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NMR Studies of the Reactions of Me_2AsH with Me_2AsNMe_2 and $Me_2As\overline{NMe_2{\cdot}B}H_3$: Synthetic Routes to $Me_2AsAsMe_2$

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Me_2AsH reacts irreversibly with Me_2AsNMe_2 and $Me_2As\overline{NMe_2{\cdot}B}H_3$ to give good yields of $Me_2AsAsMe_2$. The nitrogen-containing product is Me_2NH or $Me_2NH{\cdot}BH_3$, respectively. These reactions have been followed by using multinuclear (^1H, ^{11}B, and ^{13}C) NMR spectroscopy to elucidate the respective reaction mechanisms. Although the Me_2AsH/Me_2AsNMe_2 reaction proceeds faster initially, the overall rate of reaction is slower than that for the $Me_2AsH/Me_2As\overline{NMe_2{\cdot}B}H_3$ reaction. This is a consequence of the presence of inhibiting exchange reactions in the Me_2AsH/Me_2AsNMe_2 system that are absent when Me_2AsNMe_2 and Me_2NH are bound to BH_3 in the $Me_2AsH/Me_2As\overline{NMe_2{\cdot}B}H_3$ reaction. A detailed NMR study of the exchange reactions involving the >AsN</>NH, >AsAs</>AsH, and >AsN</>AsAs< systems is also discussed with respect to the relative impact of those systems on the rate of formation of $Me_2AsAsMe_2$.

Introduction

During the past few decades numerous publications have discussed the synthetic routes to homonuclear-bonded compounds of the group 15 elements. The majority of these reports pertain to the synthesis of N–N-[1–5] and P–P-bonded[6–14] compounds. Synthetic pathways to As–As-bonded compounds have received less attention.[15–18] Recently, however there has been renewed interest[19,20] in the synthesis of novel homonuclear-bonded compounds of P, As, and Sb that contain multiple bonding between two group 15 elements.

A survey of the literature[15–18,21–25] indicates that the general synthetic routes to di- and polyarsines involve (a) the oxidation of substituted >As–H-bonded arsines,[26–28] (b) the reduction of haloarsines or As–O-bonded derivatives,[29–32] and (c) condensation reactions involving >AsH/>AsCl,[26,33–35] >AsH/>AsOAs<,[35,36] and >AsH/>AsO[37] systems. Many of these synthetic routes give low yields of the As–As-bonded compounds and/or are plagued by side products that are difficult to remove.

Very few reports have appeared in the literature concerning the mechanistic aspects of the reactions involved in the synthesis of As–As-bonded compounds. The ^1H NMR study[38,39] of the reaction of $MeAsH_2$ with $MeAsX_2$ (X = Cl, Br, I), to produce $(MeAs)_5$ indicates the reaction involves a complex series of interrelated equilibria with exchange reactions among monomers, oligomers, and polymers to yield substituted diarsines, higher polymethylpolyarsines, MeAsHX, and HX. Similar studies on the reactions of Me_2AsH with Me_2AsX (X = Cl, Br, I, CN) to yield $Me_2AsAsMe_2$ indicate that the reactions are reversible.[40] Exchange reactions, which occur through an associative intermediate, are suggested on the basis of the experimentally determined activation parameters.

During our recent study[41] on the reactivity of $BH_3{\cdot}THF$ with Me_2AsNMe_2, we observed above −10 °C the formation of $Me_2AsAsMe_2$ as a product of adduct decomposition. We postulated that the initial step in the adduct decomposition is the formation of Me_2AsH, which reacts with undecomposed adduct, $Me_2As\overline{NMe_2{\cdot}B}H_3$, to produce $Me_2AsAsMe_2$.

$$Me_2As\overline{NMe_2{\bullet}B}H_3 \rightarrow Me_2AsH + Me_2NBH_2$$

$$Me_2As\overline{NMe_2{\bullet}B}H_3 + Me_2AsH \rightarrow Me_2AsAsMe_2 + Me_2NH{\bullet}BH_3$$

Substantiation of this postulated pathway by carrying out the independent reaction of Me_2AsH with $Me_2As\overline{NMe_2{\cdot}B}H_3$ suggested that this might prove to be a useful synthetic route to di- and polyarsines.

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In this paper, we report new and convenient synthetic pathways to $Me_2AsAsMe_2$. The reactions of Me_2AsH with Me_2AsNMe_2 and $Me_2As\overline{NMe_2{\cdot}B}H_3$ are followed by multinuclear (^1H, ^{11}B, and ^{13}C) NMR spectroscopy. A detailed NMR study of the exchange reactions involving >AsN</>NH, >AsAs</>AsH, and >AsN</>AsAs< systems is also discussed with respect to the extent to which these reactions influence the rate of formation of $Me_2AsAsMe_2$.

