Journal of Organometallic Chemistry 993 (2023) 122709

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and Characterization of 3-Aminopropyl-phenyl Germanes

Christoph Garstenauer, Roland C. Fischer, Ana Torvisco*, Frank Uhlig

University of Technology Graz, Institute of Inorganic Chemistry, Stremayrgasse 9/IV, Graz 8010, Austria

ARTICLE INFO

Article history:
Received 26 January 2023
Revised 4 April 2023
Accepted 4 April 2023
Available online 7 April 2023

Keywords:
3-aminopropyl germanes
3-aminopropyl–chloro germanes
Chloro germanes
Hydrogermylation
Bifunctional germanes

ABSTRACT

Novel synthetic pathways for different 3-aminopropyl germanes are shown in this work. For this purpose, in Synthetic Route A, a corresponding germanium compound was metalated and, *via* salt metathesis, the corresponding protected 3-aminopropyl germane was formed. After the deprotection, the corresponding amino hydrochlorides were isolated. After a neutralization reaction, the 3-aminopropyl germanes were formed. With 3-aminopropyl-diphenyl-germanium hydride, $(H_2N(CH_2)_3)Ph_2GeH$, a new bifunctional building block was isolated. To form the corresponding 3-aminopropyl–chloro germanes ($(CyHN(CH_2)_3)Ph_2GeCl$ and $(H_2N(CH_2)_3)Ph_2GeCl$), diphenyl–chloro germane was used in a hydrogermylation to form the corresponding amines (Synthetic Route B). All compounds were characterized by state-of-the-art techniques, including single crystal X-ray diffraction for selected compounds.

1. Introduction

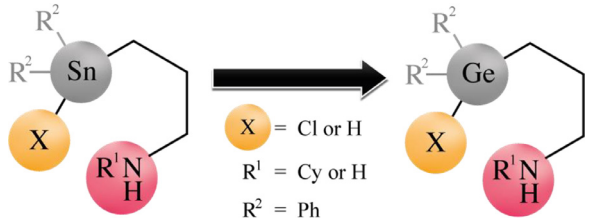
3-Aminopropyl groups are widely used in synthetic and material chemistry. Examples are in the formation of urea derivatives [1–3], the usage as an anchor function on different surfaces (e.g. carbon fiber, glass, silicon or metal oxide surfaces) [4–6] or as an anchor function in a polymer structure (e.g. in polyurethanes or epoxides) [7–9]. Also well-known is end-capping into polymeric materials in organosilicon [10–12] and organotin [13] (Scheme 1) chemistry with aminopropyl functions e.g. AMMO (3-(trimethoxysilyl)propane-1-amine) which are commercially used in STPU (silyl-terminated polyurethanes) [10–12]. In organotin chemistry, compounds of the type $R_2Sn((CH_2)_3NH_2)OAc$ (R = aryl or alkyl) are usable as a new promising class of catalysts [8,9].

A familiar reaction pathway for *N,N*-disubstituted 3-aminopropyl germanes is a salt metathesis with the corresponding Grignard compound or a lithiated species. Zickgraf [14] showed in 1997 the synthesis of mono- to tetra- substituted *N,N*-dimethyl-3-aminopropyl germanes. Additionally, Shenai-Khatkhate [15] synthesized in 2004 a (*N,N*-dimethyl-3-aminopropyl)-trimethyl germane *via* a Grignard reaction, shown in Scheme 2. In Scheme 3, an alternative synthetic route for tertiary-aminopropyl germanes is displayed *via* reduction of the corresponding acid amide [16]. In literature, only a limited number of synthetic routes for non-substituted or mono-substituted aminopropyl germanes were known. A salt metathesis was not possible in both cases due to the -NH functions which can lead to byproducts during the Grignard reaction. Alternative routes based on hydrogermylations have been described in literature, shown in Scheme 4. Hydrogermylations are in general well known, e.g. with vinyl ethers [17–20], but nevertheless for amino derivatives, the number of literature-known reactions is much lower. Lesbre synthesized 3-aminopropyl-dibutyl germane in 1963, where the starting material, a dibutyl germane, was reacted with allyl cyanide to the corresponding nitrile and afterwards, the compound was hydrogenated to afford the final product [21]. Additionally, other examples use allyl amine in a hydrogermylation on triethyl-, tributyl or triphenyl germanes to form the corresponding 3-aminopropyl germanes [22–24]. In 2001, Chazalette [17] synthesized triaryl- and trialkyl-3-aminopropyl germanes (Scheme 4). For the hydrogermylation, a radical initiator was necessary. For this purpose, AIBN (azobisisobutyronitrile) or DTBP (di-*t*–butyl peroxide) were used mainly in literature [17,21,22]. An alternative variant is the use of γ-radiation for radical initiation [23,24].

The formation of 3-aminopropyl–chloro germanes is only known for *N,N*-disubstituted aminopropyl germanes, [14] therefore a main goal of this work was the development of a novel synthetic route for 3-aminopropyl–chloro germanes with a $-(CH_2)_3)NH_2$ or $-(CH_2)_3)NHR$ function.

* Corresponding author.
E-mail address: ana.torviscogomez@tugraz.at (A. Torvisco).

https://doi.org/10.1016/j.jorganchem.2023.122709



Scheme 1. (left): aminopropyl stannanes from Pichler [8,9] (right): principal structure of the newly synthesized germanium compounds, red (R^1NH-) = the aminopropyl function for linking (e.g. in a polymer) and derivatization, yellow (X) = the second functional side for additional derivatization.

2. Results and discussion

2.1. Synthetic Route A

Pichler reported a strategy of amine protection and salt metathesis in 2014 for the synthesis of 3-aminopropyl stannane [8,9]. Similar to this strategy, the salt metathesis concept was investigated for corresponding germanium derivatives (Scheme 5). The metalation of the corresponding germanes (**1, 2a, 2b**) were performed to literature known reactions [25–27]. Starting materials were hexaphenyl digermane, (**1**) or germanium hydrides (**2a, 2b**) which were converted into highly reactive Ge^- anions (**3a-c**) by using either elemental potassium [25,26] or *t*-BuLi [27].

The germanium anions were subsequently reacted with a chloropropyl imine (**4**) to form the desired 3-iminopropyl germanes (**5, 6**), which are the protected form of the corresponding aminopropyl compounds (Scheme 6). After the deprotection and neutralization, the corresponding amines were isolated (**9, 10**).

2.1.1. Salt metathesis – synthesis of compounds 5 and 6

The anions **3a-c** (Ph_3GeK, Ph_3GeLi, $Ph_2Ge(H)Li$), shown in Scheme 6, were reacted in situ with 1–chloro-3-(2,2-dimethylpropyl-imino) propane (**4**) and the 3-iminopropyl germanes were formed (**5, 6**). From compound **4,** an excess was used to quench the residual *t*-BuLi, from the anion formation. After work up of the products, **5** and **6** were isolated and the characterization was done by ^1H, ^{13}C - NMR spectroscopy and GCMS measurements. At higher temperatures, compound **6** is decomposing, this was obtained from thermostability tests. The compound was heated up to 40, 60 and 80 °C in vacuum for 1 hour, afterwards a ^1H NMR was measured. The samples at 60 and 80 °C delivered in NMR spectra a mixture of different compounds. Upon heating **6**, the compound has two reactive sites, one is the hydride function on the Ge atom, the other behind the C_3-propyl spacer being the imine function (-N=CH-). Therefore, at higher temperatures intra- or intermolecular reactions cannot be excluded. A possible scenario is Ge-H addition on the N=C double bond or on a neighboring molecule. This theory is according to literature; a small group of Ge-H additions on -C=N- bonds are known under similar conditions [30,31]. At −20 °C under nitrogen, **6** could be stored over months, afterwards, no decomposition was observed in ^1H NMR spectra. **5** and **6** were used in the next step to form the corresponding amino hydrochlorides.

