Fluorination of Trimethylamine–Borane Using Anhydrous Hydrogen Fluoride

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Abstract: Hydrogen fluoride reacts with trimethylamine–borane in a stepwise fashion in solvents such as methylene chloride and benzene to produce trimethylamine–monofluoro-, –difluoro-, and –trifluoroborane and trimethylammonium tetrafluoroborate. The reaction can be carried out in a glass reaction vessel and monitored by proton nmr. ^{11}B and ^{19}F nmr spectra of the products are presented and discussed.

The reactions of hydrohalic acids with amine–boranes to form partially chlorinated, brominated, and iodinated derivatives are well known;[1–8] it was therefore of interest to determine whether HF would function in the same capacity producing B-fluorinated amine–boranes. During our investigation of the HF–$(CH_3)_3NBH_3$ system, we became aware of an abstract[9] of an earlier paper[1] which incorrectly reports that trimethylamine–monofluoroborane, (CH_3)-NBH_2F, had been prepared when, in fact, the investigators clearly stated that neither $(CH_3)_3NBH_2F$ nor $(CH_3)_3NBHF_2$ was isolated during their study of the reaction of anhydrous HF with trimethylamine–borane in ether solvent. Since we are not aware of other reports on partially B-fluorinated amine–boranes, we wish to give an account here of the results of our studies on the HF–$(CH_3)_3NBH_3$ reaction carried out in various solvents.

The reaction proceeds vigorously in cold benzene with the evolution of hydrogen according to

$$(CH_3)_3NBH_3 + HF \xrightarrow[\text{ice bath}]{C_6H_6} (CH_3)_3NBH_2F + H_2$$

In the presence of excess HF, the reactions proceed stepwise to produce trimethylamine–difluoroborane, trimethylamine–trifluoroborane, and finally trimethylammonium tetrafluoroborate. The monofluoro and difluoro derivatives are new compounds which have been characterized both analytically and through multinuclei nmr spectra.

We are convinced that anhydrous HF has the potential for being a useful B-fluorinating agent, not only for amine–boranes, but very probably for a number of other borane systems. The HF–$(CH_3)_3NBH_3$ reactions were initially carried out in a stainless-steel vacuum system in Kel-F vessels, but a more satisfactory method for running these reactions outside the vacuum line and on a considerably larger scale has been developed.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Varian HA-100 instrument for fluorine (94.1 MHz) and boron (32.1 MHz) spectra and a Varian T-60 instrument for proton spectra. Infrared spectra were obtained as solutions in CH_2Cl_2 or CH_3CN using double-beam techniques on a Perkin-Elmer Model 700 spectrophotometer. Melting points were obtained in sealed 1-mm capillaries in a Thiele tube and are uncorrected. All solvents (Matheson Co.), anhydrous hydrogen fluoride (Matheson Gas Co.), and trimethylamine–borane (Callery) were used as obtained.

Analyses for boron and fluorine were carried out by standard Parr bomb techniques.[10] Nitrogen analyses were carried out by the Kjeldal method. Molecular weight determinations were done cryoscopically in dimethyl sulfoxide, which has a measured cryoscopic constant of 3.78°/*m* (lit. 3.83°).[11,12]

Preparation of $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_3$. A measured quantity of $(CH_3)_3NBH_3$ was placed in a 300-ml three-necked glass flask containing about 150 ml of benzene, which was then placed in an ice bath and stirred magnetically. One neck was fitted with a $CaCl_2$ drying tube, another neck was fitted with a stainless-steel tube connected to a lecture bottle of anhydrous hydrogen fluoride, and the third neck was fitted with a rubber septum through which a long stainless-steel syringe needle was passed. Before hydrogen fluoride addition was begun, about 0.4 ml of the solution was withdrawn and placed in an nmr tube and the proton spectrum run. The contents of the nmr tube were then transferred back into the reaction vessel. Hydrogen fluoride was slowly added directly from the lecture bottle for some period of time depending on the reaction size. Another sample was withdrawn (the nmr tube cap was provided with a small hole to relieve the pressure due to small amounts of hydrogen released when the sample warmed to the temperature of the T-60 probe (35°)), the proton nmr spectrum run, and the sample returned to the reaction vessel. For a 100-mmol reaction, the first two additions of hydrogen fluoride were 10 min in duration at a rate of about one observable bubble every 2 sec. The third and fourth additions were usually for 5 min each at the same rate and, as the desired end point of the reaction was approached, additions were carried out for shorter and shorter periods of time. Near the end, the reaction was warmed to laboratory temperature between additions to ensure complete consumption of the hydrogen fluoride in solution. This procedure was continued until the methyl resonance of trimethylamine–borane had disappeared and only the methyl resonance of the desired product, $(CH_3)_3NBH_2F$, $(CH_3)_3NBHF_2$, or $(CH_3)_3NBF_3$, was observed.

