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Reactions of Me_3N with GeH_3Br: Evidence for Stabilized Germanium Dihydride Species

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Abstract

Bromogermane (GeH_3Br) and Me_3N (1:1 mole ratio) reaction at -78 °C yields $Me_3N \cdot GeH_3Br$ (1). 1 with H_2O or MeOH yields $(GeH_3)_2O$ or $MeOGeH_3$, respectively. 1 with a one molar excess of Me_3N forms $(Me_3N)_2GeH_3Br$ (2). Thermal decomposition of 2 produces mainly Ge_3H_8 (25–30%) and Me_3NHBr. GeH_3Br with excess Me_3N in Et_2O at 0 °C yields Me_3NHBr and a species in solution formulated as Me_3NGeH_2 (3). Decomposition of 3 in the presence of Me_3GeH or Me_2GeH_2 results in small quantities of $Me_3Ge_2H_3$ or $Me_2Ge_2H_4$, respectively. Above -63 °C, solid 1 undergoes intramolecular rearrangement to a product characterized as $Me_3NHBr \cdot 1/x(GeH_2)_x$ (4), a material which contains stabilized GeH_2 units. The characterization of 1–4 based on their spectral properties and reactivity towards B_2H_6 and/or HBr, and their potential in further germane syntheses, are discussed.

Introduction

The existence of germylenes (GeX_2; X = halogen, aryl, and alkyl) stabilized by coordination to bases [1] or to metals and bases [2] is well established. Germanium dihydride $(GeH_2)_x$, in the condensed phase has been reported as an intermediate or product in Ge_2H_6 [3] or $NaGeH_3$–PhBr [4] in liquid NH_3, R_3N–GeH_3Cl [5], LiX catalyzed decomposition of Ge_2H_6 [6], $KGeH_3BH_3$ [7] thermolysis, or GeH_3Cl–NH_3 [8] reactions [7–12]; however, reports of its properties vary. No clear evidence for monomeric GeH_2 other than in the gaseous phase [9–13] has appeared. Since GeH_2, $(GeH_2)_x$, or its complexes could be important in the synthesis of new germane polymers or germanium subhydrides (e.g. $GeH_{<1}$) for use as electronic materials, we have undertaken studies of its synthesis in the condensed phase. Now, in the GeH_3Br–Me_3N reaction system, we have found evidence for novel stabilized $(GeH_2)_x$ species. Our studies are reported below.

Experimental

Apparatus and Materials

All manipulations were carried out in standard vacuum lines or under a N_2 atmosphere [14]. ^1H NMR spectra were obtained with a Varian A-60A spectrometer. δ values were measured relative to Me_4Si; $+\delta$ values are downfield from the standard. Infrared and mass spectra were obtained using Beckman Model 4250 and Varian MAT CH-5 spectrometers, respectively.

Bromogermane [15], Me_2GeH_2 [16, 17], Me_3GeH [16, 18], B_2H_6 [19] and DCl [20] were prepared and purified as described previously. Me_3GeBr (Alfa Inorganics) was purified by fractional condensation. Me_2O and diglyme were distilled from $LiAlH_4$. Acetonitrile (Baker) and Me_3N (Matheson Gas) were distilled from P_4O_{10}. Deuterium oxide (>99.8% D. Mallinckrodt) and MeOH (Fischer, reagent) were used as obtained.

Reaction products from reactions below were identified by comparison of either their IR, NMR or mass spectra with published spectra.

Reactions of Me_3N with GeH_3Br

$Me_3N \cdot GeH_3Br$ (1)

Me_3N (0.117–0.135 mmol) was condensed onto GeH_3Br (0.213 mmol) at -196 °C. The mixture was warmed to -78 °C, mixed, and then warmed to -63 °C. A white solid formed immediately. Materials volatile at -63 °C were removed and measured. Typically, the Me_3N:GeH_3Br reactant ratio ranged from 1.09–0.97:1.00. In reactions involving Me_3N:GeH_3Br reactant ratios >1, small quantities (2–8% of total Ge) of GeH_4 [21], Ge_2H_6 [22, 23] and Ge_3H_8 [23, 24] formed also. Under analogous conditions, but in Me_2O solvent, identical reactant combination was observed but with less GeH_4, Ge_2H_6, or Ge_3H_8 evolution.

