Aryldiazo Complexes. Synthesis and Structure of a Five-Coordinate Complex Possessing a "Half Doubly Bent" Aryldiazo Ligand and an Intermediate Coordination Geometry, $[IrCl(N_2C_6H_5)(P(CH_3)(C_6H_5)_2)_3][PF_6]$

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Abstract: The complex $[IrCl(N_2C_6H_5)(P(CH_3)(C_6H_5)_2)_3][PF_6]$ has been prepared with the specific intent of inducing the aryldiazo ligand into a geometry intermediate between the previously observed singly and doubly bent geometries. This has been accomplished by employing ligands of intermediate bulk $(P(CH_3)(C_6H_5)_2)$ to distort the coordination geometry of the Ir atom from its electronically favored geometry. The structure of this iridium-aryldiazo complex has been determined crystallographically and consists of discrete cations and anions. The cation is five-coordinate with a highly distorted geometry about the metal which cannot be adequately described by any idealized geometry. The intermediate coordination geometry about the iridium atom is mirrored by the geometry of the aryldiazo ligand which is intermediate between singly and doubly bent. Some relevant metrical parameters are: Ir-N(1), 1.835 (8) Å; N(1)-N(2), 1.241 (11) Å; N(2)-C(11), 1.421 (11) Å; Ir-N(1)-N(2), 155.2 (7)°; N(1)-N(2)-C(11), 118.8 (8)°. The hexafluorophosphate anion is disordered. The compound crystallizes from acetone in space group C_2^2-$P2_1$ with $a = 15.767$ (7) Å, $b = 15.583$ (7) Å, $c = 9.002$ (4) Å, $\beta = 91.67$ (2)°, and $Z = 2$. The pseudo-mirror-symmetry of the cation caused great difficulty in the solution of the structure, as it was very difficult to differentiate the correct atomic positions from the mirror-related images. The correct solution was obtained by excluding those solutions which resulted in highly irregular bond angles and distances and in unreasonably short nonbonded contacts. Based on 7134 reflections with $F_o^2 \geq 3\sigma(F_o^2)$, the structural data were refined by full-matrix, least-squares methods to R indices of $R = 0.046$ and $R_w = 0.072$. The synthesis, spectra, and reaction chemistry of the complex are discussed.

There has been recent interest in the structural chemistry of coordination compounds which contain the aryldiazo ligand because these compounds can adopt a wide range of coordination geometries that can, to a large degree, be correlated with their reaction chemistry and spectroscopic properties. Although a large number of five-coordinate complexes containing aryldiazo ligands have been prepared, only three structures have been reported. The compounds $[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$[3] and $OsH(CO)(N_2Ph)(PPh_3)_2$[4,5] possess trigonal bipyramidal geometries with equatorial, singly bent aryldiazo ligands; owing to the presence of a sterically small hydrido ligand in the Os complex, the coordination geometry about the metal is somewhat distorted. The compound $[RhCl(N_2Ph)(PhP(CH_2CH_2CH_2PPh_2)_2)][PF_6]$ possesses a square pyramidal geometry with an apical, doubly bent aryldiazo ligand.[6] Of special interest is the structural and chemical behavior of a series of related iridium aryldiazo complexes, some of which are electron deficient or electron rich, e.g., $IrCl_2(N_2Ar)(PPh_3)_2$ and $IrCl(N_2Ar)(L)(PPh_3)_2^+$ which are 16-18 electron complexes, $IrCl(N_2Ar)(PPh_3)_2^+$ which is a 14-16 electron complex, and $IrCl_2(N_2Ar)(L)(PPh_3)_2$ which are 18-20 electron complexes (L = neutral 2 electron donor ligand, N_2Ar = 1 or 3 electron donor ligand).[7-9] It is noteworthy that the nitrosyl analogues of the first two classes of complexes have been known for some time but the preparation of $IrCl_2(NO)(CO)(PPh_3)_2$ was just recently reported.[10]

The structural chemistry of aryldiazo ligands seems to parallel closely that of acyldiazo, aroyldiazo, and alkyldiazo ligands prepared by the acylation or alkylation of dinitrogen complexes of molybdenum, tungsten, and rhenium[11] or by the insertion of diazoalkanes into metal-hydride bonds.[12] Indeed, diazo ligands undergo a wide range of reactions[13] and may well be models for intermediates in the chemical reduction of dinitrogen to derivatives of ammonia or hydrazine.[14]

In an effort to understand the mechanism of the singly bent to doubly bent transition in aryldiazo ligands and the influence of coordination geometry on this process, aryldiazo complexes with intermediate coordination geometries were prepared. Previous work with both five-coordinate nitrosyl and aryldiazo complexes suggested that a square pyramidal coordination geometry is associated with bent nitrosyl and doubly bent aryldiazo ligands,[6] and that a trigonal bipyramidal geometry is associated with linear nitrosyl and singly bent aryldiazo ligands.[3,4] The four-coordinate complex, $IrCl(N_2Ph)(PPh_3)_2^+$, readily adds a wide variety of neutral ligands forming cationic, five-coordinate complexes.[7] When a small ligand was added (EtNC or CO), spectroscopic evidence suggested the presence of a doubly bent aryldiazo linkage. Indeed, a doubly bent aryldiazo ligand was found in a similar cationic, five-coordinated rhodium complex, $RhCl(N_2Ph)(ppp)^+$.[6] On the other hand, when a large, bulky ligand was added (PPh_3 or $AsPh_3$), the N-N stretching frequencies were much higher suggesting that a singly bent aryldiazo linkage was present. The objective then was to attach ligands of intermediate size to the Ir atom, and both $IrCl(N_2Ph)(PMe_3)(PPh_3)_2^+$ and $IrCl(N_2Ph)(PMePh_2)_3^+$ were prepared. The value of ν(NN) for the latter Ir complex, at 1619 cm^{-1}, was higher than that observed in $RhCl(N_2Ph)(ppp)^+$ [15] (1603 cm^{-1}) and therefore suggested the desired intermediate behavior. Thus we have determined the solid state structure of the iridium complex and report it here.

Experimental Section

Crystal Preparation. The title compound was prepared by two methods described subsequently. Although several attempts at growing crystals by conventional methods yielded specimens of poor quality or ones which were too small, large orange plates were grown in situ by preparing the hexafluorophosphate complex according to method (a) using twice the amount of acetone with no stirring. Because the platelets were so thin, a larger cyrstal was chosen and fractured across the longest dimension, and then mounted on a glass fiber. The crystals thus prepared had identical elemental analyses, NMR spectra, and infrared spectra with those prepared in other ways. The crystals were stable to air.

Infrared spectra were measured in Fluorolube S-30 mulls using a Perkin-Elmer 457 spectrometer and were calibrated using a polystyrene film. There were no solid state effects evident in the infrared spectra since solution (methylene chloride) and mull spectra were essentially identical. NMR spectra were measured in CD_2Cl_2 solution at ambient temperature using Varian Associates XL-100 (^{31}P) and HR-220 (^1H) spectrometers. The spectra were calibrated using external phosphoric acid and internal tetramethylsilane. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Isotopically substituted benzenediazonium salts were prepared as previously described and carefully recrystallized before using.[16] Hydrated iridium trichloride was purchased from Engelhard Industries, Newark, N.J.

Chloro(phenyldiazo)tris(methyldiphenylphosphine)iridium Tetrafluoroborate. (a) To a solution of 1.00 g of $[IrCl(N_2Ph)(PPh_3)_2][BF_4]$[7] in 10 ml of acetone was added 1.9 g of $PMePh_2$. The green solution immediately changed color to red-orange. The mixture was stirred at room temperature for about 1 h during which time orange crystals of the product crystallized out of solution. In order to improve the yield, 5 ml of absolute ethanol and 20 ml of diethyl ether were added, and the mixture was stirred for an additional 30 min at 0-5 °C (ice bath). The mixture was filtered, washed with ether, and dried in vacuo to yield 0.86 g (80%) of orange platelets. These were soluble in chloroform and methylene chloride, but only partially soluble in acetone, ethanol, or benzene. Anal. Calcd for $C_{45}H_{44}BClF_4IrN_2P_3$: C, 52.98; H, 4.34; N, 2.75. Found: C, 53.12; H, 4.44; N, 2.61. The hexafluorophosphate salt was prepared in 89% yield using the same method. Anal. Calcd for $C_{45}H_{44}ClF_6IrN_2P_4$: C, 50.12; H, 4.11; N, 2.60. Found: C, 50.04; H, 4.05; N, 2.65. (b) Under a nitrogen atomsphere, 1.1 g of $PMePh_2$ was added dropwise to a stirring mixture of 1.00 g of $[IrCl(C_8H_{14})_2]_2$[17] in 25 ml of acetone. The mixture was stirred at room temperature for 20 min followed by the addition of 1.5 g of benzenediazonium tetrafluoroborate. The mixture was again stirred for 20 min followed by the addition of 2.0 g of the phosphine. After an additional 30 min stirring, 15 ml of absolute ethanol and 50 ml of diethyl ether were added, and the reaction mixture was handled in the same manner as in method (a). The yield was 2.25 g (74%) of an orange microcrystalline powder. Anal. Found: C, 52.75; H, 4.30; N, 2.79. The hexafluorophosphate salt was prepared in approximately the same yield by this same method.

