Determination of the Bonding Preference of Borane (BH₃) toward Aminoarsines by Multinuclear Nuclear Magnetic Resonance Spectroscopy †

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The reactions of BH_3·thf (thf = tetrahydrofuran) with selected (dialkylamino)dimethylarsines, Me_2AsNR_2 (R = Me, Et, Pr^n, or Pr^i) have been carried out as a function of temperature to determine the initial co-ordination site of boron and to elucidate the nature of any As–N, As–B, and N–B bond dissociation/formation processes in solution. The reactions were monitored by multinuclear (^1H, ^{11}B, and ^{13}C) n.m.r. spectroscopy over a temperature range of −90 to 25 °C. With Me_2AsNMe_2, a N–B bonded adduct is formed at low temperature, which decomposes at 25 °C to yield $(Me_2NBH_2)_2$, Me_2NH·BH_3, μ-$Me_2NB_2H_5$, and $Me_2AsAsMe_2$. Equimolar amounts of As–B and N–B adducts are formed at low temperature when Me_2AsNEt_2 is reacted with BH_3·thf. With increasing temperature, the As–B adduct converts to the N–B adduct, which subsequently decomposes at room temperature to μ-$Et_2NB_2H_5$, Et_2NH·BH_3, $(Et_2NBH_2)_2$, and $Me_2AsAsMe_2$. The reaction of $Me_2AsNPr^n_2$ with BH_3·thf yields more of the As–B adduct than of the N–B adduct at −90 °C, but the former rearranges to the latter on warming. Only the As–B adduct is formed in the reaction of $Me_2AsNPr^i_2$ with BH_3·thf. These results suggest that the steric bulkiness of the R_2N moiety plays an important role in determining the co-ordination site of the boron in this series of compounds.

The study of the comparative donor properties of N, P, and As atoms toward boron-containing acceptors has been of continued interest and investigation as evidenced by reports of a considerable number of borane adducts with tetrahedral (or near tetrahedral) geometry about the Group 3 and 5 atoms.[1–8] The experimental results suggest that R_3P (R = alkyl) is a stronger base than R_3N which is considerably stronger than R_3As when BH_3 is used as a reference acceptor molecule.[9–12] The major factors influencing adduct stability and the order of basicity of the donor atoms are steric and electronic contributions from the substituents on the B, N, P, and As atoms.[12–15]

The formation, exclusively, of a B–P bond in P–N-containing bases has been suggested in the interactions of $(Me_2N)_nPMe_{3-n}$,[4,7] $Me_2NCH_2PMe_2$,[2] Me_2NPF_2,[5] and $(Me_2N)_2PF$[5] with BH_3 on the basis of multinuclear n.m.r. spectral data. On the other hand, only B–N bonding has been postulated in the formation of $(Et_2NCH_2)_3P$·$3BH_3$ from the reaction of $(Et_2NCH_2)_3P$ with Et_3N·BH_3 in a 1:4 stoicheiometric ratio.[7] A large excess of Et_3N·BH_3 gives $(Et_2NCH_2)_3P$·$4BH_3$. Depending upon the stoicheiometry, $(BuPNF)_2$ adds one or two moles of BH_3.[16] $MeP[N(Me)N(Me)]_2PMe$[17] and $P[N(Me)N(Me)]_3P$[18] add two moles of BH_3 to give B–P bonded adducts.

The nature of donor-acceptor interactions where two different potential donor atoms are adjacent to each other in the same molecule, *i.e.* aminophosphines with boranes, has been discussed in terms of (a) N–P $p\pi$–$d\pi$ bonding[3,4,7] and (b) hard–soft acid–base (h.s.a.b.) concepts.[6] The chloramination of aminophosphines is known to give aminophosphonium salts in preference to phosphinohydrazinium salts[19,20] due to a decrease in electron density at nitrogen as a result of a $p\pi$–$d\pi$ bonding interaction with phosphorus. Such N–P $p\pi$–$d\pi$ bonding has been suggested from a variety of structural, stereo-chemical, and basicity observations.[1,3–7,21,22]

In contrast to aminophosphines, very little information is available on the interaction of boron acceptors with amino-arsines. The study in this area has been limited previously to the formation of BH_3 and BF_3 adducts with difluoro(dimethyl-amino)arsines.[6] The results of these studies have been discussed in terms of h.s.a.b. theory.