Results and Discussion

The reactions of Me_2AsH with Me_2AsNMe_2 and $Me_2As\overline{NMe_2{\cdot}B}H_3$ in 1:1 mole ratios in toluene solution produce $Me_2AsAsMe_2$ in good yields (76% and 72%, respectively). A 40% yield of $Me_2AsAsMe_2$ has been reported previously[31] by the reaction of Me_2AsCl with Zn dust. We have found that the Me_2AsH/Me_2AsNMe_2 condensation reaction is a straightforward and convenient synthetic route for the large-scale preparation of $Me_2AsAsMe_2$ and should be applicable to the synthesis of other symmetrical diarsines. This synthetic pathway to diarsines is irreversible and does not produce undesirable side products that are difficult to remove from the product mixture.

Reaction of Me_2AsH with Me_2AsNMe_2. The reaction of an equimolar mixture of Me_2AsH with Me_2AsNMe_2 in toluene-d_8 solution was studied as a function of temperature, time, and concentration in a sealed NMR tube and monitored by ^1H and ^{13}C NMR spectroscopy. The ^1H and ^{13}C NMR spectra at −80 °C consist of peaks of low intensity assigned to $Me_2AsAsMe_2$ and Me_2NH in addition to other peaks of high intensity corresponding to starting materials. (See Experimental Section for ^1H, ^{11}B, and ^{13}C NMR assignments.)

As the temperature of the reaction mixture is raised to −45 °C, the intensity of the ^1H and ^{13}C NMR peaks associated with $Me_2AsAsMe_2$ and Me_2NH increases, the intensity of the NMR peaks assigned to Me_2AsNMe_2 and Me_2AsH decreases, and the line width of the ^1H NMR peaks due to the Me_2N moieties of Me_2AsNMe_2 and Me_2NH broadens. The latter suggests a slow exchange process on the NMR time scale that involves the $Me_2As\mathit{NMe_2}$ and $\mathit{Me_2N}H$.

With a temperature increase to −25 °C, an increased conversion to $Me_2AsAsMe_2$ and Me_2NH occurs with coalescence of the ^1H NMR peaks associated with the Me_2N moieties. This suggests a faster exchange of the Me_2N groups with increased temperature. Narrowing of the line width of the ^1H NMR peak assigned to the Me_2N group occurs with time as the reaction consumes $Me_2AsAsMe_2$ and produces more Me_2NH. After approximately 2 h, a 42% conversion to $Me_2AsAsMe_2$ and Me_2NH has occurred and the apparent rate of reaction becomes very slow. After 6 days at −25 °C (CCl_4 slush), the ^1H and ^{13}C NMR spectra indicate complete conversion. We restricted our study to a maximum temperature of −10 °C due to the low boiling point of Me_2NH.

A plot of % tetramethyldiarsine produced vs. time (Figure 1A) indicates that the rate of reaction (0.50, 1.0, and 2.0 mmol of each reactant) is temperature-dependent and, for the initial 5.0 min in the 1.0 and 2.0 mmol cases, is essentially concentration-independent. Thereafter, the rate of formation of tetramethyldiarsine is slower and is both concentration- and temperature-dependent. These data suggest that after the initial fast formation of $Me_2AsAsMe_2$ and Me_2NH the competing reaction(s) influence(s) the rate of reaction of Me_2AsH with Me_2AsNMe_2.

We investigated several potentially competing reactions (discussed below) to determine their relative importance in the overall Me_2AsH/Me_2AsNMe_2 reaction. A quantitative kinetic study could not be carried out, because of the presence of the competing equilibria in the reaction mixture.

Reaction of Me_2AsH with $Me_2As\overline{NMe_2{\cdot}B}H_3$. The reaction of Me_2AsH with $Me_2As\overline{NMe_2{\cdot}B}H_3$ (1.0 mmol of each reactant) in toluene-d_8 solution was studied as a function of temperature and time in a sealed NMR tube and monitored by ^1H, ^{11}B, and ^{13}C NMR spectroscopy. Higher concentrations of the reactants could not be used, because of the low solubility of $Me_2As\overline{NMe_2{\cdot}B}H_3$ over the temperature range studied. The ^1H, ^{11}B, and ^{13}C NMR spectra at −80 °C consist of high-intensity peaks for starting materials and very minor peaks assigned to $Me_2AsAsMe_2$ and $Me_2NH{\cdot}BH_3$. Very little change in the relative NMR peak intensities was observed when the temperature of the reaction mixture was raised from −80 to −25 °C.

