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Borane coordination selectivity towards aminoarsines

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CONTENTS

A. Introduction 117
B. Experimental 118
  (i) General reaction of $Me_{3-n}As(NMe_2)_n$ ($n=1, 2, 3$) with $BH_3 \cdot THF$ 119
  (ii) NMR data 119
    (a) ^1H NMR spectral data 119
    (b) ^{11}B NMR spectral data 119
    (c) ^{13}C NMR spectral data 120
C. Results and discussion 120
  (i) Reactions of Me_2AsNMe_2 with $BH_3 \cdot THF$ 120
  (ii) Reactions of $MeAs(NMe_2)_2$ with $BH_3 \cdot THF$ 123
  (iii) Reactions of $As(NMe_2)_3$ with $BH_3 \cdot THF$ 126
References 128

A. INTRODUCTION

The coordination chemistry of BX_3 ($X=H$, F, 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 $BH_3 \cdot THF$ with the acyclic aminophosphine series R_2PNMe_2, $Me_2PNR'_2$, and $(Me_2N)_nPMe_{3-n}$ ($R=Me$, Et, Ph, and Cl; $R'=Me$, Et, Pr^n, Pr^i, and $SiMe_3$; and $n=1$, 2, and 3) confirmed the formation of mono P–B

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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 $MeP(NMe_2)_2$.

With Me_2NAsF_2 [41], BH_3 coordinates at the arsenic and BF_3 at the nitrogen. For the reactions of $BH_3 \cdot THF$ with Me_2AsNR_2 (1 : 1 stoichiometry; R = 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 Me_2AsNMe_2, the N atom is the exclusive BH_3 coordination site. For the Et_2N and Pr^n_2N derivatives, BH_3 binds to both the N and As atoms, with N–B bonding being preferred thermodynamically. Only with $Me_2AsNPr^i_2$ 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 $Me_2AsNR_2 \cdot BH_3$ As–N adducts leads to $Me_2AsAsMe_2$, $[R_2NBH_2]_2$, $\mu\text{-}R_2NB_2H_5$, and $R_2NH \cdot BH_3$. With $R = Pr^i$, the As–B adduct slowly disappears with the simultaneous formation of $Me_2AsAsMe_2$, Pr^i_2NH, $Pr^i_2NH \cdot BH_3$ and $\mu\text{-}Pr^i_2NB_2H_5$. 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, Me_2AsNMe_2, $MeAs(NMe_2)_2$, and $As(NMe_2)_3$. 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 $BF_3 \cdot OEt_2$ 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_2 [49–51], $[Me_2NBH_2]_2$ [49], μ-$Me_2NB_2H_5$ [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°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°C (toluene–liquid N_2 slush), agitated, and inserted into the precooled probe (−90°C) of the NMR spectrometer. The reaction was then followed at selected temperatures from −90 to 25°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. μ-$Me_2NB_2H_5$: 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). μ-$Me_2NB_2H_5$: −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 $Me_{3-n}As(NMe_2)_n$ ($n = 1, 2, 3$) and resulting borane adducts