The proton nmr spectra of the reaction sequence can be seen in Figure 1. The starting material, $(CH_3)_3NBH_3$, has a methyl resonance at 2.58 ppm (Figure 1a). As HF is added, the $(CH_3)_3NBH_3$ peak can be seen to become less intense, as the peak due to the methyl resonance of $(CH_3)_3NBH_2F$ arises at 2.42 ppm (Figure 1b). Figure 1c shows the point in the addition of hydrogen fluoride at which the reaction would be stopped if the product desired were $(CH_3)_3NBH_2F$ (a slight excess of HF has been added); however, if $(CH_3)_3NBHF_2$ is desired, more hydrogen fluoride is added, the peak due to $(CH_3)_3NBH_2F$ loses intensity, and the peak due to the methyl resonance of $(CH_3)_3NBHF_2$ arises at 2.32 ppm (Figure 1d). Figure 1e shows the reaction at the stopping point if $(CH_3)_3NBHF_2$ is the desired product. If still more HF is added, the peak at 2.32

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ppm loses intensity and a peak due to the methyl resonance of $(CH_3)_3NBF_3$ arises at 2.58 ppm (not shown). If still more hydrogen fluoride is added, the nmr peak due to the methyl resonance of $(CH_3)_3NBF_3$ disappears altogether as $(CH_3)_3NH^+BF_4^-$ forms and precipitates out of the benzene solution. The sum of peak areas in each spectrum shown in Figure 1 should be equal to the sum of the areas of the peaks in each of the other traces, since the methyl concentration is constant through the reaction. However, the peak areas decrease slightly in total intensity as the reaction progresses, due to the formation of small amounts of $(CH_3)_3NH^+BF_4^-$ which precipitate from solution.

The first step in the isolation and purification of $(CH_3)_3NBH_2F$ was the filtration of the reaction mixture followed by addition of petroleum ether (30–60°) and cooling to precipitate the product. In some cases it was necessary to remove solvent *in vacuo* and then add more petroleum ether to effectively drive the $(CH_3)_3NBH_2F$ from solution. Unless precautions were taken, the product at this point commonly contained small quantities of $(CH_3)_3NBH_3$, and no suitable method was found to separate this material from $(CH_3)_3NBH_2F$. For this reason it was made a practice to add a slight excess of HF in this preparation (monitored again by ^1H nmr) to remove all the trimethylamine–borane and cause the formation of a small amount of $(CH_3)_3NBHF_2$. The monofluoro derivative is readily separated from the amine–difluoroborane by extraction with diethyl ether, in which the latter has very low solubility, followed by recovery of the solid product upon evaporation of the solvent *in vacuo*. Finally, the $(CH_3)_3NBH_2F$ was sublimed. At pressures of 1×10^{-4} mm or less, the solid transfers slowly from the room-temperature portion of the sublimation apparatus (at 25°) to a 0° cold finger. The melting point of the purified material was 117–118°.

