$[Ru(NH_3)_5H_2O]^{2+}$)[15] or for cases where the reactions can proceed by low free energy pathways involving addition of ArN_2^+ to an electron-rich metal center (eq 1–4), outer-sphere electron transfer may not be an important competing process.

Electron transfer may play an important role in $M-N_2Ar$ chemistry in other ways. Either thermal or photochemical decomposition may occur based on initial electron transfer from metal to ligand

$$M^0\text{-}NN^+Ar \rightarrow M^I\text{-}NN^0Ar$$

or

$$M^0\text{-}NN^+Ar \xrightarrow{h\nu} M^I\text{-}NN^0Ar$$

followed by the production of Ar and either M^IN_2 or M^I + N_2 (eq 9, 14, 15). The importance of this decomposition pathway should be sensitive to the electronic structure in the $M-N_2Ar$ group and may be important for cases where the ν(NN) stretching frequency is relatively high.

The failure to observe stable diazonium complexes may also be attributable to net electron-transfer processes in certain cases. For example, reactions between $[Ru(NH_3)_5H_2O]^{2+}$ and ArN_2^+ give dinitrogen complexes[15] and between ArN_2^+ and organometallic anions like $Co(CO)_4^-$ give highly colored species at −70 °C which decompose on warming.[16] In both cases the reactions may involve initial diazonium complex formation followed by reduction of the coordinated ligand.

Experimental Section

Electronic spectra were obtained using Cary 16, Bausch and Lomb 210, and Unicam SP800 spectrophotometers. Spectrograde acetonitrile was used as solvent in the experiments described. The preparations of the diazonium salts $[Ru(bpy)_2(p\text{-}N_2C_6H_4\text{-}Y)Cl](PF_6)_2$ (Y = OCH_3, CH_3, H) have been described.[10] The diazonium salt (p-$N_2C_6H_4NO_2$)(BF_4) was prepared using a standard literature procedure. Electrochemical measurements were made vs. the saturated sodium chloride calomel electrode at 22 ± 2 °C and are uncorrected for junction potential effects. The measurements were made using a PAR Model 173 potentiostat for potential control and a PAR Model 175 universal programmar as sweep generator for cyclic voltammetry experiments.

Spectrophotometric Titrations. In a typical experiment 15 mg of the salt $[Ru(bpy)_2(p\text{-}N_2C_6H_4CH_3)Cl](PF_6)_2$ was dissolved in acetonitrile. The complex $Ru(bpy)_2Cl_2\cdot 2H_2O$ (18.6 mg) was dissolved in 100 ml of acetonitrile, aliquots of this solution were added to the solution containing the diazonium complex, and the spectrum of the resulting solution was recorded from 700 to 350 nm after each addition. The spectra contained absorption bands characteristic of $[Ru(bpy)_2(CH_3CN)Cl]^+$ (λ_{max} 480 nm) and $[Ru(bpy)_2Cl_2]^+$ (λ_{max} 380 nm) which grew in intensity as the amount of $Ru(bpy)_2Cl_2$ added was increased. The diazonium complex absorbs only weakly above 350 nm.[10] When the amount of $Ru(bpy)_2Cl_2$ added exceeded a 1:1 ratio based on the diazonium complex present initially, an absorption band characteristic of unreacted $Ru(bpy)_2Cl_2$ appeared in the spectrum at 553 nm. Plots of the OD changes at 550 and 375 nm vs. the equivalents of $Ru(bpy)_2Cl_2\cdot 2H_2O$ added gave inflection points at n = 1 showing that the stoichiometry of the reaction was 1:1.

A similar experiment was carried out using the diazonium salt p-nitrobenzenediazonium tetrafluoroborate in place of the diazonium complex. Once more plots of the OD changes at 550 and 375 nm vs. n showed that n = 1 and that the ruthenium product of the reaction was $[Ru(bpy)_2Cl_2]^+$.

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Registry No. $[Ru(bpy)_2(p\text{-}N_2C_6H_4CH_3)Cl](PF_6)_2$, 42756-26-3; $Ru(bpy)_2Cl_2$, 19542-80-4; $[Ru(bpy)_2(CH_3CN)Cl]^+$, 31847-85-5; $[Ru(bpy)_2Cl_2]^+$, 47514-47-6; (p-$N_2C_6H_4NO_2$)(BF_4), 456-27-9.

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A Two-Step Synthesis of B_2D_6 Requiring No Metal Deuterides

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A need for quantities of deuterioborane derivatives had led us to study methods for preparing diborane-d_6 without resorting to known methods[1] employing expensive metal deuterides. We wish to report here the results of that investigation.