Bromo(phenyldiazo)tris(methyldiphenylphosphine)iridium Tetrafluoroborate. This compound was prepared according to method (a) for the analogous chloro complex starting instead with $[IrBr(N_2Ph)(PPh_3)_2][BF_4]$.[7] The yield was 78% of red-orange crystals. Anal. Calcd for $C_{45}H_{44}BrF_6IrN_2P_4$: C, 50.77; H, 4.17; N, 2.63. Found: C, 51.02; H, 4.31; N, 2.76.

Crystallographic Data. Preliminary film data showed that the crystals of $[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$ belong to the monoclinic system with extinctions ($0k0$, $k = 2n + 1$) characteristic of the space groups $C_2{}^2$-$P2_1$ and $C_{2h}{}^2$-$P2_1/m$. No symmetry restrictions are necessarily imposed in space group $P2_1$; however, with two molecules in $P2_1/m$ the molecules are required to lie on the crystallographic mirror planes or the inversion centers. The centrosymmetric space group was initially chosen but was later found to be incorrect. Ultimately the space group $P2_1$ was shown to be the more consistent choice based on: (1) the successful refinement of the structure with acceptable positional parameters, thermal parameters, and agreement indices; (2) a positive second harmonic generation test; (3) the nonequivalence of the intensities of reflections of the type hkl and $h\bar{k}l$; (4) the location of all hydrogen atoms in difference Fourier syntheses. Accurate cell parameters were obtained by a least-squares analysis of the setting angles of 15 hand-centered reflections chosen from diverse regions of reciprocal space ($23.2° \leq 2\theta \leq 30.0°$, Mo $K\alpha_1$ radiation) and obtained using a narrow x-ray source. See Table I for pertinent crystal data. The crystal mosaicity was judged acceptable for the θ-2θ scan technique, based on ω scans with an open counter and narrow source.

Data were collected on a Picker four-circle diffractometer equipped with a scintillation counter and a pulse height analyzer which had been adjusted to accept 90% of the Mo $K\alpha$ peak. Background counts were measured at both ends of the scan range with stationary counter and crystal. The intensities of six standard reflections were measured every 100 reflections. All were found to decrease approximately uniformly and linearly by about 3% during the course of data collection. The observed intensities were corrected for this apparent decomposition.

Table I. Summary of Crystal Data and Intensity Collection

Compound	$[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$
Formula weight	1078.40 amu
Formula	$C_{45}H_{44}ClF_6IrN_2P_4$
a	15.767 (7) Å
b	15.583 (7) Å
c	9.002 (4) Å
β	91.67 (2)°
V	2211 Å^3
Z	2
Density	1.619 g/cm^3 (calcd) 1.60 (2) g/cm^3 (exptl)
Space group	$C_2{}^2$-$P2_1$
Crystal dimensions	0.10 × 0.65 × 0.65 mm
Crystal shape	Monoclinic prism with well-developed faces of the forms {100}, {010}, and {001}
Crystal volume	0.0346 mm^3
Temperature	20 °C
Radiation	Mo $K\alpha_1$ (λ 0.709 300 Å) monochromatized from (002) face of mosaic graphite
μ	32.7 cm^{-1}
Transmission factors	0.175–0.726
Receiving aperture	4.0 × 4.0 mm; 30 cm from crystal
Takeoff Angle	2.0°
Scan speed	2.0° in 2θ/min
Scan range	For $2\theta < 35°$, 1.0° below $K\alpha_1$ to 1.0° above $K\alpha_2$; for $2\theta \geq 35°$, 1.1° below $K\alpha_1$ to 1.0° above $K\alpha_2$
Background counts	10 s
2θ limits	1.0–62.5°
Final no. of variables	195
Unique data used $F_o{}^2 \geq 3\sigma(F_o{}^2)$	7134
Error in observation of unit weight	2.53 electrons
R	0.046
R_w	0.072

The intensities of 8664 reflections were measured for $1.0° \leq 2\theta \leq 62.5°$ using Mo $K\alpha$ radiation. Reflections of the type $\bar{h}, k, \pm l$ were collected for the complete 2θ range. In addition the $\bar{h}, \bar{k}, \pm l$ reflections were measured for the inner data sphere ($2\theta \leq 30.0°$) to give a set of reflections which would not be equivalent in space group $P2_1$. Data were processed in the usual way using a value of 0.04 for p.[18] A total of 6298 reflections of the type $\bar{h}, k, \pm l$ and 836 reflections of the type $\bar{h}, \bar{k}, \pm l$ had $F_o{}^2 \geq 3\sigma(F_o{}^2)$. Only these 7134 reflections were used in subsequent calculations. An absorption correction was applied to the data using Gaussian integration.[19]

Structure Solution and Refinement. The position of the Ir atom was obtained from a sharpened, origin-removed Patterson synthesis. Subsequent refinements and difference Fourier syntheses in the space group $P2_1/m$ led to the location of all non-hydrogen atoms. Both the anion and cation were situated on a crystallographic mirror plane. The structure was refined using full-matrix, least-squares techniques minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weights, w, are taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. Atomic scattering factors were taken from Cromer's and Waber's tabulation[20] for all atoms except hydrogen for which the values of Stewart et al.[21] were used. Anomalous dispersion terms[22] for Ir, Cl, and P were included in F_c. The isotropic model, which included all non-hydrogen atoms and seven rigid-body phenyl groups, resulted in agreement indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.102$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2} = 0.158$. In this and all subsequent refinements, group atoms were given individual isotropic thermal parameters. This centrosymmetric model, however, resulted in thermal parameters of the phenyl carbon atoms which were excessively large, up to 23 Å^2. In addition an ensuing difference Fourier synthesis indicated that the phosphine ligand on the crystallographic mirror was not as expected. In particular, a phenyl ring was located on the mirror plane, implying that the other phenyl group and the methyl group must be statistically disordered between their two positions. Alternatively the correct space group might be $P2_1$ with no crystallographically imposed mirror symmetry. This was verified by a positive second harmonic generation test.[23]

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
IR	0.221230(18)	1/4	0.23212(3)	19.85(11)	25.06(12)	64.2(3)	-0.40(28)	0.33(14)	0.7(4)
CL	0.22941(19)	0.26604(19)	-0.03646(28)	40.8(12)	44.2(19)	69.2(27)	-1.0(10)	1.4(15)	2.4(14)
P(1)	0.36633(13)	0.2485(3)	0.24395(23)	20.9(7)	27.5(8)	71.7(23)	-5.5(21)	3.6(11)	8.(3)
P(2)	0.20791(22)	0.09806(24)	0.1924(4)	26.9(13)	27.6(13)	86.(4)	-3.2(10)	-5.1(19)	-2.6(22)
P(3)	0.20465(24)	0.40089(26)	0.2499(3)	30.6(13)	28.4(13)	84.(4)	5.8(10)	3.2(20)	3.5(20)
P(4)	-0.29846(22)	0.2584(4)	0.0394(4)	34.1(12)	54.0(23)	180.(5)	6.4(18)	3.2(21)	10.(3)
N(1)	0.1495(5)	0.2407(9)	0.3881(8)	29.(3)	36.(4)	90.(9)	1.(5)	9.(4)	2.(8)
N(2)	0.1311(5)	0.2280(6)	0.5194(10)	28.(3)	40.(6)	104.(11)	-1.(3)	6.(5)	-8.(6)
C(1)	0.4182(7)	0.1661(7)	0.1331(14)	24.(4)	31.(5)	125.(18)	6.(4)	-7.(7)	-14.(7)
C(2)	0.2335(8)	0.0564(8)	0.0111(13)	36.(5)	45.(6)	92.(15)	-3.(5)	1.(7)	-22.(8)
C(3)	0.2406(8)	0.4678(8)	0.0970(12)	39.(6)	49.(6)	83.(15)	-1.(5)	29.(8)	4.(8)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP(-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL))$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

The structure was thus refined in space group $P2_1$. At first the six fluorine atoms of the PF_6^- group were not included in the calculations since in the centrosymmetric space group the anion was disordered and it was felt that this might be a consequence of the incorrect space group. However, location of the fluorine atoms again verified that the PF_6^- group is disordered. It is significant that the positions of the fluorine atoms were much more clearly defined in the noncentrosymmetric model. In all subsequent refinements the six F atoms were refined as a rigid group with these atoms at the vertices of a regular octahedron of radius 1.565 Å, similar to that observed in several well-behaved PF_6^- groups.[24] The isotropic model in space group $P2_1$ resulted in agreement indices of $R = 0.061$ and $R_w = 0.101$, clearly better than the centrosymmetric model. The thermal parameters of the phenyl carbon atoms were also improved, the largest being 8.1 Å^2.

