

Borane coordination selectivity towards aminoarsines

L.K. Krannich¹, C.L. Watkins, D.K. Srivastava and R.K. Kanjolia

Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294 (U.S.A.)

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A. INTRODUCTION

The coordination chemistry of BX_3 ($\text{X} = \text{H}, \text{F}, \text{Cl}$) with aminophosphines has been studied extensively [1–40]. On the other hand, there have been limited reports on their coordination with aminoarsine systems [12,41–44]. The Lewis base chemistry of aminophosphines and aminoarsines has been of interest since they contain adjacent, potential multiple-base coordination sites. The phosphorus atom has been considered to be the exclusive BH_3 coordination site in acyclic aminophosphines [2–8,12,13,17–19,24–29,33–35,38]. For cyclic and polycyclic aminophosphines, there may be BH_3 coordination to phosphorus only [10,11,15,16,20,21,23,29,33,36,37], phosphorus first and then N when excess BH_3 is present [9,11,12,27,29,31,33,35], or nitrogen only in the case of cyclenphosphorane and the closed form of cyclamphosphorane [29–32]. Our variable-temperature multinuclear NMR studies [39,40] on reaction systems involving $\text{BH}_3 \cdot \text{THF}$ with the acyclic aminophosphine series R_2PNMe_2 , $\text{Me}_2\text{PNR}'_2$, and $(\text{Me}_2\text{N})_n\text{PMe}_{3-n}$ ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$, and Cl ; $\text{R}' = \text{Me}, \text{Et}, \text{Pr}^n, \text{Pr}^i$, and SiMe_3 ; and $n = 1, 2$, and 3) confirmed the formation of mono P–B

¹ To whom correspondence should be addressed.

bonded adducts, but also established that bis B-P N-B bonded adducts are formed with Me_2PNMe_2 , Me_2PNEt_2 , Et_2PNMe_2 , and $\text{MeP(NMe}_2)_2$.

With Me_2NAsF_2 [41], BH_3 coordinates at the arsenic and BF_3 at the nitrogen. For the reactions of $\text{BH}_3 \cdot \text{THF}$ with Me_2AsNR_2 (1:1 stoichiometry; $\text{R} = \text{Me, Et, Pr}^n$, and Pr^i) [42,43], both mono As-B and N-B adducts can form, the results being dependent upon the nature of the R_2N group [43]. NMR spectroscopy was used to follow the reactions and establish the nature of the subsequent As-B, N-B, and As-N bond dissociation/formation processes in solution. With $\text{Me}_2\text{AsNMe}_2$, the N atom is the exclusive BH_3 coordination site. For the Et_2N and Pr^i_2N derivatives, BH_3 binds to both the N and As atoms, with N-B bonding being preferred thermodynamically. Only with $\text{Me}_2\text{AsNPr}^i_2$ is a room-temperature-stable As-B adduct obtained, presumably due to the steric nature of the NPr^i_2 group. All the BH_3 adducts of Me_2AsNR_2 are less stable than the corresponding Me_2PNR_2 adducts. The decomposition of the $\text{Me}_2\text{AsNR}_2 \cdot \text{BH}_3$ As-N adducts leads to $\text{Me}_2\text{AsAsMe}_2$, $[\text{R}_2\text{NBH}_2]_2$, $\mu\text{-R}_2\text{NB}_2\text{H}_5$, and $\text{R}_2\text{NH} \cdot \text{BH}_3$. With $\text{R} = \text{Pr}^i$, the As-B adduct slowly disappears with the simultaneous formation of $\text{Me}_2\text{AsAsMe}_2$, Pr^i_2NH , $\text{Pr}^i_2\text{NH} \cdot \text{BH}_3$, and $\mu\text{-Pr}^i_2\text{NB}_2\text{H}_5$. These data suggest a slow dissociation of the As-B adduct followed by a concerted mechanism that leads to rapid As-N bond cleavage and transfer of a hydrogen to the arsenic.

In this paper, we describe our results on the study of the coordination site selectivity of BH_3 toward the Lewis base sites in the mono, bis, and tris-dimethylamino substituted arsines, $\text{Me}_2\text{AsNMe}_2$, $\text{MeAs(NMe}_2)_2$, and $\text{As(NMe}_2)_3$. The reactions were studied by variable-temperature multinuclear NMR spectroscopy and have been investigated as a function of temperature and reactant stoichiometry. The number of dimethylamino moieties and the aminoarsine: BH_3 mol ratio influence coordination site selectivity, product stability, and the preferred thermodynamically stable reaction products. These results are correlated with those previously reported on the homologous phosphine series [40].

B EXPERIMENTAL

All compounds were stored and handled using standard high-vacuum-line techniques and a Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a Model HE-493 Dri-Train. Toluene- d_8 , THF- d_8 , and Me_4Si were purchased from Aldrich Chemical Company and stored over molecular sieves. Me_2NH was obtained from Matheson Coleman and AsCl_3 from Alfa Products. ^1H , ^{11}B , and ^{13}C NMR spectra were obtained using a GE (Nicolet) 300 MHz multinuclear FT NMR spectrometer operating at 300.1, 96.3, and 75.4 MHz, respectively, with Me_4Si as an internal reference (^1H and ^{13}C chemical shifts) and $\text{BF}_3 \cdot \text{OEt}_2$ as an external reference (^{11}B chemical shifts). The NMR studies were carried out in J. Young, VNMR valve-equipped, NMR tubes (10 mm, Pyrex) that were purchased from Wilmad. The tubes were not acid-washed to minimize the occurrence of acid-catalyzed exchange processes.

