in the Rh–C_2F_4 bonding, but we tend to discount it because it is not necessary to rationalize the observed stereochemistry and there is no evidence for it in the other Rh–ligand bonding, although it is not strictly necessary that such contraction be reflected in the remaining bonds.

There is a significant ground-state trans influence here, as the C_5H_5 group is 0.074 Å further from the Rh atom on the side trans to C_2F_4 (trans throughout is taken in a general connotation, since the ligands are not perfectly trans as seen in Figure 2). Both C_2H_4 and C_2F_4 have the potential for exerting a π-trans influence because of their inherent π-acceptor abilities coupled with the presence of a good π-bonding trans ligand (C_5H_5). The C_2F_4 ligand exerts the larger trans influence, indicating that the C_2F_4 ligand withdraws appreciably more electron density from the Rh atom *via* the d_π–π^* route than the C_2H_4 ligand, entirely consistent with our bonding description above.

The metal–ethylene geometry here is reminiscent of suggestions that ligand geometries in metal complexes may correspond to a superposition of the electronic ground-state and low-lying excited-state geometries of uncoordinated ligands.[46] However, the nature, or even existence, of this type of superposition is as yet unclear. It is not certain whether C_2H_4 has an excited state geometry close to that observed here.[47]

The structure found here confirms what was inferred from the nmr, namely, that the coordinated C_2F_4 was quite distorted from noncoordinated C_2F_4. The short Rh–C_2F_4 bond with its high π-bond order is consistent with the chemistry of this and related Rh–ethylene systems in the sense that fluorine substitution stabilizes rhodium–olefin complexes.[48] Also the higher π-bond order in Rh–C_2F_4 (*vs.* Rh–C_2H_4) is entirely consistent with its higher barrier to rotation.[2]

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Reaction of Azidopentaammineiridium(III) Cation with Acid. Intermediate Formation of Coordinated Nitrene

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Abstract: The acid decomposition of $[Ir(NH_3)_5N_3]^{2+}$ salts occurs by a mechanism involving an intermediate complex of coordinated nitrene, $[Ir(NH_3)_5NH]^{3+}$. This intermediate behaves as a powerful electrophile, reacting with HSO_4^- and Cl^- to yield $[Ir(NH_3)_5NH_2OSO_3]^{2+}$ and $[Ir(NH_3)_5NH_2Cl]^{3+}$, respectively. The characterization of these complexes is described and a study has been made of their interconversion and their reactions to form $[Ir(NH_3)_5NH_2OH]^{3+}$. Kinetic data have been obtained for the acid decomposition of $[Ir(NH_3)_5N_3]^{2+}$ salts in an attempt to elucidate the mechanism of the formation and reactions of metal nitrenes.

It has been proposed[1] that acid-catalyzed decomposition of Ru(III) azides proceeds by a mechanism involving an intermediate coordinated nitrene,[2] Ru(III)–NH, which then reacts *via* two separate pathways to yield dinitrogen complexes of Ru(II), $[Ru(NH_3)_5N_2]^{2+}$, and $[(NH_3)_5Ru–N_2–Ru(NH_3)_5]^{4+}$.

The facile reduction of Ru(III) to Ru(II) makes possible the internal redox reactions which yield these products. Several other easily reduced metal ions (Ce(IV),[3] Co(III),[4] Mn(III)[5]) react with N_3^- liberating 1.5 mol of N_2/mol of metal ion. As in the case of Ru(III), these metal ions undergo a one-electron reduction in the reaction.

Azido complexes of metal ions which readily lose one electron (Cr(II),[6] Ti(III),[7] Co(II),[8] Ni(I)[8]) show different behavior. For example, 1 mol of azide ion reacts with 2 mol of $[Cr(H_2O)_6]^{2+}$ producing 1 mol of N_2, $[Cr(H_2O)_6{}^{3+}$, and $[CrNH_3(H_2O)_5]^{3+}$. A small amount of the imido-bridged complex, $[(H_2O)_5Cr–NH–Cr(H_2O)_5]^{4+}$, is also produced and the presence of this species suggests that a coordinated nitrene intermediate might also be involved in these reactions.

We were interested in studying the reactions of coordinated nitrenes where these redox reactions are not possible. The absence of Ir(II) and Ir(IV) amine complexes[9] indicated that decomposition of Ir(III) azides (where N_2 evolution has previously been observed[10])

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might yield nitrenes which behaved differently from the above systems.

A preliminary account of the production of an Ir(III) nitrene intermediate from the decomposition of $[Ir(NH_3)_5N_3]^{2+}$ salts has already appeared.[11] The generality of this mode of reaction of Ir(III) azides has been indicated by isolation of a chloramine complex of Ir(III) from the acid decomposition of $[Ir(en)_2(N_3)_2]Cl$.[12]

Experimental Section

Materials. Iridium trichloride was a loan from the Matthey Bishop Co. Trifluoromethanesulfonic acid was obtained from the 3M Co. Dowex 50W-X2, 100–150 mesh, cation exchange resin was obtained from Sigma Chemical Co. Other chemicals were readily available commercially and were used without further purification.

Preparation of Compounds. Azidopentaammineiridium(III) Chloride. This compound was prepared by a modification of the literature method.[13] The complex $[Ir(NH_3)_5H_2O](ClO_4)_3$ (prepared as previously described[14]) (3.5 g) was dissolved in H_2O (150 ml), and NaN_3 (3.8 g) was added. The pH of the solution was adjusted to 4.7–4.8 by the dropwise addition of 6 *M* $HClO_4$ and the reaction mixture was heated in a polymer pressure bottle for 5 hr at 100°. After cooling and filtration, the reaction solution was passed through an anion exchange column (Dowex 1-X4 in the chloride form. Concentration of the eluate to 20 ml, addition of a saturated solution of LiCl, and cooling yielded the product as an off-white crystalline solid. The product was collected, washed with ethanol and ether, and air-dried. The yield was 2.1 g, 89%. *Anal.* Calcd for $[Ir(NH_3)_5N_3]Cl_2$: N, 28.72; H, 3.87; Cl, 18.17. Found: N, 28.1; H, 3.7; Cl, 18.1.

Azidopentaammineiridium(III) Perchlorate. The complex $[Ir(NH_3)_5N_3]Cl_2$ was dissolved in a minimum amount of H_2O and treated with an equal volume of a saturated solution of $NaClO_4$. The white, crystalline solid which precipitated on cooling for several hours was collected, washed with ethanol and ether, and air-dried. The purity of the compound was determined by a comparison of its uv spectrum with that of a pure sample of $[Ir(NH_3)_5N_3]Cl_2$.

