tution has a similar but smaller effect upon nitrogen protonation.

A computer fit of the NMR chemical shift vs pH curves allowed the intrinsic shifts of the various ligand protonated species, H_nL, to be obtained. The ^{31}P shifts for the various H_nL species are dependent upon protonation of the nitrogen and the phosphonate oxygen atoms, and also on the possible formation of intramolecular hydrogen bonds between NH^+ and O^- neighboring groups. Those effects are reflected in the ^{31}P chemical shifts in a complex way through σ and π contributions to the electronic structure of the phosphonate moiety.[44] The protonation shifts of the phosphonate ligands were used to obtain microscopic protonation fractions at various pH values. Although a quantitative fit of the experimental data was difficult due to pH-dependent conformational effects, the general picture of microscopic protonation of the macrocyclic phosphonate ligands is not very different from that found for the acetate couterparts.[27-29] The most basic sites are two ring nitrogens, followed by the phosphonate oxygens, which are protonated to different degrees depending on the ring structure. In the tetraaza ligand, the protonation of the pendant phosphonate oxygens is more extensive than in the triaza ligand before further protonation of the ring nitrogens occurs.

Finally, the magnitude and sign of the Na^+-induced shift on the ^1H and ^{31}P signals of the phosphonate chelates indicate that this ion binds within the macrocyclic cavities of NOTP and DOTP but not DOTRP, at least below pH 13. This may be due to an unusually high first protonation constant for DOTRP or to unique conformational features of the bridging propylenes in this chelate that precludes Na^+ binding in its cavity.

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Evidence for the Donor Capacity of Nitrogen in Acyclic Aminophosphines: A Multinuclear NMR Study

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The reactions of R_2PNMe_2, $Me_2PNR'_2$, and $(Me_2N)_nPMe_{3-n}$, where R = Me, Et, Ph, and Cl, R' = Me, Et, Pr^n, Pr^i, and $SiMe_3$, and n = 1–3, with varying mole ratios of BH_3·THF have been carried out and studied by using multinuclear NMR spectroscopy. Although P–B-bonded monoadducts were always obtained, B–P–N–B-bonded bisadducts were also obtained for Me_2PNMe_2, Me_2PNEt_2, and Et_2PNMe_2. These are the first reported examples where the nitrogen atom in acyclic aminophosphines demonstrates reactivity toward BH_3. The extent of bisadduct formation decreases dramatically in going from Me_2PNMe_2 to Me_2PNEt_2. K_{eq}, ΔH, and ΔS values were obtained for the $Me_2\overline{PNMe_2}\cdot BH_3/H_3BP(\overline{NMe_2}\cdot BH_3)Me_2$ and $Et_2\overline{PNMe_2}\cdot BH_3/H_3BP(\overline{NMe_2}\cdot BH_3)Et_2$ equilibrium systems. The results are compared with those reported previously for analogous aminoarsines. A competition study involving the Me_3N, Me_3P, Me_3As, Me_2PNMe_2, Me_2AsNMe_2, and BH_3·THF systems is discussed relative to the nature of P–N and As–N bonding.

Introduction

The borane coordination chemistry and Lewis basicity of the phosphorus and nitrogen atoms in aminophosphines have been studied extensively,[1-19] with experimental results suggesting that the phosphorus atom is the more basic site. For example, in the reactions of B_2H_6 with acyclic aminophosphines of the type $(Me_2N)_nPMe_{3-n}$,[14-17,19] Me_2NPF_2,[9] $(Me_2N)_2PF$,[9] Me_2NPBu_2,[18] and $(Me_2N)_2PBu$,[18] the BH_3 moiety binds only to the phosphorus atom. The prevailing view is that in these phosphines the nitrogen atom assumes a planar configuration and through $d\pi$–$p\pi$ multiple bonding it experiences diminished basicity, and the phosphorus atom, enhanced basicity.[20-24] Only in some constrained cyclic aminophosphines is there evidence for the binding of BH_3 to the nitrogen atom.[5,20,21,24] With $P(NMeCH_2)_3CMe$,[5] coordination to the nitrogen occurs after BH_3 binds to the phosphorus. Similarly, the constrained bicyclic $P(OCMe_2CH_2)_2N$ forms a bis(borane) adduct.[21,24]

In a recent communication,[25] we demonstrated conclusively[19] the synthesis and characterization of the first known bis(borane) adduct, $H_3BP(NMe_2\cdot BH_3)Me_2$, of an acyclic aminophosphine. Previously, the possibility of the nitrogen atom serving as a donor site in this compound was dismissed.[6,15,17] We have now extended this work to establish the generality of N–B bonding and those factors influencing P–B and N–B bonding in acyclic aminophosphine/BH_3 reaction systems. In this paper, we describe a systematic study of the reaction of BH_3·THF in varying reactant mole ratios with three series of aminophosphines: series A,