In view of these facts, we initiated an extensive and systematic study of the interaction of boron acceptors toward amino-arsines. We were interested in determining those stereochemical and/or electronic factors influencing bonding site preference in multiple Lewis base compounds, and their stability. In this paper we report an n.m.r. investigation of the reactions of BH_3·thf (thf = tetrahydrofuran) with (dialkylamino)dimethyl-arsines, Me_2AsNR_2 (R = Me, Et, Pr^n, or Pr^i) as a function of temperature. The initial reactions and subsequent bond dissociation and formation processes in solution are followed by using multinuclear (^1H, ^{11}B, and ^{13}C) n.m.r. spectroscopy. The progress of the reactions was monitored by the complete disappearance of peaks associated with the starting material and the appearance of new peaks assignable to the reaction products. Where necessary, independent reactions have been carried out in order to establish proposed reaction pathways. A synthetic route for the quantitative preparation of $Me_2AsAsMe_2$ is also discussed.

Results and Discussion

Reaction of BH_3·thf *with* Me_2AsNMe_2.—The reaction of BH_3·thf (formed by reacting B_2H_6 with $[^2H_8]$thf) with Me_2AsNMe_2 in $[^2H_8]$toluene solution was carried out in a sealed n.m.r. tube and monitored by multinuclear n.m.r. spectroscopy. This reaction was observed to take place below −90 °C. Upon raising the temperature to −70 °C, the reaction goes to completion as indicated by the disappearance of the n.m.r. peaks associated with the aminoarsine [δ_C 42.02 (Me_2N) and 9.13 p.p.m. (Me_2As)]. The ^{13}C n.m.r. spectrum at −70 °C contains two peaks: δ_C 47.26 (Me_2N) and 11.96 p.p.m. (Me_2As), Table. The ^{11}B n.m.r. spectrum at −70 °C consists of a large

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† *Non-S.I. unit employed:* mmHg = 133 N m⁻².

Table. Summary of the reactions of $BH_3 \cdot thf$ with Me_2AsNR_2 (R = Me, Et, Pr^n, or Pr^i)[a]

Compound	Temp. (°C)	δ_B/p.p.m.	δ_C/p.p.m.				δ_H/p.p.m.			
			C(α)	C(β)	C(γ)	Me-As	H-α	H-β	H-γ	Me-As
(1) Me₂AsNMe₂·BH₃	−70	−11.26	47.26			11.96	2.04 (s)			
	−40	(94.9)	(138.3)			(132.3)				
(2) Me₂AsNEt₂·BH₃	−90	−36.09	40.69 (t)	13.92 (q)		20.09 (q)[b]	2.78 (q)	0.89 (t)		1.05 (s)
		(broad)	(134.8)	(125.5)		(130.9)	(6.33)	(6.33)		
(3) Me₂AsNEt₂·BH₃	−10	−14.97	50.00 (t)	13.23 (q)		9.88 (q)	2.50 (q)	1.04 (t)		1.08 (s)
		(97.6)	(138.8)	(133.0)		(126.9)	(6.78)	(6.78)		
(4) Me₂AsNPrⁿ₂·BH₃	−60	−34.94	49.38	21.92	11.44	10.28	2.63 (t)	1.28 (m)	0.75 (t)	0.92 (s)
		(broad)	(133.4)	(125.8)	(125.0)	(134.0)	(7.43)		(7.25)	
(5) Me₂AsNPrⁿ₂·BH₃	−20	−14.15	58.29	17.72	11.84	13.40	2.52 (m)	1.75 (m)[b]	0.70 (t)	1.04 (s)
								1.48 (m)		
		(96.2)	(137.2)	(127.9)	(125.8)	(132.7)			(7.3)	
(6) Me₂AsNPrⁱ₂·BH₃	−10	−29.52	48.54	23.98		12.75	2.90 (h)	1.00 (d)		0.92 (s)
		(104.5)	(132.8)	(125.3)		(133.2)	(6.9)	(6.9)		

[a] J(X–H) values (Hz) are given in parentheses. The δ_C chemical shift assignments for (1)—(6) have been made from the coupled ^{13}C spectra and the chemical shifts of the corresponding parent compound. s = Singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet. [b] Two resonances observed due to non-equivalence.