Chloraminepentaammineiridium(III) Perchlorate. Treatment of $[Ir(NH_3)_5N_3]Cl_2$ (1.0 g) in H_2O (20 ml) with concentrated H_2SO_4 (7 ml) resulted in the vigorous evolution of gas and the precipitation of a white solid. A solution of $BaCl_2$ (2.0 g) in H_2O (10 ml) was added to a suspension of the above white solid in 0.1 *M* HCl (80 ml). The precipitated $BaSO_4$ was removed by filtration. On addition of 70% $HClO_4$ (40 ml) and cooling, white crystals of the product separated which were collected, washed with ethanol and ether, and air-dried. The yield was 1.25 g, 80% based on $[Ir(NH_3)_5N_3]Cl_2$. *Anal.* Calcd for $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$: N, 13.40; H, 2.73; ClO_4^-, 47.58; Cl, 5.65. Found: N, 13.2; H, 2.8; ClO_4^-, 47.6; Cl, 5.8.

Chloraminepentaammineiridium(III) Chloride. The complex $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ was dissolved in a minimum amount of 0.1 *M* HCl and excess $(C_6H_5)_4AsCl$ in H_2O was added. The precipitated $(C_6H_5)_4AsClO_4$ was removed by filtration, and concentrated HCl and then ethanol were added to the filtrate. The white solid which precipitated was collected, washed with ethanol and ether, and air-dried. *Anal.* Calcd for $[Ir(NH_3)_5NH_2Cl]Cl_3$: N, 19.32; H, 3.94; Cl^-, 24.45; total Cl, 32.6. Found: N, 19.1; H, 4.0; Cl^-, 25.4; total Cl, 32.6.

Hydroxylaminepentaammineiridium(III) Perchlorate. Method 1. The complex $[Ir(NH_3)_5N_3](ClO_4)_2$ (0.1 g) was dissolved in a minimum amount of 4.5 *M* H_2SO_4 (15 ml) and the solution set aside at room temperature for 48 hr. Addition of 70% $HClO_4$ (25 ml) and cooling precipitated the product as a white solid which was collected, washed with ethanol and ether, and air-dried. *Anal.* Calcd for $[Ir(NH_3)_5NH_2OH](ClO_4)_3$: N, 13.81; H, 2.98. Found: N, 13.4; H, 3.0.

Method 2. $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ (0.1 g) was dissolved in H_2O (10 ml) and the pH of the solution maintained at 5.0 by addition of NaOH solution. After 3 hr, 70% $HClO_4$ (20 ml) was added causing the immediate precipitation of the product which was collected, washed with ethanol and ether, and air-dried. The compound was identified by the identity of its properties with those of the compound prepared by method 1 above.

Hydroxylamine-*O*-sulfonatopentaammineiridium(III) Perchlorate. The complex $[Ir(NH_3)_5N_3](ClO_4)_2$ (0.09 g) was dissolved in 4.5 *M* H_2SO_4 (15 ml). Evolution of gas was observed. After 40 min ice-cold 70% $HClO_4$ (25 ml) and ethanol (5 ml) were added causing the immediate precipitation of the product. The white solid was rapidly collected at 0°, washed with ethanol and ether, and air-dried. Consistent analytical data could not be obtained for this compound, since the product was contaminated with varying amounts of $[Ir(NH_3)_5NH_2OH](ClO_4)_3$.

Hexaammineiridium(III) Chloride. Method 1. The complex $[Ir(NH_3)_6]I_3$ (prepared by a method previously described[15]) (0.22 g) was dissolved in warm H_2O (15 ml). The solution was filtered and $Na_4P_2O_7 \cdot 10H_2O$ (0.5 g) in hot H_2O (5 ml) was added to the filtrate. The complex $[Ir(NH_3)_6]HP_2O_7$ separated immediately and the white solid was isolated by filtration, air-dried, and dissolved in a minimum amount of 1.0 *M* HCl. Addition of an equal volume of concentrated HCl caused the immediate precipitation of the product which was collected, washed with ethanol and ether, and air-dried. The yield was 0.09 g, 69%. *Anal.* Calcd for $[Ir(NH_3)_6]Cl_3$: N, 20.97; H, 4.53. Found: N, 20.8; H, 4.9.

Method 2. The complex $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ (0.34 g) in H_2O (27 ml) was treated with 57% HI solution (17 ml). A golden-brown solid precipitated and the intense brown color of I_3^- was observed. After cooling the reaction mixture for 1 hr at 0°, the solid was collected and air-dried. The solid was dissolved in hot H_2O (25 ml) and $Na_4P_2O_7$ (0.9 g) in H_2O (10 ml) was added causing the immediate precipitation of $[Ir(NH_3)_6]HP_2O_7$. The white solid was collected, air-dried, and then dissolved in a minimum amount of 1 *M* HCl. Addition of an equal volume of concentrated HCl caused the immediate precipitation of the product which was collected, washed with ethanol and ether, and air-dried. The yield was 0.19 g, 84%. *Anal.* Calcd for $[Ir(NH_3)_6]Cl_3$: N, 20.97; H, 4.53. Found: N, 20.8; H, 4.5.

Quantitative Measurement of Released Gas. Reactions were carried out in a round bottom flask (100 ml) fitted with a side arm. The vessel could be connected to a vacuum line through a stopcock and o-ring seal. A weighed amount of solid was placed in the side arm and the acid solution placed in the round bottom flask. After degassing the solution and evacuating the flask, the reactants were mixed. After completion of the reaction, the solution was frozen with liquid nitrogen and the evolved gas collected and measured using a Toepler pump.[16]

Charge Determination by Ion Exchange. A column (10 cm long and 0.7 cm in diameter) was prepared from Dowex 50W-X2 resin (100–150 mesh). Elution of known cations with 2 *M* H_2SO_4 showed that mono- and dipositive cations were not appreciably retarded by the resin, whereas 100–150 ml of acid was required to elute tripositive cations. A tetrapositive cation could be eluted with 3 *M* H_2SO_4 but not by 400 ml of 2 *M* H_2SO_4. The charge on unknown cations was determined by measuring the volume of acid required to elute the unknown from the calibrated column.

Other Physical Measurements. Infrared spectra in the region 4000–400 cm^{-1} were recorded on a Perkin-Elmer 337 grating spectrophotometer calibrated against polystyrene. Ultraviolet and visible spectra were measured on a Cary 14 spectrophotometer using matched 1-cm silica cells. Magnetic susceptibilities of solids were measured on a Faraday balance. Mass spectral measurements were made on a Consolidated Electrodynamics Corp. 21-104 mass spectrograph. Nuclear magnetic resonance spectra were obtained using a Varian Associates T-60 nmr spectrometer. Solutions of complexes were titrated with standardized base using a Radiometer Titrator 11 titrigraph. Equivalent weights were determined by passing solutions of complexes through a cation exchange column in the acid form (Dowex 50W-X8) and titrating the liberated protons with standardized base. Liberated I_2 was determined volumetrically using standardized $Na_2S_2O_3$ solution.