In order to make a choice of enantiomer, all the data in the inner sphere were utilized in a structure factor calculation. The initial model gave an R value of 0.075 and an R_w value of 0.143, whereas the other enantiomer yielded values of R of 0.075 and of R_w of 0.139. This second enantiomer was judged marginally more likely. A comparison of the intensities of mirror-related reflections, hkl and $h\bar{k}l$, also favored this latter enantiomer. Refinement of this preferred enantiomer with all individual atoms vibrating anisotropically resulted in agreement indices $R = 0.051$ and $R_w = 0.081$. Two phenyl rings, however (rings 4 and 6), had unreasonable geometries with P-C-C angles of 136.5° and 127.8° and P-C distances of 1.745 and 1.966 Å, respectively. Removal of these groups, refinement without their contribution, and subsequent difference Fourier calculations reaffirmed their positions. Evidently the structure had refined to a false minimum with some of the atoms in their pseudo-mirror-related positions. For this reason the solution of the structure was reattempted starting in the noncentrosymmetric space group assuming only the positions of Ir, P(2), and P(3) from the previous solution. This arbitrarily defines the enantiomer, and all atoms were placed so as to be consistent with this choice. The positions of rings 5 and 7 were easily chosen from the images in the Fourier map since the mirror image of ring 7 produced a highly abnormal P(2)-C(51)-C(52) angle with a very short P(2)-C(51) bond. Similarly the image of ring 5 resulted in a long P(3)-C(71) distance. The positions of atoms C(2) and C(3) were chosen from "peanut-shaped" peaks. Again the correct choice resulted in approximately equal P-C distances whereas the other choice produced one long and one short P-C distance. Ring 4 was almost exactly superimposed on the image of ring 6 so these rings were input as mirror-related mates. The positions of rings 2 and 3 and of atom C(1) were chosen on the basis that their mirror-related images resulted in short intramolecular contacts with rings 5 and 7. Since neither the aryldiazo, the chloro ligand, nor their mirror images produced unacceptably short intramolecular nonbonded contacts an unambiguous choice for these positions could not be made. Instead one set of positions was arbitrarily chosen for the aryldiazo atoms and refined in a least-squares calculation. In this refinement no atom moved significantly. However, when the structure was refined with the aryldiazo group in its mirror-related position, both nitrogen atoms and the phenyl group moved across the pseudo-mirror plane to their original positions, thereby confirming the original choice. Similarly the P(1) and the Cl atoms were situated on the pseudo-mirror plane and allowed to refine to their favored locations. This resulted in reasonable P-C distances so there was no reason to believe that either of these atoms had moved in the wrong direction. Both atom P(4) and the centroid of the group of six F atoms were superimposed at $y = 1/4$. Ensuing refinements resulted in each of these on different sides of the pseudo-mirror plane. Interchange of positions followed by refinements resulted in the original positions so we assume that the centroid of the six F atoms was badly defined owing to disorder. The above model, with all individual atoms refined anisotropically, converged to values of R and R_w of 0.045 and 0.065. Again a choice of enantiomer had to be made. The other enantiomer refined to values of R and R_w of 0.046 and 0.068. Comparison of the intensities of the hkl and $h\bar{k}l$ reflections also supported the initial choice. The agreement indices (on F^2) for these inner reflections were $R = 0.086$ and $R_w = 0.207$ for the initial model and $R = 0.090$ and $R_w = 0.234$ for the other enantiomer. Since the space group $P2_1$ is polar in the y-direction, the different enantiomers result in significant shifts in the positions of the Ir, P, and Cl atoms relative to the lighter atoms and each other.[25] Therefore the two enantiomers show differing Ir-P, Ir-Cl, and P-C distances. It is encouraging that the wrong enantiomer shows a range in P-C distances of 1.778 (8)-1.842 (8) Å and chemically related Ir-P(2) and Ir-P(3) distances of 2.340 (4) and 2.433 (4) Å, whereas the correct enantiomer results in a narrower range of P-C distances (1.795 (8)-1.836 (8) Å) and Ir-P(2) and Ir-P(3) distances which are more nearly equivalent (2.372 (4) and 2.403 (4) Å). Although all hydrogen atoms were located in difference Fourier syntheses, their positions were idealized assuming trigonal and tetrahedral geometries of the phenyl and methyl carbon atoms, respectively, and using a C-H distance of 0.95 Å. Each hydrogen atom was assigned a thermal parameter of 1.0 Å^2 greater than the equivalent isotropic thermal parameter of its attached carbon atom. These data were used in the calculation of fixed contributions to F_c. The final model involving all 7134 reflections, nonequivalent in space group $P2_1$, converged to agreement indices of 0.046 and 0.072 for the 195 variables.

In a final difference Fourier synthesis the highest 20 residuals were around the PF_6^- group (3.0-1.3 e/Å^3), the Ir atom (1.1-0.9 e/Å^3), and the phenyl rings (0.9 e/Å^3). The unusually high noise about the PF_6^- group is obviously caused by the inadequacy of our model for describing the disorder of this group. A typical carbon atom on earlier syntheses had an electron density of about 3.4 e/Å^3. All but four unobserved reflections obey the relation $|F_c^2 - F_o^2| < 4\sigma(F_o^2)$. There were no trends of the quantity $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, diffractometer setting angles, or Miller indices. However, agreement between $|F_o|$ and $|F_c|$ was poor at low θ values. This is to be expected in view of the PF_6^- disorder.

The final positional and thermal parameters of the groups and non-hydrogen atoms are given in Tables II and III. The derived hydrogen atom positions are shown in Table IV[26] and the root-mean-square amplitudes of vibration are in Table V.[26] A listing of the observed and calculated structure amplitudes for the data used in the refinements is available.[26]

It is significant that the coordination geometry about the Ir atom and the geometry of the aryldiazo ligand were essentially the same for all refinements, in both the centrosymmetric and noncentrosymmetric space groups. Thus the chemical significance of the structure remains the same regardless of possible difficulties encountered in

Table III. Derived Parameters for the Rigid Group Atoms of $[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$