$(Me_3N)_2GeH_3Br$ (2)

Me_3N (0.5 mmol) was condensed onto 1 (typically, 0.100–0.145 mmol) and allowed to stand at -78 °C. After 5–14 h, excess Me_3N was removed and

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measured. The **1**:Me_3N consumed ranged from 1.0–1.05:1.00, consistent with formation of $(Me_3N)_2$-GeH_3Br (**2**).

B_2H_6 at -63 °C did not react with **2**. A 0.05 mmol sample of **2** reacted with excess HBr at -63 °C to form GeH_3Br (0.023 mmol) and traces of Ge_2H_6 and Ge_3H_8. Thermolysis of **2** at 25 °C to 80 °C produces Me_3NHBr, high yields of Ge_3H_8 (25–30%) along with H_2 and traces of GeH_4 and Ge_2H_6.

Excess Me_3N: Me_3NGeH_2 (3)

Typically, Me_3N (3–20 mmol) was allowed to react at temperatures of -78 to 0 °C with a GeH_3Br (0.10–0.41 mmol)–diglyme (3.0–4.0 ml) solution. The solution turned bright yellow and a white precipitate formed. The solution (**3**) was filtered at 0 °C. The solid was extracted with H_2O and found to contain typically 92–95% of the expected Me_3NHBr. Solution **3**, transferred at 0 °C to an NMR tube, showed only resonances due to Me_3N.

Excess HBr (3–5 mmol) was condensed onto filtrate **3** and the solution was warmed to 25 °C. The yellow solution immediately turned colorless. Unreacted HBr, GeH_3Br (typically 12–22% of initial Ge) and MeBr (0.2–0.3 mmol) were separated from the diglyme by fractional condensation. In control experiments, HBr reacted with diglyme to yield comparable amounts of MeBr under analogous reaction time and temperature conditions. No MeBr formed in a 1 h reaction of HBr with Me_3NHBr.

Solutions of **3** were prepared as above, with the addition that a 10–30 fold excess of Me_2GeH_2 or Me_3GeH was dissolved in the initial diglyme solution. The stirred solutions were warmed to 0 °C (0.3–2 h) and 25 °C (0.5–17 h). The volatile products included GeH_4 (2–10%), Ge_3H_8 (14–40%), traces of Ge_4H_{10} and $Me_2Ge_2H_4$ (with Me_2GeH_2 coreactant) and $Me_3Ge_2H_3$ (with Me_3GeH coreactant).

GeH_3Br–excess Me_3N reactions were carried out as above, except that Me_2O replaced diglyme as solvent. The reaction solution was filtered at -78 °C and the yellow solution was evaporated to dryness *in vacuo*. The yellow solid obtained was unreactive towards H_2O and yielded only traces of GeH_3Cl and Ge_3H_8 upon treatment with excess HCl at 25 °C.

Samples of neat GeH_3Br (0.12 mmol) and Me_3N (*ca.* 8 mmol) were allowed to warm to -100 °C in the probe of the ^1H NMR spectrometer. Between -80 and -40 °C, weak resonances at $\delta 3.65$ ppm (area 1) and $\delta 1.27$ ppm (area 3) relative to internal Me_3N were observed. Above -40 °C these disappeared and only the Me_3N and Me_3NH^+ resonances remained.

Gaseous phase reactions

Equimolar quantities of GeH_3Br and Me_3N (at 50 to 250 torr) were placed in separate bulbs of a double-bulb gas mixing apparatus at 23 to 90 °C. Opening a stopcock between bulbs allowed the reactants to mix. A volatile white solid formed immediately. Upon standing, the solid became nonvolatile, turned yellow, and slowly evolved GeH_4, Ge_3H_8, and traces of Ge_2H_6 and Ge_4H_{10}.

Reactions of $Me_3N \cdot GeH_3Br$ (1)

With HBr and/or B_2H_6

Samples of $Me_3N \cdot GeH_3Br$ (**1**) (0.18–0.35 mmol), prepared at -78 °C, were allowed to react with excess HBr or B_2H_6 as shown in Table I (experiments 1 and 2). After reaction, products were removed and analyzed. Reactions with HBr and B_2H_6 yielded Me_3NHBr and Me_3NBH_3 [25], respectively, GeH_3Br and traces of germanes.