Analyses. Carbon, hydrogen, and nitrogen analyses were carried out by Miss H. Beck of this department. Perchlorate was determined gravimetrically as $(C_6H_5)_4AsClO^4$ by a method previously described.[17] Chloride ion was determined by titration with standardized $AgNO_3$ solution using a Ag/AgCl standard electrode. Sulfate ion was determined gravimetrically as $BaSO_4$.

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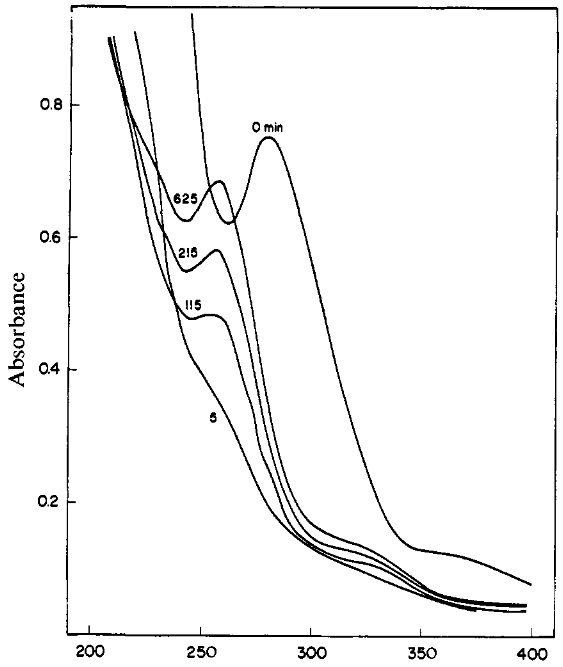

Figure 1. Ultraviolet spectral changes for the acid decomposition of $[Ir(NH_3)_5N_3]^{2+}$ in the presence of excess Cl^-: [complex] = 1.6×10^{-3} *M*, $[H_2SO_4]$ = 4.5 *M*, $[Cl^-]$ = 3.0×10^{-2} *M*, *T* = 22°.

Kinetic Studies of the Acid Decomposition of $[Ir(NH_3)_5N_3]^{2+}$. All kinetic studies were carried out at constant temperature using 10^{-3} *M* solutions of complexes. The rate of decomposition of $[Ir(NH_3)_5N_3](ClO_4)_2$ in aqueous H_2SO_4 was determined by following the decrease in intensity of the 279-nm band of the azido complex. First-order rate constants were calculated from plots of ln $(A_t - A_\infty)$ *vs.* time which were linear for at least 3 half lives. The rate of reaction of the azido complex in aqueous H_2SO_4 in the presence of excess, but small, amounts of Cl^- was determined by monitoring the change in absorbance at 258 nm (the position of the characteristic band of $[Ir(NH_3)_5NH_2Cl]^{3+}$). For Cl^- concentrations up to 0.1 *M*, plots of ln $(A_\infty - A_t)$ *vs.* time showed two reactions to be occurring. The treatment of data is discussed below. For Cl^- concentrations above 0.1 *M*, plots of ln $(A_\infty - A_t)$ *vs.* time were linear.

The rate of reaction of $[Ir(NH_3)_5N_3]^{2+}$ in aqueous HCl to give $[Ir(NH_3)_5NH_2Cl]^{3+}$ was measured by following the increase in absorbance at 258 nm. Rate constants were calculated from linear plots of ln $(A_\infty - A_t)$ *vs.* time. The rate of decomposition of $[Ir(NH_3)_5N_3](ClO_4)_2$ in aqueous $HClO_4$ was followed by monitoring the decrease in absorbance at 279 nm. Plots of ln $(A_t - A_\infty)$ *vs.* time indicated that the initial reaction was followed by a slower decrease in absorbance. Calculation of rate constants is described below.

Kinetic Studies of Other Reactions. Kinetic data were obtained in aqueous solution for the following reactions (eq 1-3). All

$$[Ir(NH_3)_5NH_2OSO_3]^{2+} + HCl \longrightarrow [Ir(NH_3)_5NH_2Cl]^{3+} + HSO_4^- \quad (1)$$

$$[Ir(NH_3)_5NH_2OSO_3]^{2+} + H_2O \longrightarrow [Ir(NH_3)_5NH_2OH]^{3+} + H_2SO_4^- \quad (2)$$

$$[Ir(NH_3)_5NH_2Cl]^{3+} + H_2O \longrightarrow [Ir(NH_3)_5NH_2OH]^{3+} + HCl \quad (3)$$

kinetic studies were carried out a constant temperature using 10^{-3} *M* solutions of complexes. First-order rate constants were calculated from plots of ln $(A_1 - A_0)$ *vs.* time, which were linear for a least 3 half lives.

The rate of reaction 1 was measured by following the change in absorbance at 258 nm. The rate of reaction 2 was determined by monitoring spectral changes at 245 nm. The rate of reaction 3 in both sodium acetate-acetic acid and sodium phosphate-phosphoric acid buffers was determined by following the decrease in absorbance at 258 nm.

Results

Acid Decomposition of $[Ir(NH_3)_5N_3]^{2+}$ Salts. When $[Ir(NH_3)_5N_3]Cl_2$ is decomposed with 4.5 *M* H_2SO_4, the vigorous evolution of a gas is observed and a white solid precipitates. Treatment of solutions of this solid with $BaCl_2$ to remove sulfate yields $[Ir(NH_3)_5NH_2Cl]^{3+}$ salts as the reaction products (eq 4). Quantitative measurements showed that 1.01 mol of gas was liberated per mole of $[Ir(NH_3)_5N_3]Cl_2$ and the gas was shown to be nitrogen by mass spectrometry. Attempts to obtain rate data for this reaction by monitoring changes in the uv spectra of 10^{-3} *M* solutions of the azido complex in 4.5 *M* H_2SO_4 showed that the 279-nm band of $[Ir(NH_3)_5N_3]^{2+}$ disappeared rapidly but that the 258-nm band of $[Ir(NH_3)_5NH_2Cl]^{3+}$ formed only very slowly (Figure 1). This behavior indicated that a stable intermediate was involved in the production of the chloramine complex. In an experiment to determine the nature of the intermediate, it was found that at least 90% of the gas produced in the overall reaction has been evolved during the disappearance of the band due to the azido complex.

$$[Ir(NH_3)_5N_3]Cl_2 + H_2SO_4 \longrightarrow [Ir(NH_3)_5NH_2Cl]^{3+} + Cl^- + SO_4^{2-} + N_2 \quad (4)$$

To further elucidate the mechanism of the formation of $[Ir(NH_3)_5NH_2Cl]^{3+}$, a kinetic study of the overall reaction was carried out in two parts: (i) the decomposition of the azido complex to the intermediate and (ii) the reaction of the intermediate to give $[Ir(NH_3)_5NH_2Cl]^{3+}$.