ATOM	X	Y	Z	B, A^2	ATOM	X	Y	Z	B, A^2
C(11)	0.0447(4)	0.2327(6)	0.5588(9)	3.52(21)	C(51)	0.2632(5)	0.0299(5)	0.3251(8)	3.27(20)
C(12)	-0.0213(5)	0.2540(7)	0.4594(7)	4.33(21)	C(52)	0.2487(5)	0.0396(5)	0.4759(9)	3.82(23)
C(13)	-0.1043(4)	0.2570(8)	0.5075(9)	5.6(3)	C(53)	0.2900(7)	-0.0135(6)	0.5791(7)	5.7(3)
C(14)	-0.1215(4)	0.2387(8)	0.6549(10)	7.3(4)	C(54)	0.3458(6)	-0.0764(6)	0.5314(10)	6.1(4)
C(15)	-0.0555(6)	0.2174(7)	0.7543(8)	5.6(3)	C(55)	0.3602(6)	-0.0860(5)	0.3806(11)	5.5(3)
C(16)	0.0275(5)	0.2144(6)	0.7062(8)	5.8(3)	C(56)	0.3189(6)	-0.0329(6)	0.2774(8)	5.5(3)
C(21)	0.4125(4)	0.2270(4)	0.4282(6)	2.69(17)	C(61)	0.0895(4)	0.4187(6)	0.2387(10)	3.25(22)
C(22)	0.3606(3)	0.2161(5)	0.5492(8)	3.26(20)	C(62)	0.0476(6)	0.4627(6)	0.3493(9)	5.0(3)
C(23)	0.3964(4)	0.2045(5)	0.6909(6)	3.81(22)	C(63)	-0.0404(6)	0.4699(6)	0.3422(9)	6.1(4)
C(24)	0.4842(5)	0.2038(5)	0.7117(6)	4.40(26)	C(64)	-0.0865(4)	0.4331(6)	0.2245(11)	5.1(3)
C(25)	0.5362(3)	0.2147(5)	0.5907(8)	3.83(23)	C(65)	-0.0446(6)	0.3891(6)	0.1139(9)	4.29(27)
C(26)	0.5003(4)	0.2263(5)	0.4490(7)	3.62(22)	C(66)	0.0434(6)	0.3819(6)	0.1210(9)	5.0(3)
C(31)	0.4164(5)	0.3464(4)	0.1890(9)	3.41(25)	C(71)	0.2427(5)	0.4521(5)	0.4194(7)	3.29(21)
C(32)	0.4326(6)	0.3615(5)	0.0401(8)	3.49(21)	C(72)	0.2584(5)	0.4020(4)	0.5451(9)	3.49(21)
C(33)	0.4693(6)	0.4385(6)	-0.0025(7)	4.60(27)	C(73)	0.2900(6)	0.4396(5)	0.6755(7)	4.04(24)
C(34)	0.4899(6)	0.5005(5)	0.1039(10)	6.1(4)	C(74)	0.3061(6)	0.5274(5)	0.6802(9)	5.7(3)
C(35)	0.4738(6)	0.4854(5)	0.2528(9)	4.78(28)	C(75)	0.2904(6)	0.5775(4)	0.5545(11)	5.8(3)
C(36)	0.4370(6)	0.4084(5)	0.2954(7)	3.53(21)	C(76)	0.2588(6)	0.5399(5)	0.4240(9)	5.4(3)
C(41)	0.0978(5)	0.0660(6)	0.2021(10)	3.53(23)	F(1)	-0.2516(9)	0.2250(10)	0.1904(13)	16.5(6)
C(42)	0.0754(5)	-0.0138(5)	0.2583(10)	4.66(28)	F(2)	-0.3453(9)	0.2754(10)	-0.1082(14)	18.0(7)
C(43)	-0.0097(6)	-0.0372(5)	0.2628(11)	5.9(3)	F(3)	-0.2323(9)	0.1974(9)	-0.0474(16)	23.6(10)
C(44)	-0.0723(5)	0.0192(7)	0.2112(12)	5.7(3)	F(4)	-0.3646(9)	0.3030(11)	0.1296(17)	28.5(12)
C(45)	-0.0499(6)	0.0990(6)	0.1551(12)	7.0(4)	F(5)	-0.3558(10)	0.1686(9)	0.0522(19)	20.0(8)
C(46)	0.0352(6)	0.1224(5)	0.1506(11)	4.19(27)	F(6)	-0.2411(9)	0.3318(8)	0.0299(16)	16.2(6)

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
RING 1	-0.0384(4)	0.2357(4)	0.6068(7)	-2.247(15)	-1.992(5)	0.973(14)
RING 2	0.4484(3)	0.2154(3)	0.5699(6)	-1.499(5)	2.729(4)	1.412(5)
RING 3	0.4532(4)	0.4234(4)	0.1464(7)	-0.395(6)	-2.912(5)	-1.467(5)
RING 4	0.0128(4)	0.0426(4)	0.2067(7)	0.290(6)	2.736(6)	-3.204(6)
RING 5	0.3045(4)	-0.0232(4)	0.4283(7)	-2.367(10)	2.286(5)	1.488(9)
RING 6	0.0015(4)	0.4259(4)	0.2316(7)	3.089(10)	2.121(6)	-0.032(10)
RING 7	0.2744(4)	0.4897(4)	0.5498(7)	-0.003(6)	2.672(5)	1.205(6)
GRP-F6	-0.2984(6)	0.2502(7)	0.0411(12)	-2.239(10)	2.585(8)	-1.475(9)

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

solving the structure. Moreover, this structure clearly indicates the utility in assessing the chemical reasonableness of a given model and the dangers in relying too heavily on "R indices" as an indication of correctness of structure, since one wrong solution refined to reasonable values of R and R_w of 0.051 and 0.081, respectively. However, the same criteria involved in assessment of chemical reasonableness cannot be applied to solid state structures as to free molecules; in fact exact equivalence of chemically related metrical parameters is the exception, rather than the rule, in the solid state.

Discussion

Description of Structure. The unit cell of $[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$ contains discrete, well-separated anions and cations, as is shown in Figure 1. A perspective view of the cation, showing the numbering scheme, is presented in Figure 2. The inner coordination sphere of the cation, with relevant bond length and angles, is shown in Figure 3 (see also Tables VI and VII).

This ionic complex has approximate mirror symmetry with the pseudo-mirror plane passing approximately through the Ir, P(1), Cl, and N(1) atoms of the cation, and atom P(4) of the anion. Within the cation the largest deviation from mirror symmetry involves the unique phosphine (P(1)) which has a methyl group (C(1)) and a phenyl group (ring 3) on opposite sides of the pseudo-mirror plane. The deviation of the substituents on the P(2) and P(3) atoms from mirror symmetry can be seen in the torsion angles about the P(2)-P(3) vector (Table VII). These angles range from −6.9 (7)° to −10.6 (5)° indicating that these substitutents are staggered slightly.

The coordination geometry about the Ir atom cannot be described accurately by any idealized polyhedron. The closest idealized geometry is square pyramidal (SP) with an apical phosphine (P(1)), two mutually trans basal phosphines, and basal chloro and aryldiazo ligands. There are, however, large distortions from the idealized SP geometry. The P(2)-Ir-P(3) angle is approximately 22° greater than the Cl-Ir-N(1) angle and atom P(1) is bent significantly off the apex towards the chloro ligand, resulting in P(1)-Ir-Cl and P(1)-Ir-N(1) angles of 88.02 (9)° and 127.0 (2)°, respectively. The second best idealized geometry is a highly distorted trigonal bipyramid (TBP) with the P(2) and P(3) atoms in the axial positions. The major deviations from this idealized geometry are in the equatorial plane, with the N(1)-Ir-Cl and Cl-Ir-P(1) angles (145.0 (3)° and 88.02 (9)°, respectively) deviating considerably from the ideal 120°. The undistorted TBP geometry would require that the Cl atom be closer to the N_2Ph group. However, this would be impossible with the substituents on the phosphines in their present orientation since extremely short contacts between the Cl atom and rings 4 and 6 would result. The Cl-H(66) contact is already short (2.91 Å). In addition both atoms P(2) and P(3) are bent off the trigonal axis by the third phosphine ligand.

The two mutually trans Ir-P(2) and Ir-P(3) distances, at 2.403 (4) and 2.372 (4) Å, respectively, compare well with other such distances in five-coordinate Ir complexes.[27-30] Although these two Ir-P distances differ by 0.031 (6) Å in the solid state, ^{31}P and ^1H NMR experiments indicate that the two phosphine ligands are chemically equivalent in solution. Similarly the two "chemically equivalent" phosphine ligands

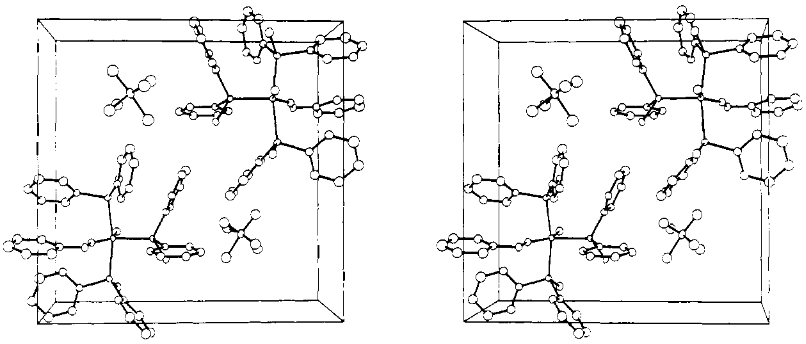

Figure 1. A stereoview of a unit cell of $[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$. The x-axis is horizontal to the right, the z-axis is perpendicular to the paper coming towards the reader, and the y-axis is vertical from bottom to top. The vibrational ellipsoids are drawn at the 20% probability level except for fluorine atoms which are drawn arbitrarily small for clarity.