Anal. Calcd for $C_3H_{11}BFN$: B, 11.9; F, 20.6; N, 15.4; mol wt, 90.9. Found: B, 12.0; F, 20.1; N, 15.2; mol wt, 91.0. The infrared spectrum has bands at 3020 (m), 2960 (m), 2375 (s), 2300 (s), 2225 (sh), 2100 (sh), 1485 (s), 1460 (s), 1410 (w), 1220 (s), 1180 (vs), 1140 (m), 1130 (m), 1115 (m), 1100 (m), 1010 (vs), 970 (s), 840 (vs), and 670 (m) cm^{-1}. The methyl proton resonance occurs at δ 2.42. The boron-11 resonance of $(CH_3)_3NBH_2F$ in methylene chloride solution occurs at δ 13.2 ppm with respect to external trimethyl borate. The observed coupling constants are J_{BF} = 88.5 and J_{BH} = 113 Hz. The fluorine-19 resonance of the same compound occurs at δ 202 ppm with respect to external trichlorofluoromethane. The coupling constants are J_{FB} = 87.2 and J_{FH} = 43.6 Hz. The analysis of the spectra is presented in Results and Discussion.

In the purification of $(CH_3)_3NBHF_2$, the reaction mixture was filtered and the product precipitated with petroleum ether as previously described. The precipitate was then washed with diethyl ether and sublimed from 90° to a 0° cold finger. Difficulties in separating the trimethylamine–difluoro- and –trifluoroboranes dictated that the addition of HF in the preparation of the former compound be stopped just short of a full stoichiometric amount (while some $(CH_3)_3NBH_2F$ was still detectable in the ^1H nmr). The sublimation was then carried out in two steps: first, the small amount of $(CH_3)_3NBH_2F$ was removed at 25° and then, when this been had completed, the sublimer was heated to 90° to recover the $(CH_3)_3NBHF_2$. The melting point of the product obtained in this manner was 124–125°.

Anal. Calcd for $C_3H_{10}BF_2N$: B, 10.0; F, 34.6; N, 12.9; mol wt, 108.9. Found: B, 9.9; F, 34.3; N, 12.7; mol wt, 110.9. The infrared spectrum has bands at 3050 (w), 3000 (w), 2960 (w), 2420 (s), 2320 (m), 2270 (w), 2230 (w), 2190 (vw), 1485 (s), 1465 (s), 1420 (w), 1270 (shw), 1250 (m), 1190 (s), 1170 (vs), 1135 (vs), 1090 (vs), 1000 (vs), and 830 (vs) cm^{-1}. The methyl proton resonance occurs at δ 2.32. The boron-11 resonance is observed at δ 14.2 ppm with respect to external trimethyl borate, and the observed coupling constants are J_{BF} = 73.2 and J_{BH} = 146 Hz. The fluorine-19 resonance of $(CH_3)_3NBHF_2$ occurs at δ 164 ppm with respect to external CCl_3F, and the coupling constants are J_{FB} = 70 and J_{FH} = 70 Hz. The analysis of the spectra is presented in Results and Discussion. Typical reactions on a 100-mmol scale had yields of 80–90% based on trimethylamine–borane.

Sublimation was also used to separate $(CH_3)_3NBF_3$ from $(CH_3)_3NH^+BF_4^-$. The former will move to a 0° cold finger *in vacuo* at 80°, while the latter is essentially nonvolatile at that temperature. The infrared, ^1H, ^{19}F, and ^{11}B nmr spectra of $(CH_3)_3NBF_3$ prepared by this method were the same as those from a sample prepared by the method of Angelici.[13] The infrared, ^1H, and ^{11}B nmr spectra of $(CH_3)_3NH^+BF_4^-$ were the same as those of a sample prepared by the method of NuHall,[14] confirming the preparation of $(CH_3)_3NBF_3$ and $(CH_3)_3NH^+BF_4^-$.

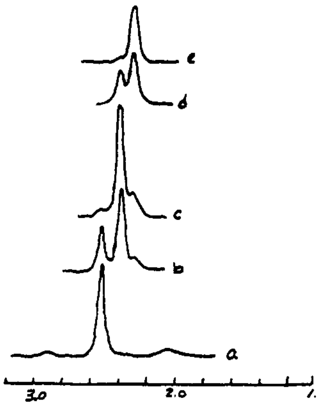

Figure 1. ^1H nmr of the HF + $(CH_3)_3NBH_3$ reaction sequence.

