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Contribution from the Department of Chemistry, Simon Fraser University,
Burnaby, British Columbia, Canada V5A 1S6

Aryldiazenido, Aryldiazene, and Arylhydrazido Complexes. Reaction of Diazonium Ions with Carbonylhydridotris(triphenylphosphine)iridium(I) and the X-Ray Structures of Iridium Complexes Containing Singly and Doubly Protonated Orthometalated Aryldiazenido Ligands

JAMES A. CARROLL, ROGER E. COBBLEDICK, FREDERICK W. B. EINSTEIN, NICHOLAS FARRELL, DEREK SUTTON,* and PETER L. VOGEL

Reaction of substituted benzenediazonium tetrafluoroborates with $IrH(CO)\{P(C_6H_5)_3\}_3$ gives orthometalated arylhydrazido complexes, $[Ir(NHNHC_6H_3R)(CO)(PPh_3)_2]BF_4$, which convert readily to the analogous diazenes, $[Ir(NHNC_6H_3R)-(X)(CO)(PPh_3)_2]BF_4$ with X = F or BF_4. Each type has been structurally characterized by x-ray crystallography. $[Ir(NHNHC_6H_3-2-NO_2)(CO)(PPh_3)_2]BF_4$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.921$ (3) Å, $b = 20.125$ (7) Å, $c = 18.061$ (5) Å, and $\beta = 97.78$ (2)°, $Z = 4$; 2069 reflections having $I > 2.3\sigma(I)$ were used for structure solution and refinement to $R = 0.042$. Two weak N—H···F hydrogen bonds connect the BF_4^- anions to the iridium complex, which has an irregular square-based pyramidal geometry with phosphines on the axis and trans to the Ir–aryl bond. The bond lengths N(1)–N(2) = 1.388 (13) Å and Ir–N(1) = 1.912 (10) Å. The solvated complex $[Ir(NHNC_6H_3-2-CF_3)-(F)(CO)(PPh_3)_2]BF_4·2CH_3OH$ crystallizes in the orthorhombic space group $Pnma$ with $a = 14.61$ (2), $b = 15.80$ (1), and $c = 20.16$ (2) Å, $Z = 4$; 624 reflections for which $I > 2.3\sigma(I)$ allowed solution of the structure and refinement to $R = 0.085$. The pseudooctahedral iridium complex contains trans phosphines related by a crystallographic mirror plane, and a fluorine ligand trans to the Ir–aryl bond of the aryldiazene chelate.
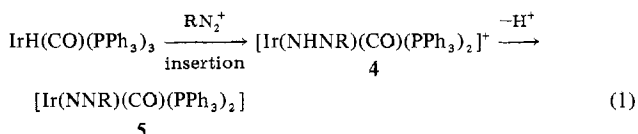
Introduction

The coordination chemistry of the diazonium ion and the chemistry of the aryldiazenido (MNNR), aryldiazene (MNHNR), and related complexes thereby obtained are currently the subject of considerable interest and activity.[1] We have previously established that reactions of diazonium ions with $IrCl(CO)(PPh_3)_2$ are dependent upon various factors including the solvent and temperature. Products include[2] aryldiazenido complexes of iridium(III) from the oxidative addition of RN_2BF_4 or RN_2Cl to give **1** or **2** as well as **3**,


1

2

3
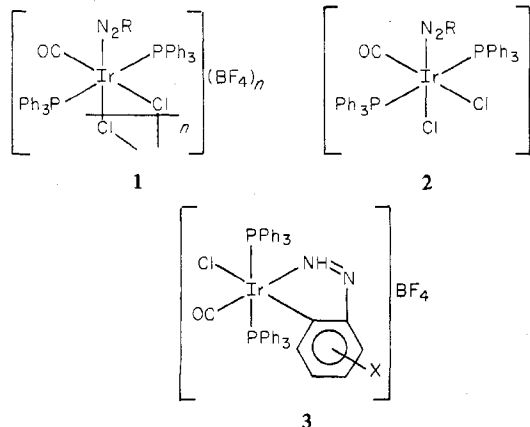
which is an isomer of **1**. Formally the latter can be derived from **1** by cyclometalation of the aryldiazenido group and protonation of the nitrogen atom N(1), but in fact the reaction mechanism is much more complicated than this.[3]

We now have obtained results on the reaction of the hydrido complex $IrH(CO)(PPh_3)_3$ with diazonium ions. Our interest here, apart from the obvious extension of the previous work, was to test the possibility that a hydrido(aryldiazenido)-iridium(III) or aryldiazeneiridium(I) complex intermediate in the formation of the orthometalated complex **3** could be isolated. If coordination alone occurred, a hydrido(aryl-diazenido) complex would result, and such complexes are scarce. If, as frequently happens for hydrido complexes, including some iridium(III) ones,[1] migration of the hydride ligand followed, the diazonium ion will have "inserted" into the Ir–H bond, to yield new aryldiazene (**4**) and aryldiazenido (**5**) complexes (eq 1).

$$IrH(CO)(PPh_3)_3 \xrightarrow[\text{insertion}]{RN_2^+} [Ir(NHNR)(CO)(PPh_3)_2]^+ \xrightarrow{-H^+}$$
$$\phantom{IrH(CO)(PPh_3)_3 \xrightarrow[\text{insertion}]{RN_2^+}} \mathbf{4}$$

$$[Ir(NNR)(CO)(PPh_3)_2] \qquad\qquad\qquad (1)$$
$$\mathbf{5}$$

In actuality, our results indicate that, while such an aryldiazene may be an intermediate, the aryl group of the diazonium ion is orthometalated in the products isolated, resulting in complexes of the hitherto unobserved type **6**, which
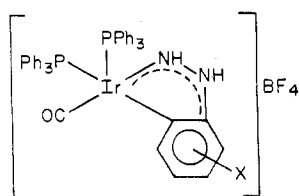
6a, X = 2-NO$_2$
  b, X = 2-CF$_3$
  c, X = 2-F
  d, X = 4-NO$_2$

have a hydrogen at each nitrogen atom. Although these species can be thought of as iridium(I) complexed by protonated diazenes, suggested practice[4] is to name them as iridium(III) hydrazido complexes. The x-ray structure of one such compound is reported here. These complexes may, during purification, convert to aryldiazene complexes with fluoride (7) or BF$_4$ ligands. The structure of one such complex has
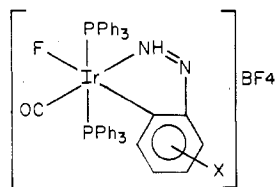
7a, X = 2-NO$_2$
  b, X = 2-CF$_3$
  c, X = 2-F
  d, X = 4-F

also been determined.

Experimental Section

IrH(CO)(PPh$_3$)$_3$ and diazonium tetrafluoroborates were synthesized by standard procedures.[5,6] All preparations were carried out using standard Schlenk apparatus connected to a double manifold for evacuation and back-filling with dry nitrogen. Infrared spectra were determined using Perkin-Elmer 457 or Beckman IR-12 instruments and samples prepared in KBr disks, in mulls, or in solution. ^{1}H NMR spectra were recorded for solutions in acetone-d_6 using a Varian XL-100 spectrometer in CW mode. Solvents were reagent grade, dried, and purified by standard methods, and saturated with dry nitrogen. Decomposition temperatures were determined in air on a Fisher-Johns melting point apparatus. Microanalyses were performed by Mr. M. K. Yang of the SFU Microanalytical Laboratory and by A. Bernhardt, Germany.

Reaction of Diazonium Ions with IrH(CO)(PPh$_3$)$_3$. *o*-Nitrobenzenediazonium Tetrafluoroborate. A solution of IrH(CO)(PPh$_3$)$_3$ (0.4 g) in toluene (25 mL) at 10 °C was treated with a solution of *o*-NO$_2$C$_6$H$_4$N$_2$BF$_4$ (0.2 g) in acetone (10 mL). The deep red solution was partially evaporated under vacuum after stirring for 10 min. A red oil formed on the walls. The supernatant liquid was poured off and the red oil solidified by stirring with hexane. Crystals of **6a** were formed by dissolving the solid in a minimum volume of methanol, adding an equal volume of Et$_2$O and then hexane, and cooling at 8 °C: mp 160–170 °C dec; ν(CO) 2000, ν(NH) 3280 cm^{-1}. X-ray quality crystals were grown by slow evaporation under N$_2$ of a saturated solution in acetone–methanol with a little added HBF$_4$. Anal. Calcd for [Ir(NHNHC$_6$H$_3$NO$_2$)(CO)(PPh$_3$)$_2$]BF$_4$: C, 52.7; H, 3.58; N, 4.28. Found: C, 52.8; H, 3.74; N, 4.09.