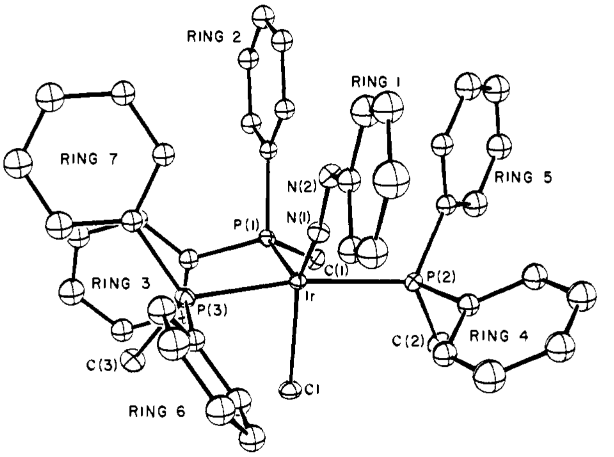

Figure 2. A perspective view of the $[IrCl(N_2Ph)(PMePh_2)_3]^+$ cation showing the numbering scheme used. The vibrational ellipsoids are drawn at the 20% probability level.

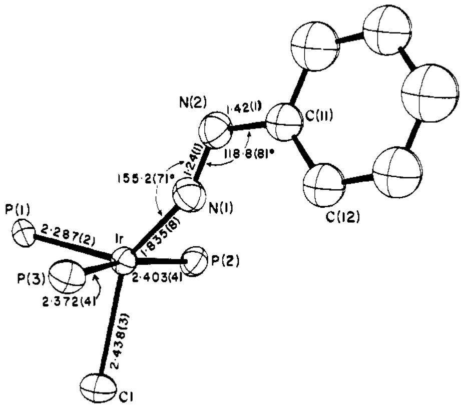

Figure 3. The inner coordination sphere of the $[IrCl(N_2Ph)(PMePh_2)_3{}^+]$ cation, with relevant bond lengths and angles shown. The vibrational ellipsoids are drawn at the 50% probability level.

in $RuCl_2(PPh_3)_3$[31] and $RuHCl(PPh_3)_3$[32] have Ru–P distances differing by 0.038 (7) and 0.032 (6) Å, respectively. The difference in the Ir–P(2) and Ir–P(3) distances in the present determination may result from steric effects. The nonbonded intramolecular contacts, listed in Table VI, indicate that there are several short contacts involving the substituents on atoms P(2) and P(3). In particular the H2C(2)–Cl and H2C(3)–Cl contacts, at 2.56 and 2.74 Å, respectively, are very short. The Ir–P(1) distance for the unique phosphine ligand, at 2.287 (2) Å, is very short and indeed is significantly shorter (~0.1 Å) than the other Ir–P distances in the complex. With no ligand

Table VI. Selected Distances (Å) in $[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$

		Bond Distances			
Ir–N(1)	1.835 (8)		P(1)–C(21)	1.823 (6)	1.813 (14)
Ir–P(1)	2.287 (2)		P(1)–C(31)	1.795 (8)	
Ir–P(2)	2.403 (4)		P(2)–C(41)	1.810 (8)	
Ir–P(3)	2.372 (4)		P(2)–C(51)	1.803 (9)	
Ir–Cl	2.438 (3)		P(3)–C(61)	1.836 (8)	
N(1)–N(2)	1.241 (11)		P(3)–C(71)	1.808 (8)	
N(2)–C(11)	1.421 (11)		P(4)–F(1)	1.615 (13)	1.57 (8)
P(1)–C(1)	1.833 (11)	1.825 (12)[a]	P(4)–F(2)	1.524 (13)	
P(2)–C(2)	1.813 (12)		P(4)–F(3)	1.628 (15)	
P(3)–C(3)	1.830 (12)		P(4)–F(4)	1.510 (15)	
			P(4)–F(5)	1.672 (15)	
			P(4)–F(6)	1.462 (14)	
		Nonbonded Distances			
Cl–H2C(2)	2.56		C(22)–H(72)	2.67	
Cl–H2C(3)	2.74		C(25)–H(55)	2.69	
Cl–H(66)	2.91		C(51)–H(42)	2.63	
N(1)–H(12)	2.55		C(56)–H3C(2)	2.53	
N(1)–H(72)	2.58		C(2)–H(56)	2.57	
N(2)–H(16)	2.54		F(5)–H(74)	2.43	
N(2)–H(72)	2.55		H(22)–H(72)	2.16	
N(2)–H(52)	2.62		H(32)–H2C(1)	2.26	
N(2)–H(22)	2.68		H(56)–H3C(2)	1.85	
C(21)–H(36)	2.70				

[a] For averaged quantities, the estimated standard deviation is the larger of an individual standard deviation or the standard deviation of a single observation as calculated from the mean.

Table VII. Selected Angles (deg) in $[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$

	Bond Angles		
N(1)–Ir–P(1)	127.0 (2)	N(2)–C(11)–C(12)	123.8 (7)
N(1)–Ir–P(2)	89.0 (4)	N(2)–C(11)–C(16)	116.2 (7)
N(1)–Ir–P(3)	87.4 (4)	P(1)–C(21)–C(22)	120.4 (5)
N(1)–Ir–Cl	145.0 (3)	P(1)–C(21)–C(26)	119.5 (4)
P(1)–Ir–P(2)	94.56 (15)	P(1)–C(31)–C(32)	120.2 (6)
P(1)–Ir–P(3)	96.85 (16)	P(1)–C(31)–C(36)	119.7 (6)
P(1)–Ir–Cl	88.02 (9)	P(2)–C(41)–C(42)	121.2 (6)
P(2)–Ir–P(3)	167.86 (9)	P(2)–C(41)–C(46)	118.8 (7)
P(2)–Ir–Cl	87.73 (11)	P(2)–C(51)–C(52)	119.5 (6)
P(3)–Ir–Cl	88.54 (10)	P(2)–C(51)–C(56)	120.5 (6)
Ir–N(1)–N(2)	155.2 (7)	P(3)–C(61)–C(62)	121.6 (6)
N(1)–N(2)–C(11)	118.8 (8)	P(3)–C(61)–C(66)	118.3 (7)
Ir–P(1)–C(1)	116.4 (4)	P(3)–C(71)–C(72)	119.0 (6)
Ir–P(2)–C(2)	117.8 (5)	P(3)–C(71)–C(76)	121.0 (6)
Ir–P(3)–C(3)	118.5 (4)	F(1)–P(4)–F(2)	171.2 (9)
Ir–P(1)–C(21)	114.6 (2)	F(1)–P(4)–F(3)	86.1 (7)
Ir–P(1)–C(31)	115.2 (3)	F(1)–P(4)–F(4)	90.1 (8)
Ir–P(2)–C(41)	110.1 (3)	F(1)–P(4)–F(5)	84.6 (8)
Ir–P(2)–C(51)	116.3 (3)	F(1)–P(4)–F(6)	91.9 (8)
Ir–P(3)–C(61)	104.9 (3)	F(2)–P(4)–F(3)	89.1 (8)
Ir–P(3)–C(71)	117.4 (3)	F(2)–P(4)–F(4)	93.7 (8)
C(1)–P(1)–C(21)	101.2 (5)	F(2)–P(4)–F(5)	87.5 (8)
C(1)–P(1)–C(31)	103.8 (4)	F(2)–P(4)–F(6)	95.7 (8)
C(21)–P(1)–C(31)	103.9 (4)	F(3)–P(4)–F(4)	171.6 (9)
C(2)–P(2)–C(41)	100.6 (5)	F(3)–P(4)–F(5)	84.2 (8)
C(2)–P(2)–C(51)	105.7 (5)	F(3)–P(4)–F(6)	91.3 (8)
C(41)–P(2)–C(51)	104.5 (4)	F(4)–P(4)–F(5)	88.0 (8)
C(3)–P(3)–C(61)	101.5 (5)	F(4)–P(4)–F(6)	96.3 (9)
C(3)–P(3)–C(71)	106.3 (5)	F(5)–P(4)–F(6)	174.5 (8)
C(61)–P(3)–C(71)	106.4 (4)		
	Torsion Angles		
Ir–N(1)–N(2)–C(11)	−179 (2)	Ir–P(3)–C(61)–C(62)	123.8 (7)
N(1)–N(2)–C(11)–C(12)	−2 (2)	Ir–P(3)–C(71)–C(72)	−17.2 (8)
Ir–P(1)–C(21)–C(22)	−2.2 (7)	C(3)–P(3)–P(2)–C(2)	−6.9 (7)
Ir–P(1)–C(31)–C(32)	−86.3 (7)	C(41)–P(2)–P(3)–C(61)	−8.8 (5)
Ir–P(2)–C(41)–C(42)	−146.6 (7)	C(51)–P(2)–P(3)–C(71)	−10.6 (5)
Ir–P(2)–C(51)–C(52)	54.4 (8)	Cl–Ir–N(1)–N(2)	172 (2)
		P(1)–Ir–N(1)–N(2)	−8 (3)
	Vector-Plane Angles		
Ir–P(2) P(1)–Cl–N(1)	174.8 (2)	Ir–P(3) P(1)–Cl–N(1)	7.0 (2)
P(2)–P(3) Ir–Cl–P(1)	−178.8 (1)	P(2)–P(3) N(1)–N(2)–C(11)	172 (1)

in the trans position competing for bonding electrons, the short Ir–P(1) bond is not surprising.