TABLE I. Reaction of 1:1 Me_3N–GeH_3Br Complex with HBr and/or B_2H_6

Experiment	Complex history[a] temperature (°C)	Complex history[a] time (h)	Acid	GeH_3Br product yield; % of Ge in initial Me_3NGeH_3Br
1	-78	1.0	HBr	97.8
2	-78	1.0	B_2H_6	92.5
3	-63	1.0	HBr	98.6
4	-63	1.0	B_2H_6	79.5
5	-23	0.5	B_2H_6	58
			HBr	23
6	23	4.0	B_2H_6	0
			HBr	<1

[a] $Me_3N \cdot GeH_3Br$ prepared at -78 °C, then warmed to the temperature for the time shown.

Thermolysis

Samples of **1** were allowed to warm to -63, -23 or 23 °C for times as shown in Table I (exps. 3–6). Samples were then treated at -78 °C with HBr or B_2H_6 followed by HBr. As above, Me_3NBH_3 along with GeH_3Br and traces of germanes formed. The percent GeH_3Br produced in each case is given in the Table. Intractable nonvolatile residues left after reaction in experiments 3–6 were not analyzed further.

1 (0.11 mmol, prepared at -78 °C) was warmed to -23 °C during 4 h in the presence of Me_3GeH (3.5 mmol). Traces of GeH_4, Ge_2H_6, and Ge_3H_8 and unreacted Me_3GeH were obtained.

With H_2O or MeOH

Water (0.051 mmol) was condensed onto **1** (0.135 mmol, prepared at -78 °C) and the mixture was allowed to warm to -63 °C. After 3 h, H_2O was consumed and $(GeH_3)_2O$ [26] (0.051 mmol) and Me_3NHBr were formed exclusively. From a **1**–D_2O reaction, $(GeH_3)_2O$ and Me_3NDBr were obtained quantitatively. The $(GeH_3)_2O$ showed no Ge–D IR spectral absorption.

MeOH (0.07 mmol) and **1** (0.108 mmol) were allowed to react at −63 °C. After 6 h, $MeOGeH_3$ [27] (0.064 mmol) was recovered.

Synthesis of $Me_3NHBr \cdot 1/x(GeH_2)_x$ (4)

Solid **1**, prepared in Me_2O at −78 °C, was warmed to 25 °C *in vacuo* during 15 min in the dark. Traces of GeH_4, Ge_2H_6, Ge_3H_8 and GeH_3Br (<5% of total germanium) evolved. The resulting solid **4** was pure white and non-volatile.

^1H NMR spectra of **4** could not be obtained owing to the insolubility of **4** in solvents in which it did not decompose, e.g. CCl_4, C_6H_6, ethers and hexane.

Freshly prepared samples of **4** were powdered and pressed into KBr disks in a darkened room under N_2 for IR spectral analysis. Preparation time varied from 15–30 min. Initial IR spectra were obtained in <0.5 h, and subsequent spectra were obtained at 48 h intervals over a 10 day period. Samples were kept in the dark between analyses. Typical spectra are shown in Fig. 1.

4 showed only slight discoloration after 7 days *in vacuo* in the dark at 25 °C; however, after 1 h in sunlight it turned deep yellow. After 6 days exposure to ambient laboratory fluorescent light, intense yellow discoloration along with evolution of traces of germanes occurred. At 250–300 °C rapid conversion of the white solid to yellow, red, brown and finally metallic grey (metallic Ge) occurred along with evolution of H_2, GeH_4 and higher germanes. Me_3NHBr (93–95%) sublimed from the pyrolysis zone.

4 did not react with B_2H_6 at 25 °C in 2 h or with HBr at 25 °C in 0.3 h. During 17 h at 25 °C, DCl (three-fold excess) reacted with **4** to produce GeH_3Cl, along with lesser amounts of GeH_2DCl (22–24% yield, overall).