A solution of **6a** in methanol–ether was allowed to stand overnight open to air. A light brown solid, **7a**, was precipitated with hexane, washed with ether, and vacuum dried. Infrared (KBr): ν(OH) from CH$_3$OH of solvation ca. 3420, ν(NH) 3140, ν(CO) 2056 cm^{-1}. Anal. Calcd for [Ir(NHNC$_6$H$_3$NO$_2$)(F)(CO)(PPh$_3$)$_2$]BF$_4$·2CH$_3$OH: C, 50.7; H, 3.98; N, 3.95; F, 8.92. Found: C, 49.6; H, 3.93; N, 3.88; F, 8.77.

o-**Trifluoromethylbenzenediazonium Tetrafluoroborate.** A solution of IrH(CO)(PPh$_3$)$_3$ (0.114 g) in toluene (10 mL) was treated slowly with a solution of *o*-CF$_3$C$_6$H$_4$N$_2$BF$_4$ (0.06 g) in acetone (3 mL) at room temperature. After 10 min the orange-brown solution was evacuated to dryness and the orange residue stirred with hexane, filtered, and dried. Infrared (KBr): ν(CO) 2000 (s) and 2050 (w), ν(NH) 3250 cm^{-1}. Although this indicates that **6b** is a major

component, attempted recrystallization of the orange solid from methanol–ether–hexane yielded yellow crystals of **7b**, mp 151–153 °C dec; ν(CO) 2050, ν(NH) 3150 cm^{-1}. It appeared from elemental analysis and IR and NMR spectroscopy that crystals from different batches variously were solvated by MeOH, Et$_2$O, or both. Anal. Calcd for [Ir(NHNC$_6$H$_3$CF$_3$)(F)(CO)(PPh$_3$)$_2$]BF$_4$·(C$_2$H$_5$)$_2$O: C, 52.5; H, 4.04; N, 2.55; F, 13.8. Found: C, 52.7, 52.7; H, 4.25, 4.12; N, 2.42, 2.46. Calcd for [Ir(NHNC$_6$H$_3$CF$_3$)(F)(CO)(PPh$_3$)$_2$]BF$_4$·2CH$_3$OH: C, 51.0; H, 3.89; N, 2.58; F, 14.0. Found: C, 51.1; H, 4.11; N, 2.44; F, 13.7.

o-**Fluorobenzenediazonium Tetrafluoroborate.** The hydride and diazonium salt were reacted in 1:2 ratio in toluene–acetone at room temperature in the usual way to give an orange solution from which solvent was stripped to give an orange solid whose IR spectrum (ν(CO) 2050, 2000 cm^{-1}) indicated the presence of both **6c** and **7c**. On recrystallization from methanol–ether–hexane a yellow solid was obtained having an IR spectrum typical of **7** (ν(CO) 2050 cm^{-1}).

p-**Fluorobenzenediazonium Tetrafluoroborate.** The hydride (0.112 g) in benzene (2 mL) was reacted with 3 equiv of diazonium salt (0.07 g) in acetone (1 mL) at room temperature to give a deep red solution. Solvent was stripped after 45 min. The resulting red oil was stirred with benzene, and the yellow-orange supernatant which separated was treated with hexane and cooled to 0 °C to yield yellow crystals of the orthometalated diazene complex, mp 152–154 °C dec. Infrared (KBr): ν(NH) 3160, ν(CO) 2038, ν(CF) 1230, δ (CH of orthometalated ring) 867, 825 cm^{-1}. Anal. Calcd for [Ir(NHNC$_6$H$_3$F)(F)(CO)(PPh$_3$)$_2$]BF$_4$: C, 53.0; H, 3.52; N, 2.88; F, 11.7. Found: C, 52.9; H, 3.55; N, 2.94; F, 11.6. Crystallization from acetone–toluene of the residue gave the corresponding tetrafluoroborato complex, mp ca. 150 °C dec; ν(NH) 3160, ν(CO) 2070 cm^{-1}. Anal. Calcd for [Ir(NHNC$_6$H$_3$F)(FBF$_3$)(CO)(PPh$_3$)$_2$]BF$_4$: C, 49.6; H, 3.29; N, 2.69; F, 16.4. Found: C, 49.6; H, 3.52; N, 2.57. In several instances crystals were obtained which showed the presence of both the fluoro and tetrafluoroborato complexes as indicated by ν(CO) 2070 and 2038 cm^{-1}, high F and low C analyses.

The red oil was crystallized from ethanol–ether or ethanol–benzene to give red crystals of the diaryltetrazene complex, identified by comparison with an authentic sample,[7] mp 148–155 °C dec, ν(CO) 2057 cm^{-1}. Anal. Calcd for [Ir{(C$_6$H$_4$F)$_2$N$_4$}(CO)(PPh$_3$)$_2$]BF$_4$·C$_6$H$_6$: C, 57.2; H, 3.85; N, 4.85. Found: C, 57.5, 57.4; H, 3.90, 4.00; N, 5.15, 5.21.

Reactions conducted in a similar way using a 1:2 ratio of hydride to diazonium salt gave rise to similar products but relatively less of the tetrazene complex.

p-**Nitrobenzenediazonium Tetrafluoroborate.** IrH(CO)(PPh$_3$)$_3$ (0.12 g) in toluene (8 mL) was treated at room temperature with 3 equiv of diazonium salt (0.085 g) in acetone (4 mL) and stirred for 1 h. The red solution was evaporated to a red oil which was stirred with toluene. The separated toluene solution yielded, on concentration and addition of ether, a brick red solid having ν(CO) 2000 (s) and 2050 (w), ν(NH) 3260 (br), and ν(BF$_4$) 1070 (vs, b) cm^{-1} which is indicated to be impure **6d** and could not be recrystallized satisfactorily. Anal. Calcd for [Ir(NHNHC$_6$H$_3$NO$_2$)(CO)(PPh$_3$)$_2$]BF$_4$: C, 52.6; H, 3.58; N, 4.28. Found: C, 55.8; H, 4.43; N, 3.15.

X-Ray Crystallography. Data Collection for [Ir(NHNHC$_6$H$_3$-2-NO$_2$)(CO)(PPh$_3$)$_2$]BF$_4$. The maroon crystals were air-stable. A single crystal of dimension 0.28 × 0.15 × 0.10 mm was used for x-ray photography and the collection of diffractometer intensity data. Weissenberg and precession photographs using Cu Kα radiation showed the crystals to be monoclinic and the systematic absences (*h0l* for *l* = 2*n* + 1 and 0*k*0 for *k* = 2*n* + 1) unambiguously defined the space group as *P*2$_1$/*c*. Accurate unit cell dimensions were obtained from a least-squares refinement of the setting angles for ten strong reflections with 2θ > 27° centered on a Picker FACS-I automatic four-circle diffractometer (using the Mo Kα_1 peak). Crystal data are as follows: C$_{43}$H$_{35}$BF$_4$IrN$_3$O$_3$P$_2$, M = 982.8, monoclinic, *P*2$_1$/*c*, a = 10.921 (3) Å, b = 20.125 (7) Å, c = 18.061 (5) Å, β = 97.78 (2)°, V = 3933.0 Å^3, ρ_o = 1.65 g cm^{-3} (by flotation), ρ_c = 1.659 g cm^{-3}, Z = 4, λ(Mo Kα_1) 0.709 26 Å, μ(Mo Kα) = 37.5 cm^{-1}, T = 25 ± 2 °C.