The solvent used in the reaction procedure described previously seems to play an important role in the quality, quantity, and ease of preparation of the products described. We have found that, of the solvents used, the most effective for this reaction are benzene and methylene chloride. In benzene or methylene chloride the reaction proceeds at a rapid but safe rate, the starting material and products (except $(CH_3)_3NH^+BF_4^-$) are soluble, and ^1H nmr resonance of the solvents does not interfere with the methyl resonance of the products. Methylene chloride has the added advantage that it has a relatively lower freezing point, allowing the reaction to be run at a lower temperature. The reaction seems to give best yields when carried out at −10 to −20°. Benzene has the advantage that the chemical shifts of the product methyl resonances are more widely separated than is the case in CH_2Cl_2, allowing for easier determination of the end point of the reaction. We have also tried toluene, diethyl ether, 1,2-dimethoxyethane, bis(2-methoxyethyl) ether, and 1,2-bis(2-methoxyethoxy)ethane, all of which were less satisfactory for reasons such as overlap of amine–borane methyl resonances with solvent resonances or substantial attack of the glass reaction vessel by the HF. Only very slight etching was observed when C_6H_6 and CH_2Cl_2 were used as solvents for the reaction.

Initially, the HF–$(CH_3)_3NBH_3$ system was studied using a metal vacuum line with Kel-F reaction tubes similar to those described by Shriver.[15] Quantities of HF were measured by weight difference of a small storage tube before and after vapor transfer of an arbitrary amount into the metal vacuum line. This method was less then satisfactory because the reactions were very difficult to control. Typical reactions set up to contain equivalent quantities of HF and $(CH_3)_3NBH_3$ produced complex mixtures of fluorinated products, presenting a very difficult separation problem. Therefore, this approach was abandoned in favor of the technique described previously.

Results and Discussion

The fluorination of trimethylamine–borane with HF under the conditions outlined produces consecutively $(CH_3)_3NBH_2F$, $(CH_3)_3NBHF_2$, $(CH_3)_3NBF_3$, and finally $(CH_3)_3NH^+BF_4^-$. The preparative method is simpler and less trying than previous methods employing metal vacuum lines for handling hydrogen fluoride, and reactions of a considerably larger scale can be readily carried out. The monofluoro and difluoro derivatives are reasonably air-stable compounds, generally intermediate in properties between $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$. The suggestion has been made that partially fluorinated amine–boranes such as $(CH_3)_3NBH_2F$ may spontaneously disproportionate to trimethylamine–borane and trimethyl-

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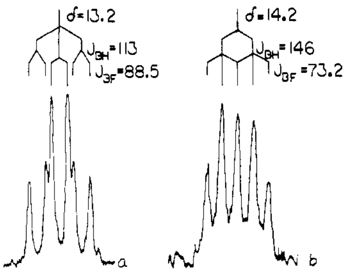

Figure 2. ^{11}B nmr spectra of $(CH_3)_3NBH_2F$ (a) and $(CH_3)_3NBHF_2$(b).

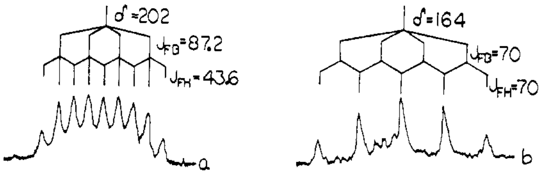

Figure 3. ^{19}F nmr spectra of $(CH_3)_3NBH_2F$ (a) and $(CH_3)_3NBHF_2$ (b).

amine–trifluoroborane.[1] We have been aware of this possibility but have found no substantial proof that such reactions occur in any of the solvents at the temperatures employed in this study. It is possible that disproportionation could occur under other conditions, but it has not detectably hindered the isolation of the partially fluorinated derivatives.[15a]