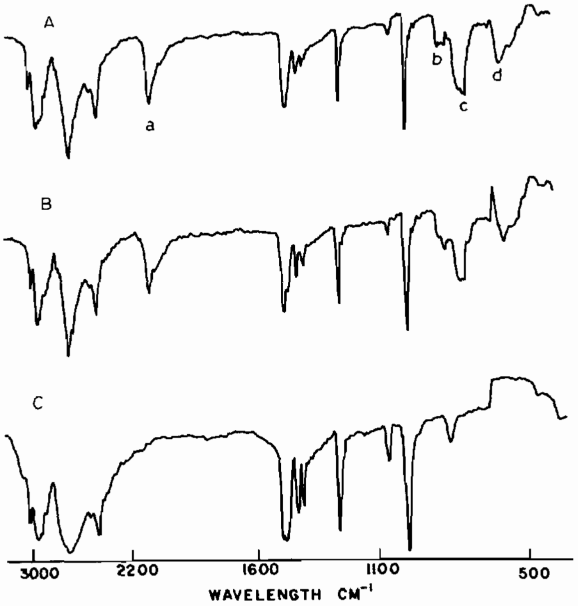


Fig. 1. Infrared spectrum of: (A), freshly prepared **4**; (B), **4** after 10 days at 25 °C; (C), pure Me_3NHBr.

4 prepared under N_2 was subjected to X-ray powder pattern analysis. After 3 h in Cu Kα irradiation, **4** turned deep yellow. The powder pattern was superimposable with that of known Me_3NHBr.

Dissolution of $Me_3NHBr \cdot 1/x(GeH_2)_x$ (4) in Acetonitrile

Freshly prepared **4** (0.10–0.15 mmol) was extracted with acetonitrile (5 ml) in the dark at 25 °C during 3 h. Partial dissolution of the solid occurs. The ^1H NMR spectrum of the acetonitrile solution showed resonances due to the Me_3NH^+ ion and acetonitrile. A grey waxy solid (**5**) remained undissolved. Evaporation of the acetonitrile solution to dryness *in vacuo* yielded Me_3NHBr (92.5–94.0% of theoretical). **5** decomposes slowly at 25 °C, although it yellows slowly upon exposure to light. Thermolysis above 150 °C causes rapid evolution of H_2, GeH_4, Ge_2H_6 and Ge_3H_8.

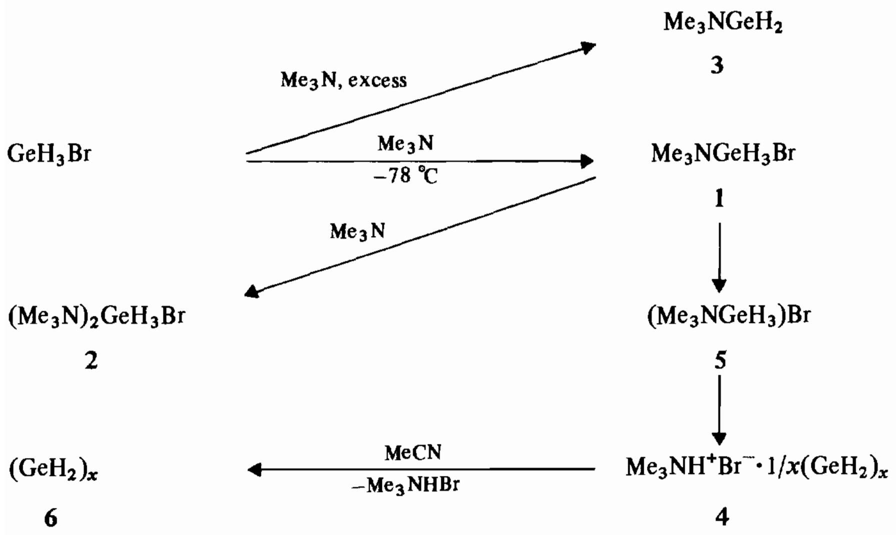
Elemental composition of **5** was determined by pyrolysis of **5** at 400 °C, followed by Toepler analysis [14] of H_2 and determination of Ge by peroxide titration of the resulting Ge metal [5, 6]. *Anal.* Calc. for GeH_2: Ge, 97.30; H, 2.70. Found: Ge, 95.8–96.4; H, 2.45–2.85%.

Reaction of Me_3GeBr with Me_3N

Typically, Me_3N (0.120 mmol) and Me_3GeBr (0.090 mmol) were allowed to mix at 25 °C and cooled to −78 °C. Excess Me_3N (0.031 mmol) was removed. Adduct $Me_3N \cdot Me_3GeBr$ (**7**) remained. During a 2 h period at −63 °C, around 20% of the adduct in an equimolar mixture of Me_3N and Me_3GeBr (determined by IR spectra) was removed *in vacuo*. Reaction of **7** with excess B_2H_6 at −78 °C resulted in consumption of a half molar equivalent of B_2H_6, and quantitative recovery, within experimental limits, of the Me_3GeBr and Me_3NBH_3.

