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The Synthesis and Characterization of Methylaminobis(difluorophosphine)–Borane(3), –Bis(borane(3)), and –Triborane(7) Complexes

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The reactions of methylaminobis(difluorophosphine), $F_2PN(CH_3)PF_2$ with diborane(6), borane carbonyl and tetraborane(10) produce the coordination complexes $F_2PN(CH_3)PF_2{\cdot}BH_3$, $F_2PN(CH_3)PF_2{\cdot}2BH_3$ and $F_2PN(CH_3)PF_2{\cdot}B_3H_7$. The new complexes have been characterized by mass, infrared, and NMR spectroscopic techniques. The relative stability of these complexes is discussed with relation to coordination complexes of other related $F_2P{-}X{-}PF_2$ ligands.

Several potentially monodentate, bidentate, and tridentate fluorophosphine ligands of the general type F_2PXPF_2 have been prepared,[1-7] and their coordination chemistry has been partially explored.[2-4,6-12] In the course of investigating the multifunctional coordination properties of F_2PXPF_2 ligands, several investigators have attempted to correlate the variety of steric, inductive, and π-overlap contributions which may be operative and decisive in determining the hapticity of the ligands toward various acceptor sites.[2-4,10,11] An apparently self-consistent bonding model has slowly evolved but new ligands and coordination complexes need to be studied before a complete understanding of the coordination behavior is available. One interesting, potentially tridentate ligand whose coordination properties have been studied little is methylaminobis(difluorophosphine), $F_2PN(CH_3)PF_2$.[5] Johnson and Nixon[8] have reported that this Lewis base can function as a bis ligand toward a single zerovalent metal center. More recently, King and co-workers[12] have shown that the ligand can also act as a biligate ligand toward two metal centers. As part of a study of synthetic routes to small ring systems containing F_2PXPF_2 moieties,[13] we have investigated the coordination chemistry of the same potentially tridentate ligand. This report describes the synthesis and characterization of the mono(borane(3)) complex $F_2PN(CH_3)PF_2{\cdot}BH_3$ (**1**), the bis(borane(3)) complex $F_2PN(CH_3)PF_2{\cdot}2BH_3$ (**2**), and the triborane(7) complex $F_2PN(CH_3)PF_2{\cdot}B_3H_7$ (**3**). A reaction of the ligand with BF_3 is also described. The properties of the new coordination complexes are discussed in the context of a previously proposed bonding model described by Parry and co-workers.[3,4,11]

Experimental Section

General Information. Standard high-vacuum synthetic techniques were used for the manipulation of the volatile compounds. Mass spectra were recorded on a Du Pont Model 21-491 spectrometer operating at 70 eV. Infrared spectra were recorded on a Perkin-Elmer Model 625 infrared spectrometer using a cell fitted with CsI windows. The NMR spectra were recorded on a Varian XL-100 instrument operating at 100.0 MHz (^{1}H), 32.1 MHz (^{11}B), and 94.1 MHz (^{19}F) in both the CW and pulse modes. A Nicolet TT-100 data system was used to drive the pulse experiments. Samples were contained in sealed 5-mm tubes rigidly placed in a 12-mm tube containing a deuterated lock sample and standard: $BF_3O(C_2H_5)_2$, ^{11}B; $CFCl_3$, ^{19}F; $(CH_3)_4Si$, ^{1}H.

Materials. Methylaminobis(difluorophosphine) was prepared by fluorination of the chloro analogue with SbF_3.[5] Borane carbonyl was prepared by the method of Carter[14] and tetraborane(10) was prepared by hot–cold tube pyrolysis of B_2H_6.[15]

Preparation of $F_2PN(CH_3)PF_2{\cdot}BH_3$. A 4.0-mmol sample of the diphosphine ligand was combined with either 4.0 mmol of BH_3CO or 2.0 mmol of B_2H_6 in a 500-mL flask. The flask was closed off by a stopcock and then held at 0 °C. The reaction was complete in less than 1 h and the CO could be quantitatively recovered using a Toepler pump system. The volatile products were vacuum distilled through cold baths: −196 °C for B_2H_6 and BH_3CO, −126 °C for $F_2PN(CH_3)PF_2$, −78 °C for $F_2PN(CH_3)PF_2{\cdot}BH_3$. The yield of the mono(borane) complex was 100%.