2.1.2. Deprotection - Formation of the amino hydrochlorides (7, 8) and amines (9, 10)

The deprotection was easily performed in a reaction of the corresponding germane with diluted aqueous HCl in an 100% excess. The compounds **5** and **6** were deprotected with HCl, shown in Scheme 6. The protecting group is cleaved off as pivalaldehyde (*t*-Bu-CHO). The aldehyde, as well the hydrochloric acid, were removed in vacuum together. **7** and **8** were fully characterized *via* ^1H-, ^{13}C NMR spectroscopy and single crystal X-ray diffraction. After deprotection, in a neutralization reaction, the amines (**9, 10**) were formed. For this purpose, the starting material (**7, 8**) were dissolved in chloroform and a simple extraction with diluted aqueous KOH was done. The products **9** and **10** were isolated in yields from over 90%.

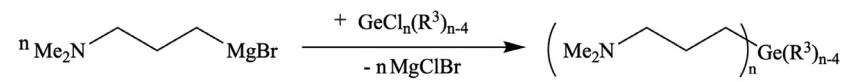
Overall through Synthetic Route A, a novel synthetic pathway is shown for triphenyl-3-aminopropyl germane (**9**), circumventing the need for the toxic allylamine in contrast to reported literature procedures [17,21,22,28,29]. A second advantage is the moderate reaction conditions in the *t*-BuLi lithiation route, in contrast to the sealed-tube-way of Chazalette [17]. Furthermore, the novel compound 3-aminopropyl-diphenyl germane (**10**) was isolated *via* this route. The compound includes two reactive sites, the Ge-H and the $-NH_2$ group. This bifunctionality makes **10** a new and exciting building block for promising subsequent compounds in organogermanium chemistry. Moreover, the 3-aminopropyl site of di- and triphenyl germanes (**9, 10**) can be furthered studied as anchoring functions to different materials in polymer or material chemistry [7–9].

2.1.3. Reactivity and stability of the 3-aminopropyl-phenyl germanes (6 - 10)

Of interest is the reactivity of the compounds **6–10**, target was the conversion of the compounds **6–10** into the corresponding 3-aminopropyl–chloro-diphenyl germane. In literature, the cleavage of the Sn-Ph bond is known from this working group. Pichler [8,9] used 1 eq. of diluted hydrochloric acid to selectively cleave off one phenyl group. Formed products were benzene and the corresponding chloro stannane. With an excess of HCl, the phenyl stannanes were completely dearylated [8,9]. Compounds **7** and **8** were reacted with an excess of diluted hydrochloric acid, however, no reaction on the Ge-Ph bond was observed. The resistance of the Ge-Ph bonds to an excess of diluted aqueous HCl is hugely different to the corresponding stannanes [8,9]. However, if concentrated HCl was used, a mixture of different compounds was obtained in an ^1H NMR measurement. Therefore, only moderate HCl concentrations and excesses are tolerated from phenyl germanes.

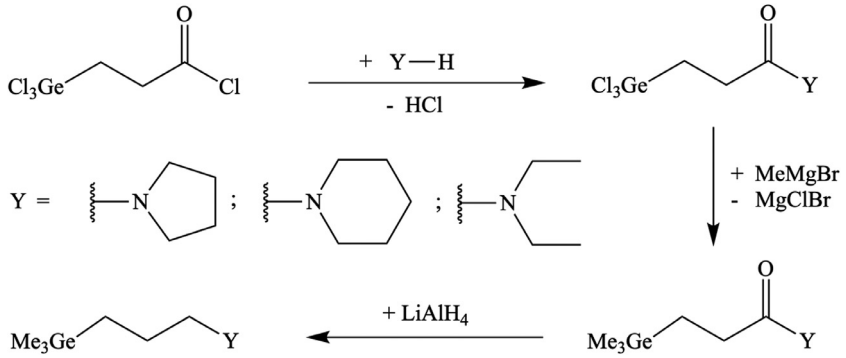
Pichler described the thermal rearrangement at 160 °C of 3-aminopropyl-phenyl stannane hydrochlorides in vacuum; 1 eq. benzene is cleaved off from the tin and the corresponding 3-aminopropyl–chloro stannane is formed [8,9]. However, compound **7** is not rearranging under the same conditions (Scheme 7). If the temperature is elevated to 200 °C, the compound is decomposing to a complex mixture of various compounds. Compound **7** cannot be used as a precursor for chloro–germanes, therefore, alternative routes were investigated.

The synthesis of a 3-aminopropyl–chloro germane, using a chloro–germanium hydride as starting material for the salt

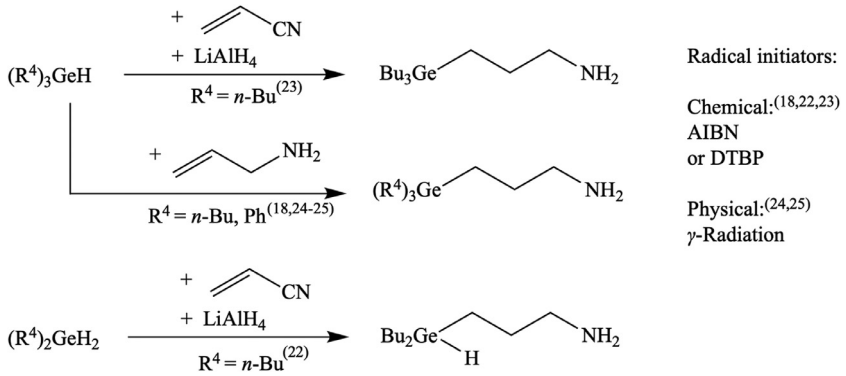


$R^3 = Ph,^{(15)}\ Me^{(16)}$ $n = 1,^{(15,16)}\ 2,^{(16)}\ 3,^{(16)}\ 4^{(16)}$

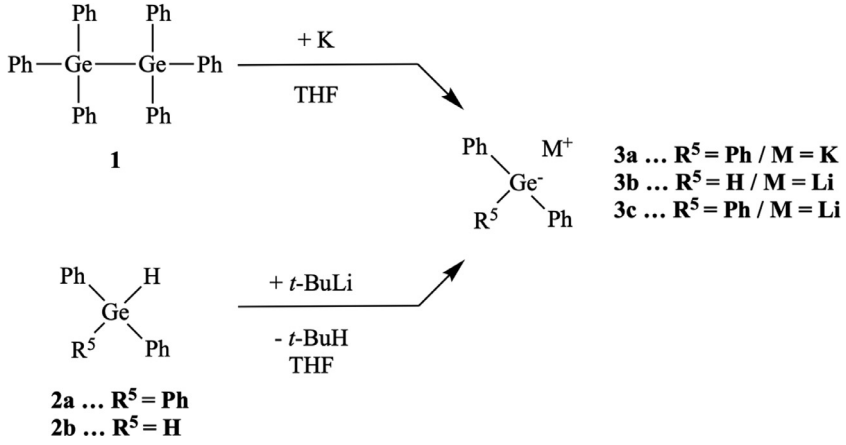
Scheme 2. Literature known synthetic route for (N,N-dimethyl)-3-aminopropyl germanes [14,15].