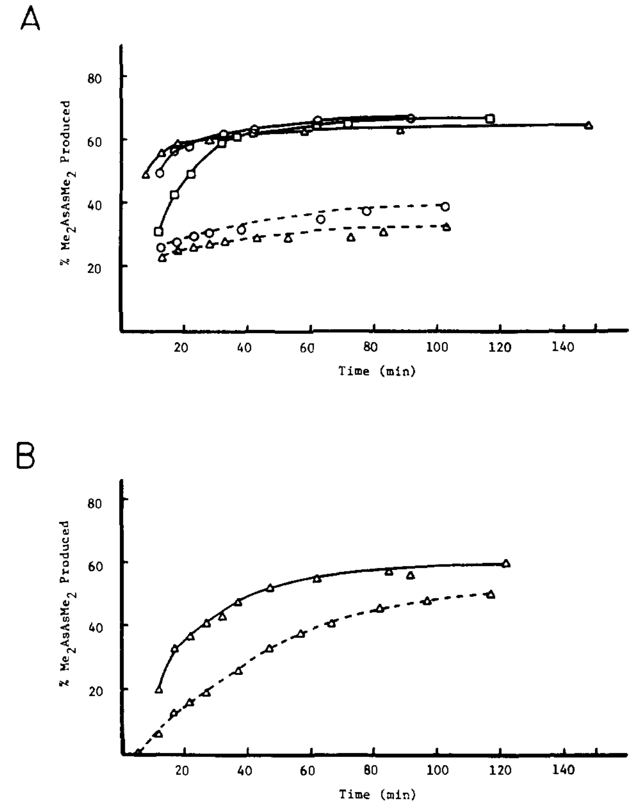

Figure 1. Percentage of $Me_2AsAsMe_2$ formed as a function of time: (A) Me_2AsH/Me_2AsNMe_2 reaction; (B) $Me_2AsH/Me_2As\overline{NMe_2{\cdot}B}H_3$ reaction. Reaction conditions: (○) 2.0, (△) 1.0, and (□) 0.50 mmol of reactants for reaction (—) at −10 °C and (--) at −25 °C.

At −25 °C, the rate of reaction was faster and the reaction proceeded smoothly. Within 2 h, a 50% conversion to $Me_2AsAsMe_2$ occurred, and after 2 days, a 65% conversion was noted. After several more days at −25 °C, the ^1H, ^{11}B, and ^{13}C NMR spectra of the reaction mixture indicated that the reaction had gone to completion. In comparison with the Me_2AsH/Me_2AsNMe_2 reaction, the absence of line broadening in the ^1H NMR spectrum of the peaks associated with the Me_2N moieties suggests that exchange involving the Me_2N moieites does not occur in the $Me_2AsH/Me_2As\overline{NMe_2{\cdot}B}H_3$ reaction. This is probably a consequence of the preferential binding of Me_2NH to BH_3.

The plot of % $Me_2AsAsMe_2$ produced vs. time (Figure 1B) indicates that the rate of reaction is temperature-dependent. Although the initial rate of formation of $Me_2AsAsMe_2$ is slower, the overall rate of reaction is faster than that observed for the Me_2AsH/Me_2AsNMe_2 reaction. The slower initial rate is attributed to the lower basicity of the nitrogen in $Me_2As\overline{NMe_2{\cdot}B}H_3$ as compared to that in Me_2AsNMe_2. The faster overall rate of reaction is a consequence of the absence of some inhibiting exchange reactions, since Me_2NH and Me_2AsNMe_2 are bound to BH_3 in $Me_2NH{\cdot}BH_3$ and $Me_2As\overline{NMe_2{\cdot}B}H_3$, respectively. The study was restricted to a maximum temperature of −10 °C due to the decomposition of $Me_2As\overline{NMe_2{\cdot}B}H_3$ above −10 °C.[41]

Factors Influencing the Rate of the Me_2AsH/Me_2AsNMe_2 Reaction. Several mixtures of potential reactants in toluene-d_8 solution were monitored to determine the extent to which various inhibiting exchange reactions involving the reactant and the product molecules might influence the overall rate of the Me_2AsH/Me_2AsNMe_2 reaction. The ^1H and ^{13}C NMR spectra of an equimolar mixture of $Me_2AsAsMe_2$ and Me_2NH show only peaks assignable to $Me_2AsAsMe_2$ and Me_2NH throughout the entire temperature range of −80 to −10 °C. Thus unlike the

$$Me_2AsCl + Me_2AsH \rightleftharpoons Me_2AsAsMe_2 + HCl$$

reaction where the reversibility of the reaction plays an important role in the synthesis of $Me_2AsAsMe_2$,[40] the

$$Me_2AsH + Me_2AsNMe_2 \rightarrow Me_2AsAsMe_2 + Me_2NH$$

reaction is irreversible over the temperature and concentration conditions of our study.

