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Photochemical Reactions of Azidopentaamminechromium(III). Evidence for a First Transition Series Coordinated Nitrene Intermediate

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Exposure of aqueous solutions of $Cr(NH_3)_5N_3^{2+}$ to 313-nm radiation results in the evolution of 1 mol of nitrogen/mol of $Cr(NH_3)_5N_3^{2+}$ decomposed. Contrary to a previous report, however, flash photolysis experiments indicate that photoredox accounts for less than 12% of the overall photochemical reaction. The reaction stoichiometry and the ability of the photolyte to oxidize iodide to iodine indicate the principal photochemical reaction to be cleavage of the azide $N-N_2$ bond to form the nitrene intermediate $Cr(NH_3)_5N^{2+}$. In the presence of HCl, $Cr(NH_3)_5N^{2+}$ is trapped to form $Cr(NH_3)_5NH_2Cl^{3+}$, a known oxidant of iodide ion. The dependence of the yield of $Cr(NH_3)_5NH_2Cl^{3+}$ on the concentration of HCl extrapolates to a limiting quantum yield in close agreement with the quantum yield of $Cr(NH_3)_5N_3^{2+}$ decomposition and establishes the primary photochemical reaction to be

$$Cr(NH_3)_5N_3^{2+} \xrightarrow[313\text{ nm}]{h\nu} Cr(NH_3)_5N^{2+} + N_2$$

Unlike $Ir(NH_3)_5NH_2Cl^{3+}$ and $Rh(NH_3)_5NH_2Cl^{3+}$, $Cr(NH_3)_5NH_2Cl^{3+}$ is unstable. In marked contrast to the rich flash photolysis spectra of $Ir(NH_3)_5N_3^{2+}$ and $Rh(NH_3)_5N_3^{2+}$, no transient absorbance is detected in the flash photolysis of $Cr(NH_3)_5N_3^{2+}$. The absence of a transient absorbance is thought to reflect the instability of the $Cr(NH_3)_5NH^{3+}$ intermediate and is attributed to a diminished $d\pi-p\pi$ overlap with the smaller 3d orbitals of the chromium(III) ion.

Introduction

The nitrene intermediate, an electron-deficient species designated NH or RN,[1] has been reported in the thermal and photochemical reactions of azide ion,[2] hydrazoic acid,[3] and numerous organic azides.[1,4] Less frequent, however, are reports of the analogous metal-coordinated nitrene intermediate, MNH.[5] Basolo and co-workers have established the nitrene intermediates $Rh(NH_3)_5NH^{3+}$ and $Ir(NH_3)_5NH^{3+}$ in the acid-catalyzed thermal decomposition of $Ir(NH_3)_5N_3^{2+}$[5c] and the photochemical reactions of $Rh(NH_3)_5N_3^{2+}$[5f] and $Ir(NH_3)_5N_3^{2+}$.[5e] However, prior to a recent communication from this laboratory, nitrene intermediates have not been detected in the thermal or photochemical reactions of first transition series azidopentaammine complexes.[6]

The characterization of a nitrene intermediate in the photolysis of $Rh(NH_3)_5N_3^{2+}$ and $Ir(NH_3)_5N_3^{2+}$ is in marked contrast to the photochemical behavior of the first transition series analogue, $Co(NH_3)_5N_3^{2+}$.[7] The photochemistry of the latter complex is dominated by an intramolecular redox reaction, whereas the iridium(III) complex reacts exclusively via a coordinated nitrene intermediate.[5e] The rhodium(III) complex, intermediate between the Co(III) and Ir(III) analogues in the cobalt triad, exhibits both photoredox and nitrene reaction modes.[5f] This change in reaction modes within the triad has been attributed to a less favorable +2 oxidation state and an increased stabilization of the nitrene intermediate by increased $d\pi-p\pi$ bonding with the heavier metal ions. These data have led to a model which attributes nitrene formation to a reaction from an azide-centered excited state whereas the redox mode originates within a CTLM state.[5c,5f,8] The relative energies and the coupling between these states then determine the observed reaction mode. This qualitative model has been further extended in the more quantitative terms of changes in the charge densities of the various charge-transfer ligand to metal, CTLM, charge-transfer metal to ligand, CTML, and ligand localized, LL, states.[9a] The calculations reinforce the proposed azide-centered excited state, the LL state, as the nitrene-forming state and predict a new reaction mode, cleavage of the metal MN_2-N bond within the CTLM state. Quite different results have been reported by Hammond and co-workers who found that direct photolysis of the azide-centered bands in $Rh(CN_5)N_3^{3-}$ and $Ir(CN)_5N_3^{3-}$ did not lead to nitrene products.[9b] Clearly, the qualitative and quantitative ideas regarding nitrene formation are speculative and must be tested with other nitrene-forming reactions.

Like the acidopentaammine complexes of Rh(III) and Ir(III), the +2 oxidation state of acidopentaamminechromium(III) is less favorable. Furthermore, previous investigations of thermal substitution reactions of $Cr(NH_3)_5N_3^{2+}$ have indicated that the Cr–N bond is unusually stable.[10] These observations led to a reexamination of the ultraviolet photolysis of $Cr(NH_3)_5N_3^{2+}$.

Contrary to a previous report,[11a] however, we find that photoredox accounts for less than 12% of the overall photochemical reaction observed on 313-nm photolysis. Evidence is presented which indicates the principal reaction mode to be cleavage of the $CrN-N_2$ bond and the formation of a coordinated nitrene intermediate, $Cr(NH_3)_5N^{2+}$. The photochemical behavior of $Cr(NH_3)_5N_3^{2+}$ is similar to that of $Ir(NH_3)_5N_3^{2+}$ and $Rh(NH_3)_5N_3^{2+}$ and is discussed in terms of the ideas postulated for these complexes. Due to the large structural changes within the azide ligand on excitation, the wavelength dependence of the quantum yield of nitrene formation is thought to reflect an inefficient coupling between the azide LL excited state and the lower energy ligand field states.

Experimental Section

Materials. Azidopentaamminechromium(III) was prepared by published methods[10] and twice recrystallized as the perchlorate salt. The infrared spectrum indicated corrdinated azide,[13] and the electronic spectrum of the complex agreed with published spectra.[10] The cobalt(III) complexes were prepared by published methods.[14] Aquopentaammine- and hexaamminecobalt(III) were recrystallized as the perchlorate salts, whereas the bromo- and chloropentaamminecobalt(III) complexes were recrystallized as the nitrate salts. The electronic spectra of the complexes agreed with published spectra. All other chemicals used in these experiments were reagent grade. Solutions were prepared with water distilled in a Corning distillation unit.