Diborane(6) was synthesized by the reaction of I_2 and $NaBH_4$ in diglyme [45] and purified by trap-to-trap fractionation. Me_2AsNMe_2 , $MeAs(NMe_2)_2$, and $As(NMe_2)_3$ were prepared by the aminolysis of Me_2AsCl , $MeAsCl_2$, and $AsCl_3$, respectively [46]. Me_2AsCl [47] and $MeAsCl_2$ [48] were synthesized by previously reported methods. All organoarsines were purified by distillation on a spinning band column and their purity was checked by 1H and ^{13}C NMR spectroscopy. Me_2NBH_3 [49–51], $[Me_2NBH_2]_2$ [49], $\mu-Me_2NB_2H_5$ [50,51], $Me_2AsAsMe_2 \cdot BH_3$ [52], and $Me_2NHBH_2NMe_2BH_3$ [53] were synthesized by previously reported procedures.

(i) General reaction of $Me_{3-n}As(NMe_2)_n$ ($n = 1, 2, 3$) with $BH_3 \cdot THF$

To the NMR tube was added 1.0 mmol of the aminoarsine, 3.0 mL of toluene- d_8 , THF- d_8 , and a drop of TMS. After degassing on the vacuum line, using several freeze-and-thaw cycles, the tube was cooled to $-196^\circ C$, the appropriate amount of B_2H_6 was condensed into it, and the VNMR valve was closed. After detaching the tube from the vacuum line, it was warmed to $-95^\circ C$ (toluene-liquid N_2 slush), agitated, and inserted into the precooled probe ($-90^\circ C$) of the NMR spectrometer. The reaction was then followed at selected temperatures from -90 to $25^\circ C$ by recording the 1H , ^{11}B , and ^{13}C NMR spectra. See spectral data below for all NMR adduct and decomposition product assignments.

(ii) NMR data

The following is a list of 1H , ^{11}B , and ^{13}C NMR spectral data (values given in ppm) in toluene- d_8 at room temperature that were determined independently on synthesized compounds. The spectral data for the parent aminoarsines and their BH_3 adducts are given in Table 1.

(a) 1H NMR spectral data

Me_2AsH : 0.77 (Me_2As), 2.39 (AsH). $Me_2AsH \cdot BH_3$: 0.80 (Me_2As). $Me_2AsAsMe_2$: 0.96. $Me_2AsAsMe_2 \cdot BH_3$: 0.97, 0.96. ($MeAs$) $_5$: 1.54, 1.50, and 1.48. Me_2NH : 2.17. $Me_2NH \cdot BH_3$: 1.96 (Me_2N). $[Me_2NBH_2]_2$: 2.24 (Me_2N). (Me_2N) $_2BH$: 2.62. $\mu-Me_2NB_2H_5$: 2.08 (Me_2N), 1.64 (BH_2), and 0.6 (BH). $Me_2NHBH_2NMe_2BH_3$: 1.81 (Me_2NH), 1.97 (BH_3), 2.01 (BH_2), 2.28 ($Me_2N<$), 4.95 ($>NH$).

(b) ^{11}B NMR spectral data

$Me_2AsH \cdot BH_3$: -33.3 . $Me_2AsAsMe_2 \cdot BH_3$: -33.8 ($^1J(BH) = 105.4$ Hz). $Me_2NH \cdot BH_3$: -14.1 ($^1J(BH) = 97.7$ Hz). Me_2NBH_2 : 37.9. $[Me_2NBH_2]_2$: 5.2. (Me_2N) $_2BH$: 27.3 ($^1J(BH) = 130$ Hz). $\mu-Me_2NB_2H_5$: -17.5 ($^1J(BH) = 130$ Hz (terminal), 31.7 Hz (bridged). $Me_2NHBH_2NMe_2BH_3$: -13.0 (BH_3 , $^1J(BH) = 108$ Hz), 2.0 (BH_2 , $^1J(BH) = 94$ Hz).

TABLE 1

Multinuclear NMR data of $\text{Me}_3\text{-}_n\text{As}(\text{NMe}_2)_n$ ($n = 1, 2, 3$) and resulting borane adducts

Compound	Chemical shift (ppm)						
	^{11}B		^{13}C		^1H		T ($^\circ\text{C}$)
	N-B	As-B	MeAs	Me_2N	MeAs	Me_2N	
$\text{Me}_2\text{AsNMe}_2$	—	—	9.15	42.01	0.70	2.39	—95
$\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ (I)	—11.3	—	12.52	47.72	0.83	2.10	—40
$\text{H}_3\text{B} \cdot \text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ (II)	—12.6	—35.3	9.57	47.94	1.27	2.24	—40
$\text{MeAs}(\text{NMe}_2)_2$	—	—	12.37	42.80	0.88	2.61	—95
$\text{MeAs}(\text{NMe}_2 \cdot \text{BH}_3)\text{NMe}_2$ (III)	—14.6	—	13.29	49.50, 45.69 ^a 38.54	1.01	2.20, 2.02	—80
$\text{MeAs}(\text{NMe}_2 \cdot \text{BH}_3)_2$ (IV)	—11.3	—	15.23	51.50, 46.15 ^a 45.68	1.37	2.53, 2.32 ^a 2.21, 2.10	—70
$\text{Me}_3\text{NBH}_2 \cdot \text{HNMe}_2$ (V)	3.2	—	—	52.8, 43.8	—	—	—70
$\text{MeAs}(\text{H})\text{NMe}_2 \cdot \text{BH}_3$ (VI)	—12.8	—	5.20	51.23	0.86(d)	2.16	—70
$\text{H}_3\text{B} \cdot \text{MeAs}(\text{H})\text{NMe}_2 \cdot \text{BH}_3$ (VII)	10.9	—32.8	10.74	48.72	1.53	2.66	—40
$(\text{Me}_2\text{N})_3\text{As}$	—	—	—	39.80	—	2.61	—95
$(\text{Me}_2\text{N})_3\text{As} \cdot \text{BH}_3$ (VIII)	—	—40.2	—	38.60	—	2.45	—70
$(\text{Me}_2\text{N})_2\text{AsNMe}_2 \cdot \text{BH}_3$ (IX)	—12.4	—	—	47.10, 40.40	—	2.43, 2.21	—70
$\text{Me}_2\text{NAs}(\text{NMe}_2 \cdot \text{BH}_3)_2$ (X)	—12.4	—	—	49.59, 48.04 44.49, 40.60	—	2.56, 2.51 2.34, 2.37	—70