Preparation of $F_2PN(CH_3)PF_2{\cdot}2BH_3$. A 4.0-mmol sample of the diphosphine ligand was treated successively with 1.0-mmol samples of BH_3CO in a 300-mL flask. After each addition the stopcock of the flask was closed, and the flask warmed to −35 °C. After several hours the flask was frozen at −196 °C and the carbon monoxide was removed into a Toepler pump system. Addition of about 10 mmol of BH_3CO was required to recover 8 mmol of CO. The final volatile products were distilled through traps cooled to −196, −126, and −78 °C. The bis(borane(3)) complex was retained at −78 °C. The yield is 90–95% based on the ligand initially present. A very small amount of the mono(borane(3)) complex always contaminates the sample, and the carbon monoxide liberated must be removed during the course of the reaction or base displacement will not proceed toward completion.

Preparation of $F_2PN(CH_3)PF_2{\cdot}B_3H_7$. A 2.5-mmol sample of diphosphine ligand was combined with 2.5 mmol of B_4H_{10} in a 300-mL flask. The flask was then warmed to 23 °C for 1 h. The volatile products were distilled through −196, −126, −78, and −45 °C baths. The triborane(7) complex was retained at −45 °C with a yield of 60–70%. Diborane(6) was quantitatively recovered at −196 °C.

Reaction of $F_2PN(CH_3)PF_2$ with BF_3. A 2.8-mmol sample of diphosphine ligand was combined with a 3.5-mmol sample of BF_3 in a sealed NMR tube. The ^{11}B and ^{19}F NMR spectra were recorded over the temperature range of −40 to 0 °C. No evidence for adduct formation was obtained from the ^{11}B or ^{19}F chemical shift data. A tensimetric titration was performed; a 1.5-mmol sample of the ligand was condensed into a standard tensimeter bulb along with 5 mL of dried, degassed CH_2Cl_2. Samples of BF_3 were added at −45 and 0 °C in 0.2-mmol portions until 3.0 mmol of BF_3 was present. Complex formation was not detected from the vapor-pressure behavior of the reaction mixture.

Properties of Coordination Complexes

(1) $F_2PN(CH_3)PF_2{\cdot}BH_3$. Vapor-pressure data are summarized by the equation $\log P(\mathrm{mm}) = -1886.8/T + 8.075$ over the temperature range −30.4 to +17.0 °C. Trouton constant, 23.6 cal deg^{-1} mol^{-1}; bp 92.0 °C (extrapolated). Molecular weight by vapor density: obsd 181.5; calcd 180.83. Mass spectrum [*m*/*e*, assignment, relative intensity]: 181–178, $F_2PN(CH_3)PF_2BH_{3-x}{}^+$, total 6; 167, $F_2PN(CH_3)PF_2{}^+$, 32; 152, $F_2PNPF_2{}^+$, 23; 148, $F_2PN(CH_3)PF^+$, 17; 133, F_2PNPF^+, 1; 114, $FPNPF^+$, 1; 98–95, $F_2PN(CH_{3-x})^+$, $PNPF^+$, total 7; 79–76, $FPNCH_{3-x}{}^+$, total 125; 69, F_2P^+, 100; 50, PF^+, 23; 45, PN^+, 14. Infrared spectrum (cm^{-1}) (gas): 2965 (m), 2910 (w), 2431 (s), 2335 (m), 1211 (m), 1100 (s), 1055 (s), 936 (s), 894 (s), 825 (vs), 732 (s), 677 (m), 590 (sh, m), 573 (m), 484 (s), 441 (m), and 373 (s). NMR spectra (neat) −40 °C: ^{1}H, δ 3.07 ppm (complex multiplet), δ 0.87 ppm (J_{BH} = 104 Hz); ^{11}B, δ 43.7 ppm (J_{BH} = 101 Hz, J_{BP} = 57 Hz); ^{19}F, δ 77.1 and 73.2 ppm ($J_{FP+FP'}$(coord) = 1215 Hz, J_{FPBH} = 16.8 Hz, $J_{FPNP'}$ = 7 Hz, $J_{FPNP'F'}$ = 4 Hz, $J_{FP+FP'}$(uncoord) = 1263 Hz). The complex is stable toward dissociation and decomposition for at least one week at 25 °C under vacuum.