Analytical Procedures. The thermal instability of chloraminepentaamminechromium(III), $Cr(NH_3)_5NH_2Cl^{3+}$, precludes the use of ion-exchange chromatography for product isolation. To circumvent this difficulty, the photolytes were treated with an aliquot of 1.0 M NaI to reduce $Cr(NH_3)_5NH_2Cl^{3+}$ to $Cr(NH_3)_6^{3+}$[5c] which was then isolated by ion-exchange chromatography on Dowex 50W-X2 (J. T. Baker, lot no. 31850). Tests with known amounts of $Cr(NH_3)_5N_3^{2+}$ and $Cr(NH_3)_6^{3+}$ indicated that $Cr(NH_3)_5N_3^{2+}$ underwent an acid-catalyzed aquation on the column. To prevent this aquation and the accompanying difficulties of trying to separate $Cr(NH_3)_5H_2O^{3+}$ from $Cr(NH_3)_6^{3+}$, the resin was washed with 2.0 M NaCl till the eluate

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was neutral. The excess NaCl was then washed from the resin with distilled water. Further tests with known samples of $Cr(NH_3)_5N_3^{2+}$ showed that eluting $Cr(NH_3)_5N_3^{2+}$ with 1.0 M HCl caused an appreciable amount of aquation; the color on the column changed from crimson-red to orange-red and both $Cr(NH_3)_5N_3^{2+}$ and $Cr(NH_3)_5H_2O^{3+}$ were confirmed by electronic and infrared spectra. If 1.0 M NaCl was used as the eluent, however, no aquation occurred and only $Cr(NH_3)_5N_3^{2+}$ was isolated. For these reasons, the photolyte which had been treated with NaI was placed on the column and rinsed with distilled water, and the unreacted $Cr(NH_3)_5N_3^{2+}$ was eluted with 1.0 M NaCl. The column was again rinsed with water and the $Cr(NH_3)_6^{3+}$ eluted with 3.0 M HCl. The HCl eluate was collected in 5-mL fractions with a Fracto-Mette 200 collector. The absorption spectra confirmed the presence of $Cr(NH_3)_6^{3+}$. Since $Cr(NH_3)_6^{3+}$ is known to phosphoresce in fluid solution whereas $Co(NH_3)_5N_3^{2+}$ and $Cr(NH_3)_5H_2O^{3+}$ do not,[15] the presence of $Cr(NH_3)_6^{3+}$ was further confirmed by emission spectroscopy. The 5-mL fraction, which absorption spectra indicated to be most concentrated, was degassed by repeated freeze–thaw cycles. The emission spectrum of the sample showed a weak emission centered at 650 nm and an excitation spectrum essentially identical with the first absorption band of $Cr(NH_3)_6^{3+}$.

The gaseous products of the reaction were characterized and quantitated by gas chromatography. A 4-mL aliquot of a 10^{-3} M $[Cr(NH_3)_5N_3](ClO_4)_2$ solution was placed in a 10-mL side arm of the photolysis cell and purged of dissolved gases on a vacuum line by repeated freeze–thaw cycles. Following photolysis, which was monitored by absorption spectroscopy, the noncondensable gas (at liquid N_2 temperature) was quantitatively transferred by a Toepler pump to a Gow-Mac Model 69-100 gas chromatograph equipped with a 6 ft × 0.25 in. Porapak Q column at room temperature and a thermal conductivity detector. The response of the GC, calibrated by transferring known amounts of N_2 to the instrument with the Toepler pump, was found to be linear over the range of 2×10^{-6} to 5×10^{-5} mol of nitrogen. To minimize any error from possible product absorption, the amount of $Cr(NH_3)_5N_3^{2+}$ decomposed during the photolysis was determined from the decrease in absorption at 280 and 265 nm.

The amount of $Cr(NH_3)_5NH_2Cl^{3+}$ formed on photolysis of HCl solutions of $Cr(NH_3)_5N_3^{2+}$ was determined by oxidation of iodide ion.[5c] The amount of I_3^- formed after the addition of an aliquot of 0.1 M NaI or KI to an aliquot of the photolyte was determined spectrally at 353 nm, ϵ 2.32×10^4 M^{-1} cm^{-1}.[5e] An equivalent aliquot of the unphotolyzed solution was treated in an identical manner. From the difference in absorbance at 353 nm, the amount of $Cr(NH_3)_5NH_2Cl^{3+}$ was determined. Azide ion was detected spectrally at 455 nm, ϵ 2.46×10^3 M^{-1} cm^{-1}, by the formation of an $Fe^{3+}–N_3^-$ complex.[16] An aliquot of the photolyte, adjusted to a pH of 6 with 0.1 M NaOH, was diluted to volume with an aliquot of 0.1 M $Fe(NO_3)_3$ and water. The concentration of the $Fe^{3+}–N_3^-$ complex was determined from the absorbance at 455 nm, relative to a reference solution prepared in the same manner with an aliquot of the unphotolyzed solution. Tests with known amounts of NaN_3 added to the solution to be photolyzed indicated that 96–97% of the added azide could be detected.

The photolyte was also analyzed for hydroxylamine, NH_2OH, by a spot test and a colorimetric procedure with α-naphthylamine at 520 nm, ϵ 1.76×10^4 M^{-1} cm^{-1}.[17] Although an extremely sensitive test, we found the absorbance to be linear with concentrations of NH_2OH of less than 5×10^{-5} M. For concentrations greater than 5×10^{-5} M the absorbance at 520-nm decreases slightly with increasing concentration. Cobalt(II) was analyzed by the thiocyanate procedure.[18] The colorimetric procedure, which measures the amount of the $Co(II)–SCN^-$ complex at 625 nm, ϵ 1.81×10^3 M^{-1} cm^{-1}, was calibrated with known amounts of $CoCl_2 \cdot 6H_2O$.

Photolysis Procedures. For product isolation and identification, preparative photolyses of 500-mL solutions containing 1.0 M HCl and 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ were carried out in a Rayonet reactor equipped with 312-nm lamps. An optical train was assembled to measure the quantum yields reported in this study. The light from a 350-W Illumination Industries high-pressure xenon–mercury arc lamp was focused onto the entrance slit of a Bausch and Lomb Model 33-86-08 grating monochromator. The wavelength scale of the monochromator was calibrated with a low-pressure mercury lamp by a procedure adapted from the calibration of a Beckman DU spectrophotometer.[19] The entrance slit, 3.48 mm, and exit slit, 1.40 mm, were calculated from the manufacturers reported dispersion of the grating to yield 90% of the radiation within a 10-nm band-pass. A quartz lens focused the light from the monochromator onto the photolysis cell which was mounted in an aluminum block. Because of the low intensity of the arc lamp below 270 nm, photolyses at 254 nm were carried out in a Rayonet reactor equipped with 254-nm lamps.

The reaction cell, a 10 × 10 × 40 mm fused quartz cell, was equipped with a 14/20 ground glass joint and could be fitted to two types of upper sections. Both types had vacuum stopcocks and 10-mL side arms for degassing the solutions by freeze–thaw techniques. One, however, had another side arm in which solid NaI was added. With this cell, the amount of complex decomposed, N_2 formed, and $Cr(NH_3)_5NH_2Cl^{3+}$ formed in the photolysis could be determined. Light intensities, $\sim 10^{-5}$ einstein L^{-1} s^{-1}, were measured by ferrioxalate actinometry before and after photolysis, and an average value was used to calculate the quantum yield. The variation in intensity was always less than 5%.

