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SYNTHESIS OF ORGANOGERMANIUM CATALYSTS AND CATALYST PRECURSORS FOR THE POLYURETHANE FORMATION

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Kurzfassung

Organozinnkatalysatoren finden in modernen Polymersynthesen kaum noch Anwendung, da diese meist als toxisch und umweltgefährdend gelten. Daher ist es Ziel moderner Forschungsarbeit, alternative Katalysatoren zu finden. Eine mögliche Alternative bieten Organogermaniumverbindungen. In der Literatur sind nur wenige Organogermanium katalysierte Polymerisationreaktionen bekannt. Da im Falle der Polyurethansynthese keine Germaniumkatalyse bekannt ist, entstand die Idee der Organogermanium katalysierten Polyurethansynthese. Basierend auf diesem Konzept war Ziel dieser Arbeit die Synthese von Organogermaniumkatalysatoren.

In Analogie zu bekannten Organozinnacetatkatalysatoren wurden Germanium analoge Verbindungen hergestellt und deren katalytische Aktivität nachgewiesen. Darüber hinaus konnten in dieser Arbeit Vorstufen eines Aminopropylgermanium basierten Katalysators syntethisiert werden. Die Aminopropylgruppe fungiert als Ankergruppe in der Polymermatrix und verhindert das "Catalyst leach out". Für die Verbindungen Triphenyl-3-aminopropylgerman und Diphenyl-3-aminopropylgerman hydrochlorid wurden neuartige Synthesewege aufgezeigt. Anzumerken ist das, Diphenyl-3-aminopropylgerman hydrochlorid nicht literaturbekannt ist und die hierfür verwendete Route in Zukunft als Universal-Syntheseroute dienen könnte. Im Allgemeinen bildet Diphenyl-3-aminopropylgerman hydrochlorid die Vorstufe für eine finale Katalysatorsynthese.

Zusammenfassend konnte in dieser Arbeit gezeigt werden, dass Organogermaniumacetate als Katalysator verwendet werden können. Zusätzlich konnten neue Syntheserouten für Aminopropylgermane gezeigt werden, welche eine Katalysatorvorstufe darstellen. Alles in allem liefert diese Arbeit die Grundlage für das neue Forschungsfeld der Amionopropylgermaniumcarboxylat basierten Katalyse.

Abstract

In modern polymer synthesis processes organotin catalysts are mostly no longer used therefore, target of modern research work is the development of alternative catalysts. A possible alternative are organogermanium catalysts. In literature only a few numbers of organogermanium catalysed polymerization reactions are known. In the case of the polyurethane formation no germanium catalyzed reaction was known, therefore the idea of germanium catalyzed polyurethane formation was born. Based on this concept the applicability of germanium compounds analogous to the common tin catalysts would be interesting. Therefore, the aim of project was the synthesis of catalytically active germanium acetates and the development of new synthesis routes.

In analogy to organotin catalysts, the formed end products are catalytic active germanium acetates and the aminopropyl anchor group including compounds triphenyl-3-aminopropyl germane and diphenyl-3-aminopropyl germane hydrochloride. The anchor group is used for covalent polymer matrix bonding to prevent a catalyst leach out. That aminopropyl germanium compounds are precursors for a noval catalyst generation based on aminopropyl germanes. Main target of this work was the synthesis of aminopropyl substituted germanes, which are used as catalyst precursors. This target was achieved with the synthesis of diphenyl-3-aminopropyl germane hydrochloride. The compound is not literature known and the synthesis route could be used as an general synthesis route for this compound type.

Overall, in this work the catalytic activity of germanium acetate was proved. In addition, novel synthesis routes for catalyst precursors with aminopropyl anchor groups were found. Therefore, this work delivers the base for the synthesis of aminopropylgermanium carboxylate catalysts.

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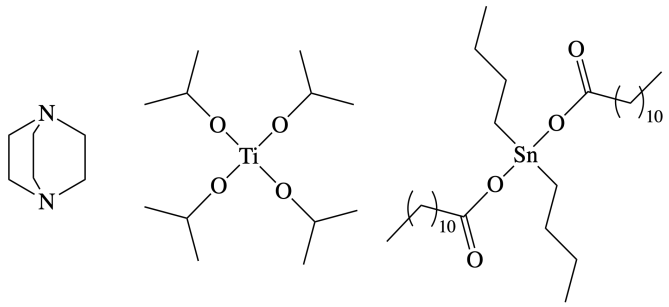
1 Introduction

Polyurethanes (PU) are widely common in the material technology for a large number of applications. PU are used for materials in different technological products. For example in foams, flexible plastics, textiles, automotive parts and electronic components.[1] A urethane is formed by reacting an alcohol (R – OH) with an isocyanate (R – N = C = O), for polyurethanes polyols and diisocyanates are used. Between these groups the reaction rate is slow, therefore a catalyst is used to accelerate the polymerization. Nowadays there are various of options for the catalysis of this reaction. Organic heterocycles or organometallic compounds are common catalysts.[2–4]



(I) (II) (III)

Scheme 1 – Example catalysts for the polymerization reaction for PU[2–4]

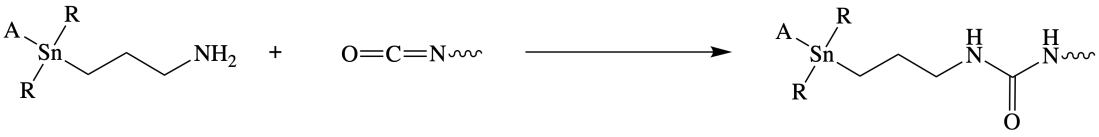
Compound (I), 1,4-diazabicyclo-[2.2.2]-octane (DABCO) is the most common catalyst for the PU synthesis. DABCO is a heterocyclic catalyst with two tertiary amine groups and used in gelling or blowing polymerizations. Steric hindrance, volatility and the molecular weight affects the catalytic activity negative. A Strong fish like smell and the toxicity in combination with the volatility (volatile organic compounds (VOCs)) are additional disadvantages.[2–4]

Compounds (II) and (III) are organometallic catalysts, an exceptionally high catalytic activity shows compound (III) dibutyltin dilaurate (DBTDL). In presence of a small amount of organotin compounds, the increase of the reaction rate is great. DBTDL can be used flexibly for the most industrial polymerization systems, moisture or light influences the process only marginally. In the polymer matrix the catalyst is not covalent bounded, environmental effects such as rain can leach out the tin compound and release them in the environment. This effect is called ”leach out effect” and is the source of various environmental problems.[2,4–6]

A huge disadvantage of organotin catalysts is the toxicity. Furthermore, the substitution pattern of the compound is in a direct relation with the toxicity. For example alkyltin compounds are more toxic than aryltin compounds. Moreover, with the number of halogen atoms the toxicity decreases: $R_3SnX > R_2SnX_2 > RSnX_3$.[2,4–6] In medical studies rats lost weight and became lethargic after the exposure of a significant amount of DBTDL.[7] The activity of the heme cytochrome P-450 decreases and affects the biotransfor-

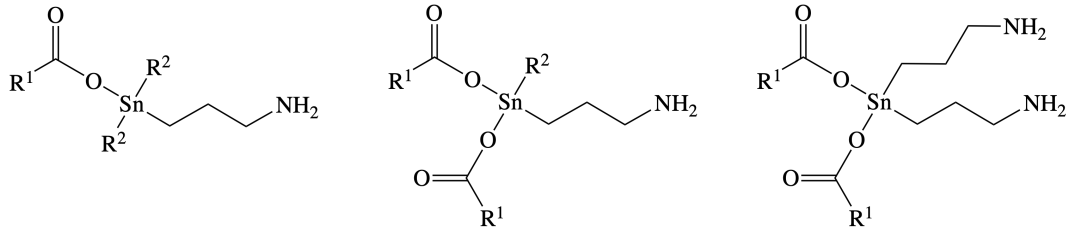
mation in the microsomes.[8] In addition, DBTDL shows an effect of the hormonal metabolism and is cytotoxic.[8,9] The European Chemicals Agency classifies DBTDL as "Toxic to Reproduction" and "Suspected to be Mutagenic". Therefore the European Union (EU) banned organotin compounds as industrial catalyst.[10]

Target of modern research work is the leach out inhibition. One possible approach was found in our working group. The idea behind it is a covalent bonding of metal containing catalysts into the polymer matrix. Aminopropyl groups were used for the matrix bounding by Pichler[6] and Müller.[5] In scheme 2 the anchor group (aminopropyl group) bonds covalently in the polymer matrix and prevents the leach out.[5]



Scheme 2 – Principle of the aminopropyl anchor system - A = carboxylate group, halogen atome, R = alkyl-, aryl-group[5]

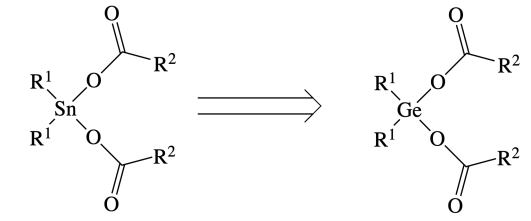
Our working group developed synthesis routes for tin catalysts with alkyl, aryl, aminopropyl and carboxylate side chains. In kinetic experiments aminopropyltin compounds show a significant catalytic activity. Futhermore, the compound typ (V) delivers a activity similar to DBTDL. Structures of the used catalysts are illustrated in the following scheme.[5,11]



(IV) (V) (VI)

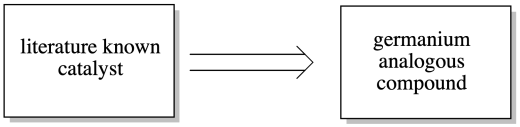
Scheme 3 – Example catalysts for the kinetic studies, $R^1 = -CH_3$, $-(CH_2)_{10}CH_3$, R^2 = alkyl-, aryl-group[5,11]

A second possible approach to avoid the known disadvantages of organotin compounds is the use of a non toxic organometallic catalyst. One of the direct neighbour elements of tin in group 14 is germanium. In contrast to tin, organogermanium compounds are not considered as toxic.[12,13] Based on this concept, organogermanium compounds are an environmentally friendly alternative to tin catalysts.



DBTDL R^1 = butyl R^2 = $-(CH_2)_{10}CH_3$

DBTDA R^1 = ethyl R^2 = $-CH_3$

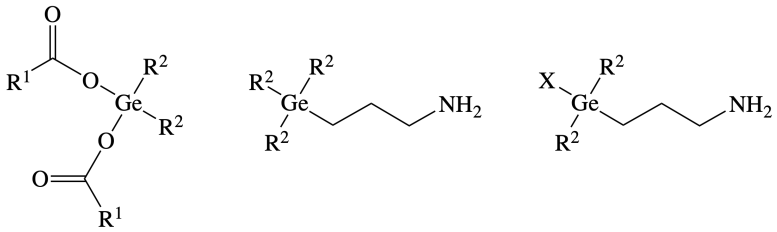


Scheme 4 – Idea and principle of the new germanium based catalysed - R^1 = alkyl- and phenyl group; R^2 = alkyl group

In addition, the combination of the approaches ”covalent bonding” and ”organogermanium catalysts” is also a possibility. Analog to tin, the resulting compounds are alkyl- or arylaminopropylgermanium acetates.

1.1 Aim of Project

Based on this concept the applicability of germanium compounds analogous to (III), (IV), (V) and (VI) would be interesting. Therefore, the aim of project was the synthesis of catalytically active germanium acetates and the development of new synthesis routes for aminopropyl germanes. For this purpose, three compound classes are interesting to synthesize, compound (VII) dialkyl- or diarylgermanium diacetates are the germanium analogous to the DBTDL-type. (VIII) Trialkyl- or triaryl-3-aminopropyl germanes and (IX) dialkyl- or diaryl-3-aminopropyl germanes are catalyst precursors or catalysts for the polyurethane formation. Furthermore, the determination of the catalytic activity is also a project target.



(VII) (VIII) (IX)

Scheme 5 – Types of germanes in the project, R^1 = alkyl, R^2 = alkyl or aryl, X = H, Cl or $-OOCCH_3$

2 Literature

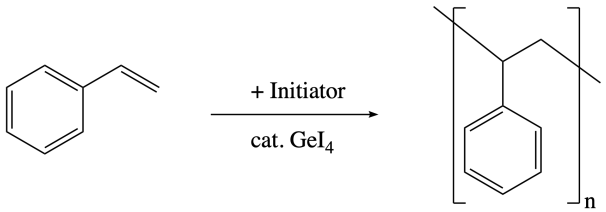
2.1 Germanium halides and organogermanium catalysts for polymerizations

Germanium catalysts can be used in different fields of polymer synthesis. Reversible chain transfer catalyzed polymerization (RTCP) is an example.[14] In literature GeI_4[15–17] and (p-tolyl)GeI_3[16] were used as transfer catalyst. For a good molar weight control a large number of activation/deactivation cycles between catalyst and polymer is necessary, in scheme 6 the cycle is illustrated. Radical transfer between $^{\bullet}GeI_3$ and the polymer chain is the principle behind the cycle. Typical monomers for RTCP are styrene or methyl methacrylate.[15–17]

$$GeI_4 + {}^{\bullet}R_{polymer} \rightleftharpoons I{-}R_{polymer} + {}^{\bullet}GeI_3 \rightleftharpoons GeI_4 + {}^{\bullet}R_{polymer}$$

Scheme 6 – Chain transfer mechanisem proposed by Goto et.al.[15–17]

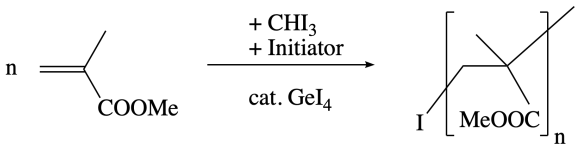
Germanium catalysts have a lower catalytic activity than the analogous tin compounds: $SnI_4 > GeI_4 >$ (p-Tolyl)GeI_3.[15–17] However, in contrast to tin (IV) iodide germanium(IV) iodide is not considered as CMR substance or environmental harmful.[13,18,19] Synthesis conditions and solvents are similar to common polymerizations. For example the polymerization of styrene is performed in THF at 70 °C for 7 h. BPO was used as initiator, as starter CHI_3 and GeI_4 as catalyst.[15–19]



Scheme 7 – GeI_4 catalysed styrene polymerization[15–17]

$GeCl_4$ is also a possible catalyst for RTCP. Known in literature is the copolymerization of vinyl acetate and acrylic acid.[20]

Furthermore, precursers for ”reversible addition fragmentation chain transfer polymerizations” (RAFT) can synthezied by germanium catalysed RTCP. An example is the preperation of the poly(methyl methacrylate) iodine. The iodine is formed by reacting methyl methacrylate with CHI_3, in presence of GeI_4 and the initiator 2,2’-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70). Synthesis conditions and solvents are similar to common polymerizations. For example the polymerization with methyl metacrylate is performed in dioxane at 40 °C.[21]

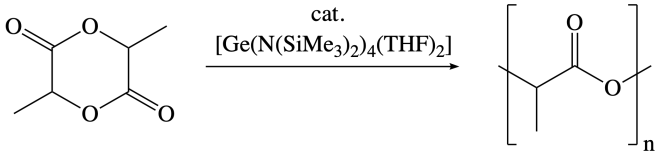


Scheme 8 – Example of a GeI_4 catalysed polymerization[21–23]

In addition to germanium halides, complexes of germanium are catalytically active. Guo and Thomas[14] used $[Ge(N(SiMe_3)_2)_4(THF)_2]$ as replacement for common tin catalysts in lactide polymerizations. Common catalyst tin(II) bis(2-ethylhexanoate) is harmful for the human organism and the environment. In a ring opening polymerization (ROP), a conversion of 97% at room temperature is achieved by using 0.5 mol% catalyst. Catalyst preperation is done by a salt metathesis of $GeCl_4$ and $Na[N(SiMe_3)_2]$ in THF.[14]

$$GeCl_4 + 4\,Na[N(SiMe_3)_2] + 2\,THF \longrightarrow [Ge(N(SiMe_3)_2)_4(THF)_2] + 4\,NaCl$$

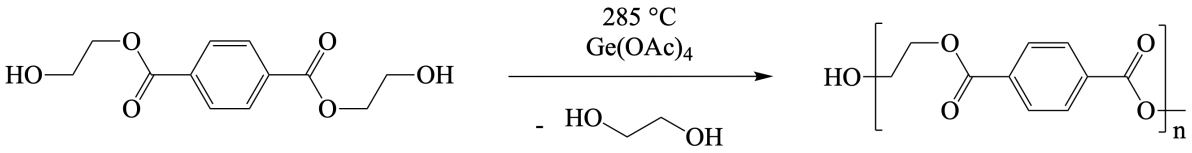
Scheme 9 – Catalyst synthesis via salt metathesis



Scheme 10 – Ring opening polymerization of the lactide[14]

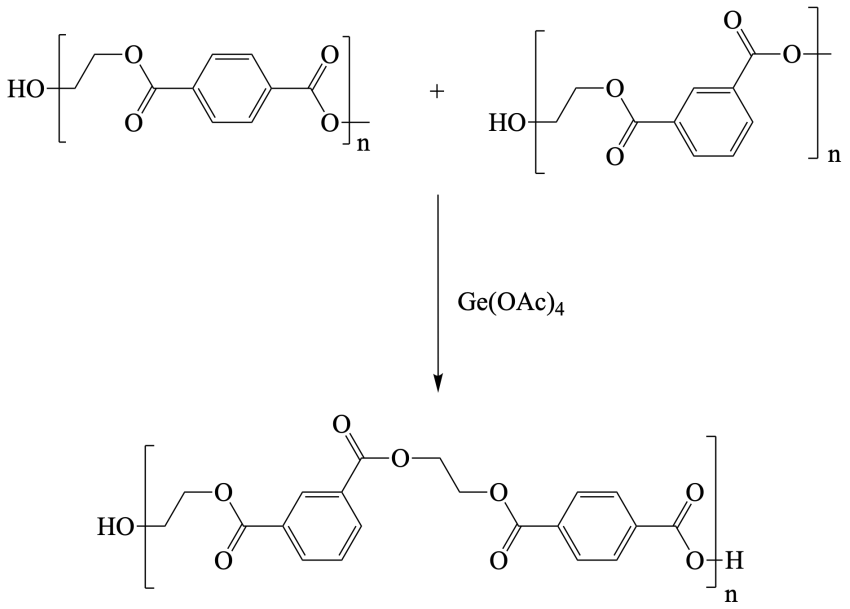
2.1.1 Germanium acetate based catalysts

In literature only a few germanium acetate based catalysts and their possible applications are known. Here by, the polycondensation of bis(2-hydroxyethyl) terephthalate with $Ge(OAc)_4$ as catalyst at high temperatures of 285 °C can be mentioned.[24]



Scheme 11 – Polycondensation of PET[24]

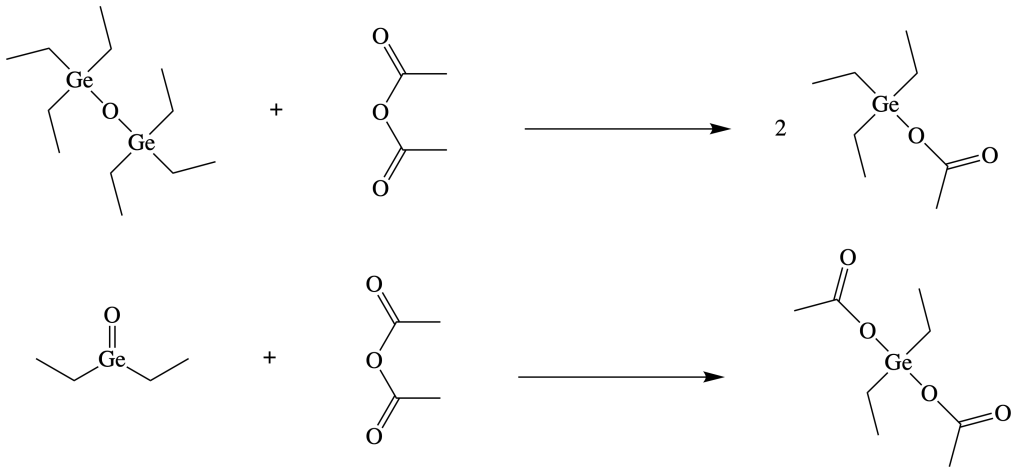
Futhermore, trans esterification between poly(ethylene isophthalate) and poly(ethylene terephthalate) with germanium acetate as catalysis is known. $Ge(OAc)_4$ is added to a melt of the polymers at aprox. 280 °C, formed is a copolymer of the ethylene terephthalate and ethylene isophthalate.[25]



Scheme 12 – $Ge(OAc)_4$ catalysed trans esterification of poly(ethylene isophthalate) and poly(ethylene terephthalate)[25]

2.2 Synthesis of germanium acetates

Anderson et.al.[26] synthesized in 1950 triethylgermanium acetate, by reacting bis-(triethylgermanium)-oxide with acetic anhydride. Diethylgermanium diacetate was synthesized from diethylgermaniumoxide and acetic anhydride. The synthesises were performed under reflux without solvents.[26]



Scheme 13 – Synthesis of ethylgermanium acetates[26]

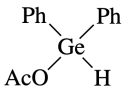
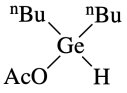
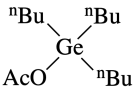
Drake et.al.[27] synthesized in 1972 germanium acetates through a reaction from the corresponding bromide with silver acetate. The synthesises was performed at room temperature without a solvent. The purification was done by fractionated condensation at - 45 °C.[27]

Scheme 14 – Synthesis of methylgermanium acetate[27]

Komanduri et.al.[28] also synthesized germanium acetates at room temperature in 2001. The germanium acetates were formed by a salt metatheses with silver acetate (1.2 eq.) from the corresponding germanium chloride (1.0 eq.) with benzene as solvent (see table 1). Benefits are the mild conditions and the yields over 85%.[28]

Scheme 15 – Synthesis of trisubstituted germanium acetates,[28] R = H, alkyl or phenyl

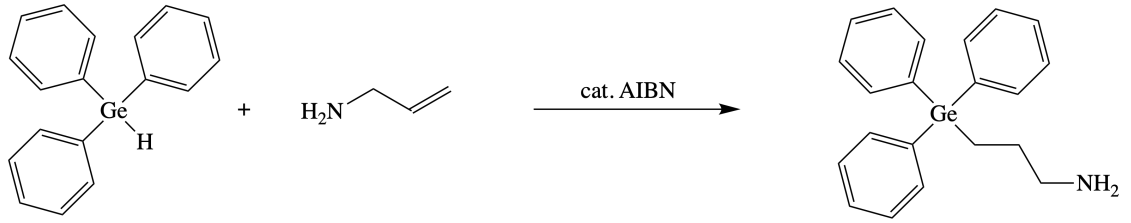
Table 1 – Synthesized compounds and yield[28]

Compound	Yield (%)
	85
	86
	94

In literature only a small group of germanium acetates are known, in addition the catalytic activity of this compounds are not known or investigated for the polyurethane formation. Therefore catalytic activity measurements are targets for research projects in the future.

