
5	2	1668	1690
5	3	1698	1567
5	5	1289	1338
5	6	1745	1700
5	7	1477	1418
5	8	830	902
5	10	1428	1406
6	1	2725	2676
6	3	1389	1391
6	5	2146	2079
6	7	1755	1941
7	1	1237	1131
7	2	1218	1060
7	3	1694	1721
7	5	764	795
7	6	1322	1324
7	7	1212	1396
7	8	802	594
8	1	1055	1108
8	2	3167	3126
8	3	1564	1599
8	4	1098	865
8	6	2055	1895
8	7	868	720
8	8	1758	1681
9	2	2334	2248
9	3	1296	1240
9	5	930	610
9	6	1530	1701
9	7	1318	1220
10	1	1788	1955
10	2	898	731
10	3	1671	1625
10	4	2517	2428
11	1	931	919
11	2	1132	1092
11	3	1272	1399
***** L = 10 *****			
0	0	3481	3613
0	4	1872	1949
0	8	1003	862
0	10	1082	1215
1	0	2660	2813
1	1	1924	1916
1	4	2124	2276
1	5	2569	2571
1	7	1570	1517
1	8	1275	1099
1	9	1533	1646
2	1	1844	1938
2	2	1412	1470
2	3	1415	1349
2	5	1121	1208
2	8	989	1101
2	9	1747	1724
3	0	1770	2012
3	1	1294	1456
3	2	1421	1589
3	3	2001	2042
3	4	2044	2120
3	6	1187	1155
3	8	2372	2277
3	9	1920	1799
4	0	2579	2562
4	3	1327	1470
4	4	2529	2569
4	5	979	857
4	6	1023	1038
4	8	2107	2101
5	0	3187	3167
5	1	1291	1321
5	2	1439	1396
5	3	1030	878
5	4	2176	2220
5	5	1945	2084
5	8	769	723
5	9	1115	1391
6	3	1044	1142
6	5	2628	2516
6	7	812	643
7	0	2378	2250
7	1	1143	1156
7	2	1280	1329
7	3	1632	1604
7	4	1572	1798
7	5	1323	1412
8	0	1210	1133
8	3	817	946
8	4	1978	1872
8	6	788	833
9	0	950	845
9	1	1059	1059
9	2	1259	1146
9	3	2440	2269
9	4	1534	1456
10	0	1001	956
10	1	1307	1352
10	2	951	804
***** L = 11 *****			
0	2	2990	2942
0	4	1366	1219
0	6	2135	2205
0	8	876	974
1	1	2687	2589
1	2	1491	1469
1	4	734	31
1	5	1099	1200
1	6	757	979
2	1	1393	1415
2	2	805	568
2	3	2933	2958
2	4	1406	1310
2	5	925	692
2	7	2546	2615
2	8	924	941
3	2	1863	1865
3	3	1948	1996
3	4	1159	1128
3	7	1744	1607
4	2	2495	2517
4	6	2665	2744
4	8	1269	1179
5	1	1183	1119
5	4	1888	1652
5	6	1949	1667
5	7	850	731
6	1	2422	2324
6	3	1675	1704
6	5	1462	1732
7	3	1106	1022
8	2	2478	2459
9	1	1103	689
***** L = 12 *****			
0	0	2990	2555
0	4	1644	1409
1	0	2693	2641
1	1	2048	1947
1	3	1106	1119
1	4	2143	2109
1	5	1493	1393
1	7	768	527
2	0	906	506
2	1	1612	1660
2	2	1079	1201
2	3	1085	988
3	0	2479	2521
3	1	1451	1292
3	3	1521	1606
3	4	1667	1659
3	5	1592	1586
4	0	1109	1053
4	1	941	933
4	3	1447	1329
4	4	1307	1334
4	5	2174	1951
5	0	1370	1315
5	1	1019	964
5	4	2247	2073
5	5	1797	1781
6	0	1052	748
7	0	1293	1450
7	1	1218	1317
***** L = 13 *****			
0	2	4045	3916
1	1	1150	1121
1	2	937	915
2	1	2540	2356
2	3	2299	2275
3	2	1562	1391
3	3	1090	1129