The flash apparatus used in these experiments is of the general design described by Porter[20] and Linschitz[21] and used in a kinetic–spectrophotometric mode. The two flash lamps, Xenon Corp. Model FP-100C, are connected in series and across a Sangamo 10-μF capacitor by 5-in. cables to minimize circuit inductance. The capacitor is charged by a Spellman Model RG10 regulated high-voltage power supply. The voltage applied to the capacitor could be varied to dissipate 100–500 J per flash. The photolyzing flash, triggered externally with a Xenon Corp. Model C trigger module, has a rise time of 5 μs, a half-peak duration of 10 μs, and a total duration of 25–30 μs. Following the flash, the chemical change is detected by monitoring the change in intensity of a collimated beam of light from a 100-W high-pressure Xe lamp powered by a Sola filtered dc power supply. The light beam from the Xe lamp is passed through the center of the reaction cell and light baffle onto a mirror which reflects the beam onto the entrance slit of a Beckman DU monochromator. The change in intensity of the analyzing beam at a given wavelength is then monitored by an RCA 31034 photomultiplier tube powered by a Pacific Photometric Instruments Model 203 regulated negative high-voltage power supply. The photomultiplier current is dropped across a 27-kΩ resistor, and the change in voltage as a function of time is displayed on a Hewlett-Packard Model 175A oscilloscope. The oscilloscope sweep is triggered by inductive coupling with the discharge of the storage capacitor. Although the RC time constant of the detection circuit is 0.81 μs, the time resolution of the apparatus is 25 μs because of the flash duration. For precise kinetic measurements, however, the time resolution is longer due to a tail in the flash profile.

The solution to be flashed is contained in a fused quartz cell. The inner cylindrical sample compartment is 17 × 1.2 cm diameter and surrounded by an outer annulus which is 20 × 3.0 cm diameter. The flash cell is connected through a 10/30 joint to an upper section having a side arm and vacuum stopcock. The apparatus could then be attached through a 10/30 joint to a vacuum line and the solution degassed by repeated freeze–thaw cycles.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer, calibrated against polystyrene. Ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer or a Techtron 635 spectrophotometer. Emission spectra were recorded on a Perkin-Elmer Hitachi MPF-2A fluorescence spectrophotometer equipped with a Hamanatsu R818 red-sensitive photomultiplier. A Beckman Expandomatic SS-2 pH meter equipped with a combination glass–calomel electrode was used to make pH measurements. This instrument was standardized with a Beckman pH 7 buffer.

Results

The absorption spectrum of $Cr(NH_3)_5N_3^{2+}$, shown in Figure 1, consists of two spin-allowed ligand-field transitions designated L_1, 499 nm, and L_2, 380 nm. Irradiation in this spectral region results in ammonia aquation with little or no aquation of the coordinated azide.[10] Irradiation in the ultraviolet region of the spectrum, which is dominated by an intense CTLM transition at 263 nm with a shoulder at 315 nm, causes a general decline in absorption and the evolution of N_2 gas. The evolution of N_2 gas and the appearance of Co(II) when $Cr(NH_3)_5N_3^{2+}$ is irradiated in the presence of $Co(NH_3)_5H_2O^{3+}$ led to the proposal of a photoredox mechanism.[11] This interpretation proposed that the initial products of the photolysis, Cr(II) and the azide radical $\cdot N_3$, arose from

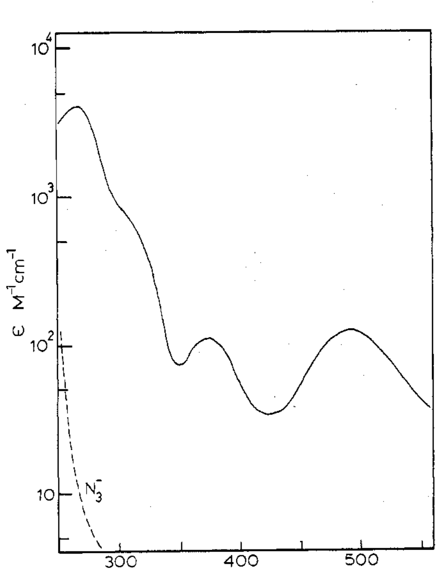

Figure 1. Absorption spectra of $Cr(NH_3)_5N_3^{2+}$ and NaN_3 in aqueous solution.

an intramolecular charge transfer. The azide radical then gave rise to N_2 and the Cr(II) reduced $Co(NH_3)_5H_2O^{3+}$ to Co(II). Our initial experiments, however, were inconsistent with this interpretation. Although we were able to confirm Vogler's observation that $Co(NH_3)_5H_2O^{3+}$ was reduced, we found that photolysis of 10^{-4} M $HClO_4$ solutions containing 10^{-2} M $Cr(NH_3)_5N_3^{2+}$ in the presence of either 10^{-2} M $Co(NH_3)_6^{3+}$, 10^{-3} M $Co(NH_3)_5Cl^{2+}$, or 5×10^{-4} M $Co(NH_3)_5Br^{2+}$ did not result in the formation of Co(II). Although the rates of reduction of acidopentaamminecobalt(III) complexes by Cr(II) are $Co(NH_3)_5Br^{2+} > Co(NH_3)_5Cl^{2+} >> Co(NH_3)_5H_2O^{3+} > Co(NH_3)_6^{3+}$,[22] the low concentrations of the bromo- and chloropentaammine complexes and the low rate of reduction of $Co(NH_3)_6^{3+}$ may not have been adequate to intercept the Cr(II) intermediate. Flash photolysis experiments, however, did indicate that photoredox is not a major reaction pathway. When degassed 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ solutions containing 10^{-4}–10^{-2} M NaI were exposed to a filtered (10^{-2} M NaI) 210-J flash, 20% of the complex was decomposed and N_2 was formed, yet we were unable to detect the absorbance of the I_2^- transient. The results of these experiments were felt to be inconclusive, however, since the rate at which I^- scavenges N_3 is not known and Cr(II), if present, might be expected to rapidly react with I_2^- preventing its detection. Because of these potential difficulties, flash photolysis experiments were carried out to detect Cr(II) directly. A degassed 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ solution was exposed to a filtered (10^{-2} M NaI) 250-J flash and analyzed at 740 nm, the absorption maximum of $Cr(H_2O)_6^{2+}$. Spectra recorded before and after the flash indicated 50% of the complex was decomposed by the flash, but no transient absorbance was detected. Although a reaction between Cr(II) and the azide radical might be postulated to account for the absence of a Cr(II) absorbance, nitrogen would not be formed; yet copious amounts of N_2 were formed in the flash experiment. At 740 nm, the extinction coefficient of $Cr(H_2O)_6^{3+}$ is only 7 M^{-1} cm^{-1}, however, and does not allow us to rule out a redox mode. Assuming a minimum signal to noise ratio of 2:1, the absence of a Cr(II) absorbance in the flash photolysis experiments indicates that under these experimental conditions $\phi_{Cr(II)} \leq 0.06$.