Compound	Chemical shift (ppm)						
	^{11}B		^{13}C		^{1}H		T (°C)
	N-B	As-B	MeAs	Me_2N	MeAs	Me_2N	
Me_2AsNMe_2	–	–	9.15	42.01	0.70	2.39	−95
$Me_2AsNMe_2 \cdot BH_3$ (**I**)	−11.3	–	12.52	47.72	0.83	2.10	−40
$H_3B \cdot Me_2AsNMe_2 \cdot BH_3$ (**II**)	−12.6	−35.3	9.57	47.94	1.27	2.24	−40
$MeAs(NMe_2)_2$	–	–	12.37	42.80	0.88	2.61	−95
$MeAs(NMe_2 \cdot BH_3)NMe_2$ (**III**)	−14.6	–	13.29	49.50, 45.69[a] 38.54	1.01	2.20, 2.02	−80
$MeAs(NMe_2 \cdot BH_3)_2$ (**IV**)	−11.3	–	15.23	51.50, 46.15[a] 45.68	1.37	2.53, 2.32[a] 2.21, 2.10	−70
$Me_2NBH_2 \cdot HNMe_2$ (**V**)	3.2	–	–	52.8, 43.8			−70
$MeAs(H)NMe_2 \cdot BH_3$ (**VI**)	−12.8	–	5.20	51.23	0.86(d)	2.16	−70
$H_3B \cdot MeAs(H)NMe_2 \cdot BH_3$ (**VII**)	10.9	−32.8	10.74	48.72	1.53	2.66	−40
$(Me_2N)_3As$	–	–	–	39.80	–	2.61	−95
$(Me_2N)_3As \cdot BH_3$ (**VIII**)	–	−40.2	–	38.60	–	2.45	−70
$(Me_2N)_2AsNMe_2 \cdot BH_3$ (**IX**)	−12.4	–	–	47.10, 40.40	–	2.43, 2.21	−70
$Me_2NAs(NMe_2 \cdot BH_3)_2$ (**X**)	−12.4	–	–	49.59, 48.04	–	2.56, 2.51	−70
				44.49, 40.60	–	2.34, 2.37	−70

[a] Non-equivalence of bound Me_2N moiety.

(c) ^{13}C NMR spectral data

Me_2AsH: 1.43. $Me_2AsH \cdot BH_3$: 3.62. $Me_2AsAsMe_2$: 5.94. $Me_2AsAsMe_2 \cdot BH_3$: 5.08 (Me_2AsB), 6.20 (Me_2As). $(MeAs)_5$: 3.78, 5.23, 6.81. $Me_2NH \cdot BH_3$: 43.89. Me_2NBH_2: 42.39. $(Me_2NBH_2)_2$: 51.68 $(Me_2N)_2BH$: 40.95. μ-$Me_2NB_2H_5$: 50.91. $Me_2NHBH_2NMe_2BH_3$, 42.58 (Me_2NH), 52.43 ($Me_2N<$).

C. RESULTS AND DISCUSSION

(i) Reactions of Me_2AsNMe_2 with $BH_3 \cdot THF$

The reactions of Me_2AsNMe_2 and $BH_3 \cdot THF$ in Me_2AsNMe_2-to-$BH_3 \cdot THF$ 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, $Me_2AsNMe_2 \cdot BH_3$, **I**, is formed at −90°C [eqn. (1)] and unreacted aminoarsine and $BH_3 \cdot THF$ 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 $Me_2AsAsMe_2$ and $Me_2NH \cdot BH_3$. Upon standing at room temperature for 12 h, the spectra indicate that further decomposition yields Me_2AsH, $Me_2AsAsMe_2$, $Me_2NH \cdot BH_3$, and $(Me_2N)_2BH$. Considerable $Me_2AsNMe_2 \cdot BH_3$ and some unreacted Me_2AsNMe_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.

$$Me_2AsNMe_2 + BH_3 \cdot THF \rightarrow Me_2AsNMe_2 \cdot BH_3 + THF \qquad (1)$$

$$Me_2AsNMe_2 \cdot BH_3 \rightarrow Me_2AsH + Me_2NBH_2 \qquad (2)$$

$$Me_2AsH + Me_2AsNMe_2 \rightarrow Me_2AsAsMe_2 + Me_2NH \qquad (3)$$

$$Me_2NBH_2 + Me_2AsNMe_2 \rightarrow Me_2AsH + (Me_2N)_2BH \qquad (4)$$

$$Me_2AsH + Me_2AsNMe_2 \cdot BH_3 \rightarrow Me_2AsAsMe_2 + Me_2NH \cdot BH_3 \qquad (5)$$

$$Me_2NH + Me_2AsNMe_2 \cdot BH_3 \rightleftharpoons Me_2NH \cdot BH_3 + Me_2AsNMe_2 \qquad (6)$$

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 $Me_2NH \cdot BH_3$ with Me_2AsNMe_2, which gives the equilibrium mixture represented in (6). This is consistent with the results from the previously reported competition reaction between Me_2AsNMe_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 $Me_2AsAsMe_2$ and $Me_2NH \cdot BH_3$ 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 Me_2AsNMe_2 in the reaction solution apparently enhances the stability of **I** due to chemical exchange [54].