Scheme 3. Literature known synthetic route for N,N-disubstituted 3-aminopropyl germanes via reduction of the corresponding amide [16].



Scheme 4. Literature known synthetic route for 3-aminopropyl germanes via hydrogermylation and hydrogenation of the corresponding germanium dihydride [17,18,21–24].

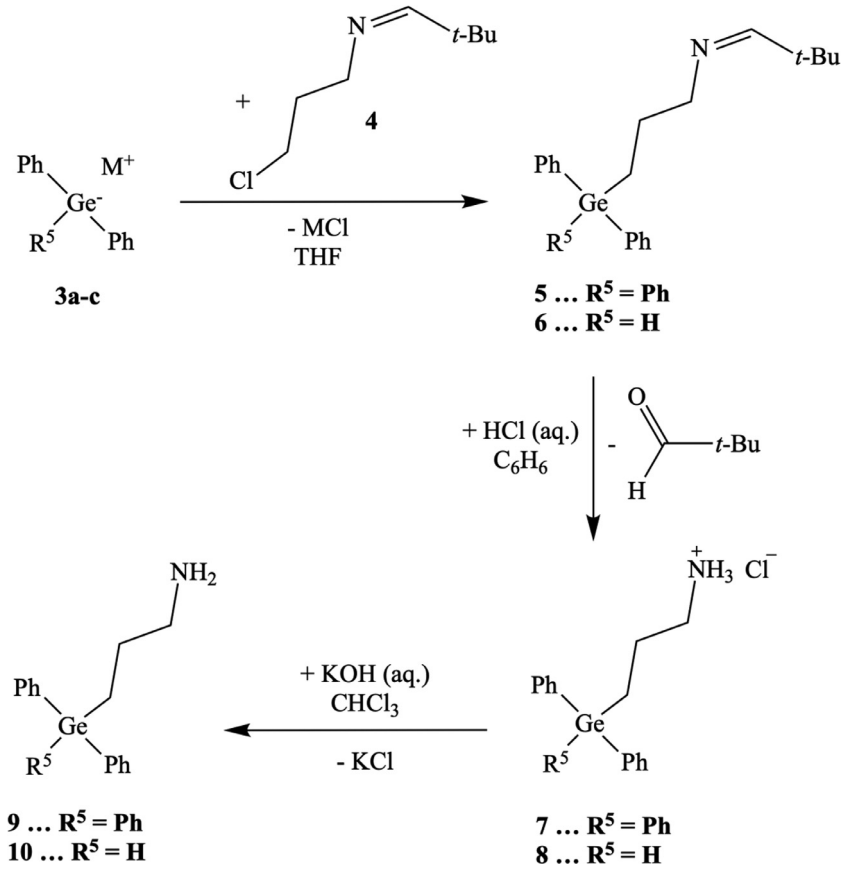


Scheme 5. Synthetic Route A, metalation of the corresponding germanes [25–27].

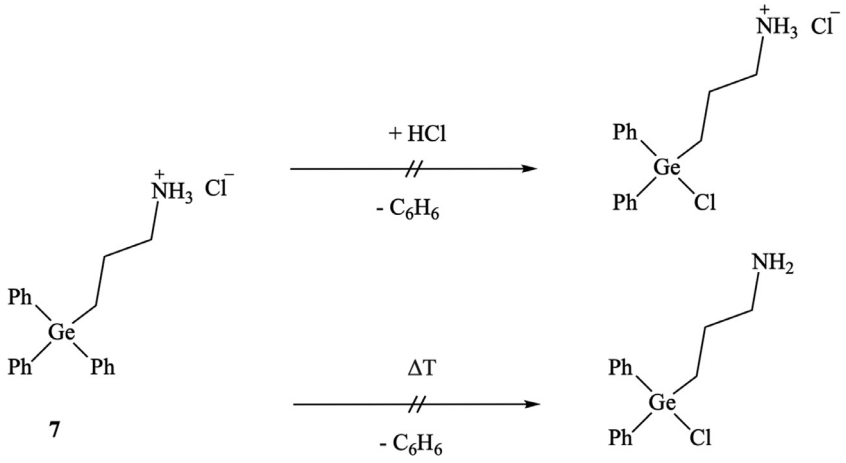
metathesis, similar to route A was not possible (Scheme 5). A lithiation of chloro–diphenyl-germanium hydrides formed a Ge polymer. An alternative way would be the chlorination of the hydride compounds (**6, 8, 10**). However, halogenation of alkyl-3-amino germanes or 3-iminoalkyl germanes (protected form) is not known in literature. Therefore, common chlorination agents were investigated [34–38]. The common agents $HCCl_3$ and LiCl were not reacting with the Ge-H functionality. CCl_4 (under AIBN catalysis), TCCA and $CuCl_2$/CuI were reacting with the -N=C- or $-NH_2$/$-NH_3^+Cl^-$ groups and an inseparable mixture of different compounds was obtained in ^1H NMR spectra. With this series of experiments, chlorination of the protected-, the hydrochloride- or the aminopropyl germanes (**6, 8, 10**) was not possible with these classic methods. Overall, a conversion of **6–10** to the corresponding chloro germane was therefore not possible, in Synthetic Route B an alternative procedure is described.

2.2. Synthetic Route B

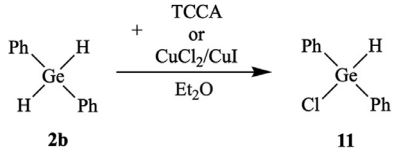
In Synthetic Route B, synthetic routes for chloro–3-aminopropyl germanes (**14, 15**) are shown (Scheme 8). For the preparation of **14** and **15,** a hydrogermylation reaction on the corresponding allyl amines was used. Hydrogermylations on the allyl amine with vinyl ethers [18–20] and allyl ethers [18–20] are known for triaryl- and trialkyl germanes [17]. However, this type of hydrogermylation is not known for diaryl–chloro germanes. Therefore, a novel synthetic route was developed to prepare 3-aminopropyl–chloro-diphenyl germanes. For this reaction, two starting materials were necessary, a hydridic chloro germane and an allyl amine derivative. The diphenyl–chloro germane ($Ph_2Ge(H)Cl$, **11**) was synthesized according to known procedures by using TCCA (trichloroisocyanuric acid) [37] or copper-(II)-chloride, using diphenyl germane (**2b**) as a starting material [38–40].



Scheme 6. Synthetic Route A, alkylation, deprotection, and neutralization of the corresponding germanium anion.



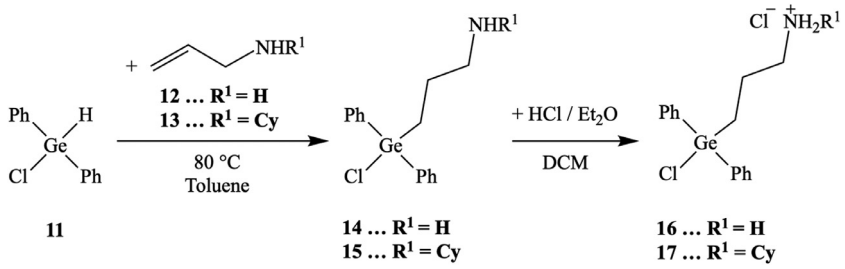
Scheme 7. Stability and reactivity of 7.