^aNon-equivalence of bound Me_2N moiety.(c) ^{13}C NMR spectral data

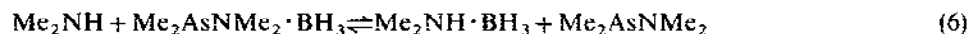
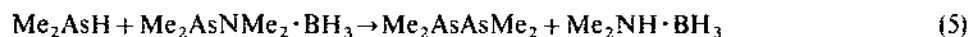
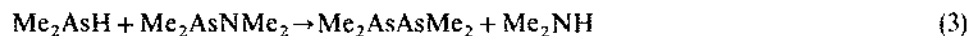
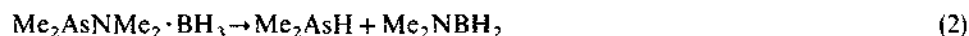
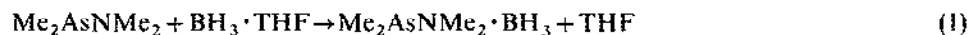
Me_2AsH : 1.43. $\text{Me}_2\text{AsH} \cdot \text{BH}_3$: 3.62. $\text{Me}_2\text{AsAsMe}_2$: 5.94. $\text{Me}_2\text{AsAsMe}_2 \cdot \text{BH}_3$: 5.08 (Me_2AsB), 6.20 (Me_2As). $(\text{MeAs})_5$: 3.78, 5.23, 6.81. $\text{Me}_2\text{NH} \cdot \text{BH}_3$: 43.89. Me_2NBH_2 : 42.39. $(\text{Me}_2\text{NBH}_2)_2$: 51.68 ($\text{Me}_2\text{N})_2\text{BH}$: 40.95. $\mu\text{-Me}_2\text{NB}_2\text{H}_5$: 50.91. $\text{Me}_2\text{NHBH}_2\text{NMe}_2\text{BH}_3$: 42.58 (Me_2NH), 52.43 ($\text{Me}_2\text{N} <$).

C. RESULTS AND DISCUSSION

(i) Reactions of $\text{Me}_2\text{AsNMe}_2$ with $\text{BH}_3 \cdot \text{THF}$

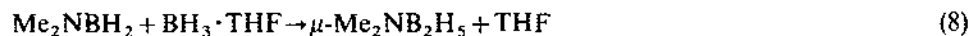
The reactions of $\text{Me}_2\text{AsNMe}_2$ and $\text{BH}_3 \cdot \text{THF}$ in $\text{Me}_2\text{AsNMe}_2$ -to- $\text{BH}_3 \cdot \text{THF}$ mol ratios ranging from 1:0.9 to 1:4.4 were studied as a function of temperature

and time. Regardless of the mol ratio, $\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$, **I**, is formed at -90°C [eqn. (1)] and unreacted aminoarsine and $\text{BH}_3 \cdot \text{THF}$ are observed. At a mol ratio of 1:0.9, there is a 40% conversion to the N-B bonded adduct, which increases with increasing temperature to a maximum conversion occurring at -20°C . At 0°C , a slow decomposition of the adduct commences to give $\text{Me}_2\text{AsAsMe}_2$ and $\text{Me}_2\text{NH} \cdot \text{BH}_3$. Upon standing at room temperature for 12 h, the spectra indicate that further decomposition yields Me_2AsH , $\text{Me}_2\text{AsAsMe}_2$, $\text{Me}_2\text{NH} \cdot \text{BH}_3$, and $(\text{Me}_2\text{N})_2\text{BH}$. Considerable $\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ and some unreacted $\text{Me}_2\text{AsNMe}_2$ still remain in solution. The NMR data suggest that reactions represented by eqns. (2)–(6) occur at 0°C and above to give the observed products.



Reactions described by (1) [43], (2) [43], (3) [54], and (5) [43] have been reported previously. Equation (6) has been established by carrying out the reaction of $\text{Me}_2\text{NH} \cdot \text{BH}_3$ with $\text{Me}_2\text{AsNMe}_2$, which gives the equilibrium mixture represented in (6). This is consistent with the results from the previously reported competition reaction between $\text{Me}_2\text{AsNMe}_2$ and Me_3N for BH_3 [40]. Due to the highly facile nature of (3) [54], the much slower reaction (5) [54] plays a minor role in the production of $\text{Me}_2\text{AsAsMe}_2$ and $\text{Me}_2\text{NH} \cdot \text{BH}_3$ in this reaction system. We have independently carried out the reaction represented by eqn. (4). Since **I** readily decomposes above 0°C [43], the presence of $\text{Me}_2\text{AsNMe}_2$ in the reaction solution apparently enhances the stability of **I** due to chemical exchange [54].