The broadening of the peaks assigned to $Me_2AsN\mathit{Me}_2$ and Me_2NH in the ^1H NMR spectrum suggests that exchange of Me_2N groups between Me_2AsNMe_2 and Me_2NH, i.e. self-transamination, occurs in the Me_2AsH/Me_2AsNMe_2 reaction. This is not unexpected, since transamination reactions are a known synthetic pathway to dialkylamino-substituted arsines.[42,43] Alder and Kober[44] have established the dimethylamino group exchange in the Me_2NH/Me_2AsNMe_2 system through NMR studies involving isotopic labeling. An equimolar mixture of Me_2AsNMe_2 and Me_2NH in toluene-d_8 solution was monitored as a function of temperature (−80 to −10 °C), and concentration by using ^1H and ^{13}C NMR spectroscopy to establish the importance of transamination in influencing the rate of formation of $Me_2AsAsMe_2$ and Me_2NH in the Me_2AsH/Me_2AsNMe_2 reaction. The results of this study indicate minimal Me_2N exchange below −60 °C, increasing exchange with increasing temperature, fast exchange at −10 °C, and reversibility of the transamination reaction under our reaction conditions. A concentration study establishes that the exchange rate is concentration-dependent. Thus self transamination is an important contributing factor in slowing down the rate of formation of $Me_2AsAsMe_2$ in the Me_2AsH/Me_2AsNMe_2 reaction when the reaction mixture contains appreciable concentrations of Me_2AsNMe_2 and Me_2NH.

The possibility of exchange between Me_2AsH and $Me_2AsAsMe_2$ was investigated as a function of temperature (−80 to −10 °C) by monitoring the ^1H NMR spectra of an equimolar ratio of $Me_2AsAsMe_2$ and Me_2AsH in toluene-d_8 solution. The ^1H NMR spectra undergo no change over the entire temperature range. These data suggest either no exchange or very slow exchange on the NMR time scale for this system. Because of the indistinguishability of the reactants and the products, the information concerning slow exchange could not be obtained from the $Me_2AsH/Me_2AsAsMe_2$ system. Thus we investigated the $Me_2AsH/Et_2AsAsEt_2$ system to determine if slow exchange occurs on the NMR time scale. At −80 °C, the ^1H and ^{13}C NMR spectra consist of high-intensity peaks assignable to Me_2AsH and $Et_2AsAsEt_2$ and very low intensity peaks assignable to $Me_2AsAsEt_2$ and Et_2AsH. At −40 °C, the peaks are now of comparable intensity and a new peak assignable to $Me_2AsAsMe_2$ is observed. Within $2^1/_2$ h at −10 °C, an equilibrium is established between the $Et_2AsAsEt_2/Me_2AsH$ and $Me_2AsAsEt_2/Me_2AsAsMe_2/Et_2AsH$ systems as indicated by no further significant change in the intensities of the peaks over the next 20 days. The ^1H NMR spectral data indicate the presence of 41% $Et_2AsAsEt_2$, 9% Me_2AsH, 18% $Me_2AsAsEt_2$, 26% Et_2AsH, and 5% $Me_2AsAsMe_2$ in the reaction mixture. Thus the exchange reaction involving Me_2AsH and $Et_2AsAsEt_2$ attains equilibrium rapidly, but the exchange process is slow on the NMR time scale.

The formation of $Me_2AsAsMe_2$ from the reaction of $Et_2AsAsEt_2$ with Me_2AsH suggests that $Me_2AsAsEt_2$ can undergo self-exchange with symmetrization and/or participate in an exchange process with Me_2AsH. To determine if diarsines undergo self-exchange of R_2As moieites, an equimolar mixture of $Et_2AsAsEt_2$ and $Me_2AsAsMe_2$ in toluene-d_8 solution was monitored by using ^1H and ^{13}C NMR spectroscopy. The spectral data indicate an exchange of the R_2As groups to give an equilibrium mixture of $Me_2AsAsMe_2$, $Et_2AsAsEt_2$, and $Me_2AsAsEt_2$ with 25%, 25%, and 50% yields at room temperature (as obtained from ^1H NMR peak intensity data), respectively.

The possibility of exchange involving $Me_2AsAsMe_2$ and Me_2AsNMe_2 was studied by monitoring the ^1H NMR spectra of a 1:1 mole ratio of these species in a toluene-d_8 solution as a function of temperature (−80 to −10 °C) and time. Only sharp peaks assignable to $Me_2AsAsMe_2$ and Me_2AsNMe_2 were observed over the entire temperature range. These results indicate that any exchange must be very slow on the NMR time scale for this system. Since the products and the reactants are indistinguishable, we investigated the $Et_2AsAsEt_2/Me_2AsNMe_2$ system as a function of temperature (−80 to −10 °C) and time by using equimolar ratios of the reactants in a toluene-d_8 solution. From −80 to −30 °C the ^{13}C NMR spectrum contains only peaks associated with Me_2AsNMe_2 and $Et_2AsAsEt_2$. Thus exchange of Et_2As and Me_2As groups does not occur over this temperature range. At −25 °C, very low intensity peaks corresponding to $Me_2AsAsEt_2$ and Et_2AsNMe_2 appear. At −10 °C, the intensities of these peaks increase with time as those of the starting material peaks decrease. After 5 h at this temperature, a peak assignable to $Me_2AsAsMe_2$ appears and increases in intensity with time. Thus the unsymmetrical diarsine undergoes symmetrization. After 5 days at −10 °C, the reaction reaches equilibrium. The ^1H NMR spectral data at equilibrium indicate the presence of 18% Me_2AsNMe_2, 34% $Et_2AsAsEt_2$, 24% Et_2AsNMe_2, 20% $Me_2AsAsEt_2$, and 4% $Me_2AsAsMe_2$ in the reaction mixture. This study suggests the following equilibria are established in solution:

