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Interaction of Neutral Diazo Molecules with Iridium(I) and Rhodium(I): Synthesis, Characterization, and Reaction Chemistry of Iridium(I) and Rhodium(I) Diazo Complexes

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A series of new four-coordinate Ir(I) complexes $IrCl(N_2C_5X_4)(PR_3)_2$ (X = Cl, Br; R = phenyl, *p*-fluorophenyl, *p*-tolyl) has been prepared by allowing the neutral diazo molecule to react with "$IrCl(PR_3)_2$". The complexes have been characterized spectroscopically: Ir is in a square-planar environment with trans phosphine ligands and with the $N_2C_5X_4$ ligand attached in the singly bent fashion through the terminal nitrogen atom. The complex $IrCl(N_2C_5Cl_4)(PPh_3)_2$ reacts with PMe_3, PMe_2Ph, $PMePh_2$, *t*-BuNC, and NO^+ to form the respective five-coordinate complexes. In these complexes, which have been characterized by the usual analytical and spectroscopic techniques, the $N_2C_5Cl_4$ molecule remains coordinated in an η^1 fashion. The complex $IrCl(N_2C_5Cl_4)(PPh_3)_2$ reacts with HCl to form the six-coordinate Ir(III) oxidative addition product. Reaction of this complex, prepared in situ, with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide yields the six-coordinate nitrosyl/diazo complex $IrCl_2(N_2C_5Cl_4)(NO)(PPh_3)_2$. An orthometalated hydrido species $\overline{\mathrm{IrHCl(2,7\text{-}Br_2N_2C}}\mathrm{_{13}H_5)(PPh_3)_2}$ is formed in the reaction of $IrCl(N_2)(PPh_3)_2$ with 2,7-dibromo-9-diazofluorene in the presence of ethanol. The analogous four-coordinate Rh systems, $RhCl(N_2C_5X_4)(PR_3)_2$ (X = Cl, Br; R = Ph, *i*-Pr, *p*-FC_6H_4, Cy, *t*-Bu), were generated as transient intermediates but could not be isolated even at low temperature. The significant differences in the chemistries of $IrCl(N_2C_5Cl_4)(PPh_3)_2$ and $IrCl(N_2Ph)(PPh_3)_2^+$ are contrasted.

Introduction

In various transition-metal systems aryldiazo and aryldiazene ligands have been of great interest in recent years because of their close relationship to dinitrogen and nitrosyl ligands. Recent work has shown that diazo ligands can be prepared from coordinated dinitrogen in Re, Mo, and W complexes,[1-3] that diazene ligands can be prepared from diazo ligands by reaction with protic acids,[3-6] and that diazene ligands in Rh and Pt complexes can be reduced under mild conditions by using hydrogen in the presence of a catalyst[5,6] to form hydrazine ligands. These reactions suggest the possibility of reducing dinitrogen through this chemical route under mild conditions with the aid of transition metals. Indeed, Parshall[6] and Sutton[7a] have suggested that aryldiazene complexes may be useful models for studying the reduction of dinitrogen in synthetic and biological systems.

Until recently the majority of the synthetic, structural, and reaction chemistry studies of organonitrogen ligands coordinated to transition metals has focused on the aryl- and alkyldiazo cations RN_2^+. However, at this time the complexation properties of neutral diazo molecules, RN_2, as well as their versatile reaction chemistry are just beginning to be explored. The interaction of neutral diazo molecules with organometallic complexes generally proceeds in one of two ways: (1) loss of dinitrogen to form a transient carbene species which may or may not be stabilized by the metal or (2) coordination of the intact diazo molecule. A number of organometallic carbene species have been strongly implicated in the polymerization of olefins[8] and in the formation of cyclopropanes.[9-11] In a few instances, stable organometallic carbene complexes have been isolated.[12] Aliphatic diazo compounds are also important precursors in the formation of stable μ-methylene complexes, where the $-CH_2$ moiety acts as a bridging group between two metal centers.[13,14] A number of complexes have been reported recently where the diazo molecule is bonded to one metal center in a monodentate or bidentate fashion[9,11,15-19] or where the intact diazo molecules are incorporated into the products as unusual bridging species.[20-22] To date the interactions of neutral diazo molecules with Ir and Rh systems and of neutral aromatic diazo molecules with transition metals in general are virtually unexplored. We now report the syntheses and characterization of a variety of new Ir complexes of the type $IrCl(N_2C_5X_4)(PR_3)_2$ (X = Cl, Br; R = Ph, *p*-FC_6H_4, *p*-tol),[23] $IrCl(N_2C_5Cl_4)(PPh_3)_2L$ (L = NO^+, *t*-BuNC, PMe_3, PMe_2Ph, $PMePh_2$), and $IrCl_2L'(N_2C_5Cl_4)(PPh_3)_2$ (L′ = H, NO). We also report the attempted isolation of $RhCl(N_2C_5X_4)(PR_3)_2$ (X = Cl, Br; R = Ph, *i*-Pr, *p*-FC_6H_4, Cy, *t*-Bu). The preparation and characterization of $\overline{\mathrm{IrHCl(2,7\text{-}Br_2N_2C}}\mathrm{_{13}H_5)(PPh_3)_2}$, an ortho-

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(23) Abbreviations: Ph = phenyl; *t*-BuNC = *tert*-butyl isocyanide; Me = methyl; *i*-Pr = isopropyl; Cy = cyclohexyl; *t*-Bu = *tert*-butyl; *p*-tol = *p*-tolyl; Cp = cyclopentadiene.