2.3 Synthesis of aminopropyl germanes

Second interesting compound class in this work are aminopropyl germanes, because the amino function should be used as anchor for the catalyst in the polymer matirx. According to literature only a few aminopropyl germane synthesis routes are known. An approach is from Chazalette et.al.[29] based on a hydrogermylation of triphenyl germane with allyl amine. THF, the starting materials and the initiator AIBN were heated up at 100 °C for 3 days in a sealed tube. Triphenyl-3-aminopropyl germane was isolated, with a yield of 45 %.[29]



Scheme 16 – Synthesis of triphenyl-3-aminopropyl germane

Disadvantages of this route are the relatively harsh conditions, this route will maybe not work easily with the before mentioned germanium carboxylates or germanium halides. Therefore this route must be critically reviewed as synthesis way for other aminopropyl germanium compounds. Other building blocks and alternative synthesis routes for aminopropyl germanes are based on germanium di- and -trihydrides. For this purpose, in the following section a synthesis route is shown.

2.4 Synthesis of germanium hydrides

Germanium hydrides can be used as universal building block in the synthesis of alkyl substituted germanes (for example for aminopropyl germanes), therefore is in this section a simple and common synthesis route for mono-, di- and trihydrides is described.

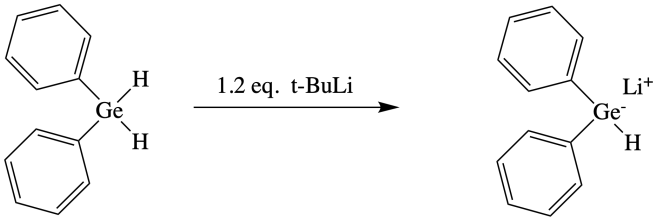
Germanium hydrides can be synthesized from the corresponding halogen compound. In literature, hydrogenation with lithium aluminium hydride (LAH) is very common. The synthesis is performed in diethyl ether at room temperature[30,31] The formed hydrides are used in the next section for the formation of highly reactive germanium anions.

$$\begin{aligned} R_3GeX &\xrightarrow{LAH} R_3GeH \\ R_2GeX_2 &\xrightarrow{LAH} R_2GeH_2 \\ RGeX_3 &\xrightarrow{LAH} RGeH_3 \end{aligned}$$

Scheme 17 – Hydrogenation of halogen germanes, R = alkyl or aryl, X = Br or Cl

2.5 Synthesis of germanium anions

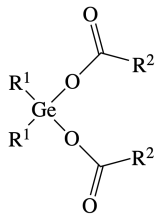
Germanium anions are very important in the synthesis of alkyl substituted germanes (for example for aminopropyl germanes), therefore is in this section a synthesis route is shown. The anions can be formed in a reaction from germanium hydrides with 1.0 - 1.2 eq. t-butyl lithium. In 1989 Castel et.al.[32] synthesized Ph_2HGeLi from H_2GePh_2. The synthesis was carried out in THF at - 40 °C, in yields of 90%.[32] The formed germanium anion could be used as starting material in salt metathesis reactions to form alkyl substituted germanes.



Scheme 18 – Lithiation of diphenyl germane[32]

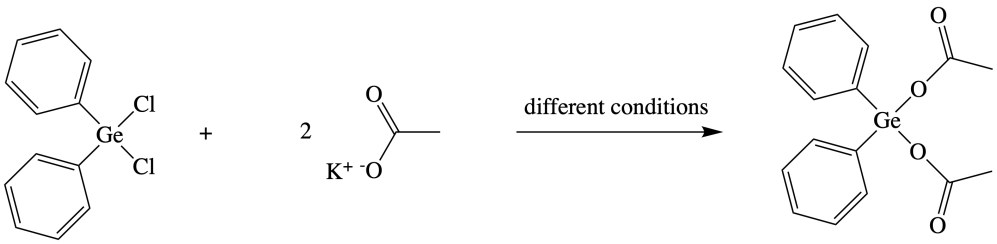
3 Results and Discussion

3.1 Synthesis of germanium acetates



Scheme 19 – Germanium analogous compound to the DBTDL Type - R^1 = alkyl- and phenyl group; R^2 = alkyl group

The principle idea was the synthesis of germanium analogous compounds to dibutyltin dilaurate (DBTDL) and dibutyltin diacetate (DBTDA). For tin halides a salt metathesis with potassium acetate is known in literature.[5] Therefore, the applicability of this salt metathesis should also be tested for germanium compounds. For this test synthesis, diphenylgermanium dichloride was used as starting material.



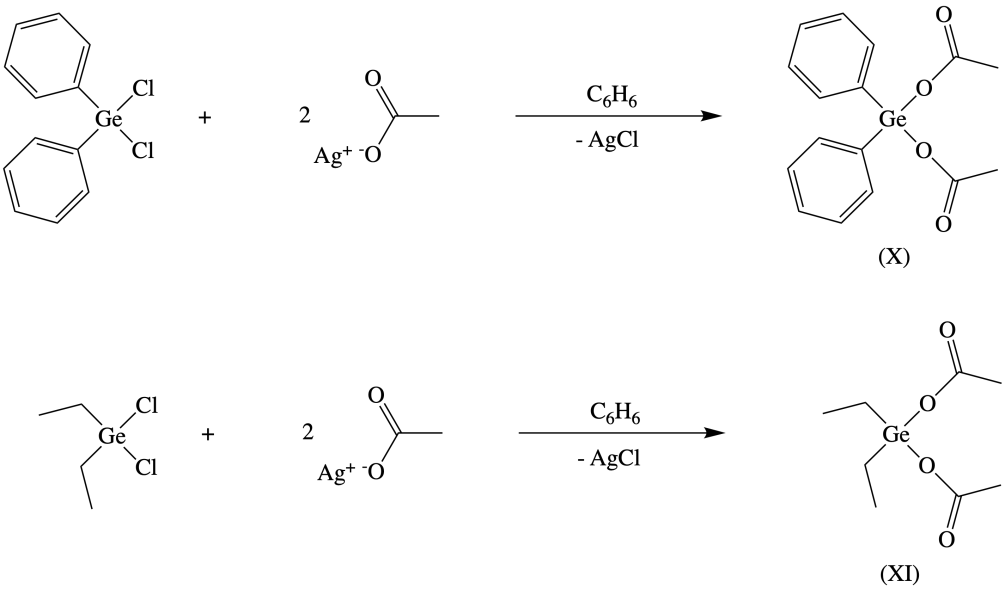
Scheme 20 – Principle of the salt metathesis with potassium acetate

The first experiment was performed in analogy to the corresponding tin compound.[5] For this purpose dichlorodiphenyl germane was reacted with potassium acetate in methanol, at room temperature and at various reaction times (30 min., 60 min. and 180 min.). After the workup ^{1}H and ^{13}C - NMR were measured, however many side products could be observed in the NMR - spectra. The second experiment was done under reaction conditions which are known from allyl tin compounds.[33] A salt metathesis from potassium acetate and diphenyldichloro germane in methanol at - 50 °C was performed. The isolated product was also not pure and many side products were formed. From a ^{1}H - NMR spectrum the yield was determined. The $-CH_3$ singlet of the acetate group in the ^{1}H-NMR spectra was integrated and a main product yield of 65% was achieved in relation to the side products. Possible side products are formed by an acetoxylation of the acetate on the phenyl ring. Different phenyl acetates were formed and in literature also similar reactions on benzene are known.[34] Sodium acetate was used alternatively to potassium acetate in a third experiment. Two stirring times were tested, 2 and 16 hours in tolouene. It was also not possible to isolate the product and a mixture of different substances was obtained in the NMR - spectra.
Overall, the salt metathesis with potassium or sodium acetate is working but a pure product could not be

isolated. Hence, a literature known salt metathesis with silver (I) acetate[28] instead of alkali metal acetates was used for the following reactions.

3.1.1 Salt metathesis with silver (I) acetate

In analogy to a literature known way from Komanduri et.al.,[28] diphenylgermanium acetate (X) and diethylgermanium acetate (XI) were synthezied. Disadvantages are photo sensitivity of silver acetate and costs of silver salts. Positive aspects are a high yield and the simple work up. In order to remove traces of acetic acid, the silver (I) acetate was washed 3-times with dry THF. The synthesis was performed at room temperature in dry benzene and under exclusion of light. Diphenylgermanium acetate (X) is an air instable white powder and diethylgermanium acetate (XI) is an air instable transparent liquid. Characterisation of this compounds was done via ^{1}H and ^{13}C - NMR spectroscopy.



Scheme 21 – Synthesis of diphenylgermanium acetate and diethylgermanium acetate

Compounds (X) and (XI) were used in the following experiment as catalyst and the catalytic activity of the compounds were determined.

3.2 Application as catalyst and kinetic studies of germanium acetates

Müller et.al.[35] developed a NMR based system for catalytic activity measurements of tin compounds. To compare germanium to tin catalysts the same experiment was implemented. The reaction of phenyl isocyanate with methanol and a 3 mol% catalyst solution in deuterated chloroform has been used for the activity determination. For this purpose in-situ ^{1}H - NMR spectra with a 60 MHz benchtop NMR were measured and by integration of methanol and product H-atoms signals the reaction progress was tracked. The used shift of methanol is located between 3.18 ppm to 3.59 ppm and for phenyl isocyante between 3.60

ppm to 4.01 ppm. To set a benchmark for the catalytic activity of each catalyst, the time ($t_{50\%}$) is measured until a 50% conversion of product and methanol. In figure 1 the principle of reaction tracking is illustrated.

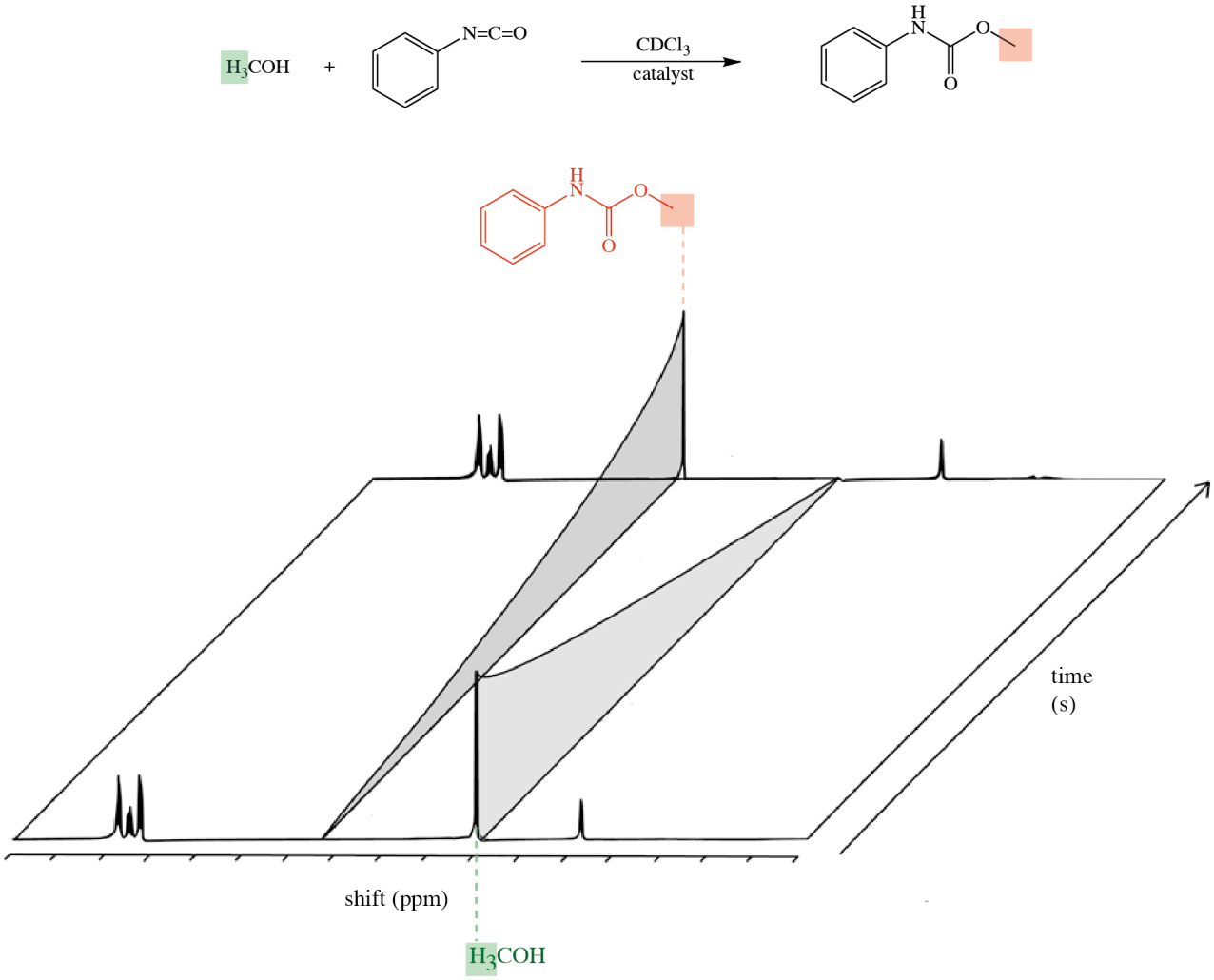


Figure 1 – Principle of the activity determination based on ^{1}H - NMR measurements, used catalysts in this work: $Ph_2Ge(OAc)_2$, $Et_2Ge(OAc)_2$ and DBTDL

3.2.1 Catalytic activity of diphenylgermanium diacetate and diethylgermanium diacetate

Under $Ph_2Ge(OAc)_2$ catalysis the model reaction delivered a $t_{50\%}$ of 950 s. In analogy $Et_2Ge(OAc)_2$ was used as a catalyst in the model reaction under the same conditions and delivers a $t_{50\%}$ of 1000 s. In a time - area diagram (figure 2) the conversion is illustrated, the increasing amount of the product is visualized in red and the decreasing amount of methanol in green.

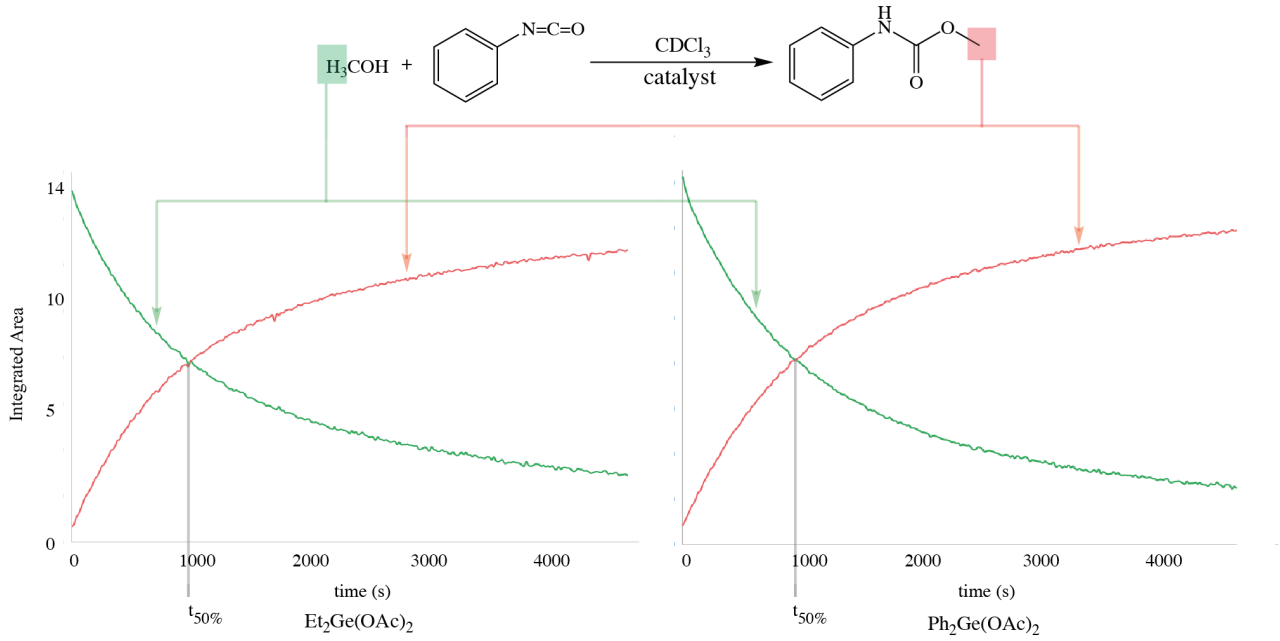


Figure 2 – Catalysis test of $Et_2Ge(OAc)_2$ left and $Ph_2Ge(OAc)_2$ right

3.2.2 Comparison and discussion of the catalytic activity

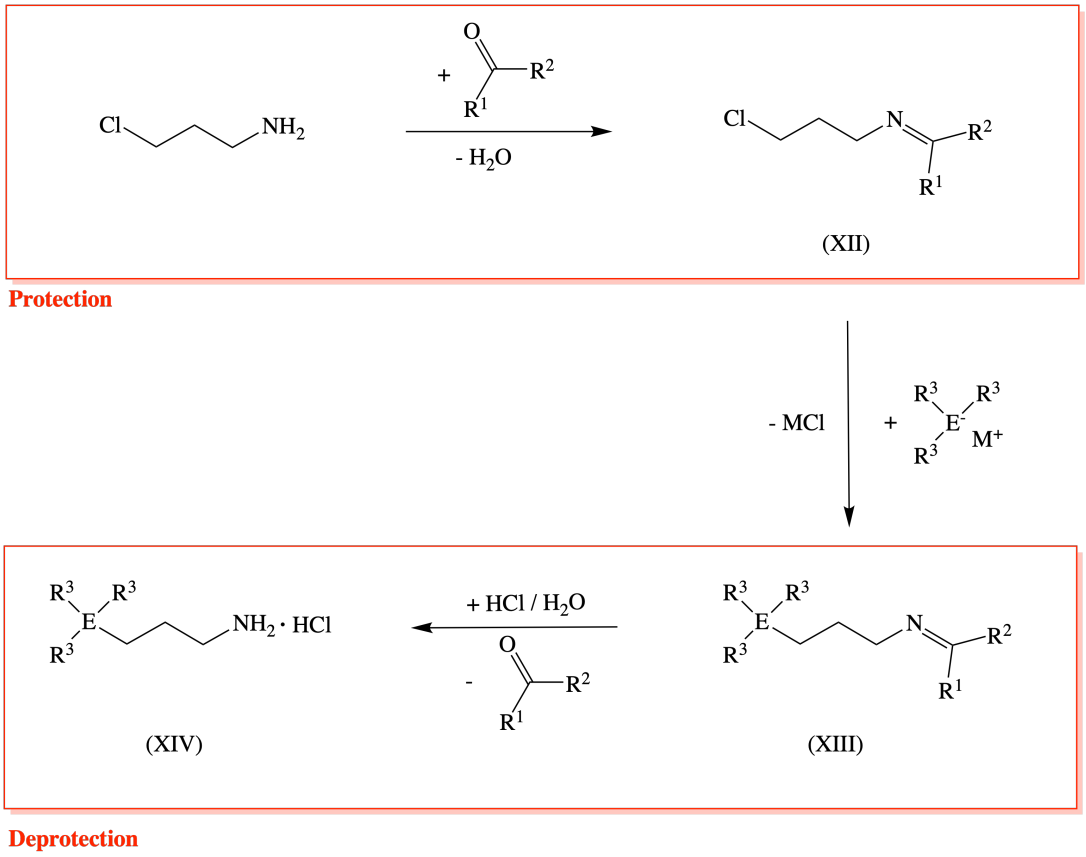
Table 2 – Summery of the catalytic activity, conditions: 3M of phenyl isocyante and 3M of methanol, each solved in $CDCl_3$, 3 mol% catalyst in $CDCl_3$, Temperature 25 °C,

Compound	$t_{50\%}$ (s)
DBTDL	5
$Ph_2Ge(OAc)_2$	950
$Et_2Ge(OAc)_2$	1000
blanc	3800

Next to the two germanium catalysts, DBTDL was used as benchmark and yielded a product conversion of 50 % in 5 s. Under the same experimental conditions the reaction without a catalyst (blanc) was tested. The uncatalyzed (blanc) reaction needed 3800 s for 50% conversion.

DBTDL is much more active than the germanium compounds but a benefit of germanium catalysts are the low toxicity. Also the possibility for an industrial use is given because germanium compounds are not banned from the industrial use.[10] Nevertheless, to come up with a final judgement for the organo germanium compounds further experiments and optimizations too carried out the reaction conditions must be done. In comparison, the germanium acetates deliver a 3.8 times faster conversion as the reaction without a catalyst. In summary, it can be shown that germanium acetate compounds are possible catalysts and an alternative to common tin compounds.