(i) **Decomposition of $[Ir(NH_3)_5N_3]^{2+}$.** The rate of decomposition of the azido complex to form the intermediate was found to be a function of H_2SO_4 concentration and the rate data are given in Table I.

Table I. Rate Data for the Acid Decomposition of $[Ir(NH_3)_5N_3]^{2+}$ at 22°

Acid	Acid concn, *M*	h_0[a]	$10^4 k_{obsd}$, sec^{-1}
H_2SO_4	4.30	94.4	11.3
H_2SO_4	4.30	94.4	12.1
H_2SO_4	3.23	29.8	5.53
H_2SO_4	2.15	8.20	1.82
H_2SO_4	1.08	1.99	0.45
HCl	6.00	132	15.1
HCl	4.00	25.1	5.38
HCl	2.00	4.90	1.21
$HClO_4$	1.90	5.30	0.98
$HClO_4$	1.90	5.30	0.93

[a] Values obtained from data given in ref 18.

The analysis of these kinetic data was complicated by the high ionic strengths involved. Under these conditions, the molarity of the acid is not a useful measure of the acidity of the medium. Effective acidity scales have been developed for strong acid solutions of which the most widely used is the h_0 function.[18] A plot of k_{obsd} *vs.* h_0 is not linear, leveling off at high h_0 values. Similar behavior was observed by Davis and Lalor[19] for the acid-catalyzed aquation of $[Rh(NH_3)_5N_3]^{2+}$. This behavior was interpreted as involving a preequilibrium to form $[Rh(NH_3)_5N_3H]^{3+}$, which subsequently solvolyzes to yield $[Rh(NH_3)_5$-

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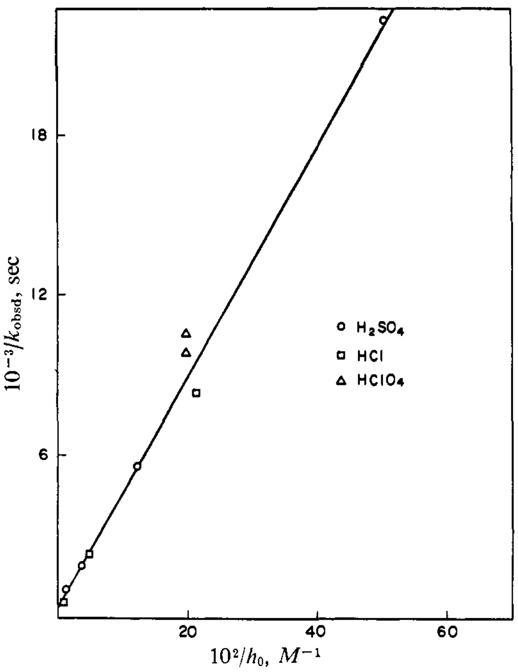

Figure 2. Plot of $1/k_{obsd}$ *vs.* $1/h_0$ for the acid decomposition of $[Ir(NH_3)_5N_3]^{2+}$ in various acids at 22°.

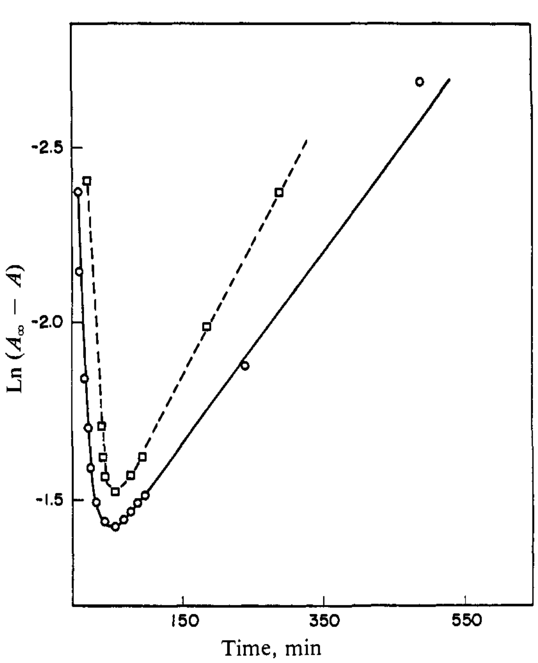

Figure 3. Observed (—) and simulated (- - - -) plots of ln (A_∞ − A_t) *vs.* time for the acid decomposition of $[Ir(NH_3)_5N_3]^{2+}$ in the presence of excess Cl^-: [complex] = 2.0×10^{-2} *M*, [H_2SO_4] = 4.3 *M*, [Cl^-] = 1.5×10^{-2} *M*, *T* = 22°. (The position of the simulated plot on the vertical axis is arbitrary.)

$H_2O]^{3+}$. In addition, the ability of HN_3 to act as a ligand has been confirmed by isolation of a hydrazoic acid complex of Co(III), $[Co(NH_3)_5N_3H](ClO_4)_3$.[20]

The results on the acid decomposition of $[Ir(NH_3)_5N_3]^{2+}$ were analyzed in terms of a similar protonation (eq 5 and 6). Equations 7 and 8 give two forms of the

$$[Ir(NH_3)_5N_3]^{2+} + H^+ \overset{K_1}{\rightleftharpoons} [Ir(NH_3)_5N_3H]^{3+} \qquad (5)$$

$$[Ir(NH_3)_5N_3H]^{3+} \xrightarrow{k_1} \text{stable intermediate} + N_2 \qquad (6)$$

$$k_{obsd} = k_1K_1h_0/(1 + K_1h_0) \qquad (7)$$

$$1/k_{obsd} = 1/k_1 + 1/k_1K_1h_0 \qquad (8)$$

expression for the observed rate constant derived from the above mechanism. Equation 8 predicts that a plot of $1/k_{obsd}$ *vs.* $1/h_0$ should be linear if the mechanism is correct and Figure 2 shows this plot for the data given in Table I. The excellent linearity of this plot supports the mechanism, and further the pK_a of −2.1 for $[Ir(NH_3)_5N_3H]^{3+}$ derived from the slope and intercept of the plot agrees with that of −2.2 obtained by Davis and Lalor[19] for $[Rh(NH_3)_5N_3H]^{3+}$. A limiting rate of 3.04×10^{-3} sec^{-1} for k_1 at 22° was determined from Figure 2.

The product which was isolated from the reaction of $[Ir(NH_3)_5N_3](ClO_4)_2$ with 4.5 *M* H_2SO_4 after 40 min (at which time the 279-nm band due to the azido complex had disappeared) was $[Ir(NH_3)_5NH_2OSO_3](ClO_4)_2$ (see below). This suggests that the stable intermediate above is the *O*-sulfonate complex. This was confirmed by showing that HCl converted the *O*-sulfonate to the chloramine complex and by kinetic studies.