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Table I. Analytical Data for Iridium Diazo Complexes

compd	color	% found (calcd) C	H	N	Cl or Br
$IrCl(N_2C_5Cl_4)(PPh_3)_2 \cdot C_7H_8$ (I)	dark green	52.50 (53.66)	3.41 (3.54)	2.66 (2.61)	16.68 (16.51)
$IrCl(N_2C_5Cl_4)(P(p\text{-tol})_3)_2$ (II)	dark green-brown	52.75 (52.93)	4.06 (3.94)	2.41 (2.41)	16.88 (16.63)
$IrCl(N_2C_5Cl_4)(P(p\text{-}FC_6H_4)_3)_2$ (III)	dark green	46.05 (45.15)	1.90 (2.20)	2.51 (2.57)	15.85 (16.27)
$IrCl(N_2C_5Br_4)(PPh_3)_2$ (IV)	dark green	42.73 (42.45)	2.62 (2.59)	2.32 (2.41)	26.06 (27.58)
$IrCl(N_2C_5Br_4)(P(p\text{-}CH_3C_6H_4)_3)_2 \cdot C_7H_8$ (V)	olive green	47.00 (48.53)	4.42 (3.75)	1.96 (2.10)	20.83 (23.94)
$IrCl(N_2C_5Br_4)(P(p\text{-}FC_6H_4)_3)_2$ (VI)	dark green	36.79 (38.83)	1.73 (1.89)	1.98 (2.21)	25.37 (25.22)
$IrCl(N_2C_5Cl_4)(PMe_3)(PPh_3)_2$ (VII)	yellow-orange	49.52 (49.93)	3.71 (3.69)	2.22 (2.65)	17.31 (16.76)
$IrCl(N_2C_5Cl_4)(PMe_2Ph)(PPh_3)_2$ (VIII)	red	52.78 (52.53)	4.28 (3.66)	2.10 (2.50)	14.18 (15.83)
$IrCl(N_2C_5Cl_4)(PMePh_2)(PPh_3)_2$ (IX)	red-brown	54.50 (54.85)	3.94 (3.64)	1.87 (2.37)	13.23 (15.00)
$IrCl(N_2C_5Cl_4)(t\text{-}BuNC)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$ (X)	dark purple	50.08 (50.37)	3.71 (3.61)	3.47 (3.79)	18.33 (19.20)
$[IrCl(N_2C_5Cl_4)(NO)(PPh_3)_2][PF_6] \cdot CH_3CN$ (XI)	yellow-orange	43.44 (43.09)	3.02 (2.76)	4.70 (4.68)	14.01 (14.80)
$IrCl_2H(N_2C_5Cl_4)(PPh_3)_2$ (XIIa)	yellow-orange	48.27 (48.34)	3.21 (3.05)	2.55 (2.75)	
$IrCl_2(N_2C_5Cl_4)(NO)(PPh_3)_2 \cdot C_7H_8$ (XIII)	yellow	49.38 (50.58)	3.29 (3.34)	3.25 (3.69)	17.66 (18.68)
$IrHCl(N_2C_{13}H_5Br_2)(PPh_3)_2$ (XIV)	orange-yellow	50.00 (49.16)	3.40 (2.95)	2.09 (2.29)	

metalated product of diazofluorene with iridium, are also reported. A preliminary report of this work has appeared.[15]

Experimental Section

All reactions were performed in freshly distilled solvents under a nitrogen atmosphere. Typical reactions involved ca. 0.1 mmol of metal complexes. The following compounds were synthesized by the respective literature methods: $IrCl(N_2)(PPh_3)_2$,[24] $[IrCl(C_8H_{14})_2]_2$,[25] $N_2C_5Cl_4$,[26] $N_2C_5Br_4$,[27] 9-diazofluorene,[28] 2,7-dibromo-9-diazofluorene,[29] *tert*-butyl isocyanide,[30] $[RhCl(C_8H_{14})_2]_2$.[31] All of the precious metal was obtained from Johnson Matthey, Inc., Malvern, Penn. All the phosphines used were purchased from Strem Chemicals, Inc., Newburyport, Mass.; the anhydrous HCl gas was from Matheson Gas Products, Joliet, Ill.; 9-fluorenone was purchased from Aldrich Chemicals, Milwaukee, Wis., and was used without further purification. Elemental analyses were performed by H. Beck of the Northwestern University Analytical Services Laboratory and by Micro-Tech Laboratories, Inc., Skokie, Ill. The results of these analyses appear in Table I. Infrared spectra were recorded in perfluorohydrocarbon, hexachlorobutadiene, and Nujol mulls by using a Perkin-Elmer 283 double-beam spectrometer and calibrated by using a polystyrene film. The NMR spectra were obtained on Varian CFT-20 (^1H) and JEOL FX90Q (^{31}P) spectrometers, with C_6D_6 or $CDCl_3$ as the solvent using Me_4Si and 85% phosphoric acid as the respective external reference standards. The resonance Raman spectra of the majority of these complexes were recorded on a 0.85 Spec 1401 double-monochromator spectrometer with photon-counting detection.[32] A light-stabilized Spectra Physics 164 Ar^+ laser was employed; the spectra were taken at room temperature with 4579-Å excitation by utilizing the 180° backscattering geometry and spinning samples. To avoid excessive decomposition, we employed a power of 20 mW, with 10 mW at the sample.

Syntheses. Bis(triphenylphosphine)(tetrachlorodiazocyclopentadiene)chloroiridium, $IrCl(N_2C_5Cl_4)(PPh_3)_2$ (I). Method a. Equimolar quantities of $IrCl(N_2)(PPh_3)_2$ and $N_2C_5Cl_4$ were dissolved in a minimum amount of solvent[33] at 0 °C. The solution immediately became dark green and was stirred at 0 °C overnight. Hexane was added and the product isolated as dark green microcrystalline powder. The yield was 96% on the basis of the $IrCl(N_2)(PPh_3)_2$ starting material. The material crystallizes from toluene as the monosolvate.

Method b. Di-μ-chloro-tetrakis(1,5-cyclooctene)diiridium(I) and triphenylphosphine were combined in a 1:4 molar ratio in a minimum amount of solvent[33] for 20 min at room temperature. This solution of "$IrCl(PPh_3)_2$"[34] was cooled to 0 °C, 2 equiv of the diazo molecule was added, and stirring was continued overnight at 0 °C. A dark green microcrystalline solid was isolated as in method a, washed with diethyl ether to remove the cyclooctene, and dried in vacuo.