peak at δ_B −11.26 p.p.m., assigned to a N-co-ordinated BH_3 group,[23,24] and a small peak at δ_B −1.26 p.p.m., due to a slight excess of $BH_3 \cdot thf$ in the mixture. These ^{11}B n.m.r. data, in conjunction with the larger downfield shift upon adduct formation of the Me_2N peak (5.24 p.p.m.) as compared to that of the Me_2As peak (2.83 p.p.m.) in the ^{13}C spectrum, suggest the formation of a B–N adduct, $Me_2AsNMe_2 \cdot BH_3$ (1). The adduct (1) is stable from −70 to 0 °C. Above 0 °C, (1) decomposes as indicated by changes in the n.m.r. spectra. At 25 °C, the δ_B values observed in the ^{11}B n.m.r. spectrum suggest the presence of $(Me_2NBH_2)_2$ (4.59 p.p.m.), $Me_2AsNMe_2 \cdot BH_3$ (−11.35 p.p.m.), $Me_2NH \cdot BH_3$ (−13.65 p.p.m.), and μ-$Me_2NB_2H_5$ (−18.25 p.p.m.) (see Experimental section for ^{11}B and ^{13}C n.m.r. assignments). The corresponding δ_C values for these compounds are observed at 51.68, 47.95 and 12.84, 43.95, and 42.39 p.p.m. respectively. A peak at δ_C 5.96 p.p.m. is assigned to $Me_2AsAsMe_2$. After keeping the reaction mixture at room temperature for 3 d, the n.m.r. spectra indicate the complete absence of (1) and the presence of $(Me_2NBH_2)_2$, $Me_2NH \cdot BH_3$, μ-$Me_2NB_2H_5$, and $Me_2AsAsMe_2$.

Analysis of the n.m.r. data suggests the occurrence of reactions (1)—(5); reactions (4) and (5) are established.[8,25]

Adduct formation (−90 °C)

$$Me_2AsNMe_2 + BH_3 \cdot thf \longrightarrow Me_2AsNMe_2 \cdot BH_3 \quad (1)$$

Adduct decomposition (0 °C and above)

$$Me_2AsNMe_2 \cdot BH_3 \longrightarrow Me_2AsH + Me_2NBH_2 \quad (2)$$

Subsequent reactions (above 0 °C with time)

$$Me_2AsNMe_2 \cdot BH_3 + Me_2AsH \longrightarrow$$
$$Me_2AsAsMe_2 + Me_2NH \cdot BH_3 \quad (3)$$

$$2Me_2NBH_2 \longrightarrow (Me_2NBH_2)_2 \quad (4)$$

$$Me_2NBH_2 + BH_3 \cdot thf \longrightarrow \mu\text{-}Me_2NB_2H_5 \quad (5)$$
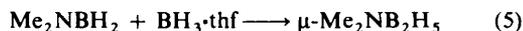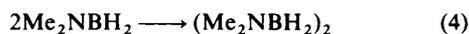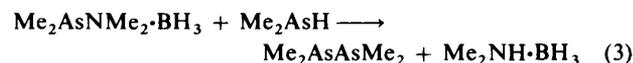
Because of the presence of excess $BH_3 \cdot thf$ in the reaction mixture, Me_2NBH_2 is converted to μ-$Me_2NB_2H_5$. Decompositions analogous to reaction (2) have been observed previously for $F_2AsNMe_2 \cdot BF_3$[6] and $F_2PNMe_2 \cdot BF_3$.[5]

The postulated reaction (3) was confirmed by carrying out an independent reaction of (1) with Me_2AsH in [$^2H_8$]toluene solution, which was monitored from −90 to 25 °C by multinuclear n.m.r. spectroscopy. Reaction occurs below −90 °C and progresses gradually with increasing temperature. Peaks in the ^{13}C and ^{11}B n.m.r. spectra that are assignable to (1) and Me_2AsH (δ_C 1.56 p.p.m.) decrease continually in intensity with a simultaneous increase in intensity of peaks associated with the following species: $Me_2NH \cdot BH_3$ (δ_C 43.97, δ_B −14.16 p.p.m.), $Me_2AsAsMe_2$ (δ_C 5.94 p.p.m.). The reaction goes to completion on reaching −10 °C. In addition, minor peaks assignable to $Me_2AsH \cdot BH_3$ are noted at δ_C 3.23 and δ_B −34.22 p.p.m. in the n.m.r. spectra. This reaction is particularly interesting, since it provides a potential pathway to the quantitative synthesis of As–As bonded compounds. We are currently investigating the reactions of dialkylarsines with aminoarsines to determine the general applicability of this synthetic route.