(1) Cowley, A. H.; Dewar, M. J. S.; Jackson, W. R.; Jennings, W. B. *J. Am. Chem. Soc.* **1970**, *92*, 5206.
(2) Verkade, J. G. *Coord. Chem. Rev.* **1972/73**, *9*, 1.
(3) Romming, C.; Songstad, J. *Acta Chem. Scand.* **1978**, *A32*, 689.
(4) Dakternieks, D.; DiGiacomo, R. *Phosphorus Sulfur* **1985**, *24*, 217.
(5) Kroshefsky, R. D.; Verkade, J. G.; Pipal, J. R. *Phosphorus Sulfur* **1979**, *6*, 377.
(6) Riess, J. G. *Phosphorus Sulfur* **1986**, *27*, 93.
(7) Jessup, J. S.; Paine, R. T.; Campana, C. F. *Phosphorus Sulfur* **1981**, *9*, 279.
(8) Paine, R. T. *Inorg. Chem.* **1977**, *16*, 2996.
(9) Fleming, S.; Parry, R. W. *Inorg. Chem.* **1972**, *11*, 1.
(10) Lundberg, K. L.; Rowatt, R. J.; Miller, N. E. *Inorg. Chem.* **1969**, *8*, 1336.
(11) Morris, E. D., Jr.; Nordman, C. E. *Inorg. Chem.* **1969**, *8*, 1673.
(12) La Prade, M. D.; Nordman, C. E. *Inorg. Chem.* **1969**, *8*, 1669.
(13) Holmes, R. R.; Carter, R. P., Jr. *Inorg. Chem.* **1963**, *2*, 1146.
(14) Holmes, R. R.; Wagner, R. P. *J. Am. Chem. Soc.* **1962**, *84*, 357.
(15) Laurent, J. P.; Jugie, G.; Commenges, G. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1353.
(16) Jugie, G.; Laussac, J. P.; Laurent, J. P. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3455.
(17) Jouany, C.; Laurent, J. P.; Jugie, G. *J. Chem. Soc., Dalton Trans.* **1974**, 1510.
(18) Noeth, H.; Vetter, H. J. *Chem. Ber.* **1963**, *96*, 1298.
(19) Burg, A. B.; Slota, P. J., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 2145.
(20) Grec, D.; Hubert-Pfalzgraf, L. G.; Grand, A.; Riess, J. G. *Inorg. Chem.* **1985**, *24*, 4642.
(21) Febvay, J.; Casabianca, F.; Riess, J. G. *Inorg. Chem.* **1985**, *24*, 3235.
(22) Dupart, J. M.; Le Borgne, G.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 1202.
(23) Dupart, J. M.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 1051.
(24) Grec, D.; Hubert-Pfalzgraf, L. G.; Riess, J. G.; Grand, A. *J. Am. Chem. Soc.* **1980**, *102*, 7133.
(25) Kanjolia, R. K.; Watkins, C. L.; Krannich, L. K. *Inorg. Chem.* **1987**, *26*, 222.

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Table I. Multinuclear NMR Data for R_2PNMe_2 (R = Me, Et, Ph, Cl) and Resulting Borane Adducts at 25 °C

	chemical shift, ppm				coupling const, Hz		
			^{13}C				
compd	^{11}B	^{31}P	R_2P	$-*C-N-P$	$^1J_{PB}$	$^1J_{PC}$	$^2J_{PNC}$ or $^2J_{PCC}$
Me_2PNMe_2		39.7	14.2 (d)	39.2 (d)		18.3	13.1
$Me_2\overline{PNMe_2{\cdot}BH_3}$ (I)	−38.3	63.7	11.8 (d)	37.3	68.7	40.6	<0.5
$Me_2PNMe_2{\cdot}2BH_3$ (II)	−11.8 (B-N) −40.7 (B-P)	109.4	10.3 (d)	48.0 (d)	49.4	36.3	3.3
$Me_2\overline{PNMe_2{\cdot}BH_3}$[a] (III)	−15.8	83.7	12.9 (d)	46.9 (d)		25.6	6.8
Et_2PNMe_2		63.8	21.9 (d) ($P-CH_2$) 9.9 (d) (CH_3-)	40.0 (d)		14.1	13.4 16.1
$Et_2\overline{PNMe_2{\cdot}BH_3}$ (IV)	−42.2	77.4	19.2 (d) ($P-CH_2$) 6.9 (CH_3-)	37.7	67.9	40.2	<0.5 <0.5
$Et_2PNMe_2{\cdot}2BH_3$ (V)	−44.6 (B-P) −11.8 (B-N)	123.8	17.0 (d) ($P-CH_2$) 8.0 (CH_3-)	49.1	48.8	31.9	<0.5 <0.5
Cl_2PNMe_2		165.7		36.9 (d)			21.9
$Cl_2\overline{PNMe_2{\cdot}BH_3}$	−31.4	143.4		37.3 (d)	31.6		4.0
Ph_2PNMe_2[b]		65.7	139.5 (16.1) (C-1) 132.4 (19.9) C-2,6) 128.4 (5.7) (C-3.5) 128.5 (C-4)	41.8 (d)		16.1	15.0
$Ph_2\overline{PNMe_2{\cdot}BH_3}$[b]	−37.9	70.9	131.6 (28.1) (C-1) 132.6 (10.5) (C-2,6) 128.6 (9.9) (C-3,5) 131.2 (C-4)	38.7	63.4	28.1	<0.5

[a] Data at −70 °C. [b] Respective J_{P-C} values are given in parentheses; C-1 = ipso carbon.

R_2PNMe_2 (R = Me, Et, Ph, Cl); series B, Me_2PNR_2 (R = Me, Et, Pr^n, Pr^i, $SiMe_3$); series C, $(Me_2N)_nPMe_{3-n}$ (n = 1-3). These results are compared with those obtained previously[26,27] for analogous acyclic aminoarsines. This study also establishes the influence that the substituents on the phosphorus and nitrogen atoms have on the initial coordination site and investigates the equilibrium and kinetics of the bis- versus mono(borane) adduct formation. Lastly, a competition study suggests the role these substituents play in determining the BH_3 binding site in multiple intermolecular Lewis base site systems.

