Syntheses and Characterization of 1-Haloazagermatranes

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Germanium, Azagermatranes

The reaction of tris(dimethylamino)halogermanes, (Me2N)3GeHal (7, Hal = Cl; 8, Hal = Br), with tris(2-aminoethyl)amines, N(CH2CH2NHR)3 (5, R = H; 6, R = Me), yield 1-halo-N,N',N"-azagermatranes (1, X = Cl, R = H; 2, X = Br, R = H; 3, X = Cl, R = Me; 4, X = Br, R = Me). Treatment of 4 with n-butyllithium affords 1-n-butyl-N,N',N"-trimethylazagermatrane (14) in high yield. Reactions of n-BuLi with 7 or (Me2N)4Ge (13) lead to the formation of (Me2N)3Ge-n-Bu (15). On treatment of 15 with 5 the 1-n-butylazagermatrane 16 was obtained. The molecular composition and the structures of all new compounds were established by elemental analyses, 1H and 13C NMR spectroscopy and mass spectrometry.

Results and Discussion

Starting materials 7 and 8 (Scheme 1) were readily prepared by redistribution reactions between GeHal4 and (Me2N)4Ge (13) following a literature method [7].

Table 1. 1H NMR data (δ(Me2N), C6D6, ppm) of (dimethylamino)germanes 7 - 13.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ</th>
<th>Compound</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Me2N)3GeCl</td>
<td>2.53</td>
<td>Me2NGeCl3</td>
<td>1.22</td>
</tr>
<tr>
<td>(Me2N)3GeBr</td>
<td>2.50</td>
<td>Me2NGeBr3</td>
<td>1.22</td>
</tr>
<tr>
<td>(Me2N)2GeCl2</td>
<td>2.44</td>
<td>(Me2N)2Ge</td>
<td>1.24</td>
</tr>
<tr>
<td>(Me2N)2GeBr2</td>
<td>2.34</td>
<td>(Me2N)2Ge</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Introduction

During our studies concerning the syntheses and reactions of functionally substituted metallatranes (metal = Si, Ge) we became interested in using simple and easily available metallatranes bearing apical groups which have the capability for further derivatisation at the silicon or germanium atom [1]. One common structural feature of these compounds is their hypervalent metal centre. The design of the atrane building block and the substituents at the metal atoms have an influence on the reaction pathways [1, 2, a-c]. In contrast to extensive studies on germatranes [1, 2], the chemistry of azagermatranes has barely been explored. First examples of azagermatranes, N(CH2CH2NR)3GeX (R = H, Me; X = Me, tert-Bu, NMe2), have been reported as late as 1993 [3]. Recently we have described new azagermatranes, N(CH2CH2NR)3GeAllyl (R = H, Me, SiMe3) [4]. We were now interested to find a simple route to 1-haloazagermatranes and to compare their reactivity with that of 1-halogermatranes [1, 5] and 1-haloazasilatranes [6]. In this context, we here report the syntheses and some preliminary experiments on the reactivity of 1-haloazagermatranes (1 - 4) in order to obtain information on nucleophilic substitution reactions at the penta-coordinated germanium atom.

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The new (dimethylamino)halogermanes 9 - 12 were synthesized similarly and their 1H NMR spectra recorded in CöDö (Table 1).

\[ n \text{GeHal}_4 + (4 - n)(\text{Me}_2\text{N})_4\text{Ge} \rightarrow (\text{Me}_2\text{N})_4-n\text{GeHal}_n \] (1)

After the purity check of 7 and 8 by 1H NMR spectra these reagents were used without further purification.

Transamination reactions were applied for the syntheses of 1-haloazagermatranes 1 - 4 (Scheme 1). Tris(2-aminoethyl)amine 5 smoothly reacts within a few minutes with 7 and 8 in toluene at room temperature with evolution of dimethylamine to afford white solids which proved to be complexes with Me₂NH (according to 1H NMR spectra). The overall composition of the complex 1 · Me₂NH was established by elemental analysis. Dimethylamine is retained in this complex firmly enough so that even heating at 110 °C (1 Torr) for 3 h results only in partial removal of Me₂NH from the sample, and finally 1 decomposes. For 2 the coordination with Me₂NH is not that strong and no analytically pure complex 2 · Me₂NH was obtained. NMR and mass spectra show that a compound from the reaction of 5 and 8 contains only 2 and Me₂NH, which decomposes on heating.