Reaction of $BH_3 \cdot thf$ with Me_2AsNEt_2.—The reaction of $BH_3 \cdot thf$ with Me_2AsNEt_2 occurs below −90 °C as evidenced by the multinuclear n.m.r. spectra of the reaction mixture. The ^{11}B n.m.r. spectrum consists of two signals of equal intensity at δ_B −36.09 and −14.97 p.p.m., which are assigned to the As–B and N–B bonded adducts, $Me_2AsNEt_2 \cdot BH_3$ (2) and $Me_2AsNEt_2 \cdot BH_3$ (3) respectively. The presence of two sets of peaks in the ^{13}C spectrum [(2): δ_C 40.69, 20.09, and 13.92 p.p.m.; (3): δ_C 50.00, 13.23, and 9.88 p.p.m.] and the absence of parent Me_2AsNEt_2 peaks further support these assignments (Table). A downfield δ_C n.m.r. shift of 6.1 p.p.m. in the C(α) carbon chemical shift occurs upon N–B bond formation, while a downfield δ_C n.m.r. shift of 8.0 p.p.m. in the Me_2As carbon chemical shift occurs upon As–B bond formation. Upon warming the reaction mixture, peaks associated with (2) decrease in intensity with a concomitant increase in intensity of those associated with (3). These data suggest that (2) undergoes rearrangement to (3). Some minor peaks, which are associated with a trace of decomposition of (2), are observed. At −10 °C, the exclusive presence of (3) is confirmed by peaks in the ^{13}C n.m.r. spectrum at δ_C 50.00 [C(α)], 13.23 [C(β)], and 9.88 p.p.m. (Me_2As); and a quartet in the ^{11}B n.m.r. spectrum at δ_B −14.97 p.p.m. [J(B–H) = 97.6 Hz].

The N–B bonded adduct decomposes above 0 °C to give Me_2AsH and Et_2NBH_2. Subsequent secondary reactions occur which lead to the formation of μ-$Et_2NB_2H_5$, $Et_2NH \cdot BH_3$,

$(Et_2NBH_2)_2$, and $Me_2AsAsMe_2$ upon standing at room temperature.[8] These reactions are analogous to reactions (2)—(5) and proceed slowly with time. Within 3 d the decomposition of $Me_2AsNEt_2 \cdot BH_3$ is complete.

Reaction of $BH_3 \cdot thf$ *with* $Me_2AsNPr^n_2$.—The reaction of $BH_3 \cdot thf$ with $Me_2AsNPr^n_2$ occurs below -90 °C as evidenced by the multinuclear n.m.r. spectra of the reaction mixture. At -90 °C, the ^{11}B n.m.r. spectrum shows broad peaks at -1.03, -13.32, and -36.43 p.p.m. assignable to $BH_3 \cdot thf$, the N–B bonded adduct (5), and the As–B bonded adduct (4) respectively. The As–B adduct is found to be in greater yield than the N–B adduct. The adduct formation reactions go to completion at -60 °C to give equimolar amounts of $Me_2As-NPr^n_2 \cdot BH_3$ (4) and $Me_2AsNPr^n_2 \cdot BH_3$ (5). The ^{11}B peak at -34.94 p.p.m. is assigned to the As–B adduct and that at -13.16 p.p.m. to the N–B compound. The presence of only (4) and (5) at -60 °C is further substantiated by the occurrence of two sets of ^{13}C n.m.r. peaks. The peaks at 10.28, 11.44, 21.92, and 49.38 p.p.m. in the ^{13}C n.m.r. spectra have been assigned to the CH_3As, $CH_3CH_2CH_2$, $CH_3CH_2CH_2-$, and $-CH_2N$ carbons of (4) respectively. The peaks at 13.40, 11.84, 17.72, and 58.29 p.p.m. in the ^{13}C n.m.r. spectrum are assigned to the analogous respective carbon resonances of (5). The peak assignments have been made from the analysis of the coupled ^{13}C n.m.r. spectra and the changes in the relative intensities of the spectral lines with temperature.

As the temperature is raised from -60 to -20 °C, the ^{11}B and ^{13}C peaks corresponding to (4) decrease in intensity while those of (5) increase in intensity. This interconversion of (4) to (5) is complete at -20 °C. However, at this temperature a minor peak due to $Pr^n_2NH \cdot BH_3$ is observed at -16.52 p.p.m. in the ^{11}B n.m.r. spectrum. The ^1H n.m.r. spectrum at -20 °C also confirms the complete absence of (4) at this temperature. The presence of two multiplets at 1.75 and 1.48 p.p.m. in the spectra of (5) between -20 and 25 °C indicates the non-equivalence of the two $N-CH_2-CH_2-CH_3$ protons. The spectra do not undergo any change when the temperature of the reaction mixture is raised to 25 °C; (5) appears to be fairly stable at room temperature.