Results and Discussion

Me_2PNMe_2/BH_3·THF System.[28] A detailed NMR study of the Me_2PNMe_2/BH_3·THF system was undertaken to determine the kinetic and thermodynamic stabilities of the P-B-, N-B-, and B-P-N-B-bonded borane adducts of Me_2PNMe_2. The reactions of Me_2PNMe_2 and BH_3·THF in Me_2PNMe_2:BH_3·THF mole ratios ranging from 1:0.5 to 1:3.0 were studied by ^1H, ^{11}B, ^{13}C, and ^{31}P NMR spectroscopy as a function of temperature and time. Regardless of the reactant mole ratio, the formation of $Me_2\overline{PNMe_2{\cdot}BH_3}$ (I), $H_3BP(\overline{NMe_2{\cdot}BH_3})Me_2$ (II), and $Me_2\overline{PNMe_2{\cdot}BH_3}$ (III) is always observed at −90 °C (NMR data, Table I). However, the relative quantities of I-III were found to be dependent upon the reactant mole ratio, temperature, and time. When the Me_2PNMe_2:BH_3·THF mole ratio is 1:<1, the intensities of the NMR peaks of II and III decrease and those of I increase with an increase in temperature and/or time. After 12 h at room temperature, the spectra indicate complete conversion of II and III to I.

At reactant mole ratios of 1:≥1, the intensities of the NMR peaks associated with I and III decrease and those of II increase as the reaction mixture is warmed from −90 to −60 °C. After 24 h at −60 °C, complete conversion to the bisadduct, II, occurs when the reactant mole ratio is 1:≥2. Thus, formation of the P-B-bonded monoadduct, I, is kinetically favored at low temperatures, while the bisadduct, II, is the most thermodynamically stable product at Me_2PNMe_2:BH_3·THF mole ratios 1:≥2. In all cases, the N-B-bonded adduct, III, is much less stable than the P-B-bonded adduct, I.

Upon warming of the −60 °C solution to −30 °C, the NMR spectra indicate the reconversion of a small amount of II to I. Above −30 °C, a measurable equilibrium mixture of I and II exists. The intensities of the peaks of I increase with a concomitant decrease in those of II as the temperature is increased to 25 °C. Equilibrium constant values for several independent samples were calculated by using ^{31}P and ^{11}B NMR integration data. The K_{eq} values at −30, −17, 0, and 25 °C were 1.1×10^3, 5.2×10^2, 2.7×10^2, and 1.1×10^2, respectively, where $K_{eq} = [II]/[I][BH_3]$. A van't Hoff plot of ln K_{eq} versus $1/T$ shows excellent linearity (r = 0.998). The resulting ΔH and ΔS values are −24.3 kJ/mol and −42.5 eu, respectively.

These large K_{eq} values indicate that the formation of the bisadduct is still favored thermodynamically at room temperature. Thus, by choice of the appropriate experimental conditions, II was synthesized and isolated in the following manner. The reaction of Me_2PNMe_2 with BH_3·THF in a 1:2.2 mole ratio was carried out at −35 °C for 6 h. An 85% yield of a white crystalline product, $Me_2PNMe_2{\cdot}2BH_3$ (NMR spectral data, Table I), was obtained after distillation of all volatiles while the reaction flask was maintained at −10 °C.[25]

The formation and isolation of the bisadduct, II, and the formation of the thermodynamically less stable N-B-bonded adduct, III, are the first examples where the nitrogen atom in an acyclic aminophosphine demonstrate a definite basicity toward borane. $^1J_{P-B}$ coupling constant data suggest that π bonding in the P-N bond is considerably less in the bis- (49.4 Hz) than in the monoadduct (68.7 Hz).[20]

Series A: R_2PNMe_2, Where R = Me, Et, Ph, and Cl. The reactions of R_2PNMe_2 with BH_3·THF were studied to determine any electronic and/or steric effects that variation of the substituent on the phosphorus may have on the bonding selectivity of BH_3 and on the kinetic and thermodynamic stabilities of the resulting products. The reaction of Et_2PNMe_2 with BH_3·THF (1:1 mole ratio) at −90 °C yields $Et_2\overline{PNMe_2{\cdot}BH_3}$ (IV, NMR data, Table I), which is the exclusive product from −90 to 25 °C. At Et_2PNMe_2:BH_3·THF mole ratios of 1:≥1, only IV is observed initially at −90 °C. However, with increasing time and/or temperature, the formation of the bisadduct, $H_3BP(\overline{NMe_2{\cdot}BH_3})Et_2$ (V), is noted. The relative amounts of IV and V depend upon time, initial reactant mole ratio, and temperature. When addi-

(26) Kanjolia, R. K.; Krannich, L. K.; Watkins, C. L. *Inorg. Chem.* **1985**, *24*, 445.
(27) Kanjolia, R. K.; Krannich, L. K.; Watkins, C. L. *J. Chem. Soc., Dalton Trans.* **1986**, 2345.
(28) This work published in part as a short communication.[25]