Scheme 8. Synthesis of 11.

In respect to the allyl amine starting material, allyl amine (**12**) or *N*-cyclohexylallyl amine (**13**) were used (Scheme 9). Allyl amine is suspected by the National Research Council (US) as being cardiovascularly toxic [28,29]. Therefore, the less toxic *N*-cyclohexylallyl amine (**13**) was also used in this work as an alternative starting material.

Compound **11** was reacted with the corresponding allyl amine (**12** or **13**) in toluene, with AIBN as radical initiator and the mixture was heated up to 80 °C (Scheme 9). The amount of AIBN is significant for product formation; with amounts bigger than 5 mol% of AIBN, the formation of byproducts was observed in ^{1}H- and ^{13}C NMR spectra. However, isolation of pure 3-aminopropyl germane was not possible. Therefore, 1.6 mol% of AIBN was used for the synthesis of the novel compounds **14** and **15.** The characterization was done by GCMS, ^{1}H- and ^{13}C NMR. The compounds **14** and **15** include two reactive sites, the Ge-Cl and the -N(H)R^{1} group. This bifunctionality makes **14** and **15** potential precursors for dif-



Scheme 9. Synthesis of the corresponding 3-aminopropyl germanes and hydrochlorides.

ferent synthesis processes in the future. The chlorine function can be derivatized to form new substructures in polymers/surfaces or in polymer catalysis chemistry. For examples, these new germanes could be utilized as starting material for a salt metathesis or other substitution reactions. In addition, the 3-aminopropyl anchor of these derivatives can be linked to different structures (polymers or surfaces) [7–9].

In order to get a better understanding of structural features, the corresponding hydrochlorides were formed. The compounds **14** and **15** were protonated with hydrochloric acid dissolved in diethyl ether. Both hydrochlorides (**16, 17**) were isolated as powders and the characterizations were done *via* ^{1}H-, ^{13}C NMR spectroscopy. However, only **17** was able to be recrystallized from a benzene/pentane mixture yielding colorless crystals suitable for single crystal X-ray analysis.

2.3. Characterization

2.3.1. NMR measurements

In this work, novel 3-aminopropyl-phenyl germanes were characterized. Interesting to mention are the proton NMR shifts of the directly bonded groups on the germanium atom. For the rest of the molecule (N-bonded and phenyl groups), and the ^{1}H and ^{13}C shifts are matching with the literature known data [8,9,17].

For the triphenyl compounds (**5, 7, 9**), the corresponding ^{1}H - shift for Ge-CH_2- is nearly in the same range (1.52 to 1.56 ppm). The bifunctional 3-aminopropyl-diphenyl germanes (**6, 8, 10, 14**) deliver an upfield ^{1}H - shift for Ge-CH_2- also in a similar range between 1.27 to 1.44 ppm.

The germanium atom (substituents H or Cl) and the nitrogen are influencing these shifts marginally. For the Ge-H compounds **6, 8, 10**, a ^{1}H - shift was obtained in a similar range (5.01 to 5.19 ppm) for the Ge-H function, this shift is in accordance to typical shifts of trisubstituted germanium hydrides [27].

2.3.2. Single crystal X-ray diffraction of the 3-aminopropyl germane hydrochlorides (7, 8, 17)

Compounds **7, 8** and **17** were isolated as powders and afterwards recrystallized. These crystals are the first examples of 3-aminopropyl germane hydrochloride structures in literature. The isolated hydrochloride **7** was recrystallized from chloroform and is shown in Fig. 1. One molecule water is interacting with the protonated aminopropyl group. The source of water was the aqueous hydrochloric acid from the deprotection reaction.

The isolated hydrochloride **8** was recrystallized from chloroform displayed in the supporting information. In Fig. 3, the extended structure of **8** is shown. **17** was crystalized from a benzene/pentane mixture. Compound **17** is shown in Fig. 2 which crystallized with two solvent molecules of benzene.

The average Ge-C bond length for crystallized hydrochlorides (**7, 8, 17**) is 1.9422(3) Å and compares well with the averaged Ge-C bond length in $GePh_4$ (1.9559(2) Å) [32,33] In comparison, between the shown hydrochlorides and The Ge-Ph bonding length in all

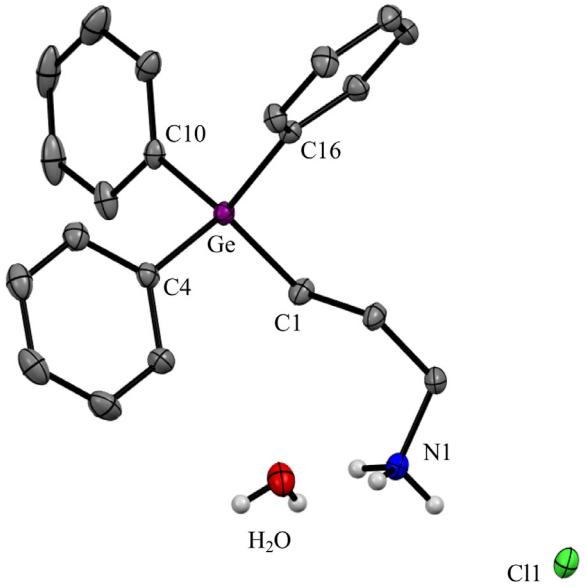


Fig. 1. Crystal structure of 7 - Ge-C_1 = 1.963(3) Å, Ge-C_4 = 1.951(3) Å, Ge-C_{10} = 1.950(3) Å, Ge-C_{16} = 1.944(3) Å; C_{16}-Ge_1-C_{10} = 106.95(11)°, C_{16}-Ge_1-C_4 = 111.02(11)°, C_{10}-Ge_1-C_4 = 109.56(11)°, C_{16}-Ge_1-C_1 = 109.93(11)°, C_{10}-Ge_1-C_1 = 110.74(11)°, C_4-Ge_1-C_1 = 108.65(12)°; one molecule H_2O is interacting with NH_3^+; All non-hydrogen atoms shown as 30% shaded ellipsoids. Carbon bound hydrogen atoms omitted for clarity.

three molecules (**7, 8, 17**) and in $GePh_4$ is in a similar range. With the crystal structure of compound **8**, the first crystal structure of an aminopropyl substituted germanium hydride is shown and therefore, a comparison with triphenyl germanium hydride was done. The length of the Ge-H bond in **8** is longer (1.67(6) Å) than the literature known compound Ph_3GeH, (Ge-H bond 1.495(4) Å) [40]. A reason for this difference could be the different substitution pattern with alkyl and aryl residues on the germanium atom. With the crystal structure of compound **17**, the first crystal structure of an aminopropyl substituted chloro germane is shown and therefore, a comparison with chloro–triphenyl germane was done. The Ge-Cl bond length in **17** is 2.1910(4) Å. The literature known compound Ph_3GeCl has a similar Ge-Cl length with 2.191(2) Å [41]. The angles between the Ph, H, Cl and germanium atoms are in a similar range, and around 6° +/- to the theoretical 109.5° tetrahedral angle. Overall, the shown crystal structures are the first structures of the compound class of 3-aminopropyl germane hydrochlorides in literature.