Although five-coordinate, tris-phosphine complexes most often display TBP geometry with equatorial phosphine ligands,[33,34] the TBP geometry with two axial and one equatorial phosphine ligand[35,36] and the SP geometry with one apical and two basal phosphine ligands[31,32] are also observed. The present complex fits most aptly into this last category and can be compared with other closely related five-coordinate and pseudo-five-coordinate tris-phosphine complexes. In all of these examples, as in the present complex, the apical metal–phosphine distances are shorter than the corresponding basal distances. Thus in $RuCl_2(PPh_3)_3$[31] and $RuHCl(PPh_3)_3$[32] the apical Ru–P distances (2.230 (8) and 2.206 (4) Å) are significantly shorter than the basal Ru–P distances (2.412 (6), 2.374 (4); and 2.361 (4), 2.329 (4) Å, respectively). The complexes $RuH(O_2CCH_3)(PPh_3)_3$[37] and $RuH(O_2CH)(PPh_3)_3$[38] can be regarded as pseudo-square-pyramidal with the bidentate acetate and formate ligands each occupying one coordination site. Again the apical Ru–P distances are shorter than the average basal distances by ca. 0.13 and 0.08 Å, respectively. Although the hydrido ligands were not located in all these above structures it is still possible to compare their geometries with the present Ir complex, based on the other metrical parameters within the molecules and a projected hydrido position. Thus these hydrido complexes seem to distort from SP geometry in a manner similar to the $[IrCl(N_2Ph)(PMePh_2)_3]^+$ cation with the apical phosphine ligand bent off the apex towards the least sterically encumbered ligand (H in the Ru complexes, Cl in the Ir complex).

The geometries of the methyldiphenylphosphine ligands are normal, comparing well with earlier determinations.[39] The average P–C(methyl) distance of 1.825 (12) Å is marginally longer than the average P–C(phenyl) distance of 1.813 (14) Å. This trend is expected owing to the hybridization differences of the carbon atoms.

The Ir–Cl distance (2.438 (3) Å) is within the range found in other five-coordinate iridium complexes. However, it is significantly longer than those distances observed in two closely related complexes $[IrCl(NO)(CO)(PPh_3)_2]^+$[27] and $IrCl_2(NO)(PPh_3)_2$[28] (2.343 (3) and 2.348 (2) Å, respectively). This lengthening in the present complex is possibly a consequence of the very short contacts between the Cl atom and the substituents on atoms P(2) and P(3), the shortest being those previously mentioned with atoms H2C(2) and H2C(3). The Ir–Cl distance is, however, still significantly shorter than the extremely long Ir–Cl distance of 2.619 (6) Å observed in $IrCl(CO)(PMe_2Ph)_3$.[35]

As mentioned, the PF_6^- anion is disordered (not an uncommon characteristic of PF_6^- salts)[40] resulting from the almost spherical nature of the anion. The range in P(4)–F distances and F–P(4)–F angles, shown in Tables VI and VII,

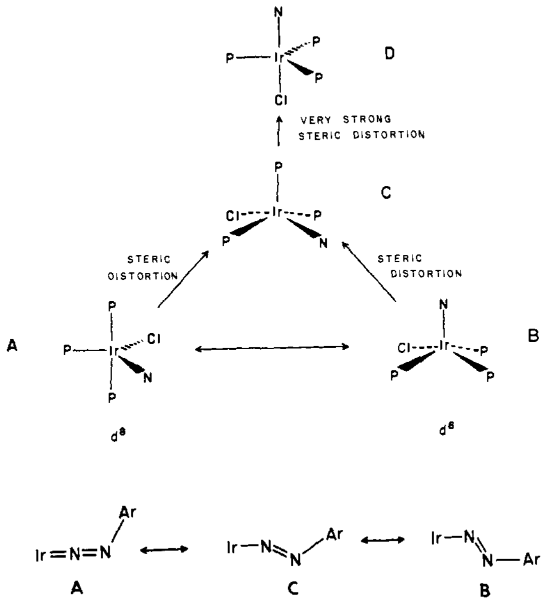

Figure 4. Steric distortions in five-coordinate complexes when three bulky ligands are present. Also shown is the transformation from a singly bent to a doubly bent N_2Ph ligand.

even though the six F atoms were refined as a rigid group, results from the noncoincidence of the P(4) position and the centroid of the F_6 rigid group.

It is of interest to examine the intermediate geometry of the $[IrCl(N_2Ph)(PMePh_2)_3]^+$ cation further in order to understand the reason for this unusual geometry. If one regards the singly bent aryldiazo ligand as N_2Ph^+ and the doubly bent ligand as N_2Ph^-, then the Ir atom is correspondingly either Ir(I) (d^8) or Ir(III) (d^6). Five-coordinate d^8 metal complexes seem to prefer TBP coordination whereas five-coordinate d^6 metal complexes seem to prefer SP coordination (see Figure 4). Ignoring steric effects, the complex $IrCl(CO)(PR_3)_3$ should have geometry A, and indeed such a complex, $IrCl(CO)(PMe_2Ph)_3$, has geometry A though it is distorted towards C apparently as a result of steric effects caused by phosphine-phosphine interactions.[35] On the other hand, the hypothetical cationic complex $IrCl_2(PR_3)_3^+$ should have a square pyramidal geometry (C) analogous to $RuCl_2(PPh_3)_3$. In this case, geometry C is preferred over B for both steric and electronic reasons; geometry C allows the three phosphine ligands to adopt larger phosphorus-metal-phosphorus angles and it places the ligand with the strongest trans effect in the apical position. Again ignoring steric effects, our Ir-N_2Ph complex would have geometry A if N_2Ph^+ were present, as in $Fe(CO)_2(N_2Ph)(PPh_3)_2^+$,[3] or it would have geometry B if N_2Ph^- were present, as in $RhCl(N_2Ph)(ppp)^+$.[6] We would expect the latter case because Ir(I) with several tertiary ligands attached is readily oxidized, and N_2Ph^+ is readily reduced. Furthermore, geometry B would be preferred over C because the reduced N_2Ph^- must preferentially occupy the apical position. In fact, the phosphine ligands in the Ir-N_2Ph complex exert a significant steric influence and distort the coordination about the iridium away from geometry B towards a geometry more closely approximating C. The unique phosphine ligand forces the two mutually trans phosphine ligands away from itself, and this in turn opens up the N-Ir-Cl angle. The aryldiazo ligand clearly reflects the distorted geometry about the iridium and adopts an intermediate geometry between the commonly found singly bent and doubly bent geometries. Using the above reasoning, we would expect our Ir-N_2Ph complex to approach geometry B more closely if less bulky phosphine ligands were present, and we would expect its geometry to distort more strongly away from B if more bulky phosphine ligands were present. A very strong steric repulsion will lead to a greater steric distortion resulting in structure D. The complexes, $RhH(CO)(PPh_3)_3$,[41] $RuH(NO)(PPh_3)_3$,[42] and $[IrH(NO)(PPh_3)_3]^+$ (one form),[34] all have geometry D. In these complexes three bulky triphenylphosphine ligands are present; furthermore, the electronic requirements of the hydrido ligand seem to favor it being in the axial position.

Viewing the coordination geometry in Figures 2 and 3, it becomes evident why the Ir-aryldiazo complex does not adopt the electronically favored geometry B. Although the three phosphine ligands approach their desired meridional arrangement quite closely, with P(1)-Ir-P(2), P(1)-Ir-P(3), and P(2)-Ir-P(3) angles of 94.6 (2)°, 96.9 (2)°, and 167.86 (9)°, respectively, the resulting orientations of their substituents, in particular rings 4 and 6, block the coordination site trans to P(1). In doing so they prevent the Cl atom from assuming the position trans (or pseudo trans) to atom P(1), as is required in geometry B. By moving towards this site trans to atom P(1) several extremely short nonbonded contacts would result, three of the more obvious being Cl-H(66), Cl-H(46), and Cl-H(16). Unable to assume the electronically most favored geometry B, the complex assumes an intermediate configuration that is a compromise between the electronic and steric requirements, a highly distorted SP geometry with an apical phosphine ligand.