The rates of decomposition of $[Ir(NH_3)_5N_3]^{2+}$ in HCl solutions, where $[Ir(NH_3)_5NH_2Cl]^{3+}$ is formed, and in $HClO_4$ solutions are given in Table I. In $HClO_4$ a two-step reaction is observed and the kinetic data have been analyzed in terms of two consecutive first-order reactions.[21] This analysis gives the rate of decomposition of the azido complex and the rate of the subsequent reaction of the intermediate. No attempt was made to characterize either the intermediate or the final product of the decomposition in the case of $HClO_4$ solutions. The rate constants, which are plotted against h_0 in Figure 2, show that at the same h_0 the rate of decomposition of $[Ir(NH_3)_5N_3]^{2+}$ in HCl or $HClO_4$ is almost identical with the rate observed in H_2SO_4. The independence of this rate on the nature of the acid anion shows the absence of nucleophilic-assisted loss of nitrogen.

(ii) **Reactions of $[Ir(NH_3)_5NH_2OSO_3]^{2+}$.** In the presence of small, but excess, amounts of Cl^-, the decomposition of $[Ir(NH_3)_5N_3]^{2+}$ in 4.5 *M* H_2SO_4 takes place in two steps. Measurement of the changes in absorbance at 258 nm clearly indicates these two steps as shown in Figure 3 which gives a plot of ln (A_∞ − A_t) *vs.* time for this reaction. The first step of this reaction is due to formation of $[Ir(NH_3)_5NH_2OSO_3]^{2+}$ and the second step is due to reaction of this intermediate to form $[Ir(NH_3)_5NH_2Cl]^{3+}$ as shown in eq 9 and 10.

$$[Ir(NH_3)_5N_3]^{2+} + H_2SO_4 \xrightarrow{k_2} [Ir(NH_3)_5NH_2OSO_3]^{2+} + N_2 \qquad (9)$$

$$[Ir((NH_3)_5NH_2OSO_3]^{2+} + Cl^- \xrightarrow{k_3} [Ir(NH_3)_5NH_2Cl]^{3+} + SO_4^{2-} \qquad (10)$$

Treatment of the data according to the theory of consecutive first-order reactions[21] yields the two rate constants k_2 (the observed first-order rate constant for eq 9 which is identical with k_{obsd} (of eq 7) and k_3 (the pseudo-first-order rate constant for eq 10). The kinetic data for these reactions as a function of Cl^- concentration are given in Table II. The values obtained for k_2 of

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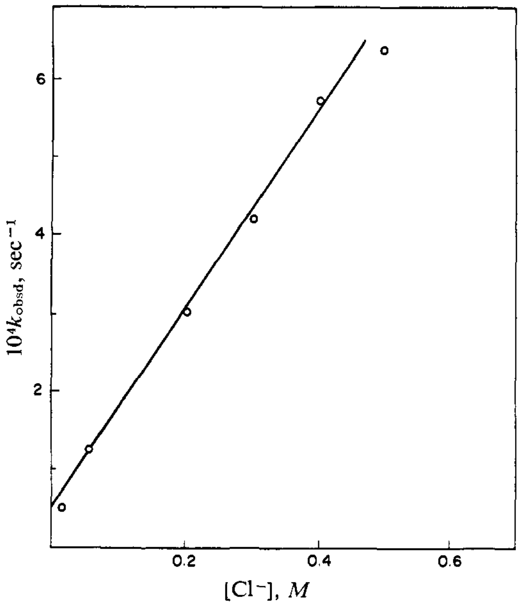

Figure 4. Plot of k_{obsd} *vs.* [Cl$^-$] for the formation of $[Ir(NH_3)_5NH_2Cl]^{3+}$ from $[Ir(NH_3)_5NH_2OSO_3]^{2+}$: $[H_2SO_4]$ = 4.3 M, T = 22°.

1.0×10^{-3} and 1.1×10^{-3} sec^{-1} agree well with the k_{obsd} values shown in Table I for the decomposition of $[Ir(NH_3)_5N_3]^{2+}$ in 4.3 M H_2SO_4 in the absence of Cl$^-$. This agreement shows the validity of the analysis of the rate data in terms of eq 9 and 10. In addition, the independence of the initial rate on Cl$^-$ concentration provides further evidence that the decomposition of $[Ir(NH_3)_5N_3]^{2+}$ does not involve a nucleophilic-assisted loss of nitrogen.

Table II. Rate Data for Decomposition of 10^{-3} M Solutions of $[Ir(NH_3)_5N_3]^{2+}$ in 4.5 M H_2SO_4 in the Presence of Cl$^-$ at 22°

[Cl$^-$], M	10^3k_2, sec^{-1} [a]	10^4k_3, sec^{-1} [b]
0.015	1.0	0.47
0.056	1.1	1.22
0.205		2.98
0.316		4.15
0.415		5.70
0.504		6.42

[a] k_2 is the first-order rate constant for eq 9. [b] k_3 is the pseudo-first-order rate constant for eq 10.

The rate of formation of $[Ir(NH_3)_5NH_2Cl]^{3+}$ from $[Ir(NH_3)_5NH_2OSO_3]^{2+}$ (k_3) is plotted as a function of Cl$^-$ concentration in Figure 4. A second-order rate constant of 1.25×10^{-3} M^{-1} sec^{-1} was obtained from the linear relationship between k_3 and [Cl$^-$].

The nonzero intercept in Figure 4 indicates a further reaction of $[Ir(NH_3)_5NH_2OSO_3]^{2+}$ which is independent of the Cl$^-$ concentration and which competes with the reaction to form $[Ir(NH_3)_5NH_2Cl]^{3+}$. In the absence of Cl$^-$, the final product from the acid decomposition of the azido complex is $[Ir(NH_3)_5NH_2OH]^{3+}$ (see below). The rate of reaction of the intermediate (which was formed *in situ*) to form the hydroxylamine complex was measured by following spectral changes at 245 nm and found to be 5.50×10^{-5} sec^{-1}. This rate constant agrees well with the value of 4.33×10^{-5} sec^{-1} found for the intercept in Figure 4 and further supports the interpretation of the data given above.

In addition, it was possible to simulate the plot of ln ($A_\infty - A_t$) *vs.* time shown in Figure 3 by substitution of the determined rate constants and the extinction coefficients of the various species at 258 nm into the exact rate expression. The agreement between the observed and simulated plots is excellent as shown in Figure 3 and this agreement provides additional support for the reaction sequence.