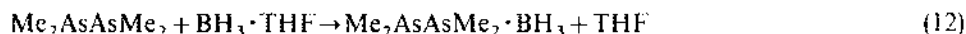
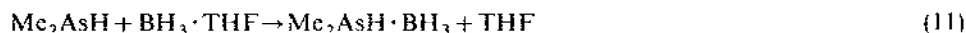
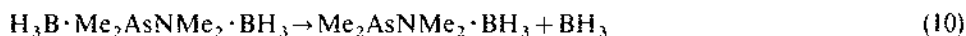
When the $\text{Me}_2\text{AsNMe}_2 : \text{BH}_3 \cdot \text{THF}$ mol ratio is 1:slightly >1 [43], reaction (1) goes to completion at -20°C . At 0°C , decomposition of **I** begins and continues with time at room temperature to give a final product mixture containing $\text{Me}_2\text{AsAsMe}_2$, $[\text{Me}_2\text{NBH}_2]_2$, $\text{Me}_2\text{NH} \cdot \text{BH}_3$, and a trace of $\mu\text{-Me}_2\text{NB}_2\text{H}_5$ [43]. $[\text{Me}_2\text{NBH}_2]_2$ arises from the dimerization of Me_2NBH_2 (eqn. (7)) [43] after the slight excess of $\text{BH}_3 \cdot \text{THF}$ is consumed in the formation of $\mu\text{-Me}_2\text{NB}_2\text{H}_5$ (eqn. (8)) [49–51].



In this case, the reactions represented by (3), (4), and (6) are of little importance since all the $\text{Me}_2\text{AsNMe}_2$ is consumed in the formation of **I**.

At $\text{Me}_2\text{AsNMe}_2:\text{BH}_3\cdot\text{THF}$ mol ratios of $1:\geq 2$, peaks in the NMR spectra assignable to $\text{H}_3\text{B}\cdot\text{Me}_2\text{AsNMe}_2\cdot\text{BH}_3$, **II**, are observed in addition to those for **I**. Over the temperature range of -90 to -20°C , the parent $\text{Me}_2\text{AsNMe}_2$ is consumed to yield more **I** and **II**. The relative amount of **II** is dependent upon the reaction stoichiometry. With a reactant mol ratio of $1:4.4$, the maximum **I**:**II** ratio ($1:1.3$) is obtained. Above -20°C , **II** dissociates into **I** and BH_3 . **I** then begins to decompose, as evidenced by the formation of $\text{Me}_2\text{AsH}\cdot\text{BH}_3$ and $\mu\text{-Me}_2\text{NB}_2\text{H}_5$. The expected initial decomposition products [Me_2AsH , Me_2NBH_2 , and $(\text{Me}_2\text{NBH}_2)_2$] [43] are not observed since the available $\text{BH}_3\cdot\text{THF}$ reacts with Me_2NBH_2 to form $\mu\text{-Me}_2\text{NB}_2\text{H}_5$ and with Me_2AsH to give $\text{Me}_2\text{AsH}\cdot\text{BH}_3$ [42]. When the solution stands at room temperature, the conversion of **II** to **I** goes to completion and **I** slowly decomposes to give a product mixture of $\mu\text{-Me}_2\text{NB}_2\text{H}_5$ and $\text{Me}_2\text{AsH}\cdot\text{BH}_3$ with trace amounts of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and $\text{Me}_2\text{AsAsMe}_2\cdot\text{BH}_3$ [52].

The NMR data suggest that, as the $\text{Me}_2\text{AsNMe}_2:\text{BH}_3\cdot\text{THF}$ mol ratio increases from $1:0.9$ to $1:4.4$, the importance of reactions (3)-(6) rapidly diminishes as that of reactions (2), (8), and the following increase.



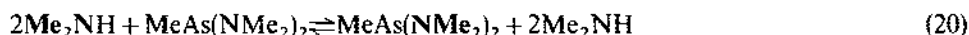
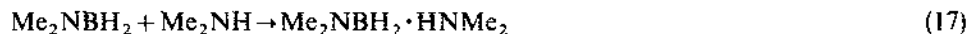
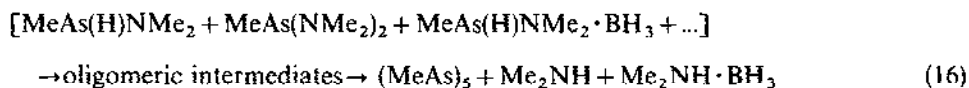
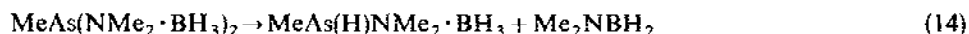
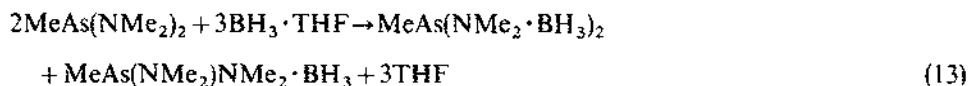
Reactions represented by (11) [42] and (12) [52] have been carried out independently. Thus, with increasing $\text{Me}_2\text{AsNMe}_2$ -to- $\text{BH}_3\cdot\text{THF}$ ratios, the formation of $\mu\text{-Me}_2\text{NB}_2\text{H}_5$, $\text{Me}_2\text{AsH}\cdot\text{BH}_3$, $\text{Me}_2\text{AsAsMe}_2\cdot\text{BH}_3$, and $\text{Me}_2\text{NH}\cdot\text{BH}_3$ is favored and $(\text{Me}_2\text{N})_2\text{BH}$ does not form.