Previous studies[2,3] of the hydrogen-exchange characteristics of trimethylamine–borane afforded a solution to the basic problem of how to achieve the B–H to B–D conversion without employing deuterides. Those studies showed that trimethylamine–borane undergoes reasonably facile D–H exchange on the borane group (eq 1) upon treatment with

$$(CH_3)_3N\cdot BH_3 \xrightarrow{D_2O/DCl} (CH_3)_3N\cdot BD_3 \qquad (1)$$

acidified D_2O.

Although we were not able to precisely duplicate the literature results,[2] small modifications of the reported procedure afforded acceptable yields of trimethylamine–borane-d_6. In a typical synthesis 1.00 g (13.7 mmol) of $(CH_3)_3N\cdot BH_3$ (Callery Chemical Corp.) in 50 ml of anhydrous diethyl ether was stirred with 20 ml of 1.2 N DCl (99%) in D_2O (99.7%) for 5 h. The ether layer was separated and dried over barium oxide, and the solution was fractionated using a trap held at −20 °C to stop $(CH_3)_3N\cdot BD_3$. The solid was sublimed giving an isolated yield of 0.73 g (70%) and the extent of B-deuteration was estimated by IR methods to be at least 90%. Longer reaction times resulted in lower isolated yields due to the slow hydrolysis of trimethylamine–borane,[4] but no noticeable increase in the percent of deuteration could be achieved by this approach. The earlier investigators[2] reported a 95% yield of $(CH_3)_3N\cdot BD_3$ which was 98% deuterated, but others[3] found a 60–65% yield with no deuterium content given.

Samples of $(CH_3)_3N\cdot BD_3$ with greater deuterium content were produced by carrying out two sequential exchange reactions. In a typical synthesis 1.50 g (20.5 mmol) of $(CH_3)_3N\cdot BH_3$ in 80 ml of anhydrous ether was stirred in succession with two 30-ml portions of 1.2 N DCl in D_2O for 5 h each time. The ether was dried and stripped off as described previously and the residue was sublimed to give 9.35 g (60%) of $(CH_3)_3N\cdot BD_3$ which showed no appreciable B–H stretch in the IR region. This product was used later for the synthesis of B_2D_6. It should be noted that exposure of the product to air causes reappearance of the B–H IR absorption after several minutes. Evidently hydrogen reexchange with moisture in the air occurs readily. The melting point of $(CH_3)_3N \cdot BD_3$ was 93–94 °C (lit.[2] mp 94 °C).

Nöth and Beyer[5] reported a method for the generation of diborane from trimethylamine–borane involving the apparent Lewis acid displacement reaction shown in eq 2. Their report indicates the use of diethyl ether as solvent for the reaction but, in our hands, dichloromethane was preferable. (Our attempted use of ether as a solvent gave only 20–30% isolated yields of diborane.) In a typical reaction 2.10 g (27.4 mmol) of $(CH_3)_3N \cdot BD_3$ was placed in a 250-ml flask connected to a vacuum line via a Teflon valve and glass O-ring joint. The bulb was evacuated and 40 ml of dry CH_2Cl_2 along with 24.0 mmol of BF_3 condensed in at −196 °C. (Note: trimethylamine–borane is appreciably volatile at 25 °C and is rapidly pumped away if not cooled during evacuation.) The Teflon valve was then closed and the reaction mixture allowed to warm to room temperature with stirring. After 18 h the contents of the flask were fractionated through traps at −78, −130, and −196 °C until no more B_2D_6 collected in the −196 °C trap. The yield was 11.6 mmol (96.6%, based on BF_3) and the product was identified by its IR spectrum. Careful comparison of the spectra of the product and those of B_2D_5H and B_2D_6[6] showed that little if any of the former was present.

$$(CH_3)_3N \cdot BH_3 + BF_3 \cdot O(C_2H_5)_2 \xrightarrow{(C_2H_5)_2O} (CH_3)_3N \cdot BF_3 + (C_2H_5)_2O + {}^1/_2 B_2H_6 \qquad (2)$$

In order to avoid contamination of the product with BF_3 it is essential to use at least a 15 mol % excess of $(CH_3)_3N \cdot BD_3$, which may be recovered from the solid residue of the reaction by fractional sublimation. Trifluoroborane is difficult to fractionate from B_2D_6 but can be removed from BF_3/B_2D_6 mixtures by reaction with additional $(CH_3)_3N \cdot BD_3$. We have found in earlier studies[7] that about 3 mol % of $(CH_3)_3N \cdot BF_2H$ is formed in this reaction but this was considered a negligible loss of yield. Other acids such as BCl_3 and BBr_3 are unsuitable for the displacement because of halogen–hydrogen exchange.