When the $Me_2AsNMe_2 : BH_3 \cdot THF$ 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 $Me_2AsAsMe_2$, $[Me_2NBH_2]_2$, $Me_2NH \cdot BH_3$, and a trace of μ-$Me_2NB_2H_5$ [43]. $[Me_2NBH_2]_2$ arises from the dimerization of Me_2NBH_2 (eqn. (7)) [43] after the slight excess of $BH_3 \cdot THF$ is consumed in the formation of μ-$Me_2NB_2H_5$ (eqn. (8)) [49–51].

$$2Me_2NBH_2 \rightarrow (Me_2NBH_2)_2 \qquad (7)$$

$$Me_2NBH_2 + BH_3 \cdot THF \rightarrow \mu\text{-}Me_2NB_2H_5 + THF \qquad (8)$$

In this case, the reactions represented by (3), (4), and (6) are of little importance since all the Me_2AsNMe_2 is consumed in the formation of **I**.

At $Me_2AsNMe_2:BH_3\cdot THF$ mol ratios of $1:\geqslant 2$, peaks in the NMR spectra assignable to $H_3B\cdot Me_2AsNMe_2\cdot BH_3$, **II**, are observed in addition to those for **I**. Over the temperature range of −90 to −20°C, the parent Me_2AsNMe_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 $Me_2AsH\cdot BH_3$ and μ-$Me_2NB_2H_5$. The expected initial decomposition products [Me_2AsH, Me_2NBH_2, and $(Me_2NBH_2)_2$] [43] are not observed since the available $BH_3\cdot THF$ reacts with Me_2NBH_2 to form μ-$Me_2NB_2H_5$ and with Me_2AsH to give $Me_2AsH\cdot BH_3$ [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 μ-$Me_2NB_2H_5$ and $Me_2AsH\cdot BH_3$ with trace amounts of $Me_2NH\cdot BH_3$ and $Me_2AsAsMe_2\cdot BH_3$ [52].

The NMR data suggest that, as the $Me_2AsNMe_2:BH_3\cdot THF$ 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.

$$Me_2AsNMe_2 + 2BH_3\cdot THF \rightarrow H_3B\cdot Me_2AsNMe_2\cdot BH_3 \tag{9}$$

$$H_3B\cdot Me_2AsNMe_2\cdot BH_3 \rightarrow Me_2AsNMe_2\cdot BH_3 + BH_3 \tag{10}$$

$$Me_2AsH + BH_3\cdot THF \rightarrow Me_2AsH\cdot BH_3 + THF \tag{11}$$

$$Me_2AsAsMe_2 + BH_3\cdot THF \rightarrow Me_2AsAsMe_2\cdot BH_3 + THF \tag{12}$$

Reactions represented by (11) [42] and (12) [52] have been carried out independently. Thus, with increasing Me_2AsNMe_2-to-$BH_3\cdot THF$ ratios, the formation of μ-$Me_2NB_2H_5$, $Me_2AsH\cdot BH_3$, $Me_2AsAsMe_2\cdot BH_3$, and $Me_2NH\cdot BH_3$ is favored and $(Me_2N)_2BH$ does not form.