In the extended solid state, compounds **7, 8** and **17** all display halide interactions (N—H···Cl) between the amino functionality and the respective chlorine atoms of neighboring molecules (Table 1). In the case of **7** and **8**, the molecules arrange themselves to optimize these interactions resulting in layered two-dimensional sheets (Fig. 3) similar to hydrophilic/hydrophobic bilayer structural motifs. All other extended structures are in the Supporting Infor-

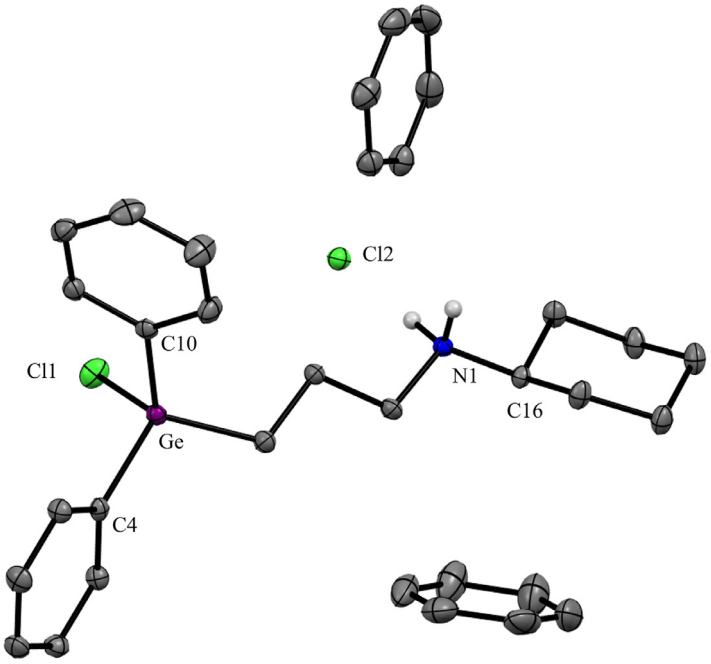


Fig. 2. Crystal structure of compound 17 - Ge-C_1 = 1.9416(15) Å, Ge-C_4 = 1.9339(14) Å, Ge-C_{10} = 1.9224(15) Å, Ge-Cl_1 = 2.1910(4) Å; C_1-Ge_1-Cl_1 = 106.07(5)°, C_4-Ge_1-C_1 = 110.72(6)°, C_4-Ge_1-Cl_1 = 105.79(4)°, C_{10}-Ge_1-C_1 = 116.26(6)°, C_{10}-Ge_1-Cl_1 = 106.12(5)°, C_{10}-Ge_1-C_4 = 111.11(6)°; All non-hydrogen atoms shown as 30% shaded ellipsoids. Carbon bound hydrogen atoms omitted for clarity.

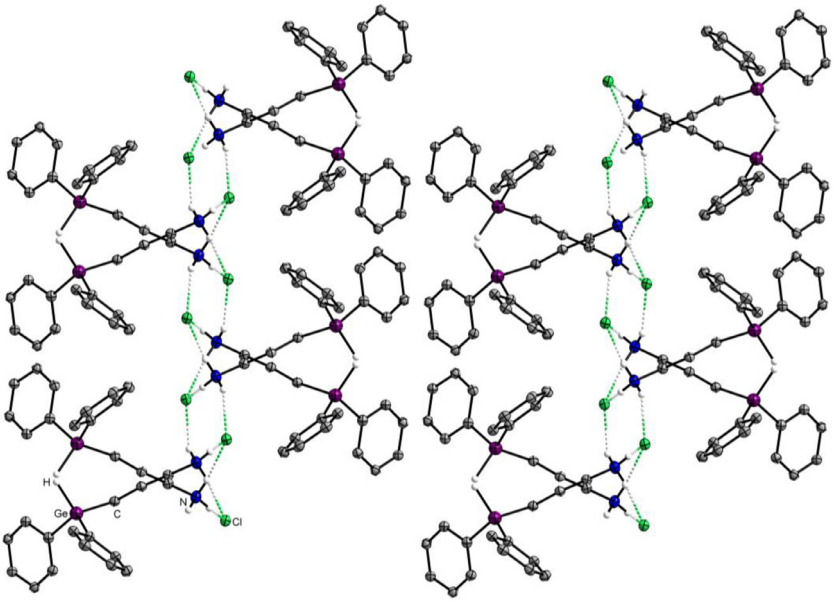


Fig. 3. Extended bilayer structure of 8. N—H···Cl interactions highlighted by dashed bonds. All non-hydrogen atoms shown as 30% shaded ellipsoids. Carbon bound hydrogen atoms omitted for clarity.

Table 1
Halide interactions in the extended solid state.

Compound	N—H···Cl (Å)
7	2.31-2.43
8	2.32-2.35
17	2.16-2.56

mation. Additional hydrogen bonding interactions are observed in **7** through the water of crystallization with neighboring chlorine atoms and amine groups in the hydrophilic region of the bilayer. There are no classical π-interactions observed intra-or intermolecularly through the phenyl groups for either **7** or **8**. In case of compound **17**, due to the co-crystallized benzene molecules, a three-dimensional network is observed propagated by N—H···Cl interactions and edge to face C—H···π interactions between the cyclohexyl substituents and benzene molecules (2.95-3.00 Å). The range of halide interactions distances in **17** is broader, possibly due to the higher steric demand of the cyclohexyl substituent.

3. Conclusion

A novel synthetic route for 3-aminopropyl-triphenyl germane under moderate reaction conditions is reported (**9**). Moreover,

the first bifunctional 3-aminopropyl-diphenyl germanes (**10**) could be reported. A hydrogermylation was also used to form the novel bifunctional 3-aminopropyl–chloro-diphenyl germanes (**14, 15**). These routes and compounds deliver the base for following studies in the field of organogermanium implementation on surfaces and in polymers.

4. Experimental

General information about materials (starting materials, sources of chemicals, solvents) and analytic methods are shown in the Supporting Information [43–55].

*4.1. Synthesis of 3-(2,2-dimethylpropyl-imino)propyl-triphenyl germane (5) (*via *anion 3a and 3c)*

For the compound **5**, 3-(2,2-dimethylpropyl-imino)propyl-triphenyl germane two synthetic routes are shown one over anion **3a** and one over anion **3c**.

4.1.1. Route via *anion 3a (Ge_2Ph_6 and K)*

In a 100 mL Schlenk tube, 9.49 g (15.6 mmol) of hexaphenyl germane (**1**) were mixed with 50 mL THF. To this white suspension, 1.22 g (30.5 mmol) of potassium were added and refluxed for 8 h, a dark green solution was resulting. Afterwards, 5.55 g (17.2 mmol) of 1–chloro-3-(2,2-dimethylpropyl-imino)propane (**4**) was added and was stirred for 4 h. The solvent was removed under vacuum and 15 mL *n*-pentane was added. After 15 min. of stirring, the mixture was filtered through a 20 μm syringe filter. The *n*-pentane was removed and the product was dried under vacuum at 40 °C. Product **5** was isolated as a slightly yellow oil, yield: 4.61 g (69%).