Characterization and Reactions of $[Ir(NH_3)_5NH_2Cl]^{3+}$ Salts. The decomposition of $[Ir(NH_3)_5N_3]^{2+}$ in HCl, or in H_2SO_4 in the presence of added Cl$^-$, yields $[Ir(NH_3)_5NH_2Cl]^{3+}$ which was isolated as the ClO_4^- salt and converted to the Cl$^-$ salt. The complex $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ is a white, diamagnetic solid. The charge on the complex was determined as 3+ using ion exchange techniques and this result was confirmed by an equivalent weight determination which showed a charge of 3.06 ± 0.05 per iridium atom.

The presence of coordinated NH_2Cl in this complex was confirmed by studies of its uv and nmr spectra, its reactivity toward Ag$^+$, and its oxidizing properties. Decomposition of $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ in basic solution followed by acidification and treatment with Ag$^+$ gave a quantitative yield of AgCl. However, treatment of the complex in acid solution with Ag$^+$ gave no precipitate. Similarly titration of $[Ir(NH_3)_5NH_2Cl]Cl_3$ with Ag$^+$ showed 3 mol of Cl$^-$ whereas after base hydrolysis of the complex 4 mol of Cl$^-$/mol of complex were titrated. Such behavior is characteristic of free NH_2Cl.[22]

On reaction of $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ with I$^-$, I_2 is liberated. The iridium-containing product of this reaction was isolated as its Cl$^-$ salt and shown to be $[Ir(NH_3)_6]Cl_3$ by comparison of its properties (elemental analysis, uv spectrum, conductivity, and equivalent weight) with those of an authentic sample. Determination of the liberated I_2 showed that 1.0 mol was formed per mole of $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ according to eq 11. The quantitative liberation of I_2 from I$^-$ is

$$[Ir(NH_3)_5NH_2Cl]^{3+} + 2I^- + H^+ \longrightarrow [Ir(NH_3)_6]^{3+} + I_2 + Cl^- \quad (11)$$

characteristic of both free[22] and coordinated[23] NH_2Cl.

The nmr spectrum of $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ in neat CF_3SO_3H contains two resonances, one at δ 3.7 (relative intensity 15) assigned to the NH_3 protons[24] and the second at δ 7.0 (relative intensity 2) assigned to the NH_2Cl protons. The uv spectra of the $[Ir(NH_3)_5NH_2Cl]^{3+}$ salts contain a strong band at 258 nm (ϵ 870) which is atypical for $[Ir(NH_3)_5X]^{n+}$ salts.[13] This band can be attributed to the same transition which gives rise to the band at 243 nm (ϵ 458)[25] observed for aqueous solutions of free NH_2Cl.

Titration of an aqueous solution of the complex with standardized base showed 1 mol of protons with pK_a = 5.9 and 1 mol of protons with pK_a = 9.4. The first end point is assigned to deprotonation of the coordinated NH_2Cl. The relatively strong acidity of this ligand is consistent with the strong acid behavior (pK_a <

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1) of coordinated $NHCl_2$.[26] The second end point (pK_a = 9.4) is assigned to the deprotonation of $[Ir(NH_3)_5NH_2OH]^{3+}$ which is formed rapidly in basic solution according to eq 12. In accordance with eq 12,

$$\underset{pK_a = 5.9}{[Ir(NH_3)_5NH_2Cl]^{3+}} + H_2O \longrightarrow \underset{pK_a = 9.4}{[Ir(NH_3)_5NH_2OH]^{3+}} + Cl^- + H^+ \quad (12)$$

titration of solutions which have been allowed to stand for 1 hr shows 20% of 1 mol of strongly acidic protons ($pK_a < 1$), 80% of 1 mol of protons with $pK_a = 5.9$, and 1 mol of protons with $pK_a = 9.4$. The production of $[Ir(NH_3)_5NH_2OH]^{3+}$ in this hydrolysis (eq 12) was confirmed by isolation of its ClO_4^- salt which was characterized by the identity of its properties with those of a sample prepared by a different method (see below).

The rate of the above hydrolysis reaction is pH dependent and a kinetic study of this reaction was carried out both in acetic acid–sodium acetate buffers (pH 3.5–5.5) and in phosphoric acid–sodium phosphate buffers (pH 6–7.5) at a constant ionic strength of 0.2 *M*. Table III gives the rate for hydrolysis of $[Ir(NH_3)_5NH_2Cl]^{3+}$. The plot is linear at low concentrations of OH^- with a slope of approximately unity although some deviation from linearity is observed at higher $[OH^-]$.

Table III. Rate Data for the Hydrolysis of $[Ir(NH_3)_5NH_2Cl]^{3+}$ in Buffered Solution at 25°

pH	10^4k_{obsd}, sec^{-1}
3.93	3.53
3.93	3.52
4.30	8.28
4.30	8.23
4.78	23.0
4.78	23.3
5.28	64.2
5.28	64.8
6.11	360
6.11	460
7.01	1630
7.01	1900

There are two reasonable mechanisms for the production of $[Ir(NH_3)_5NH_2OH]^{3+}$ by base hydrolysis of $[Ir(NH_3)_5NH_2Cl]^{3+}$. One involves the direct displacement of Cl^- by OH^- (eq 13), whereas the second mechanism consists of deprotonation of the chloramine ligand in a rapid preequilibrium followed by decomposition of the deprotonated species (eq 14 and 15).

$$[Ir(NH_3)_5NH_2Cl]^{3+} + OH^- \xrightarrow{k_4} [Ir(NH_3)_5NH_2OH]^{3+} + Cl^- \quad (13)$$

$$[Ir(NH_3)_5NH_2Cl]^{3+} \overset{K_5}{\rightleftharpoons} [Ir(NH_3)_5NHCl]^{2+} + H^+ \quad (14)$$

$$[Ir(NH_3)_5NHCl]^{2+} + H_2O \xrightarrow{k_5} [Ir(NH_3)_5NH_2OH]^{3+} + Cl^- \quad (15)$$

Two forms of the rate law for the mechanism shown in eq 14 and 15 are given in eq 16 and 17. Unfortunately for the direct reaction of eq 13, the rate law is identical with that shown in eq 16. The plot of $1/k_{obsd}$ *vs.* $[H^+]$ suggested by eq 17 is linear with a positive *y* intercept. In addition, the value of the equilibrium constant (K_5 in eq 14) calculated from the slope and intercept of the above plot ($K_5 = 1.68 \times 10^{-6}$) agrees well with the value of this equilibrium constant determined by direct titration of $[Ir(NH_3)_5NH_2Cl]^{3+}$ ($K = 1.26 \times 10^{-6}$).

$$k_{obsd} = k_5K_5/(K_5 + [H^+]) \quad (16)$$

$$1/k_{obsd} = [H^+]/k_5K_5 + 1/k_5 \quad (17)$$

Although the kinetic data presented do not conclusively prove either of the two mechanisms outlined above, we prefer an SN2 displacement of Cl^- by OH^- (eq 13). The hydrolysis of free NH_2Cl to NH_2OH follows the same SN2 mechanism.[27]

Characterization and Reactions of $[Ir(NH_3)_5NH_2OSO_3](ClO_4)_2$. Treatment of $[Ir(NH_3)_5N_3](ClO_4)_2$ with 4.5 *M* H_2SO_4 and addition of 70% $HClO_4$ to the reaction mixture after 40 min precipitates a white, diamagnetic solid which has been characterized as predominantly $[Ir(NH_3)_5NH_2OSO_3](ClO_4)_2$. This product is indefinitely stable in the solid state in dry air. However, it is usually obtained contaminated with a small amount of $[Ir(NH_3)_5NH_2OH](ClO_4)_3$ as evidenced by the presence of weak bands at 2890 and 939 cm^{-1} (bands characteristic of NH_2OH, see below) in its ir spectrum. In moist air the compound decomposes to the hydroxylamine complex as shown by the increasing intensity of these bands.