$$Et_2AsAsEt_2 + Me_2AsNMe_2 \rightleftharpoons Et_2AsNMe_2 + Me_2AsAsEt_2$$

$$2Me_2AsAsEt_2 \rightleftharpoons Et_2AsAsEt_2 + Me_2AsAsMe_2$$

Since the line widths of all the peaks in the ^1H and ^{13}C NMR spectra over the entire temperature range remain very narrow, we conclude that the exchange of Me_2As and Et_2As moieties is very slow on the NMR time scale.

Our study indicates that the following exchange reactions can play a role in influencing the overall rate of the Me_2AsH/Me_2AsNMe_2 reaction:

$$Me_2AsNMe_2 + \mathbf{Me_2}NH \rightleftharpoons Me_2AsN\mathbf{Me_2} + Me_2NH \quad (1)$$

$$Me_2AsAsMe_2 + \mathbf{Me_2As}H \rightleftharpoons Me_2AsAs\mathbf{Me_2} + Me_2AsH \quad (2)$$

$$Me_2AsAsMe_2 + \mathbf{Me_2AsAsMe_2} \rightleftharpoons Me_2As\mathbf{AsMe_2} + \mathbf{Me_2As}AsMe_2 \quad (3)$$

$$Me_2AsAsMe_2 + \mathbf{Me_2As}NMe_2 \rightleftharpoons Me_2As\mathbf{AsMe_2} + Me_2AsNMe_2 \quad (4)$$

Although the exchange processes represented by eq 2–4 undoubtedly occur in the reaction solution, these processes appear to be slow on the NMR time scale and thus of minor importance in influencing the overall rate of reaction. The NMR data suggest that the exchange process involving the Me_2N group in Me_2AsNMe_2 and Me_2NH represented by eq 1 plays the most significant role in influencing the rate of formation of $Me_2AsAsMe_2$. Although this self-transamination process is of minor importance in influencing the rate of formation of $Me_2AsAsMe_2$ at low concentrations of Me_2NH (initial stages of the Me_2AsH/Me_2AsNMe_2 reaction), it is of prime importance at higher concentrations of Me_2AsNMe_2 and Me_2NH (>20% conversion to $Me_2AsAsMe_2$). This is further demonstrated by the fact that the rate of formation of $Me_2AsAsMe_2$ in the reaction containing 0.50 mmol of each reactant is quite fast within the first 30 min (as compared to the first 5 min in the 1.0 and 2.0 mmol reactions) even though the overall rate of reaction is found to be very slow in all three concentration studies.

Factors Influencing the Rate of the $Me_2AsH/Me_2\overline{AsNMe_2{\cdot}B}H_3$ Reaction. The $Me_2AsH/Me_2\overline{AsNMe_2{\cdot}B}H_3$ reaction is irreversible over the temperature range of our study. Since the Me_2NH is bound to the BH_3 upon formation of $Me_2AsAsMe_2$, the exchange process represented by eq 1 cannot occur. The ^1H, ^{11}B, and ^{13}C NMR spectra at −10 °C of an equimolar mixture of $Et_2AsAsEt_2$

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and $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$ in toluene-d_8 solution show only peaks assignable to $\mathrm{Et_2AsAsEt_2}$ and $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$ even when the reaction is maintained at −10 °C overnight. Thus the exchange process represented by eq 4 cannot occur. On the other hand, those exchange reactions indicated by eq 2 and 3 can occur in solution and can influence the rate of formation of $\mathrm{Me_2AsAsMe_2}$, but are of minor importance.

All the exchange processes that have been studied probably involve the formation of a four-centered intermediate,[14,42,45] which undergoes bond making and breaking to give the observed equilibrium mixture of the exchange products. Undoubtedly, the relative basicity of the group 15 atom, As and/or N, in these arsines influences the ease of formation of the four-centered intermediate and the resultant bond fomration and disruption.