The previous study which proposed that photoredox occurred on 313-nm photolysis of $Cr(NH_3)_5N_3^{2+}$ reported the yield of N_2 to be 90% of the expected 1.5 mol of N_2/mol of complex decomposed.[11] Our experiments, however, yield an average value of the number of moles of N_2 which is less than that previously reported. The gas liberated during the photolysis was characterized and quantitated by gas chromatography. A 10^{-3} M $[Cr(NH_3)_5N_3](ClO_4)_2$ solution containing 0.3 M HCl was degassed by repeated freeze–thaw cycles. The spectrum of the solution was recorded before and after photolysis and the number of moles of $Cr(NH_3)_5N_3^{2+}$ decomposed was determined from the decrease in absorbance at 280 and 265 nm. The noncondensable gas (at liquid N_2 temperature) was quantitatively transferred by a Toepler pump to a Gow-Mac gas chromatograph. The GC trace indicated N_2 was the only gaseous product and a series of five experiments yielded 1.1 ± 0.2 mol of N_2/mol of $Cr(NH_3)_5N_3^{2+}$ decomposed. The apparent excess of N_2 may be due to an inability to account for a possible absorption of the product(s) in determining the number of moles of complex decomposed and/or secondary photolysis[5d] or thermal instability of the primary product of the photochemical reaction (see below).

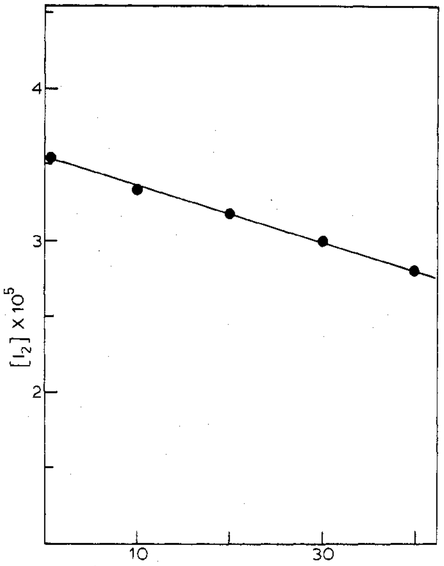

Figure 2. The time dependence of the ability of the photolyte to oxidize iodide ion to iodine following 313-nm photolysis of a 0.3 M HCl solution containing 3×10^{-3} M $Cr(NH_3)_5N_3^{2+}$.

When 10^{-3} M $[Cr(NH_3)_5N_3](ClO_4)_2$ solutions containing 1.0 M $HClO_4$ are exposed to 313-nm radiation, nitrogen is evolved, but the photolyte does not oxidize iodide ion. In 1.0 M HCl, however, 313-nm photolysis of a 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ solution yielded a photolyte which oxidized iodide to iodine. These results indicate that the initial photochemical product is a chromium nitrene intermediate, $Cr(NH_3)_5NH^{3+}$, which in the presence of HCl is trapped to form the chloramine, known to oxidize iodide to iodine.[5c–f] As previously reported,[6] secondary photolysis occurs extensively at 313 nm and, as mentioned above, may account in part for the high yield of nitrogen relative to the amount of complex decomposed.[5d] Additional experiments also indicate $Cr(NH_3)_5NH_2Cl^{3+}$ is thermally unstable. A 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ solution containing 1.0 M HCl was photolyzed to 5% consumption of the starting material. The photolyte was then stored in the dark at 25 °C in a Haake FK2 constant-temperature bath and aliquots taken periodically were tested with iodide ion. As indicated by Figure 2, the ability of the photolyte to oxidize iodide to iodine had decreased by 18% in 30 min. This thermal instability precluded the use of conventional ion-exchange chromatography to isolate $Cr(NH_3)_5NH_2Cl^{3+}$. It is known, however, that coordinated chloramine can be reduced to the coordinated ammine by iodide ion.[5c] Thus the photolytes were treated with 1.0 M NaI to reduce the unstable $Cr(NH_3)_5NH_2Cl^{3+}$ to the stable Cr-

$(NH_3)_6^{3+}$. The treated photolyte was charged onto a Dowex 50-X2 ion-exchange column and after elution of the unreacted $Cr(NH_3)_5N_3^{2+}$ with 1.0 M NaCl, the column was eluted with 3.0 M HCl. The initial HCl eluate, which had absorption bands at 480 and 355 nm, appeared to contain a small amount of $Cr(NH_3)_5H_2O^{3+}$. Since a small amount of $Cr(NH_3)_5H_2O^{3+}$ was also detected in the eluates of known samples of $Cr(NH_3)_5N_3^{2+}$ (see Experimental Section), the $Cr(NH_3)_5H_2O^{3+}$ is thought to arise from an acid-catalyzed aquation of $Cr(NH_3)_5N_3^{2+}$ on the column rather than a photochemical reaction. The visible–UV spectra of the following fractions of the HCl eluate showed two absorption bands of equal intensity at 465 and 350 nm, characteristic of $Cr(NH_3)_6^{3+}$. A weak luminescence centered at 650 nm with an excitation spectrum identical with the first absorption band of $Cr(NH_3)_6^{3+}$ also confirmed the presence of $Cr(NH_3)_6^{3+}$ in a degassed aliquot of the eluate.[15]

Our flash photolysis and Co(III) scavenging experiments yield an upper limit of $\phi_{Cr(II)} \leq 0.06$ which is in reasonable agreement with a value of 0.02 for photoredox reported by Sriram and Endicott.[11b] On the other hand, the ability of photolytes containing HCl to oxidize iodide ion and the isolation of $Cr(NH_3)_6^{3+}$ from iodide-treated photolytes establish the primary photochemical reaction to be cleavage of the CrN–N_2 bond. In the presence of HCl, the nitrene intermediate $Cr(NH_3)_5NH^{3+}$ is trapped to form the chloramine[5c–f] $Cr(NH_3)_5NH_2Cl^{3+}$

$$Cr(NH_3)_5N_3^{2+} \xrightarrow[313\text{ nm}]{h\nu} Cr(NH_3)_5N^{2+} + N_2 \tag{1}$$

$$Cr(NH_3)_5N^{2+} + 2H^+ + Cl^- \rightarrow Cr(NH_3)_5NH_2Cl^{3+} \tag{2}$$

As previously reported,[6] the dependence of the quantum yield of $Cr(NH_3)_5NH_2Cl^{3+}$, ϕ_{NH_2Cl}, on the concentration of HCl extrapolates to a limiting yield of 0.5 ± 0.17. The agreement between the limiting yield of $Cr(NH_3)_5NH_2Cl^{3+}$ and the quantum yield for $Cr(NH_3)_5N_3^{2+}$ decomposition at 313 nm, 0.48, indicates the principal photochemical reaction to be nitrene formation. The uncertainty in the limiting yield is large, however, and prevents establishing the nitrene reaction mode as the exclusive reaction pathway at 313 nm. Nevertheless, the results of the flash photolysis and Co(III) scavenging experiments reported above and the results reported by Sriram and Endicott[11b] indicate that the photoredox accounts for less than 12% of the overall photodecomposition of $Cr(NH_3)_5N_3^{2+}$. Although nitrene formation is the principal reaction mode at 313 nm, other photochemical reactions appear to occur at 254 nm. In 1.0 M HCl, the ratio of ϕ_{NH_2Cl} to ϕ_{dec} decreases from 0.48 at 313 nm to 0.33 at 254 nm.