Results and Discussion

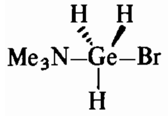
Bromogermane (GeH_3Br) reacts with Me_3N to form the products summarized in Scheme 1. At −78 °C, Me_3N with excess GeH_3Br reacts neat or in Me_2O solvent to form a 1:1 $Me_3N \cdot GeH_3Br$ complex (**1**) in a process analogous to that which occurs between GeH_3Cl and Me_3N reported in brief form earlier [5, 26]. Even in the absence of solvent, GeH_3Br–Me_3N reactions are remarkably clean and are accompanied by formation of only traces of GeH_4, Ge_2H_6 and Ge_3H_8. Adduct **1** is a colorless solid, which appears unchanged after several hours at −78 °C; however, upon warming it undergoes conversion to material(s) with different physical and chemical properties.



Scheme 1.

$Me_3N + GeH_3Br \longrightarrow Me_3N{\cdot}GeH_3Br$ (1)

Three formulations for the $Me_3N{\cdot}GeH_3Br$ adduct can be considered: **I**, a five-coordinate structure in which Me_3N is coordinatively bonded to the Ge atom of GeH_3Br; **II**, a salt in which a GeH_3^+ moiety has been transferred to the Me_3N to form a quaternary salt; and **III**, a bromogermanide salt in which Me_3N has abstracted a H^+ from GeH_3Br to form the GeH_2Br^- ion.



$Me_3N{-}GeH_3{-}Br$

I

$[Me_3N\text{-}GeH_3^+]Br^-$

II

$[Me_3NH]^+[GeH_2Br]^-$

III

Precedents for species analogous to **I**–**III** exist. Five-coordinated silicon and germanium halides, where coordination involves amine, phosphine or ether bases are well known [9, 11, 28]. Type **II** complexes, e.g. $[Me_3NSiH_3^+]Br^-$ and $[Me_3N(Me_3Ge)^+]Br^-$, analogs of tetraalkylammonium ions, from Me_3N–SiH_3Br and Me_3N–Me_3GeBr reactions, respectively, have been tentatively reported by Srivastava and Onyszchuk [29]. A type **III** species would be analogous to the GeH_3^- anion formed upon deprotonation of GeH_4 [30a] or the $SiCl_3^-$ ion formed in reaction of Me_3N with $HSiCl_3$ [30b]. Although GeH_4 requires bases stronger than Me_3N for deprotonation [30, 31] it is possible that GeH_3Br, because of the electron withdrawing effect of the Br atom, might be more acidic.

Characterization of **1** by spectral data (IR and ^1H NMR) was unsuccessful because of the low thermal stability and solubility of **1** in solvents with which it did not react. However, from its chemical reactivity properties, definitive structural inferences can be made. **1** reacts quantitatively with H_2O (or D_2O) or HBr and in high (*ca.* 90%) yield with B_2H_6 or MeOH as shown in eqns. (2)–(5)

$$Me_3N{\cdot}GeH_3Br \longrightarrow \begin{cases} \xrightarrow[-Me_3NHBr]{HBr} GeH_3Br & (2)\\ \xrightarrow[-Me_3NBH_3]{B_2H_6} GeH_3Br & (3)\\ \xrightarrow[-Me_3NHBr]{H_2O} (GeH_3)_2O & (4)\\ \xrightarrow[-Me_3NHBr]{MeOH} MeOGeH_3 & (5) \end{cases}$$

Substitution of D_2O for H_2O yields Me_3NDBr and $(GeH_3)_2O$; within experimental error no incorporation of deuterium into the germyl ether occurs. Reactions in eqns. (4) and (5) are in fact good preparative syntheses for $(GeH_3)_2O$ and $MeOGeH_3$ [32], species which otherwise have been difficult to obtain in reasonable yields.

Of the structures possible for $Me_3N{\cdot}GeH_3Br$ (**I**–**III**), **I** seems most likely. Since **1** reacts quantitatively with D_2O to form $(GeH_3)_2O$ and no $(GeD_3)_2O$, the complex must contain an intact GeH_3 unit; hence formulation **III** is ruled out. Since GeH_3Br is easily displaced from the complex by B_2H_6, we conclude the GeH_3 unit is not bonded to nitrogen in a quaternary cationic species as in **II**.