An analogous study involving $Me_2PNMe_2/BH_3\cdot THF$ systems of varying mol ratios [39,40] indicates that a mixture of $Me_2\underline{P}NMe_2\cdot BH_3$, $H_3BP(NMe_2\cdot BH_3)Me_2$, and $Me_2P\underline{N}Me_2\cdot BH_3$ forms. The bis adduct is favored thermodynamically and can be isolated as a room-temperature-stable compound from reaction mixtures with $Me_2PNMe_2/BH_3\cdot THF$ mol ratios of $1:\geqslant 2$. The mono N–B adduct is the least stable species and decomposes above −70°C. In contrast, the $Me_2AsNMe_2/BH_3\cdot THF$ 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 $Me_2AsNMe_2:BH_3\cdot THF$ 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 $Me_2AsNMe_2:BH_3\cdot THF$ mol ratios of $1:\geqslant 2$, dissociates above −20°C to the mono N–B adduct.

(ii) Reactions of $MeAs(NMe_2)_2$ with $BH_3 \cdot THF$

The reactivity of $BH_3 \cdot THF$ towards $MeAs(NMe_2)_2$ was studied as a function of temperature and time with $MeAs(NMe_2)_2 : BH_3 \cdot THF$ mol ratios ranging from 1:0.5 to 1:3. At −90°C, the formation of $MeAs(NMe_2 \cdot BH_3)NMe_2$, **III**, and $MeAs(NMe_2 \cdot BH_3)_2$, **IV**, was always observed, in addition to the presence of unconsumed reactants. For the 1:0.5 and 1:1 mol ratio systems, unreacted $MeAs(NMe_2)_2$ 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 $(Me_2N)_2BH$, $Me_2NBH_2 \cdot HNMe_2$, **V**, and various transient MeAs(H)- and $MeAs(NMe_2)$-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 $(Me_2N)_2BH$ and the appearance of peaks assignable to $(MeAs)_5$, Me_2NH, $Me_2NHBH_2NMe_2BH_3$ [53,55], and $Me_2NH \cdot BH_3$. 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 $(Me_2N)_2BH$. Above −70°C, spectral line width broadening suggests that Me_2N-group exchange occurs between Me_2NH, $(Me_2N)_2BH$, $MeAs(NMe_2)_2$, 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.

$$\begin{aligned}&2MeAs(NMe_2)_2 + 3BH_3 \cdot THF \rightarrow MeAs(NMe_2 \cdot BH_3)_2\\&\quad + MeAs(NMe_2)NMe_2 \cdot BH_3 + 3THF\end{aligned} \tag{13}$$

$$MeAs(NMe_2 \cdot BH_3)_2 \rightarrow MeAs(H)NMe_2 \cdot BH_3 + Me_2NBH_2 \tag{14}$$

$$Me_2NBH_2 + MeAs(NMe_2)_2 \rightarrow MeAs(H)NMe_2 + (Me_2N)_2BH \tag{15}$$

$$\begin{aligned}&[MeAs(H)NMe_2 + MeAs(NMe_2)_2 + MeAs(H)NMe_2 \cdot BH_3 + \ldots]\\&\quad \rightarrow \text{oligomeric intermediates} \rightarrow (MeAs)_5 + Me_2NH + Me_2NH \cdot BH_3\end{aligned} \tag{16}$$

$$Me_2NBH_2 + Me_2NH \rightarrow Me_2NBH_2 \cdot HNMe_2 \tag{17}$$

$$Me_2NBH_2 \cdot HNMe_2 \rightarrow (Me_2N)_2BH + H_2 \tag{18}$$

$$\mathbf{Me_2}NH + MeAs(NMe_2)NMe_2 \cdot BH_3 \rightleftharpoons Me_2NH + MeAs(\mathbf{NMe_2})NMe_2 \cdot BH_3 \tag{19}$$

$$2\mathbf{Me_2}NH + MeAs(NMe_2)_2 \rightleftharpoons MeAs(\mathbf{NMe_2})_2 + 2Me_2NH \tag{20}$$

$$\mathbf{Me_2}NH + Me_2NBH_2 \cdot HNMe_2 \rightleftharpoons \mathbf{Me_2}NBH_2 \cdot HNMe_2 + Me_2NH \tag{21}$$