4.1.2. Route via *anion 3c (Ph_3GeH and* t*-BuLi)*

In a 100 mL Schlenk tube, 0.7 g (2.30 mmol) triphenyl germane (**2a**) was dissolved in 20 mL THF. After cooling to −50 °C, 1.45 mL (2.76 mmol) of a *t*-BuLi solution (1.9 M in *n*-pentane) was added and stirred for 1 h. A clear brownish solution was resulting, 0.56 g (3.44 mmol) of 1–chloro-3-(2,2-dimethylpropyl-imino)propane (**4**) was added dropwise and this mixture was stirred for 2 h. The solvent was removed under vacuum and the residue was suspended in 15 mL benzene. After 15 min. of stirring, the mixture was filtered through a 20 μm syringe filter, afterwards the benzene was removed and the product was dried under vacuum at 40 °C. Product **5** was isolated as a slightly yellow oil, yield: 0.72 g (73%).

3-(2,2-dimethylpropyl-imino)propyl-triphenyl germane (5) **$C_{26}H_{31}GeN$** found: 72.3% C (calcd. 72.6%), found: 7.4% H (calcd. 7.3%); **GC–MS:** $t_R = 18.4$ min, MS: 416.2 (R-N=CH-C^+Me_2), 388.1 (R-N=CH-CH_2^+), 374.1 (R-N=CH^+), (R=$Ph_3Ge(CH_2)_3$), 354.2 ($Ph_2Ge^+(CH_2)_3$-N=CHCMe_3=-), 305.1 (Ph_3Ge^+), 227.0 (Ph_2Ge^+), 201.0 ($Ge^+(CH_2)_3$-N=CHCMe_3=-), 151.0 ($PhGe^+$); **^{1}H NMR:** (300 MHz, C_6D_6) δ 7.55 (m, 6H, *o*-phenyl-H), 7.32 (s, 1H, C=NH-), 7.15 (m, 9H, *m,p*-phenyl-H,), 3.32 (t, 2H, -CH_2N), 1.93 (m, 2H, -$CH_2CH_2CH_2$-), 1.56 (m, 2H, -CH_2-Ge), 1.01 (s, 9H, -CH_3) **^{13}C NMR:** (75.5 MHz, C_6D_6) δ 170.5 (-C=N), 137.3 (phenyl-C, Ge-C), 135.0 (*o*-phenyl-C), 128.8 (*p*-phenyl-C), 128.2 (*m*-phenyl-C), 63.7 (1C, -CH_2-N), 26.9 (-CH_3), 26.7 (-$CH_2CH_2CH_2$-), 11.4 (-CH_2-Ge) ppm.

*4.2. Synthesis of 3-(2,2-dimethylpropyl-imino)propyl-diphenyl germane (6) (*via *anion 3b)*

In a 250 mL Schlenk tube, 2.6 g (11.4 mmol) diphenyl germane (**2b**) was dissolved in 50 mL THF. After cooling to −50 °C, 8 mL (13.7 mmol) of a *t*-BuLi solution (1.7 M in *n*-pentane) was added and stirred for 1 h. A clear yellow solution was resulting and 2.78 g (17.2 mmol) of 1–chloro-3-(2,2-dimethylpropyl-imino)propane (**4**) was added dropwise and was stirred for 2 h. At 40 °C, the solvent was removed under vacuum and the residue was suspended in 10 mL *n*-pentane. After 15 min. of stirring, the mixture was filtered through a 20 μm syringe filter, afterwards the *n*-pentane was removed. The product was dried in vacuum at 40 °C. **6** was isolated as a slightly yellow oil, yield: 4.15 g (78%). **$C_{20}H_{27}GeN$** found: 65.7% C (calcd. 67.8%), found: 7.91% H (calcd. 7.69%), found: 4.07% N (calcd. 3.96%); **GC–MS:** $t_R = 15.3$ min, MS: 354.2 (M^+), 340.2 (Me_2C^+-C=N-R), 326.1 (MeC^+-C=N-R), 312.1 (C^+-C=N-R), 298.1 ($^+$C=N-R) (R = $Ph_2Ge(H)(-(CH_2)_3$-), 278.1 ($Ge^+Ph(H)(-(CH_2)_3$-N=CHCMe_3=-), 268.1 $Ph_2Ge(H)(-CH_2)_3^+$, 229.0 $Ph_2Ge^+(H)$, 151.0 $Ge^+Ph(H)$; **^{1}H NMR:** (300 MHz, C_6D_6) δ 7.46 (m, 4H, *o*-phenyl-H), 7.28 (t, 1H, -NH=), 7.12 (m, 6H, *m,p*-phenyl-H), 5.19 (t, 1H, Ge-H) $^3J(^1H–^1H)$ H-Ge-CH_2- = 5.1 Hz, 3.27 (td, 2H, -CH_2N), 1.83 (m, 2H, -$CH_2CH_2CH_2$-), 1.30 (m, 2H, -CH_2-Ge), 1.27 (s, 9H, -C(CH_3)$_3$); **^{13}C NMR:** (75.5 MHz, C_6D_6) δ 170.9 (-C=N), 137.0 (phenyl-C, Ge-C), 135.1 (*o*-phenyl-C), 129.1 (*p*-phenyl-C), 128.6 (*m*-phenyl-C), 63.7 (-CH_2N), 36.1 (quart.-C), 27.6 (-$CH_2CH_2CH_2$–), 27.2 (-C(CH_3)$_3$), 11.2 (-CH_2-Ge) ppm.

4.3. Synthesis of 3-aminopropyl-triphenyl germane hydrochloride (7) and 3-aminopropyl-diphenyl germane hydrochloride (8)

In a 20 mL Schlenk tube, the corresponding germane was solved in 5 mL benzene. To the colourless solution, 2 eq. of hydrochloric acid (0.5 M, aq.) was added and stirred for 2 h. The product precipitated as a white solid. The solid was separated, washed 3 times with *n*-pentane/benzene mixture (1:1) and was dried in vacuum at 40 °C.

4.3.1. 3-aminopropyl-triphenyl germane hydrochloride (7)

corresponding germane: 0.2 g (0.46 mmol) 3-(2,2-dimethylpropyl-imino)propyl-triphenyl germane (**5**), 1.86 mL HCl (0.5 M, aq.) (0.92 mmol); The product **7** was crystallized from chloroform and isolated as colourless crystals, yield: 0.18 g (90%); **mp**: 167 °C; **$C_{21}H_{24}GeNCl$** found: 63.43% C (calcd. 63.3%), found: 6.01% H (calcd. 6.07%), found: 3.54% N (calcd. 3.51%); **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 8.29 (bs, 3H, -NH_3^+), 7.44 (m, 6H, *o*-phenyl-H), 7.31 (t, 9H, *m,p*-phenyl-H), 2.82 (d, 2H, -CH_2-N), 1.87 (m, 2H, -CH_2-CH_2-CH_2-), 1.52 (m, 2H, -CH_2-Ge); **^{13}C NMR:** (75.5 MHz, $CDCl_3$) δ 136.2 (phenyl-C, Ge-C), 134.9 (*o*-phenyl-C), 129.2 (*p*-phenyl-C), 128.4 (3C, *m*-phenyl-C), 42.3 (CH_2-N), 23.4 (-CH_2-CH_2-CH_2-), 10.9 (-CH_2-Ge) ppm. The X-ray crystallography data is located in the Supporting Information.