Upon warming slightly or standing at −63 °C, the character of **1** changes dramatically and its reactivity toward H_2O and B_2H_6 decreases. After 1 h at −63 °C (exp. 3), the $Me_3N{\cdot}GeH_3Br$ complex with B_2H_6 produces only 79.5% of the theoretically expected GeH_3Br, although it still is in such a form that GeH_3Br can be displaced quantitatively (exp. 4) by HBr. Later, after 3 h at −23 °C, the GeH_3Br that can be displaced by B_2H_6 has dropped further to 58%. Again, considerable reactivity towards HBr is retained. After reaction with B_2H_6, HBr displaces another 23% of the GeH_3Br from the product. This behavior suggests involvement of a transient (intermediate) species whose formulation is different from **1** and that of the subsequently formed product **4**. Such an intermediate could be $[Me_3NGeH_3^+]Br^-$ (**5**; Scheme 1), a species which contains a GeH_3 unit bonded to a quaternized nitrogen center as a result of cleavage of the Ge–Br bond in **1**. Again, a species such as $[Me_3NH^+][GeH_2Br]$ (type **III**, above) appears ruled out because in reactions with D_2O the digermyl ether obtained shows no significant Ge–D IR absorptions.

Further warming of the 1:1 $Me_2N{\cdot}GeH_3Br$ product to ambient room temperature (23 °C) yields a pure white, light sensitive solid (**4**) which is essentially unreactive towards B_2H_6, HBr (exp. 6, Table I) and H_2O. **4** is stable at ambient temperatures in the absence of light for periods of days, showing only barely decomposition and traces of germane evolution.

Solid **4** dissolves partially and slowly (3 h) in acetonitrile or water at room temperature. A colorless solution, which upon evaporation was found to contain 92–95% of the expected Me_3NHBr, and a grey unstable gum (**6**) are formed. Compound **6** after drying *in vacuo*, analyzed closely for $(GeH_2)_x$. Upon heating, **6** discolors to yellow, orange and finally brown. During this decomposition GeH_4, Ge_2H_6 and Ge_3H_8 evolve. Final heating at >300 °C yields a black residue which was presumed to be metallic germanium. It should be noted that dissolution of **4** is markedly different from that of Me_3NHBr.

The IR spectra of **4**, as a function of time, provide some insight into its composition. Spectral data are shown in Fig. 1. The spectrum of pure Me_3NHBr (Fig. 1C) is shown for comparison purposes. The initial spectrum of a freshly prepared sample (Fig. 1A) which had been exposed minimally to light prior to spectral analysis showed absorptions clearly attributable to the Me_3NH^+ ion. In addition, strong absorptions at 2045 (a), 755 (c), and 610 (d) cm^{-1}, and a weak absorption at 860 (b) cm^{-1} is present. Absorption a occurs in the characteristic Ge–H stretching mode region. Figure 1B shows the spectrum after 10 days at 25 °C. During this period, the sample was intentionally exposed to ambient laboratory light. A noticeable decrease in the intensity of absorptions a, b and c is evident along with some absorption line broadening. These are assigned to germanium hydride species. Although our data do not allow unambiguous characterization of **4**, or the material to which it decomposes thermally or photochemically, they do show that **4** contains Me_3NH^+ ions from the outset, and in a concentration which seems invariant with time.

It is known that **4** forms from **1**, with no change in overall compound composition (excepting loss of traces of germanes due to decomposition), that **4** contains Me_3NH^+ ions from the outset, and that **4** yields Me_3NHBr upon dissolution in acetonitrile. Thus, a reasonable formulation for **4** is $Me_3NH^+Br^-{\cdot}1/x(GeH_2)_x$, a composition containing Me_3NH^+ and Br^- ions and (GeH_2) units. The germylene unit is written as $(GeH_2)_x$, since GeH_2 monomers are likely not the main species present. Mono GeH_2 species can be present only to a minor degree, since only 20–25% reaction with HBr to GeH_3Br occurs. It is assumed that $(GeH_2)_x$ is less reactive than the mono GeH_2 and therefore forms no GeH_3Br upon treatment with HBr. Also, **4** with Me_3GeH gave no $Me_3Ge_2H_3$, suggesting that the GeH_2 species present is not very reactive towards insertion into Ge–H bonds.