tion is 4.58 Å. The closest approach between the BF_4^- group and the cation is an O_2–F separation of 3.27 Å. The molecule of benzene solvent is packed so as to be as far as possible from the phosphine groups on the neighboring cations, its location in the unit cell being closest to the NO group and the I atom. The shortest H · · · H separation between the benzene molecule and the phosphine groups is 2.55 Å. The closest approaches of the benzene molecule to the inner coordination sphere of the cation are an O_2–H separation of 2.95 Å and an I–H distance of 3.71 Å. All of these interactions are normal.

The B_1–B_2 separation is 0.15 Å, and so the two orientations of the BF_4^- group do not have a common center. The polyhedron formed by the eight F atoms from the two orientations of the BF_4^- group is irregular. One can generate approximately the second orientation of the BF_4^- group by rotating the first group 60° around one of the B–F vectors.

A selection of intramolecular distances and angles in the cation is given in Table IV. These distances are all within one standard deviation of the values obtained after the attempt to refine the atoms of the carbonyl and nitrosyl groups anisotropically. The root-mean-square amplitudes of vibration of the atoms which were refined anisotropically range from 0.12 to 0.28 Å. The directions of the principal axes of the ellipsoids are displayed, at least in part, in the figures.

The geometry of the cation is very similar to that found in the chloro analog,[2] and a comparison of the bond lengths and angles found in the two cations is also given in Table IV. The difference of 0.323 Å between the Ir–I and Ir–Cl distances is approximately equal to

TABLE IV
SELECTED INTRAMOLECULAR DISTANCES AND ANGLES
IN $IrX(CO)(NO)P(C_6H_5)_3)_2^+$

Intramolecular dist, Å			Angle, deg		
	X = I	X = Cl[a]		X = I	X = Cl[a]
Ir-N	1.89 (3)	1.97 (1)	N-Ir-P1	94 (1)	90.1 (3)
Ir-P1	2.37 (1)	2.408 (3)	N-Ir-P2	97 (1)	91.3 (3)
Ir-P2	2.35 (1)	2.407 (3)	N-Ir-X	101 (1)	101.3 (3)
Ir-X	2.666 (3)	2.343 (3)	N-Ir-C	101 (2)	97.4 (5)
Ir-C	1.70 (5)	1.86 (1)	P1-Ir-P2	168.2 (3)	175.7 (1)
Ir-O1	2.89 (3)	3.02 (1)	P1-Ir-X	87.6 (3)	88.9 (1)
Ir-O2	2.74 (3)	2.79 (1)	P1-Ir-C	90 (1)	91.2 (3)
N-O2	1.17 (4)	1.16 (1)	P2-Ir-X	86.1 (3)	86.8 (1)
C-O1	1.20 (4)	1.16 (1)	P2-Ir-C	91 (1)	92.7 (3)
N-P1	3.13 (4)	3.11 (1)	X-Ir-C	158 (1)	161.3 (3)
N-P2	3.20 (3)	3.15 (1)	Ir-C-O1	176 (4)	178.1 (9)
N-X	3.56 (3)	3.35 (1)	Ir-N-O2	125 (3)	124.1 (9)
N-C	2.78 (6)	2.88 (2)	C1[b]-P-C1[b]	104.5	105.9
P1-P2	4.70 (2)	4.811 (4)	(av of 6)		
P1-X	3.49 (1)	3.328 (4)			
P1-C	2.92 (5)	3.07 (1)			
P2-X	3.44 (1)	3.265 (4)			
P2-C	2.94 (5)	3.11 (1)			
X-C	4.28 (3)	4.15 (1)			
P-C1[b]	1.81	1.81			
(av of 6)					

[a] Reference 2. [b] Phenyl C atom.