Bis(tri-*p*-tolylphosphine)(tetrachlorodiazocyclopentadiene)chloroiridium, $IrCl(N_2C_5Cl_4)(P(p\text{-tol})_3)_2$ (II). This compound was prepared exactly as was I in method b using tri-*p*-tolylphosphine in toluene or dichloromethane. The solution of "$IrClP_2$" was cooled to −78 °C, 2 equiv of the diazo ligand was added, and stirring at −78 °C was continued for 3 h. Chilled hexane was added to precipitate a dark green-brown solid which was filtered quickly at room temperature, washed with chilled diethyl ether, and dried in vacuo. The yield was 27%.

Bis(tris(*p*-fluorophenyl)phosphine)(tetrachlorodiazocyclopentadiene)chloroiridium, $IrCl(N_2C_5Cl_4)(P(p\text{-}FC_6H_4)_3)_2$ (III). This compound was prepared exactly as was II by using tri-*p*-fluorophenylphosphine. The yield was 70%.

Bis(tri-*p*-tolylphosphine)(tetrabromodiazocyclopentadiene)chloroiridium, $IrCl(N_2C_5Br_4)(PPh_3)_2$ (IV). This compound was prepared in the manner of Ia by using $N_2C_5Br_4$ as the diazo ligand in chloroform solution. The dark green product was filtered, washed with diethyl ether, and dried in vacuo. The yield was 70%.

Bis(tri-*p*-tolylphosphine) (tetrabromodiazocyclopentadiene)chloroiridium, $IrCl(N_2C_5Br_4)(P(p\text{-tol})_3)_2$ (V). This compound was prepared by using $N_2C_5Br_4$ as the diazo ligand and the procedure for II. The yield was 38%.

Bis(tris(*p*-fluorophenyl)phosphine)(tetrabromodiazocyclopentadiene)chloroiridium, $IrCl(N_2C_5Br_4)(P(p\text{-}FC_6H_4)_3)_2$ (VI). This compound was prepared in the manner of III by using $N_2C_5Br_4$ as the diazo molecule. The yield was 50%.

Bis(triphenylphosphine)(trimethylphosphine)(tetrachlorodiazocyclopentadiene)chloroiridium, $IrCl(N_2C_5Cl_4)(PMe_3)(PPh_3)_2$ (VII). Compound I was generated in situ in toluene or dichloromethane solution by method a and cooled to −78 °C. One equivalent of PMe_3 was added to give a dark red solution which was stirred for 30 min at −78 °C. The complex was precipitated with chilled hexane, filtered at low temperature, washed with chilled hexane, and dried in vacuo to yield a yellow-orange product. The yield was 71% on the basis of the $IrCl(N_2)(PPh_3)_2$ starting material.

Bis(triphenylphosphine)(dimethylphenylphosphine)(tetrachlorodiazocyclopentadiene)chloroiridium, $IrCl(N_2C_5Cl_4)(PMe_2Ph)(PPh_3)_2$ (VIII). This compound was prepared exactly as was VII by using 1 equiv of dimethylphenylphosphine. The yield of bright red solid was 87%.

Bis(triphenylphosphine)(methyldiphenylphosphine)(tetrachlorodiazocyclopentadiene)chloroiridium, $IrCl(N_2C_5Cl_4)(PMePh_2)(PPh_3)_2$ (IX). The same procedure as for VII was used with 1 equiv of methyldiphenylphosphine. The yield of red-brown solid was 66%.

Bis(triphenylphosphine)(*tert*-butyl isocyanide)(tetrachlorodiazocyclopentadiene)chloroiridium, $IrCl(N_2C_5Cl_4)(t\text{-}BuNC)(PPh_3)_2$ (X). This compound was prepared in the manner of VII by using 1 equiv

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of *tert*-butyl isocyanide. Yield of dark purple solid was 80%.

Bis(triphenylphosphine)nitrosyl(tetrachlorodiazocyclopentadiene)chloroiridium Hexafluorophosphate, $[IrCl(N_2C_5Cl_4)(NO)(PPh_3)_2][PF_6]$ (XI). Compound I was generated in situ in chloroform solution by method a. One equivalent of $NOPF_6$ in acetonitrile was added to give an orange-brown solution. Stirring was continued overnight at 0 °C. The solvent was removed, and the crude product was recrystallized from dichloromethane/hexane to yield a yellow-orange semicrystalline solid. The yield was 80%.

XIIa from Reaction of $IrCl(N_2C_5Cl_4)(PPh_3)_2$ with HCl. Compound I was generated in situ in toluene by method a and cooled to −78 °C. One equivalent of HCl[35] was added, and the solution was stirred at −78 °C for 8 h to yield a deep red solution. Chilled hexane was added. The resultant yellow-orange product was filtered at low temperature, washed with hexane, and dried in vacuo. The yield was 84% of a complex which analyzes correctly for the HCl adduct.

XIIb from Reaction of $IrCl(N_2C_5Cl_4)(PPh_3)_2$ with DCl. This compound was prepared exactly as was XIIa by using 1 equiv of DCl.[36] The yield was 87% of a complex which analyzes correctly for the DCl adduct.

Bis(triphenylphosphine)nitrosyl(tetrachlorodiazocyclopentadiene)dichloroiridium (XIII). Compound XIIa was generated in situ at −78 °C in dichloromethane. An acetonitrile solution containing 1 equiv of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide was added and the solution warmed to 0 °C. Stirring was continued overnight at 0 °C to yield an orange-brown solution. The solvent was removed and the residue recrystallized from toluene/hexane to give a yellow solid which was washed with copious amounts of methanol and then diethyl ether and dried to give a light yellow solid. The yield was 76% of the crude product. The IR spectrum of this material still showed significant *N*-methyl-*p*-toluenesulfonamide impurity (ν_{NH} = 3178 cm^{-1}, $\nu_{S=O}$ = 1182 cm^{-1}). Hexane was allowed to diffuse slowly into a dichloromethane solution of the crude product to yield a yellow-orange microcrystalline solid, which was filtered, washed with ether, and dried in vacuo.