Intensity data were collected with the crystal mounted with its needle *a* axis approximately coincident with the Φ axis of the diffractometer. A graphite monochromator and a scintillation counter with pulse-height analysis were used. A total of 2504 reflection intensities with 0 < 2θ < 35° were measured using a θ–2θ scan with a base width of 1.3° increased for dispersion and a scan speed of 2°/min in 2θ. Background

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measurements of 4-s duration were made on either side of the scan limits. Two standard reflections were measured after every 70 measurements to test for radiation damage. A variation of ±3% in I was found, with no decay. Reflections for which $I > 2.3\sigma(I)$, where $\sigma(I) = [S + (t_s/t_b)^2 B + (0.03I)^2]^{1/2}$ with S the total scan count, B the total background count, and t_s and t_b the scan and background count times, respectively, were classed as observed. The intensities were corrected for Lorentz and polarization effects but not for absorption. The extreme error in F arising from this is estimated to be ±4%.

Structure Solution and Refinement of [Ir(NHNHC$_6$H$_3$-2-NO$_2$)-(CO)(PPh$_3$)$_2$]BF$_4$ (6a). A three-dimensional unsharpened Patterson synthesis yielded the positions of the iridium and phosphorus atoms, and the remaining nonhydrogen atoms were located from electron-density difference syntheses. Full-matrix least-squares refinement initially with isotropic temperature parameters for all of the atoms and then with anisotropic thermal parameters for the iridium atom gave $R = 0.090$ where $R = \sum |(|F_o| - |F_c|)|/\sum|F_o|$. An electron-density difference map located most of the phenyl group hydrogen atoms and indicated anisotropic motion of the fluorine atoms of the BF$_4$ and the oxygen atoms of the nitro group. Calculated positions for the aromatic hydrogens were determined using a C–H bond distance of 0.97 Å. Inclusion of these atoms in fixed positions and anisotropic refinement of the fluorine and oxygen atoms reduced R to 0.045. An electron-density difference map gave peaks of the order of 3–4$\sigma(\rho)$, the majority of which were near the iridium atom but included two (which had appeared on earlier difference maps) at reasonable positions for hydrogens bonded to N(1) and N(2) of ca. 3$\sigma(\rho)$. The two hydrogen atoms were included in fixed positions indicated by the difference map peaks and after another two cycles of refinement the final R was 0.042 for the 2069 observed reflections, with a maximum shift to estimated standard deviation ratio of 0.15 for any parameter. The only peak greater than 3$\sigma(\rho)$ in an electron-density difference synthesis was near the iridium atom.

In the final stages of refinement, weights (w) were used where $w = 1/\sigma(F_o)^2$ and analysis showed no unusual variation of average values of $w(|F_o| - |F_c|)^2$ in terms of either F_o or $(\sin\theta)/\lambda$. Atomic scattering factors for all the atoms and anomalous dispersion corrections for the iridium atom were taken from ref 8. Programs used in the structure determination have been noted elsewhere.[9] Final atomic fractional coordinates and thermal parameters are listed in Table I and selected interatomic distances and angles are given in Table II. The equations and deviations of atoms for least-squares planes relevant to the discussion are given in Table III. Observed and calculated structure amplitudes are listed in Table IV (supplementary material).

Data Collection for [Ir(NHNC$_6$H$_3$-2-CF$_3$)(F)(CO)(PPh$_3$)$_2$]BF$_4$·2CH$_3$OH (7b). A yellow-orange crystal in the shape of an approximate rectangular block of dimensions 0.42 × 0.18 × 0.18 mm was used for photography and data collection. Preliminary oscillation and Weissenberg photographs showed the space group to be orthorhombic *Pnma* or *Pn2$_1$a*. Accurate cell dimensions were obtained at 24 °C by least-squares analysis of the setting angles of six accurately centered reflections in the range $2\theta = 22$–32° using a Picker FACS-1 automatic diffractometer and Mo Kα_1 radiation with the crystal mounted with a along the Φ axis. Crystal data: C$_{46}$H$_{42}$BF$_8$IrN$_2$O$_3$P$_2$, mol wt 1087.8, *Pnma*, $a = 14.61$ (2) Å, $b = 15.80$ (1) Å, $c = 20.16$ (2) Å, $V = 4654$ Å^3, $Z = 4$, λ 0.709 26 Å, μ(Mo Kα) = 32.3 cm^{-1}.

Intensity data were collected in the range $2\theta < 30°$ with the crystal slightly misset with respect to Φ, using the θ–2θ scan technique with a scan rate of 2°/min in 2θ, with a base width of 1.7°, and with background counts of 20-s duration taken at each side of the reflection. Two standard reflections were measured at frequent intervals to monitor possible crystal decomposition or orientation changes. Data collection was interrupted for a period of 5 days, after about half the reflections had been measured, owing to generator breakdown, and upon resumption the intensities of the standard reflections were approximately 50% smaller than before. There were no available crystals of superior quality, so data collection using this crystal was resumed. A total of 1018 unique reflection intensities were measured, of which 624 were classed as observed ($I > 2.3\sigma(I)$). Intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure Solution and Refinement of [Ir(NHNC$_6$H$_3$-2-CF$_3$)(F)-(CO)(PPh$_3$)$_2$]BF$_4$·2CH$_3$OH (7b). Patterson synthesis followed by successive cycles of full-matrix least-squares refinement and electron density difference synthesis located the nonhydrogen atoms (excluding boron). In the centrosymmetric space group *Pnma* there is a
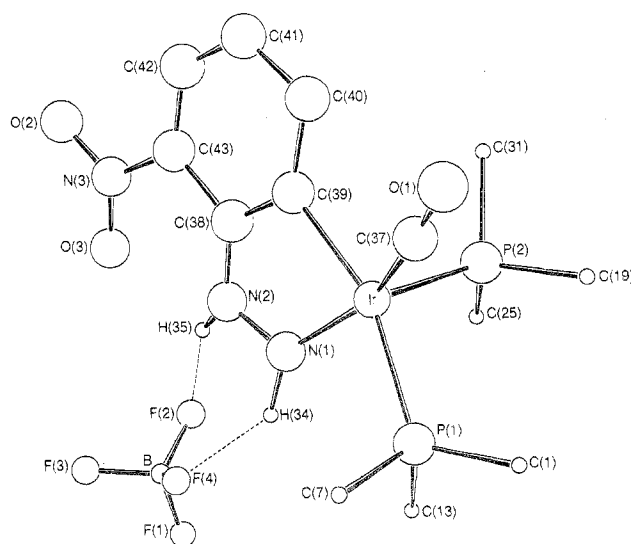
Figure 1. A perspective view of a molecule in [Ir(NHNHC$_6$H$_3$-2-NO$_2$)(CO)(PPh$_3$)$_2$]BF$_4$.

crystallographically imposed mirror plane which relates the two triphenylphosphine groups. All the other atoms of the cationic complex except two fluorines of the CF$_3$ lie in this plane. There was no reason to attempt refinement in the noncentric group *Pn2$_1$a* with the data set available.

With anisotropic temperature factors included for iridium and phosphorus atoms refinement with unit weights gave a final $R = 0.085$. The main features of the structure, including the orthometalation of the aryldiazene ring, were clearly evident at this point. The remaining problems were to describe properly the BF$_4$ group and to identify residual peaks near the diazo moiety. A peak at the calculated center of the BF$_4$ group was evident in an electron-density difference map, but the model did not behave satisfactorily upon the inclusion of the boron atom (so that it was not possible to refine the parameters for this atom). The remaining peaks in an electron-density difference synthesis were in positions expected for solvent hydrogen bonded to N(1) but the poor quality of the x-ray data did not allow interpretation of these peaks in terms of reasonable distances and angles. While we are satisfied with the correctness of the basic description of the complex cation (the main feature of interest in the structure) the failure to achieve a reasonable degree of agreement and the high standard deviations are cause for some concern. However, in view of the limited new information likely to accrue, it was decided that additional crystallographic work was not warranted. Final positional and thermal parameters are listed in Table V, and selected distances and angles in Table VI. Observed and calculated structure amplitudes are listed in Table VII (supplementary material).