3.3 General synthesis strategy for aminopropyl germanes



Scheme 22 – General synthesis strategy - process of protection, synthesis of the aminopropyl germanium or tin compound via salt metathesis and deprotection of the amine, R^1 = H or alkyl, R^2 = alkyl, R^2 = aryl, alkyl or H, E = Ge or Sn

The synthesis of aminopropyl germanes is a major target of this work, because the aminopropyl group can be use as an anchor group for covalent polymer matrix bonding. Pichler and Müller[5,6] used that principle to prevent tin catalyst leach out from the polymer matrix.

Based on that concept, a general synthetic route for aminopropyl germanes is necessary. General idea is a salt metathesis because a simple work process could be used furthermore, high yields are typically for that reaction typ. But a direct salt metathesis with an aminopropyl compound is not possible because the amino group is also reactive and many by-products would be formed. To solve this problem a protection group is used for the amine.[36] For this purpose the reaction of aldehydes and ketons with 1-chloro-3-propylamine were used to prepare the protected amines, called 1-chloro-3-propylimines (XII).

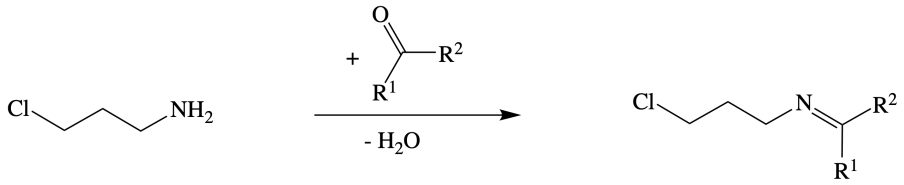
After the protection the compound is used in an usual salt metathesis. The formation of a highly reac-

tive germanium anion as reaction partner in the salt metathesis is the next step. In the following sections different strategies for germanium anion formation are test and described. Next step is the salt metathesis, an organo tin or germanium anion $(R^3)_3E^-$ reacted with the protected amine and (XIII) is formed.[6] After the reaction of germanium anion and protected amine (salt metathesis) the amine group is deprotected with hydrochloric acid and the amino hydrochloride (XIV) is formed. By-product is the corresponding aldehyd or ketone.[5,6]

Overall, there are two independent pre-steps for the formation of the aminopropyl germanes – one is the synthesis of the protected amine the other one is the germanium anion formation. Therefore, the investigation of the amine protection is the first step and which aldehyde or ketone could be used for the amine protection. Therefore, a overview is given in the following section.

3.4 Precursor synthesis - protection of amine groups

The reaction of aldehydes and ketons with 1-chloro-3-propylamine were used to protect amines and a 1-chloro-3-propylimines (XII) are formed. For the side groups called R^1 and R^2 in scheme 23 different approaches were tested. One requirement is a high volatility of the formed aldehyde/ketone after the deprotection, because a removal in vacuum is planned. Furthermore, a high storage stability is demanded from the compound.

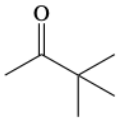
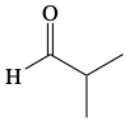
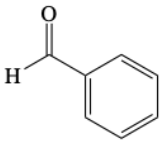
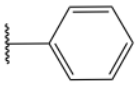
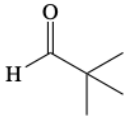


(XV)

Scheme 23 – Synthesis of the imine (protected amine)

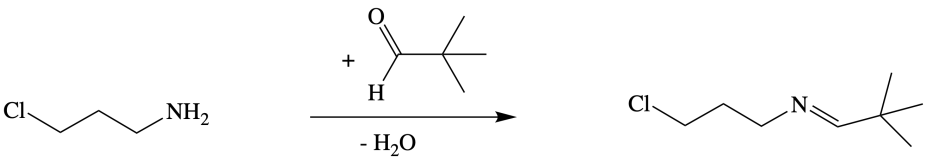
Five different ketones and aldehydes were tested for the protection of propylamines (see table 3). The educts was reacted with 1-chlor-3-propylamine under water separation. The formed products from 3,3-dimethyl-2-butanone and 2-methyl-propionaldehyde delivered a yield under 10%. Therefore, those approaches were rejected. Benzaldehyde, acetone and pivaldehyde delivered a yield of more than 75%. In the deprotection step after the salt metathesis a high volatility is helpful. Therefore the approaches protecting with acetone or pivaldehyde were used for further experiments and invastigations, because the reformed aldehydes are much more volatile as benzaldehyde. Furthermore, the protection with pivaldehyde was known in literature[5,6] , but the costs of the starting material pivaldehyde are relatively high. Therefore, the cheaper route was also interesting and is discussed in the following section.

Table 3 – Overview of the tested aldehydes/ ketones for the amine protection

Educt		Rests on the Product	
		R^1	R^2
3,3-Dimethyl-2-butanone			
2-Methyl-propionaldehyde			
Benzaldehyde			
Acetone			
Pivaldehyde			

3.4.1 2,2-Dimethylpropyl-imino protection group

Pichler and Müller[5,6] showed the use of 2,2-dimethylpropyl-imino groups as a good and practicable protecting group.[6] A negative factor of this route is the high price of the starting material, pivaldehyde. Benefits are the high stability, an easy synthesis route, high storage stability and appropriate volatility. Pivaldehyde and 1-chloro-3-propylamine hydrochloride were used for the 1-chloro-3-(2,2-dimethylpropyl-imino)propane (XV) formation.

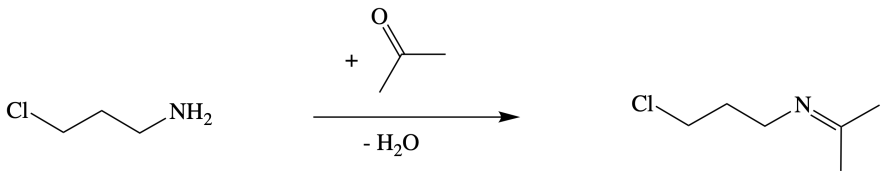


(XV)

Scheme 24 – Synthesis of 1-chloro-3-(2,2-dimethylpropyl-imino)propane[5,6]

3.4.2 iso-Propylimino protection group

Alternatively to the literature known approach, a new protection group based on an iso-propylimino group is invastigated. Acetone and 1-chloro-3-propylamine hydrochloride were used as starting material for the 1-chloro -3-(iso-proyl-imino)propane formation. After the work up, 1-chloro-3-(iso-propyl-imino)propane (XVIII) was isolated as slightly yellow oil and was characterized by ^{1}H and ^{13}C - NMR spectroscopy. 1-chloro-3-(iso-propylimino)propane (XVIII) is more air- and temperature- sensitive as 1-chloro-3-(2,2-dimethylpropyl-imino)propane (XV), but under nitrogen also storable for longer periods. The biggest benefit of this route is the massive lower price of the starting material acetone. Futhermore, the synthesis route is simpler and the volatility is better as the 2,2-dimethylpropyl-imine (XV) protecting group.



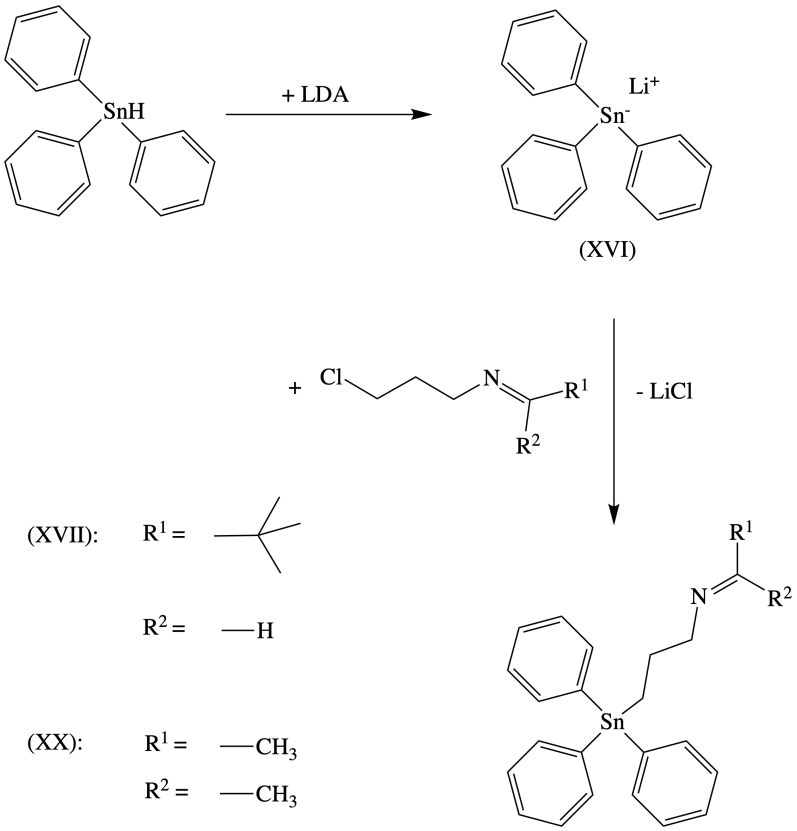
(XVIII)

Scheme 25 – Synthesis of 1-chloro-3-(iso-propylimino)propane

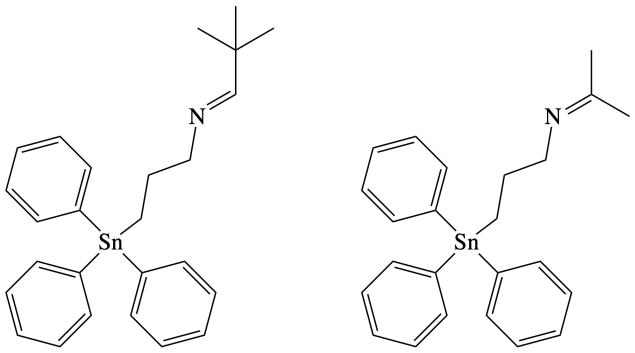
3.4.3 Salt metathesis test in a model reaction

To use this compounds in the development of new reactions on the germanium the protection group system must work in a salt metathesis. In order to test this, a literature known reaction was used. The use of 1-chloro-3-(2,2-dimethylpropyl-imino)propane in a salt metathesis with triphenyl stannane is known in literature[5,6,35] and 1-chloro-3-(iso-propylimino)propane was tested as alternative compound. The protected amine 1-chloro-3-(2,2-dimethylpropyl-imino)propane (XV) or 1-chloro-3-(iso-propylimino)propane (XVIII) was reacted with the tin anion (XVI).[5,6] The anion is formed by a lithilation of triphenyltin hydride with LDA. After the work up, the corresponding stannane was isolated. Triphenyl-3-(2,2-dimethylpropyl-imino)propyl stannane (XVII) and was isolated as colourless oil and 1-chloro-3-(iso-propylimino)propyl stannane (XX) was isolated as colourless crystals. The characterization of both compounds were done by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. As side note, triphenyl-(iso-propylimino)propyl stannane (XX) is not

known in literature and in addition, a new cheaper protecting group for amines was developed in comparison to the already known 2,2-dimethylpropyl-imine way.



Scheme 26 – Formation of the stannane in the model reaction



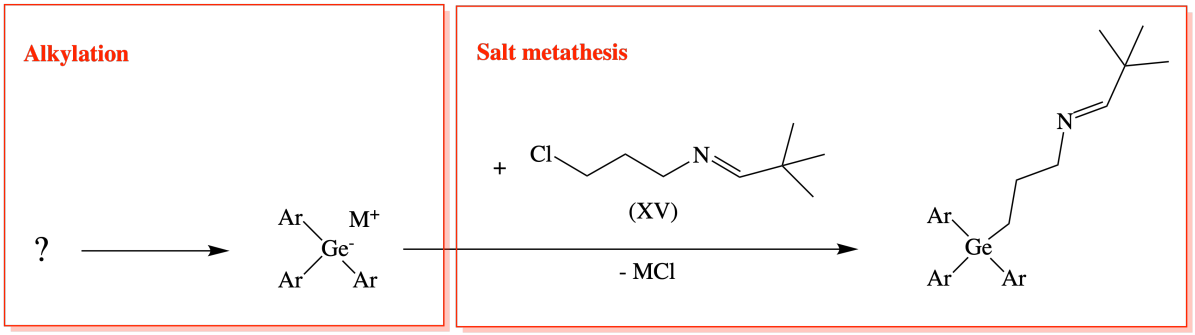
(XVII) (XX)

Scheme 27 – Isolated compounds from the salt metathesis test

To summarize, both described ways are possible for the protection of amines. For following synthesis steps 2,2-dimethylpropyl-imino groups are used as an protection group, because a better air- and temperature-tolerance is nessesary for the development process. After that development process of new routes, the process could be eventually changed to the cheaper iso-propylimino group approach.

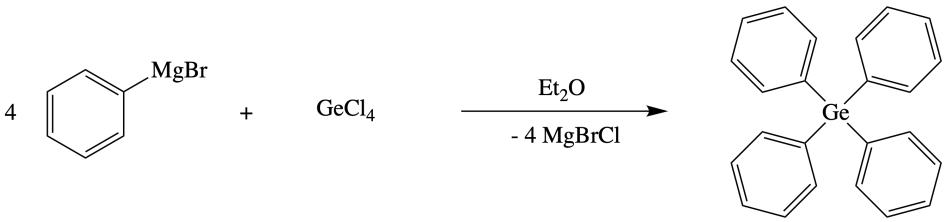
3.5 Synthesis of triaryl-3-(2,2-dimethylpropyl-imino)propyl germanes

In section 3.4.3 the synthesis of triphenyl-3-(2,2-dimethylpropyl-iminopropyl) stannane (XVII) was shown. This stannane is used in literature[5,6,35] as a precurser in the synthesis of various catalytic active tin carboxylates. Therefore, similar steps are planned with the germanium analogous compounds to form a catalyst. For this purpose, triaryl-3-(2,2-dimethylpropyl-iminopropyl) germanes were synthesised as a precursor for catalysts in analogy to the tin compounds from section 3.4.3. Triaryl-3-(2,2-dimethylpropyl-imino)propyl germanes include the important amino anchor group (in protected form) and also 3 aryl groups. This aryl groups are potential reaction sides for substitution or rearrangement reactions. To form this germanium compound, a synthesis way via salt metathesis in particular was not known in literature. Therefore, different ways are tested and investigated. Basic principle of all routes is the forming of a germanium anion (alkylation) and afterwards a salt metathesis. One of the first steps was the triphenyl-3-(2,2-dimethylpropyl-iminopropyl)germane synthesis via lithilation of tetraphenyl germane.



Scheme 28 – Principle of the triaryl-3-(2,2-dimethylpropyl-imino)propyl germane synthesis, M = Li or K, Ar = aryl group

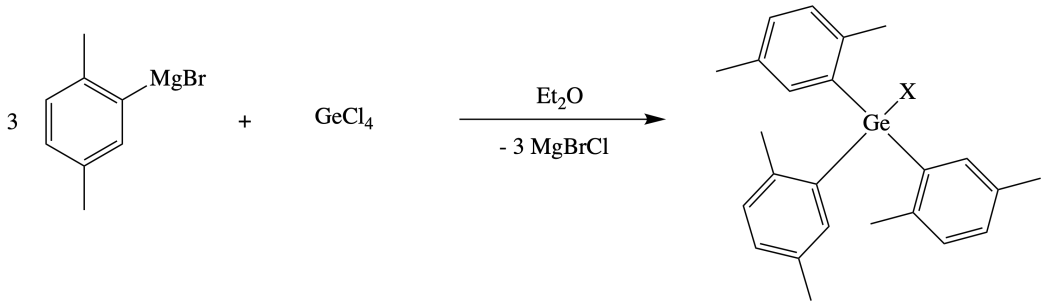
In step one, tetraphenyl germane was formed by reacting the grignard compound phenylmagnesium bromide with germanium tetrachloride.



(XXI)

Scheme 29 – Synthesis of tetraphenyl germane

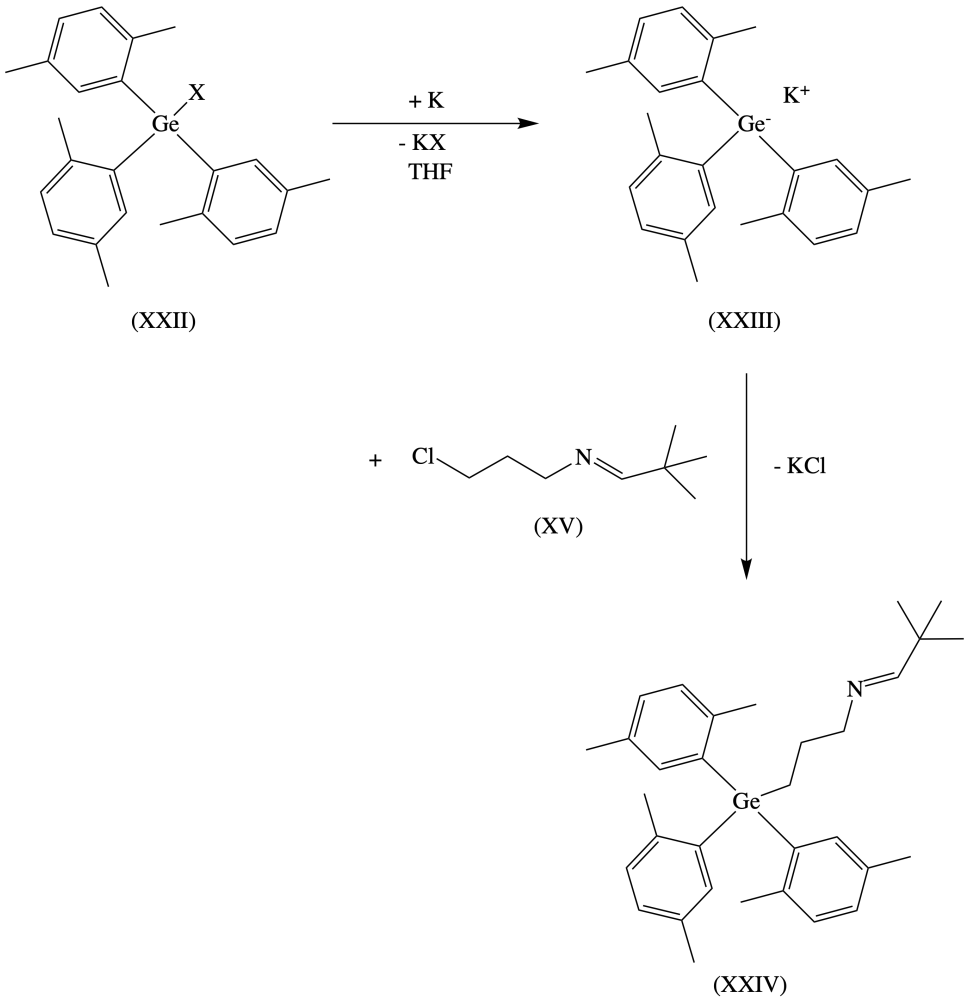
For step two, tetraphenyl germane was reacted with 1 eq. metallic lithium in THF. A brownish suspension is formed, 1-chloro-3-(2,2-dimethylpropyl-imino)propane (XV) was added and after the workup in the ^{1}H and ^{13}C - NMR spectra only a mixture of compounds could be determined. Therefore this approach was rejected for following steps. The second approach was the tris-(2,5-xylyl)-3-(2,2-dimethylpropyl-imino)propyl germane synthesis via potassium salt metathesis. The starting material was synthesised by using a method developed by Wolf and Traxler.[31,37] Tri-(2,5-xylyl)germanium halides were formed by reacting the grignard compound 2,5-xylylmagnesium bromide with germanium tetrachloride.



(XXII)

Scheme 30 – Synthesis of tris-(2,5-xylyl)-germanium halides, X = Cl or Br

For step two, the tris-(2,5-xylyl)-germanium halide was stirred with metallic potassium for 18 h in THF. A red brownish solution was formed, 1-chloro-3-(2,2-dimethylpropyl-imino)propane (XV) was added, after the workup ^{1}H and ^{13}C - NMR spectroscopy and GC/MS were measured. The major product of the reaction (scheme 31) was tris-(2,5-xylyl)-3-(2,2-dimethylpropyl-imino)propyl germane, but in addition by-products were obtained. A seperation via column chromatorgaphie was not successful, hence the route was also rejected for follow-up reactions.

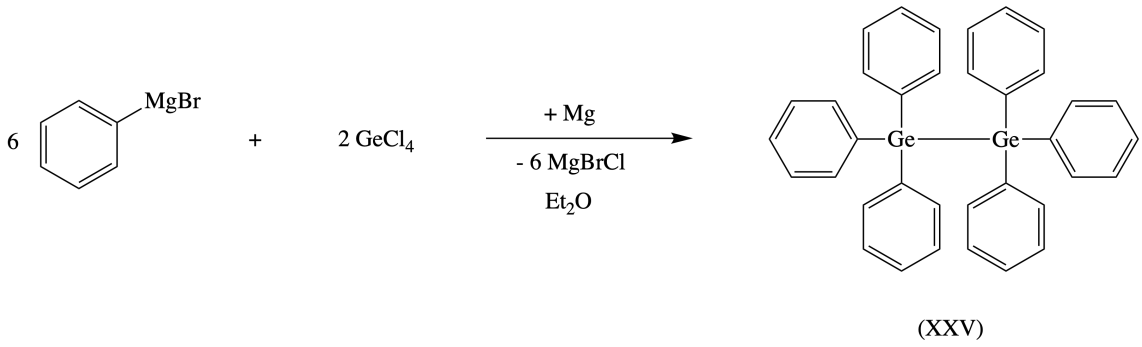


Scheme 31 – Synthesis of tris-(2,5-xylyl)-3-(2,2-dimethylpropyl-imino)-propyl germane, X = Cl or Br

Overall, the synthesis with the corresponding triaryl germanium compounds was only partially successful. Major problem is the preparation of the anion without the forming of by-products. Therefore, an alternative route based on digermanes was investigated.