the value of 0.34 Å calculated for the difference between the single-bond covalent radii of I and Cl.[20] The Ir-P lengths of 2.35 (1) and 2.37 (1) Å found in the iodo complex are normal, being similar to the values of 2.33 (1) and 2.36 (1) Å in the SO2 complex[4] and the values of 2.36 (1) and 2.38 (1) Å in the chloro–oxygen complex;[5] the lengths of 2.407 (3) and 2.408 (3) Å found in the chloro complex[2] are slightly longer than normal. The Ir-C and Ir-N lengths show a significant shortening on substitution of I for Cl, the Ir-N being shortened by 0.08 (3) Å and the Ir-C by 0.16 (5) Å; this is because in both bonds the metal donates electrons to the ligand, and the increased electron density at the metal in the iodo complex makes it a better donor. On this basis we might have expected the Ir-P distances to be longer in the iodo complex; yet they appear to be slightly, but significantly, shorter. The high standard deviations on the Ir-C and Ir-N bond lengths preclude any quantitative discussion of this bond shortening. The M-C bond lengths which have been determined for the 14 second- and third-row transition metal carbonyls which could be found in the literature fall in the range 1.81–2.08 Å; it is apparent that the Ir-C length of 1.86 (1) Å in the chloronitrosyl complex is normal but that of 1.70 (5) Å in the iodo complex is short.

The increase in the N-Ir-P angles in the iodo complex is presumably the result of the shortening of the Ir-N bond. If the N-Ir-P1 angle were 90° in the iodo complex (as it is in the chloro complex), the N-P separation would be only 3.06 Å as compared with 3.11 Å in the chloro complex. It has been shown[21] that in a

series of closely related complexes of Re and Os containing M-P and M-N bonds, the N···P interaction is remarkably constant. Accordingly, it is not surprising that the N···P interactions should be constant in the present two compounds, and that N-Ir-P angles should be different.

The Ir-N bond length in the iodo complex is significantly longer than the Ir-C bond length, the difference being 0.19 (6) Å; this difference is probably not significantly different from the value of 0.11 (2) Å found in the chloro complex. This lack of any significant difference is a good indication that the mode of attachment of the NO group is the same in both complexes. It is important to note that this difference in bond lengths is not a steric factor; the van der Waals radius of nitrogen is about 0.04 Å less than the van der Waals radius of carbon, and so on steric grounds one would expect the Ir-C bond to be slightly longer than the Ir-N bond. The shortness of the Ir-C bond relative to the Ir-N bond is taken as evidence for much less π contribution in the Ir-N bond than in the Ir-C bond, the metal being a π donor to the carbonyl group and a σ donor to the nitrosyl group.

There is further evidence for this belief that the nitrosyl group is acting as a Lewis acid ligand in these systems. Large changes in the bonding at the nitrogen would have been expected if the NO moiety were involved in π bonding with the metal, as is found in the molecular oxygen complexes $IrX(CO)(O_2)(P(C_6H_5)_3)_2$,[5,6] where the O-O length changes from 1.30 to 1.51 Å on substitution of Cl for I. In the nitrosyl case, however, the N-O bond length in unchanged, and, more significantly, the Ir-N-O angle of 125 (3)° found in the iodo complex is essentially the same as the value of 124 (1)° found in the chloro analog.[2] This lack of any real change in the bonding at the nitrogen, plus the continued shortness of the Ir-C bond as compared with the Ir-N bond, is excellent support for our hypothesis that in these systems the NO+ ligand is acting as a σ acceptor (Lewis acid) and is involved in σ bonding to the Ir, the hybridization at the N being sp². This is in agreement with the finding[22] that $IrCl(CO)(P(C_6H_5)_3)_2$ will serve as a Lewis base toward boron-containing Lewis acids.

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(22) R. N. Scott, D. F. Shriver, and L. Vaska, *J. Am. Chem. Soc.*, **90**, 1079 (1968).