The ir spectrum of $[Ir(NH_3)_5NH_2OSO_3](ClO_4)_2$ contains bands at 1273, 1235, and 587 cm^{-1} (in addition to the expected amine and ClO_4^- bands) characteristic of both HSO_4^-[28] and NH_3OSO_3.[29] Addition of an equivalent of $BaCl_2$ to an aqueous solution of $[Ir(NH_3)_5NH_2OSO_3](ClO_4)_2$ precipitates only 0–55% of the theoretical amount of $BaSO_4$ (depending on the extent of hydrolysis). However, decomposition of the hydroxylamine-*O*-sulfonic acid complex in base followed by acidification and addition of a stoichiometric amount of $BaCl_2$ gives greater than 90% of the stoichiometric amount of $BaSO_4$. This behavior indicates the presence of bound sulfate. Likewise, recrystallization of the complex from $HClO_4$ removed very little of the sulfate, merely increasing the amount of $[Ir(NH_3)_5NH_2OH](ClO_4)_3$ in the recovered solid. This result confirms that the sulfate in the product is not present as a free anion.

Titration of an aqueous solution of the complex with standardized base showed 1 mol of strongly acidic protons ($pK_a < 2$) and 1 mol of protons with pK_a = 9.4. The strong acid end point is assigned to the titration of the coordinated NH_2OSO_3. Free hydroxylamine-*O*-sulfonic acid, which exists as the zwitterion NH_3OSO_3,[30] similarly shows 1 mol of protons with pK_a = 1.5.[31] The second end point (pK_a = 9.4) is assigned to titration of $[Ir(NH_3)_5NH_2OH]^{3+}$ which is rapidly formed from $[Ir(NH_3)_5OSO_3]^{2+}$ as the solution becomes basic (eq 18). This hydrolysis occurs more slowly in acidic solution (in 0.1 *M* $HClO_4$, k_{obsd} = 6.0

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$$\underset{\mathrm{p}K_a < 2}{[Ir(NH_3)_5NH_2OSO_3]^{2+}} + H_2O \longrightarrow \underset{\mathrm{p}K_a = 9.4}{[Ir(NH_3)_5NH_2OH]} + HSO_4^- \quad (18)$$

$\times$ 10^{-5} sec^{-1}). Free NH_3OSO_3 is also hydrolyzed rapidly in base and slowly in acid ($k \sim 5 \times 10^{-5}$ sec^{-1}) to give NH_2OH.[31]

The reactivity of $[Ir(NH_3)_5NH_2OSO_3]^{2+}$ is identical with that of the intermediate discussed above. In addition to giving the same hydrolysis product at about the same rate, the complex also reacts with HCl to give $[Ir(NH_3)_5NH_2Cl]^{3+}$ (eq 19) at a rate in rough agreement

$$[Ir(NH_3)_5NH_2OSO_3]^{2+} + HCl \longrightarrow [Ir(NH_3)_5NH_2Cl]^{3+} + HSO_4^- \quad (19)$$

with that expected from studies on the decomposition of $[Ir(NH_3)_5N_3]^{2+}$ (in 4 *M* HCl: $k_{obsd} = 1.8 \times 10^{-3}$ sec^{-1}; $k_{expected} = 5.0 \times 10^{-3}$ sec^{-1}). The uv spectrum of $[Ir(NH_3)_5NH_2OSO_3](ClO_4)_2$ is also very similar to that of the intermediate observed in the kinetic studies discussed above containing bands at 245 nm (ϵ 170) and 305 (sh, 38). Bands in this region but of somewhat lesser intensity are typical for $[Ir(NH_3)_5X]^{n+}$ salts.[13]

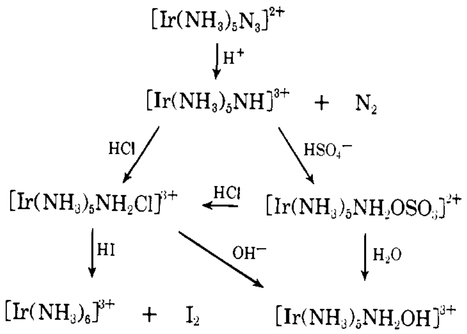
Characterization of $[Ir(NH_3)_5NH_2OH](ClO_4)_3$. Treatment of $[Ir(NH_3)_5N_3](ClO_4)_2$ with 4.5 *M* H_2SO_4 for 48 hr yields $[Ir(NH_3)_5NH_2OH](ClO_4)_3$ on addition of 70% $HClO_4$. The ir spectrum of the white, diamagnetic solid contains bands at 2890 and 939 cm^{-1} characteristic of coordinated NH_2OH.[32] The uv spectrum of the complex is typical of $[Ir(NH_3)_5X]^{n+}$ salts[13] containing weak bands at 246 nm (ϵ 103) and 296 (sh, 33). The charge on the complex was shown to be 3.06 ± 0.05 from equivalent weight determinations. Titration of an aqueous solution of the complex with standardized base gives an end point with $\mathrm{p}K_a = 9.4$ corresponding to 1 mol of protons/mol of complex. This value compares favorably wtih $\mathrm{p}K_a$ values of 8–9 for Pt(II)–NH_2OH complexes.[33]

No reaction of $[Ir(NH_3)_5NH_2OH](ClO_4)_3$ occurs with HCl or I^-. The complex is stable in acidic solution but decomposes in base to yield gaseous products identified as N_2 and N_2O.