However, complete disappearance of (5) was noted after keeping the reaction solution for 6 d. Analysis of spectral data indicates the presence of $(Pr^n_2NBH_2)_2$ (δ_B 2.24 p.p.m.), $Pr^n_2NH \cdot BH_3$ (δ_B 16.00 p.p.m.), $Pr^n_2NB_2H_5$ (δ_B -19.25 p.p.m.), $Me_2AsAsMe_2$ (δ_C 5.98 p.p.m.), and Me_2AsH (δ_C 1.36 p.p.m.). The decomposition of (5) after several days at room temperature and subsequent reactions to form the products whose ^{11}B and ^{13}C n.m.r. peaks are observed are analogous to reactions (2)—(5).

Reaction of $BH_3 \cdot thf$ *with* $Me_2AsNPr^i_2$.—$Me_2AsNPr^i_2$ reacts with $BH_3 \cdot thf$ in $[^2H_8]$toluene solution below -90 °C to give exclusively the As–B adduct $Me_2AsNPr^i_2 \cdot BH_3$ (6). No significant spectral changes occur in the ^{11}B and ^{13}C spectra over the temperature range -90 to 25 °C. The coupled ^{11}B n.m.r. spectrum shows a quartet at δ_B -29.52 p.p.m. $[J(B-H) = 104.5$ Hz], which is in the region expected for an As–B bonded adduct. There is no n.m.r. spectral evidence for the formation of a N–B bonded adduct. Peaks in the ^{13}C n.m.r. spectrum assigned to (6) are δ_C 48.54 $[C(\alpha)]$, 23.98 $[C(\beta)]$, and 12.75 p.p.m. (Me_2As). Both the parent $C(\alpha)$ and Me_2As chemical shifts are shifted slightly downfield and the $C(\beta)$ chemical shift is shifted slightly upfield upon adduct formation. Thus the ^{13}C n.m.r. resonances of the parent arsine are only slightly dependent upon quaternization of the arsenic atom upon adduct formation, in this case. Perhaps this is a consequence of a minimal hybridization change about the arsenic atom because of the degree of steric crowding in the parent molecule.[26]

To confirm that the ^{13}C n.m.r. peaks correspond to the adduct and not to unreacted arsine, nor are a consequence of an exchange process involving adduct and parent aminoarsine, a few drops of $Me_2AsNPr^i_2$ were added to the solution of (6). The resulting ^{13}C n.m.r. spectrum showed separate peaks corresponding to adduct and unreacted aminoarsine.

No appreciable decomposition of the adduct occurred overnight at room temperature. Since the spectrum remains unchanged over the entire temperature range, this suggests that (6) is stable up to 25 °C. After keeping the reaction mixture for 2 weeks at room temperature, the spectra indicated complete decomposition of (6) to $Pr^i_2NH \cdot BH_3$ (δ_B -21.60 p.p.m.), $Pr^i_2NBH_2$ (δ_B 34.23 p.p.m.), and $Me_2AsAsMe_2$ (δ_C 5.96 p.p.m.).

The results of this study suggest that when $BH_3 \cdot thf$ reacts with Me_2AsNR_2 ($R = Me$, Et, Pr^n, or Pr^i) both the As and N atoms can serve as potential Lewis base co-ordination sites. When $R = Me$, Et, or Pr^n, formation of the respective N–B bonded adducts is the thermodynamically preferred reaction pathway. Only when $R = Pr^i$ is an As–B bonded adduct obtained as the exclusive product at room temperature.

