

should exhibit ORD-CD behavior analogous to that of the present examples.

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Electrophilic Behavior of Nitrene Coordinated to Iridium(III)

Sir:

It has been proposed¹ that acid-catalyzed decomposition of ruthenium(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).

The facile reduction of Ru(III) to Ru(II) makes possible the internal redox reactions which yield these products. We were interested in studying the reactions of coordinated nitrenes where these redox reactions were not possible. The absence of Ir(II)-amine complexes³ indicated that decomposition of Ir(III) azides (where nitrogen evolution has been previously observed⁴) might yield nitrenes which behaved differently from the Ru(III) systems.

We wish to report the production of an Ir(III) nitrene intermediate from the acid decomposition of $[\text{Ir}(\text{NH}_3)_5\text{N}_3]^{2+}$ salts. An Ir(III)-chloramine complex and an Ir(III)-hydroxylamine complex have been characterized as products of reaction of the Ir(III) nitrene.

Treatment of $[\text{Ir}(\text{NH}_3)_5\text{N}_3]\text{Cl}_2$ (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. A solution of BaCl_2 (2.0 g) in H_2O (10 ml) was added to a suspension of A (1.25 g) 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 $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{Cl}](\text{ClO}_4)_3$ (B) separated, which were collected, washed with ethanol and ether, and air-dried. The yield was 1.25 g, 80% based on $[\text{Ir}(\text{NH}_3)_5\text{N}_3]\text{Cl}_2$. *Anal.* Calcd for $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{Cl}](\text{ClO}_4)_3$: 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.

Quantitative measurements showed that 1.01 mol of gas was liberated per mole of $[\text{Ir}(\text{NH}_3)_5\text{N}_3]\text{Cl}_2$ and the gas was shown to be nitrogen by mass spectrometry.

Compound B is an air-stable, diamagnetic, white crystalline solid which is stable in aqueous acid but decomposes in neutral or basic solutions. Compound B was characterized by a determination of its charge as 3+ using ion-exchange techniques. On reaction of B with I^- , I_2 is liberated quantitatively (eq 1), a reaction characteristic of free⁵ and coordinated⁶ NH_2Cl . De-

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(2) The term nitrene throughout this paper refers to the molecule NH.

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(6) I. I. Chernyaev, G. S. Muraveiskaya, and L. S. Korablina, *Zh. Neorg. Khim.*, **10**, 300 (1965); *Russ. J. Inorg. Chem.*, **10**, 158 (1965);

composition of B in basic solution followed by acidification and treatment with Ag^+ gave a quantitative yield of AgCl . However, treatment of B in acid solution with Ag^+ gave no precipitate. Similar behavior is observed for free NH_2Cl .⁵

Decomposition of $[\text{Ir}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$ with 4.5 M H_2SO_4 in the complete absence of Cl^- for 2 days, followed by addition of 70% HClO_4 , yielded a white solid, C, which was identified as $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{OH}](\text{ClO}_4)_3$. *Anal.* Calcd for $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{OH}](\text{ClO}_4)_3$: N, 13.81; H, 2.98. Found: N, 13.4; H, 3.0.

Compound C was characterized by a determination of its charge as 3+ using ion-exchange techniques. Titration of C with base showed the presence of 1.0 mol of ionizable protons with $\text{p}K_a = 9.4$ (literature $\text{p}K_a$ values for NH_2OH complexes of Pt(II) are 8-9).⁷ The ir spectrum of C showed bands characteristic of NH_2OH at 2890 (ν_{OH}) and 939 cm^{-1} (ν_{NO})⁸ in addition to the expected amine and perchlorate bands.

Kinetic studies of the reaction of 10^{-3} M solutions of $[\text{Ir}(\text{NH}_3)_5\text{N}_3]\text{Cl}_2$ with 4.5 M H_2SO_4 showed that the azide complex decomposed rapidly (monitored by the decreasing intensity of the 279-nm band of this complex), and that this reaction was accompanied by the quantitative loss of nitrogen. However, the formation of $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{Cl}]^{3+}$ under these conditions is a much slower reaction, as shown by the gradual increase of the 258-nm band characteristic of this product. If the reaction products from the decomposition of $[\text{Ir}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$ in 4.5 M H_2SO_4 were isolated by precipitation with 70% HClO_4 after 40 min, a different product, D, was obtained, contaminated with some C.