Presently we are investigating in detail the steric and electronic effects of various substitutents on the ease of the exchange of $\mathrm{R_2As}$ moieties in $\mathrm{R_2AsAsR_2/R'_2AsAsR'_2}$, $\mathrm{R_2AsAsR_2/R'_2AsH}$, and $\mathrm{R'_2AsAsR'_2/R_2AsNMe_2}$ systems.

Experimental Section

Standard high-vacuum-line techniques and a Vacuum Atmospheres Model HE-43 Dri-lab equipped with a Model HE-493 Dri-Train were used for storing and handling of all compounds. $\mathrm{Me_2NH}$ (Matheson Gas products) was dried over sodium metal and was distilled on the vacuum line prior to use. THF-d_8, toluene-d_8 and $\mathrm{Me_4Si}$ were purchased from Aldrich Chemical Co. and were stored over molecular sieves. Diborane(6),[46] $\mathrm{Me_2AsNMe_2}$ (108 °C),[47] $\mathrm{Me_2AsAsMe_2}$ (60 °C/25 torr),[31] $\mathrm{Me_2AsH}$ (36 °C),[48] $\mathrm{Me_2AsCl}$ (106 °C),[49] $\mathrm{Et_2AsCl}$ (73–76 °C/73 torr),[50] and $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$[41] were synthesized by previously reported methods. $\mathrm{Et_2AsAsEt_2}$ (185 °C) was synthesized by the reaction of $\mathrm{Et_2AsCl}$ with Zn dust.[31] The purity of the compounds was checked by NMR spectroscopy prior to use. ^{1}H, ^{11}B and ^{13}C NMR spectra were recorded on a Nicolet 300-MHz multinuclear FT NMR spectrometer operating at 300.1, 96.3, and 75.4 MHz, respectively. Chemical shift values for the ^{11}B resonance were measured relative to that of $\mathrm{BF_3{\cdot}OEt_2}$, the high-field shift being negative. ^{1}H and ^{13}C NMR chemical shifts were measured with respect to tetramethylsilane as an internal reference. All NMR spectra were obtained in toluene-d_8 as solvent. The integration of the peaks in the ^{1}H NMR spectra of a sample was done with respect to the constant integration value of $\mathrm{Me_4Si}$ throughout a given study. See spectral data below for all NMR assignments.

Synthesis of $\mathrm{Me_2AsAsMe_2}$ from the Reaction of $\mathrm{Me_2AsNMe_2}$ with $\mathrm{Me_2AsH}$. A 20.0-mmol sample of dimethylarsine was condensed onto 20 mL of a toluene solution containing 20.0 mmol (3.0 g) of (dimethylamino)dimethylarsine at −196 °C by using standard vacuum-line techniques. The reaction was slowly warmed to 10 °C and stirred for 2 h. The toluene and dimethylamine were fractionally distilled under reduced pressure in the vacuum line. The product (3.9 g or 93% yield) thus obtained was purified on a spinning band-distillation column. The fraction boiling at 60 °C/25 torr was collected (yield 3.2 g or 76% yield).

Synthesis of $\mathrm{Me_2AsAsMe_2}$ from the Reaction of $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$ with $\mathrm{Me_2AsH}$. A 5.0-mmol sample of $\mathrm{B_2H_6}$ was condensed onto a mixture of toluene (15 mL) and THF (2 mL) maintained at −196 °C by using standard vacuum-line techniques. The reaction mixture was warmed to room temperature. The vessel was recooled to −196 °C, and 1.5 g (10.0 mmol) of $\mathrm{Me_2AsNMe_2}$, previously dissolved in 2 mL of toluene, was condensed into it. The solution was stirred at 0 °C for 1 h. A 10.0-mmol sample of $\mathrm{Me_2AsH}$ was condensed onto the frozen mixture at −196 °C. The mixture was warmed to 0 °C and stirred for 4 hrs. Trap-to-trap distillation gave crude $\mathrm{Me_2AsAsMe_2}$ in the −10 °C (ethylene glycol slush) trap. Fractional distillation on a spinning band column gave 1.5 g (72% yield) of $\mathrm{Me_2AsAsMe_2}$ boiling at 60 °C/25 torr.

Reactions of $\mathrm{Me_2AsNMe_2}$ with $\mathrm{Me_2AsH}$, $\mathrm{Me_2NH}$, $\mathrm{Me_2AsAsMe_2}$, and $\mathrm{Et_2AsAsEt_2}$. The reactions of $\mathrm{Me_2AsNMe_2}$ with equimolar amounts of $\mathrm{Me_2AsH}$ (0.5, 1.0, and 2.0 mmol), $\mathrm{Me_2NH}$ (0.5 and 1.0 mmol), $\mathrm{Me_2AsAsMe_2}$ (1.0 mmol), and $\mathrm{Et_2AsAsEt_2}$ (1.0 mmol) in toluene-d_8 were carried out by using the following general procedure. The stochiometric amount of the less volatile arsine dissolved in toluene-d_8 and a drop of $\mathrm{Me_4Si}$ (total volume 3.0 mL) were added into the NMR tube (10 mm × 22.5 cm, Pyrex) equipped with a greaseless vacuum stopcock. The tube was degassed by using standard vacuum-line techniques. At −196 °C, an equimolar amount of the more volatile arsine was condensed into the NMR tube. The tube was sealed, agitated gently at −95°C (toluene slush), and inserted into the precooled (−90 °C) probe of NMR spectrometer. The reaction was then followed at the selected temperature or over the temperature range of −80 to −10 °C by recording ^{1}H and/or ^{13}C NMR spectra as a function of time.