Table II. Multinuclear NMR Data for Me_2PNR_2 (R = Me, Et, Pr^n, Pr^i, $NSiMe_3$) Borane Adducts at 25 °C

	chem shift, ppm						coupling const, Hz			
			^{13}C							
compd	^{11}B	^{31}P	$*CH_3-P$	N-*C- or N-Si-*C	N-C-*C-	N-C-C-*C or N-C-(*CH_3)$_2$	$^1J_{PB}$	$^1J_{PC}$	$^2J_{PNC}$	$^3J_{PNCC}$ or $^3J_{PNSiC}$
$Me_2PN(SiMe_3)_2$		32.6	19.4 (d)	4.7[a] (d)				23.3		8.2
$Me_2PN(SiMe_3)_2{\cdot}BH_3$	−31.4	54.4	19.9 (d)	5.5[b]			63.4	40.8		<0.5
Me_2PNEt_2		34.8	16.7 (d)	42.4 (d)	15.4			17.6	14.4	<0.5
$Me_2PNEt_2{\cdot}BH_3$	−38.1	60.6	14.5 (d)	40.3	14.6		69.7	41.3	<0.5	<0.5
$Me_2PN(Pr^n_2)$		36.1	16.6 (d)	50.8 (d)	22.9	11.6		18.1	13.4	<0.5
$Me_2PN(Pr^n_2){\cdot}BH_3$	−37.9	61.5	14.4 (d)	48.2	22.2	11.2	69.8	41.5	<0.5	<0.5
$Me_2PN(Pr^i_2)$		7.2	16.3 (d)	44.9 (d)		23.9 (d)		16.6	7.6	7.1
$Me_2PN(Pr^i_2){\cdot}BH_3$	−34.3	52.4	16.2 (d)	48.0		23.2	65.7	43.4	<0.5	<0.5

[a] ^{29}Si = 6.5 ppm; ^2JSi-P = 4.7 Hz. [b] ^{29}Si = 9.9 ppm; ^2JSi-P = <0.5 Hz.

tional BH_3·THF is added to a solution containing IV and V, and bisadduct, V, forms.

Equilibrium studies were conducted between −30 and 25 °C on several solutions with Et_2PNMe_2:BH_3·THF mole ratios of 1:≥2. The equilibrium constant values, K_{eq}, were calculated by using ^{31}P and ^{11}B NMR integration data. The K_{eq} values at −30, −17, 0, and 25 °C were 35.1, 24.2, 14.7, and 7.5, respectively, where $K_{eq} = [V]/[IV][BH_3]$. The ΔH and ΔS values were calculated to be −16.7 kJ/mol and −39.0 eu (r = 0.999), respectively. All attempts to isolate the bisadduct gave V with some contamination due to IV.

The optimum temperature for studying the kinetics of IV → V conversion was determined to be −60 °C. At this temperature, the kinetics can be followed by NMR spectroscopy. K_{eq} for the formation of V is so large that only the forward reaction (IV + BH_3·THF → V) is important. Several solutions with Et_2PNMe_2:BH_3·THF mole ratios of 1:≥2 were investigated. In each case, formation of exclusively IV was first achieved at −90 °C. Then the temperature was raised directly to −60 °C for the kinetic studies. A second-order kinetics plot of ln {[IV]/[BH_3]} versus t at −60 °C shows excellent linearity (R = 0.998). k was determined to be 3.1×10^{-2} L/(mol min). Thus, IV → V conversion seems to follow a simple second-order pathway.

In the reactions of Ph_2PNMe_2 with BH_3·THF for Ph_2PNMe_2:BH_3·THF mole ratios 1:≥2, only the P–B-bonded monoadduct is observed over the temperature range −90 to 25 °C. The analogous Cl_2PNMe_2/BH_3·THF reactions also gave only the P–B-bonded adduct. However, the Cl_2PNMe_2 P–B adduct is not stable at room temperature and decomposes upon standing.

A comparison of the K_{eq} values for the mono → bis conversion in the Me_2PNMe_2 and Et_2PNMe_2 cases indicates that the substitution of an Et for a Me group on phosphorus favors formation of the P–B-bonded monoadduct. This substituent effect on phosphorus is electronic rather than steric in nature, since similar ΔS values are obtained for both systems, while the ΔH values are significantly different. This apparent inductive effect is further substantiated by the Ph_2PNMe_2 and Cl_2PNMe_2 reaction results. In both cases, only P–B-bonded adducts are obtained when more electron-withdrawing groups are on the P. Thus, as expected, the Ph and Cl groups appear to be very effective in lowering the basicity of the nitrogen atom.[1,4]

Series B: Me_2PNR_2, Where R = Me, Et, Pr^n, Pr^i, and $SiMe_3$. The reactions of Me_2PNR_2 with BH_3·THF were carried out to note what effect the variation of the substituent on the nitrogen has on BH_3 bonding selectivity and to compare these results and any subsequent decomposition mechanisms with those obtained previously with the analogous aminoarsines, Me_2AsNR_2 (R = Me, Et, Pr^n, and Pr^i).[26,27] The reaction of a 1:2.5 mole ratio of Me_2PNEt_2 and BH_3·THF at −90 °C yields $Me_2PNEt_2{\cdot}BH_3$ (NMR spectral data, Table II) and less than 5% of the B–P–N–B-bonded bis species, $Me_2PNEt_2{\cdot}2BH_3$. Both adducts were stable over the entire temperature range from −90 to 25 °C with no noticeable interconversion occurring between the mono- and bisadducts. The reactions of $Me_2PN(Pr^n)_2$, $Me_2PN(Pr^i)_2$, and $Me_2PN(SiMe_3)_2$ with BH_3·THF gave only the respective P–B-bonded monoadducts (NMR spectral data, Table II).

Thus, the extent of bisadduct formation decreases dramatically upon substituting an Et group for a Me group in the NR_2 moiety, with no evidence of bisadduct formation for the Pr^n, Pr^i, and $SiMe_3$ derivatives. B–N bond formation must be very dependent upon the steric requirements about the nitrogen atom in the parent aminophosphine. This is consistent with the series C results.