(2) $F_2PN(CH_3)PF_2{\cdot}2BH_3$. Vapor pressure and gas density data were not collected for this compound because of its decomposition rate at 25 °C. Mass spectrum [*m*/*e*, assignment, relative intensity]: 195–190, $F_2P(BH_{3-x})N(CH_3)PF_2(BH_{3-y})^+$, total 2; 181–178, $F_2PN(CH_3)PF_2(BH_{3-y})^+$, total 5; 167, $F_2PN(CH_3)PF_2{}^+$, 18; 152, $F_2PNPF_2{}^+$, 12; 148, $F_2PN(CH_3)PF^+$, 10; 133, F_2PNPF^+, 2; 129, $FPN(CH_3)PF^+$, 2; 114, $FPNPF^+$, 1; 110, $FPN(CH_3)P^+$, 1; 98–95, $F_2PN(CH_{3-x})^+$, $PNPF^+$, total 14; 79–76, $FPNCH_{3-x}{}^+$, total 135; 69, F_2P^+, 100; 50, PF^+, 20; 45, PN^+, 12. Infrared spectrum (cm^{-1}) (gas): 2965 (m), 2910 (w), 2838 (vw), 2429 (s), 2372 (w), 1217 (m), 1097 (s), 1052 (s), 928 (vs), 835 (vs), 809 (s), 722 (m), 690 (m), 612 (sh, m), 572 (m), 498 (m), 378 (m). NMR spectra (neat) −10 °C: ^{1}H, δ 3.33, 1.05 ppm (J_{BH} = 103 Hz); ^{11}B, δ 43.3 ppm (J_{BH} = 105 Hz, J_{BP} = 53 Hz); ^{19}F, δ 66.3 ppm (J_{FP} = 1241 Hz, J_{FPBH} = 18 Hz). The complex decomposes irreversibly at 25 °C forming B_2H_6, ligand, and a unidentified yellow oil.

(3) $F_2PN(CH_3)PF_2{\cdot}B_3H_7$. Vapor pressure and gas density data were not collected for this compound due to its low volatility at 25 °C and its decomposition above 25 °C. Mass spectrum [*m*/*e*, assignment, relative intensity]: 207–204, $F_2PN(CH_3)PF_2B_3H_{7-x}{}^+$, total 1; 193–190, $F_2PN(CH_3)PF_2B_2H_{4-x}{}^+$, total 15; 181–178, $F_2PN(CH_3)PF_2BH_{3-x}{}^+$, 2; 167, $F_2PN(CH_3)PF_2{}^+$, 60; 152, $F_2PNPF_2{}^+$, 22; 148, $F_2PN(CH_3)PF^+$, 19; 133, F_2PNPF^+, 7; 129, $FPN(CH_3)PF^+$, 1; 98–95, $F_2PN(CH_{3-x})^+$, $PNPF^+$, total 31; 79–76, $FPNCH_{3-x}{}^+$, total 157; 69, $PF_2{}^+$, 100; 50, PF^+, 23; 45, PN^+, 12; 40–33, $B_3H_{7-x}{}^+$, total 29. Infrared spectrum (cm^{-1}) (gas): 2957 (m), 2897 (w), 2810 (vw), 2561 (m), 2480 (m), 1600 (br, w), 1473 (br, m), 1402 (br, m), 1193 (m), 1097 (s), 887 (vs), 843 (s), 810 (vs), 671 (m), 550 (m), 473 (s), 421 (m). NMR spectra (neat) −10 °C: ^{1}H, δ 3.3 ppm; ^{11}B, $\delta_{2,3}$ 98.6 ppm, δ_1 136.4 ppm ($J_{B_{2,3}H}$ = 112 Hz, $J_{BH} \simeq J_{BP}$ = 101 Hz); ^{19}F, δ 72.9 ppm (J_{PF} = 1285 Hz), δ 80.5 ppm (J_{PF} = 1191 Hz). The complex decomposes irreversibly at 25 °C to B_2H_6, ligand, and several unidentified compounds. The decomposition is qualitatively less rapid than the decomposition of **2**.

The NMR splitting patterns for each of the above complexes are described in the text.

Competitive Base-Displacement Reactions

The base-displacement reaction

$$F_3P{\cdot}BH_3 + F_2PN(CH_3)PF_2 \xrightleftharpoons{CFCl_3} F_3P + F_2PN(CH_3)PF_2{\cdot}BH_3$$

was studied in both directions. The reactants on the left or right were initially combined in a 1:1 ratio, sealed in NMR tubes, and thermostated for up to one 1 week. The product mixtures were analyzed by ^{19}F NMR. The resulting peak areas indicate that the reaction lies approximately 87% to the right. A reliable equilibrium constant was not obtained due in part to the lack of solubility data for the reactants in $CFCl_3$ and the slow approach to equilibrium from the left side.