4.3.2. 3-aminopropyl-diphenyl germane hydrochloride (8)

0.26 g (0.73 mmol) 3-(2,2-dimethylpropyl-imino)propyl-diphenyl germane (**6**), 2.94 mL HCl (0.5 M, aq.) (1.47 mmol); The product **8** was isolated as a white powder and recrystalized from chloroform yielding white crystals, yield: 0.24 g (91%). **mp**: 102 °C; **$C_{21}H_{24}GeNCl$** found: 55.59% C (calcd. 55.88%), found: 6.37% H (calcd. 6.25%), found: 4.39% N (calcd. 4.34%); **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 8.19 (bs, 3H, -NH_3^+), 7.50 (d, 4H, *o*-phenyl-H), 7.36 (t, 6H, *m,p*-phenyl-H), 5.01 (d, 1H, Ge-H), 2.96 (s, 2H, -CH_2-N), 1.96 (t, 2H, -CH_2-CH_2-CH_2-), 1.38 (t, 2H, -CH_2-Ge); **^{13}C NMR:** (75.5 MHz, $CDCl_3$) δ 135.7 (phenyl-C, Ge-C), 134.8 (*o*-phenyl-C), 129.2 (*p*-phenyl-C), 128.5 (*m*-phenyl-C), 42.3 (CH_2-N), 24.1 (-CH_2-CH_2-CH_2-), 10.2 (-CH_2-Ge) ppm. The X-ray crystallography data is located in the Supporting Information.

4.4. Synthesis of 3-aminopropyl-triphenyl germane (9) and 3-amino-propyl-diphenyl germane (10)

In a 20 mL Schlenk tube, the corresponding germane was solved in 5 mL chloroform. The colourless solution was extracted 2 times with 2 mL of KOH (0.5 M, aq.). The chloroform phase was

dried and the chloroform was removed under vacuum. The product was dried in vacuum at 40 °C.

4.4.1. 3-aminopropyl-triphenyl germane (9)

100 mg (0.25 mmol) 3-aminopropyl-triphenyl germane hydrochloride (**7**). The product **9** was isolated as a colourless oil, yield 95 mg (95%) **$C_{21}H_{23}GeN$** found: 69.3% C (calcd. 67.8%), found: 6.46% H (calcd. 7.69%), found: 3.79% N (calcd. 3.96%); **GC–MS:** $t_R = 17.5$ min, MS: 363.1 (M^+), 334.09 (Ph_3GeCH_2-CH_2^+), 305.0 (Ph_3Ge^+), 286.0 (Ph_2Ge^+(-CH_2)$_3$-NH_2), 227.0 (Ph_2Ge^+), 151.0 ($PhGe^+$), 78.0 (Ph^+); **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 7.53 (m, 6H, *o*-phenyl-H), 7.41 (t, 9H, *m,p*-phenyl-H), 2.76 (t, 2H, -CH_2-N), 1.71 (m, 2H, -CH_2-CH_2-CH_2-), 1.55 (m, 2H, -CH_2-Ge), 1.51 (bs, 2H, -NH_2); **^{13}C NMR:** (75.5 MHz, $CDCl_3$) δ 137.1 (phenyl-C, Ge-C), 134.9 (*o*-phenyl-C), 128.9 (*p*-phenyl-C), 128.2 (*m*-phenyl-C), 45.4 (-CH_2-N), 29.4 (-CH_2-CH_2-CH_2-), 11.2 (-CH_2-Ge) ppm.

4.4.2. 3-aminopropyl-diphenyl germane (10)

0.2 g (0.7 mmol) 3-aminopropyl-diphenyl germane hydrochloride (**9**); The product **10** was isolated as a colourless oil, yield: 0.18 g (92%). **$C_{15}H_{19}GeN$** found: 63.3% C (calcd. 63.0%), found: 5.03% H (calcd. 4.90%), found: 4.39% N (calcd. 4.34%); **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 7.48 (d, 4H, *o*-phenyl-H), 7.34 (t, 6H, *m,p*-phenyl-H), 5.04 (s, 1H, GeH), 2.77 (s, 2H, -CH_2-N), 2.02 (bs, 2H, -NH_2), 1.72 (t, 2H, -CH_2-), 1.39 (t, 2H, -CH_2-Ge); **^{13}C NMR:** (75.5 MHz, C_6D_6) δ 136.8 (phenyl-C, Ge-C), 134.8 (*o*-phenyl-C), 128.8 (*p*-phenyl-C), 128.2 (*m*-phenyl-C), 44.8 (-CH_2-N), 30.0 (-CH_2-CH_2-CH_2-), 10.4 (-CH_2-Ge) ppm.

4.5. Synthesis of chloro–diphenyl germane (11)

For the compound **11,** chloro–diphenyl germane two synthesis ways are shown in this work.

4.5.1. Route via *TCCA as chlorination agent*

In a 500 mL three-necked round-bottom flask, 14.85 g (65.1 mmol) diphenyl germane (**2b**) was dissolved in 350 mL diethyl ether. After cooling to −80 °C, 5.03 g (21.7 mmol) of TCCA was very slowly added (200 mg every 10 min) and stirred for 48 h. A white suspension was resulting. At 40 °C, the solvent was removed under vacuum and the residue was suspended in 250 mL *n*-pentane. After 45 min. of stirring, the mixture was filtered and the *n*-pentane was removed under vacuum. The product **11**, a clear colourless liquid, was dried in vacuum at 40 °C, yield: 14.86 g (87%).

4.5.2. Route via *$CuCl_2$ as chlorination agent*

In a 50 mL three-necked round-bottom flask, 2.20 g (9.6 mmol) diphenyl germane (**2b**) was dissolved in 25 mL THF. 1.29 g (9.6 mmol) of $CuCl_2$ and 18 mg (0.096 mmol) CuI were added and refluxed for 24 h. A brownish suspension was resulting and the solid was filtered off. At 50 °C, the solvent was removed under vacuum and the residue was suspended in 25 mL *n*-pentane. After 45 min. of stirring, the mixture was filtered, the *n*-pentane was removed and the resulting yellow oil was distilled in the vacuum, **bp** = 128 °C (0.5 mbar). The product **11** is a clear colourless liquid, yield: 2.15 g (85%).

Chloro-diphenyl germane (11) $C_{12}H_{11}GeCl$ found: 54.9% C (calcd. 54.7%), found: 4.2% H (calcd. 4.2%); **GC–MS:** $t_R = 11.7$ min, MS: 263.0 (M^+), 227.0 (Ph_2Ge^+(H)), 185.9 ($PhGe^+$(Cl)), 151.0 ($PhGe^+$), 108.9 ($ClGe^+$), 78.0 (Ph^+); **^{1}H NMR:** (300 MHz, C_6D_6) δ 7.47 (q, 4H, *o*-phenyl-H), 7.11 (m, 6H, *m,p*-phenyl-H,), 6.39 (s, 1H, Ge-H); **^{13}C NMR:** (75.5 MHz, C_6D_6) δ 134.5 (phenyl-C, Ge-C), 133.6 (*o*-phenyl-C), 130.4 (*p*-phenyl-C), 128.6 (*m*-phenyl-C) ppm.

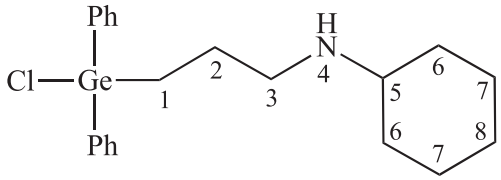


Fig. 4. Numbering of the N-cyclohxyl-aminopropyl substituent.