For analogous $Me_2PNR_2{\cdot}BH_3$ and $Me_2AsNR_2{\cdot}BH_3$[26,27] species, as expected, the P–B-bonded adducts are more thermally stable than the As–B-bonded adducts. N–B-bonded adducts are favored thermodynamically in the aminoarsines, except where N–B bonding is blocked in the sterically hindered $Me_2AsN(Pr^i)_2$. Owing to the lability of the As–N bond, all the aminoarsine/borane adducts are thermally unstable at room temperature. On the other hand, P–B-bonded adducts are favored kinetically and thermodynamically for all the aminophosphines studied, except for Me_2PNMe_2 where the bis adduct is favored thermodynamically.

Series C: $(Me_2N)_nPMe_{3-n}$, Where n = 1–3. In this series, the successive substitution of the Me_2N moiety for a Me group increases the number of potential N atom base sites, increases the competition between the electron lone pairs on the nitrogens for the available vacant d orbital on phosphorus (P–N $d\pi$–$p\pi$ bonding), and changes the molecular conformation. The literature states that both $(Me_2N)_2PMe$ and $(Me_2N)_3P$ react with B_2H_6 to form exclusively the P–B-bonded monoadducts, regardless of the reactant mole ratio.[15-17] Because of the unexpected results with the R_2PNMe_2 system, the $(Me_2N)_nPMe_{3-n}$ series was reinvestigated to determine what effect the replacement of one and two Me groups by Me_2N moieties has on adduct formation under our reaction conditions.

In contrast to the literature reports,[17] the exclusive formation of the B–P–N–B-bonded bisadduct, $H_3B(Me)P(NMe_2{\cdot}BH_3)NMe_2$ (VI), was observed in the room-temperature reaction of $(Me_2N)_2PMe$ with B_2H_6 (1:1.5 mole ratio). The peaks at −11.7 and −41.2 ppm in the ^{11}B NMR spectrum were assigned to the N–BH_3 and P–BH_3 units, respectively. The ^{31}P resonance was observed at 122.4 ppm. The ^{13}C NMR spectrum shows signals for the uncoordinated NMe_2 at 39.9 ppm and the coordinated NMe_2 at 48.0 and 48.6 ppm.

The reaction of a 1:3 mole ratio of $(Me_2N)_2PMe$ and BH_3·THF was studied from −90 to 25 °C. At −90 °C, the NMR spectra indicated the formation of $(Me_2N)_2PMe{\cdot}BH_3$ (VII) and VI (NMR spectral data, Table III). The relative amounts of VI and VII were temperature and time dependent. With increasing temperature and/or time, the formation of VI is favored. At −90 °C, the ^{13}C NMR spectrum indicates restricted rotation about the P–C and N–C bonds for the P–Me, $BPNMe_2$, and $PNMe_2$ groups of VI. Upon increase of the temperature to −70 °C, the ^{13}C NMR resonance is a sharp singlet for the PMe group. However, both Me_2N moieties show Me group nonequivalence. When the temperature is raised, there is conformational averaging

Table III. Multinuclear NMR Data for $(Me_2N)_nPMe_{3-n}$ (n = 1–3) and Resulting Borane Adducts at 25 °C

	chemical shift, ppm				coupling const, Hz		
			^{13}C				
compd	^{11}B	^{31}P	P–*C	P–N–*C	$^1J_{PB}$	$^1J_{PC}$	$^2J_{PNC}$
$Me_2NPMe_2{\cdot}2BH_3$	−11.8 (B–N)	109.4	10.3 (d)	48.0 (d)	49.4	36.3	3.3
	−40.7 (B–P)						
$(Me_2N)_2PMe$		87.4	13.1 (d)	40.4 (d)		7.7	13.7
$(Me_2N)_2PMe{\cdot}2BH_3$ (VI)	−11.7 (B–N)	122.4	9.4 (d)	39.9		53.7	
	−41.2 (B–P)			48.0 (d)	64.7		2.8
				48.6 (d)			2.8
$(Me_2N)_2PMe{\cdot}BH_3$[a] (VII)	−41.0 (B–P)	94.6	11.1 (d)	37.6	96.7	60.9	<0.5
$(Me_2N)_3P$		122.9		37.9 (d)			18.9
$(Me_2N)_3P{\cdot}BH_3$[21]	−43.4 (B–P)	105.9		36.9 (d)	97.6		3.9

[a] Data at −70 °C.

for the uncoordinated NMe_2 group until coalescence is observed at −20 °C. Above −20 °C rapid conformational averaging occurs as indicated by line-width narrowing of the singlet with increasing temperature. However, the nonequivalence of the two carbon methyls of the coordinated NMe_2 moiety remains up to room temperature, suggesting conformationally restricted motion. The ^{11}B NMR spectra show no evidence of BH_3 exchange between the two nitrogen atoms. No evidence was noted for the formation of a BH_3 trisadduct.

The reaction of $(Me_2N)_3P$ with $BH_3{\cdot}THF$ (1:4 mole ratio) yielded only the P–B-bonded adduct $(Me_2N)_3P{\cdot}BH_3$ (NMR spectral data, Table III), as reported previously.[22] The ^{11}B and ^{31}P NMR spectra indicate trace formation of a B–N-bonded monoadduct.