The Aryldiazo Ligand. The most striking feature of the aryldiazo ligand is the Ir-N(1)-N(2) angle of 155.2 (7)°, which represents the first clear-cut example of a "half doubly bent" ligand geometry intermediate between the known singly bent and doubly bent geometries.[3,6] The N(1)-N(2)-C(11) angle of 118.8 (8)° is indicative of sp^2 hybridization about atom N(2), and the N(1)-C(11) distance of 1.421 (11) Å is typical of such distances in other aryldiazo ligands, both singly bent and doubly bent. The N(1)-N(2) distance of 1.241 (11) Å is the longest yet observed for any aryldiazo ligand and is virtually identical with the N—N double bond distance found in free HN=NH,[43] CH_3N=NCH_3,[44] and PhN=NPh.[45] The metal-nitrogen distance in this Ir complex is 1.835 (8) Å, which is longer than corresponding distances for singly bent aryldiazo ligands, but shorter than those for doubly bent ligands.[46] The Ir-N-N-Ph linkage is almost completely coplanar and lies in the plane containing Ir, Cl, and P(1), and it is almost perpendicular to the P(2)-P(3) vector (see Table VII). The dihedral angles around N(1)-N(2) and N(2)-C(11) are −179(2)° and −2(2)°, respectively.

We can estimate the approximate metrical parameters for the hypothetical doubly bent and singly bent Ir-N-N-C linkages. Using $RhCl(N_2Ph)(ppp)^+$ [6] as a model for the doubly bent ligand, we estimate the Ir-N, N-N, N-C distances and the Ir-N-N, N-N-C angles to be 1.96 Å, 1.17 Å, 1.44 Å, 125°, and 120°, respectively. Using $Fe(CO)_2(N_2Ph)(PPh_3)_2^+$ [3] and $ReCl_2(N_2Ph)(PMe_2Ph)_3$[47] as models for the singly bent ligand and making corrections for differences in metal, charge, and coordination number, we estimate these same distances and angles to be 1.76 Å, 1.23 Å, 1.42 Å, 175° and 120°, respectively. By averaging the respective distances and angles expected for the two extreme forms of the aryldiazo ligand, we obtain the following values which should resemble those expected for an aryldiazo ligand of intermediate geometry: Ir-N, 1.86 Å; N-N, 1.20 Å; N-C, 1.43 Å; Ir-N-N, 150°; N-N-C, 120°. With the possible exception of the N-N distance these distances and angles compare favorably with those actually found in the present Ir complex: 1.835 (8) Å, 1.24 (1) Å, 1.42 (1) Å, 155.2 (7)°, 118.8 (8)°. Note that the above complexes are 16-18 electron systems and that the metrical parameters of a doubly bent aryldiazo ligand in the Rh complex may well be different from those in an 18-20 electron system.

Now that one "half doubly bent" aryldiazo ligand has been

Table VIII. Infrared N–N Stretching Frequencies

Compound	Observed ν(NN)[a]	ν(NN)[b]	Coupling frequency[b]
$[IrCl(L)(PMePh_2)_3][PF_6]$			
L = C_6H_5–^{14}N–^{14}N	1569 (20), 1644 (43)	1619	1594
C_6H_5–^{14}N–^{15}N	1561 (20), 1624 (21)	1593	1592
C_6H_5–^{15}N–^{15}N	1547 (45), 1610 (20)	1566	1591
$[IrBr(L)(PMePh_2)_3][BF_4]$			
L = C_6H_5–^{14}N–^{14}N	1574 (20), 1650 (72)	1633	1591

[a] Frequencies given as wavenumbers, cm^{-1}; relative intensities (A') appear in parentheses. [b] See ref 15 for calculations.

Table IX. ^{31}P and ^1H Nuclear Magnetic Resonance Data[a]

Compound	Pattern-area	Shift[b] (δ)	Coupling constant
$[IrCl(N_2Ph)(PMePh_2)_3][BF_4]$	doublet-2P	−21.16	12 Hz: $^2J_{PP}$
	triplet-1P	1.34	12 Hz: $^2J_{PP}$
	triplet-6H	1.75	9 Hz: $^2J_{PH} + {}^4J_{PH}$
	doublet-3H	2.06	12 Hz: $^2J_{PH}$
$[IrBr(N_2Ph)(PMePh_2)_3][BF_4]$	doublet-2P	−24.58	12 Hz: $^2J_{PP}$
	triplet-1P	1.18	12 Hz: $^2J_{PP}$
	triplet-6H	1.87	9 Hz: $^2J_{PH} + {}^4J_{PH}$
	doublet-3H	2.18	12 Hz: $^2J_{PH}$

[a] Spectra were measured in CD_2Cl_2 solutions at ambient temperature, about 30 °C. Protons were decoupled (noise decoupling) in the phosphorus spectra. [b] The ^1H reference is internal Me_4Si, and the ^{31}P reference is external H_3PO_4.

discovered, where are others likely to be found? Conceivably, they could be found in almost any complex which had properly arranged molecular orbitals. In fact, partial bending is rare. Based on this work and previous work with nitrosyl ligands, an answer to the question may be ventured. Partially doubly bent aryldiazo ligands or partially bent nitrosyl ligands may be found (1) in five-coordinate, 15–17 electron systems which possess square pyramidal geometries about the metal, (2) in six-coordinate, 17–19 electron systems, (3) in five-coordinate, 16–18 electron systems which possess a distorted coordination geometry about the metal intermediate between square pyramidal and trigonal bipyramidal, (4) in four-coordinate, 16–18 electron systems which possess a distorted coordination geometry about the metal, intermediate between square planar and pseudotetrahedral. Although the structural data are difficult to interpret owing to disorder, the five-coordinate, 15–17 electron nitrosyl complexes $Fe(NO)(dtc)_2$[48] and $Fe(NO)(mnt)_2^{2-}$[49] seem to possess partially bent nitrosyl ligands. The six-coordinate, 17–19 electron nitrosyl complex Fe(NO)(L)(TPP)[50] also has a partially bent nitrosyl ligand (L = 1-methylimidazole). No structures of similar complexes containing second- or third-row metals are known. With the exception of the present Ir complex, there are as yet no well-documented five-coordinate, 16–18 electron nitrosyl or aryldiazo complexes with intermediate coordination geometries.[51]

Synthesis and Spectra. The five-coordinate, cationic complex of Ir was prepared by two different methods. When 1 equiv of $PMePh_2$ adds to $IrCl(N_2Ph)(PPh_3)_2^+$, the blood-red, five-coordinate product $IrCl(N_2Ph)(PMePh_2)(PPh_3)_2^+$ is formed in quantitative yield. However, the addition of a large excess of $PMePh_2$ results in the formation of the trismethyldiphenylphosphine complex through the displacement of all triphenylphosphine ligands (reaction 1). This reaction proceeds smoothly, rapidly, and efficiently at room temperature. In contrast, the same reaction with the analogous nitrosyl complex takes a different course (reaction 3), and all four ligands are displaced by the $PMePh_2$.[52] In view of the greater affinity of Ir(I) for NO^+ in preference to PhN_2^+,[7] it is difficult to rationalize the displacement of the nitrosyl ligand but not the aryldiazo ligand, unless perhaps the much more bulky aryldiazo ligand inhibits the attack of the fourth phosphine ligand on the tris(methyldiphenylphosphine) complex.

$$IrX(N_2Ph)(PPh_3)_2^+ + \text{xs } PMePh_2 \xrightarrow[X\,=\,Cl,\,Br]{} IrX(N_2Ph)(PMePh_2)_3^+ + 2PPh_3 \quad (1)$$

$$\tfrac{1}{2}\,[IrCl(C_8H_{14})_2]_2 + 3PMePh_2 + PhN_2^+ \rightarrow IrCl(N_2Ph)(PMePh_2)_3^+ + C_8H_{14} \quad (2)$$

$$IrCl(NO)(PPh_3)_2^+ + \text{xs } PMePh_2 \rightarrow Ir(PMePh_2)_4^+ \quad (3)$$

$$IrCl(N_2Ph)(PPh_3)_2^+ + L \rightarrow IrCl(N_2Ph)(L)(PPh_3)_2^+ \quad (4)$$

$$L = PR_3, AsR_3, SbR_3, NH_3, NH_2R, PF_3, RNC, CO, \text{pyridine}$$

The title compound was also prepared via another route, reaction 2, which is similar to the addition of PhN_2^+ to $IrCl(PPh_3)_3$.[7] "$IrCl(PMePh_2)_2$" was prepared in situ by adding 1.5–2.0 equiv of the phosphine to chlorobis(cyclooctene)iridium(I)[53] and allowing this mixture to react with excess phenyldiazonium salt. Finally more of the phosphine was added to complete the preparation. The several color changes during the course of the reaction suggest to us the presence of several intermediates. NMR spectra, infrared spectra, and elemental analyses were identical for the complexes prepared by the two different methods.