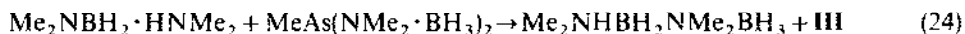
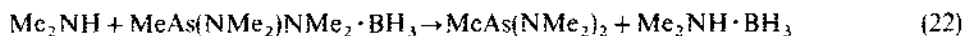
An analogous study involving $\text{Me}_2\text{PNMe}_2/\text{BH}_3\cdot\text{THF}$ systems of varying mol ratios [39,40] indicates that a mixture of $\text{Me}_2\text{PNMe}_2\cdot\text{BH}_3$, $\text{H}_3\text{BP}(\text{NMe}_2\cdot\text{BH}_3)\text{Me}_2$, and $\text{Me}_2\text{PNMe}_2\cdot\text{BH}_3$ forms. The bis adduct is favored thermodynamically and can be isolated as a room-temperature-stable compound from reaction mixtures with $\text{Me}_2\text{PNMe}_2:\text{BH}_3\cdot\text{THF}$ mol ratios of $1:\geq 2$. The mono N-B adduct is the least stable species and decomposes above -70°C . In contrast, the $\text{Me}_2\text{AsNMe}_2:\text{BH}_3\cdot\text{THF}$ study indicates that the mono N-B bonded adduct, **I**, is favored kinetically and thermodynamically. There is no spectral evidence for the formation of a mono As-B bonded adduct, even at a $\text{Me}_2\text{AsNMe}_2:\text{BH}_3\cdot\text{THF}$ mol ratio of $1:4.4$. Due to the lability of the As-N bond, **I** decomposes above 0°C . The nature of these decomposition products depends upon the reaction stoichiometry. Whereas the bis B-P-N-B bonded adduct can be isolated as a stable compound, the analogous B-As-N-B bonded adduct, **II**, which is obtained only at $\text{Me}_2\text{AsNMe}_2:\text{BH}_3\cdot\text{THF}$ mol ratios of $1:\geq 2$, dissociates above -20°C to the mono N-B adduct.

(ii) Reactions of $\text{MeAs}(\text{NMe}_2)_2$ with $\text{BH}_3 \cdot \text{THF}$

The reactivity of $\text{BH}_3 \cdot \text{THF}$ towards $\text{MeAs}(\text{NMe}_2)_2$ was studied as a function of temperature and time with $\text{MeAs}(\text{NMe}_2)_2 : \text{BH}_3 \cdot \text{THF}$ mol ratios ranging from 1:0.5 to 1:3. At -90°C , the formation of $\text{MeAs}(\text{NMe}_2 \cdot \text{BH}_3)\text{NMe}_2$, **III**, and $\text{MeAs}(\text{NMe}_2 \cdot \text{BH}_3)_2$, **IV**, was always observed, in addition to the presence of unconsumed reactants. For the 1:0.5 and 1:1 mol ratio systems, unreacted $\text{MeAs}(\text{NMe}_2)_2$ remained at room temperature, but was consumed with time through secondary reactions as discussed below.

In the 1:0.5 and 1:1 systems, decomposition of **IV** is observed at -80°C . New peaks appearing in the NMR spectra are assignable to $(\text{Me}_2\text{N})_2\text{BH}$, $\text{Me}_2\text{NBH}_2 \cdot \text{HNMe}_2$, **V**, and various transient $\text{MeAs}(\text{H})$ - and $\text{MeAs}(\text{NMe}_2)$ -moiety-containing species (δ_c , 52–40 and 8.0–1.0 ppm spectral regions). Over the temperature range of -80 to -50°C , the decomposition of **IV** is accompanied by an increase in intensity of peaks associated with **V** and $(\text{Me}_2\text{N})_2\text{BH}$ and the appearance of peaks assignable to $(\text{MeAs})_3$, Me_2NH , $\text{Me}_2\text{NHBH}_2\text{NMe}_2\text{BH}_3$ [53,55], and $\text{Me}_2\text{NH} \cdot \text{BH}_3$. The intensity of the ^{11}B peak (3.60 ppm) associated with **V** reaches a maximum at -60°C . Thereafter, a decrease in the intensity of this peak occurs with a concomitant increase in that (28.60 ppm) for $(\text{Me}_2\text{N})_2\text{BH}$. Above -70°C , spectral line width broadening suggests that Me_2N -group exchange occurs between Me_2NH , $(\text{Me}_2\text{N})_2\text{BH}$, $\text{MeAs}(\text{NMe}_2)_2$, and unbound Me_2N moieties of **III**, **IV**, and **V**. The decomposition of **IV** is complete by -60°C ; that of **V** by -40°C . These data suggest that reactions represented by eqns. (13)–(24) occur readily over the -90 to -40°C temperature range.