Similar reactions of tris(2-N-methylaminoethyl)amine 6 with the aminogermanes 7 and 8 are slow and conversion is complete only after heating for a prolonged reaction time (24 h) in refluxing benzene or toluene. The moisture sensitive compounds 3 and 4 can be isolated in yields of 94% and 85%, respectively. These azagermatranes do not contain any Me₂NH.

It is worth noting that the results of these reactions differ from those of (Me₂N)₃SiCl with 5 and 6, which gave mixtures of polymers [8]. For this reason a convenient approach to 1-haloazasilatranes is essentially a complex multistep process [6].

We have studied some reactions of the 1-bromoazagermatrane (4) and obtained preliminary data for a comparison of the reactivities of 1-bromogermatrane and 1-chloro-N,N',N''-trimethylazasilatran.

We have shown that replacement of bromine in N(CH₂CH₂O)₃GeBr in a reaction with organoxytrialkylstannanes is a useful method for the preparation of a variety of 1-organoxygermatranes [5]. However, our attempts to react the azagermatrane 4 with Et₃SnOMe under similar conditions failed.

Treatment of azagermatrane 4 with n-BuLi affords 1-n-butyl-N,N',N''-trimethylazagermatrane 14 in 90% yield as a colourless liquid (eq. (2)).

In this reaction no products of a breakdown of the “atrane” cage are found. This result for 4 differs from that for 1-bromogermatrane, which on reacting with n-BuLi can undergo both alkylation at the Ge-Br bond and cleaving of the Ge-O bonds of the germatran cage [1]. In these reactions the germanium atom may become hexacoordinated and nucleophilic substitution may occur via transition the states Y or Z (Scheme 2).

Our attempts to react 4 with other lithium reagents [CpLi, FluLi, LiN(SiMe₃)₂, Li(OMe)] failed; we obtained either the starting materials or very complex product mixtures (1H NMR control).

For a comparison of the reactivity of azagermatrane 4 and its tetra-coordinated analogue, chlorotris(dimethylamino)germane 7, we have studied the reaction of 7 with n-BuLi. The reaction of 7 with one equivalent of n-BuLi is exothermic (0 °C, benzene, 5 min) and produces (Me₂N)₃Ge-n-Bu 15 in 88% yield (eq. (3)).

Reaction of n-BuLi with equimolar amounts of tetrakis(dimethylamino)germane 13 also resulted in the formation of 15. However, in this case completion of the reaction is only achieved after 24 h at 20 °C (eq. (3)).

\[ (\text{Me}_2\text{N})_3\text{GeCl} \rightarrow (\text{Me}_2\text{N})_3\text{GeBu-n} \] (15)

\[ 7 \rightarrow (\text{Me}_2\text{N})_4\text{Ge} \] (13)
Thus, both approaches leading to compounds \((\text{Me}_2\text{N})_3\text{Ge}\,\text{X}\) (eq. 3) are promising reactions, in particular in cases, where the precursors are not available by standard reactions. Treatment of tris-(dimethylamino)-\(n\)-butylgermane 15 with amine 5 led to azagermatrane 16 in 43\% yield (eq. 4).

In conclusion, our experiments prove that 1-bromoazagermatrane 4 is less reactive in nucleophilic reactions than 1-bromogermatrane, 1-chloro-\(N,\,N',\,N''\)-trimethylazasilatrane and more so than chlorotris(dimethylamino)germate 7.

**Experimental**

All reactions were carried out under an argon atmosphere; solvents were dried by standard methods and distilled prior to use. Starting materials 13 [6, 9] and 6 [10] were prepared according to the literature. 5 was distilled in vacuo from LiAlH₄ before use. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department, Moscow State University. NMR spectra were recorded at 25 °C on a Varian VXR-400 spectrometer, C₆D₆ was used as a solvent and for internal deuterium lock. Chemical shifts of \(^1\)H and \(^{13}\)C NMR are given in \([\text{ppm}]\) relative to internal TMS. Assignments of the \(^{13}\)C NMR data were supported by APt experiments. Mass spectra (EI-MS) were recorded on a Varian CH-7a device using electron impact with an ionization energy of 70 eV; all assignments were made with reference to the most abundant isotopes.