In the presence of 0.1 M NaCl, the quantum yield of $Cr(NH_3)_5NH_2Cl^{3+}$ was found to be independent of the concentration of hydrogen ion. The hydrogen ion concentration was varied with $HClO_4$ over the range of 10^{-1} to 10^{-4} M. Although the majority of experiments reported in this study were carried out with solutions degassed by freeze–thaw cycles or with N_2 saturated solutions, ϕ_{NH_2Cl} was, within experimental error, independent of the dissolved oxygen.

Unlike $Ir(NH_3)_5N_3^{2+}$ and $Rh(NH_3)_5N_3^{2+}$, which have rich flash photolysis spectra,[5e,23a,25] no transient absorbance lasting longer than 20 μs is detected in the flash photolysis of $Cr(NH_3)_5N_3^{2+}$ under a variety of experimental conditions over the 300- to 800-nm range.

Direct photolysis of $Co(NH_3)_5H_2O^{3+}$ at 313 nm does lead to photoreduction with a quantum yield of 1.1×10^{-2}. The yield of Co(II) on direct photolysis was found to be independent of the concentration of $HClO_4$ over the range 10^{-3}–10^{-4} M. The inefficiency of the photoreduction process, however, ruled out a trivial direct photolysis of $Co(NH_3)_5H_2O^{3+}$ in the presence of $Cr(NH_3)_5N_3^{2+}$. Photolysis of a weakly acidic, 10^{-4} M $HClO_4$, solution 5×10^{-3} M in $Cr(NH_3)_5N_3^{2+}$ and containing 10^{-2} M $Co(NH_3)_5H_2O^{3+}$, 95% of the 313-nm radiation is absorbed by $Cr(NH_3)_5N_3^{2+}$, led to the formation of Co(II) with a quantum yield, $\phi_{Co(II)}$, of 0.48. A trivial mechanism also could not account for the striking pH dependence of the yield of Co(II). For solutions 5×10^{-3} M in $Cr(NH_3)_5N_3^{2+}$ and 10^{-2} M in $Co(NH_3)_5H_2O^{3+}$, varying the pH with $HClO_4$ caused $\phi_{Co(II)}$ to decrease from 0.48 at pH 4 (0.1 M $NaClO_4$) to $<10^{-3}$ at pH 1. As shown in Figure 3, the yield of Co(II) on 313-nm photolysis of 5×10^{-3} M $Cr(NH_3)_5N_3^{2+}$ solutions containing 10^{-2} M $Co(NH_3)_5H_2O^{3+}$ also decreased as the concentration of HCl increased. The dependence of $\phi_{Co(II)}$ on the concentration of $Co(NH_3)_5H_2O^{3+}$ was determined with 10^{-4} M $HClO_4$ solutions containing 5×10^{-3} M $Cr(NH_3)_5N_3^{2+}$ and varying amounts of $Co(NH_3)_5H_2O^{3+}$. Again the solutions were irradiated at 313 nm and the results of these experiments are shown in Figure 4. The yield of Co(II), $\phi_{Co(II)}$, was also found to be independent of oxygen. Unfortunately, no transient absorbance was observed on flash photolysis of identical solutions containing 10^{-2} M $Co(NH_3)_5H_2O^{3+}$.

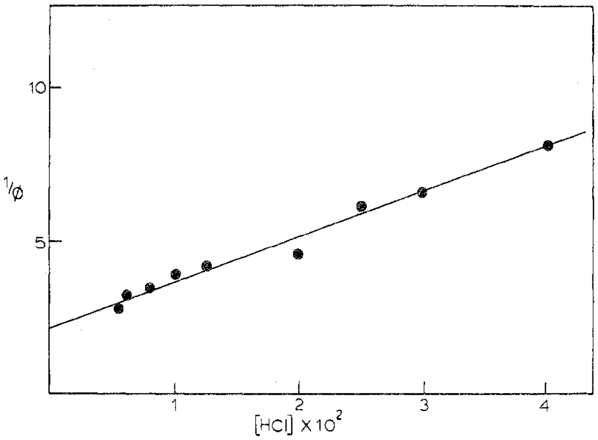

Figure 3. Dependence of the reciprocal of the Co(II) quantum yield, $\phi_{Co(II)}$, on the concentration of HCl. Initial concentrations of $[Cr(NH_3)_5N_3](ClO_4)_2$ and $[Co(NH_3)_5H_2O](ClO_4)_3$ are 3.0×10^{-3} and 1.0×10^{-2} M, respectively.

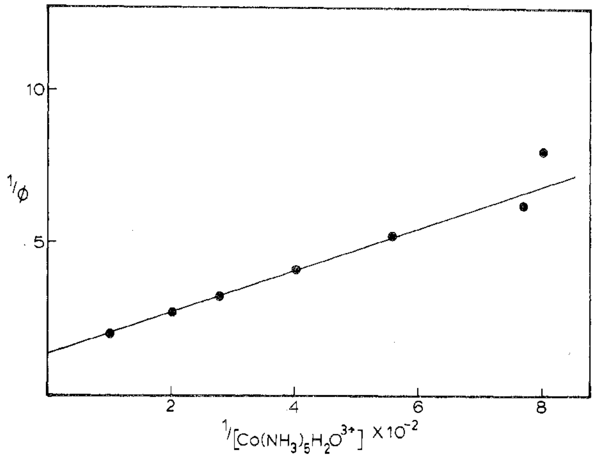

Figure 4. Dependence of the reciprocal of the quantum yield of Co(II) on reciprocal of the concentration of $Co(NH_3)_5H_2O^{3+}$. Initial concentration of $[Cr(NH_3)_5N_3](ClO_4)_2$ in 10^{-4} M $HClO_4$ is 3.0×10^{-3} M.

Discussion

Irradiation of aqueous solutions of $Cr(NH_3)_5N_3^{2+}$ results in the evolution of 1.1 ± 0.2 mol of N_2/mol of complex decomposed. In the presence of $Co(NH_3)_5H_2O^{3+}$, photolysis of $Cr(NH_3)_5N_3^{2+}$ leads to extensive formation of Co(II).

However, similar reductions are not obtained with other acidopentaamminecobalt(III) complexes, and flash photolysis experiments indicate that $\phi_{\mathrm{Cr(II)}} \leq 0.06$.[11b] In the presence of HCl, however, the photolyte will oxidize iodide to iodine and $\mathrm{Cr(NH_3)_6^{3+}}$ is isolated from the reduced photolyte. These results suggest that the principal reaction mode is the formation of a coordinated nitrene intermediate, $\mathrm{Cr(NH_3)_5NH^{3+}}$, which can be scavenged by HCl to form the chloramine, a known oxidant of iodide ion.