The ^{11}B and ^{19}F nmr spectra confirm the stoichiometries indicated by the analytical results. The ^{11}B spectrum of $(CH_3)_3NBH_2F$ (Figure 2a) consists of a sextet with component peak areas in the ratios of 1:1:2:2:1:1 which can be interpreted as triplet (J = 113 Hz), each component of which is further split into a doublet (J = 88.5 Hz). The ^{19}F spectrum of the same sample (Figure 3a) consists of a nonet with areas 1:2:2:2:2:2:2:2:1, most probably arising from a 1:1:1:1 quartet due to spin coupling of the ^{11}B nucleus ($I(^{11}B) = {}^3/_2$) with the fluorine (J_{FB} = 87.2 Hz), each member of which is split into a 1:2:1 triplet (J = 43.6 Hz). The near equality of the doublet coupling constant in the ^{11}B spectrum and the quartet splitting in the ^{19}F spectrum supports the assignment of the former doublet splitting to a single fluorine (*i.e.*, J_{BF} = 88.5 Hz). Then the triplet splitting in the ^{11}B and ^{19}F spectra is indicative of two protons, confirming the $(CH_3)_3NBH_2F$ stoichiometry.

The ^{11}B nmr spectrum of trimethylamine–difluoroborane (Figure 2b) shows a quintet with peak areas in the ratio of 1:2:2:2:1, which we believe arises from a doublet (J = 146.4 Hz) in which each member shows triplet multiplicity (J = 73.2 Hz). Evidence for the splitting assignments comes from the ^{19}F spectrum (Figure 3b), which also consists of a 1:2:2:2:1 quintet, arising in this case from a quartet with equal peak areas (J = 70 Hz) due to coupling with the ^{11}B nucleus, each member of which is split into a doublet (J = 70 Hz). The quartet in the ^{19}F spectrum is attributed to F–B coupling. The near equality of the ^{19}F B–F splitting and ^{11}B triplet splitting (J_{BF} = 73.2 Hz $\cong J_{FB}$) supports the assignment of the triplet splitting to two fluorines. The doublet splitting in the ^{19}F and ^{11}B spectra is indicative of coupling with a single proton, confirming the stoichiometry, $(CH_3)_3NBHF_2$.

It is of some interest to note that for $(CH_3)_3NBH_2F$, $J_{BF} \sim 2J_{FH}$, and for the difluoro derivative $J_{BF} \cong J_{FH}$. Such coupling constant relationships are not likely to be purely coincidental, since similar cases are fairly common in the literature describing other amine–boranes,[16] and it has been observed that, when two or more spin–spin couplings involve the same atom, the coupling constants are frequently integral multiples of one another.[16] The reasons for such behavior are not yet clear, and further study would seem to be indicated.

A matter of some interest deals with the influence of added fluorines on the bonding between the amine and the borane segments of the adduct. While it is recognized that thermodynamic studies will be required to define the coordinate bond strengths in a rigorous way, some preliminary insights may be drawn from the nmr data. Assuming no exchange processes are active,[17] the relative chemical shifts of the methyl protons on the free amine and the coordinated amine have been taken as a rough measure of the coordinate bond strength of the adduct. The greater the change in methyl proton shift (toward lower field) upon coordination, the stronger the indicated donor–acceptor strength in a given series of compounds.[18,19] On this basis our results suggest that the relative acid strengths toward trimethylamine are

$$BH_3 \cong BF_3 > BH_2F > BHF_2$$

The approximate equality of BH_3 and BF_3 acid strength toward trimethylamine is in agreement with known heats of dissociation for the adducts in nitrobenzene.[19] The indication that both BH_2F and BHF_2 are weaker acceptors than BH_3 and BF_3 is surprising and not readily explained at this time.

Neither the ^{11}B or ^{19}F chemical shift data (Experimental Section) are particularly informative in the matter of adduct stabilities. Although a comparison of ^{11}B shifts among analogous compounds has been used to determine relative donor–acceptor strengths,[20] the absence of a satisfactory ^{11}B chemical shift theory suggests that such practices should be used with caution. Thus it is perhaps not surprising that the ^{11}B chemical shifts of the fluorinated trimethylamine–boranes can be readily correlated neither with inductive effects nor with the tentative order of adduct strengths obtained from ^1H nmr data. The ^{19}F shifts, on the other hand, do seem to be understandable in terms of the inductive influence of the group to which fluorine is bound. Thus as the number of fluorines on the molecular adduct increases, the ^{19}F shift moves to lower field presumably as the diamagnetic shielding of the fluorine nucleus decreases.