Thus, for the $(Me_2N)_nPMe_{3-n}$ series, when n = 1 and 2, P–B monoadduct formation is favored kinetically, but B–P–N–B bisadduct formation is favored thermodynamically. When n = 2, conformationally restricted motion suggests steric crowdedness at the NMe_2 moieties. This may explain why only one nitrogen atom is accessible to BH_3 coordination and a BH_3 trisadduct is not formed. When n = 3, the kinetically and thermodynamically stable adduct is the P–B-bonded monocompound. The replacement of the last Me group with a NMe_2 group may create sufficient steric constraints at the N atoms to preclude the formation of an N–B adduct.

$Me_2PNMe_2/Me_2AsNMe_2/BH_3{\cdot}THF$ Competition Study. The reactions of solutions containing equimolar ratios of Me_2PNMe_2 and Me_2AsNMe_2 with varying mole ratios of $BH_3{\cdot}THF$ were studied to determine the relative basicity of the P–N and As–N bonds toward BH_3. At −90 °C a reaction system containing a 1:1:0.8 mole ratio of Me_2PNMe_2:Me_2AsNMe_2:$BH_3{\cdot}THF$ gave a mixture of $Me_2PNMe_2{\cdot}BH_3$ (I), $Me_2AsNMe_2{\cdot}BH_3$ (VIII), and unreacted aminoarsine and aminophosphine. The NMR spectra indicated surprisingly a greater concentration of VIII than of I (1.4:1) and no evidence for the formation of the bisadduct, II. When the relative mole ratios were changed to 1:1:1.8, the aminoarsine was preferentially consumed with VIII and I being formed at −90 °C in a 2:1 mole ratio. No significant change in the relative amounts of VIII and I occurred with increasing temperature.

Due to these unexpected results, we studied the reactions of $BH_3{\cdot}THF$ toward a series of solutions containing competing mono- and/or bis(Lewis base) (group 15) site compounds. All reaction systems containing equimolar amounts (1 mmol) of each reactant were studied in toluene-d_8 at −20 °C to minimize interfering adduct decomposition reactions.[27] The nature and composition of the reaction mixtures were determined by multinuclear NMR spectroscopy. The resulting products and product mole ratios for each system are summarized in Table IV. These data indicate the following order of reactivity of these Lewis bases toward BH_3 in displacing THF from $BH_3{\cdot}THF$ in toluene-d_8 solutions:

$$Me_3N \simeq Me_2AsNMe_2 > Me_2PNMe_2 \simeq Me_3P > Me_3As$$

Such an ordering follows that expected for Me_3E (E = N, P, As), on the basis of the relative electronegativities of the respective group 15 atoms. This is in contrast to the order of base strength, i.e. $R_3P > R_3N > R_3As$, toward BH_3 determined from displacement reactions.[29,30] Substitution of Me_2As for the Me group in Me_3N apparently produces no change in nitrogen basicity. Thus, the aminoarsine As and N atoms compete independently for BH_3 with the As–N base pair behaving as an amine nitrogen in displacing THF from $BH_3{\cdot}THF$. This is consistent with the absence or substantially diminished importance of $d\pi$–$p\pi$ bonding in the As–N bond due to the large size of As and diffuseness of its d orbitals.

Table IV. Competition Study Systems (−20 °C)

syst	adduct	mole ratios
$Me_2AsNMe_2/Me_3N/BH_3{\cdot}THF$	VIII	1
	$Me_3N{\cdot}BH_3$	1.0
$Me_2AsNMe_2/Me_3P/BH_3{\cdot}THF$	$Me_3P{\cdot}BH_3$	1
	VIII	1.3
$Me_2AsNMe_2/Me_3As/BH_3{\cdot}THF$	VIII only	
$Me_2AsNMe_2/Me_2PNMe_2/BH_3{\cdot}THF$	I	1
	VIII	1.3
$Me_2PNMe_2/Me_3N/BH_3{\cdot}THF$	I	1
	$Me_3N{\cdot}BH_3$	1.3
$Me_2PNMe_2/Me_3P/BH_3{\cdot}THF$	$Me_3P{\cdot}BH_3$	1
	I	1.1
$Me_2PNMe_2/Me_3As/BH_3{\cdot}THF$	$Me_3As{\cdot}BH_3$	1
	I	33.3
$Me_3N/Me_3As/BH_3{\cdot}THF$	$Me_3N{\cdot}BH_3$ only	
$Me_3P/Me_3As/BH_3{\cdot}THF$	$Me_3As{\cdot}BH_3$	1
	$Me_3P{\cdot}BH_3$	7.7
$Me_3N/Me_3P/BH_3{\cdot}THF$	$Me_3P{\cdot}BH_3$	1
	$Me_3N{\cdot}BH_3$	1.4

Me_2PNMe_2 is slightly more effective than Me_3P in competing for BH_3 where the phosphorus atoms behave as the Lewis base sites. Substitution of the less electronegative Me moiety for the Me_2N in Me_2PNMe_2 to give Me_3P (theoretical electronegativities: Me, 2.27; Me_2N, 2.40)[31,32] should enhance the basicity of the P atom. On the other hand, $d\pi$–$p\pi$ P–N bonding considerations[1,2,14–17] suggest that the aminophosphine P and N atoms compete cooperatively through the P–N bond with this base pair behaving as a phosphine phosphorus atom. Thus, our results suggest that $d\pi$–$p\pi$ bonding is an important factor and it counters the group electronegativity effect in the intermolecular, aminophosphine/phosphine competition toward BH_3 in displacing THF.