Consider first the reaction mode which leads to $\mathrm{Cr(NH_3)_5NH_2Cl^{3+}}$. The results suggest and are consistent with a reaction mechanism, eq 3–10, which postulates a coordinated

$$\mathrm{Cr(NH_3)_5N_3^{2+}} \xrightarrow[313\text{ nm}]{\mathrm{Ia}} {}^*\mathrm{Cr(NH_3)_5N_3^{2+}} \tag{3}$$

$$ {}^*\mathrm{Cr(NH_3)_5N_3^{2+}} \xrightarrow{k_4} \mathrm{Cr(NH_3)_5N_3^{2+}} + \text{heat} \tag{4}$$

$$ {}^*\mathrm{Cr(NH_3)_5N_3^{2+}} \xrightarrow{k_5} \mathrm{Cr(NH_3)_5N^{2+}} + \mathrm{N_2} \tag{5}$$

$$\mathrm{Cr(NH_3)_5N^{2+}} + \mathrm{H^+} \xrightarrow{k_6} \mathrm{Cr(NH_3)_5NH^{3+}} \tag{6}$$

$$\mathrm{Cr(NH_3)_5NH^{3+}} + \mathrm{HCl} \xrightarrow{k_7} \mathrm{Cr(NH_3)_5NH_2Cl^{3+}} \tag{7}$$

$$\mathrm{Cr(NH_3)_5NH^{3+}} + \mathrm{H_2O} \xrightarrow{k_8} \mathrm{Cr(NH_3)_5NH_2OH^{3+}} \tag{8}$$

$$\mathrm{Cr(NH_3)_5NH^{3+}} + \mathrm{OClO_3^-} \xrightarrow[k_9]{+\mathrm{H^+}} \mathrm{Cr(NH_3)_5NH_2OClO_3^{3+}} \tag{9}$$

$$\mathrm{Cr(NH_3)_5NH_2Cl^{3+}} \xrightarrow{k_{10}} \mathrm{P}\ (\text{slow}) \tag{10}$$

nitrene intermediate. The product P in eq 10 represents the product of the thermal decomposition of $\mathrm{Cr(NH_3)_5NH_2Cl^{3+}}$. The decomposition is slow, however, compared to the other reactions in the sequence and is neglected in the following analysis. The data gathered in this study do not distinguish the sequence of steps leading to $\mathrm{H^+}$ and $\mathrm{Cl^-}$ addition. Thus, to simplify the analysis, we have specified, in eq 7, a single addition of HCl to the nitrene rather than a series of reaction steps. This does not affect the kinetic analysis, however, since $\phi_{\mathrm{NH_2Cl}}$ is independent of pH. Although the mechanism for the formation of $\mathrm{Cr(NH_3)_5NH_2Cl^{3+}}$ is essentially identical with that observed with $\mathrm{Ir(NH_3)_5NH_2Cl^{3+}}$ and $\mathrm{Rh(NH_3)_5NH_2Cl^{3+}}$, the difference in the rate constants suggests $\mathrm{Cr(NH_3)_5NH^{3+}}$ is substantially less electrophilic. Steady-state analysis of the mechanism yields

$$\frac{1}{\phi_{\mathrm{NH_2Cl}}} = \frac{1}{\phi_{\mathrm{N}}} + \frac{k_8[\mathrm{H_2O}] + k_9[\mathrm{ClO_4^-}]}{\phi_{\mathrm{N}} k_7 [\mathrm{HCl}]} \tag{11}$$

where ϕ_{N} is the quantum yield of the nitrene intermediate. The ratio of the intercept to the slope from Figure 4 yields a value of 0.48 $\mathrm{M^{-1}}$ for $k_7/(k_8[\mathrm{H_2O}] + k_9[\mathrm{ClO_4^-}])$. Comparison of this value, 0.48 $\mathrm{M^{-1}}$, with the values determined for $\mathrm{Rh(NH_3)_5NH^{3+}}$, 23.3 $\mathrm{M^{-1}}$, and $\mathrm{Ir(NH_3)_5NH^{3+}}$, 1740 $\mathrm{M^{-1}}$, suggests that the electrophilicity of a first transition series nitrene is substantially less than nitrenes of heavier metals. This appears somewhat arbitrary to us, however, since the charges on the metal ions and nitrene nitrogens are the same. Nor do we feel the small value indicates the $\mathrm{Cr(NH_3)_5NH^{3+}}$ is a triplet nitrene which would be expected to be less electrophilic than the singlet nitrenes[5c] $\mathrm{Rh(NH_3)_5NH^{3+}}$ and $\mathrm{Ir(NH_3)_5NH^{3+}}$. The yield of $\mathrm{Cr(NH_3)_5NH_2Cl^{3+}}$ is independent of oxygen, an efficient scavenger of triplet arylnitrenes.[26] Rather, we suggest that the diminished reactivity toward $\mathrm{Cl^-}$ reflects the instability of the $\mathrm{Cr(NH_3)_5NH^{3+}}$ intermediate. This interpretation, which is consistent with the idea that the stability of a coordinated nitrene is due to an enhanced dπ–pπ overlap with the heavier metal ions,[5c] is indirectly suggested by flash photolysis experiments. The absence of transient spectra in these experiments indicates that the chromium nitrene intermediates are short lived, $\tau < 20$ μs, and is in marked contrast to the rich flash photolysis spectra observed with the rhodium(III) and iridium(III) analogues.

Table I. Quantum Yields of $\mathrm{Cr(NH_3)_5NH_2Cl^{3+}}$ and Decomposition in 1.0 M HCl at Various Wavelengths

$10^3 \times [\mathrm{Cr(NH_3)_5N_3^{2+}}]$, M	λ_{ex}, nm	$\phi_{\mathrm{NH_2Cl}}$	ϕ_{dec}
5.04	406	$\leq 10^{-3}$	–[b]
5.04	366	2.8×10^{-3}[a]	–[b]
3.00	313	0.23[a]	0.48
0.48	302	0.20[a]	0.46
0.48	254	0.14[a]	0.43

[a] Values obtained by extrapolation of ϕ_{obsd} to zero irradiation time. [b] Ligand aquation appears to be other principal reaction mode (ref 10 and 11).

The data gathered in this study on the 313-nm photolysis of $\mathrm{Cr(NH_3)_5N_3^{2+}}$ do not rule out an intramolecular photoredox process but rather suggest that photoredox is a minor reaction mode. We do not question that photoredox occurs on 313-nm photolysis. We question whether it occurs in amounts adequate to account for the reduction of $\mathrm{Co(NH_3)_5H_2O^{3+}}$ and whether scavenging with Co(III) complexes is a reliable measure of the redox yield. Previous studies have attributed the formation of Co(II) to the reaction

$$\mathrm{Cr^{2+}} + \mathrm{Co(NH_3)_5H_2O^{3+}} \rightarrow \mathrm{Cr^{3+}} + \mathrm{Co^{2+}} + 5\mathrm{NH_3} + \mathrm{H_2O}$$