The overall yield in the synthesis of B_2D_6 depended strongly on the extent of deuteration desired. When 90–93% deuterium sufficed, the overall yield was about 68%, but, if nearly quantitative deuteration was desired, the yield decreased to about 58% (assumes recovery of excess $(CH_3)_3N \cdot BD_3$ used in the second step).

Scale-up of the reaction appears to be limited only by the capacity of the fractionation train used to isolate the B_2D_6. Thus far the largest single reaction we have carried out produced 25 mmol of B_2D_6. A possible hazard exists during the second step if air is inadvertently admitted to the reaction vessel.

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Registry No. $(CH_3)_3N \cdot BH_3$, 75-22-9; $(CH_3)_3N \cdot BD_3$, 1538-39-2; B_2D_6, 20396-66-1.

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Gas-Phase Reaction of Ammonia with Thionyl Chloride

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The gas-phase reaction of ammonia with thionyl chloride was reported by Schenk in 1942.[3] The products of the reaction were observed to be thionyl imide, HNSO, and ammonium chloride according to the reaction

$$SOCl_2(g) + 3NH_3(g) \rightarrow HNSO(g) + 2NH_4Cl(s) \qquad (1)$$

Subsequent to this initial preparation of thionyl imide its infrared,[4] microwave,[5] ultraviolet,[6] and photoelectron spectra[7] and the photolysis of matrix-isolated[8] HNSO have been reported. In addition to the stoichiometric products shown in eq 1, SO_2 was also observed in varying amounts depending upon the experimental conditions.[4–6] The most obvious explanation for the production of SO_2 involves the reaction[9]

$$HNSO + H_2O \rightarrow SO_2 + NH_3 \qquad (2)$$

which could result from water contamination of either the reagents or the vacuum line. Kirchoff[5] noted that the relative amount of SO_2 could be decreased by carrying out the reaction at low pressures (12 Torr of NH_3 and 4 Torr of $SOCl_2$) and that the amount of SO_2 remained relatively constant with time whereas the amount of HNSO decreased. This was an indication that SO_2 was formed during the initial reaction only.

The subject of this note is that thiazyl chloride, NSCl, has been detected as one of the products in the gas-phase reaction of $SOCl_2$ with NH_3. This fact points to a side reaction that is consistent with the production of SO_2 in the initial reaction even when stringent experimental conditions have excluded moisture from the reagents and the vacuum line.

Experimental Section

A standard Pyrex vacuum line utilizing a mercury diffusion pump was employed. A liquid air trap was used to protect the vacuum line from mercury vapor and to protect the mechanical pump and the diffusion pump from ammonia and thionyl chloride vapors. Greaseless "O-ring" seal joints and "O-ring" taps were employed throughout. These joints and taps are capable of 10^{-6} Torr and were purchased from J. Young Ltd., Acton, London. The segment of the vacuum line used for preparing thionyl imide had three greaseless O-ring taps and a vacuum gauge purchased from Gallenkamp (GJ 330), London. This gauge can measure pressures 0–760 Torr with an accuracy of about 10 Torr. One of the O-ring taps had socket joints to connect the 10-cm infrared cell or the 10-cm optical cell for visible and ultraviolet spectra. The other two O-ring taps had socket joints to which the reaction vessel and the ammonia cylinder (Matheson lecture bottle) could be joined.

The reaction vessel was a 1-l. bulb fitted with two greaseless O-ring taps. The upper tap had a greaseless O-ring ball joint to fit the socket on the vacuum line and the lower tap had an O-ring seal joint to connect the tube containing thionyl chloride, $SOCl_2$ (Fluka AG). This tube was fitted with an O-ring seal joint and a few milliliters of $SOCl_2$ was introduced in the dry box. Prior to carrying out any reaction the NH_3 and $SOCl_2$ were degassed of noncondensable vapors by carrying out several freeze–thaw cycles with liquid air. In addition, the ammonia was passed over KOH pellets in a U-tube and subsequently condensed over small pieces of sodium metal to ensure dryness. Ultraviolet and visible spectra were recorded on a Perkin-Elmer 450 instrument and infrared spectra were recorded on a Perkin-Elmer 137 instrument.

Two methods were employed in the preparation of thionyl imide. In the "higher" pressure runs the $SOCl_2$ was first admitted to the 1-l. reaction bulb at a pressure of 70 Torr. Ammonia gas was then admitted in three aliquots which previous calibration experiments showed would give a final NH_3 pressure of 210 Torr. Upon release of the NH_3 gas into the 1-l. reaction bulb containing $SOCl_2$ vapor,