The comparable base strengths of Me_3N and Me_2PNMe_2 toward BH_3 were also investigated by using a displacement reaction involving an equimolar mixture of $Me_3N{\cdot}BH_3$ and Me_2PNMe_2. A very slow reaction occurred. After 4 days at room temperature a 1:2 molar ratio of $Me_3N{\cdot}BH_3$:$Me_2PNMe_2{\cdot}BH_3$ was observed. No displacement reaction occurred between Me_2PNMe_2 and

(29) Parshall, G. W. In *The Chemistry of Boron and Its Compounds*; Muetterties, E., Ed.; Wiley: New York, 1967; pp 617–667.
(30) Coyle, T. D.; Stone, F. G. A. In *Progress in Boron Chemistry*; Steinberg, H., McCloskey, A. L., Eds.; Macmillan: New York, 1964; Vol 1, pp 83–160.
(31) Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284.
(32) Mann, B. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 30.

$Me_3P{\cdot}BH_3$ over an extended period of time. Thus, under the conditions of our competition studies, displacement reactions are not important.

Experimental Section

All experimental manipulations were carried out in a standard high-vacuum line and a Vacuum Atmosphere HE-43 Dri-Lab equipped with an He-493 Dri-Train. The NMR data were obtained by using a Nicolet 300-MHz multinuclear Fourier Transform NMR Spectrometer operating at 75.5 MHz for ^{13}C, 300.1 MHz for ^{1}H, 121.5 MHz for ^{31}P, 96.3 MHz for ^{11}B, and 59.6 MHz for ^{29}Si. The ^{11}B and ^{31}P chemical shift values were measured relative to external $BF_3{\cdot}OEt_2$ and 85% H_3PO_4, respectively, high-field shifts being taken as negative. δ_H, δ_C, and δ_{Si} were measured by using Me_4Si as an internal standard. THF-d_8 and toluene-d_8 were purchased from Aldrich and stored over molecular sieves (note: use of fresh THF-d_8 is recommended). Low-resolution EI–MS data were recorded on a HP 5986A GC/MS/DS mass spectrometer operated at 70 eV, 2400-V electron multiplier, and with a direct-insert probe. The source temperature was maintained at 200 °C, and the probe temperature, at 25 °C.

Diborane(6) was synthesized by the reaction of $NaBH_4$ and I_2 in $(MeOCH_2CH_2)_2O$ and purified by trap-to-trap fractionation.[33] The aminophosphines, $R_2PNR'_2$, were synthesized by two general methods: (a) the reaction of Me_2NPCl_2 with $EtMgX$[34–36] and (b) the reaction of Me_2PCl with the corresponding secondary amine, R'_2NH (R′ = Me, Et, Pr^n, Pr^i).[35] Method b was also used for the preparation of Ph_2PNMe_2. $(Me_3Si)_2NPMe_2$ was synthesized by reacting $(Me_3Si)_2NLi$ with PCl_3 and subsequently using MeMgBr via a Grignard reaction.[37] Me_2AsNMe_2 was synthesized by the aminolysis of Me_2AsCl.[38] The reaction of Me_3Al with As_2O_3 yielded Me_3As.[39]

$Me_2\overline{PNMe_2{\cdot}BH_3}$ (I) and $H_3BP(\overline{NMe_2{\cdot}BH_3})Me_2$ (II) were synthesized as previously reported.[25] Satisfactory elemental analyses of II (mp 117 °C) were obtained from Schwarzkopf Microanalytical laboratory. Calcd: C, 36.23; H, 13.74; B, 16.29. Found: C, 36.92; H, 13.57; B, 16.96. The EI–MS data (greater than 20% abundance) of II suggest the following peak assignments {[species], m/z (relative abundance)}: $[Me_2PNMe_2{\cdot}2BH_3]^+$, 133 (22); $[Me_2NPH_3]^+$, 78 (100); $[Me_2NPH_2]^{\cdot+}$, 77 (22); $[Me_2PB]^{\cdot+}$, 72 (21); $[Me_2PH_2]^+$, 63 (88); $[Me_2PH]^{\cdot+}$, 62 (54); $[Me_2NBH_2]^{\cdot+}$, 57 (29); $[Me_2NBH]^+$, 56 (52); $[MePH]^+$, 47 (25); $Me_2NH]^{\cdot+}$, 45 (45); $[Me_2N]^+$, 44 (47).

All aminophosphines were purified by distillation on a spinning-band column: Me_2PNMe_2 (100 °C), Me_2PNEt_2 (136–138 °C), $Me_2PNPr^n_2$ (172–174 °C), $Me_2PNPr^i_2$ (166 °C), $(Me_3Si)_2NPMe_2$ (55–60 °C/4 Torr), Et_2PNMe_2 (86 °C/146 Torr), Ph_2PNMe_2 (96 °C/0.1 Torr), Me_2NPCl_2 (150 °C). $(Me_2N)_2PMe$, $(Me_2N)_3P$, and Me_3P were obtained from Strem Chemicals Co., and Me_3N was obtained from Matheson. The purity of these compounds was checked by ^{1}H and ^{13}C NMR spectroscopy.

$Me_3N{\cdot}BH_3$, $Me_3P{\cdot}BH_3$, and $Me_3As{\cdot}BH_3$ were synthesized by the direct reaction of B_2H_6 with the respective Lewis base in the vacuum line. The purity of these adducts was determined from their ^{11}B, ^{13}C, and ^{31}P NMR spectra in toluene-d_8 at room temperature (all δ values in ppm): $Me_3N{\cdot}BH_3$ [δ_B, −7.53; δ_C, 53.54], $Me_3P{\cdot}BH_3$ [δ_B, 36.71 (d), $^{1}J_{PB}$ = 58.0 Hz; δ_C, 12.38 (d), $^{1}J_{PC}$ = 36.7 Hz; δ_P, −1.28 (q)], $Me_3As{\cdot}BH_3$ [δ_B, −33.18; δ_C, 8.48].