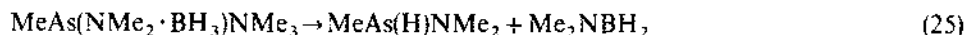


Equations (14) and (15) are analogous to those discussed for the $\text{Me}_2\text{AsNMe}_2/\text{BH}_3 \cdot \text{THF}$ systems and account for the low-temperature formation of $(\text{Me}_2\text{N})_2\text{BH}$ and transient $\text{MeAs}(\text{H})$ - and $\text{MeAs}(\text{NMe}_2)$ -moiety-containing species. Based upon the previous work of Rheingold et al. involving the $\text{MeAsH}_2/\text{MeAsI}_2$ system [56] and our results from studying the $\text{MeAsH}_2/\text{Me}_2\text{AsNMe}_2$ system [57], the pathway to $(\text{MeAs})_5$ (eqn. (16)) is very complex and facile. Any species having an $>\text{As}(\text{H})$ group in a reaction medium with an $>\text{AsNMe}_2$ moiety-containing species should be unstable relative to condensation/ Me_2NH -elimination reactions. For example, via the formation of a concerted, four-centered activated intermediate [56,58], $>\text{As}-\text{H}$ bonded species undergo very facile exchange reactions with any other $>\text{As}-\text{H}$ and $>\text{AsNMe}_2$ moiety-containing species. These, in turn, undergo rapid condensation/ Me_2NH -elimination reactions [57] to yield intermediate $\text{Me}(\text{H})\text{As}(\text{AsMe})_x\text{As}(\text{Me})\text{NMe}_2$ oligomers, which readily cyclize via Me_2NH elimination to the thermodynamically stable $(\text{MeAs})_5$ (eqn. (16)).

From previously studied systems [54,57,59] and the observed spectral line broadening, we also expect that the overall reaction involves several competing exchange equilibria between $\text{MeAs}(\text{NMe}_2)_2$, various $>\text{AsNMe}_2$ and $>\text{As}(\text{H})$ moiety-containing intermediates, and Me_2NH that influence the relative rates of consumption of $\text{MeAs}(\text{NMe}_2)_2$ and formation of $(\text{MeAs})_5$ (eqns. (19)–(21)). The Me_2NH can also compete for the bound BH_3 in III and IV to give $\text{Me}_2\text{NH} \cdot \text{BH}_3$ (eqns. (22) and (23)), which is analogous to the reaction previously established (see eqn. (6)) [40].

Although spectral peaks for Me_2NBH_2 are not observed, reactions of Me_2NBH_2 with Me_2NH and $\text{MeAs}(\text{NMe}_2)_2$ (corresponding to eqns. (15), (17), and (18)) were carried out independently to yield $(\text{Me}_2\text{N})_2\text{BH}$. Thus, in the presence of $\text{MeAs}(\text{NMe}_2)_2$ and Me_2NH , any Me_2NBH_2 should be consumed immediately. We also propose that $\text{Me}_2\text{NHBH}_2\text{NMe}_2\text{BH}_3$ forms from the reaction of $\text{Me}_2\text{NBH}_2 \cdot \text{HNMe}_2$ with IV (eqn. (24)) since $\text{Me}_2\text{NHBH}_2\text{NMe}_2\text{BH}_3$ forms only while IV is present in solution.

When the 1:0.5 and 1:1 reaction mixtures stand overnight at room temperature, all of III decomposes, $\text{MeAs}(\text{NMe}_2)_2$ is completely consumed, and the final product mixture contains Me_2NH , $\text{Me}_2\text{NH} \cdot \text{BH}_3$, $(\text{Me}_2\text{N})_2\text{BH}$, $(\text{MeAs})_5$ and a dark red solid. The latter is analogous to the brick red oligomers that often form in the synthesis of $(\text{MeAs})_5$ [56]. We assume that decomposition of III proceeds via the equation



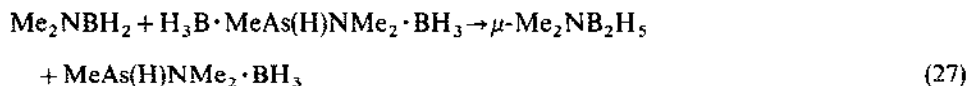
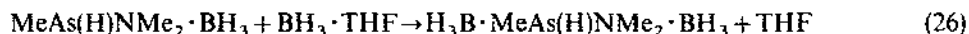
with $\text{MeAs}(\text{H})\text{NMe}_2$ and Me_2BH_2 being involved subsequently in reactions corre-

sponding to eqns. (15)–(17). Equations (19), (20), and (22) suggest the role that Me_2NH plays in influencing the relative rate of reaction and formation of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ at room temperature.