Structural Results

Structure of [Ir(NHNHC$_6$H$_3$-2-NO$_2$)(CO)(PPh$_3$)$_2$]BF$_4$ (6a). The structure consists of discrete cationic pentacoordinate iridium complexes linked through weak N—H$\cdots$F bonds to tetrafluoroborate anions. A diagram illustrating one ion pair is shown in Figure 1. Figure 2 gives the packing in the unit cell. The coordination geometry about each iridium is best described as an irregular square-based pyramid. The basal plane is made up of a phosphorus, the carbonyl carbon atom, and both ligating atoms of an orthometalated 2-nitrophenylhydrazido group. The apical position is occupied by a second phosphorus atom. The hydrogen atom bonded to C(12) of the basal triphenylphosphine does approach the iridium atom (Ir–H ~ 3.0 Å) beneath the plane.

The atoms P(1), N(1), C(37), and C(39) comprising the square base are not coplanar within the limits of error. The iridium lies 0.37 Å above the mean plane through the four atoms. (Mean plane calculations for this and other pertinent planes are given in Table III.)

The apical Ir–P bond of 2.322 (4) Å is significantly shorter than the equatorial Ir–P bond of 2.402 (4) Å. This is a larger

Table I. Final Atomic Coordinates, Isotropic Temperature Factors, and Anisotropic Thermal Parameters for
[Ir(NHNHC$_6$H$_3$-2-NO$_2$)(CO)(PPh$_3$)$_2$]BF$_4$

(a) Final Atomic Coordinates^a and Isotropic Temperature Factors

Atom	x	y	z	10^3U, A^2
Ir	17582 (5)	40139 (3)	33810 (3)	
P(1)	2310 (4)	2913 (2)	3034 (2)	
P(2)	3363 (3)	4608 (2)	2973 (2)	
F(1)	−1947 (10)	3285 (8)	435 (6)	
F(2)	−1606 (14)	4183 (6)	1113 (7)	
F(3)	−3360 (10)	3628 (6)	1071 (6)	
F(4)	−1628 (8)	3233 (4)	1686 (5)	
O(2)	−3061 (12)	5933 (7)	3016 (9)	
O(3)	−2561 (9)	5175 (6)	2278 (8)	
B	−2106 (26)	3604 (14)	1056 (16)	84 (7)
N(1)	332 (10)	3960 (6)	2642 (6)	48 (3)
N(2)	−583 (10)	4440 (6)	2632 (6)	48 (4)
N(3)	−2334 (18)	5513 (9)	2843 (10)	96 (6)
O(1)	2931 (8)	3980 (5)	4958 (5)	52 (3)
C(1)	3818 (11)	2543 (6)	3403 (7)	25 (3)
C(2)	4436 (13)	2108 (7)	2977 (7)	47 (4)
C(3)	5478 (13)	1788 (7)	3322 (8)	50 (4)
C(4)	5883 (12)	1870 (7)	4037 (8)	44 (4)
C(5)	5309 (12)	2282 (7)	4472 (7)	45 (4)
C(6)	4277 (13)	2631 (6)	4140 (7)	43 (4)
C(7)	1277 (11)	2309 (6)	3357 (7)	31 (4)
C(8)	1562 (13)	1633 (7)	3409 (8)	59 (5)
C(9)	737 (15)	1181 (8)	3650 (9)	66 (5)
C(10)	−373 (14)	1380 (8)	3851 (8)	63 (5)
C(11)	−684 (14)	2031 (9)	3806 (9)	70 (5)
C(12)	124 (14)	2500 (7)	3542 (8)	56 (5)
C(13)	2147 (12)	2802 (6)	2032 (7)	35 (4)
C(14)	1061 (13)	2613 (7)	1631 (8)	46 (4)
C(15)	899 (15)	2613 (8)	843 (9)	67 (5)
C(16)	1866 (15)	2801 (8)	488 (9)	68 (5)
C(17)	2923 (14)	2977 (8)	850 (9)	65 (5)
C(18)	3112 (12)	2999 (7)	1637 (8)	46 (4)
C(19)	4905 (11)	4273 (6)	3305 (7)	32 (4)
C(20)	5590 (12)	3964 (7)	2821 (7)	44 (4)
C(21)	6732 (14)	3654 (8)	3115 (9)	61 (5)
C(22)	7098 (14)	3681 (8)	3842 (9)	65 (5)
C(23)	6423 (13)	3980 (7)	4329 (8)	52 (4)
C(24)	5298 (12)	4280 (6)	4048 (7)	40 (4)
C(25)	3220 (12)	4700 (7)	1968 (7)	41 (4)
C(26)	4216 (14)	5005 (7)	1675 (8)	57 (5)
C(27)	4089 (15)	5115 (8)	894 (10)	74 (5)
C(28)	3053 (16)	4965 (8)	455 (9)	72 (5)
C(29)	2068 (15)	4688 (8)	730 (9)	72 (5)
C(30)	2171 (13)	4550 (7)	1507 (8)	58 (5)
C(31)	3436 (12)	5490 (6)	3244 (7)	30 (4)
C(32)	2428 (12)	5883 (7)	2991 (7)	48 (4)
C(33)	2435 (14)	6560 (7)	3163 (8)	55 (4)
C(34)	3450 (14)	6826 (8)	3558 (9)	63 (5)
C(35)	4508 (14)	6458 (8)	3797 (8)	60 (5)
C(36)	4475 (12)	5776 (7)	3645 (7)	44 (4)
C(37)	2493 (10)	3981 (6)	4303 (6)	25 (3)
C(38)	−363 (13)	4871 (7)	3172 (8)	47 (4)
C(39)	678 (12)	4806 (6)	3670 (7)	36 (4)
C(40)	1007 (13)	5245 (7)	4267 (8)	56 (5)
C(41)	132 (15)	5749 (8)	4360 (9)	66 (5)
C(42)	−880 (14)	5822 (8)	3897 (9)	61 (5)
C(43)	−1195 (14)	5421 (8)	3341 (9)	59 (5)
H(34)	0	360	220	48
H(35)	−110	445	215	48

(b) Anisotropic Thermal Parameters^b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	277 (4)	261 (4)	390 (4)	0 (4)	55 (4)	−28 (4)
P(1)	37 (3)	25 (2)	34 (2)	−3 (2)	0 (2)	−2 (2)
P(2)	32 (3)	30 (3)	39 (3)	−2 (2)	4 (2)	−1 (2)
F(1)	106 (9)	313 (19)	72 (8)	34 (11)	−8 (7)	−40 (10)
F(2)	270 (17)	123 (11)	156 (12)	−100 (11)	−115 (11)	77 (9)
F(3)	94 (9)	153 (11)	134 (10)	48 (8)	−13 (7)	−20 (8)
F(4)	70 (6)	90 (7)	77 (7)	−2 (6)	−11 (5)	6 (6)
O(2)	119 (11)	143 (13)	213 (16)	80 (11)	98 (11)	85 (13)
O(3)	26 (7)	65 (9)	173 (14)	8 (6)	1 (8)	58 (9)

^{a} Values ×10^5 for Ir, ×10^4 for P, F, O, N, C, and B, and ×10^3 for H. Estimated standard deviation is in parentheses. ^{b} In the form exp[−2π^2($h^2a^{*2}U_{11}$ + ... + 2$hka^*b^*U_{12}$ + ...)]. Values are ×10^4 A^2 for Ir and ×10^3 A^2 for P, F, and O. Esd's in parentheses.