(15a) NOTE ADDED IN PROOF. After sitting in a screw cap vial on the shelf for 6 months, a sample of $(CH_3)_3NBHF_2$ was found to be wet with H_2O and the ^1H nmr showed the presence of ~10% $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$. Under the same conditions no change was noted for $(CH_3)_3NBH_2F$.

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Electronic Structure of Oxo-Bridged Iron(III) Dimers

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Abstract: Magnetic susceptibility results and extensive electronic, infrared, and Mössbauer spectral data are presented for $enH_2[(FeHEDTA)_2O]\cdot 6H_2O$, $Na_4[(FeEDTA)_2O]\cdot 12H_2O$, $FeHEDTA\cdot H_2O$, and $NaFeEDTA\cdot 3H_2O$ (HEDTA = *N*-hydroxoethylethylenediaminetriacetate, EDTA = ethylenediaminetetraacetate, and enH_2^{2+} = ethylenediammonium cation). The magnetic and spectral data establish an electronic structural model for the oxo-bridged dimers in which pairs of $S = {}^5/_2$ Fe(III) ions interact antiferromagnetically, with $J \simeq -95\ cm^{-1}$. The oxo-bridged dimers show marked intensity enhancement of the one-center Fe(III) ligand-field bands. There are also several uv bands which are interpreted as arising from simultaneous electronic excitations of Fe(III) pairs. A simple high-spin ligand-field model modified by spin–spin interaction is judged to be considerably more appropriate than the Dunitz–Orgel molecular orbital approach as a vehicle for describing oxo-bridged Fe(III) dimers.

There has recently been considerable interest in oxo-bridged iron(III) dimeric systems. Several complexes of this type have been synthesized and characterized by magnetic susceptibility measurements and Mössbauer spectra.[4–8] Infrared frequencies associated with the oxo-bridging unit have been identified,[4,9] and in certain cases X-ray structures have been obtained.[10–13] Particular importance can be attached to these model complexes in view of the presence of dimeric and polymeric species in the aqueous chemistry of Fe(III) and the probable occurrence of dimeric Fe(III) species in biochemical systems such as the protein hemerythrin.[14] Dimeric ferriporphyrins containing the Fe–O–Fe structural unit have also been characterized.[13,15,16]

In order to formulate a useful electronic structural model for oxo-bridged Fe(III) complexes, we have chosen to study in considerable detail the spectral and magnetic properties of $enH_2[(FeHEDTA)_2O]\cdot 6H_2O$.[17,18] This choice is felicitous because the compound is of known structure[10] and the HEDTA ligand itself does not interfere significantly in the spectral regions of interest. In addition, the closely related complex $Na_4[(FeEDTA)_2O]\cdot 12H_2O$ is available for comparative study, as are the monomers $NaFeEDTA\cdot 3H_2O$ and $FeHEDTA\cdot 1.5H_2O$. The latter complexes provide a reference point for identifying the electronic structural features that are peculiar to the Fe–O–Fe bridging unit.

The present paper reports magnetic and spectroscopic properties over a wide temperature range for $enH_2[(FeHEDTA)_2O]\cdot 6H_2O$ and related compounds. The results are discussed in terms of a ligand-field (LF) model featuring spin–spin interaction of pairs of high-spin Fe(III) ions. This spin–spin-modified ligand-field description is shown to be superior to the Dunitz–Orgel molecular orbital model for these particular oxo-bridged systems.

Experimental Section

$enH_2[(FeHEDTA)_2O]\cdot 6H_2O$, $Na_4[(FeEDTA)_2O]\cdot 12H_2O$, and $NaFeEDTA\cdot 3H_2O$ were prepared as previously described.[17,19] Solutions of FeHEDTA were prepared by adding 3 equiv of NaOH to solutions of equimolar amounts of ferric chloride and the free ligand.

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