$$\mathrm{Me_2NH + MeAs(NMe_2)NMe_2{\cdot}BH_3 \rightarrow MeAs(NMe_2)_2 + Me_2NH{\cdot}BH_3} \tag{22}$$

$$\mathrm{Me_2NH + MeAs(NMe_2{\cdot}BH_3)_2 \rightarrow MeAs(NMe_2)NMe_2{\cdot}BH_3 + Me_2NH{\cdot}BH_3} \tag{23}$$

$$\mathrm{Me_2NBH_2{\cdot}HNMe_2 + MeAs(NMe_2{\cdot}BH_3)_2 \rightarrow Me_2NHBH_2NMe_2BH_3} + \mathbf{III} \tag{24}$$

Equations (14) and (15) are analogous to those discussed for the Me_2AsNMe_2/$BH_3{\cdot}THF$ systems and account for the low-temperature formation of $(Me_2N)_2BH$ and transient MeAs(H)-and MeAs(NMe_2)-moiety-containing species. Based upon the previous work of Rheingold et al. involving the $MeAsH_2$/$MeAsI_2$ system [56] and our results from studying the $MeAsH_2$/Me_2AsNMe_2 system [57], the pathway to $(MeAs)_5$ (eqn. (16)) is very complex and facile. Any species having an $>$As(H) group in a reaction medium with an $>$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], $>$As–H bonded species undergo very facile exchange reactions with any other $>$As–H and $>$AsNMe_2 moiety-containing species. These, in turn, undergo rapid condensation/Me_2NH-elimination reactions [57] to yield intermediate $Me(H)As(AsMe)_xAs$-$(Me)NMe_2$ oligomers, which readily cyclize via Me_2NH elimination to the thermodynamically stable $(MeAs)_5$ (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 $MeAs(NMe_2)_2$, various $>$AsNMe_2 and $>$As(H) moiety-containing intermediates, and Me_2NH that influence the relative rates of consumption of $MeAs(NMe_2)_2$ and formation of $(MeAs)_5$ (eqns. (19)–(21)). The Me_2NH can also compete for the bound BH_3 in **III** and **IV** to give $Me_2NH{\cdot}BH_3$ (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 $MeAs(NMe_2)_2$ (corresponding to eqns. (15), (17), and (18)) were carried out independently to yield $(Me_2N)_2BH$. Thus, in the presence of $MeAs(NMe_2)_2$ and Me_2NH, any Me_2NBH_2 should be consumed immediately. We also propose that $Me_2NHBH_2NMe_2BH_3$ forms from the reaction of $Me_2NBH_2{\cdot}HNMe_2$ with **IV** (eqn. (24)) since $Me_2NHBH_2NMe_2BH_3$ 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, $MeAs(NMe_2)_2$ is complete consumed, and the final product mixture contains Me_2NH, $Me_2NH{\cdot}BH_3$, $(Me_2N)_2BH$, $(MeAs)_5$ and a dark red solid. The latter is analogous to the brick red oligomers that often form in the synthesis of $(MeAs)_5$ [56]. We assume that decomposition of **III** proceeds via the equation

$$\mathrm{MeAs(NMe_2{\cdot}BH_3)NMe_3 \rightarrow MeAs(H)NMe_2 + Me_2NBH_2} \tag{25}$$

with $MeAs(H)NMe_2$ and Me_2BH_2 being involved subsequently in reactions corresponding 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 $Me_2NH \cdot BH_3$ at room temperature.