3.5.1 Synthesis of hexaphenyl digermane

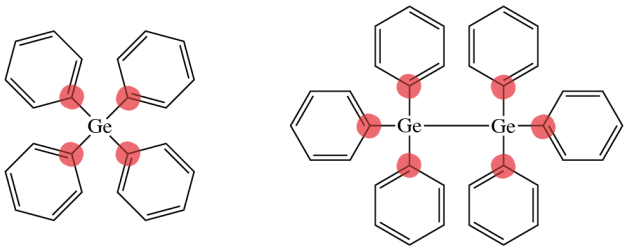
Both routes (lithilation of tetraphenyl germane and synthesis via potassium salt metathesis) deliver also various by-products. To avoid this problem a possible approach is the use of hexaaryl digermanes following by a Ge-Ge bond cleavage with potassium. For this purpose hexaphenyl digermane was synthesized by wurz coupling described by Zaitsev et.al..[38] The reaction of phenylmagnesiumbromide with germanium tetrachloride and magnesium was used to prepare hexaphenyl digermane (XXV). The product solubility in ether is limited, as a result hexaphenyl digermane precipitate as white solid in the ether phase. Therefore a simple separation from the by-product tetraphenyl germane was possible, because the solubility of tetraphenyl germane in ether is much better.



(XXV)

Scheme 32 – Synthesis of hexaphenyl digermane

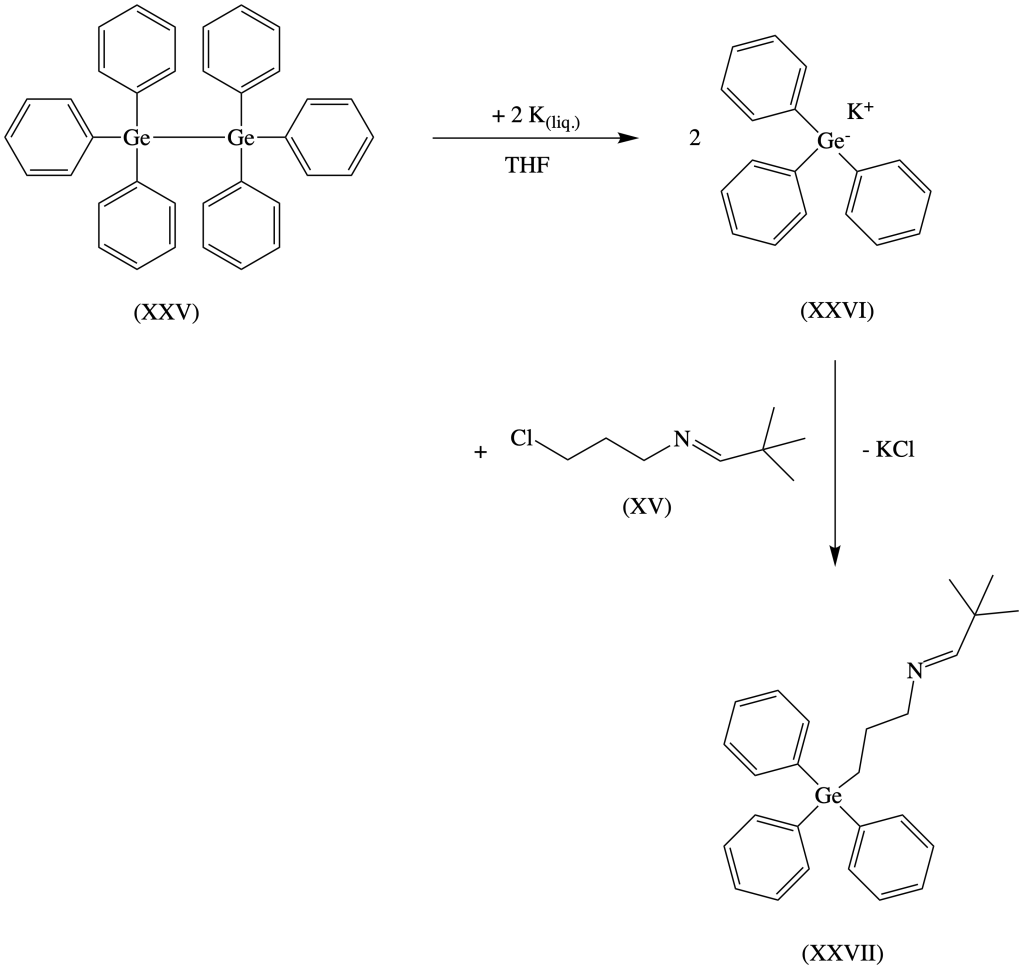
The characterisation is done via ^{1}H and ^{13}C - NMR spectroscopy, in addition the melting point was measured. In ^{13}C NMR only one C-atom delivers a significant other shift as tetraphenyl germane, therefore the melting point was used as a second characterisation attribute. The measured melting point of the product is 330 - 332 °C and is in full agreement with the literature.[39] As side note, the melting point of tetraphenyl germane is 230 - 235 °C.[40] The ^{13}C NMR shift of the C-atoms bonded to the germanium are used for the differentiation between the compounds, marked in red in scheme 33.



Scheme 33 – ^{13}C - NMR shifts - the in red marked atoms deliver the given shift

3.5.2 Synthesis of triphenyl-3-(2,2-dimethylpropyl-imino)propyl germane via Ge-Ge bond cleavage

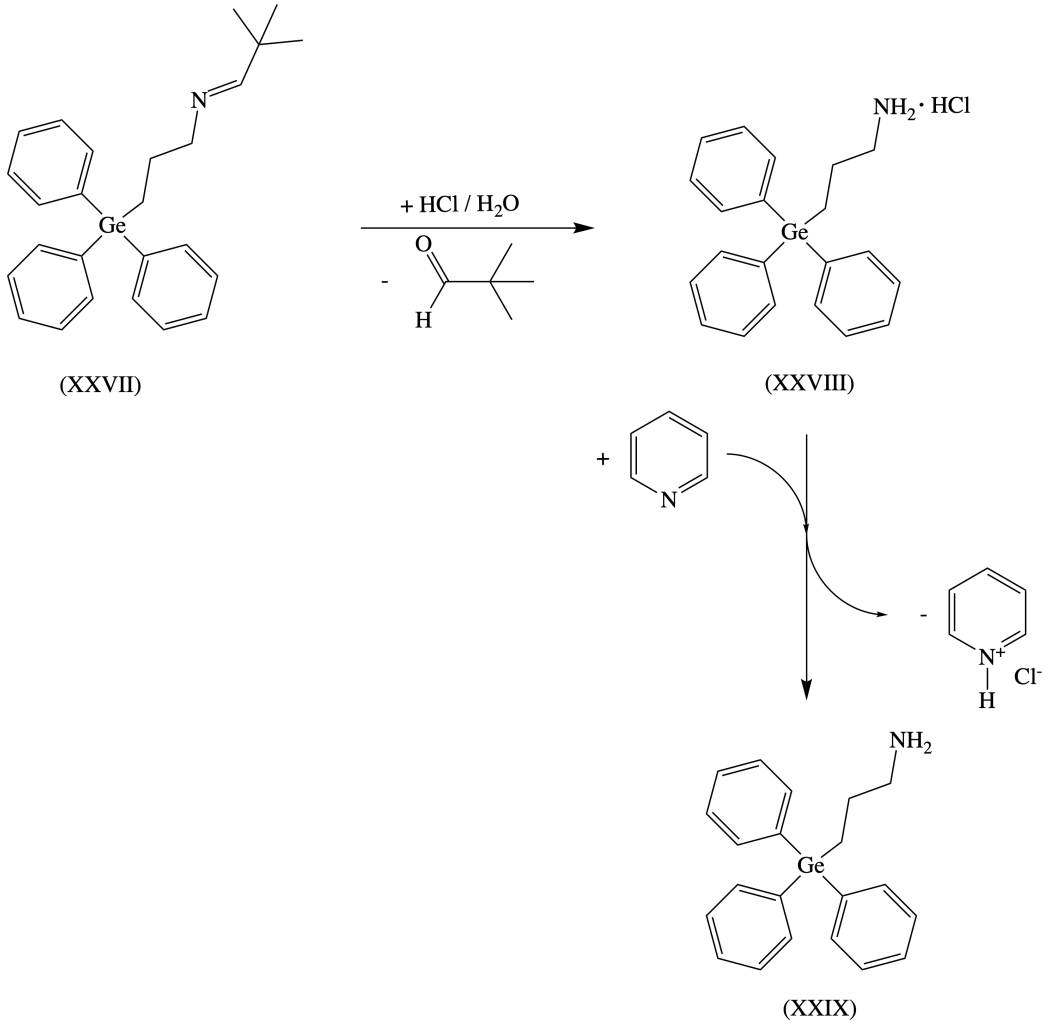
In the section before hexaphenyl digermane was synthesized for the purpose of Ge-Ge bond cleavage to prepare selectively germanium anions. Hexaphenyl digermane was suspended in THF and potassium was added. The white suspension was refluxed and the potassium was melted and a suspension was formed. On this point the choice of a solvent with a boiling point higher as the melting point of potassium is important. Boiling point of THF is 66.0 °C[41] and the melting point of potassium is 63.5 °C.[42] The formed anion is in THF solution dark green, after 1-chloro-3-(2,2-dimethylpropyl-imino)propane (XV) adding a colour change to white brownish was obtained. After the work up, the product was isolated as a slightly yellow oil. The characterization was done by ^{1}H, ^{13}C - NMR spectroscopy and a GC/MS measurement.



Scheme 34 – Synthesis of triphenyl-3-(2,2-dimethylpropyl-imino)propyl germane via Ge-Ge bond cleavage

3.5.3 Synthesis of triphenyl-3-aminopropyl germane

To synthesize triphenyl-3-aminopropyl germane the iminopropyl group was deprotected. The reaction of hydrochloric acid with the corresponding imine (XXVII) was used to prepare the amino hydrochloride (XXVIII). Afterwards in a neutralisation reaction the free amine (XXIX) was formed. For this purpose, in a first experiment potassium hydroxide in methanol was used. The product isolation and separation from the byproduct potassium chloride was complicated. Therefore, pyridine was used as base in the neutralisation step and the expected free amine was isolated in a yield of 95 %.



Scheme 35 – Synthesis of triphenyl-3-aminopropyl germane and neutralisation of the amino hydrochloride

The characterisation of the hydrochloride (XXVIII) was done via ^{1}H, ^{13}C - NMR spectroscopy and x-ray crystallography. The crystal structure is illustrated and discussed on the following pages. For the free amine compound (XXIX) ^{1}H and ^{13}C - NMR were used as characterisation methods.

In figure 3 the crystal structure of (XXVIII) is given, phenyl and protonated aminopropyl ligands are visable. In addition, a molecule water interacted via H-bond with the protonated aminopropyl group. The source of water was hydrochloric acid from the deprotection.

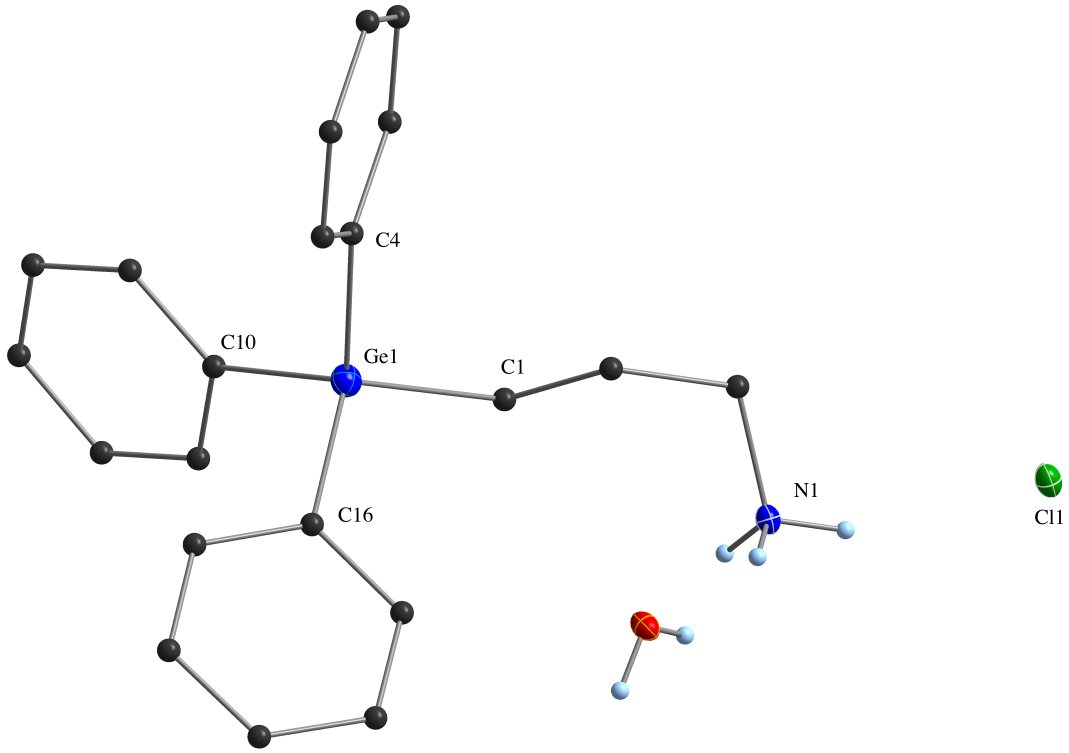


Figure 3 – Crystal structure of triphenyl-3-aminopropyl germane hydrochloride (XXVIII), complete atom numbering is illustrated in the appendix

Table 4 – Crystal structure - important bond and angle parameters of compound (XXVIII)

Triphenyl-3-aminopropyl germane hydrochloride			
Atoms	Distance (Å)	Atoms	Angele (°)
Ge-C16	1.944	C10-Ge-C16	106.95
Ge-C10	1.950	C16-Ge-C4	111.02
Ge-C4	1.951	C10-Ge-C4	109.56
Ge-C1	1.963	C16-Ge-C1	109.93
N1-Cl1	3.151	C4-Ge-C1	108.65

Table 5 – Bonding distances and angels from similar compounds from literature[43,44]

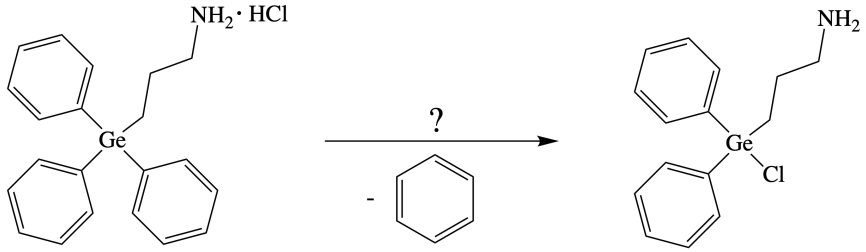
Diphenyl-ethyl-3-aminopropyl stannane hydrochloride			
Atoms	Distance (Å)	Atoms	Angele (°)
Sn1-C4	2.149	C4-Sn1-C1	114.90
Sn1-C1	2.151	C12-Sn1-C1	107.30
Sn1-C6	2.157	C12-Sn1-C6	106.41

Tetraphenyl germane			
Atoms	Distance (Å)	Atoms	Angele (°)
Ge-C	1.9559	C(I)-Ge-C(II)	108.80
Tetraphenyl germane is symetric, therefore only one Ge-C distance is given			

The crystal structure of the novel compound (XXVIII) is compared with a similar tin compound in table 5. In table 5 Sn is the central atome C4 and C1 are the atoms on the phenylgroup, C6 on the propyl rest. Both hydrochlorids from table 5 and 4 are tetrahedral and the ammonium group is not coordinated to corresponding hetero atom (Ge or Sn). Reason for this is the missing free electron pair at the N-atom, no coordination to the central atom (Ge or Sn) occurs. The Sn - phenyl bond is circa 0.2Å longer as the Ge - phenyl bond, in comparison with $GePh_4$ the bonding length is nearly the same. The distance $Ge-CH_2$ is a little bit longer as the phenyl bonding length. At the diphenyl-ethyl-3-aminopropyl stannane hydrochloride the bonding length is circa 0.2Å longer. The tetrahedral angle of (XXVIII) and from the tin compound are not exactly the theoretical expected angle of 109.5°.[36] In a symetric molecule like $GePh_4$ the angle is nearly on the theoretical angle. Main reason of this differences is the volume of the ligands, because the phenyl group needs more space as the propyl group. A secound is the atomic radius of germanium and tin, germanium is smaller therefore, the ligands can better distribute around the atom.

3.6 Attempts for the cleavage of germanium-phenyl bonds

In literature the cleavage of the phenyl - Sn bond is known, for this purpose hydrochloric acid in diethyl ether is used.[5,6] One molecule of HCl is needed to cleave one tin phenyl bond. For example, diphenyl-3-aminopropyl-chloro stannane was synthesized from the corresponding triphenyl derivative as catalyst precursor, from Müller.[5,11] Also trifluoroacetic acid (TFA) can cleave the tin phenyl bond, reaction product is the corresponding tin trifluoracetate. In addition, Pichler[6] showed a thermal rearrangement of 3-aminopropyl stannane hydrochloride. The chloro atome of the hydrochloride substitute one of the phenyl groups and the corresponding chloro stannane and benzene are formed. The reaction is performed in vacuum at 160 °C. For that reason cleaving of the phenyl germanium bond in order to form the corresponding diphenylchloro germane was a target in this work.[36,43,44]



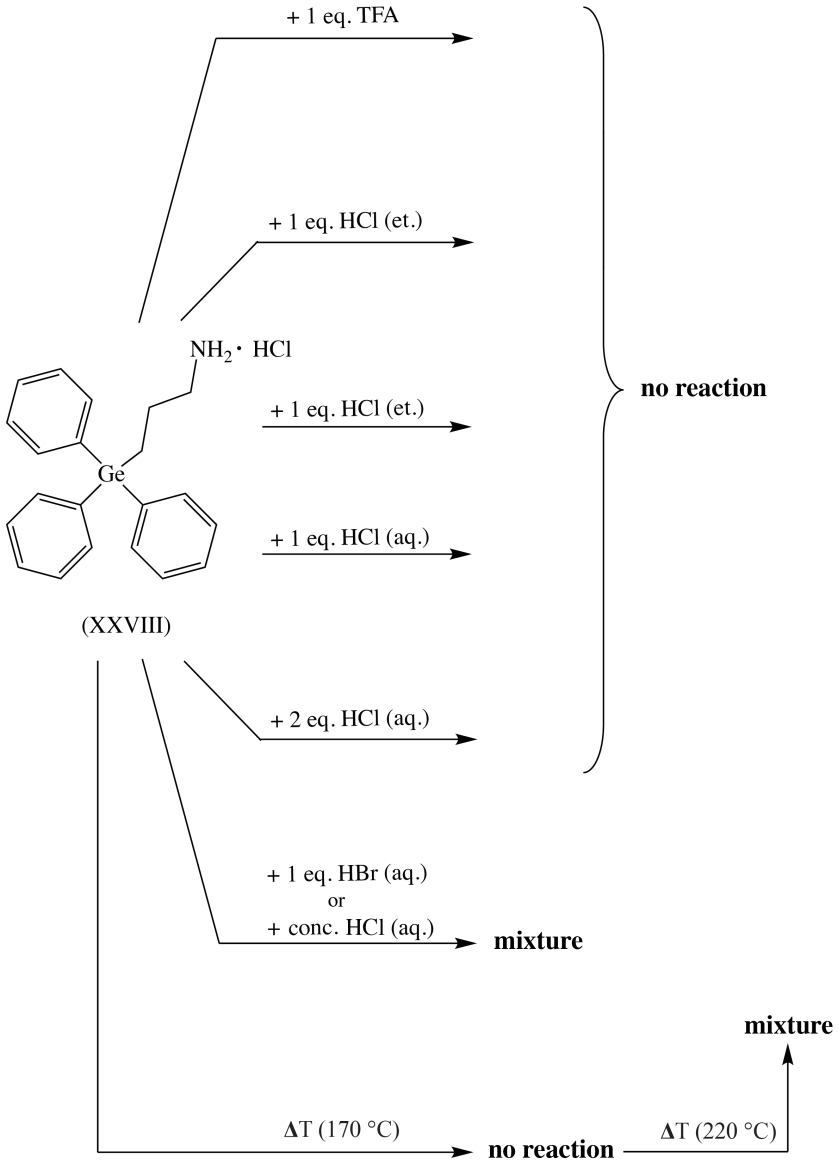
(XXXIX)

Scheme 36 – Target and principle of the Ge-phenyl bond cleavage

Therefore, in analogy to known reactions from phenyl stannanes, the applicability of analog germanium compounds was investigated, the characterisation was done via ^{1}H - NMR spectroscopy. First of all, 1 eq. of hydrochloric acid in diethyl ether was used at room temperature. In the NMR spectra no change between the shifts was obtained, therefore no reaction was suspected. Same behavior was obtained with 2 eq. of hydrochloric acid diethyl ether at the same conditions. Next approach was hydrochloric acid in a water/THF mixture. In relation to the starting material there was no ^{1}H - NMR shift change to be obtained, neither with 1 eq. nor with 2 eq.. Therefore a approach with 1 eq. trifluoroacetic acid (TFA) at room temperature was tested, the reaction was tracked by ^{19}F - NMR spectroscopy, because a significant ^{19}F - signal shifting must be obtained in case of a bonding between trifluoroacetate group and germanium. In ^{19}F - NMR no shift change was obtained, this induces the assumption that there was no reaction between germanium compound and TFA. In addition a stronger acid as TFA and HCl was used, 1 eq. hydrobromic acid in a water/THF mixture at room temperature was tested. At same conditions an excess of 12 M hydrochloric acid was used, this reaction is known form the complete dephenylation of the analogous tin compound.[5,6] In the measured ^{1}H - NMR spectra a mixture of various products was obtained in both cases. A possible scenario is the phenyl - germanium bond and in addition the propyl - germanium bond was broken and many reactive fragments were formed. Afterwards there are various possibilities to react and to form new substances. Through the various number of reaction possibilities a mixture of different substances could be obtained in the NMR spectra.