The n.m.r. data also suggest that the steric size of the R_2N group greatly influences the relative amounts of As–B and N–B adducts formed and the kinetics of B–N bond formation. For example, when $R = Me$, there is no evidence to suggest As–B adduct formation at -90 °C. The small size of the Me_2N group and the greater nucleophilicity of the N atom as compared to that of the As atom in the aminoarsine leads only to formation of the N–B adduct (1). This result is unexpected from h.s.a.b. theory and the reported $F_2AsNMe_2 \cdot BH_3$ adduct.[6] The substitution of the more bulky Et group for the Me group in the R_2N moiety leads to an equimolar mixture of N–B and As–B adducts below -90 °C. Thus the nucleophilic character of both the As and N atoms is displayed. This results despite the fact that the Lewis basicity of the N atom should be greater as a consequence of this substitution. With increasing temperature, rearrangement of the As–B adduct (2) to the more thermodynamically stable N–B adduct (3) occurs. Again, both As–B and N–B adducts are obtained in the $R = Pr^n$ case, but more of the As–B adduct (4) is formed at -90 °C as expected from steric considerations. Rearrangement of (4) to the more thermodynamically stable N–B adduct (5) takes place from -90 to -20 °C. Only an As–B bonded adduct, (6), forms when $R = Pr^i$. These results suggest that the Pr^i group sterically blocks BH_3 bonding at the nitrogen atom.

Formation of the As–B and N–B adducts is further substantiated by the nature of the final products of the subsequent decomposition reactions. For both the N–B and As–B adducts, decomposition proceeds with breaking of the As–N bond to give a variety of side products. Some of these undergo further reaction to produce thermodynamically stable end products. Me_2AsH, μ-$R_2NB_2H_5$, $Me_2AsAsMe_2$, $R_2NH \cdot BH_3$, and R_2NBH_2 are observed as products from the decomposition of the respective N–B adducts.

The behaviour of the As–B and N–B adducts formed in this study is in contrast to that of previously reported aminophosphine—BH_3 adducts[7] where the stable P–B bonded adducts were isolated. No stable As–B adducts have been isolated in the present study. Our recent work on the reaction of Me_2NPMe_2 with $BH_3 \cdot thf$ [27] indicates the formation of N–B, P–B, and bis adducts. However, the N–B adduct is observed only at low temperatures and rearranges to the P–B adduct upon warming. The results may be explainable in terms of stronger N–P bonding and greater Lewis base character of the P atom that arises from N–P $p\pi$–$d\pi$ interaction.[1,2,7]

Experimental

Standard high-vacuum line techniques and a Vacuum Atmospheres HE-43 Dri-Lab equipped with a HE-493 Dri-

Train were used during the handling of all compounds. Boron-11, ^{13}C, and ^1H n.m.r. spectra were recorded on a Nicolet 300-MHz multinuclear Fourier transform n.m.r. spectrometer operating at 96.3, 75.4, and 300.1 MHz, respectively (^{11}B and ^{13}C n.m.r. assignments are given below). Chemical shift values for the ^{11}B resonance signals were measured relative to $BF_3\cdot OEt_2$, high-field shifts being taken as negative. The ^1H and ^{13}C n.m.r. chemical shifts were measured with respect to $SiMe_4$ as internal reference. [$^2H_8$]Tetrahydrofuran and [$^2H_8$]toluene were purchased from Wilmad Glass Company and stored over molecular sieves. [NOTE: The use of freshly acquired [$^2H_8$]thf is important when carrying out the reactions to avoid undesired side reactions.] Me_2NH (b.p. 7.4 °C), Et_2NH (56.3 °C), Pr^n_2-NH (109 °C), and Pr^i_2NH (84 °C) were stored over sodium metal and distilled *in vacuo* prior to use. Diborane (B_2H_6) was synthesized by the dropwise addition of a $(MeOCH_2CH_2)_2O$ solution of iodine to $NaBH_4$ in $(MeOCH_2CH_2)_2O$.[28] Trap-to-trap distillation afforded pure diborane in the -126 °C trap. Me_2AsNMe_2 (74 °C/108 mmHg), Me_2AsNEt_2 (80.5 °C/90 mmHg), $Me_2AsNPr^n_2$ (107—109 °C/84 mmHg), and $Me_2AsNPr^i_2$ (78 °C/28 mmHg) were synthesized by the reaction of Me_2AsCl with a stoicheiometric excess of the corresponding amine and/or by the transamination of Me_2AsNMe_2.[29,30] The aminoarsines were purified on a spinning band distillation column prior to use and their purity was checked by ^1H and ^{13}C n.m.r. spectroscopy. Me_2AsH was synthesized by the reduction of $Me_2AsO(OH)$ in the presence of a Zn/Hg amalgam and hydrochloric acid.[31] The purity of this arsine was checked by ^1H and ^{13}C n.m.r. spectroscopy.