Table II. Selected Interatomic Distances and Angles for
[Ir(NHNHC$_6$H$_3$-2-NO$_2$)(CO)(PPh$_3$)$_2$]BF$_4$^{a}

(a) Distances, Å

Ir–P(1)	2.402 (4)	Ir–P(2)	2.322 (4)
Ir–C(37)	1.750 (12)	Ir–N(1)	1.912 (10)
Ir–C(39)	2.091 (13)	P(1)–C(1)	1.848 (12)
P(1)–C(7)	1.808 (13)	P(1)–C(13)	1.808 (13)
P(2)–C(19)	1.837 (13)	P(2)–C(25)	1.811 (13)
P(2)–C(31)	1.840 (13)	B–F(1)	1.324 (26)
B–F(2)	1.286 (26)	B–F(3)	1.375 (25)
B–F(4)	1.400 (27)	N(1)–N(2)	1.388 (13)
N(2)–C(38)	1.302 (15)	C(38)–C(39)	1.357 (17)
C(38)–C(43)	1.490 (18)	C(39)–C(40)	1.403 (17)
C(40)–C(41)	1.418 (18)	C(41)–C(42)	1.300 (18)
C(42)–C(43)	1.300 (18)	C(43)–N(3)	1.444 (20)
N(3)–O(2)	1.229 (18)	N(3)–O(3)	1.224 (17)
C(37)–O(1)	1.215 (12)	Mean C–C (phenyl groups)	1.378 (5)

(b) Angles, Deg

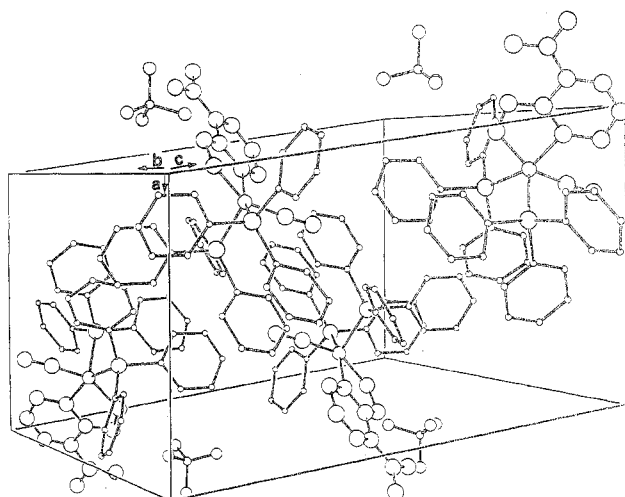|			
P(1)–Ir–P(2)	99.5 (1)	P(1)–Ir–C(37)	96.6 (4)
P(1)–Ir–N(1)	88.6 (3)	P(1)–Ir–C(39)	159.8 (4)
P(2)–Ir–C(37)	93.0 (4)	P(2)–Ir–N(1)	112.7 (3)
P(2)–Ir–C(39)	99.4 (4)	N(1)–Ir–C(37)	152.6 (5)
N(1)–Ir–C(39)	77.5 (5)	C(37)–Ir–C(39)	89.6 (5)
Ir–P(1)–C(1)	121.4 (4)	Ir–P(1)–C(7)	110.3 (4)
Ir–P(1)–C(13)	112.4 (4)	C(1)–P(1)–C(7)	100.2 (6)
C(1)–P(1)–C(13)	105.9 (6)	C(7)–P(1)–C(13)	105.0 (6)
Ir–P(2)–C(19)	113.9 (4)	Ir–P(2)–C(25)	113.9 (5)
Ir–P(2)–C(31)	114.8 (4)	C(19)–P(2)–C(25)	108.4 (6)
C(19)–P(2)–C(31)	105.2 (6)	C(25)–P(2)–C(31)	99.3 (6)
F(1)–B–F(2)	113.8 (24)	F(1)–B–F(3)	106.2 (22)
F(1)–B–F(4)	110.6 (21)	F(2)–B–F(3)	112.3 (23)
F(2)–B–F(4)	108.1 (22)	F(3)–B–F(4)	105.4 (20)
Ir–N(1)–N(2)	119.1 (8)	N(1)–N(2)–C(38)	113.2 (11)
C(39)–C(38)–C(43)	114.5 (13)	N(2)–C(38)–C(39)	119.0 (13)
N(2)–C(38)–C(43)	126.3 (14)	Ir–C(39)–C(38)	111.0 (10)
Ir–C(39)–C(40)	125.3 (10)	C(38)–C(39)–C(40)	123.6 (13)
C(39)–C(40)–C(41)	115.8 (13)	C(40)–C(41)–C(42)	122.2 (15)
C(41)–C(42)–C(43)	122.6 (16)	C(38)–C(43)–C(42)	121.0 (15)
C(38)–C(43)–N(3)	117.8 (15)	C(42)–C(43)–N(3)	121.1 (16)
C(43)–N(3)–O(2)	117.5 (18)	C(43)–N(3)–O(3)	120.5 (18)
O(2)–N(3)–O(3)	121.9 (20)	Ir–C(37)–O(1)	175.4 (10)

^{a} Esd's in parentheses.

difference than that of 0.042 Å in the structure of carbonylbis(triphenylphosphine)(1,4-di-*p*-fluorophenyltetrazene)-iridium tetrafluoroborate[10] although the mean of the two bond lengths is identical in both structures. The short axial Ir–P bond reflects the lack of any significant interaction at the trans site. Bonding of the carbonyl and phenyl groups is typical.

Figure 2. Molecular packing in a unit cell of [Ir(NHNHC$_6$H$_3$-2-NO$_2$)(CO)(PPh$_3$)$_2$]BF$_4$.

Atoms N(1), N(2), C(38), and C(39) of the chelating, orthometalated 2-nitrophenylhydrazido ligand are coplanar (Plane 9, Table III). The iridium is 0.094 Å above this plane toward the axial phosphine.

Bond distances in the metallocycle are one of the most interesting aspects of this structure determination, in as much as they suggest a large contribution from the formal valence structure depicted as 6a'. This can be seen by reference to
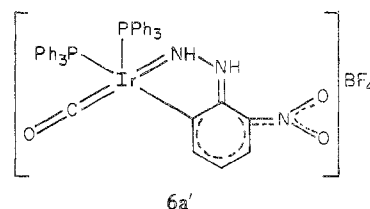

6a'

Table VIII for which the analogous or appropriate bond lengths of several structures are compared with that of 6a. Clearly the structure suggests that the N–N bond order has been considerably reduced at the expense of other bonds, though not to the same extent as in a coordinated phenylhydrazine, and that the bonding is distinctly different from that in the known aryldiazene complexes.

Table III. Least-Squares Planes,^{a} and Deviations of Atoms Therefrom, Calculated for [Ir(NHNHC$_6$H$_3$-2-NO$_2$)(CO)(PPh$_3$)$_2$]BF$_4$

Plane	Atoms defining plane	l	m	n	p	χ^2
1	P(1), N(1), C(37), C(39)	0.710	0.5184	−0.4752	1.7217	48.11^b
2	C(1), C(2), C(3), C(4), C(5), C(6)	0.6145	0.7529	−0.2355	4.4750	2.90
3	C(7), C(8), C(9), C(10), C(11), C(12)	−0.3018	−0.1381	−0.9433	−6.4719	3.37
4	C(13), C(14), C(15), C(16), C(17), C(18)	−0.3226	0.9465	−0.0108	4.7048	1.50
5	C(19), C(20), C(21), C(22), C(23), C(24)	0.5002	0.8589	−0.1101	9.0053	0.85
6	C(25), C(26), C(27), C(28), C(29), C(30)	0.3915	−0.9079	−0.1499	−7.9353	3.01
7	C(31), C(32), C(33), C(34), C(35), C(36)	0.4890	0.1876	−0.8519	−1.4166	5.03
8	C(38), C(39), C(40), C(41), C(42), C(43)	0.5515	0.6013	−0.5782	1.9474	6.04
9	N(1), N(2), C(38), C(39)	0.5758	0.5792	−0.5770	1.7242	0.14

Plane	Atoms and dev (Å) from plane
1	P(1), 0.003; N(1), −0.038; C(37), −0.040; C(39), 0.060; Ir, 0.368
2	C(1), −0.005; C(2), −0.006; C(3), 0.011; C(4), −0.002; C(5), −0.011; C(6), 0.014; P(1), −0.246
3	C(7), −0.010; C(8), 0.001; C(9), 0.010; C(10), −0.005; C(11), −0.011; C(12), 0.018; P(1), 0.003
4	C(13), −0.002; C(14), −0.005; C(15), 0.006; C(16), 0.003; C(17), −0.013; C(18), 0.010; P(1), 0.210
5	C(19), 0.005; C(20), 0.000; C(21), −0.007; C(22), 0.008; C(23), 0.000; C(24), −0.005; P(2), −0.154
6	C(25), 0.009; C(26), −0.017; C(27), 0.013; C(28), 0.004; C(29), −0.011; C(30), 0.002; P(2), −0.128
7	C(31), −0.009; C(32), 0.017; C(33), −0.007; C(34), −0.014; C(35), 0.019; C(36), −0.005; P(2), 0.064
8	C(38), 0.018; C(39), −0.016; C(40), 0.015; C(41), −0.010; C(42), 0.010; C(43), −0.014; N(1), −0.046; N(2), −0.003; Ir, 0.014
9	N(1), 0.001; N(2), −0.002; C(38), 0.004; C(39), −0.002; Ir, 0.094

^{a} Equations of the planes are of the form $lX + mY + nZ - p = 0$ referred to an orthogonal set of axes with X parallel to the a axis, Z parallel to the c^* axis, and Y in the ab plane. ^{b} These atoms are not coplanar.