The thermal rearrangement of the hydrochloride (XXVIII) was invastigated in vacuum at 170 °C. ^{1}H - NMR shifts are equivalent to the starting material and a thermal rearrangement is improbable. Based on this knowledge, the temperature is increased to 220 °C. After the reaction, a mixture of different compounds could be obtained in the ^{1}H - spectra. The phenyl - germanium bond and in addition the propyl - germanium bond is maybe cleaved. Afterwards reactive fragments were formed and the reactivity is supported as well by the high temperature. This fragments have a various number of possibilities to react and to form new compounds. Through the various number of reaction possibilities a mixture of different substances were formed.

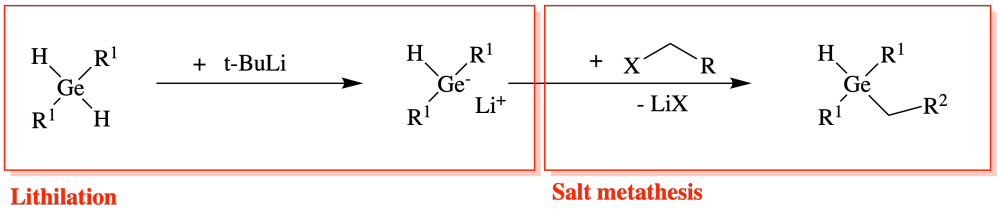
The summary of the studies to the cleavability of the phenyl-germanium bond on triphenyl-3-aminopropyl germane is given in scheme 37. Overall, the cleavability of the germanium-phenyl bonds needs more extensive investigations and experiments to determine what exactly happened with protic reagents. Also the thermal rearrangement need more complex investigations. At this point the analogous reactions to tin were not working and for the synthesis of alkyl substituted diphenyl germanes a alternative route was used.



Scheme 37 – Studies to the cleavability of the phenyl-germanium bond on triphenyl-3-aminopropyl germane hydrochloride

3.7 Synthesis of diphenyl-alkyl germanes

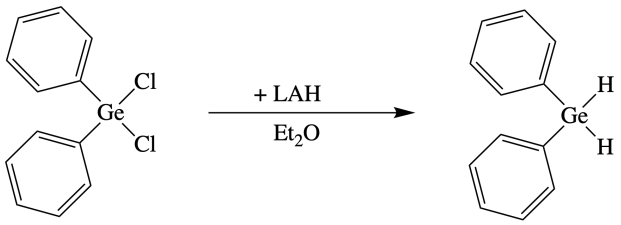
In section 3.6 a triphenyl germane should be converted in a diphenyl germane, because in literature triphenyl stannanes are used as starting material for substituted diphenyl stannanes. This diphenyl stannanes are the final precursor of a catalyst. For example diphenyl-3-aminopropyl-chloro stannane was used as catalyst precurser from Müller.[5,6,11] But in the section 3.6 a selective cleavage of the germanium-phenyl bond was not realised in analogy to tin, because some cleavaging agents (HCl or HBr) delivered mixtures and significant numbers of reactions were gernerlly not work. Therefore, a new synthesis way based on the general strategy of a salt metathesis was necessary. Target of this section was the synthesis of the germanium analogous compound to diphenyl-3-aminopropyl-chloro stannane. For this purpose, a new starting point was used and starting material was diphenyldichloro germane which, can be simple hydrogenated to the corresponding dihydride. As following step a germanium dihydride lithilation with a following salt metathesis was selected and an alkyl substituted diphenyl germane was formed. This molecule has one high reactive H-atome, that can be used in the next synthesis steps.



Scheme 38 – Principle of the substitution of germanium dihydrides, R^1 = aryl, R^2 = alkyl and X = Cl or Br

3.7.1 Precursor synthesis - hydrogenation of diphenylchloro germane

In literature, the hydrogenation of germanes is well known.[30,31] Diphenyldichloro germane is hydrogenated with lithium aluminium hydride (LAH). After the work up, pure diphenyl germane (diphenyl germane dihydride) is isolated and used as starting material in the following lithilation experiments.



(XXX)

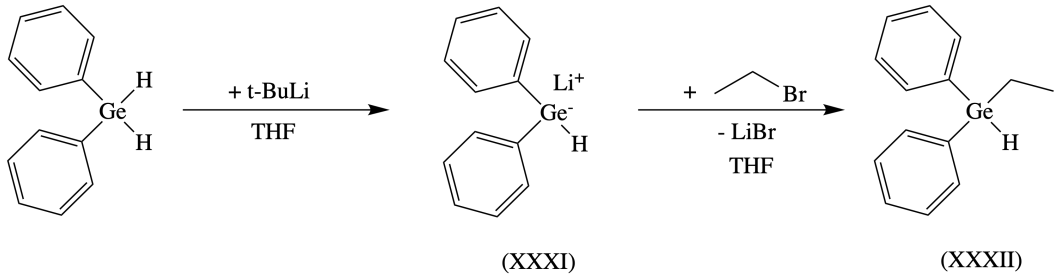
Scheme 39 – Hydrogenation of diphenylchloro germane

3.7.2 Synthesis of diphenyl-ethyl germane

In this work a major target is the synthesis of aminopropyl substituted germanes. But in a first step, a novel substitution method based on a salt metathesis must be developed. For that process the determination of

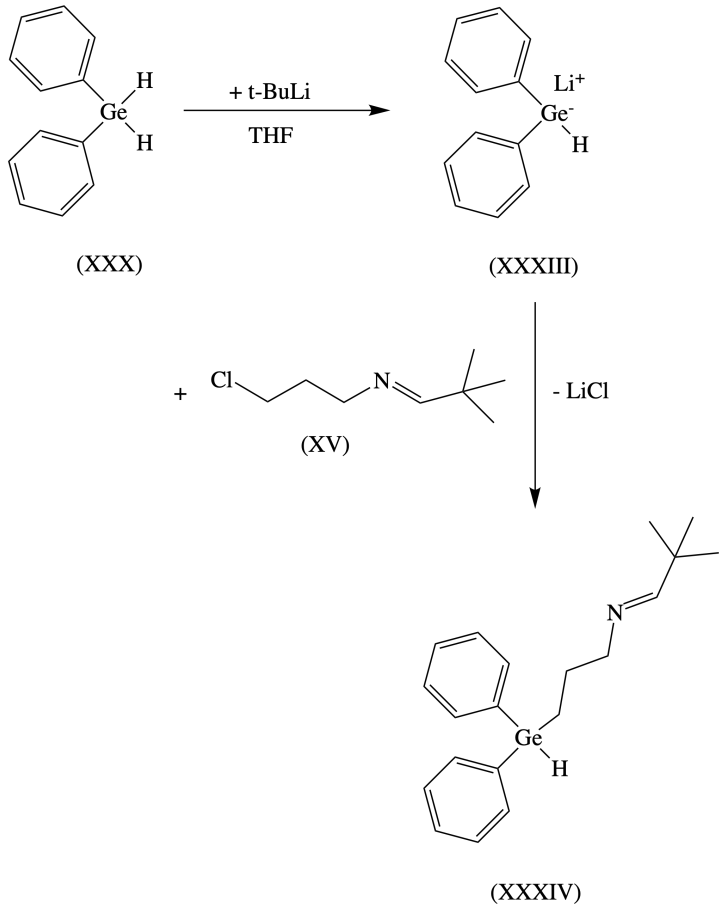
the best fitting reaction conditions was necessary. Therefore, the reaction of a simple alkyl halide (ethyl bromide) with a germanium anion was used as a model and test reaction. Ethyl bromide is often used as test compound for possible reactions (e.g. salt metathesis) and for the parameter determination, in contrast to a propylimine.

To form in the first step the germanium anion, diphenylgermanium dihydride (XXX) was reacted in THF with 1.1 eq. of t-butyl lithium at - 40 °C,[32] yielding a yellow germanium anion (XXXI) in solution. To this solution 1.3 eq. ethyl bromide were added and the product is isolated after the work up as a colourless liquid. Characterization was done by GC/MS, ^{1}H and ^{13}C - NMR spectroscopy. The ethyl bromide excess was used for quentching the 0.2 eq. of t-butyl lithium and the remaining ethyl bromide was evaporated after the reaction. This novel synthesis route is universal, not known in literature and built the base for the synthesis of 3-aminopropyl and 3-iminopropyl germanes. As a side notice, the equivalents of t-butyl lithium influence the formation of R_2HGe^- anion, more than 1.2 eq. of t-butyl lithium delivers a parallel formation of the dianion R_2Ge^{2-} and following a mixture of monoethyl and diethyl diphenyl germane.



Scheme 40 – Synthesis of diphenyl-ethyl germane

3.7.3 Synthesis of diphenyl-3-(2,2-dimethylpropyl-imino)propyl germane



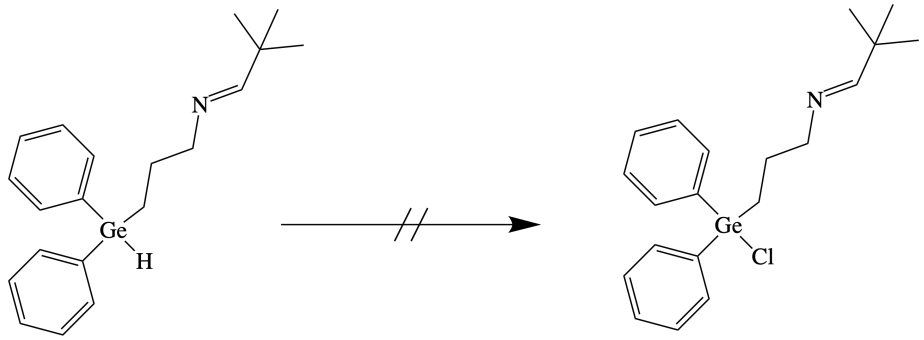
Scheme 41 – Synthesis diphenyl-3-(2,2-dimethylpropyl-imino)propyl germane

With the information from the model reaction in the section before the synthesis of diphenyl-3-(2,2-dimethyl-propyl-imino)propyl germane was performed. Diphenyl germane was reacted with 1.2 eq. of t-butyl lithium, at - 40 °C in THF to form the anion (XXXIII). To this anion solution, 1.3 eq. of 1-chloro-3-(2,2-dimethylpropyl-imino) propane were added and the mixture was worked up, yielding a colourless oil. The characterization was done by ^{1}H and ^{13}C - NMR spectroscopy. A GC/MS measurement was also done, but the compound stability during the GC measurement was problematic. In a series of measurements, the pure product delivered a second peak with a higher retention time in the GC measurement. As side notice the product was pure in a NMR measurement. In order to clarify that problem a distillation of (XXXIV) was done, in an NMR - spectra of the distillate a mixture of compounds was obtained. Based on this knowlege a thermolysis is assumed. In addition to clarify a possible reaction with the column material of the GC, a simple column chromatography was done with the clean compound. Afterwards a ^{1}H spectra was measured and a mixture of various compounds was obtained. With this information from the GC/MS series and from the distillation experiment as well as from the column chromatography, the product is suspected to ther-

mal decompose or rearranging during the GC measurement. Resulting from that notice, a GC/MS must be considered critically for this compound type.

3.7.4 Chlorination experiments on diphenyl-3-(2,2-dimethylpropyl-imino)propyl germane

In literature diphenylchloro tin compounds are formed by Sn phenyl bond cleavage. Deprotection and Sn-phenyl bond cleavage can be done in one step, because in both cases hydrochloric acid can be used. For example, Müller[5,35] used triphenyl-3-(2,2-dimethylpropyl-imino)propyl stannane and added 2 eq. of hydrochloric acid for deprotection and chlorination. The product diphenyl-3-(2,2-dimethylpropyl-imino)-chloro stannane was used as a precursor for the final synthesis of a catalytically active compound. For that reason, trying to form diphenyl-3-(2,2-dimethylpropyl-imino)propyl-chloro germane was an obvious choice. Therefore, the chlorination of (XXXIV) was a logical next step.



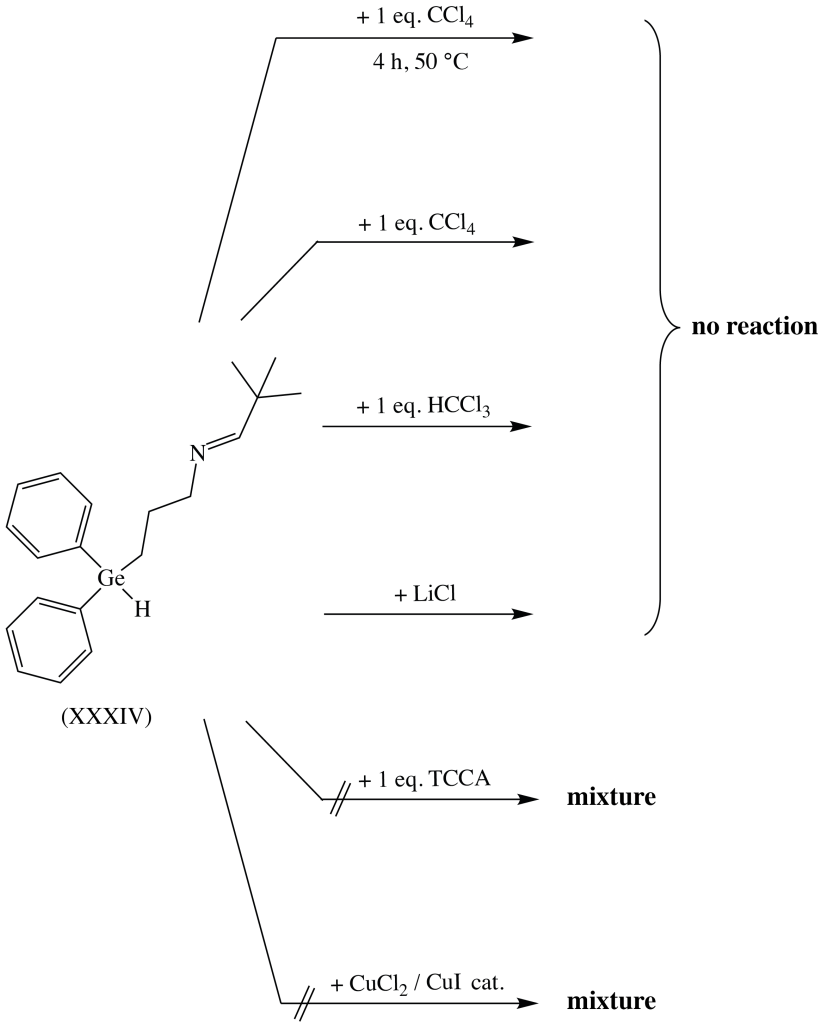
(XXXIV)

Scheme 42 – Chlorination problem with compound (XXXIV)

The chlorination of germanes is commonly known but most approaches are based on a radical reactions at high temperatures.[31,37,45–48] For example, typical chlorination agents are carbon tetrachloride or chloroform under reflux. There are many problems with the chlorination at this point, one problem are the radical transitions states in the common reactions, because they can also react with the imine group in compound (XXXIV). In addition, for diphenyl-3-(2,2-dimethylpropyl-imino)propyl germane (XXXIV) the reflux conditions were not possible, because a thermosensitivity is not excluded, details in section 3.7.3. Facing this temperature limitation, the first experiment was performed in pure carbon tetrachloride at 50 °C for 4 h. The following two experiments were stirred overnight in the pure carbon tetrachloride and chloroform, respectively. A suspension of lithium chloride in THF was stirred overnight as well. The reaction progress was obtained via ^{1}H - NMR spectroscopy, for this reason the integral of the hydride H-atome (Ge-H) was used. The experiments with carbon tetrachloride, chloroform and lithium chloride delivered no integral change of the hydride H-atomes in the ^{1}H - NMR, therefore a chlorination on the germanium is excluded. Additionally and in analogy to known chlorinations TCCA (trichloroisocyanuric acid) was used.[49,50] At - 80 °C TCCA was reacted in THF with the corresponding germanium compound. The reaction progress was tracked by ^{1}H - NMR spectroscopy and a mixture of various components was obtained. As a last approach, chlorination

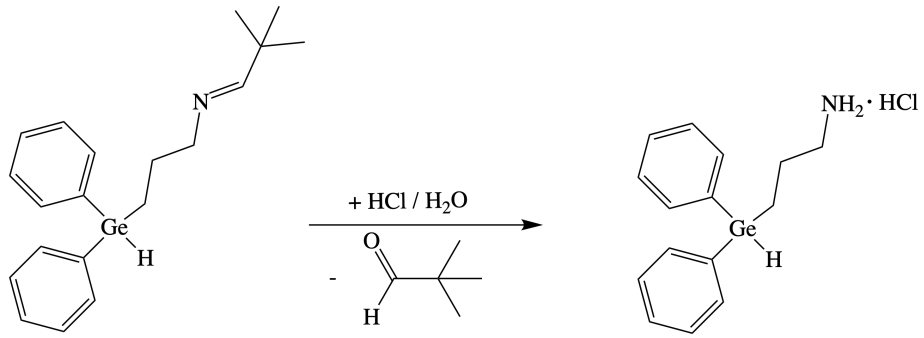
with 1 eq. copper(II)chloride and catalytic amounts of copper(I)iodine[45,48] in THF was tested at room temperature over night. In the ^{1}H - NMR spectra various components were obtained as well. The imine group was maybe also a target of the chlorination and delivered a fragmentation of this group. This fragments can also react with the germanium compound or with other fragments to form compounds the can not separated from the product. Therefore this approaches were rejected for following synthesis steps.

Overall, various chlorination agents did not lead towards the expected results, therefore the idea ”chlorination of diphenyl-3-(2,2-dimethylpropyl-imino)propyl germane (XXXIV)” was rejected. In this section it has been shown, that a chlorination is difficult or even impossible to perform, because the imine group can also react with the chlorination agents. As a new approach, the chlorination of the free amine or the hydrochloride can be the target of new projects.



Scheme 43 – Studies to the chlorination of diphenyl-3-(2,2-dimethylpropyl-imino)propyl germane

3.7.5 Synthesis of diphenyl-3-aminopropyl germane hydrochloride



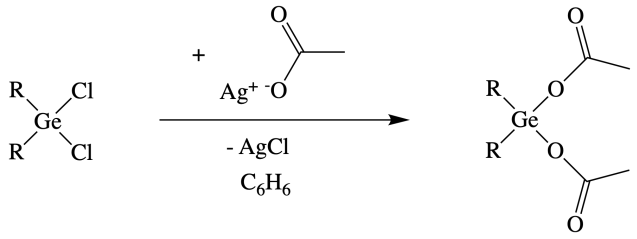
(XXXIV) (XXXV)

Scheme 44 – Synthesis of triphenyl-3-aminopropyl germane

In section 3.7.4 the problems of 3-(2,2-dimethylpropyl-imino)propyl germane chlorination was described. A possible explanation of the problems with the chlorination are side reactions of the imino-function with the chlorination agent. The imino group is used only as protection group for the amine during the salt metathesis. As alternative way the hydrochlorid (unprotected form) could be used as starting material for following chlorination experiments. Based on this knowledge a chlorination of the deprotected form (hydrochloride form) is target in the future. For that reason, the corresponding imine was deprotected and the hydrochlorid was isolated, this compound can be used as direct precursor for a final catalyst synthesis. The product was synthesized by deprotection of the iminopropyl group, 1 eq. hydrochloric acid was reacted with diphenyl-3-(2,2-dimethylpropyl-imino)propyl germane (XXXIV) and diphenyl-3-aminopropyl germane hydrochloride (XXXV) was formed. The characterisation of the hydrochloride (XXXV) was done via ^{1}H and ^{13}C - NMR spectroscopy. The product was isolated as a colourless powder with traces of solvents.
Diphenyl-3-aminopropyl germane hydrochloride (XXXV) is not known in literature and can be used as precursor for following chlorination experiments. Furthermore, this compound is the analogous substance to tin catalyst precursors. This compound delivers the base for the build up of functional aminopropyl germane catalysts and is a central building block for germanium catalysts in the future.