where $\mathrm{Cr^{2+}}$ is the product of the photoredox step.[11] On extrapolation to infinite $\mathrm{Co(NH_3)_5H_2O^{3+}}$ concentration, Figure 4 indicates the limiting yield of Co(II) to be 0.55 ± 0.15. Flash photolysis experiments, however, indicate that the photoredox yield is much less, $\phi_{\mathrm{Cr(II)}} \leq 0.06$. To account for this difference, it has been proposed that Cr(II) is scavenged by the nitrene intermediate. Although such a reaction is possible, in our opinion, it does not adequately explain these results. Assuming that both photoredox and nitrene formation occur, $\phi_{\mathrm{N}} + \phi_{\mathrm{Cr(II)dec}}$ must be equal to ϕ_{dec}. Using the limiting yield of Co(II) as a measure of $\phi_{\mathrm{Cr(II)}}$ and the limiting yield of $\mathrm{Cr(NH_3)_5NH_2Cl^{3+}}$ as a measure of ϕ_{N}, our results yield ϕ_{dec} to be 1.05 ± 0.32. Although the uncertainty is large, the calculated value of ϕ_{dec} is larger than the value of 0.48 measured in this work and that reported by Vogler.[11a] The data gathered in this study do not explicitly elucidate the reaction sequence leading to the reduction of $\mathrm{Co(NH_3)_5H_2O^{3+}}$, but the similarity of the limiting quantum yields of decomposition, chloramine formation, and Co(II) lead us to suggest that the reduction of $\mathrm{Co(NH_3)_5H_2O^{3+}}$ may also involve $\mathrm{Cr(NH_3)_5NH^{3+}}$ or a product of this intermediate. The decreasing yield of Co(II) with increasing concentration of HCl, however, rules out $\mathrm{Cr(NH_3)_5HH_2Cl^{3+}}$ or its thermal decomposition product as the reductant. Tests of photolyte with α-napthylamine also indicate that $\mathrm{NH_2OH}$ is not formed in adequate amounts, $\phi_{\mathrm{NH_2OH}} \leq 10^{-3}$, to suggest it is the reductant.

In the absence of HCl, the coordinated hydroxylamine, $\mathrm{Cr(NH_3)_5NH_2OH^{3+}}$, is the expected product, eq 8.[5e] If the redox reaction is postulated to be

$$\mathrm{Cr(NH_3)_5NH_2OH^{3+}} + \mathrm{Co(NH_3)_5H_2O^{3+}} \rightarrow \mathrm{Co(II)} + \mathrm{Cr(III)} \tag{12}$$

where Cr(III) and Co(II) represent the oxidation and reduction products, the mechanism is not consistent with the kinetic data. Steady-state analysis of the reaction mechanism, including eq 12, leads to

$$\frac{1}{\phi_{\mathrm{Co(II)}}} = \frac{1}{\phi_{\mathrm{N}}} + \frac{k_7[\mathrm{HCl}]}{\phi_{\mathrm{N}} k_8 [\mathrm{H_2O}] + k_9 [\mathrm{ClO_4^-}]} \tag{13}$$

From Figure 3, the ratio slope to intercept, $k_7/(k_8[\mathrm{H_2O}] + k_9[\mathrm{ClO_4^-}])$, yields a value of 71.4 $\mathrm{M^{-1}}$. Since this value of 71.4 $\mathrm{M^{-1}}$ differs substantially from the value of 0.48 $\mathrm{M^{-1}}$ obtained from the dependence of $\phi_{\mathrm{NH_2Cl}}$ on HCl, such a reaction seems implausible.

Since the coordinated hydroxylamines are weak acids, pK_a ~ 8–10[5c,27] and $\phi_{\mathrm{Co(II)}}$ is pH dependent, we suggest that the conjugate base of the hydroxylamine, $\mathrm{Cr(NH_3)_5NHOH^{2+}}$, or a decomposition product of this species may be involved in the reduction of $\mathrm{Co(NH_3)_5H_2O^{3+}}$.

Previous investigations of the photochemical reactions of $\mathrm{Rh(NH_3)_5N_3^{2+}}$ and $\mathrm{Ir(NH_3)_5N_3^{2+}}$ have led to the suggestion that the nitrene reaction pathway, cleavage of an $\mathrm{MN{-}N_2}$ bond, originates in an azide-centered excited state.[5e,f] Spectral studies have indicated that this first allowed singlet state of the azide chromophore is bent.[12a,b] This distortion from the linear ground state gives rise to a large Stoke's shift between the vertical Franck–Condon absorption and the fluorescence from the thermally equilibrated bent excited state. For example, Deb reports the fluorescence of alkali metal azides to be centered at 480 nm.[12c] Based on these observations, it was proposed that cleavage of the $\mathrm{MN{-}N_2}$ bond takes place within the internal azide centered excited state which is lower in energy and is populated by internal conversion from the ligand field excited states of the rhodium(III) and iridium(III) complexes.

The ligand field excited states of $\mathrm{Cr(NH_3)_5N_3^{2+}}$ are much lower in energy than those of the rhodium(III) and iridium(III) analogues. The long wavelength tail of the first absorption band of $\mathrm{Cr(MH_3)_5N_3^{2+}}$ indicates the thermally equilibrated $\mathrm{L_1}$ state lies at $<1.7\ \mu\mathrm{m}^{-1}$, whereas the fluorescence maxima reported by Deb indicates the thermally equilibrated azide-centered excited state lies at 2.0–2.1 $\mu\mathrm{m}^{-1}$.[12c] If the cleavage of the $\mathrm{CrN{-}N_2}$ bond arises from this low energy azide excited state, the singularity of the reaction mode observed in these experiments indicates little internal conversion between the thermally equilibrated azide-centered excited state and the ligand field excited state. Since the energy of the azide-centered state is greater than that of the $\mathrm{L_1}$ state, the absence of internal conversion cannot be attributed to energetic barriers. Rather, we suggest that the barrier to internal conversion arises from quantum mechanical consideration. The width of the $\mathrm{L_1}$ absorption band reflects the difference in the equilibrium nuclear configuration of the excited state relative to the ground state.[29] Since the $\mathrm{L_1}$ excited state of the chromium(III) complex has the electronic configuration $t_{2g}^{\,2}\, e_g^{\,1}$, assuming O_h microsymmetry, the metal–ligand bond strength within the excited complex is reduced and a change in the size and shape of the complex is expected. This weakening of the metal–ligand bonds would not be expected to cause a distortion within the azide ligand per se. We propose that the vibrational manifold of the $\mathrm{L_1}$ state may not contain a vibration of proper symmetry to yield a nonzero vibrational overlap integral with the vibrational manifold of the thermally equilibrated azide-centered excited state.[30] The negligible or zero value of the integral would then prevent internal conversion between the states and lead exclusively to the observed nitrene reaction pathway.

The minimum energy required to cleave the $\mathrm{HN{-}N_2}$ bond is calculated to be 0.33 $\mu\mathrm{m}^{-1}$/mol.[31] Although the minimum energy required to cleave the $\mathrm{MN{-}N_2}$ bond may be somewhat different, it would be a small fraction of the excitation energies of 2.2–4.0 $\mu\mathrm{m}^{-1}$ used in these experiments and those of $\mathrm{Ir(NH_3)_5N_3^{2+}}$ and $\mathrm{Rh(NH_3)_5N_3^{2+}}$. Thus the wavelength dependence of the quantum yield of the nitrene reaction mode does not reflect energetic barriers but as previously proposed is thought to reflect differences in the efficiency of internal conversion to the reactive low-energy azide-centered excited state.[5e] Qualitatively, the wavelength dependence of ϕ_{N} for $\mathrm{Cr(NH_3)_5N_3^{2+}}$ is similar to that previously observed,[5e] but other factors also appear to be important. For lower energy excitations, $\lambda_{\mathrm{ex}} > 313$ nm, a larger fraction of the exciting radiation is absorbed by the overlapping $\mathrm{L_2}$ absorption band. With higher energy radiation, $\lambda_{\mathrm{ex}} < 302$ nm, the ratio ϕ_{N} to ϕ_{dec} decreases indicating another reaction mode is competitive with the nitrene reaction mode. Although the maximum in ϕ_{N} at 312 nm could be attributed to a more efficient conversion from the state populated at this wavelength to the reactive azide-centered excited state, it is also possible that excitation at this wavelength results in direct population of an azide excited state. Clossen and Gray have observed a weak absorption at 300 nm in alkylazides.[12a]

Clearly, this proposed model contrasts with the findings of Miskowski, et al.,[9b] where direct irradiation of the near-UV absorption of coordinated azide did not lead to a nitrene intermediate. As pointed out by these authors, a possible explanation of the difference may lie in the effect of $\mathrm{CN^-}$ ligation or $\mathrm{NH_3}$ ligation on the back-bonding in the nitrene intermediate. Another alternative explanation, of course, lies in the rate and efficiency of various decay paths which may be quite different in the cyano and ammine complexes.