Table V. Final Atomic Coordinates, Isotropic Temperature Factors, and Anisotropic Thermal Parameters for [Ir(NHNC$_6$H$_3$-2-CF$_3$)(F)(CO)(PPh$_3$)$_2$]BF$_4$·2MeOH

(a) Final Atomic Coordinates^a and Isotropic Temperature Factors

Atom	x	y	z	$10^3 U$, A^2
Ir	661 (3)	2500	1958 (2)	
P	747 (13)	4001 (11)	1985 (9)	
F	199 (3)	250	247 (2)	59 (14)
F(1)	5 (3)	318 (3)	−71 (2)	134 (17)
F(2)	−116 (4)	250	−99 (3)	128 (24)
F(11)	39 (7)	250	−540 (4)	215 (40)
F(12)	15 (6)	319 (6)	−469 (4)	305 (40)
F(13)	129 (9)	250	−472 (6)	280 (55)
C(1)	6 (8)	250	253 (6)	64 (31)
O(1)	−58 (4)	250	299 (3)	47 (16)
N(1)	130 (5)	250	111 (4)	47 (24)
N(2)	88 (5)	250	57 (3)	58 (25)
C(11)	−16 (6)	250	72 (5)	55 (32)
C(12)	−95 (7)	250	20 (5)	63 (32)
C(13)	−179 (7)	250	40 (4)	50 (29)
C(14)	−203 (7)	250	105 (5)	77 (34)
C(15)	−135 (7)	250	164 (4)	44 (29)
C(16)	−41 (5)	250	132 (4)	25 (26)
C(17)	−46 (9)	250	−48 (7)	139 (50)
C(21)	171 (4)	447 (4)	156 (3)	42 (20)
C(22)	245 (5)	397 (4)	159 (3)	53 (22)
C(23)	330 (4)	433 (4)	125 (3)	66 (22)
C(24)	325 (5)	520 (4)	101 (3)	68 (24)
C(25)	243 (5)	563 (4)	101 (3)	79 (23)
C(26)	163 (5)	528 (5)	132 (3)	82 (25)
C(31)	76 (5)	443 (4)	280 (3)	59 (20)
C(32)	95 (5)	403 (4)	337 (4)	72 (27)
C(33)	98 (5)	437 (5)	402 (4)	85 (25)
C(34)	76 (5)	521 (5)	402 (4)	79 (22)
C(35)	56 (6)	570 (4)	350 (4)	87 (23)
C(36)	70 (5)	540 (4)	285 (3)	87 (22)
C(41)	−29 (5)	443 (4)	160 (3)	71 (26)
C(42)	−101 (4)	471 (4)	196 (3)	56 (19)
C(43)	−185 (6)	509 (5)	163 (4)	120 (31)
C(44)	−181 (5)	508 (5)	93 (4)	99 (28)
C(45)	−103 (5)	475 (5)	58 (5)	88 (28)
C(46)	−26 (4)	450 (4)	94 (4)	70 (24)
B^b	47	250	−490	

(b) Anisotropic Thermal Parameters ($\times 10^3$ A^2)^c

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	21 (3)	66 (3)	40 (4)	0 (4)	9 (4)	0 (4)
P	51 (13)	82 (14)	41 (11)	1 (13)	2 (18)	5 (13)

^{a} Values $\times 10^4$ for Ir and P and $\times 10^3$ for F, O, N, and C. Estimated standard deviations in parentheses. ^{b} Calculated values. ^{c} In the form $\exp[-2\pi^2(h^2 a^{*2} U_{11} + \ldots 2hka^*b^* U_{12} + \ldots)]$. Estimated standard deviations are in parentheses.

Table VI. Selected Distances and Angles^a for [Ir(NHNC$_6$H$_3$-2-CF$_3$)(F)(CO)(PPh$_3$)$_2$]BF$_4$·2MeOH

(a) Distances, Å

Ir–P	2.38 (1)	N(1)–N(2)	1.24 (6)
Ir–C(16)	2.02 (6)	N(2)–C(11)	1.56 (9)
Ir–N(1)	1.95 (5)	Mean P–C(PPh$_3$)	1.81 (3)
Ir–F	2.21 (4)	Mean C–C(phenyl)	1.36 (2)

(b) Bond Angles, Deg

P–Ir–P	173.4 (4)	C(1)–Ir–F	99 (3)
P–Ir–C(1)	90.8 (4)	C(16)–Ir–N(1)	80 (3)
P–Ir–C(16)	93.2 (4)	C(16)–Ir–F	169 (2)
P–Ir–N(1)	89.7 (4)	N(1)–Ir–F	89 (3)
P–Ir–F	86.7 (4)	Ir–N(1)–N(2)	122 (4)
C(1)–Ir–C(16)	92 (3)	N(1)–N(2)–C(11)	108 (7)
C(1)–Ir–N(1)	171 (3)		

^{a} Esd's are in parentheses.

In order to check that the least-squares estimated standard deviations in bonds between light atoms were reasonable, we compared the error in a typical C–C bond (ca. 0.02 Å) with that derived from the root mean square variation of the 36 C–C bonds of the phenyl groups (0.032 Å). Taking into
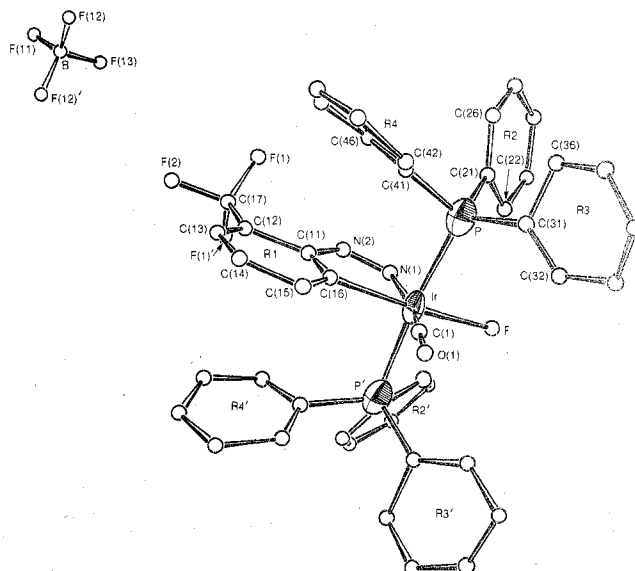

Figure 3. A perspective view of the cation and anion in the structure of [Ir(NHNC$_6$H$_3$-2-CF$_3$)(F)(CO)(PPh$_3$)$_2$]BF$_4$·2MeOH.

account that the latter value is an overestimate due to the evident systematic variation in the phenyl C–C bonds due to thermal motion, the least-squares errors do seem reasonable.

Considering the C(38)–N(2) double bond character, the lack of uniformity of bond length and possible loss of planarity in the metal-bound aryl ring is not surprising. Carbon–carbon bond distances do not vary in a regular pattern around the ring. Conjugation with the nitro group is indicated, as the dihedral angle between the aryl mean plane and the NO$_2$ plane is only 7°. This is in contrast to an angle of 50° in the structure of [IrCl$_2$(2-N$_2$C$_6$H$_4$NO$_2$)(CO)(PPh$_3$)$_2$]·2(CH$_3$)$_2$CO, where the large twist is attributed[2] to the steric interaction between a nitro oxygen atom and the N(2) nitrogen atom of the diazo group (O···N = 2.82 Å). In this work the corresponding distance is O(3)···N(2) = 2.63 Å, and it is likely that there is a weak hydrogen bond (H(35)···O(3) = 2.20 Å) between the nitro oxygen atom and the acidic hydrogen atom bonded to N(2). The same hydrogen atom is involved in bonding to BF$_4^-$.