Reactions of $\mathrm{Me_2AsAsMe_2}$ with $\mathrm{Me_2NH}$, $\mathrm{Me_2AsH}$, and $\mathrm{Et_2AsAsEt_2}$ and of $\mathrm{Et_2AsAsEt_2}$ with $\mathrm{Me_2AsH}$ and $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$. The reactions of $\mathrm{Me_2AsAsMe_2}$ with equimolar amounts of $\mathrm{Me_2NH}$ (1.0 mmol), $\mathrm{Me_2AsH}$ (1.0 mmol), and $\mathrm{Et_2AsAsEt_2}$ (0.50 mmol) and of $\mathrm{Et_2AsAsEt_2}$ with equimolar amounts of $\mathrm{Me_2AsH}$ (1.0 mmol) and $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$ (1.0 mmol) were carried out in toluene-d_8 by using the above-described procedure.

Reaction of $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$ with $\mathrm{Me_2AsH}$. The reaction of 1.0 mmol of $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$ with 1.0 mmol of $\mathrm{Me_2AsH}$ in toluene-d_8 (total volume 3.0 mL) was carried out by using the following procedure. The desired stoichiometric amount of $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$ was synthesized in the NMR tube according to the procedure previously described in the literature.[41] An equimolar quantity of $\mathrm{Me_2AsH}$ was condensed onto the frozen toluene-d_8 solution (−196 °C) of $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$. The tube was sealed, agitated gently at −95 °C, and inserted into the precooled (−90 °C) probe of the NMR spectrometer. The reaction was then followed at selected temperatures in the −80 to −10 °C range by monitoring the ^{1}H, ^{13}C, and ^{11}B resonances as a function of time.

^{1}H NMR Spectral Data. The following −10 °C ^{1}H NMR spectral data (δ values in ppm) were determined independently on prepurified or synthesized compounds. $\mathrm{Me_2NH}$: $\delta_\mathrm{H} = 2.17$. $\mathrm{Me_2NH{\cdot}BH_3}$: $\delta_\mathrm{H} = 1.96$ ($\mathrm{Me_2N}$, doublet), 3.99 (NH, $^3J_\mathrm{HCNH} = 5.73$ Hz). $\mathrm{Me_2AsH}$: $\delta_\mathrm{H} = 0.77$ ($\mathrm{Me_2As}$, doublet, $^3J_\mathrm{HH} = 7.0$ Hz), 2.39 (AsH, septet, $^3J_\mathrm{HH} = 6.9$ Hz). $\mathrm{Me_2AsNMe_2}$: $\delta_\mathrm{H} = 0.79$ ($\mathrm{Me_2As}$), 2.42 ($\mathrm{Me_2N}$). $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$: $\delta_\mathrm{H} = 0.82$ ($\mathrm{Me_2As}$), 2.09 ($\mathrm{Me_2N}$). $\mathrm{Et_2AsH}$: $\delta_\mathrm{H} = 1.08$ (triplet, $^3J_\mathrm{HH} = 7.56$ Hz, $\mathrm{C\mathit{H}_3CH_2As}$), 1.19–1.55 (complex multiplet, $\mathrm{CH_3C\mathit{H}_2As}$), 2.51 (AsH, $^3J_\mathrm{HH} = 7.56$ Hz), $\mathrm{Et_2AsNMe_2}$: $\delta_\mathrm{H} = 1.08$ ($\mathrm{C\mathit{H}_3CH_2As}$, multiplet), 1.45 ($\mathrm{CH_3C\mathit{H}_2As}$, multiplet), 2.56 ($\mathrm{Me_2N}$). $\mathrm{Me_2AsAsMe_2}$: $\delta_\mathrm{H} = 0.96$. $\mathrm{Me_2AsAsEt_2}$: $\delta_\mathrm{H} = 1.01$ ($\mathrm{Me_2As}$), 1.13 ($\mathrm{C\mathit{H}_3CH_2As}$, $^3J_\mathrm{HH} = 7.70$ Hz), 1.48 ($\mathrm{CH_3C\mathit{H}_2As}$). $\mathrm{Et_2AsAsEt_2}$: $\delta_\mathrm{H} = 1.16$ ($\mathrm{CH_3C\mathit{H}_2As}$, $^3J_\mathrm{HH} = 7.70$ Hz), 1.54 ($\mathrm{CH_3C\mathit{H}_2As}$).