Conclusion

The absence of transients in these flash photolysis experiments suggests that the chromium nitrene, $\mathrm{Cr(NH_3)_5NH^{3+}}$, is less stable than the nitrene analogues of the heavier metals. This result is thought to reflect a smaller $d\pi$–$p\pi$ overlap which appears necessary for a stable coordinated nitrene. These results also question the use scavenging with Co(III) complexes as a measure of the photoredox yield.

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Registry No. $\mathrm{Cr(NH_3)_5N_3^{2+}}$, 22317-10-8; $\mathrm{Cr(NH_3)_5NH_2Cl^{3+}}$, 61245-62-3; $\mathrm{Co(NH_3)_5H_2O^{3+}}$, 14403-82-8.

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Complex Halides of the Transition Metals. 24.[1] Reactions of Dimeric Molybdenum(II) Halide Complexes Containing Strong Metal–Metal Bonds with Bidentate Tertiary Phosphines and Arsines. Evidence for the Staggered Configuration in Dimers of Molybdenum(II)

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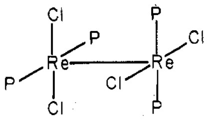
The reactions of $K_4Mo_2Cl_8$ and $Mo_2X_4(PR_3)_4$, where X = Cl or Br and R = Et or *n*-Bu, with the bidentate phosphine and arsine donors bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1-diphenylphosphino-2-diphenylarsinoethane (arphos), 1,2-bis(diphenylarsino)ethane (dpae), and *o*-phenylenebis(dimethylarsine) (diars) produce metal–metal bonded complexes of the type $Mo_2X_4(LL)_2$. The dimeric complex $Mo_2Cl_4(dppm)_2$ shows spectral similarities to $Mo_2Cl_4(PR_3)_4$ and the rhenium analogue $Re_2Cl_4(dppm)_2$ and it is believed to possess a similar structure to the latter complex with an eclipsed ligand configuration and bridging dppm molecules. The dppe complex $Mo_2Cl_4(dppe)_2$ exists in both α and β forms, which are believed to exhibit quite different structures. α-$Mo_2Cl_4(dppe)_2$ possesses a $\sigma^2\pi^4\delta^2$ ground-state configuration and available evidence indicates that it contains chelating dppe molecules and a cis disposition of Mo–Cl bonds within the individual $[MoCl_2P_2]$ units. β-$Mo_2Cl_4(dppe)_2$ exhibits very similar infrared and electronic absorption spectral properties to $Mo_2Cl_4(arphos)_2$ and $Mo_2Cl_4(dpae)_2$ implying that this group of complexes possesses closely related structures. Since β-$Mo_2Cl_4(dppe)_2$, $Mo_2Cl_4(arphos)_2$, $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ are isomorphous, it seems likely that these molybdenum complexes have the same structure as their rhenium analogues, namely, a staggered noncentrosymmetric structure, wherein the dppe, arphos, and dpae ligands assume a novel bonding mode in which they bridge the rhenium atoms within the dimer. This is the first instance where a metal–metal quadruple bond ($\sigma^2\pi^4\delta^2$) has been modified to a triple bond ($\sigma^2\pi^4$) without an accompanying change in the metal oxidation state. $Mo_2Br_4(dppe)_2$ is probably related structurally to β-$Mo_2Cl_4(dppe)_2$ rather than to the α isomer. The diars complexes $Mo_2Cl_4(diars)_2$ and $Re_2Cl_4(diars)_2$ do not appear to be isostructural. The electronic absorption spectrum of $Re_2Cl_4(diars)_2$ provides evidence for the oxidation of this complex by O_2 to form $[Re_2Cl_4(diars)_2]^+$ of some electronically related species. The x-ray photoelectron spectra of the new molybdenum complexes are in accord with their formulation as derivatives of the molybdenum(II) chlorides.

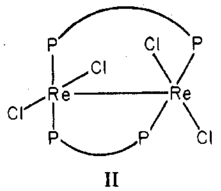
Introduction

In exploring the factors which influence the electronic structures of low oxidation state halide complexes of molybdenum and rhenium which contain strong metal–metal bonds (double, triple, or quadruple),[2] we recently established[3] that the metal–metal bonded dimers $Re_2Cl_4(LL)_2$, where LL = 1,2-bis(diphenylphosphino)ethane (dppe) or 1-diphenylphosphino-2-diphenylarsinoethane (arphos), differ structurally from the related complexes with monodentate tertiary phosphines, $Re_2Cl_4(PR_3)_4$.[4,5] In contrast to the latter systems, which possess an eclipsed noncentrosymmetric D_{2d} structure I,[5] the complexes with dppe and arphos were suggested to have



I

the staggered structure II,[3] wherein the dppe and arphos



II

ligands assume a novel bonding mode in which they bridge the rhenium atoms *within* the dimer. The latter structure formulation was based upon differences between the electronic absorption spectra and magnetic properties of $Re_2Cl_4(PR_3)_4$ and $Re_2Cl_4(LL)_2$ and experiments with scaled molecular models which were constructed to minimize unfavorable steric interactions. Earlier attempts to solve the crystal structure of either $Re_2Cl_4(dppe)_2$ or $Re_2Cl_4(arphos)_2$ were thwarted by a disorder problem and small crystal size. Accordingly, as an alternative approach to aid us in establishing whether our structural conclusions were correct, we set out to synthesize and characterize the related molybdenum(II) complexes of this type. This investigation has led us to study the reactions of the complexes $K_4Mo_2Cl_8$ and $Mo_2X_4(PR_3)_4$, where X = Cl or Br and R = Et or *n*-Bu, with the bidentate ligands dppe, arphos, bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylarsino)ethane (dpae), and *o*-phenylenebis(dimethylarsine) (diars), the results of which are reported herein. Since the completion of this study, our original suggestion[3] concerning the structures of $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ has been confirmed by a single-crystal x-ray structural analysis of $Re_2Cl_4(dppe)_2$.[6]

Experimental Section

Starting Materials. The following compounds were prepared by standard literature procedures: $K_4Mo_2Cl_8$,[7] $Mo_2Cl_4(PEt_3)_4$,[8] $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$,[9] and $Mo_2Br_4(PEt_3)_4$.[8] Commercial reagents and

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