Compound D reacts with HCl to give $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{Cl}]^{3+}$ and with H_2O to give $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{OH}]^{2+}$, and appears to be an intermediate in the production of B and C. Preliminary characterization of D shows the presence of 1 mol of bisulfate ion per mole of complex. Addition of Ba^{2+} to an acidic solution of D precipitates only a small portion of the HSO_4^- . However, decomposition of D in basic solution followed by acidification and treatment with Ba^{2+} gives an almost quantitative yield of BaSO_4 . On this basis, D is formulated as $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{OSO}_3](\text{ClO}_4)_2$ (containing bound sulfate). Free NH_2OSO_3 and D undergo similar reactions.⁹

The formation of B, C, and D can be rationalized in terms of Scheme 1, which involves the intermediacy of a coordinated nitrene. The dependence of the rate of decomposition of $[\text{Ir}(\text{NH}_3)_5\text{N}_3]^{2+}$ on sulfuric acid strength is a function of h_0 , similar to the behavior observed by Davis and Lalor¹⁰ for $[\text{Rh}(\text{NH}_3)_5\text{N}_3]^{2+}$. In HCl where $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{Cl}]^{3+}$ is formed, and in HClO_4 , at the same h_0 , the rate of decomposition of the azido complex is almost identical with the rate in H_2SO_4 . The independence of this rate on the anion of the acid shows the absence of nucleophilic-assisted loss of nitrogen, and gives strong support to the intermediacy of a coordinated nitrene.

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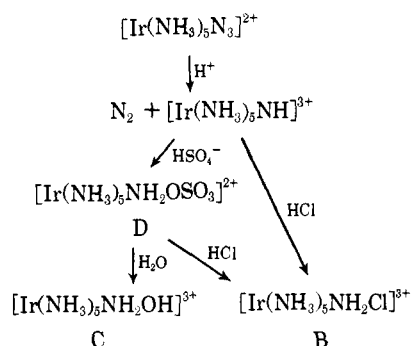
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Scheme I



The intermediate nitrene complex behaves as an extremely powerful electrophile as does nitrene (NH) itself, which gives analogous products (NH₂Cl and NH₂OH) in aqueous solution.¹¹ Such behavior is expected for singlet nitrenes, where a valence-shell orbital is unoccupied, and is observed for the singlet aminonitrenes, R₂N-N.¹²

The formation of coordinated nitrene from the Ir(III) azide is in marked contrast to the behavior found for many other azido complexes, where only acid-catalyzed aquation occurs.^{10,13} The difference could be attributed to a lowering of the energy of the transition state for nitrene formation by π donation from the t_{2g} orbitals on Ir(III). This proposed $d\pi \rightarrow p\pi$ 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, R₂N-N.¹²

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Reactions of Methylene in Solution. Selective Abstraction Reactions of ¹CH₂ and ³CH₂

Sir:

Recently we utilized chemically induced nuclear spin polarization (CIDNP) to assign singlet (triplet) spin multiplicity to methylene generated by direct irradiation (photosensitized decomposition) of diazomethane.¹ However, one important question remained unanswered. In carbon tetrachloride the same abstraction-recombination product was formed from both spin multiplicities, and thus the same signal was enhanced (in emission or absorption) during both modes of decomposition. Therefore, it was impossible to decide whether methylene was formed exclusively in

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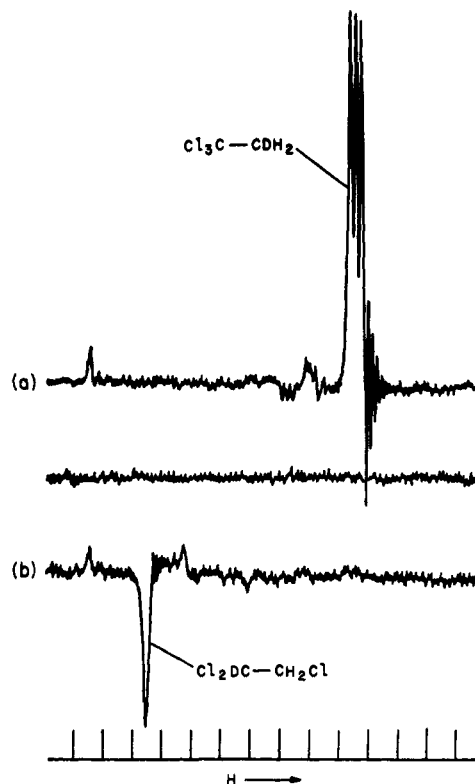


Figure 1. Proton nmr spectra (60 MHz) of diazirine solutions in deuteriotrichloromethane during triplet-sensitized (a) and direct (b) photolysis. A spectrum of the same region without irradiation is shown between traces a and b. A frequency scale (10.6 Hz between two markers) is given below trace b. The resonance of diazirine (~ 200 Hz upfield of **3**) is not included in the spectra.

one spin state or only predominantly in one state and to a lesser extent in the other one.²⁻⁶ This ambiguity can be resolved by studying multiplicity-specific reactions of methylene. Reactions of this type were found in the gas phase, where methylene attacks substrates containing both hydrogen and halogen atoms in a selective and multiplicity-specific manner.^{7,8} Although reactions in solution are not necessarily comparable to those in the gas phase, we investigated reactions of methylene in solutions of substrates similar to those successfully employed in the gas phase.

In this study we used diazirine (**1**)⁹ as the source of methylene because diazomethane is so readily decomposed by even relatively stable free radicals (such as trichloromethyl).^{1,10} Deuteriotrichloromethane was chosen as substrate because the nmr spectra of its po-

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