Results and Discussion

The combination of B_2H_6 or $BH_3{\cdot}CO$ and the potentially tridentate ligand $F_2PN(CH_3)PF_2$ at 0 °C produces the stable mono(borane(3)) complex **1** according to the equation

$$^1/_2B_2H_6 \text{ or } BH_3{\cdot}CO + F_2PN(CH_3)PF_2 \xrightarrow{0\,°C} \underset{\mathbf{1}}{F_2PN(CH_3)PF_2{\cdot}BH_3}$$

Base-displacement studies show that the same reaction occurs when $F_3P{\cdot}BH_3$ is the borane source and an equilibrium is established which favors the formation of $F_2PN(CH_3)PF_2{\cdot}BH_3$. Under the conditions explored here, it is not possible to add a second BH_3 group when the borane source is B_2H_6. A bis(borane(3)) complex, **2**, however, is obtained when excess borane carbonyl is used.

$$2BH_3{\cdot}CO + F_2PN(CH_3)PF_2 \xrightarrow{-35\ ^\circ C} F_2PN(CH_3)PF_2{\cdot}2BH_3$$

2

Complex **2** is considerably less stable to decomposition than is complex **1**, and the decomposition of **2** is complex and irreversible. The combination of B_4H_{10} and the ligand under the conditions employed here produces only a monoligate triborane(7) complex **3** according to the equation

$$B_4H_{10} + F_2PN(CH_3)PF_2 \xrightarrow{25\ ^\circ C} F_2PN(CH_3)PF_2{\cdot}B_3H_7 + {}^1/_2B_2H_6$$

3

The formation of a bis(triborane(7)) complex or a mixed mono(borane(3))-mono(triborane(7)) complex has not yet been detected. Likewise evidence for the formation of a BF_3 complex is not found in the temperature range −40 to 0 °C.

The molecular structures of only two compounds directly related to **1**–**3** have been determined. Morris and Nordman[16a] studied the crystal structure of $(CH_3)_2NPF_2$ and found that the molecule possesses mirror symmetry with a planar C–N–P skeleton and short P–N bond distance 1.628 Å. Further, La Prade and Nordman[16b] studied the crystal structure of the coordination complex $(CH_3)NPF_2{\cdot}B_4H_8$ and found that the structure contains a B–P coordinate bond. Structural analogy, mass spectra, infrared frequencies, and NMR spectra now provide a sound structural assignment for **1**–**3**. The observation of a parent ion in the mass spectra of **1**–**3** establishes the proposed composition for each complex. Infrared spectra are similar to the spectra obtained from related complexes: $(CH_3)_2NPF_2{\cdot}BH_3$,[17] $(CH_3)_2NPF_2{\cdot}B_3H_7$,[17] $F_2PN(CH_3)N(CH_3)PF_2{\cdot}BH_3$, and $F_2PN(CH_3)N(CH_3)PF_2{\cdot}2BH_3$.[6] The absorption which has been tentatively assigned to the B–P stretching mode in this series appears to be relatively constant in the range 586–542 cm^{-1}; the absorptions for **1** (573 cm^{-1}), **2** (572 cm^{-1}), and **3** (550 cm^{-1}) fall in this range.

The NMR spectra for **1**–**3** are complex. Nixon[5] has studied the ^{19}F and ^{31}P spectra of the uncoordinated ligand and the spectra are consistent with the assignment of an $XX'AA'X''X'''$ spin system. The parameters obtained from this work include $\delta(^{19}F)$ 74.6 ppm (upfield of $CFCl_3$) and J_{PF} = 1264 Hz. In the new coordination complexes, **1**–**3**, some of the spectral complexity is retained. The ^{19}F NMR spectrum of **1** consists of a pair of widely spaced doublets. The lower field doublet δ 73.2 ppm, $J_{PF+PF'}$ = 1263 Hz, retains a second-order coupling pattern, and it corresponds to the uncoordinated F_2P segment (Figure 1). The higher field pair, δ 77.1 ppm, corresponds to the complexed PF_2 group with $J_{PF+PF'}$ = 1215 Hz. Expansion of one member of the latter doublet reveals fine structure which can be simulated by assuming J_{FPBH} = 16.8 Hz, $J_{FPNP'}$ = 7 Hz, and $J_{FPNP'F''}$ = 4 Hz. The proton NMR spectrum consists of a low field complex multiplet, δ −3.07 ppm, which has not been simulated successfully and a high field quartet, δ −0.87 ppm, which is assigned to the protons of the BH_3 group, J_{BH} = 104 Hz. The ^{11}B NMR spectrum further supports the presence of a B–P coordinate bond; the spectrum consists of a resonance at 43.7 ppm (upfield from $BF_3{\cdot}O(C_2H_5)_2$). This peak is split into a quartet, J_{BH} = 101 Hz, each member of which is further split into a doublet, J_{BP} = 57 Hz.