By comparison, in the 1:3 system, $MeAs(NMe_2)_2$ is almost completely consumed at −80°C to give a mixture of **III**, **IV**, unreacted $BH_3 \cdot THF$, and a trace of **V**. By −70°C, decomposition of **IV** has begun and peaks assignable to **V**, Me_2NBH_2, and $MeAs(H)NMe_2 \cdot BH_3$, **VI**, are observed in the spectra. Over the next 20 degree temperature interval, μ-$Me_2NB_2H_5$ and $Me_2NH \cdot BH_3$ form; **III** and $BH_3 \cdot THF$ are consumed; spectral peaks assignable to a second As–B bonded adduct, $H_3B \cdot MeAs(H)NMe_2 \cdot BH_3$, **VII**, appear; peaks in the ^{13}C (1.40 ppm) and ^{11}B (−40.63 ppm) spectra suggest the presence of an $(MeAs)_xAs(H)Me \cdot BH_3$ 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 $(MeAs)_5$ are first observed. With increasing temperature, the intensities of the peaks associated with μ-$Me_2NB_2H_5$, $Me_2NH \cdot BH_3$, and $(MeAs)_5$ 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 $[Me_2NBH_2]_2$, **V**, $Me_2NH \cdot BH_3$, μ-$Me_2NB_2H_5$, Me_2NH, and $(MeAs)_5$. $[Me_2NBH_2]_2$ results from the dimerization of Me_2NBH_2 once $BH_3 \cdot THF$ 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 $BH_3 \cdot THF$ 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. $(MeAs)_5$ was only very slowly produced at room temperature. The final reaction products were $(MeAs)_5$, μ-$Me_2NB_2H_5$, and $Me_2NH \cdot BH_3$.

These data suggest that, in addition to reactions corresponding to eqns. (13)–(16), and (19)–(25), the following also occur when sufficient unreacted $BH_3 \cdot THF$ is present in solution.

$$MeAs(H)NMe_2 \cdot BH_3 + BH_3 \cdot THF \rightarrow H_3B \cdot MeAs(H)NMe_2 \cdot BH_3 + THF \qquad (26)$$

$$Me_2NBH_2 + H_3B \cdot MeAs(H)NMe_2 \cdot BH_3 \rightarrow \mu\text{-}Me_2NB_2H_5 + MeAs(H)NMe_2 \cdot BH_3 \qquad (27)$$

$$Me_2NH + BH_3 \cdot THF \rightarrow Me_2NH \cdot BH_3 + THF \qquad (28)$$

Thus, when $BH_3 \cdot THF$ is in a stoichiometric excess relative to the available nitrogen base sites in the aminoarsine, the additional $BH_3 \cdot THF$ minimizes the importance of eqns. (17)–(24), stabilizes the MeAs(H) intermediates as adducts **VI** and **VII**, slows down the rate of oligomerization and formation of $(MeAs)_5$ (eqn. (16)), and increases the importance of eqns. (26)–(28) in determining the relative composition of the final product mixture.

In the $MeP(NMe_2)_2$–$BH_3\cdot THF$ systems [40], the bis B–P–N–B bonded adduct, $H_3B(Me)P(NMe_2\cdot BH_3)NMe_2$, which forms regardless of the stoichiometric ratio of aminophosphine and $BH_3\cdot THF$, is stable at room temperature. At a 1:3 mol ratio, a P–B bonded adduct, $(Me_2N)_2PMe\cdot BH_3$ 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 $BH_3\cdot THF$ with $MeAs(NMe_2)_2$ 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 $(MeAs)_5$ 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 $BH_3\cdot THF$ [40].

(iii) Reactions of $As(NMe_2)_3$ with $BH_3\cdot THF$

The reactivity of $BH_3\cdot THF$ towards $As(NMe_2)_3$ was studied as a function of temperature and time at 1:1 and 1:3 $As(NMe_2)_3$:$BH_3\cdot THF$ mol ratios. For the 1:1 system, at −90°C, the formation of $(Me_2N)_3As\cdot BH_3$, **VIII**, $(Me_2N)_2AsNMe_2\cdot BH_3$, **IX**, and $Me_2NAs(NMe_2\cdot BH_3)_2$, **X**, are observed in approximately a 1:1.5:0.25 mol ratio. Some unreacted $As(NMe_2)_3$ and $BH_3\cdot THF$ remain in solution. By −70°C, all the $BH_3\cdot THF$ 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**, $Me_2NH\cdot BH_3$, and a trace of $(Me_2N)_2BH$. 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 $Me_2NH\cdot BH_3$. Upon standing overnight at room temperature, the decomposition of **IX** is complete. The product mixture in solution consists of $(Me_2N)_2BH$, $Me_2NH\cdot BH_3$, Me_2NH, unreacted $As(NMe_2)_3$ and a trace of $[Me_2NBH_2]_2$. 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 $As(NMe_2)_3$. After 5 days at room temperature, all the $As(NMe_2)_3$ is consumed, the mixture contains a 2:1 mol ratio of $(Me_2N)_2BH$ and $Me_2NH\cdot BH_3$, a trace of $(Me_2NBH_2)_2$, 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.