^{11}B NMR Spectral Data. The following −10 °C ^{11}B NMR data (δ values in ppm) were determined independently in this laboratory on the following prepurified or synthesized compounds. $\mathrm{Me_2NH{\cdot}BH_3}$: $\delta_\mathrm{B} = -14.05$ ($^1J_\mathrm{BH} = 97.7$ Hz). $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$: $\delta_\mathrm{B} = -11.36$ ($^1J_\mathrm{BH} = 98.7$ Hz).

^{13}C NMR Spectral Data. The following −10 °C ^{13}C NMR data (δ values in ppm) were determined independently in this laboratory on the following prepurified or synthesized compounds. $\mathrm{Me_2NH}$: $\delta_\mathrm{C} = 38.87$ ($^1J_\mathrm{CH} = 131.9$ Hz, $^3J_\mathrm{CH} = 6.0$ Hz). $\mathrm{Me_2NH{\cdot}BH_3}$: $\delta_\mathrm{C} = 43.82$ ($^1J_\mathrm{CH} = 138.7$ Hz, $^{2,3}J_\mathrm{CH} = 4.6$ Hz). $\mathrm{Me_2AsH}$: $\delta_\mathrm{C} = 1.43$ ($^1J_\mathrm{CH} = 132.5$ Hz, $^{2,3}J_\mathrm{CH} = 3.0$ Hz). $\mathrm{Et_2AsH}$: $\delta_\mathrm{C} = 10.96$ ($\mathrm{C\mathit{H}_3CH_2As}$), 13.82 ($\mathrm{CH_3C\mathit{H}_2As}$). $\mathrm{Me_2AsNMe_2}$: $\delta_\mathrm{C} = 9.70$ ($\mathrm{Me_2As}$, $^1J_\mathrm{CH} = 130.6$ Hz, $^3J_\mathrm{CH} = 4.0$ Hz), 41.92 ($\mathrm{Me_2N}$, $^1J_\mathrm{CH} = 132.7$ Hz, $^3J_\mathrm{CH} = 5.3$ Hz). $\mathrm{Me_2As\overline{NMe_2{\cdot}B}H_3}$: $\delta_\mathrm{C} = 12.63$ ($\mathrm{Me_2As}$, $^1J_\mathrm{CH} = 132.7$ Hz), 47.76 ($\mathrm{Me_2N}$, $^1J_\mathrm{CH} = 138.4$ Hz). $\mathrm{Et_2AsNMe_2}$: $\delta_\mathrm{C} = 10.48$ ($\mathrm{C\mathit{H}_3CH_2As}$, $^1J_\mathrm{CH} = 126.5$ Hz), 19.45 ($\mathrm{CH_3C\mathit{H}_2As}$, $^1J_\mathrm{CH} = 130.8$ Hz), 42.56 ($\mathrm{Me_2N}$, $^1J_\mathrm{CH} = 132.5$ Hz, $^3J_\mathrm{CH} = 5.2$ Hz). $\mathrm{Me_2AsAsMe_2}$: $\delta_\mathrm{C} = 5.94$ ($^1J_\mathrm{CH} = 132.6$ Hz). $\mathrm{Me_2AsAsEt_2}$: $\delta_\mathrm{C} = 6.15$ ($\mathrm{Me_2As}$, $^1J_\mathrm{CH} = 132.7$ Hz, $^3J_\mathrm{CH} = 4.2$ Hze, 12.63 ($\mathrm{C\mathit{H}_3CH_2As}$, $^1J_\mathrm{CH} = 125.6$ Hz, $^3J_\mathrm{CH} = 3.5$ Hz), 15.15 ($\mathrm{CH_3C\mathit{H}_2As}$, $^1J_\mathrm{CH} = 132.3$ Hz). $\mathrm{Et_2AsAsEt_2}$: $\delta_\mathrm{C} = 12.80$ ($\mathrm{C\mathit{H}_3CH_2As}$, $^1J_\mathrm{CH} = 125.8$ Hz, $^2J_\mathrm{CH} = 3.6$ Hz), 14.63 ($\mathrm{CH_3C\mathit{H}_2As}$, $^1J_\mathrm{CH} = 132.4$ Hz, $^2J_\mathrm{CH} = 4.1$ Hz).

Registry No. $\mathrm{Me_2AsAsMe_2}$, 471-35-2; $\mathrm{B_2H_6}$, 19287-45-7; $\mathrm{Me_2AsH}$, 593-57-7; $\mathrm{Me_2AsNMe_2}$, 30880-19-4.

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