It has been pointed out by Rudolph and Schultz[18] that considerable care must be employed when comparing Lewis acid–base coordinate bond strengths with experimental parameters such as J_{BP} or ν_{BP}. This is appropriately demonstrated by comparing stability, coupling constant, and B–P stretching frequencies of **1** and $F_3P{\cdot}BH_3$. Competition reactions clearly indicate that **1** is a stronger complex than $F_3P{\cdot}BH_3$. This is in line with the coupling constants (**1**, 57 Hz; $F_3P{\cdot}BH_3$, 39 Hz) but opposed to the B–P stretching fundamentals (**1**, 573 cm^{-1}; $F_3P{\cdot}BH_3$, 609 cm^{-1}).[19]

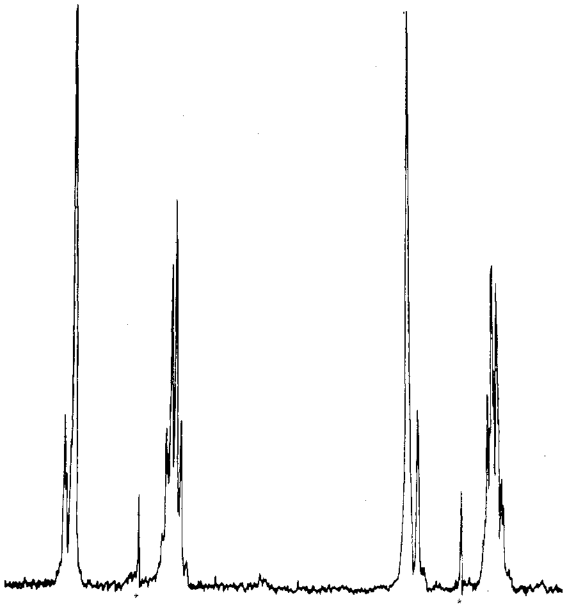

Figure 1. ^{19}F NMR spectrum of $F_2PN(CH_3)PF_2{\cdot}BH_3$ at −40 °C. The asterisk indicates some free ligand impurity.

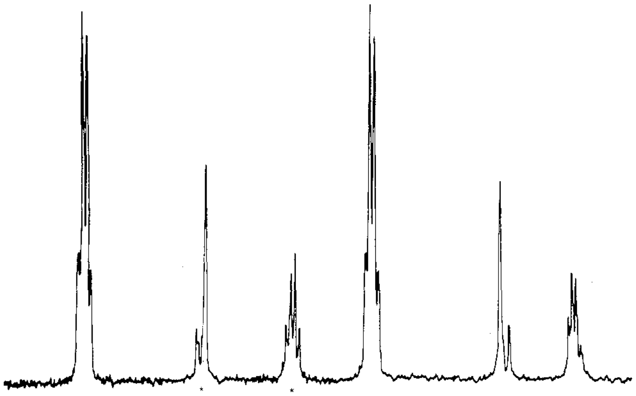

Figure 2. ^{19}F NMR spectrum of a mixture of $F_2PN(CH_3)PF_2{\cdot}BH_3$ (indicated by an asterisk) and $F_2PN(CH_3)PF_2{\cdot}2BH_3$ at −40 °C.

Figure 2 shows a ^{19}F NMR spectrum containing both the mono(borane(3)) (**1**) and bis(borane(3)) (**2**) complexes. Complex **2** shows a widely spaced doublet, δ 66.3 ppm (J_{PF} = 1241 Hz), each member of which is split into a quartet J_{FPBH} = 17.7 Hz. No further coupling has been resolved. The ^{11}B NMR spectrum consists of a resonance at δ 43.3 ppm (J_{BH} = 105 Hz and J_{BP} = 53 Hz). These J_{BP} coupling constants are comparable to that observed for $(CH_3)_2NPF_2BH_3$ J_{BP} = 79 Hz.[17] Where there are comparable data, the correspondence of **1** and **2** with $F_2PN(CH_3)N(CH_3)PF_2{\cdot}BH_3$ and $F_2PN(CH_3)N(CH_3)PF_2{\cdot}2BH_3$ is also very good.