The tetrafluoroborate anion is bonded to the complex cation by two weak N—H···F bonds. Relevant contact distances are N(2)···F(2) = 2.87 Å and N(1)···F(4) = 2.95 Å. These and the distances and angles about the hydrogen atoms agree with similar dimensions for weak N—H···F bonds observed in other structures.[13,14]

Structure of [Ir(NHNC$_6$H$_3$-2-CF$_3$)(F)(CO)(PPh$_3$)$_2$]BF$_4$· 2CH$_3$OH (7b). The cation (Figure 3) is an orthometalated aryldiazene complex of the type previously identified in the reactions of [IrCl(CO)(PPh$_3$)$_2$] with diazonium ions.[11] The main objective of the structure determination was to obtain structural confirmation of the identity and stereochemistry of the complex 7 resulting from the oxidation of the hydrazido complex 6. No detailed discussion is warranted, especially in view of the limited accuracy. The dimensions of related complexes[11,12] are compared in Table VIII.

Synthetic Results and Discussion

Like Robinson et al.[15] we found that stoichiometric 1:1 reactions of aryldiazonium salts with IrH(CO)(PPh$_3$)$_3$ did not yield identifiable products, which we ascribe to the diazonium ion being largely consumed in reacting with triphenylphosphine.[16] By using 2 or 3 equiv of diazonium salt, nitrogen-containing iridium complexes are formed and these are exclusively bis(phosphine) complexes. Their nature, ease of isolation, and stability are dependent on the choice and position of the substituent on the aryldiazonium ion.

Table VIII. Bond Lengths in Å Useful for Comparison with Those of **6a** and **7b**

Compd	Ir–N	N–N	N–C(aryl)	C–C of metallocycle	Ir–C(aryl)	Ref
[Ir(NHNHC$_6$H$_3$-2-NO$_2$)(CO)(PPh$_3$)$_2$]BF$_4$	1.912 (10)[a]	1.388 (13)	1.302 (15)	1.357 (18)	2.091 (13)[b]	This work
[Ir{(C$_6$H$_4$-4-F)$_2$N$_4$}(CO)(PPh$_3$)$_2$]BF$_4$·C$_6$H$_6$	1.941 (13)[a]	1.400 (16)	[1.270 (16)][c]	[1.350 (16)][c]	[1.971 (10)][d]	10
[Ir(NHNC$_6$H$_3$-4-F)Cl(CO)(PPh$_3$)$_2$]BF$_4$·(CH$_3$)$_2$CO	2.04 (3)[a]	1.28 (3)	1.39 (3)	1.38 (4)	2.01 (3)[e]	11
[Ir(NHNC$_6$H$_3$-2-CF$_3$)F(CO)(PPh$_3$)$_2$]BF$_4$·2CH$_3$OH	1.96 (5)[a]	1.28 (6)	1.44 (9)	1.30 (8)	2.04 (6)[f]	This work
[Ir(NHNC$_6$H$_3$-4-OCH$_3$)Cl$_2$(PPh$_3$)$_2$]·CHCl$_3$	1.990 (7)[e]	1.272 (9)	1.376 (12)	1.409 (12)	2.011 (8)[e]	12
[IrCl$_2$(N$_2$C$_6$H$_4$-2-NO$_2$)(CO)(PPh$_3$)$_2$]·2(CH$_3$)$_2$CO	2.05 (4)[e]	1.19 (4)	1.47 (4)			2
[PtCl(NH$_2$NHC$_6$H$_4$-4-F){P(C$_2$H$_5$)$_3$}$_2$]·BF$_4$		1.436 (11)	1.408 (11)			13

[a] Trans to CO. [b] Trans to P. [c] Distance of analogous bond. [d] Ir–N bond trans to P. [e] Trans to Cl. [f] Trans to F.

Two equivalents of o-NO$_2$C$_6$H$_4$N$_2$BF$_4$ react with the hydride to produce, after workup, crystals of the iridium complex **6a**, having an IR spectrum with ν(CO) 2000 cm^{-1} and typical absorptions for PPh$_3$, NO$_2$, and BF$_4$ groups. No absorption due to ν(NN) could be identified, but ν(NH) occurred prominently at 3280 cm^{-1}. In the ^{1}H NMR peaks due to the two NH groups occurred at 12.66 and 14.16 ppm downfield from Me$_4$Si, and these disappeared on addition of D$_2$O. The structure of **6a** has been established further by x rays as described above.

Neutralization with 1 equiv of base (e.g., 0.05 M K$_2$CO$_3$ in aqueous methanol) gave a violet complex having ν(CO) 1965 and ν(NH) 3250 cm^{-1}, which is assigned the diazene structure **8** with the H atom arbitrarily placed on N(1). The
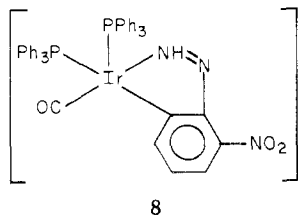
8

stereochemistry of **8** is at present unknown. The ν(CO) value of **8** is typical for neutral iridium(I) complexes. Addition of HBF$_4$ regenerates the red complex **6a**, and ν(CO) is increased by about 35 cm^{-1}. By reference to the cation–neutral pairs [HC(pz)$_3$Mo(CO)$_2$(N$_2$Ph)]$^+$ [17]–[HB(pz)$_3$Mo(CO)$_2$(N$_2$Ph)],[18] [(C$_5$H$_4$PPh$_3$)Mo(CO)$_2$(N$_2$C$_6$H$_4$OCH$_3$)]$^+$ [19]–[(C$_5$H$_5$)Mo(CO)$_2$(N$_2$C$_6$H$_4$OCH$_3$)],[20] and [(C$_5$H$_4$PPh$_3$)Mo(CO)(N$_2$C$_6$H$_4$OCH$_3$)(PPh$_3$)]$^+$ [19]–[(C$_5$H$_5$)Mo(CO)(N$_2$C$_6$H$_4$CH$_3$)(PPh$_3$)],[20] the effect on ν(CO) due to an additional charge alone is expected to be ∼10–15 cm^{-1}. It appears that protonation of **8** effects an increase in oxidation state of the iridium, yet ν(CO) in **6** is rather low for typical cationic complexes of Ir(III) which generally absorb near 2050 cm^{-1}, e.g., [IrCl(CO)(NO)(PPh$_3$)$_2$]$^+$. We feel that the features of the complex cation in **6a**, including the low ν(CO) value and short Ir–N(1) bond, can be rationalized in terms of the following scheme in which it is envisaged that the Ir(III) achieves an 18-electron configuration by the donation of an electron pair from N(1) of the hydrazido-type ligand
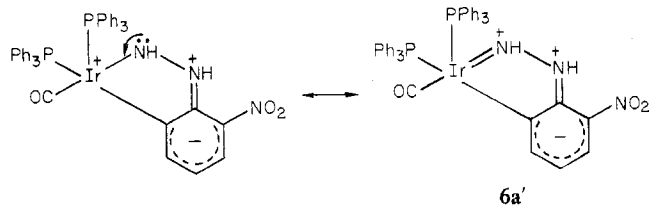
6a'

The red 4-NO$_2$ analogue **6d** has also been isolated, but not obtained pure, using the diazonium salt in 1:2 or 1:3 ratios, and has been identified by its similar properties including ν(CO) 2000, ν(NH) 3250 cm^{-1}, and reaction with base.

In the case of o-CF$_3$C$_6$H$_4$N$_2$BF$_4$ the crude orange solid product had an IR spectrum with ν(CO) principally at 2000 cm^{-1} and presumably contained the analogous complex **6b**.