**Chlorotris(dimethylamino)germane (7)**

Tetrakis(dimethylamino)germane (13) (5.60 g, 22.5 mmol) was added dropwise to GeCl₄ (1.60 g, 7.5 mmol). After 10 min at r.t. the reaction was complete: \(^1\)H NMR spectroscopy (C₆D₆) revealed only the presence of 7 with \(\delta = 2.53\). 7.20 g (100\%) of 7 were obtained as a pure, colourless liquid which was used without purification in further experiments. Analysis for C₆H₁₈ClGeN₃ (240.27): calcd. C 29.99, H 7.55, Ge 30.21; found C 29.81, H 7.62, Ge 30.48.

Using 13 together with GeX₄ (X = Cl, Br) in the required ratios, new compounds 7-12 were obtained according to the procedure described above and characterized by \(^1\)H NMR spectroscopy (Table 1).

**Complex of 1-chloroazagermatrane (1) with dimethylamine: N\((\text{CH}_2\text{CH}_2\text{NH})_2\text{GeCl}\cdot\text{Me}_2\text{NH}\)**

5 (0.75 g, 5.1 mmol) was added to a solution of 7 (1.24 g, 5.2 mmol) in toluene (5 ml). Immediate evolution of Me₂NH and formation of a precipitate were observed. The mixture was stirred for 24 h at r.t., then a white solid was filtered off, washed with \(n\)-hexane (2 \(\times\) 5 ml) and dried in vacuo. Yield 1.38 g (91\%), m.p. 120 - 122 °C (decomp.).

\(^1\)H NMR: \(\delta = 2.53\) (t, 6H, NCH₂), 2.22 (t, 6H, NCH₂), 2.19 (6H, NMe₂), 1.85 (m, 4H, NH). EI-MS, \(m/z\) (rel. int., assign.): 252 (0.2\%, M⁺=\(\text{N}(\text{CH}_2\text{CH}_2\text{NH})_2\text{GeCl}\)), 223 (2\%, M⁺-\(\text{CH}_2\text{NH}\)), 217 (5\%, M⁺-Cl), 194 (5\%, M⁺-\(2\text{CH}_2\text{NH}\)), 85 (100\%, \(\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}\)). Analysis for C₉H₂₁ClGeN₄ (293.33): calcd. C 36.85, H 7.03, N 18.85.

**Complex of 1-bromoazagermatrane (2) with dimethylamine: N\((\text{CH}_2\text{CH}_2\text{NH})_2\text{GeBr}\cdot\text{Me}_2\text{NH}\)**

According to the procedure described for 1 \cdot Me₂NH, 1.02 g of 2 Me₂NH, m.p. 135 - 140 °C (decomp.) were prepared from 8 (1.00 g, 3.5 mmol) and 5 (0.50 g, 3.4 mmol) in benzene (10 ml).

\(^1\)H NMR: \(\delta = 2.51\) (t, 6H, NCH₂), 2.21 (t, 6H, NCH₂), 2.19 (6H, NMe₂), 1.45 (m, 4H, NH). EI-MS, \(m/z\) (rel. int., assign.): 296 (0.2\%, M⁺=\(\text{N}(\text{CH}_2\text{CH}_2\text{NH})_2\text{GeBr}\)), 267 (11\%, M⁺-\(\text{CH}_2\text{NH}\)), 238 (11\%, M⁺-\(2\text{CH}_2\text{NH}\)), 217 (18\%, M⁺-Br), 85 (100\%, \(\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}\)).

**I-Chloro-N,\,N',\,N''-trimethylazasilatrane, N\((\text{CH}_2\text{CH}_2\text{NMe})_2\text{GeCl}\text{Cl}\)**

A solution of 6 (0.29 g, 1.5 mmol) and 7 (0.38 g, 1.6 mmol) in benzene (10 ml) was refluxed for 24 h, then a white solid was filtered off, washed with \(n\)-hexane (2 \(\times\) 5 ml) and dried in vacuo. Yield 0.41 g (94\%).