The complex $IrCl(N_2Ph)(PMePh_2)_3^+$ exhibits unusual chemical behavior. At room temperature, $IrCl(N_2Ph)(CO)(PPh_3)_2^+$ reacts with LiCl to form $IrCl_2(N_2Ph)(CO)(PPh_3)_2$, and $IrCl(N_2Ph)(PPh_3)_3^+$ also reacts with LiCl to form $IrCl_2(N_2Ph)(PPh_3)_2$ with the displacement of 1 equiv of triphenylphosphine. However, $IrCl(N_2Ph)(PMePh_2)_3^+$ will not react with chloride ion under the same conditions. In the first reaction, chloride ion simply adds to the cationic carbonyl complex. To the tris(triphenylphosphine) complex, Cl^- probably will not add owing to the steric hindrance of the third phosphine ligand which is displaced with the addition of chloride ion. Apparently, the third phosphine ligand in the tris(methyldiphenylphosphine) complex inhibits the addition of the chloride ion, and yet is sufficiently tightly bound so that it cannot be displaced.

The infrared spectra of the title complex and its bromo analogue show the presence of two bands which change position upon ^{15}N substitution and are associated with ν(NN). Resonance interaction between ν(NN) and other phenyl vibrational modes has been observed before in similar types of aryldiazo and aryldiazene complexes.[15] Calculation of the N–N stretching frequency in the absence of vibrational resonance yields values of ν(NN) of 1619 cm^{-1} for the chloro complex and 1633 cm^{-1} for the bromo complex (see Table VIII). These bands seem to be coupled with a weak phenyl mode near 1592 cm^{-1}. The 14 cm^{-1} increase in frequency in the bromo complex as compared with the chloro complex is not large, but the change is in the wrong direction if electronic effects of the bromo ligand are responsible. On the other hand, since a bromo ligand is larger than a chloro ligand the geometry of the bromo complex may approach more closely that of a trigonal bipyramid, thus resulting in a slightly higher N–N stretching frequency. The value of the modified N–N stretching frequency (ν')[54] for the chloro complex is 1559 cm^{-1} which is relatively low but still higher than 1513 cm^{-1} for $RhCl(N_2Ph)(ppp)^+$.[55] It is certainly encouraging to find that the 1559-cm^{-1} value of ν' corresponds to an intermediate geometry for the aryldiazo ligand, since this value is near the borderline between values corresponding to singly bent and doubly bent geometries for aryldiazo ligands. Yet, we feel that the coincidence may be fortuitous for we do not believe that values of ν' are sufficiently accurate to reveal subtle differences.

Both the ^{1}H and ^{31}P NMR spectra show the presence of two equivalent phosphines and one unique phosphine ligand (Table IX). In the chloro complex there is a doublet at δ 2.06 corresponding to the protons attached to atom C(1) and a 1:2:1 triplet at δ 1.75 corresponding to the protons attached to atoms C(2) and C(3). Despite the significant deviation of the P(2)–Ir–P(3) angle from linearity (167.86 (9)°), the perfectly formed triplet attests to the strong virtual coupling of the protons on atoms C(2) and C(3) to both atoms P(2) and P(3). The ^{1}H NMR spectra of the bromo complex are very similar. The proton decoupled ^{31}P spectra of the chloro complex shows a triplet at δ 1.34 corresponding to atom P(1) and a doublet at δ −21.16 corresponding to atoms P(2) and P(3). The P–P coupling constant of 12 Hz is typical for a cis arrangement of phosphine ligands. Although clearly crystallographically distinct in the solid state, the phosphine ligands associated with atoms P(2) and P(3) have very similar metrical parameters and conformations and are undoubtedly equivalent in solution. With the exception of the phenyl and methyl substituent groups on atom P(1), the Ir complex would possess an approximate mirror plane of symmetry through which P(2) would be related to P(3). For steric reasons, it is unlikely that the unique phosphine ligand could ever possess internal mirror symmetry, but rotation about the Ir–P(1) bond would give effective mirror symmetry to the whole molecule. The ^{31}P NMR spectra of the bromo complex is similar to that of the chloro complex with one exception. The resonance from the two equivalent phosphine groups is shifted up field by 3.4 ppm to δ −24.58; yet, the position of the unique phosphine resonance remains essentially unchanged. As noted earlier, the bulkier bromo ligand may cause small changes in the coordination geometry of the molecule affecting atoms P(2) and P(3) but not atom P(1). It is anticipated that the structural properties and reaction chemistry of other compounds of the type $IrCl(N_2Ph)(L)(PR_3)_2^+$ will yield valuable information concerning the bending process in nitrosyl and aryldiazo ligands.

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Supplementary Material Available: The table of observed and calculated structure amplitudes, the idealized phenyl H positions (Table IV), and the root-mean-square amplitudes of vibration (Table V) (51 pages). Ordering information is given on any current masthead page.

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(5) Abbreviations: Ph = C_6H_5, Me = CH_3, Et = C_2H_5, ppp = $PhP(CH_2CH_2CH_2PPh_2)_2$, Ar = aryl group, R = organic group, L = neutral ligand, X = anionic ligand, mnt = $S_2C_2(CN)_2^{2-}$, dtc = $S_2CNMe_2^{-1}$, TPP = tetraphenylporphinato ligand, Tol = $C_6H_4CH_3$.

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Charge-Transfer Complexes. NH_3–O_3, NH_3–SO_2, and $N(CH_3)_3$–SO_2[1]

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Abstract: The donor–acceptor complex between trimethylamine and sulfur dioxide is the strongest (in terms of its dissociation energy to $N(CH_3)_3$ plus SO_2) such complex yet to be studied experimentally in the gas phase. Ab initio self-consistent-field theory has been applied to this and two related complexes, NH_3O_3 and NH_3SO_2. Minimum basis sets were used for all three complexes, while for NH_3SO_2 two considerably larger sets (double ζ and double ζ plus sulfur d functions) were employed. The equilibrium structure of these complexes was predicted by an investigation of many points on the respective potential energy surface. To a surprising degree, the O_3 or SO_2 molecule is found to lie in a plane nearly perpendicular to the amine C_{3v} axis. Further, the central atom in O_3 and SO_2 is predicted to lie only slightly off the amine C_{3v} axis. With these guidelines, the prediction of further structures of this type essentially reduces a one-dimensional search for the central atom–N distance. Using a minimum basis set, the three predicted binding energies are 2.24, 5.00, and 4.06 kcal/mol. Using the double ζ basis set the NH_3–SO_2 dissociation energy is increased to 10.40 kcal/mol. When a set of sulfur d functions is added to the latter set, the binding energy becomes 9.30 kcal/mol in the absence of geometry reoptimization.

Experimental[2] and theoretical[3-5] progress in the study of charge-transfer (or donor–acceptor, a term we use interchangeably) complexes has rapidly accelerated in recent years. The goal of most chemical research in this area is the elucidation of the structure, energetics (especially dissociation energies), and electronic spectroscopy of such species. As an example of the recent theoretical developments we note the ab initio study by Lathan, Pack, and Morokuma[4] of the carbonyl cyanide–benzene complex. In addition to carrying out self-consistent-field (SCF) calculations, they were able to estimate the dispersion energy or electron correlation contribution to the binding or dissociation energy. At the present time, theory appears particularly well suited to the study of charge-transfer complexes, since experimental determinations of their equilibrium geometries are extremely difficult and hence quite rare.[6] The structures and energetics of these molecular complexes are very important to our understanding of molecular interactions, since they lie somewhere between van der Waals molecules[7] and chemically bound systems,[8] and are much less well understood than traditional hydrogen bonding situations.[9]

As pointed out clearly in the recent review of Tamres,[10] there exists at least one major roadblock to the fundamental understanding of charge-transfer complexes. This is the fact that, while existing theoretical models[11,12] and detailed studies[3-5] are appropriate to gas-phase situations, most experimental studies[2] have been made in solution. An example of this dilemma is given by our recent theoretical study[13] of the NH_3 and $N(CH_3)_3$ complexes with the halogens F_2, Cl_2, and ClF. While the theoretical methods predict the ammonia complexes