Attempted Synthesis of Bis(phosphine)(tetrachlorodiazocyclopentadiene)chlororhodium. Di-μ-chloro-tetrakis(1,5-cyclooctene)dirhodium(I) and phosphine[37] were combined in a minimum amount of solvent (dichloromethane, toluene, or acetone). The red-orange "$RhClP_2$" solution was cooled to −78 °C, and 2 equiv of the diazo molecule was added. The solution immediately became dark green or green-brown, indicative of the formation of the $RhCl(N_2C_5Cl_4)P_2$ product. However, attempts to isolate these complexes proved unsuccessful.

Reaction of $IrCl(N_2)(PPh_3)_2$ with 9-Diazofluorene. Equimolar quantities of $IrCl(N_2)(PPh_3)_2$ and 9-diazofluorene were dissolved in a minimum amount of solvent[33] at room temperature. The resultant deep red-brown solution was stirred in the dark for 1–2 h. The product was chromatographed on Fluorisil to yield bright red crystals of fluorenone ketazine[29] (75% yield). This reaction was repeated by using shorter reaction times and lower temperatures (0, −78 °C), and in each case the ketazine was obtained.

Synthesis of $\overline{\mathrm{IrHCl(N_2C}}\mathrm{_{13}H_5Br_2)(PPh_3)_2}$ (XIV). Equimolar quantities of $IrCl(N_2)(PPh_3)_2$ and 2,7-dibromo-9-diazofluorene were dissolved in a mixture of chloroform/ethanol (3:1 volume ratio) at 0 °C with stirring for 3 h. A bright red-orange solution was obtained from which a 50% yield of the orange-yellow orthometalated product was isolated. When the reaction was carried out in the absence of ethanol, no nitrogen-containing products were obtained.

Reaction of $IrCl(N_2C_5Cl_4)(PPh_3)_2$ with CO and SO_2. Compound I was generated in situ in toluene and cooled to −78 °C. CO or SO_2 was bubbled through the solution for about 2–3 min, during which time the solution changed from dark green to bright yellow. Hexane was added, and the product was filtered at low temperature. The products, identified by their infrared spectra and elemental analyses, are $IrCl(CO)(PPh_3)_2$[38] and $IrCl(SO_2)_n(PPh_3)_2$[39] (n = 1, 2).

Reaction of $IrCl(CS)(PPh_3)_2$ or $IrCl(CO)(PPh_3)_2$ with $N_2C_5Cl_4$. Equimolar quantities of $IrCl(CS)(PPh_3)_2$[40] and the diazo molecule were dissolved in toluene at room temperature, and the solution was stirred for 2 days. Precipitation with hexane gave only the thiocarbonyl starting material. Under similar conditions no reaction occurred between $IrCl(CO)(PPh_3)_2$ and $N_2C_5Cl_4$.

Discussion

Preparation and Characterization of Four-Coordinate Complexes. The neutral diazo molecules $N_2C_5Cl_4$ and $N_2C_5Br_4$ react smoothly with $IrCl(N_2)(PPh_3)_2$ with evolution of N_2 gas to afford the four-coordinate complexes $IrCl(N_2C_5X_4)(PPh_3)_2$ (X = Cl (I), Br (IV)) (eq 1). The diazo molecules also react

$$IrCl(N_2)(PPh_3)_2 + N_2C_5X_4 \rightarrow IrCl(N_2C_5X_4)(PPh_3)_2 + N_2 \quad (1)$$

with "$IrClP_2$", generated from the μ-chloro-bis(cyclooctene)iridium(I) dimer and 4 equiv of phosphine,[37] to yield the analogous four-coordinate complexes (eq 2). These

$$[IrCl(C_8H_{14})_2]_2 + 4PPh_3 + 2N_2C_5X_4 \rightarrow 2IrCl(N_2C_5X_4)(PPh_3)_2 + 4C_8H_{14} \quad (2)$$

complexes are thermally unstable in solution; the triphenylphosphine systems decompose within a week at room temperature, while the *p*-tolylphosphine derivatives decompose within 1 day.[41]

The structure of complex I has been determined.[15,42,43] The geometry of the η^1-coordinated diazo molecule is singly bent, consistent with the value of the NN stretching frequency (1872 cm^{-1}) obtained by resonance Raman experiments. The other four-coordinate iridium diazo complexes (II–VI) also exhibit Raman bands in the region 1858–1915 cm^{-1} [ν(NN)], and thus the diazo ligands in these complexes also assume the singly bent geometry. The trends (Table II) of the solid-state NN stretching frequencies with change of phosphine in these four-coordinate complexes are interesting. The phosphines, which are of approximately equal steric bulk, increase in basicity in the order $P(p\text{-}FC_6H_4)_3 < PPh_3 < P(p\text{-}tol)_3$.[44] On the basis of observed trends[44] with other π-ligand systems we would expect the NN stretching frequency to decrease as the basicity of the phosphine increases. This does not occur here. In the known structure of the PPh_3 complex the disposition of the diazo molecule is very effective for creation of an extended delocalized π system utilizing the carbon pπ orbitals of the Cp ring, the N pπ orbitals, and the filled d_{xy} orbitals of Ir.[43] With the resultant delocalized system there may be competition between metal and Cp ring for π donation into the π^* orbitals of the NN fragment, competition to which the NN stretching frequency would be sensitive. This disposition of the Cp ring, known for the PPh_3 system, could depend on solid-state packing effects, since the N–C(Cp) bond has only partial double-bond character and rotation of the Cp ring about this bond is possible in response to packing demands brought about by change of phosphine. It may be that changes in the

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(35) Owing to the extremely small quantities of HCl for this reaction (~0.1–0.2 mmol), dry, degassed benzene was saturated with anhydrous HCl gas. An aliquot of this solution was suspended in water and titrated to determine the concentration (usually 0.17–0.18 mM). A stoichiometric amount of HCl could then easily be used for subsequent reactions.