4.6. Synthesis of 3-aminopropyl–chloro-diphenyl germane (14) and N-cyclohexyl-3-aminopropyl–chloro-diphenyl germane (15)

In a 250 mL Schleck flask, chloro–diphenyl germane (**11**) was dissolved in toluene, the corresponding amine was added and the corresponding amount of AIBN was also added. This mixture was heated up to 80 °C for 20 h. A white suspension was formed, the solid was separated and from the filtrate the solvent was removed. The resulting white powder was washed 3 times with *n*-pentane and dried in vacuum for 10 h at 30 °C.

4.6.1. 3-aminopropyl–chloro-diphenyl germane (14)

2.03 g (7.7 mmol) chloro–diphenyl germane (**11**); 55 mL toluene; 0.77 g (13.8 mmol) corresponding amine: allyl amine (**12**); 20 mg of AIBN. The product **14** was isolated as a white powder, yield: 1.65 g (67%); **mp** = 77 °C; **$C_{15}H_{18}GeClN$** found: 54.5% C (calcd. 56.2%), found: 5.9% H (calcd. 5.7%), found: 3.9% N (calcd. 4.4%); **GC–MS:** $t_R = 13.8$ min, MS: 285.0 (Ph_2Ge^+(CH2)$_3$$NH_2$), 257.0 ($Ph_2ClGe^+$), 228.0 ($Ph_2Ge^+$(H)), 151.0 ($PhGe^+$), 124.9 ($Cl(CH_3)Ge^+$), 78.0 ($Ph^+$); **mp** = 77 °C; **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.37 (m, 4H, *o*-phenyl-H), 7.29 (m, 6H, *m,p*-phenyl-H,), 3.02 (t, 2H, -CH_2-N), 2.42 (s, -NH_2), 2.09 (t, 2H, -CH_2-CH_2-CH_2-), 1.44 (m, 2H, Ge-CH_2); **^{13}C NMR:** (100.6 MHz, $CDCl_3$) δ 137.6 (phenyl-C, Ge-C), 134.0 (*o*-phenyl-C), 129.5 (*p*-phenyl-C), 128.2 (*m*-phenyl-C), 42.4 (-CH_2-N), 22.8 (-CH_2-CH_2-CH_2), 14.1 (CH_2-Ge) ppm.

4.6.2. N-*cyclohexyl-3-aminopropyl–chloro-diphenyl germane (15)*

1.0 g (3.7 mmol) chloro–diphenyl germane (**11**); 55 mL toluene; 0.79 g (5.7 mmol), corresponding amine: *N*-cyclohexyl-3-allyl amine (**13**); 10 mg AIBN. The product (**15**) was isolated as a white powder, yield: 1.49 g (55%); For the positions in the *N*-Cy-aminopropyl substituent the numbering from Fig. 4 was used. **mp** = 132 °C; **$C_{21}H_{28}GeNCl$** found: 60.7% C (calcd. 62.7%), found: 7.1% H (calcd. 7.0%), found: 3.3% N (calcd. 3.5%); **GC–MS:** $t_R = 16.8$ min, MS: 367.0 (Ph_2Ge^+(R)), 339.1 ($PhGe^+$(Cl)(R^2), 324.1 ($PhGe^+$(Cl)(R)), (R= -(CH_2)$_3$-N(H)Cy), (R^2=-(CH_2)$_3$-N(H-CH_2Me)-CH_2Me), 227.0 (Ph_2Ge^+), 151.0 ($PhGe^+$), 108.9 ($ClGe^+$), 77.0 (pH^+); **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.34 (m, 6H, *o*-phenyl-H), 7.26 (q, 4H, *m,p*-phenyl-H), 3.01 (t, 2H, 3), 2.49 (quin, 2H, 2), 2.35 (d, 1H, 5), 1.89 - 1.69 (bm, 4H, 6), 1.69 (bm, 2H, 8), 1.36 (m, 2H, 1), 1.36 – 1.25 (bm, 4H, 7), 0.92 (t, 1H, 4); **^{13}C NMR:** (100.6 MHz, $CDCl_3$) δ 137.8 (phenyl-C, Ge-C), 133.8 (*o*-phenyl-C), 129.4 (*p*-phenyl-C), 128.0 (*m*-phenyl-C), 58.1 (3), 45.7 (5), 29.1 (6), 24.8 (2), 21.5 (8), 20.6 (7), 14.3 (1) ppm.

4.7. Synthesis of 3-aminopropyl–chloro-diphenyl germane hydrochloride (16) and N-*cyclohexyl-3-aminopropyl–chloro-diphenyl germane hydro-chloride (17)*

In a 50 mL Schleck flask, the corresponding 3-aminopropyl–chloro-diphenyl germane was dissolved in 10 mL DCM. Afterwards, 1 eq. of HCl solved in diethyl ether (2 M HCl) was added and stirred for 15 min. The solvent was removed, the resulting white solid was dried in vacuum for 3 h and was recrystallized.

4.7.1. 3-aminopropyl–chloro-diphenyl germane hydrochloride (16)

corresponding germane: 300 mg (0.94 mmol) 3-aminopropyl–chloro-diphenyl germane (**14**); The product **16** was isolated as a white powder, yield: 310 mg (93%); **mp** = 112 °C; **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 8.26 (bs, 3H, -NH_3^+), 7.55 (d, 4H, *o*-phenyl-H), 7.37 (s, 6H, *m,p*-phenyl-H,), 2.94 (bs, 2H, -CH_2-NH_3^+), 2.00 (bs, 2H, Ge-CH_2), 1.67 (bs, 2H, -CH_2-CH_2-CH_2-NH_2); **^{13}C NMR:** (75.5 MHz, $CDCl_3$) δ 135.1 (phenyl-C, Ge-C), 133.6 (*o*-phenyl-C), 130.6 (*p*-phenyl-C), 128.9 (*m*-phenyl-C), 41.8 (CH_2-N), 22.4 (-CH_2-CH_2-CH_2-), 15.5 (CH_2-Ge) ppm.

4.7.2. N-cyclohexyl-3-aminopropyl–chloro-diphenyl germane hydrochloride (17)

corresponding germane: 350 mg (0.79 mmol) 3-aminopropyl–chloro-diphenyl germane (**15**); The product **17** was recrystallized from a benzene/pentane mixture (1:1) and was isolated as colourless crystals, yield: 290 mg (91%); **mp** = 178 °C; For the positions in the *N*-Cy-aminopropyl substituent, the numbering from Fig. 4 was used. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 9.46 (bs, 2H, -NH_2^+-), 7.63 (d, 4H, *o*-phenyl-H), 7.45 (s, 6H, *m,p*-phenyl-H,), 2.97 (bs, 2H, 3), 2.29 (quin, 2H, 2), 2.11 (d, 1H, 5), 1.80 (m, 4H, 6), 1.76 (m, 2H, 8), 1.54 (m, 2H, 1), 1.18 (bm, 4H, 7); **^{13}C NMR:** (100.6 MHz, $CDCl_3$) δ 135.2 (phenyl-C, Ge-C), 133.4 (*o*-phenyl-C), 130.4 (*m*-phenyl-C), 128.8 (*p*-phenyl-C), 56.9 (3), 45.7 (5), 29.0 (6), 24.8 (2), 24.6 (8), 20.6 (7), 15.9 (1) ppm. The X-ray crystallography data is located in the Supporting Information.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This work was supported by the NAWI Graz project, a collaboration between the Graz University of Technology and the Graz University.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2023.122709.

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