Discussion

We feel that all of our results are best explained by postulating that the initial reaction of the azide complex with acid produces an unstable nitrene complex of iridium(III), $[Ir(NH_3)_5NH]^{3+}$. The formula of such a complex is, of course, indistinguishable from that of an imide complex of Ir(V). Our choice of nomenclature is based on the characteristic reactions of such a species. These are shown in Scheme I, together with the other reactions we have observed. The reactions and interconversions of the NH_2X (X = OSO_3^-, Cl, OH) ligands proceed similarly to those of the free species.[22,27,31] These results provide an interesting example of ligand transformations. The wide variety of reactions undergone by free NH_2Cl[22] suggests that many interesting compounds could be synthesized from $[Ir(NH_3)_5NH_2Cl]^{3+}$ salts. However, our primary interest was in the production and reactivity of a coordinated nitrene. The data presented above show that this coordinated nitrene behaves as an extremely powerful electrophile. Such behavior is expected for singlet nitrenes, in which a valence shell orbital is unoccupied, and is observed for the singlet aminonitrenes, R_2N–N.[34] When nitrene is produced photochemically from HN_3 in aqueous solutions, a process which should yield the singlet form, NH_2OH and NH_2Cl (in HCl) are the main products.[35] Hence, the coordinated nitrene produced in this work shows behavior typical of singlet nitrenes.

Scheme I



These reactions of coordinated nitrene are novel and differ from those observed for the Ru(III) systems.[1] The difference in behavior can be attributed to the ease of reduction of Ru(III) to Ru(II), a reaction pathway not available for Ir(III).

The action of acid on azido complexes often results in solvolysis of the complex, liberating HN_3, rather than decomposition of the coordinated azide.[19,36] In many cases, this difference in behavior can be attributed to the lability of the metal–nitrogen bond and the poor coordinating ability of HN_3. This explanation is not valid for the solvolysis[19] of $[Rh(NH_3)_5N_3]^{2+}$ to $[Rh(NH_3)_5H_2O]^{3+}$, since the rate of solvolysis of this azido complex in acid is slower than the rate of decomposition of $[Ir(NH_3)_5N_3]^{2+}$ to $[Ir(NH_3)_5NH]^{3+}$ under the same conditions. However, the difference can be attributed to a lowering of the energy of the transition state for nitrene formation by π donation from the filled t_{2g} orbitals on Ir(III). This explanation implies that the d orbital electrons are more available for π donation in Ir(III) than in Rh(III) and is in keeping with the observed increased in metal basicity going down a group in the periodic table.[37] This $d\pi \rightarrow p\pi$ interaction is analogous to the $p\pi \rightarrow p\pi$ interaction which is invoked to explain the unusual stability and the singlet (rather than triplet) ground state of the aminonitrenes, R_2N–N.[34]

Such $d\pi \rightarrow p\pi$ donation would be expected to be particularly favorable in Re(III) and Ir(I) complexes, since complete donation of an electron pair would give well-known, stable oxidation states for these metals, Re(V) and Ir(III). Indeed many compounds of these metals have been prepared which can be formulated as nitrene complexes of Re(III)[38] and Ir(I),[39]

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e.g., $[Re\{P(C_6H_5)(C_2H_5)_2\}_2Cl_3(NC_6H_5)]$ and $[Ir\{P(C_6H_5)_3\}_2Cl(NC_6H_5)]$. These Re complexes, unlike $[Ir(NH_3)_5NH]^{3+}$, do not show the electrophilic behavior of singlet nitrene and appear to be quite stable to nucleophilic attack. Hence, the electron distribution in these complexes may be more correctly indicated by formulating them as Re(V) alkyl- and arylimido complexes after Chatt.[38]

Treatment of $[Re\{P(C_6H_5)_2CH_3\}_2CH_3]$ with NaN_3 yields $[Re\{P(C_6H_5)_2CH_3\}_3Cl_2N]$,[40] which can also be prepared by a different method.[40] This complex has been formulated as a nitrido complex of Re(V) but could also be viewed as a complex of Re(III) with a deprotonated nitrene ligand. This complex, like the alkyl- and arylimido compounds discussed above, is unreactive toward nucleophilic attack reacting only with Lewis acids, *e.g.*, BF_3.[41] It therefore should not be considered as a complex of singlet nitrene.

Hence, although some $d\pi \rightarrow p\pi$ donation appears to be necessary for the formation of $[Ir(NH_3)_5NH]^{3+}$ from $[Ir(NH_3)_5N_3]^{2+}$, extensive electron transfer leads to loss of nitrene-like properties of the resulting ligand. We propose the name "coordinated nitrene" to describe the NH ligand in $[Ir(NH_3)_5NH]^{3+}$ as a means of distinguishing compounds of this type from the formally similar alkyl- and arylimido and nitrido ligands of $[Re\{P(CH_3)_2C_6H_5\}_2Cl_3NR)$ and $[Re\{P(CH_3)_2C_6H_5\}_3Cl_2N]$ which show very different chemical behavior.

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Mixed Complex Formation between Methyllithium and Lithium Bromide or Iodide in Diethyl Ether[1]

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Abstract: Methyllithium forms mixed complexes with both LiBr and LiI in ether. The association of LiBr in ether at 0° varies from 2.8 at 0.025 *F* to 3.2 at 0.25 *F*, whereas LiI association varies from 1.24 at 0.024 *F* to 1.97 at 0.24 *F*. On the basis of ^7Li and 220-MHz ^1H spectra in the range -50 to $-90°$ for solutions of $LiCH_3$ and LiBr in various ratios, the species present in solution are assigned as $Li_4(CH_3)_4$, $Li_4(CH_3)_3Br$, $Li_4(CH_3)_2Br_2$, and $(LiBr)_n$. Analogous studies on the iodide system show that only $Li_4(CH_3)_4$, $Li_4(CH_3)_3I$, and $(LiI)_n$ are present. Intermolecular exchanges between the various species present are most rapid for the species richest in halide.

It has been reported on several occasions that the reactivity of an organolithium reagent[3–7] is influenced by the presence of lithium halide. Ternary organolithium–lithium halide–etherate complexes have been isolated by Talalaeva and coworkers.[8] Glaze and West have also reported the isolation of butyllithium–lithium bromide complexes of variable composition from hydrocarbon solution.[9] On the basis of this earlier work it is reasonable to suppose that organolithium compounds enter into mixed complex formation with lithium halides in solution, especially in those solvents in which the lithium halides possess considerable solubility. The existence of such mixed complex formation between methyllithium and lithium bromide or iodide in diethyl ether was revealed through ^7Li nmr studies by Brown and Wells.[10] Waack and coworkers reported low temperature ^7Li spectra of THF solutions of $LiCH_3$ and LiBr which showed a limited degree of mixed complex formation.[11]

We report here the results of extensive ^7Li and proton nmr studies of mixed complex formation between methyllithium and lithium bromide or lithium iodide in diethyl ether.

Experimental Section

All operations were performed in a glove box under an argon atmosphere. Removal of traces of oxygen and water was effected by continuous circulation of the box atmosphere through molecular sieve (4A and 13X) and manganese(II) oxide columns as described previously.[12] The water content of this atmosphere was always

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