By comparison, in the 1:3 system, $\text{MeAs}(\text{NMe}_2)_2$ is almost completely consumed at -80°C to give a mixture of **III**, **IV**, unreacted $\text{BH}_3\cdot\text{THF}$, and a trace of **V**. By -70°C , decomposition of **IV** has begun and peaks assignable to **V**, Me_2NBH_2 , and $\text{MeAs}(\text{H})\text{NMe}_2\cdot\text{BH}_3$, **VI**, are observed in the spectra. Over the next 20 degree temperature interval, $\mu\text{-Me}_2\text{NB}_2\text{H}_5$ and $\text{Me}_2\text{NH}\cdot\text{BH}_3$ form; **III** and $\text{BH}_3\cdot\text{THF}$ are consumed; spectral peaks assignable to a second As–B bonded adduct, $\text{H}_3\text{B}\cdot\text{MeAs}(\text{H})\text{NMe}_2\cdot\text{BH}_3$, **VII**, appear; peaks in the ^{13}C (1.40 ppm) and ^{11}B (-40.63 ppm) spectra suggest the presence of an $(\text{MeAs})_x\text{As}(\text{H})\text{Me}\cdot\text{BH}_3$ intermediate adduct; and numerous new peaks in the 52–44 ppm and 8–2 ppm regions of the ^{13}C and the N– BH_3 region of the ^{11}B spectra NMR emerge. At -50°C , peaks assignable to $(\text{MeAs})_5$ are first observed. With increasing temperature, the intensities of the peaks associated with $\mu\text{-Me}_2\text{NB}_2\text{H}_5$, $\text{Me}_2\text{NH}\cdot\text{BH}_3$, and $(\text{MeAs})_5$ increase while those of **VI** and the other uncharacterized N–B-bonded adducts and Me_2N moiety-containing species decrease. **VII** decomposes over the -20 to 0°C temperature range. At room temperature, the product mixture consists of $[\text{Me}_2\text{NBH}_2]_2$, **V**, $\text{Me}_2\text{NH}\cdot\text{BH}_3$, $\mu\text{-Me}_2\text{NB}_2\text{H}_5$, Me_2NH , and $(\text{MeAs})_5$. $[\text{Me}_2\text{NBH}_2]_2$ results from the dimerization of Me_2NBH_2 once $\text{BH}_3\cdot\text{THF}$ has been consumed [43].

In a separate experiment, the reaction was followed up to -70°C , quenched to -196°C (liquid nitrogen), and a large excess of $\text{BH}_3\cdot\text{THF}$ was added. With increasing temperature, more **VI** and **VII** formed than in the 1:3 system. Then the decomposition of **VI** and **VII** occurred near room temperature. $(\text{MeAs})_5$ was only very slowly produced at room temperature. The final reaction products were $(\text{MeAs})_5$, $\mu\text{-Me}_2\text{NB}_2\text{H}_5$, and $\text{Me}_2\text{NH}\cdot\text{BH}_3$.

These data suggest that, in addition to reactions corresponding to eqns. (13)–(16), and (19)–(25), the following also occur when sufficient unreacted $\text{BH}_3\cdot\text{THF}$ is present in solution.



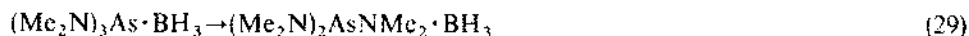
Thus, when $\text{BH}_3\cdot\text{THF}$ is in a stoichiometric excess relative to the available nitrogen base sites in the aminoarsine, the additional $\text{BH}_3\cdot\text{THF}$ minimizes the importance of eqns. (17)–(24), stabilizes the $\text{MeAs}(\text{H})$ intermediates as adducts **VI** and **VII**, slows down the rate of oligomerization and formation of $(\text{MeAs})_5$ (eqn. (16)), and increases the importance of eqns. (26)–(28) in determining the relative composition of the final product mixture.

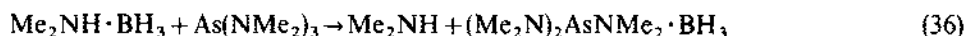
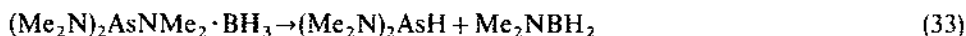
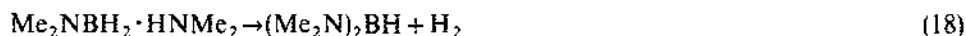
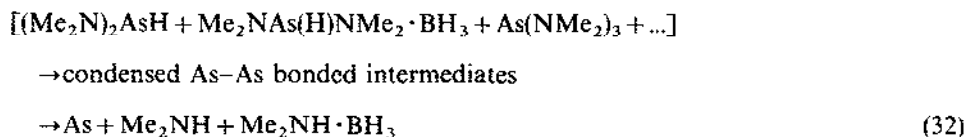
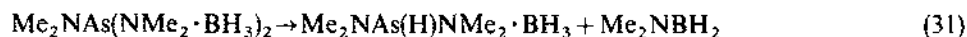
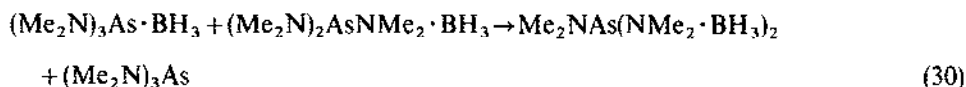
In the $\text{MeP}(\text{NMe}_2)_2\text{-BH}_3\cdot\text{THF}$ systems [40], the bis B-P N-B bonded adduct, $\text{H}_3\text{B}(\text{Me})\text{P}(\text{NMe}_2\cdot\text{BH}_3)\text{NMe}_2$, which forms regardless of the stoichiometric ratio of aminophosphine and $\text{BH}_3\cdot\text{THF}$, is stable at room temperature. At a 1:3 mol ratio, a P-B bonded adduct, $(\text{Me}_2\text{N})_2\text{PMe}\cdot\text{BH}_3$ also forms. With increasing temperature and time, this P-B bonded adduct converts to the bis B-P N-B adduct. In contrast, the reactions of $\text{BH}_3\cdot\text{THF}$ with $\text{MeAs}(\text{NMe}_2)_2$ yield the mono and bis N-B bonded adducts, with the bis adduct being quite unstable and the mono adduct decomposing at room temperature. Regardless of the reaction stoichiometry, the final arsenic-containing product is always $(\text{MeAs})_5$ and red polymer. The nature of the final N-B bonded products depends upon the reaction stoichiometry. Whereas the P and N atoms compete cooperatively for the BH_3 group, the As and N atoms appear to compete independently with the N atom being more effective in displacing the THF from $\text{BH}_3\cdot\text{THF}$ [40].