The ^{19}F NMR spectrum of **3** shows a pair of widely spaced doublets centered at δ 72.9 ppm (J_{PF} = 1285 Hz) and δ 80.5 ppm (J_{PF} = 1191 Hz). The former corresponds to the uncoordinated PF_2 group and the latter to the B_3H_7-coordinated PF_2 group. The uncoordinated PF_2 retains a second order coupling pattern while the coordinated PF_2 shows no well-resolved fine structure. The ^{11}B NMR spectrum is similar to spectra of $F_2XP{\cdot}B_3H_7$ complexes.[20,21] There is a low-field

Table I. Summary of $F_2PXPF_2 \cdot BH_3$ Coordination Complexes

Ligand	BH_3	$(BH_3)_2$	BF_3
F_2PPF_2	$+^{a,11}$	$+^{9}$	–
F_2POPF_2	$+^{2}$	$-^{b,2}$	–
$F_2PCH_2PF_2$	$+^{3}$	$+^{3}$	–
$F_2PCH_2CH_2PF_2$	$+^{7}$	$+^{7}$	Unknown
F_2PSPF_2	$+^{3,4}$	$-^{3,4}$	–
$F_2PC(CF_3)_2OPF_2$	$+^{3}$	$-^{3}$	–
$F_2PN(CH_3)N(CH_3)PF_2$	$+^{6}$	$+^{6}$	+
$F_2PN(CH_3)PF_2$	$+^{c}$	$+^{c}$	–
$F_2PN(CH_3)_2$	$+^{17}$	$-^{17}$	$+^{17}$

[a] + implies a complex has been characterized. [b] – implies a complex has not been detected. [c] This study.

triplet at 98.6 ppm ($J_{B_{2,3}H} = 112$ Hz) and a high-field multiplet resembling a quartet δ 136.4 ppm ($J_{BH} \simeq J_{BP} = 101$ Hz).

From the characterization data the molecular connectivities of **1**–**3** are established. The aminofluorophosphine in each case binds to the borane acid through the phosphorus atom(s). Furthermore, it is definitely established that $F_2PN(CH_3)PF_2$ can act as a bidentate ligand toward two BH_3 groups and that the nitrogen donor site is not susceptible to coordination by BH_3 or BF_3.

It is now appropriate to place this coordination chemistry in perspective with the known coordination properties of other tetrafluorodiphosphines, $F'_2P'XPF_2$. In Table I are summarized the coordination properties of the ligands with X = absent, O, $N(CH_3)N(CH_3)$, $N(CH_3)$, CH_2, C_2H_4, S, and $C(CF_3)_2O$. From these data a qualitative bonding model can be derived. Considering the $F'_2P'XPF_2$ ligands to be derivatives of PF_3, where the substituent is $F'_2P'X$, it would be expected that the fluorine atoms on phosphorus will withdraw electron density and reduce the lone electron pair availability of the phosphorus atoms to which they are attached. This charge flow away from phosphorus should be enhanced by electron withdrawal due to the $F'_2P'X$ group. These ligands to some degree should inductively resemble PF_3 and they should be expected to form weak σ-bonded mono(borane(3)) complexes. Only if electron withdrawal by $F'_2P'X$ becomes considerably greater than electron withdrawal by fluorine should the phosphorus base site become unattractive for coordination by BH_3. Once the PF_2 group is coordinated by one acceptor molecule the expectation is that the basicity of the second phosphorus site in $F'_2P'X$ will be reduced by electron withdrawal by its own fluorine atom pair, by the $PF_2(BH_3)$ group, and in X = O, $N(CH_3)$, S and $C(CF_3)O$ by the intervening group.

π-electron delocalization may be expected to enhance the inductive electron pattern outlined above. It is often suggested[22] that the normally diffuse 3d orbitals on phosphorus are contracted by fluorine atoms such that if substituent ($F'_2P'X$) orbitals of the proper symmetry are available then $p\pi$–$d\pi$ delocalization may occur. For the ligands of interest here delocalization should be expected for X = O, $N(CH_3)$, S, and perhaps $N(CH_3)N(CH_3)$ and for P_2F_4. Delocalization should be blocked when X = CH_2, C_2H_4, and $C(CF_3)_2O$. Coordination of the PF_2 site by BH_3 should enhance $p\pi$–$d\pi$ delocalization in the P′XP backbone if X can π electron conduct. Such delocalization in turn should *reduce* the lone-pair availability on the uncoordinated $P'F'_2$ site.

Steric factors are difficult to assess for these ligands since P_2F_4 is the only ligand for which a molecular structure determination has been completed.[10,23] P_2F_4 displays a trans configuration with a P–P bond distance of 2.22 Å. It is not known, however, if this stereochemistry prevails in the other ligands, but model building reveals no serious structural restrictions for the ligands in any configuration.