(36) Anhydrous DCl gas was generated from benzoyl chloride and D_2O according to the method of: Shoemaker, D. P.; Cowland, C. W. "Experiments in Physical Chemistry"; McGraw-Hill: New York, 1962; p 314. Dry, degassed benzene was saturated with the anhydrous DCl gas.

(37) Phosphines used included PPh_3, $P(i\text{-}Pr_3)$, $P(p\text{-}FC_6H_4)_3$, $P(p\text{-}tol)_3$, PCy_3, and $P(t\text{-}Bu_3)$.

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(41) Decomposition via loss of dinitrogen also occurs slowly in the solid state for the four-coordinate iridium(I) complexes; within a few months at room temperature a significant decrease (14–50%) in the nitrogen analyses was observed. This general instability prevented us from getting totally satisfactory analyses in some instances.

(42) The data crystal for the X-ray structure determination came from the same batch of crystals that was used for elemental analysis. While the elemental analysis is poor, the structure determination establishes composition without a doubt.

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Table II. Infrared and Resonance Raman Spectral Data (cm^{-1}) for Iridium Diazo Complexes

compd	$\nu(NN)^a$	other
$IrCl(N_2C_5Cl_4)(PPh_3)_2 \cdot C_7H_8$ (I)	1872	$\nu(IrCl)$ 348; $C_5Cl_4{}^b$ 1263 (s)
$IrCl(N_2C_5Cl_4)(P(p\text{-tol})_3)_2$ (II)	1874	$\nu(IrCl)$ 345
$IrCl(N_2C_5Cl_4)(P(p\text{-}FC_6H_4)_3)_2$ (III)	1858	$\nu(IrCl)$ 360
$IrCl(N_2C_5Br_4)(PPh_3)_2$ (IV)	1915	$\nu(IrCl)$ 345; C_5Br_4 1249 (s), 1332 (m)
$IrCl(N_2C_5Br_4)(P(p\text{-tol})_3)_2 \cdot C_7H_8$ (V)	1908	$\nu(IrCl)$ 349
$IrCl(N_2C_5Br_4)(P(p\text{-}FC_6H_4)_3)_2$ (VI)	1867	$\nu(IrCl)$ 342
$IrCl(N_2C_5Cl_4)(PMe_3)(PPh_3)_2$ (VII)	1541	C_5Cl_4 1288
$IrCl(N_2C_5Cl_4)(PMe_2Ph)(PPh_3)_2$ (VIII)	1635	
$IrCl(N_2C_5Cl_4)(PMePh_2)(PPh_3)_2$ (IX)	1640	C_5Cl_4 1282
$IrCl(N_2C_5Cl_4)(t\text{-}BuNC)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$ (X)	1520, 1453^c	$\nu(CN)$ 2210; $\nu(IrCl)$ 314 (br) C_5Cl_4 1278 (m), 1232 (s)
$[IrCl(N_2C_5Cl_4)(NO)(PPh_3)_2][PF_6] \cdot CH_3CN$ (XI)	1525, 1485, 1448^d 1523, 1449^c	$\nu(NO)$ $1499,^d$ $\nu(IrCl)$ 330 C_5Cl_4 1271; PF_6 837
$IrCl_2H(N_2C_5Cl_4)(PPh_3)_2$ (XIIa)	1614^c	$\nu(IrH)$ 2104; $\nu(IrD)$ 1607 C_5Cl_4 1281; $\nu(IrCl)$ 322 (br)
$IrCl_2(N_2C_5Cl_4)(NO)(PPh_3)_2 \cdot C_7H_8$ (XIII)	1502, 1482, 1440^d 1504, 1443^c	$\nu(NO)$ $1490,^d$ $\nu(IrCl)$ 306, 338 C_5Cl_4 1277
$IrHCl(N_2C_{13}H_5Br_2)(PPh_3)_2$ (XIV)	*e*	$\nu(IrH)$ 2224; $\nu(IrCl)$ 298

[a] NN stretching frequencies obtained from the resonance Raman experiment using 4579-Å excitation unless otherwise noted. [b] Assigned as a C_5X_4 ring vibration. See: Reimer, K. J.; Shaver, A. *Inorg. Chem.* **1975**, *14*, 2707–16. [c] NN stretching frequencies observed in the infrared. [d] The specific band assignments for $\nu(NN)$ are made by comparison with other complexes. Positive identification of these bands awaits ^{15}N isotopic labeling studies. [e] The NN stretching frequency cannot be accurately assigned since it is obscured by fluorenyl bands between 1400 and 1600 cm^{-1}.

Table III. Proton and Phosphorus Nuclear Magnetic Resonance Spectra for Iridium Diazo Complexes[a]

compd	^1H chem shift[b]	^{31}P chem shift[c]
$IrCl(N_2C_5Cl_4)(PPh_3)_2 \cdot C_7H_8$ (I)	7.54 (m, C_6H_5)	10.07 (s)[d]
$IrCl(N_2C_5Cl_4)(P(p\text{-tol})_3)_2$ (II)	2.28 (s, CH_3, 18 H) 7.29 (m, C_6H_4, 24 H)	8.81 (s)
$IrCl(N_2C_5Cl_4)(P(p\text{-}FC_6H_4)_3)_2$ (III)	7.29 (m, C_6H_4)	8.00 (s)
$IrCl(N_2C_5Br_4)(PPh_3)_2$ (IV)	7.40 (m, C_6H_5)	10.25 (s)
$IrCl(N_2C_5Br_4)(P(p\text{-tol})_3)_2 \cdot C_7H_8$ (V)	2.28 (s, CH_3, 18 H) 7.36 (m, C_6H_4, 24 H)	9.09 (s)
$IrCl(N_2C_5Br_4)(P(p\text{-}FC_6H_4)_3)_2$ (VI)	7.30 (m, C_6H_4)	8.15 (s)
$IrCl(N_2C_5Cl_4)(PMe_3)(PPh_3)_2$ (VII)	1.42 (m, CH_3, 9 H) 7.49 (m, C_6H_5, 30 H)	−16.33 (d, 2P) $^2J(PP) = 15$ Hz −51.86 (t, 1P)
$IrCl(N_2C_5Cl_4)(t\text{-}BuNC)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$ (X)	1.17 (s, *t*-Bu, 9 H) 7.47 (m, C_6H_5, 30 H)	−10.22 (s)
$[IrCl(N_2C_5Cl_4)(NO)(PPh_3)_2][PF_6] \cdot CH_3CN$ (XI)	2.13 (s, CH_3, 3 H) 7.51 (m, C_6H_5, 30 H)	−15.38 (s)
$IrCl_2H(N_2C_5Cl_4)(PPh_3)_2$ (XIIa)	7.56 (m, C_6H_5)[e]	−17.34 (s)
$IrCl_2(N_2C_5Cl_4)(NO)(PPh_3)_2 \cdot C_7H_8$ (XIII)	7.56 (m, C_6H_5)	−20.29 (s)
$IrHCl(N_2C_{13}H_5Br_2)(PPh_3)_2$ (XIV)	7.53 (m, C_6H_5) −26.93 (t, IrH) $^2J(PH) = 14.7$ Hz	9.62 (s)