However, attempts to purify this complex repeatedly failed since it converted rapidly upon workup to the orthometalated iridium(III) aryldiazene complex formulated as **7b**, for which the x-ray structure has been described above. For example, yellow crystals of **7b** were obtained by crystallization of a solution of the orange compound even in degassed methanol, and these exhibited ν(CO) 2050, ν(NH) 3150 cm^{-1} and properties identical with those of the previously synthesized[3] analogous aryldiazene complexes **3**.

In preliminary reactions with other ortho-substituted benzenediazonium salts the results suggest that there is a general tendency for **6** to convert to **7** upon workup and that this is least for an o-NO$_2$ substituent. The change from complex **6** to **7** involves (a) loss of one H$^+$ from N(2), (b) loss of two electrons, (c) shift of a phosphine to the site, vacant in **6**, trans to the other phosphine, and (d) addition of a fluoride ion. It is not clear whether the hydrazido species **6** or the diazene **8** (or both) is oxidized, but these complexes are extremely sensitive to oxidation in solvents which have been degassed by normal procedures. The greater stability of the nitro-substituted complexes is consistent with the electron-withdrawing power of this group. The phosphine shift, though not required a priori, is not exceptional, and an ambient temperature ^{31}P NMR for **6a** produced only one signal, indicating equivalent phosphines in solution, probably due to fluxionality.

Using para-substituted diazonium salts it was evident that reaction proceeded somewhat differently. Thus, whereas o-FC$_6$H$_4$N$_2$BF$_4$ had yielded orange solutions, p-FC$_6$H$_4$N$_2$BF$_4$ reacted to give a deep red solution, and in addition to the yellow orthometalated aryldiazene complex **7d**, the red diaryltetrazene complex [Ir{(FC$_6$H$_4$)$_2$N$_4$}(CO)(PPh$_3$)$_2$]BF$_4$ was isolated in reasonable purity from several runs. It appeared to be formed in increased yield when a hydride:diazonium ion ratio of 1:3 was employed suggesting electrophilic attack of excess diazonium ion on an intermediate iridium–aryldiazene or –aryldiazenido complex such as **4** or **5**. The high nitrogen content of some products from reactions with p-NO$_2$ diazonium ion suggested tetrazene complexes to be present also, but these were not isolated in pure condition.

It was also noticeable, especially with the p-fluorophenyldiazene complex, that the nature of the anionic ligand in the complexes **7** seems to be variable and is probably dependent upon the availability and concentration of anionic ligands in the synthetic procedure. In the complexes designated as **7** it was found to be fluoride, but in repeated syntheses of complexes with p-F and some other substituents, several instances of coordination of FBF$_3$ rather than F have occurred. We do not know whether the usual F ligand occurs as a result of solvolysis of an initial FBF$_3$ ligand or arises from free fluoride generated in solution.

In summary, the observed reactions follow this general pattern. Nitro groups in ortho and para positions yield **6** and are relatively slow to convert to **7**. Fluorine or CF$_3$ appear to give rise to **6**, but these do not easily survive purification procedures and convert to **7**. With para substituents significant amounts of the diaryltetrazene complexes are formed, whereas

this reaction is largely inhibited for ortho substituents.

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Supplementary Material Available: Tables IV and VII, observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Di-μ-adeninium-disilver(I) Perchlorate Monohydrate

CAROLE GAGNON, JOSEPH HUBERT, ROLAND RIVEST, and ANDRÉ L. BEAUCHAMP*

Crystals of the title compound belong to space group $P2_1/c$, with $a = 15.533$ (12) Å, $b = 7.356$ (6) Å, $c = 13.019$ (8) Å, $\beta = 117.43$ (5)°, and $Z = 4$ monomeric units. They contain planar centrosymmetric $[(\text{adeninium})_2\text{Ag}_2]^{4+}$ cations in which two adjacent silver atoms are bridged by two N(3),N(9)-bidentate adeninium cations. N(1) is protonated and the acidic proton originally attached to N(9) in adenine is displaced to N(7) in the complex. Each silver atom is coordinated to N(3) of one ligand (Ag–N(3) = 2.194 (10) Å) and N(9) of the other (Ag–N(9) = 2.155 (10) Å). The distortion at Ag (N(3)–Ag–N(9) = 164.1 (2)°) is ascribed to the arrangement of donor atoms in the ligand. No silver–silver bonding is assumed to exist in spite of the lack of intervening ligand and the relatively short Ag–Ag separation (3.002 (1) Å). Perchlorate ions of one type are involved in tridentate interactions with silver atoms: one oxygen in the molecular plane forms a weak ionic bond to silver (Ag–O = 2.635 (6) Å), whereas two more oxygens interact very weakly by bridging a pair of silver atoms on another complex ion (Ag–O = 2.903 (5) and 3.009 (4) Å). The water molecule is strongly hydrogen bonded to N(7)–H(7), but all other hydrogen bonds are rather weak. Complex cations and the latter set of perchlorate ions form layers between which another set of weakly hydrogen-bonded perchlorate ions is inserted.

Introduction

As part of a program of crystallographic studies on silver and mercury complexes with heterocyclic bases of nucleic acids, we recently reported the crystal structure of a silver nitrate complex with 9-methyladenine.[1] Those crystals contain infinite chains of digonally coordinated silver ions and bridging N(1),N(7)-bidentate ligands. The title compound was prepared from adenine and silver perchlorate in 2 M HClO₄. At that acidity, N(1) and N(9) would be occupied by protons in the free ligand, which would leave N(7) and N(3) as potential binding sites for silver. However, in multidentate ligands, protons are often transferred to other acceptors by entering metal ions. The crystal structure was investigated in order to determine unambiguously the distribution of silver and hydrogen ions on the various basic sites available on the ligand.

Experimental Section

Preparation. Adenine (0.70 g) was dissolved in 500 mL of warm water and 54 mL of a 2% AgClO₄ solution (from Ag₂O and HClO₄) was added, followed by 125 mL of concentrated HClO₄. On standing in the dark at room temperature, the mixture yielded 0.20 g of well-formed colorless crystals.

Crystal data: formula C₅H₈AgCl₂N₅O₉; fw 460.95; monoclinic; space group $P2_1/c$; $a = 15.533$ (12) Å; $b = 7.356$ (6) Å; $c = 13.019$ (8) Å; $\beta = 117.43$ (5)°; $V = 1320.3$ Å³; $d_{\text{calcd}} = 2.32$ g/cm³; $d_{\text{obsd}} =$ 2.30 g/cm³ (flotation in bromoform–bromobenzene); $Z = 4$; μ(Mo Kα) = 19.55 cm⁻¹; $T = 23$ °C; λ(Mo Kα) = 0.710 69 Å (graphite monochromator).

Crystallographic Measurements. A drawing showing the shape and dimensions of the crystal used is part of the supplementary material.

Space group $P2_1/c$ was indicated from a set of precession photographs. Accurate cell parameters were obtained by refining the setting angles of 15 reflections automatically centered and indexed on a Syntex $P\bar{1}$ diffractometer.

Intensities of 2340 independent hkl and $hk\bar{l}$ reflections within a sphere $2\theta \leq 50°$ were measured with the $P\bar{1}$ diffractometer using the $2\theta/\theta$ scan technique. The peaks were scanned from $[2\theta(\text{K}\alpha_1) - 1.0]°$ to $[2\theta(\text{K}\alpha_2) + 1.0]°$. The scan rate was 1° ($2\theta$)/min for most reflections, but higher rates (up to 24°/min) were automatically selected by the autocollection program for strong reflections. Stationary-background counts were taken at each limit of the scan. Counting time was selected to make the background time-to-scan time ratio equal to 0.40. Three standard reflections (310, 040, 014) measured every 50 reflections showed maximum fluctuations of ±3% from average during data collection.

Net intensities I were obtained from $I = (I_t - B/0.40)S$, where I_t is the total scan count, B is the total background count, and S is the scan rate. $\sigma(I)$ was calculated from $\sigma^2(I) = (I_t + B/0.16)S^2 + (0.02I)^2$. A total of 476 reflections (including the systematic absences) with $I/\sigma(I) < 2.5$ were considered as "unobserved". Lorentz and polarization corrections were applied. An absorption correction based on the crystal geometry was applied at a later stage (Program NRC-3,