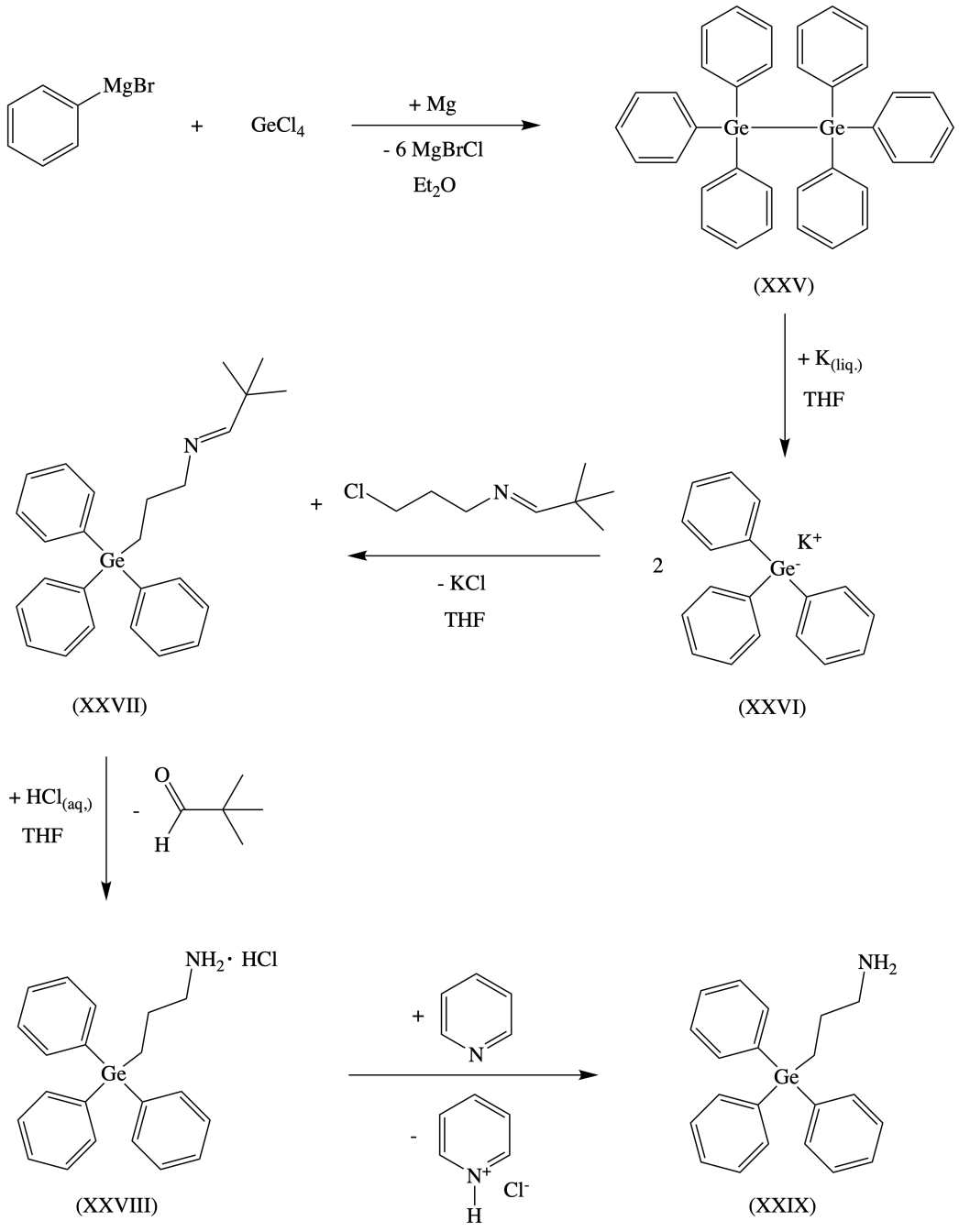
3.8 Summary

In this section an overview of all successful reactions is given. For various organo germanium compounds synthesis routes were found, formed end products are the catalytic active germanium acetates and the aminopropyl anchor group including compounds triphenyl-3-aminopropyl germane (XXIX) and diphenyl-3-aminopropyl germane hydrochloride (XXXV). (XXXV) and (XXIX) are precursors for a noval catalyst generation based on aminopropyl germanes.
The acetates are formed by reacting silver (I) acetate with the corresponding germanium dichlorides. Synthesized products are diphenylgermanium diacetate (IX) and diethylgermanium diacetate (X). Both compounds are catalytically active and accelerate the carbamate formation approximately 3.8 times.



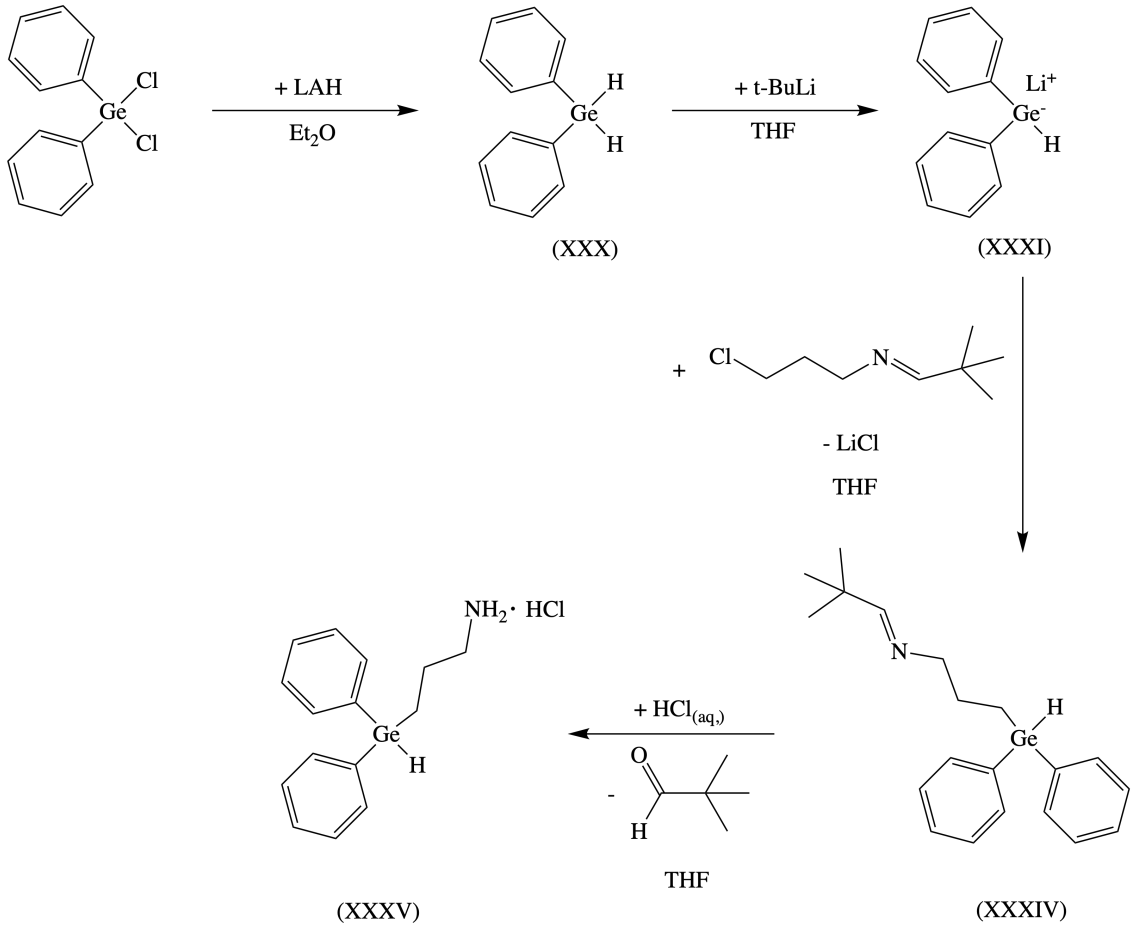
Scheme 45 – Synthesis of germanium acetates, R = phenyl or ethyl group

Triphenyl-3-aminopropyl germane (XXIX) is formed via a multistep synthesis, starting material was hexaphenyl digermane (XXV). The Ge-Ge bond is cleaved with potassium and the formed germanium anion is directly reacted with 1-chloro-3-(2,2-dimethylpropyl-imino) propane (XV). Afterwards, the formed triphenyl-3-(2,2-dimethylpropyl-imino)propyl germane (XXVII) is deprotected with hydrochloric acid to triphenyl-3-aminopropyl germane hydrochloride. The free amine (XXIX) is formed in a neutralization reaction of the hydrochloride (XXVIII) with pyridine.



Scheme 46 – Synthesis of triphenyl-3-aminopropyl germane

Diphenyl-3-aminopropyl germane hydrochloride (XXXV) is formed via a multistep synthesis, starting the corresponding germanium dihydride (XXX). The hydride is lithilated with t-butyllithium and the formed germanium anion is directly reacted with (XV). Afterwards, (XXXV) is deprotected with hydrochloric acid to diphenyl-3-aminopropyl germane hydrochloride (XXXV). This hydrochloride is used as a precursor for a catalyst synthesis in the future.

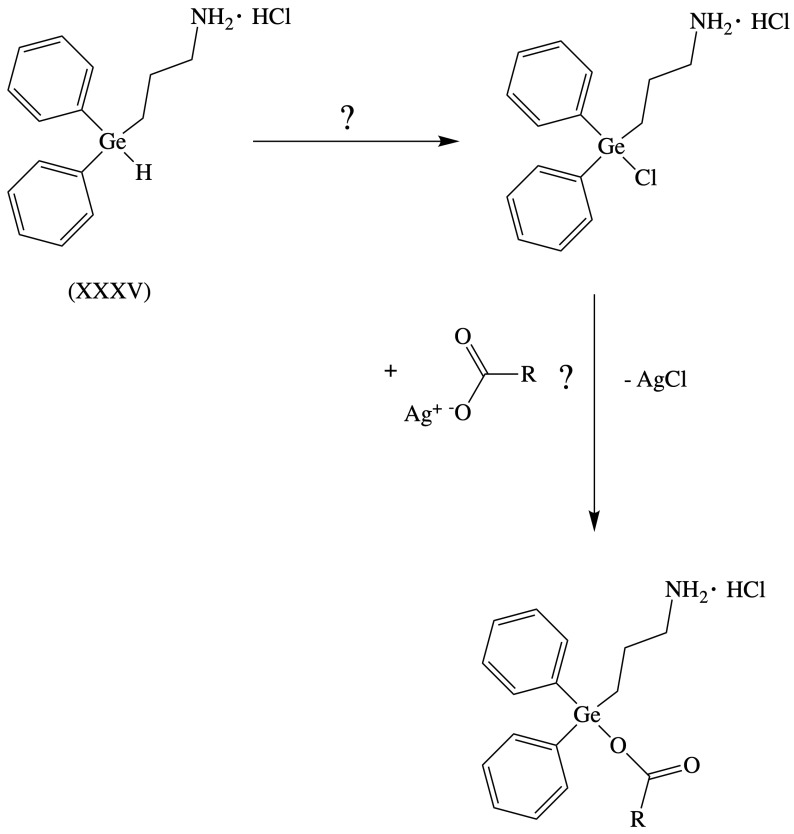


Scheme 47 – Synthesis of diphenyl-3-aminopropyl germane hydrochloride

4 Conclusion and Outlook

The synthesis and catalytic activity determination of germanium acetates was shown. The synthesis is known from literature but the use as catalyst for carbamate formation and activity determination is novel. From these studies a new research field is opened and shows new possibilities in organo germanium catalysed polymer synthesis. In the future, a target is the synthesis and activity determination of other germanium carboxylates, for example the dilaurates in direct analogy to DBTDL.

Furthermore, a novel synthesis route for triphenyl-3-aminopropyl germane was found as well as studies to the cleavability of the phenyl – germanium bond was done. The cleavage of this bond is not that simple therefore, a deeper and more complex investigations will be necessary in order to use this route for further synthesis ways in the future. Main target of this work was the synthesis of aminopropyl substituted germanes, which are used as catalyst precursors. This target was achieved with the synthesis of diphenyl-3-aminopropyl germane hydrochloride (XXXV). The compound is not literature known and the synthesis route could be used as an universal synthesis route for this compound type. In the future a target is the synthesis of a various number of aminopropyl substituted germanes and in the following the synthesis of the corresponding carboxylates. A possible way to achieving this is shown in the following scheme in analogy to the well-known acetates.



Scheme 48 – Target for following projects: chlorination and carboxylate synthesis

In scheme 48 the synthesis of the corresponding germanium halide from the hydride is shown and could be a mandatory aim for following projects and studies. For this purpose, different chlorination agents must be investigated to chlorinate the germanium hydride. For the second step of scheme 48 the applicability of the silver (I) carboxylate metathesis must be verified.
Overall, in this work was the catalytic activity of germanium acetate was proved. In addition, novel synthesis routes for catalyst precursors with aminopropyl anchor groups were found. Therefore, this work delivers a base for the synthesis of aminopropyl germanium carboxylate based catalysts.

5 Experimental Section

5.1 General section

Nitrogen atmosphere and standard schlenk line techniques were used for all operations and experiments. Toluene, pentane, diethyl ether, benzene and THF were prepared on a solvent drying system (Innovative Technology Inc., Molecular sieve pore size 4 Å). In addition, THF was distilled under nitrogen and over LAH. To remove traces of acidic acid, silver (I) acetate was washed 3-times with dry THF and dryed over night in vacuum under light exclusion. All Chemicals were bought from commercial sources.

5.1.1 NMR - spectroscopy

^{1}H (300.22 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded at 25 °C on a Mercury 300 MHz spectrometer from Varian. Relative to TMS (δ = 0.00 ppm) the chemical shifts δ are given in parts per million (ppm) for ^{1}H, ^{13}C and ^{119}Sn spectra.

Table 6 – Used letters for the signal types

letter	signal typ
s	singlet
bs	broad singlet
d	doublet
t	triplet
q	quartett
dt	doublet of a triplet
tt	triplet of a triplet
m	multiplett

5.1.2 XRAY - crystallography

All crystals suitable for single crystal X-ray diffractometry were removed from a vial or a Schlenk and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold nitrogen stream provided by an Oxford Cryosystems cryostream. XRD data collection was performed for compound (XXVII), on a Bruker APEX II diffractometer with use of an Incoatec microfocus sealed tube of Mo Kα radiation (λ = 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS or TWINABS.[51–53] The structures were solved with use of the intrinsic phasing option in SHELXT and refined by the full-matrix least-squares procedures in SHELXL.[53–55] The space group assignments and structural solutions were evaluated using PLATON.[53,56–58] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to nitrogen in compound was located in a difference map. All other hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles. All crystal structures representations were made with the program Diamond. Table 10 contains crystallographic data and details of measurements and refinement for compound (XXVIII).

5.1.3 GC/MS measurements

Used GC/MS sysetem: Agilent Technologies 7890A GC system coupled to an Agilent Technologies 5975C VLMSD mass spectrometer using a HP5 column (30 m x 0.250 mm x 0.025 μm) and helium as a carrier gas (gasflow: 0.92726 mL/min). For injection a hot-needle manual injection method at an injector temperature of 280 °C was used. The GC methods which are used for this work are presented in the appendix.
MS conditions: positive EI ionization with an ionization energy of 70 eV and a full scan mode (50–500 m/z). Interpretation of the MS was done by comparison with common fragmentation pattern.[59,60]

5.2 Determination of the catalyst activity

To the determine the activity a NMR based reaction tracking was used.[61–64] For this purpose, 3 stock solutions in deuterated chloroform were prepared in a 20 mL volometric flask:

Table 7 – Stock solutions for the catalytic activity measurements

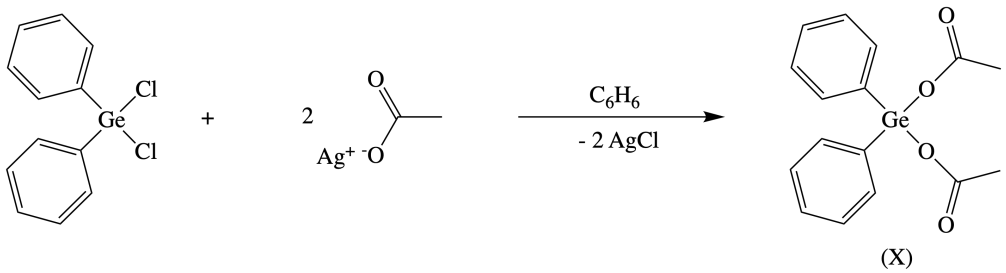
solution	compound	concentration
A	methanol	3 M
B	phenylisocyante	3 M
C	catalyst	3 %mol

In a commercial NMR - tube, 0.3 mL of solution A, B and C were mixed at 25 °C, afterwards a series of in-situ ^{1}H NMR spectra were measured to follow the reaction progress. Used NMR was a 60 MHz bench top NMR from Nanalysis (NMReady-60e), for the series of in-situ ^{1}H measurements the application "Kinetics package capabilities for reaction monitoring" from Nanalysis was used.[65,66] The used shift of methanol is located between 3.18 ppm to 3.59 ppm and for phenyl isocyante between 3.60 ppm to 4.01 ppm. From the kinetic setup of the NMR spectrometer a time / area table of the peaks was delivered. To set a benchmark for the catalytic activity of each catalyst, the time ($t_{50\%}$) was determined until a 50% conversion of product and methanol. The time / area tables for the measurements are presented in the appendix. Invastigated catalysts were DBTDL, diphenylgermanium diacetate (X), diethylgermanium diacetate (XI) and in addition the blanc reaction (without any catalyst) was invastigated. The results of the measurements are illustrated in table 8.

Table 8 – Summery activity results

Compound	$t_{50\%}$ (s)
DBTDL	5
$Ph_2Ge(OAc)_2$	950
$Et_2Ge(OAc)_2$	1000
blanc	3800

5.3 Diphenylgermanium diacetate (X)



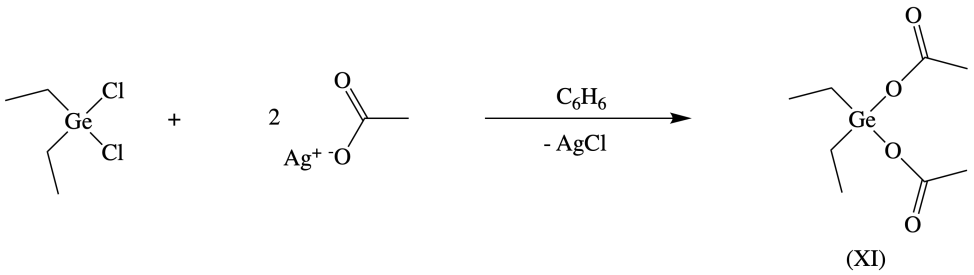
Scheme 49 – Synthesis of diphenylgermanium diacetate (X)

In a 50 mL Schlenk tube coated with aluminium foil (for light exclusion), 0.50 g (1.7 mmol) of diphenylgermanium dichloride were solved in 20 mL benzene. To the colourless solution, 0.74 g (4.4 mmol) of silver (I) acetate were added and stirred for 18 h at room temperature. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the white powder was dried in oil vacuum at 40 °C. The product was isolated as a white powder, yield: 0.52 g (89%).

^{1}H - NMR (C_6D_6, 300 MHz) δ: 1.69 (s, 6H, $-OOC-CH_3$); 7.92 (m, 4H o – Ph); 7.13 - 7.10 (m, 6H m, p – Ph) ppm.

^{13}C - NMR (C_6D_6, 75.5 MHz) δ: 20.2 (2C, $-CH_3$); 173.9 (2C, $-OOC-$); 134.2 (2C, Ge – Ph); 131.1 (4C, o – Ph); 128.5 (4C, m, p – Ph); ppm.

5.4 Diethylgermanium diacetate (XI)



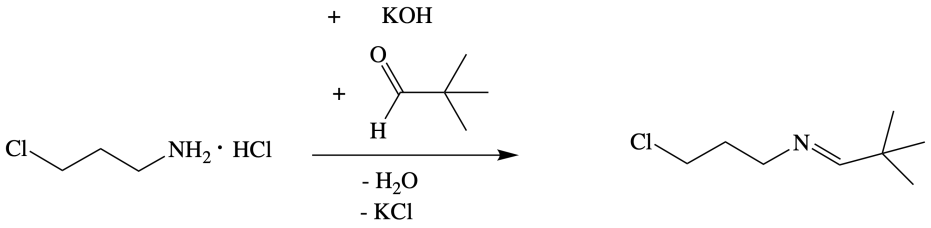
Scheme 50 – Synthesis of diethylgermanium diacetate (XI)

In a 50 mL Schlenk tube coated with aluminium foil (for light exclusion), 0.50 g (1.7 mmol) of diethylgermanium dichloride were solved in 20 mL benzene. To the colourless solution, 0,74 g (4.4 mmol) of silver (I) acetate were added and stirred for 18 h at room temperature. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the white powder was dried in oil vacuum at 40 °C. The product was isolated as a white powder, yield: 0.63 g (90%).

^{1}H - NMR (C_6D_6, 300 MHz) δ: 1.47 (s, 6H, $-OOC-CH_3$); 1.21 (dt, 4H $-CH_2-$); 0.83 (t, 6H $-CH_3$); ppm.

^{13}C - NMR (C_6D_6, 75.5 MHz) δ: 6.7 (2C, $-CH_3$); 12.8 (2C, $-CH_2-$); 20.6 (2C, $-OOC-CH_3$); 174.6 (2C, $-OOC-$); ppm.

5.5 1-Chloro-3-(2,2-dimethylpropyl-imino) propane (XV)



(XV)

Scheme 51 – Synthesis of 1-chloro-3-(2,2-dimethylpropyl-imino)propane (XV)

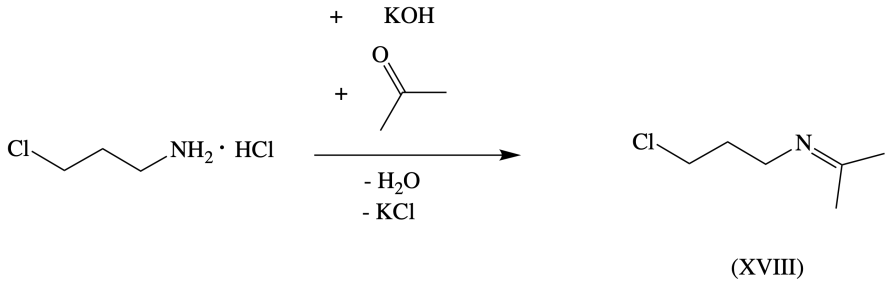
In a 500 mL round-bottom flask with a Dean–Stark apparatus and a reflux condenser, 6.5 g (5 mmol) of 1-chloro-3-propylamino hydrochloride were solved in 200 mL benzene. To the colourless solution, 4.3 g (5 mmol) of pivaldehyde and potassium hydroxide (2.5 g, 5 mmol) were added and refluxed for 3 h (water seperation was finished). At 40 °C the solvent was removed under vacuum and 100 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated. The n-pentane was removed and the slightly yellow oil was dried in oil vacuum at 40 °C. After a vacuum destiallation, the product was isolated as a colourless oil, yield: 6.98 g (80%).