[a] All spectra were obtained at −55 °C unless otherwise noted. The solvent was $CDCl_3$. [b] Chemical shift given in δ referenced to Me_4Si. [c] Chemical shift given in δ; positive δ indicates downfield from H_3PO_4. [d] Spectrum obtained at room temperature. [e] Hydride resonance not observed.

disposition of the Cp ring could be one factor in the unusual trends seen in the NN stretching frequencies.

Comparison of the reaction chemistry of $IrCl(N_2C_5Cl_4)(PPh_3)$ with that of $[IrCl(N_2Ph)(PPh_3)_2][PF_6]$[4] (vide infra) shows some very interesting differences which may indeed arise from changes in the delocalization of electrons throughout the M–N–N–R system in going from IrN_2Cp to IrN_2Ph^+.

Preparation and Characterization of Five-Coordinate Complexes. The compound $IrCl(N_2C_5Cl_4)(PPh_3)_2$ (I) reacts with phosphines at low temperature to give bright red solutions from which highly colored five-coordinate products, $IrCl(N_2C_5Cl_4)(PR_3)(PPh_3)_2$ (VII, VIII, IX), can be isolated. Although these solids appear to be only slightly air sensitive, they are thermally sensitive and decompose slowly at room temperature. In solution these complexes decompose rapidly at room temperature. The IR spectra of these complexes show no bands attributable to $\nu(NN)$. Presumably, as in the four-coordinate complexes, the NN stretching frequencies of these five-coordinate complexes are very weak in the infrared; however, these complexes do exhibit resonance Raman bands in the region 1640–1541 cm^{-1}, which we assign to $\nu(NN)$ (Figure 1). These values are comparable with those obtained for related IrN_2Ph^+ systems, i.e., $IrCl(N_2Ph)(PPh_3)_3{}^+$[4] ($\nu(NN) = 1651$ cm^{-1}) and $IrCl(N_2Ph)(PMePh_2)_2{}^+$[45] ($\nu(NN) = 1644$, 1569 cm^{-1}). From the known structure of $[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$[45] it is likely that the present complexes have the $N_2C_5Cl_4$ ligand attached to the Ir center in a singly bent fashion, although it may be that in the PMe_3 complex, which shows a markedly lower value of $\nu(NN)$, the attachment is intermediate between singly bent and doubly bent.

The ^{31}P NMR spectrum (Table III) of VII, the PMe_3 derivative, consists of a 1:1 doublet and a 1:2:1 triplet with a P–P coupling constant of 15 Hz, comparable with the value of 12 Hz reported for the complex $IrCl(N_2Ph)(PMePh_2)_3{}^+$,[45] suggestive of a similar geometry about the Ir center in the two compounds. ^{31}P NMR spectra of the other two phosphine complexes (VIII and IX) do not show this expected doublet–triplet pattern. Very complicated spectra were obtained

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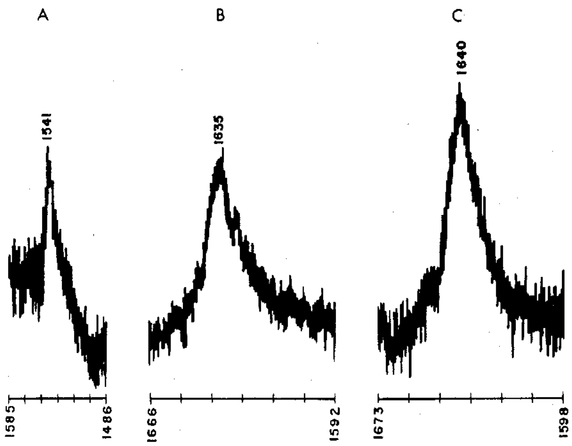

Figure 1. Resonance Raman spectra (4579-Å excitation) of five-coordinate phosphine complexes: A, $IrCl(N_2C_5Cl_4)(PMe_3)(PPh_3)_2$; B, $IrCl(N_2C_5Cl_4)(PMe_2Ph)(PPh_3)_2$; C, $IrCl(N_2C_5Cl_4)(PMePh_2)(PPh_3)_2$.

which may indicate that phosphine dissociation equilibria are involved with these bulkier phosphines PMe_2Ph and $PMePh_2$. Note that we could not isolate $IrCl(N_2C_5Cl_4)(PPh_3)_3$.