(iii) *Reactions of $\text{As}(\text{NMe}_2)_3$ with $\text{BH}_3\cdot\text{THF}$*

The reactivity of $\text{BH}_3\cdot\text{THF}$ towards $\text{As}(\text{NMe}_2)_3$ was studied as a function of temperature and time at 1:1 and 1:3 $\text{As}(\text{NMe}_2)_3\text{:BH}_3\cdot\text{THF}$ mol ratios. For the 1:1 system, at -90°C , the formation of $(\text{Me}_2\text{N})_3\text{As}\cdot\text{BH}_3$, **VIII**, $(\text{Me}_2\text{N})_2\text{AsNMe}_2\cdot\text{BH}_3$, **IX**, and $\text{Me}_2\text{NAs}(\text{NMe}_2\cdot\text{BH}_3)_2$, **X**, are observed in approximately a 1:1.5:0.25 mol ratio. Some unreacted $\text{As}(\text{NMe}_2)_3$ and $\text{BH}_3\cdot\text{THF}$ remain in solution. By -70°C , all the $\text{BH}_3\cdot\text{THF}$ is consumed. With increasing temperature, peaks associated with **VIII** begin to decrease in intensity as those assigned to **IX** and **X** increase. This conversion is complete by -50°C . Exchange averaging of the unbound Me_2N moieties on the bis adduct occurs and decomposition of this bis adduct commences with the formation of **V**, $\text{Me}_2\text{NH}\cdot\text{BH}_3$, and a trace of $(\text{Me}_2\text{N})_2\text{BH}$. Decomposition of **X** is complete by -20°C and the tube is coated with an arsenic mirror. **IX** begins to decompose with the formation of additional **V** and $\text{Me}_2\text{NH}\cdot\text{BH}_3$. Upon standing overnight at room temperature, the decomposition of **IX** is complete. The product mixture in solution consists of $(\text{Me}_2\text{N})_2\text{BH}$, $\text{Me}_2\text{NH}\cdot\text{BH}_3$, Me_2NH , unreacted $\text{As}(\text{NMe}_2)_3$ and a trace of $[\text{Me}_2\text{NBH}_2]_2$. In addition to the arsenic mirror, the tube contains a brown black solid. Line broadening in the ^1H spectra indicates Me_2N group exchange between Me_2NH and $\text{As}(\text{NMe}_2)_3$. After 5 days at room temperature, all the $\text{As}(\text{NMe}_2)_3$ is consumed, the mixture contains a 2:1 mol ratio of $(\text{Me}_2\text{N})_2\text{BH}$ and $\text{Me}_2\text{NH}\cdot\text{BH}_3$, a trace of $(\text{Me}_2\text{NBH}_2)_2$, and a large quantity of black solid, which is probably impure elemental arsenic.

The NMR spectral data suggest that the following reactions occur at -70°C and above.





In the 1:3 system, analogous results are obtained below -50°C . At -50°C , a small amount of $\mu\text{-Me}_2\text{NBH}_2\text{H}_5$ forms due to the availability of unreacted $\text{BH}_3 \cdot \text{THF}$ (eqn. (8)). At -20°C , peaks assignable to $\text{Me}_2\text{NHBH}_2\text{NMe}_2\text{BH}_3$ are observed in addition to those for $(\text{Me}_2\text{N})_2\text{BH}$ and $\text{Me}_2\text{NH} \cdot \text{BH}_3$. This suggests that, when more $\text{BH}_3 \cdot \text{THF}$ is available, the $\text{Me}_2\text{NBH}_2 \cdot \text{HNMe}_2$ (eqn. (17)) reacts with $\text{BH}_3 \cdot \text{THF}$ (eqn. (37)).



The final reaction mixture contains $\text{Me}_2\text{NHBH}_2\text{NMe}_2\text{BH}_3$, $\text{Me}_2\text{NH} \cdot \text{BH}_3$, $(\text{Me}_2\text{N})_2\text{BH}$, $[\text{Me}_2\text{NBH}_2]_2$, and Me_2NH .

In the $\text{P}(\text{NMe}_2)_3\text{-BH}_3 \cdot \text{THF}$ systems [40], the only product observed over the entire temperature range is the P-B adduct, $(\text{Me}_2\text{N})_3\text{P} \cdot \text{BH}_3$, [2,7,12], which is stable at room temperature. The observation that a distribution of As-B and N-B bonded adducts are obtained at low temperature suggest that the As and N atoms compete independently for the BH_3 group [40]. In $(\text{Me}_2\text{N})_3\text{As}$, the N atom is more effective than the As atom in displacing the THF from the $\text{BH}_3 \cdot \text{THF}$. The As-B adduct dissociates with formation of the N-B adducts, which decompose at moderately low temperatures (bis adduct, -50 to -20°C ; mono adduct, -20°C to room temperature) to yield a mixture of room-temperature-stable N-B bonded species and elemental arsenic. The nature of the N-B bonded compounds depends upon the initial mol ratio of $(\text{Me}_2\text{N})_3\text{As}$ and $\text{BH}_3 \cdot \text{THF}$.

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