To date it has not been possible to predict a priori which of the above factors would predominate and determine the hapticity of a given F'_2PXPF_2 ligand toward even a single reference acid such as BH_3. Some qualitative deductions can be made in light of the experimental results listed in Table I. All of the F'_2PXPF_2 ligands studied to date form at least a single, phosphorus bound, BH_3 complex. This requires that the combination of bonding factors does not override such coordination. It is important to note that for X = O and $C(CF_3)_2O$ the complexes are very weak and unstable to dissociation at 25 °C[2-4] and for X = S[3,4] and P_2F_4[11] the complexes are relatively more stable to dissociation, but they do decompose on standing at 25 °C. The remaining mono(borane(3)) complexes are very stable at 25 °C. Table I shows that only F_2PPF_2,[9] $F_2PCH_2PF_2$,[3] $F_2PCH_2CH_2PF_2$,[7] $F_2PN(CH_3)PF_2$, and $F_2PN(CH_3)N(CH_3)PF_2$[6] form bis(borane(3)) complexes with the $F_4P_2 \cdot BH_3$ being noticeably less stable than the others to dissociation. Attempts to prepare the double adduct of F_2PSPF_2 resulted in the formation of $F_2PSSPF_2 \cdot 2BH_3$ with the borane groups on adjacent sulfur atoms.[3] The other ligands resist addition of the second BH_3. Last, only those complexes which contain an X with a nitrogen atom bind BF_3, and $F_2PN(CH_3)PF_2$ does not appear to add BF_3 under conditions employed here.

The observations on bis(borane(3)) complex formation can be rationalized using an inductive-localized electron-dominated bonding argument. π-electron delocalization is expected in P_2F_4 and only a mono(borane) complex should result. Hodges[10] has pointed out, however, that the trans structure suggests a lone-pair localized model, and the observation[9] of a weak bis(borane) adduct also is consistent with that conclusion. The CH_2- and C_2H_4-bridged diphosphines, of course, require localized lone pairs on phosphorus and little inductive interaction between coordination sites. It would be predicted that bis(borane(3)) adducts should result, and they are observed. When the bridging group is O or S, inductive electron withdrawal and π delocalization should greatly reduce the basicity of the second lone pair and bis(borane(3)) coordination is not found. The observation of strong bis(borane(3)) complexes when X = $N(CH_3)$ or $N(CH_3)N(CH_3)$ may then be taken to suggest that these ligands have well-localized phosphorus lone pairs which do not strongly interact by π-electron delocalization or inductive effects. Inductive effects are of some importance since these bis(borane(3)) complexes are less stable than the mono(borane(3)) complexes.

Further tests of this evolving model are required and coordination and structural studies of several new related ligands would be timely.

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Registry No. 1, 63937-12-2; **2**, 63937-13-3; **3**, 63915-15-1; $F_2PN(CH_3)PF_2$, 17648-18-9; BH_3CO, 13205-44-2; B_2H_6, 19287-45-7; B_4H_{10}, 18283-93-7.

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Acid-Catalyzed Hydrolysis of Trimethylamine–Azidoborane

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The rate of $Me_3N\cdot BH_2N_3$ hydrolysis at 25 °C is relatively insensitive to $[H^+]$ at pH >1 but increases markedly with increasing acidity above 0.1 M H^+ reaching a maximum in 8.1 M H_2SO_4. A decrease in rate, observed with a further increase in acidity to 10 M H_2SO_4, is attributed to a commensurate lowering of the activity of water. In HCl, $HClO_4$, and H_2SO_4 solution, the kinetics are described by $-d[Me_3N\cdot BH_2N_3]/dt = k_2[Me_3N\cdot BH_2N_3]a_w$ where a_w denotes water activity with k_2 showing a dependence on the Hammett acidity function, h_0, as depicted by the expression $k_2 = k_rKh_0/(1 + Kh_0)$. Thus, the logarithm of k_2 is linear with $-H_0$ with near unit slope in the range $H_0 = +1$ to -3 but approaches a limiting value, k_r, in 8.1 M H_2SO_4 and becomes invariant with further changes in acidity from $H_0 = -4$ to -5. In the acid-dependent region, rates in water and D_2O at a given H_0 (D_0) are nearly equal; however, $k_{H_2O}/k_{D_2O} \simeq 2.2$ in 8.1 M H_2SO_4 (D_2SO_4) at 25 °C. An A-2 mechanism involving rapid preequilibrium protonation of substrate followed by rate-limiting attack by H_2O on substrate conjugate acid is strongly suggested. The limiting rate, therefore, is viewed as that of the bimolecular reaction of water with $Me_3NBH_2N_3H^+$, which is formed stoichiometrically at high acidity. A value $K \sim 3 \times 10^{-4}\ M^{-1}$ is calculated for the equilibrium constant for protonation of $Me_3N\cdot BH_2N_3$ at 25 °C. From studies of temperature dependence, the values $\Delta H^\circ = 6.6$ kcal/mol and $\Delta S^\circ = 6.1$ eu are estimated for protonation of the azidoborane, and $\Delta H^\ddagger = 16.9$ kcal/mol and $\Delta S^\ddagger = -21.8$ eu for the subsequent hydrolytic decomposition of $Me_3N\cdot BH_2N_3H^+$. It is suggested that protonation occurs at the azide ligand enabling its departure as the relatively labile HN_3 species. A comparable pathway may exist for the acid-catalyzed hydrolysis of $Me_3N\cdot BH_2F$.