\(^1\)H NMR: \(\delta = 3.09\) (s, 9H, NCH₃), 2.56 (t, 6H, NCH₂), 1.93 (t, 6H, NCH₂). \(^{13}\)C NMR: \(\delta = 49.72\) (NCH₂); 48.92 (NCH₂); 39.39 (CH₃). ES-MS, \(m/z\) (rel. int., assign): 294 (0.8\%, M⁺), 259 (7\%, M⁺-Cl), 251 (3\%, M⁺-\(2\text{CH}_2\text{NCH}_2\text{CH}_3\)), 237 (3\%, M⁺-\(3\text{CH}_2\text{NCH}_2\text{CH}_3\)), 208 (2\%, M⁺-\(2\text{CH}_2\text{NCH}_2\text{CH}_3\)), 99 (100\%, \(\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_3\)). Analysis for C₉H₂₀ClGeN₄ (293.33): calcd. C 36.85, H 7.22, N 19.10; found C 36.53, H 7.03, N 18.85.

**1-Bromo-N,\,N',\,N''-trimethylazasilatrane, N\((\text{CH}_2\text{CH}_2\text{NMe})_2\text{GeBr}\)**

According to the procedure described for 3, 3.46 g (yield 85\%) of 4 was prepared from 8 (3.46 g, 12.2 mmol) and 6 (2.27 g, 12.0 mmol) in toluene (20 ml).

\(^1\)H NMR: \(\delta = 3.08\) (s, 9H, NCH₃), 2.56 (t, 6H, NCH₂), 1.91 (t, 6H, NCH₂). \(^{13}\)C NMR: \(\delta = 50.20\) (NCH₂); 49.24 (NCH₂); 40.17 (CH₃). ES-MS, \(m/z\) (rel. int., assign): 338 (4\%, M⁺), 295 (10\%, M⁺-\(2\text{CH}_2\text{NCH}_3\)), 281 (9\%,
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M⁺·CH₂CH₂NCH₃), 259 (32%, M⁺·Br), 252 (27%, M⁺·2CH₂NCH₃), 237 (12%, M⁺·CH₂CH₂NCH₃·CH₂NCH₃), 196 (12%, M⁺·2CH₂NCH₃·CH₂NCH₃), 237 (12%, M⁺·CH₂CH₂NCH₂·CH₂NCH₃), 196 (12%, M⁺·2CH₂NCH₂·CH₂NCH₃), 99 (100%, CH₂CH₂NCH₂·CH₂NCH₃). Analysis for C₉H₂¹BrGeN₄ (337.78): calcd. C 32.00, H 6.27, N 16.59, found C 31.63, H 6.03, N 16.13.

1-n-Butyl-1,1,4,4-tetramethylazagermatrane (14)

A solution of n-BuLi (0.4 ml, 0.65 mmol) [1.63 M solution in n-hexane] was added to a suspension of 4 (0.22 g, 0.65 mmol) in benzene (25 ml) at r.t. The reaction mixture was refluxed for 24 h with stirring; after cooling to r.t. about two thirds of the volatiles were evaporated in vacuo. A white precipitate was filtered off and residual volatiles were removed in vacuo. Distillation of the residue gave 0.18 g (88%) of 14 as a colourless liquid, b.p. 135 - 137 °C/2 Torr.

¹H NMR: δ = 2.68 (s, 9H, NMe), 2.64 (t, 6H, NCH₂), 2.26 (t, 6H, NCH₂), 0.97 - 1.83 (m, 9H, GeBu-n).

n-Butyltris(dimethylamino)germane (15)

a) From (Me₂N)₃GeCl (7)

To 3 ml of a n-hexane solution of 1.12 g (4.7 mmol) of (Me₂N)₃GeCl 7, cooled to 0°C, 2.95 ml of 1.66 M n-BuLi solution in n-hexane (4.9 mmol) was added. The reaction mixture was stirred for 5 min and then a solid was filtered off. Distillation of the filtrate gave 1.07 g (87%) of 15 as a colourless liquid, b.p. 82 - 83 °C/1 Torr.

¹H NMR: δ = 2.62 (s, 18H, Me), 0.82 - 1.47 (m, 9H, GeBu-n).
¹³C NMR: δ = 52.80 (NCH₂), 38.69 (NCH₂), 25.40, 24.96, 14.00, 13.17 (GeBu-n). Analysis for C₁₃H₃₀GeN₄ (327.83): calcd. C 44.02, H 8.87, Ge 20.54; found C 43.81, H 8.54, Ge 20.09.

Azagermatranes 1 - 4, 14 and 16 are hygroscopic compounds and may decompose under moisture to give the corresponding amines.

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