The GeH_2 species obtained in **4** seems different from that reported previously [3–5, 12]. The $(GeH_2)_x$ from Ge_2H_6 disproportionation or GeH_3^-–RBr reactions reportedly decomposes quickly above −63 or 25 °C, respectively, to germanes and $(GeH_{<2})$ polymer. The $(GeH_2)_x$ in **4** does not discolor or evolve germane in significant quantities for days. This suggests that the $(GeH_2)_x$ moieties are stabilized in the solid either by the Me_3NH^+ ion or the Br^- ion, or both. It is known that bases stabilize GeX_2 species in general [1, 2, 10], and there are cases where GeX_2 units are stabilized by coordination both to a base and an acid, e.g. to $Fe(CO)_4$ and THF, in THF–GeX_2–$Fe(CO)_4$ [2]. In **4**, weak coordination of $(GeH_2)_x$ species by Br^- (acting as a base) and/or by Me_3NH^+ (acting as an acid) could occur. In this way **4** represents a unique system in which $(GeH_2)_x$ becomes stabilized and displays behavior unique from that of other reported species.

Compound **6**, the product left after acetonitrile extraction of Me_3NHBr from **4**, analyzes for GeH_2. It also is more stable than previously reported $(GeH_2)_x$. It is unreactive towards HBr and shows no photodecomposition or significant thermal decomposition over moderately long periods. Either it contains entrapped Me_3NHBr in concentrations below what we could detect by our analytical techniques, which stabilizes it, or it contains GeH_2 units bonded differently from other known systems. Timms has suggested that solid $(GeH_2)_x$ might contain Ge–Ge bonds [12]. However, another arrangement involving Ge–H–Ge bonding analogous to that in GeX_2 [10] is possible. **6** might be of the former type, and thus is expected to be unreactive towards HBr. Further studies of compound **6** and its properties are warranted.

Bromogermane with excess Me_3N yields products which are more complex. Compound **1** with an additional equivalent of Me_3N reacts to form a 2:1 complex as

$$Me_3N + Me_3N{\cdot}GeH_3Br \longrightarrow (Me_3N)_2GeH_3Br \qquad (6)$$

The structure of the 2:1 complex is unclear. Since it is relatively unreactive towards B_2H_6, it likely is not a simple six-coordinate complex of GeH_3Br. A more complex formulation such as $[Me_3NH^+][Me_3NGeH_2Br^-]$, in which the second Me_3N deprotonates the acidic Me_3NGeH_3Br complex is possible. However, complete characterization awaits further study.

In the presence of Me_3N in large excess, Me_3N and GeH_3Br yield Me_3NHBr and a yellow solution. Based on reaction stoichiometry data and the fact that Me_3NHBr is recovered quantitatively, reaction appears to occur as

$$2Me_2N + GeH_3Br \longrightarrow Me_3NHBr + Me_3NGeH_2 \qquad (7)$$

a reaction similar to what has been noted previously in the formation of the ylid Me_3NCH_2 from Me_3N and CH_3I [33]. The species in solution, formulated as Me_3NGeH_2 (**3**), decomposes rapidly but for a time retains reactivity towards Ge–H bonds. Reaction of **3** with Me_2GeH_2 or Me_3GeH results in low yield formation of $Me_2Ge_2H_4$ and $Me_3Ge_2H_3$, respectively, in addition to substantial quantities (13–37%) of Ge_3H_8. Similar behavior has been noted previously for the ylid Me_3NCH_2 [33].

Reaction of Me_3N with Me_3GeBr results in formation of a 1:1 complex $Me_3N{\cdot}Me_3GeBr$ (**7**) as

$$Me_3N + Me_3GeBr \longrightarrow Me_3N{\cdot}Me_3GeBr \qquad (8)$$

analogous to that which occurs between Me_3N and GeH_3Br and reported earlier for Me_3GeBr with amines [5, 28]. Reaction of **7** with B_2H_6 yields Me_3NBH_3 quantitatively; complex **7** is partially dissociated even at −63 °C to the extent that Me_3GeBr and Me_3N can be removed slowly *in vacuo*. However, beyond this, the similarity between **7** and **1** ends. Upon warming, **7** dissociates without formation of other products. In excess Me_3N, it shows no tendency to form products analogous to those in eqn. (7). Clearly, because the GeH_3Br has transferrable H atoms, it is unique in the products it can form.

Acknowledgements

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