Introduction

The influence of boron-bonded ligands on the kinetics and mechanistic pathways of hydrolysis of amine–boranes, $R_nNH_{3-n}\cdot BH_yX_{3-y}$, has been reported for X = aryl[1-3], as well as hydride,[4-7] cyanide,[8] and various halide ions.[9,10] Similarities in the reactions of such species and selected organic and transition-metal complex substrates also have been noted, including the anomalous effect of the F^- ligand both in the hydrolysis of trimethylamine–haloboranes and in the aquation of haloammine complexes of cobalt(III).[11-13] In each of these systems, an acid-catalyzed pathway is favored presumably involving protonation of the strongly electronegative fluoride ion and its subsequent departure in the form of the conjugate acid, HF. In order to further explore such ligand effects, and in view of the reported similarity of N_3^- and F^- in promoting the acid-catalyzed aquation of substituted amminecobalt(III) complexes,[14,15] we were prompted to explore the hydrolytic properties of trimethylamine–azidoborane.

Experimental Section

Materials. Trimethylamine–borane was obtained from Aldrich Chemical Co. and sublimed in vacuo before use. Trimethylamine was obtained from Matheson Gas Products, hydrogen iodide (57% aqueous solution) from Matheson Coleman and Bell, and sodium azide from Alfa Inorganics. Deuterium oxide (99.8 atom % D) and deuteriosulfuric acid (>98% D_2SO_4 in D_2O) were obtained from Diaprep Inc. Solutions of DCl in D_2O were prepared by the method of Brown and Groot[16] from D_2O and benzoyl chloride. Trimethylammonium iodide was prepared by treatment of aqueous HI with gaseous Me_3N. After evaporation of water, the solid was recrystallized from hot MeOH and dried in vacuo. Stock solutions of H_2SO_4, $HClO_4$, and HCl were prepared from the concentrated reagents and standardized with NaOH.

Analyses and Spectra. Carbon, total hydrogen, and nitrogen analyses were performed by MHW Laboratories, Garden City, Mich. Hydridic hydrogen was determined by measurement of the H_2 evolved during hydrolysis of the substrate. The corresponding hydrolysate was employed for the determination of boron by a titrimetric procedure.[17] Mass spectra were recorded on a Finnigan 1015 S/L mass spectrometer operating at an ionizing voltage of 70 eV. Visible and UV spectra were obtained on a Cary Model 15 recording spectrophotometer, and infrared spectra of samples of amine–azidoboranes (neat liquids) on a Beckman IR-10. The ^1H NMR spectra were recorded on a Varian A-60A spectrometer at 60 MHz using Me_4Si as internal standard and ^{11}B NMR spectra on a Varian HA-100 spectrometer at 32.1 MHz using $(MeO)_3B$ (sealed capillary) as external standard. Sidebands generated by an external Hewlett-Packard (HP) 200 CD oscillator were used to calibrate the spectra by measuring frequencies with a HP 5211 B frequency counter.

Bis(trimethylamine)dihydroboron(1+) Iodide. A modification of the method of Miller and Muetterties[18] was employed as follows. A 12-in. length of 1.5-in. diameter iron pipe was fitted with cast iron caps, one having been tapped and threaded to hold a stainless steel stopcock through which the apparatus could be attached to a high-vacuum apparatus. A Pyrex sleeve sealed at one end was constructed to fit within the metal tube to hold reactant materials. In a typical run, the desired weighed amounts of Me_3NHI and $Me_3N\cdot BH_3$ were placed in the glass sleeve and a loose wad of glass wool placed in the top of the sleeve to reduce loss of powder on subsequent evacuation. After the apparatus was fully assembled, air was slowly removed, following which the tube and contents were heated in a drying oven for 12 h at 100 °C and 8 h at 175 °C. While warm, the pipe again was attached to the vacuum apparatus and volatile material, including unreacted $Me_3N\cdot BH_3$, was removed by sublimation. The remaining product was cooled under dry nitrogen and extracted and recrystallized from hot ethanol. Typically, 20–25-g quantities