^{1}H - NMR ($CDCl_3$, 300 MHz) δ: 7.48 (s, 1H, – N=CH –); 3.43 (t, 2H, Cl–CH_2 –) 3.40 (t, 2H, – CH_2–N) 1.93 (tt, 2H, – CH_2 –) 0.98 (s, 9H –CH_3) ppm.

^{13}C - NMR ($CDCl_3$, 75.5 MHz) δ: 42.6 (1C, – CH_2–N); 33.2 (1C, – CH_2 –); 57.6 (1C, CH_2–Cl); 36.3 (1C, C–quart); 27.0 (3C, CH_3 –); 173.3 (1C, C=N); ppm.

Boiling point: 63 °C (at 15 mbar)

5.6 1-Chloro-3-(iso-propylimino)propane (XVIII)



(XVIII)

Scheme 52 – Synthesis of 1-chlor-3-(iso-propylimino)propane (XVIII)

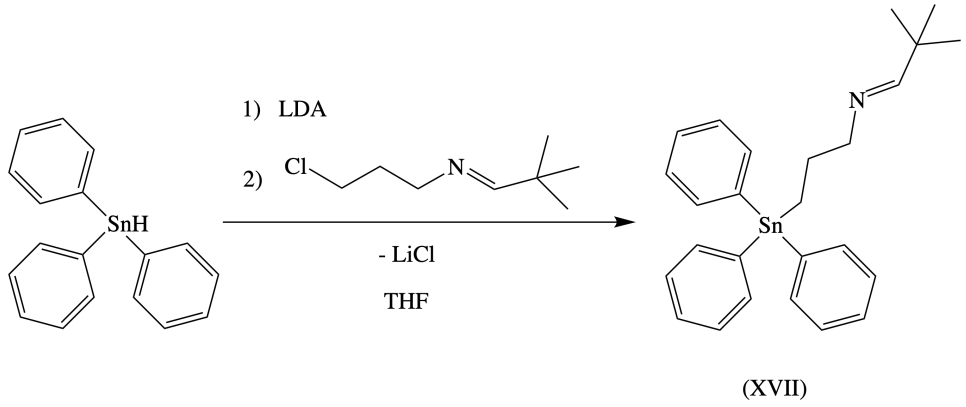
In a 500 mL round-bottom flask with a Dean–Stark apparatus and a reflux condenser, 6.5 g (5 mmol) of 1-chloro-3-propylamino hydrochloride were solved in 200 mL benzene. To the colourless solution, 6 g (11 mmol) of acetone and potassium hydroxide (2.5 g, 5 mmol) were added and refluxed for 3 h (water seperation was finished). At 30 °C the solvent was removed under vacuum (500 mbar) and 100 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated. The n-pentane was removed and the slightly yellow oil was dried in vacuum (15 mbar) at room temperature. The product was isolated as a yellow oil, yield: 6.4 g (79%).

^{1}H - NMR (C_6D_6, 300 MHz) δ: 2.92 (t, 2H, $-CH_2-Cl$); 2.08 (t, 2H, $-CH_2-N$); 1.50 (tt, 2H, $-CH_2-$); 1.09 (s, 6H $-CH_3$) ppm.

^{13}C - NMR (C_6D_6, 75.5 MHz) δ: 27.9 (1C, CH_3-); 27.4 (1C, CH_3-); 52.5 (1C, CH_2-Cl); 17.7 (1C, $C-N$); 9.5 (1C, $-CH_2-$); 168.5 (1C, $-C=N$);

Boiling point (decomposition): 51 °C (15 mbar)

5.7 Triphenyl-3-(2,2-dimethylpropyl-imino)propyl stannane (XVII)



(XVII)

Scheme 53 – Synthesis of triphenyl-3-(2,2-dimethylpropyl-imino)propyl stannane

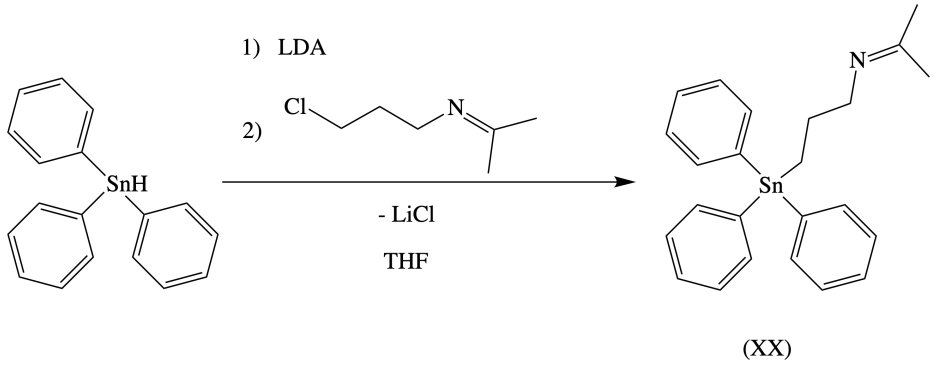
In a 50 mL Schlenk tube, 0.80 g (7.5 mmol) of LDA were solved in 40 mL THF. To the colourless solution, 2.5 g (7.1 mmol) of triphenyl stannane were added and stirred for 1 h at - 80 °C. Afterwards, 1.14 g (7.0 mmol) 1-chloro-3-(2,2-dimethylpropyl-imino)propane were dropwise added and stirred over night. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the oil was dried in oil vacuum at 40 °C. The product was isolated as a slightly white oil, yield: 3.04 g (91%).

^{1}H - NMR (C_6D_6, 300 MHz) δ: 7.59 (m, 6H, o-Ph); 7.24 - (s, 1H $-N=C-H$) 7.05 - 7.14 (m, 9H m, p-Ph) 2.60 (t, 2H $Sn-CH_2-$) 1.81 (tt, 2H $-CH_2-$) 1.23 (t, 2H $-CH_2-N$) 0.72 - (s, 9H t-butyl)

^{13}C - NMR (C_6D_6, 75.5 MHz) δ: 170.7 (1C, $-C=N-$); 136.3 (3C, Ph); 134.3 (6C, Ph); 129.6 (6C, Ph); 128.4 (3C, Ph); 63.5 (1C, $=N-CH_2-$); 35.8 (1C, C−quart); 27.7 (3C, CH_3); 27.9 (1C, $-CH_2-$); 10.9 (1C, $Sn-CH_2-$); ppm.
$^{1}J(^{13}C-^{119}Sn)$ = 392 Hz

^{119}Sn - NMR (C_6D_6, 112 MHz) δ: -108.5 ppm.

5.8 Triphenyl-3-(iso-propylimino)propyl stannane (XX)



(XX)

Scheme 54 – Synthesis of triphenyl-3-(iso-propylimino)propyl stannane

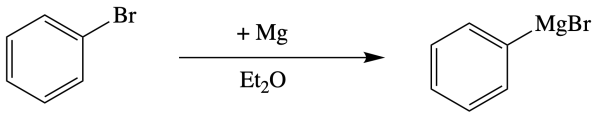
In a 50 mL Schlenk tube, 0.80 g (7.5 mmol) of LDA were solved in 40 mL THF. To the colourless solution, 2.5 g (7.1 mmol) of triphenyl stannane were added and stirred for 1 h at - 80 °C. Afterwards, 1.09 g (7.3 mmol) 1-chloro-3-(iso-propylimino)propane were dropwise added and stirred over night. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the white powder was dried in oil vacuum at 40 °C. The product was isolated as a colourless crystals, yield: 3.04 g (91%).

^{1}H - NMR (C_6D_6, 300 MHz) δ: 7.58 (m, 6H, o-Ph); 7.24 (s, 1H, $-N{=}C{-}H$) 7.05 - 7.14 (m, 9H, m, p – Ph) 2.92 (t, 2H, $-CH_2{-}N$) 1.81 (tt, 2H, $-CH_2-$) 1.22 (t, 2H, $Sn{-}CH_2-$) 1.09 (s, 6H $-CH_3$) ppm.

^{13}C - NMR (C_6D_6, 75.5 MHz) δ: 170.7 (1C, $-C{=}N-$); 136.3 (3C, Ph); 134.3 (6C, Ph); 129.6 (6C, Ph); 128.4 (3C, Ph); 53.7 (1C, $=NCH_2-$); 27.4 (1C, CH_3); 27.9 (1C, CH_3); 9.55 (1C, $Sn{-}CH_2-$); 17.73 (2C, $-CH_2-$); ppm. $^{1}J(^{13}C-^{119}Sn)$ = 392 Hz

^{119}Sn - NMR (C_6D_6, 112 MHz) δ: -108.2 ppm.

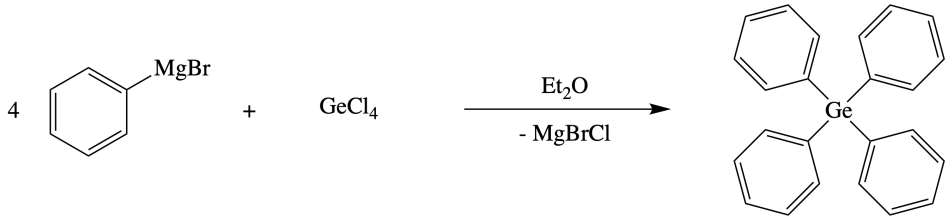
5.9 Phenylmagnesium bromide



Scheme 55 – Synthesis of phenylmagnesium bromide

In a 4000 mL three-necked round flask with dropping funnel, KPG - stirrer and reflux condenser, 80 g (3.33mol) of magnesium were suspended in 2000 mL diethylether. To this mixture, a solution of 437 g (2.79mol) of bromobenzene solved in 500 mL diethylether were added dropwise (after adding of 10% a dynamic reflux was obtained). Afterwards, the brownish suspension was refluxed for 3 h. After the cool down the mixture was filtrated to seperate the magnesium. The formed brownish solution was used as stock solution for following steps. Determination of the concentration was done via titration with HCl (0.1 M) , 0.87 mol/L (yield: 90%).

5.10 Tetraphenyl germane (XXI)



Scheme 56 – Synthesis of tetraphenyl germane (XXI)

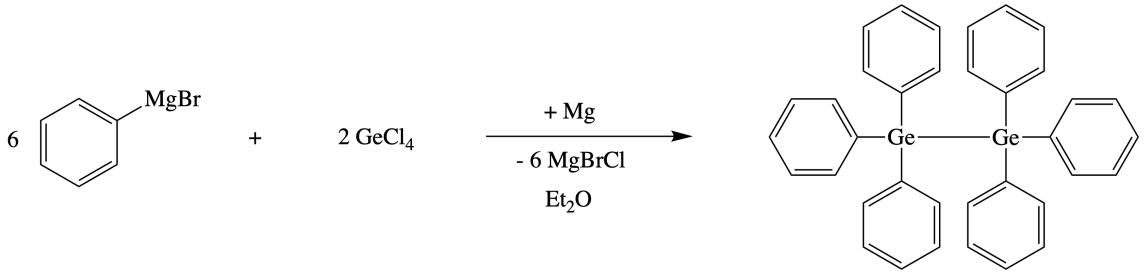
In a 250 mL Schlenk tube, 1.87 g (8.7 mmol) of germanium tetrachloride were solved in 50 mL diethylether. To the colourless solution, 100 mL (87 mmol) of phenylmagnesium bromide solution (0.87 M in diethyl ether) were added and stirred for 4 h at room temperature. 50 mL of cold water were added and the phases were separated. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the white powder was dried in oil vacuum at 40 °C. The product was isolated as a white powder,
yield: 2.83 g (85%).

^{1}H - NMR ($CDCl_3$, 300 MHz) δ: 7.22 - 7.18 (o,m,p - Ph, 20H, Ph); ppm.

^{13}C - NMR ($CDCl_3$, 75.5 MHz) δ: 128.2 (p - Ph, 4C); 128.7 (m - Ph, 8C); 135.5 (o -Ph, 4C);
134.7 (Ge - Ph, 8C);

Melting point: 232 °C

5.11 Hexphenyl digermane (XXV)



(XXV)

Scheme 57 – Synthesis of hexphenyl digermane (XXV)

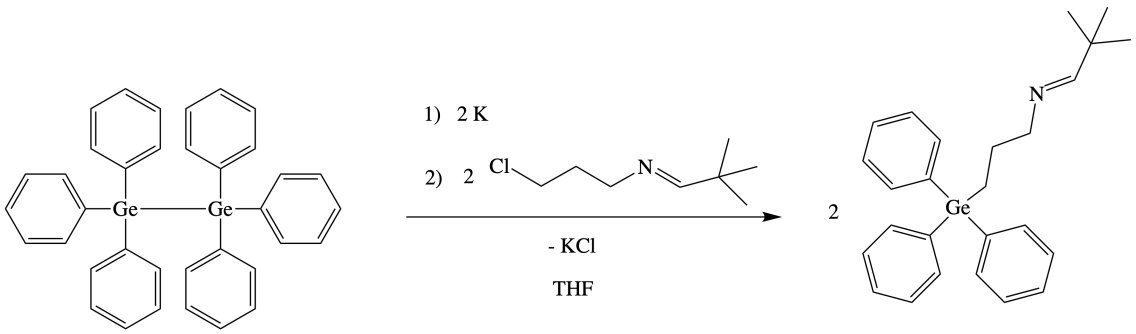
In a 250 mL Schlenk tube charged with 0.4 g magnesium (17.4 mmol), 1.87 g (8.7 mmol) of germanium tetrachloride were solved in 50 mL diethylether. To the colourless solution, 100 (87 mmol) of phenylmagnesium bromide solution (0.87 M) were added and stirred for 8 h at room temperature. 100 mL of cold water were added and the phases were separated. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the white powder was dried in oil vacuum at 40 °C. The product was isolated as a white powder, yield: 2.33 g (70%).

^{1}H - NMR ($CDCl_3$, 300 MHz) δ: 7.23 - 7.16 (o,m,p - Ph, 30H, Ph); ppm.

^{13}C - NMR ($CDCl_3$, 75.5 MHz) δ: 128.1 (p - Ph, 6C,); 128.8 (m - Ph, 12C,); 135.4 (o -Ph, 12C,); 137.3 (Ge - Ph, 6C,); ppm.

Melting point: 330 - 332 °C

5.12 Triphenyl-3-(2,2-dimethylpropyl-imino)propyl germane (XXVII)



(XXV) (XXVII)

Scheme 58 – Synthesis of triphenyl-(3-2,2-dimethylpropyl-imino)propyl germane (XXVII)

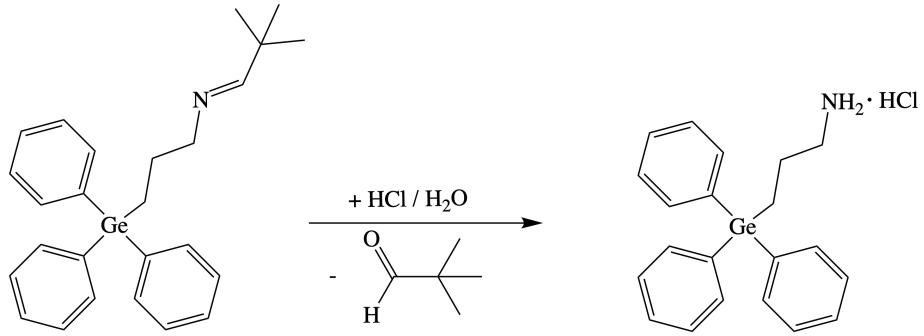
In a 250 mL Schlenk tube, 9.49 g (15.6 mmol) of hexaphenyl germane were solved in 50 mL THF. To the white suspension, 1.22 g (30.5 mmol) of potassium were added and refluxed for 8 h. To this dark green solution 5.55 g (17.2 mmol) of 1-chloro-3-(2,2-dimethylpropyl-imino)propane were added and was stirred for 4 h. At 40°C the solvent was removed under vacuum and 15 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the slightly yellow oil was dried in oil vacuum at 40 °C. The product was isolated as a slightly yellow oil, yield: 4.61 g (69%).

^{1}H - NMR ($CDCl_3$, 300 MHz) δ: 7.63 (m, 6H, o-Ph); 7.34 (s, 1H $-N{=}C-H$); 7.18 (m, 9H m, p – Ph); 2.70 (t, 2H $-CH_2-N{=}$); 1.85 (tt, 2H $-CH_2-$); 1.27 (t, 2H $Ge-CH_2-$); 0.72 - (s, 9H t-butyl) ppm.

^{13}C - NMR ($CDCl_3$, 75.5 MHz) δ: 170.7 (1C, $-C{=}N-$); 136.3 (3C, Ph); 134.5 (6C, Ph); 129.2 (6C, Ph); 128.4 (3C, Ph); 63.4 (1C, $-CH_2-N$); 35.8 (1C, $C-$quart$\cdot$); 27.2 (3C, CH_3); 10.3 (1C, $Ge-CH_2-$); 27.7 (1C, $-CH_2-$); ppm.

GCMS (Methode 1) : t_r = 21. 2 min. **m/z:** 430.3 (M+•); 374.1 ($R-N{=}C^+$); 305.1 (Ph_3Ge^+); 227.0 (Ph_2Ge^+); 150.9 ($PhGe^+$); 77.0 (Ph^+);

5.13 Triphenyl-3-aminopropyl germane hydrochloride (XXVIII)



(XXVII) (XXVIII)

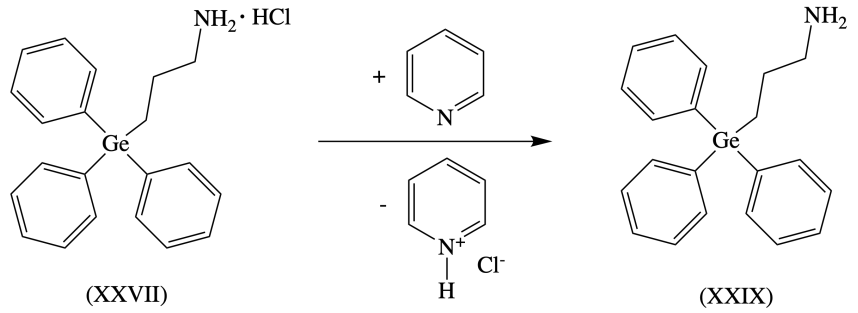
Scheme 59 – Synthesis of triphenyl-3-aminopropyl germane hydrochloride (XXVIII)

In a 100 mL Schlenk tube, 0.5 g (1.16 mmol) of triphenyl-3-(2,2-dimethylpropyl-imino)propyl germane were solved in 50 mL THF. To the colourless solution, 11.6 mL (1.16 mmol) of hydro chloric acid (0.1 M) were added and stirred for 1 h at room temperature. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the white powder was dried in oil vacuum at 40 °C, afterwards the powder was recrystallized in chloroform. The product was isolated as colourless crystals, yield: 0.44 g (95%).

^{1}H - NMR ($CDCl_3$, 300 MHz) δ: 7.31 (m, 6H, o – Ph); 7.23 - 7.14 (m, 9H, m, p – Ph);
2.71 (t, 2H, $-CH_2-N=$); 2.04 (tt, 2H, $-CH_2-$); 1.73 (t, 2H, $Ge-CH_2$) ppm.

^{13}C - NMR ($CDCl_3$, 75.5 MHz) δ: 136.1 (3C, Ge – Ph); 134.9 (6C, o – Ph); 129.1 (6C, m – Ph); 128.3 (3C, p – Ph); 42.3 (1C, $-CH_2-N=$); 23.3 (1C, $-CH_2-$); 10.8 (1C, $Ge-CH_2-$); ppm.

5.14 Triphenyl-3-aminopropyl germane (XXIX)



(XXVII) (XXIX)

Scheme 60 – Synthesis of triphenyl-3-aminopropyl germane (XXIX)

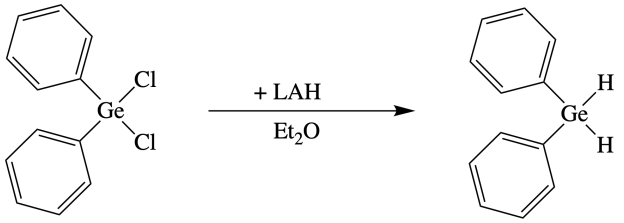
In a 100 mL Schlenk tube, 0.5 g (1.38 mmol) of triphenyl-3-aminopropyl germane hydrochloride were solved in 50 mL THF. To the colourless solution, 0.12 g (1.44 mmol) of pyridine were added and stirred for 3 h at room temperature. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the oil was dried in oil vacuum at 40 °C. The product was isolated as a colourless oil, yield: 0.43 g (95%).

^{1}H - NMR ($CDCl_3$, 300 MHz) δ: 7.31 (m, 6H, o – Ph); 7.23 - 7.14 (m, 9H m, p – Ph); 2.65 (t, 2H $-CH_2-NH_2$); 1.54 (tt, 2H $-CH_2-$); 1.44 (t, 2H $-CH_2-$Ge) ppm.

^{13}C - NMR ($CDCl_3$, 75.5 MHz) δ: 136.1 (3C, Ge–Ph); 134.9 (6C, o – Ph); 129.1 (6C, m – Ph); 128.3 (3C, p – Ph); 45.4 (1C, $CH_2-N=$); 29.3 (1C, $-CH_2-$); 11.09 (1C, Ge–CH_2-); ppm.