General Reaction of Me_2AsNR_2 *with* $BH_3\cdot thf$.—[$^2H_8$]-Toluene (3.0 cm^3) and [$^2H_8$]thf (*ca.* 0.5 cm^3, 2 mmol), along with a drop of $SiMe_4$, were added to the n.m.r. reaction tube (12 mm × 22.5 cm, Pyrex; equipped with a greaseless vacuum stopcock). The tube was degassed using standard vacuum line techniques. At -196 °C, *ca.* 1.0 mmol of B_2H_6 was condensed onto the toluene–thf mixture. The reaction was allowed to warm to 20 °C to assure complete formation of $BH_3\cdot thf$. The n.m.r. tube was recooled to -196 °C and the appropriate aminoarsine Me_2AsNR_2 (2.0 mmol) was condensed into it. The n.m.r. tube was sealed, agitated gently at -95 °C (toluene–liquid N_2 slush), and inserted into the precooled (-90 °C) probe of the n.m.r. spectrometer. The ^{13}C, ^{11}B, and ^1H n.m.r. spectra of the reaction mixture were recorded from -90 °C to 25 °C at temperature intervals of 10 °C. The n.m.r. spectral data are given in the Table.

Reaction of Me_2AsH *with* $Me_2AsNMe_2\cdot BH_3$.—[$^2H_8$]-Toluene (3.0 cm^3) and [$^2H_8$]thf (0.5 cm^3), along with a drop of $SiMe_4$, were added to the n.m.r. tube. $Me_2AsNMe_2\cdot BH_3$ (2.0 mmol) was synthesized in an n.m.r. tube using the procedure described above. The reaction mixture was not warmed above 0 °C, to minimize decomposition of this adduct. After cooling the n.m.r. tube to -196 °C, Me_2AsH (2.0 mmol) was condensed into it. The reaction tube was sealed, agitated gently at -95 °C, and inserted into the precooled (-90 °C) probe of the spectrometer. The reaction was followed by acquiring ^{13}C, ^{11}B, and ^1H n.m.r. spectra as a function of temperature.

δ_B *Chemical Shifts for Compound Identification.*—Reaction products were identified by comparing observed chemical shift values (p.p.m.) with the following reported values (ref. 24 unless stated otherwise): $Me_2NH\cdot BH_3$ (-14.2), $Et_2NH\cdot BH_3$ (-16.9), $Pr^n_2NH\cdot BH_3$ (-15.9), $Pr^i_2NH\cdot BH_3$ (-21.0), μ-$Me_2NB_2H_5$ (-18.6), μ-$Et_2NB_2H_5$ (-19.0), μ-$Pr^n_2NB_2H_5$ (-18.6), μ-$Pr^i_2NB_2H_5$ (-21.0), Me_2NBH_2 (37.9),[25] $(Me_2NBH_2)_2$ (3.9), Et_2NBH_2 (36.18), $(Et_2NBH_2)_2$ (1.90), $Pr^n_2NBH_2$ (37.8),[25] $Me_2AsH\cdot BH_3$ (-34.2),[8] $Me_2AsAsMe_2\cdot BH_3$ (-33.0).[32]

δ_C *Chemical Shifts for Compound Identification.*—Reaction products were identified by comparing observed shift values (p.p.m.) as follows. (*a*) From compounds synthesized independently in this laboratory: Me_2AsNMe_2 [41.91 (Me_2N) and 9.94 (Me_2As)], Me_2AsNEt_2 {43.91 [$C(\alpha)$], 15.00 [$C(\beta)$], and 11.93 (Me_2As)}, $Me_2AsNPr^n_2$ {53.19 [$C(\alpha)$], 23.43 [$C(\beta)$], 12.12 [$C(\gamma)$], and 11.68 (Me_2As)}, $Me_2AsNPr^i_2$ {46.46 [$C(\alpha)$], 25.03 [$C(\beta)$], and 12.18 (Me_2As)}, Me_2NH (38.90), Me_2AsH (1.35), $Me_2AsH\cdot BH_3$ (3.64), $Me_2AsAsMe_2$ (5.96). (*b*) Reported literature values:[33] Et_2NH {44.2 [$C(\alpha)$] and 15.4 [$C(\beta)$]}, Pr^n_2NH {52.34 [$C(\alpha)$], 23.94 [$C(\beta)$], and 11.98 [$C(\gamma)$]}, Pr^i_2NH {45.30 [$C(\alpha)$] and 23.72 [$C(\beta)$]}.

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