General Reaction of $R_2PNR'_2$ with $BH_3{\cdot}THF$. A Pyrex NMR tube (10 mm × 22.5 cm) equipped with a greaseless vacuum adapter and stopcock containing 3.0 mL of toluene-d_8, 0.5 mL of THF-d_8, and 1 drop of TMS was degassed on the vacuum line by using freeze-and-thaw cycles. The appropriate amount of B_2H_6 was condensed into it at −196 °C. The reaction mixture was allowed to warm to 20 °C to ensure complete formation of $BH_3{\cdot}THF$. The NMR tube was recooled to −196 °C, and the appropriate amount of $R_2PNR'2$ was condensed (or added by using an addition tube) into it. The NMR tube was sealed, agitated at −95 °C (toluene/liquid N_2 slush), and inserted into the precooled probe of the NMR spectrometer. The ^{1}H, ^{11}B, ^{13}C, and ^{31}P NMR spectra of the reaction mixture were recorded at different temperatures. The NMR data for all the adducts formed in these reactions are listed in Tables I–III.

(33) Freeguard, G. F.; Long, L. M. *Chem. Ind.* **1965**, 471.
(34) Burg, A. B.; Slota, P. J., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 1107.
(35) Maier, L. *Helv. Chim. Acta* **1964**, *47*, 2129.
(36) King, R. B.; Sadanani, N. D. *Synth. React. Inorg. Met.-Org. Chem.* **1985**, *15*, 149.
(37) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1982**, *21*, 3568.
(38) Moedritzer, K. *Chem. Ber.* **1959**, *92*, 2637.
(39) Stamm, W.; Breindel, A. *Angew. Chem.* **1964**, *76*, 99.

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Insertion of Nitriles into the Nitrogen–Chlorine Bond. Synthesis of Polyfluoro- and (Perfluoroalkyl)tetrazanes

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Photolysis of $CF_3N(CF_2CFXCl)Cl$ with ClCN leads to $CF_3N(CF_2CFXCl)N{=}CCl_2$ (X = Cl, F). Similarly, RCN (R = CF_3, Cl) with $CF_3(C_2F_5)NCl$ forms $CF_3(C_2F_5)NN{=}C(Cl)R$. Chlorine fluoride adds readily to the carbon–nitrogen double bond in $CF_3(C_2F_5)NN{=}C(Cl)R$ to give $CF_3(C_2F_5)NN(Cl)CClFR'$ (R′ = F, CF_3). While photolysis of $CF_3(C_2F_5)NN(Cl)CF_2Cl$ results in a tetrazane, $[CF_3(C_2F_5)NNCF_2Cl]_2$, under analogous conditions chlorine is eliminated from $CF_3(C_2F_5)NN(Cl)CClFCF_3$ to form $CF_3(C_2F_5)NN{=}CFCF_3$. Addition of chlorine fluoride to the latter compound followed by photolysis produces a tetrazane with perfluorinated alkyl substituents, $[CF_3(C_2F_5)NNCF_2CF_3]_2$. With CsF, $CF_3(C_2F_5)NN{=}CCl_2$ gives a rearranged perfluoro dimer, $CF_3(C_2F_5)NN{=}CFN(CF_3)N(C_2F_5)CF_3$. Photolysis of the product obtained after reacting the latter with ClF results in a highly substituted tetrazane, $[CF_3(C_2F_5)NN(CF_3)CF_2NN(C_2F_5)CF_3]_2$. These highly catenated nitrogen compounds are thermally and hydrolytically stable.

Introduction

The study of the chemistry of nitrogen–halogen bonds in fluorinated compounds has been ongoing for nearly 35 years, but heretofore the reactivity of these bonds has not been utilized in the preparation of fluorinated, highly catenated nitrogen-containing compounds. It has been shown that both fluorinated and nonfluorinated olefins can be inserted with ease into the nitrogen–halogen bond, e.g., hexafluoropropane or ethylene into the nitrogen–halogen bond of bromo- or iodobis(trifluoromethyl)amine[1–5] or olefins into chlorobis(trifluoromethyl)amine.[6–7] More recently we reported the stepwise insertion of $CF_2{=}CFX$ (X = Cl, F) into the N–Cl bonds of dichloro(perfluoroalkyl)amines.[8] Insertions of cyanogen chloride and/or trifluoroacetonitrile into nitrogen–chlorine bonds, e.g., in chlorobis(trifluoromethyl)amine,[9]

(1) Young, J. A.; Tsoukalas, S. N.; Dresdner, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 3604.
(2) Alexander, E. S.; Haszeldine, R. N.; Newlands, M. J.; Tipping, A. E. *J. Chem. Soc. C* **1968**, 796.
(3) Emeléus, H. J.; Tattershall, B. W. *Z. Anorg. Allg. Chem.* **1964**, *327*, 147.
(4) Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc.* **1965**, 6141.
(5) Barlow, M. G.; Fleming, G. L.; Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc. C* **1971**, 2744.
(6) Fleming, G. L.; Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc. C* **1971**, 3829.
(7) Fleming, G. L.; Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc. C* **1971**, 3833.
(8) Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1989**, *28*, 2187.

0020-1669/89/1328-3345$01.50/0