Compound I, $IrCl(N_2C_5Cl_4)(PPh_3)_2$, reacts with $NOPF_6$ to form the stable five-coordinate complex $[IrCl(N_2C_5Cl_4)(NO)(PPh_3)_2][PF_6]$ (XI). The infrared spectrum of this complex is assigned in Table II, but in the absence of ^{15}N-labeling experiments we cannot separate $\nu(NO)$ from $\nu(NN)$ with certainty. But all of the possible bands are at low frequencies (1523, 1499, 1449 cm^{-1}), and hence it is very likely that this complex is a square pyramid with a bent NO ligand at the apex. This assignment is consistent with the single resonance at δ −15.38 in the ^{31}P NMR spectrum corresponding to a trans disposition of P ligands in the base of the square pyramid. In addition, the high value of 330 cm^{-1} for $\nu(IrCl)$ in this system is consistent with a square-pyramidal geometry (compare the values of 320 cm^{-1} [46] in $IrCl(CO)(NO)(PPh_3)_2^+$ and 329 cm^{-1} [47] in $IrCl_2(NO)(PPh_3)_2$ both of which are square-pyramidal complexes with bent, apical NO ligands as established by diffraction studies[48,49]). The mode of attachment of the $N_2C_5Cl_4$ ligand cannot be assigned on the basis of the present data, although the almost certain five-coordinate nature of the Ir center indicates an η^1 coordination for this ligand. The low values for $\nu(NN)$ suggest the possibility of distortion away from an idealized singly bent geometry.

Both *t*-BuNC and CH_3CN react instantaneously with $IrCl(N_2C_5Cl_4)(PPh_3)_2$ to form bright purple solutions at −78 °C. The five-coordinate complex $IrCl(N_2C_5Cl_4)(t\text{-}BuNC)(PPh_3)_2$ (X) is isolated at −78 °C; the dark purple solid is stable for only a short period of time at room temperature. The infrared spectrum of this complex is assigned in Table II. Assignment of the structure of this complex cannot be made from the available data. The high value of $\nu(IrCl)$ of 314 cm^{-1} again is suggestive of a square-pyramidal coordination geometry and is consistent with the single resonance at δ −10.22 in the ^{31}P NMR spectrum. But the close correspondence of the values of $\nu(NN)$ to those in the NO^+ complex suggests a similar disposition of the $N_2C_5Cl_4$ ligand in the two systems. If this ligand is in the basal plane of a square pyramid in the *t*-BuNC complex X, this puts the *t*-BuNC in the apical position, not a likely possibility. Clearly more spectral and especially more definitive structural data on a wider range of these five-coordinate N_2R complexes are needed before structures may be reliably deduced from spectral data alone.

Other attempts to make five- or six-coordinate complexes from the reaction of $IrCl(N_2C_5Cl_4)(PPh_3)_2$ with various substrates have been unsuccessful. The reaction with CO yields $IrCl(CO)(PPh_3)_2$ with loss of the diazo molecule. Similarly, reaction with SO_2 yields $IrCl(SO_2)_n(PPh_3)_2$ ($n = 1, 2$). Reactions with H_2, HPF_6, and NO have yielded uncharacterized compounds which contain no nitrogen.

Preparation and Characterization of Six-Coordinate Complexes. Complex I, $IrCl(N_2C_5Cl_4)(PPh_3)_2$, reacts with a stoichiometric amount of HCl at −78 °C to give a bright yellow-orange solid (XII) which analyzes for 1 equiv of HCl/Ir. On the basis of infrared and ^{31}P NMR evidence, compound XII is most probably the six-coordinate $IrCl_2H(N_2C_5Cl_4)(PPh_3)_2$ oxidative addition product. The trans disposition of PPh_3 ligands is established from the ^{31}P NMR spectrum. A medium-weak band at 2104 cm^{-1} in the infrared region shifts to 1607 cm^{-1} when the compound is prepared with the use of DCl in place of HCl. This band is reasonably assigned to $\nu(IrH)$. However, there is no evidence for a hydride resonance in the ^1H NMR spectrum. It is conceivable that in solution there is a rapid equilibrium between the six-coordinate hydride and the five-coordinate product $IrCl_2(HNNC_5Cl_4)(PPh_3)_2$ formed by transfer of the hydride ligand to the coordinated diazo molecule. In this regard the reaction of $[IrCl(N_2Ph)(PPh_3)_2][PF_6]$ with HCl yields the diazene complex $IrCl_3(HNNPh)(PPh_3)_2$.[4] The hydride ligand in XII is certainly labile as judged by the reappearance of the 2104-cm^{-1} band when the deuterated compound, in a Nujol mull, is exposed to moist air. The reaction chemistry of XII is also consistent with its formulation as an Ir(III) hydride. When XII is allowed to react with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS), the nitrosyl complex $IrCl_2(N_2C_5Cl_4)(NO)(PPh_3)_2$ (XIII) is obtained. Although the reaction of MNTS[50] or pentyl nitrite[51] with preformed metal hydride complexes to yield nitrosyl derivatives is well-known, nitrosyl complexes have been generated from nonhydrido metal species as well;[52,53] Robinson and Uttley[52,53] have proposed that formation of these latter nitrosyl complexes occurs by attack of NO on hydride intermediates formed in situ by the reaction of metal halides with the alcoholic solvent. Thus, the formation of an Ir(III) hydride in the reaction of $IrCl(N_2C_5Cl_4)(PPh_3)_2$ with HCl and the subsequent reaction of it with MNTS to form the nitrosyl product appear entirely feasible.

The six-coordinate NO complex $IrCl_2(N_2C_5Cl_4)(NO)(PPh_3)_2$ (XIII) shows a slight lowering of both $\nu(NO)$ and $\nu(NN)$ (Table II) relative to the five-coordinate complex $[IrCl(N_2C_5Cl_4)(NO)(PPh_3)_2][PF_6]$ (XI). The single resonance in the ^{31}P NMR spectrum is consistent with a trans disposition of PPh_3 ligands and the two Ir–Cl stretching frequencies (306, 338 cm^{-1}) in the infrared spectrum suggest the cis disposition of chloro ligands.