$$(Me_2N)_3As\cdot BH_3 \rightarrow (Me_2N)_2AsNMe_2\cdot BH_3 \qquad (29)$$

$$(Me_2N)_3As\cdot BH_3+(Me_2N)_2AsNMe_2\cdot BH_3\rightarrow Me_2NAs(NMe_2\cdot BH_3)_2 + (Me_2N)_3As \quad (30)$$

$$Me_2NAs(NMe_2\cdot BH_3)_2\rightarrow Me_2NAs(H)NMe_2\cdot BH_3+Me_2NBH_2 \quad (31)$$

$$[(Me_2N)_2AsH+Me_2NAs(H)NMe_2\cdot BH_3+As(NMe_2)_3+...] \rightarrow \text{condensed As–As bonded intermediates} \rightarrow As+Me_2NH+Me_2NH\cdot BH_3 \quad (32)$$

$$Me_2NBH_2+Me_2NH\rightarrow Me_2NBH_2\cdot HNMe_2 \quad (17)$$

$$Me_2NBH_2\cdot HNMe_2\rightarrow (Me_2N)_2BH+H_2 \quad (18)$$

$$(Me_2N)_2AsNMe_2\cdot BH_3\rightarrow (Me_2N)_2AsH+Me_2NBH_2 \quad (33)$$

$$Me_2NH+(Me_2N)_2AsNMe_2\cdot BH_3\rightarrow Me_2NH\cdot BH_3+As(NMe_2)_3 \quad (34)$$

$$Me_2NBH_2\cdot HNMe_2+As(NMe_2)_3\rightarrow Me_2NH+(Me_2N)_2AsH+(Me_2N)_2BH \quad (35)$$

$$Me_2NH\cdot BH_3+As(NMe_2)_3\rightarrow Me_2NH+(Me_2N)_2AsNMe_2\cdot BH_3 \quad (36)$$

In the 1:3 system, analogous results are obtained below −50°C. At −50°C, a small amount of μ-$Me_2NB_2H_5$ forms due to the availability of unreacted $BH_3\cdot THF$ (eqn. (8)). At −20°C, peaks assignable to $Me_2NHBH_2NMe_2BH_3$ are observed in addition to those for $(Me_2N)_2BH$ and $Me_2NH\cdot BH_3$. This suggests that, when more $BH_3\cdot THF$ is available, the $Me_2NBH_2\cdot HNMe_2$ (eqn. (17)) reacts with $BH_3\cdot THF$ (eqn. (37)).

$$Me_2NBH_2\cdot HNMe_2+BH_3\cdot THF\rightarrow Me_2NHBH_2NMe_2BH_3+THF \quad (37)$$

The final reaction mixture contains $Me_2NHBH_2NMe_2BH_3$, $Me_2NH\cdot BH_3$, $(Me_2N)_2BH$, $[Me_2NBH_2]_2$, and Me_2NH.

In the $P(NMe_2)_3$–$BH_3\cdot THF$ systems [40], the only product observed over the entire temperature range is the P–B adduct, $(Me_2N)_3P\cdot BH_3$, [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 $(Me_2N)_3As$, the N atom is more effective than the As atom in displacing the THF from the $BH_3\cdot THF$. 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 $(Me_2N)_3As$ and $BH_3\cdot THF$.

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