Reactions of Diazofluorenes with Ir(I) Systems. Among many possibilities, we chose to extend our studies of the reactions of diazo molecules with Ir(I) systems through the use of diazofluorenes, since diazofluorene itself was known to form stable η^2 complexes with Ni(0),[9] Ru(0),[43] and Pt(0).[43] The reaction of diazofluorene with $IrCl(N_2)(PPh_3)_2$ did not yield a complex containing the diazofluorene molecule but rather produced fluorenone ketazine. We believe that the instability of the hypothetical $IrCl(diazofluorene)(PPh_3)_2$ molecule is

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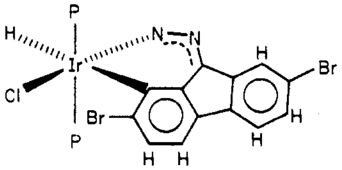
Table IV. Comparison of the Reactions of $IrCl(N_2R)(PPh_3)_2$ with L

L	N_2R	
	$N_2C_5Cl_4$ [a]	N_2Ph^+ [b]
PR_3	$IrCl(N_2C_5Cl_4)(PR_3)(PPh_3)_2$	$IrCl(N_2Ph)(PR_3)(PPh_3)_2^+$
t-BuNC	$IrCl(N_2C_5Cl_4)(t\text{-BuNC})(PPh_3)_2$	$IrCl(N_2Ph)(t\text{-BuNC})(PPh_3)_2^+$
CO	$IrCl(CO)(PPh_3)_2$	$IrCl(N_2Ph)(CO)(PPh_3)_2^+$
SO_2	$IrCl(SO_2)(PPh_3)_2$	?
NO^+	$IrCl(N_2C_5Cl_4)(NO)(PPh_3)_2^+$	$IrCl(NO)(PPh_3)_2^+$
HCl	$IrCl_2H(N_2C_5Cl_4)(PPh_3)_2$	$IrCl_2(HN_2Ph)(PPh_3)_2^+$

[a] This work. [b] Reference 4.

electronic in origin, as space-filled models indicate that there are no serious steric constraints on the molecule. A rough indication of the electronic nature of a given N_2R molecule may be obtained from the pK_a value of the parent R molecule, as the ability to stabilize negative charge within the carbon framework is certainly related to the stability of the possible N_2R complex. The pK_a of $C_5Cl_4H_2$ we estimate to be around 10–13 on the basis of the known pK_a of cyclopentadiene (18.0).[54] The pK_a of fluorene is 22.6.[55] Since the pK_a of 2,7-dibromofluorene is 17.9,[55] we chose to study the reaction of 2,7-dibromo-9-diazofluorene with Ir(I) systems. When 2,7-dibromo-9-diazofluorene is allowed to react with $IrCl(N_2)(PPh_3)_2$ in the presence of ethanol, a yellow-orange solid, XIV, is obtained. The elemental analysis is consistent with the formulation of one diazo molecule per iridium center. Such a complex is not obtained in the absence of ethanol. The compound is not the simple diazo adduct, as the proton NMR spectrum exhibits a 1:2:1 triplet (^2J = 14.7 Hz) at δ −26.93, indicative of a hydride ligand coupled to two equivalent phosphorus nuclei. A very strong infrared band at 2224 cm^{-1} may be assigned to ν(IrH). We believe that a possible structure for compound XIV is the orthometalated hydrido complex



where the positions of the H and Cl ligands could equally well be reversed. Such an orthometalated complex is similar to known orthometalated aryldiazene complexes of iridium.[56] That these complexes also do not form in the absence of ethanol has been discussed by Sutton and Gilchrist.[56] Clearly the reactions of substituted diazofluorenes with $IrCl(N_2)(PPh_3)_2$ are interesting and deserving of further study.

Comparison of the Reaction Chemistry of $IrCl(N_2R)(PPh_3)_2$ (N_2R = $N_2C_5Cl_4$, N_2Ph^+). The reaction chemistry of $IrCl(N_2C_5Cl_4)(PPh_3)_2$ resembles, to a point, the chemistry of the cationic aryldiazonium complex $[IrCl(N_2Ph)(PPh_3)_2][PF_6]$.[4] The chemistries are compared in Table IV. Both compounds form five-coordinate complexes with phosphines and isocyanides and exhibit similar decreases in the values of ν(NN) upon coordination of these ligands. However, the reactions with CO, HCl, and NO^+ are very different. The coordination of the nitrosyl ligand to $IrCl(N_2C_5Cl_4)(PPh_3)_2$ is especially surprising since NO^+ displaces the phenyldiazonium ligand from $IrCl(N_2Ph)(PPh_3)_2^+$.[4] Presumably the subtle electronic changes engendered in going from N_2Ph^+ to the presumably poorer π-acceptor $N_2C_5Cl_4$ are sufficient to alter the chemistry, even though the structures are very similar. Electronic changes manifest themselves in other ways. Our attempts to isolate discrete rhodium complexes $RhCl(N_2C_5Cl_4)P_2$ were unsuccessful, although these complexes were observed as transient species in solution. Evidently the much decreased basicity of the rhodium center does not provide the proper electronic balance for the isolation of stable diazo complexes. Similarly, the basicity[44] of the phosphine ligand is critical. When "$IrCl(PPh_2(OMe))_2$", generated in situ from the μ-chloroiridium cyclooctene dimer and $PPh_2(OMe)$, was allowed to react with $N_2C_5Cl_4$, no isolable diazo complex was obtained. It is apparent that these neutral diazo molecules as well as the diazonium cations are capable of coordinating only to those metal systems which display rather specific electronic properties.

Acknowledgment. We are indebted to Johnson Matthey, Inc., for the loan of precious metals used in this study. This work was kindly supported by the National Science Foundation (Grant CHE76-10335).

Registry No. I, 66973-33-9; II, 73396-32-4; III, 73396-31-3; IV, 73396-30-2; V, 73396-29-9; VI, 73396-28-8; VII, 73396-27-7; VIII, 73453-94-8; IX, 66970-19-2; X, 66970-20-5; XI, 73465-12-0; XIIa, 73396-26-6; XIIb, 73396-25-5; XIII, 73396-24-4; XIV, 73396-23-3; $IrCl(N_2)(PPh_3)_2$, 21414-18-6; $[IrCl(C_8H_{14})_2]_2$, 12246-51-4; fluorenone ketazine, 2071-44-5; 9-diazofluorene, 832-80-4; *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, 80-11-5.

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