GCMS (Method 3) : t_r = 15.3 min. **m/z:** 362.2 (M+•); 334.1 (Ph_3GeEt^+); 305.0 (Ph_3Ge^+); 286.0 ($Ph_2Ge(CH_2CH_2CH_2NH_2)^+$); 227.0 ($Ph_2Ge^+$); 151.0 ($PhGe^+$); 78.0 ($Ph^+$);

5.15 Diphenyl germane (XXX)



Scheme 61 – Synthesis of diphenylgermane (XXX)

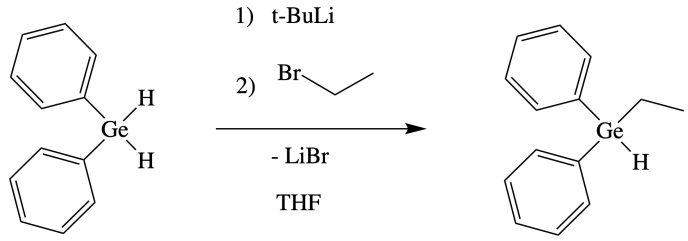
In a 500 mL Schlenk tube, 1.28 g (33.6 mmol) of LAH were suspended in 200 mL diethyl ether. To this grey suspension, 5 g (16.8 mmol) of diphenyl germanium dichlorid were dropwise added and stirred for 6 h at room temperature. 150 mL of cold water (degassed) were very slowly added and the phases were separated. At 40 °C the solvent was removed under vacuum and 200 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the remaining liquid was dried in oil vacuum at 40 °C. The product was isolated as a colourless liquid, yield: 3.45 g (91%).

^{1}H - NMR (C_6D_6, 300 MHz) δ: 7.69 (m, 4H, o – Ph); 7.50 - 7.48 (m, 6H m, p – Ph); 5.26 (s, 2H Ge–H);

^{13}C - NMR (C_6D_6, 75.5 MHz) δ: 135.3 (2C, Ge–Ph); 134.1 (4C, o – Ph); 129.2 (4C, m – Ph); 128.5 (2C, p – Ph); ppm.

GCMS (Method 3) : t_r = 10.3 min. **m/z:** 227 (M+•); 150.8 ($GeHPh_2^+$); 77.0 (Ph^+); 51.0 ($C_4H_3^+$)

5.16 Diphenyl-ethyl germane (XXXII)



(XXXII)

Scheme 62 – Synthesis of diphenyl-ethyl germane (XXXII)

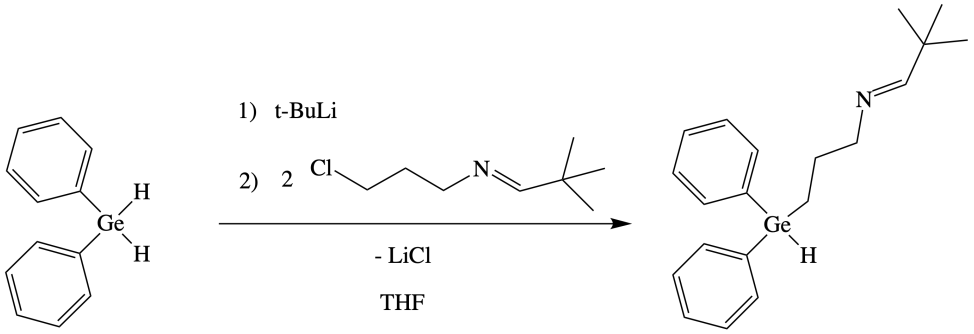
In a 250 mL Schlenk tube, 2.6 g (11.4 mmol) of diphenyl germane were solved in 70 mL THF. To the colourless solution, 8.0 mL g (13.7 mmol) of t-butyllithium (in pentane 1.7 mol/L) were added and stirred for 1 h at - 50 °C. Afterwards, 1.64 g (15.0 mmol) ethylbromide (destilled and stored under nitrogen) were dropwise added and stirred over night. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the remaining liquid was dried in oil vacuum at 40 °C. The product was isolated as a colourless liquid, yield: 2.47 g (85%).

^{1}H - NMR (C_6D_6, 300 MHz) δ: 7.39 (m, 4H, o – Ph); 7.05 - 7.08 (m, 6H, m, p – Ph); 4.98 (t, 1H, Ge – H); 0.88 (tt, 2H, $-CH_2-$); 0.79 (t, 3H, $-CH_3$) ppm. $^{3}J(^{1}H-^{1}H)$ $HGe-CH_2$ = 4.9 Hz

^{13}C - NMR (C_6D_6, 75.5 MHz) δ: 136.3 (2C, Ph); 134.3 (4C, Ph); 129.6 (4C, Ph); 128.4 (2C, Ph); 27.9 (1C, $-CH_2-$); 10.9 (1C, $-CH_3$); ppm.

GCMS (Method 3) : t_r = 11.4 min. **m/z:** 243 ($Ge-CH_2^+$); 180 ($HGe^+CH_2CH_3$); 227.0 (Ph_2Ge^+); 150.9 ($PhGe^+$); 78.0 (Ph^+);

5.17 Diphenyl-3-(2,2-dimethylpropyl-imino)propyl germane (XXXIV)



(XXX) (XXXIV)

Scheme 63 – Synthesis of diphenyl-(3-2,2-dimethylpropyl-imino)propyl germane (XXXIV)

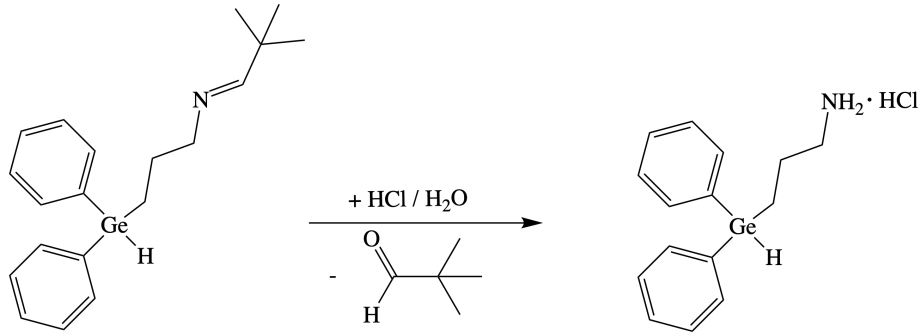
In a 250 mL Schlenk tube, 2.6 g (11.4 mmol) of diphenyl germane were solved in 70 mL THF. To the colourless solution, 8.0 mL g (13.7 mmol) of t-butyllithium (in pentane 1.7 mol/L) were added and stirred for 1 h at - 50 °C. Afterwards, 2.42 g (15.0 mmol) 1-chloro-3-(2,2-dimethylpropyl-imino)propane (distilled and stored under nitrogen) were dropwise added and stirred over night. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the oil was dried in oil vacuum at 40 °C. The product was isolated as a colourless oil, yield: 3.19 g (79%).

^{1}H - NMR (C_6D_6, 300 MHz) δ: 7.41 (m, 4H, o-Ph); 7.05 - 7.09 (m, 6H m, p-Ph); 7.22 (s, 1H N=CH^{-}); 5.21 (t, 1H, Ge–H); 3.22 (tt, 2H, $-CH_2-$N); 1.78 (t, 2H, $-CH_2-$); 1.05 - 1.12 (tt, 2H, Ge–CH_2); 0.93 (s, 9H $C(CH_3)_3$) ppm. $^{3}J(^{1}H-{}^{1}H)$ HGe–CH_2 = 4.9 Hz

^{13}C - NMR (C_6D_6, 75.5 MHz) δ: 170.5 (1C, N=C –); 136.6 (2C, Ph); 134.7 (4C, Ph); 128.7 (4C, Ph); 128.2 (2C, Ph); 63.3 (1C, NCH_2); 35.7 (1C, C – quart·); 27.9 (3C, $-CH_3$); 26.8 (1C, $-CH_2-$); 10.77 (1C, Ge–CH_2); ppm.

GCMS (Method 3) : t_r = 15.3 min. **m/z:** 340.1 ($^{+}C(CH_2)_2(-C=N)$); 298.1 ($-N=C^{+}$); 278.1 (Ph(Imin)HGe^{+}); 229.0 (Ph_2Ge^{+}); 151.0 ($PhHGe^{+}$);

5.18 Diphenyl-3-aminopropyl germane hydrochloride (XXXV)



(XXXIV) (XXXV)

Scheme 64 – Synthesis of diphenyl-3-aminopropyl germane hydrochloride (XXXV)

In a 100 mL Schlenk tube, 0.41 g (1.16 mmol) of diphenyl-3-(2,2-dimethylpropyl-imino)propyl germane were solved in 50 mL THF. To the colourless solution, 11.6 mL (1.16 mmol) of hydrochloric acid (0.1 M) were added and stirred for 1 h at room temperature. At 40 °C the solvent was removed under vacuum and 10 mL n-pentane were added. After 15 min. of stirring the mixture was filtrated through a 20 µm syringe filter. The n-pentane was removed and the white powder was dried in oil vacuum at 40 °C. The product was isolated as a white powder - in the NMR spectra traces of solvents could be obtained, yield: 0.39 g (94%).

^{1}H - NMR (C_6D_6, 300 MHz) δ: 7.29 (m, 4H, o – Ph); 7.23 - 7.14 (m, 6H m, p – Ph) 5.99 (bs, 2H NH_2) 5.09 (t, 1H Ge – H) 2.88 (t, 2H $-CH_2-$N) 2.15 (tt, 2H $-CH_2-$) 1.24 (tt, 2H Ge – CH_2-) ppm. $^{3}J(^{1}H-{}^{1}H)$ $HGe-CH_2$ = 4.9 Hz

^{13}C - NMR (C_6D_6, 75.5 MHz) δ: 136.1 (2C, Ge – Ph); 134.9 (4C, o – Ph); 129.1 (4C, m – Ph); 128.3 (2C, p – Ph); 42.3 (1C, $-CH_2-$N); 24.9 (1C, $-CH_2-$); 10.1 (1C, Ge – CH_2-); ppm.

6 Appendix

6.1 GC/MS methods

Table 9 – GC/MS methods

Method No.	Typ	Rate (°C/min.)	Value (°C)	Hold time (min.)
Method 1	Initial	-	40	2
	Ramp 1	18	280	10
Method 2	Initial	-	45	2
	Ramp 1	12	280	10
Method 3	Initial	-	40	2
	Ramp 1	20	100	-
	Ramp 2	16	200	-
	Ramp 3	12	320	20

6.2 Crystallographic data and details of measurement

Table 10 – Crystallographic data and details of measurements for compound (XXVIII)

Mo Kα (λ=0.71073Å). R1= Σ/ $|F_o|$- $|F_c|$/|Σ|F_d; wR2 = $[\Sigma_w(F_o^2-F_2^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$

Compound	**(XXVII)**
Formula	$C_{21}H_{24}GeN\cdot Cl\cdot H_2O$
Fw (g mol^{-1})	416.47
a (Å)	15.1514(7)
b (Å)	37.6769(19)
c (Å)	7.2797(3)
α (°)	90
β (°)	90
γ (°)	90
V ($Å^3$)	4155.7(3)
Z	8
Crystal size (mm)	0.08 × 0.07 × 0.07 mm
Crystal habit	15.1514(7)
Crystal system	Orthorhombic
Space group	*Iba*2
d_{calc} (Mg/m^{-3})	1.331
μ (mm^{-1})	1.61
T (K)	100(2)
2*θ* range (°)	2.7–29.2
F(000)	1728
R_{int}	0.086
independent reflns	7956
No. of params	7956
R1, wR2 (all data)[a]	R1 = 0.0423 wR2 = 0.0844
R1, wR2 (>2*σ*)[b]	R1 = 0.0364 wR2 = 0.0813

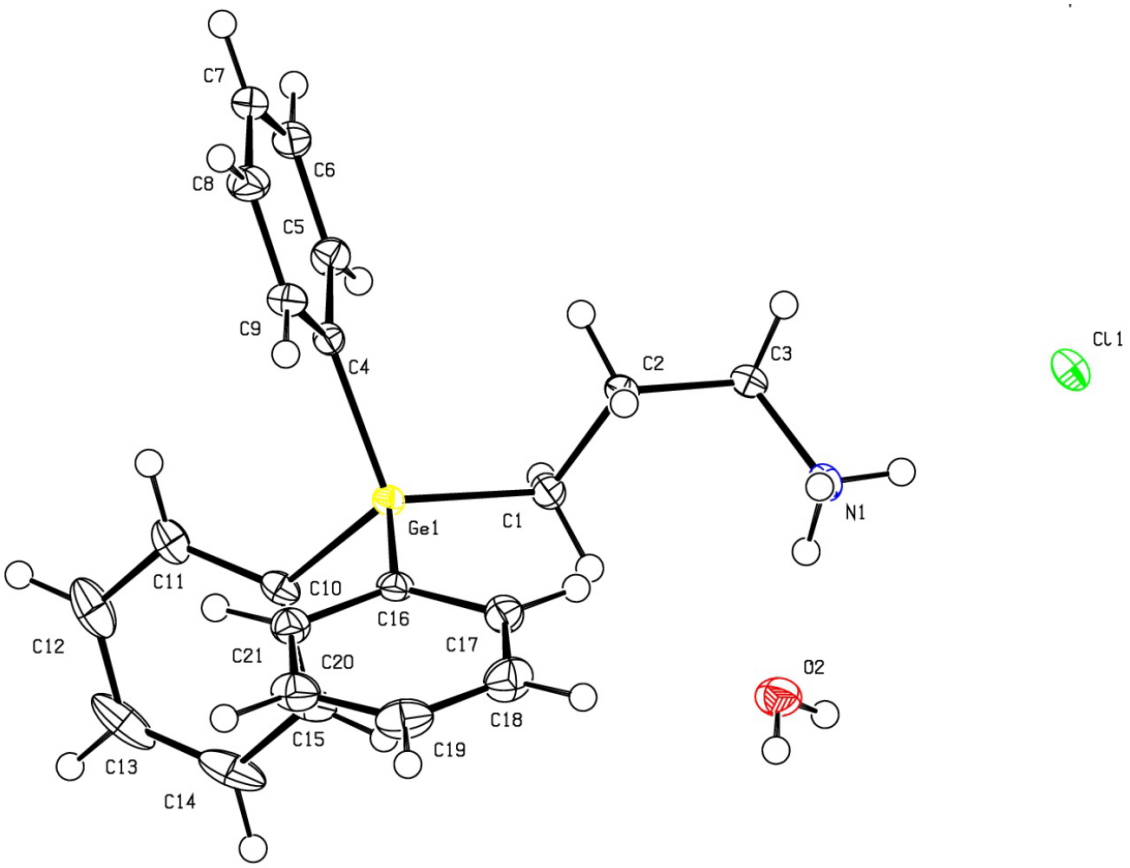


Figure 4 – Atome numbering in the crystal structure of (XXVIII)

6.3 NMR data catalytic activity measurements

6.3.1 Diphenylgermanium diacetate

Table 11 – Measured datas from the catalytic activity measurements MeOH = methanol ; PhIC = phenyl isocyanate

Time (s)	Integral (MeOH)	Integral(PhIC)	Time (s)	Integral (MeOH)	Integral(PhIC)
0	162501	8875,48	886,281	85443,8	78579,5
18,0555	157765	10731,5	904,335	83307,5	80671,8
36,0484	154566	12766,5	922,47	82598,4	81298,4
54,1199	151420	14896,8	940,513	81929,8	81393,8
72,2017	148759	17191,7	958,579	81363,8	82127,1
90,2779	146650	18410,6	976,66	80970,9	82847,2
108,39	145140	20381,5	994,746	80023,4	83453,3
126,479	142382	23103,8	1012,79	79179	84697,4
144,548	141004	23822	1030,87	78631,4	85330,9
162,579	139021	26132,6	1050,04	77342,2	86747
180,625	136718	28371,6	1068,12	75805,1	87969
198,71	134939	29898,3	1086,18	75923,3	87746,3
216,761	133206	31758,2	1104,19	75386,8	88371,9
234,815	131488	33759,1	1122,27	74794,6	89067,2
252,833	130189	34436,5	1140,37	73757	90142,9
270,944	128074	36531,2	1158,41	73016,5	90406,8
288,952	126490	38114,8	1176,5	72730,4	91349
307,018	125254	39261,9	1194,5	71689,4	92216,5
325,075	123284	41484,4	1212,58	71356,9	92574,5
343,192	121668	42890,1	1230,69	70370,4	93255,9
361,194	120094	44366,9	1248,79	70164,7	93417,6
379,31	118075	46500,3	1266,85	68729,3	94971,3
397,398	116915	47640,1	1284,94	68484,4	95469,2
415,47	114964	49251,5	1303,02	67514,1	96166,9
433,577	113859	50558,5	1321,1	67231	96880,6
451,644	112588	51517,6	1339,21	66437,2	97288
469,694	111520	52660,3	1357,25	66407,2	97395,8
487,796	110277	54038,6	1375,39	65827	97952,5
505,857	108653	55756,2	1393,54	64817,8	98850,1
523,877	106930	57322,3	1411,61	64398,3	99321,3
541,969	105691	58526,1	1429,69	64131,7	99357,9
560,027	104797	59062,6	1447,83	63728,8	100044
578,179	103056	60985,5	1465,9	63069,5	101109
596,253	102279	61908	1484,03	62681,6	101259
614,306	100597	63205,3	1502,1	62206,4	101728
632,374	99610,1	64454,2	1520,16	61912,9	101912
650,402	98326,1	65653,7	1538,24	61058,1	102532
668,545	97542,2	66504,8	1556,3	59604,6	104099
686,589	96531,6	67590,5	1575,37	59864,5	103983
704,62	94831,2	69236,7	1593,54	59241,4	104556
723,711	94124	70059,7	1611,57	59394,2	104802
741,738	93066,3	70682,3	1629,69	58470,4	105303
759,863	91043,5	72629,3	1648,77	57855,2	105581
777,934	90442,5	73223	1666,79	57480,9	106056
796,054	89880,6	74083	1684,9	57102,5	106420
814,078	88178,3	76014,5	1702,99	56120,2	107440
832,135	87851,6	76106,1	1721,16	55884,1	107795
850,209	86854	76732,4	1739,21	56480,4	107574
868,222	86148,6	77625,9	1757,23	55452,3	108574

Time (s)	Integral (MeOH)	Integral(PhIC)	Time (s)	Integral (MeOH)	Integral(PhIC)
1812,46	53832	109667	2755,19	38820,4	124791
1830,54	54303,4	109965	2773,26	39513	124755
1848,63	53461,3	110454	2791,31	38268,9	125342
1866,68	53235,8	110299	2809,38	39344,4	124691
1884,83	52816,8	111263	2827,47	38964,9	125030
1902,84	52920,8	110896	2845,53	38182,1	125762
1920,92	51776,8	111594	2863,65	38582,9	125783
1938,99	51704,3	112345	2881,82	39033,8	125363
1957,15	51475,7	112616	2899,98	38260,3	125839
1975,21	50864,7	113135	2918,03	36939,7	126654
1993,29	50418,2	113461	2936,11	37593,4	126426
2011,33	49873,6	113708	2954,15	37326,6	126963
2029,43	49729	113998	2972,26	37126,3	126785
2047,46	49443,3	114057	2990,31	36843,3	127088
2065,54	49098,2	114288	3008,44	36767,1	127184
2083,61	47672,8	115674	3027,53	36286,8	127858
2101,74	48244,5	115309	3045,6	37058	127348
2119,81	48251,8	115493	3063,72	36271,3	128058
2191,53	46609,9	117129	3081,77	35935,8	128021
2209,59	46520,9	117545	3099,89	35822,7	128307
2227,68	46331,1	117838	3117,94	36546,4	127954
2245,8	45956,2	117696	3136,07	34609	129164
2263,86	45402,3	118337	3154,19	34794,3	128724
2281,91	45374,8	118291	3172,31	35130,3	129143
2299,98	44920,2	118665	3190,42	34124,2	129834
2318,12	45020,5	118369	3208,5	34770,4	129071
2336,12	43956,9	119498	3226,54	34423,4	129590
2355,29	44431	119728	3244,6	35180	129065
2373,33	44036,6	120082	3262,68	34198,8	129930
2391,42	43841,1	119714	3280,77	34834,2	129412
2409,49	43899,8	120025	3298,79	33754,1	130511
2427,61	42739,9	120832	3316,9	33177,6	130617
2445,73	42097,5	121337	3334,96	33852,6	130508
2463,84	42274,1	121787	3353,02	33125,9	130793
2481,96	43248,9	120706	3371,07	32900,6	130893
2500	43036,8	121247	3389,12	33306,4	131106
2518,09	42301,7	121641	3407,18	32570,3	131206
2536,2	41190,2	122376	3425,27	32147,3	132000
2554,23	41497,4	122147	3443,36	32602,3	131604
2573,26	41686,9	122541	3461,47	33151,2	130864
2591,39	41554,4	122509	3479,51	32173,2	131856
2609,5	41250,4	122724	3497,59	33466,1	131150
2627,52	40781,1	123009	3515,75	31625,5	132684
2645,68	40512,4	123292	3533,76	32269,5	131938
2663,76	40038,2	124015	3551,84	31894,8	132173
2681,9	39559	124221	3569,9	31259,5	132974
2700,99	39607,4	123998	3587,98	31391	133076
2719,02	39925,8	124089	3606,06	31503,9	132299
2737,14	39484,2	124374	3624,13	32305,3	132441

Time (s)	Integral (MeOH)	Integral(PhIC)	Time (s)	Integral (MeOH)	Integral(PhIC)
3679,45	30881,3	133248	4618,99	24713,1	139101
3698,59	30796	133655	4637,04	25837,6	138669
3768,14	30702,3	133536	4655,1	25345,2	138762
3786,2	30186,1	134127	4673,2	25068,1	139263
3804,3	30858,8	133807	4691,23	25505,3	138424
3823,45	30066,2	134038	4709,25	26135,7	138518
3841,49	29643,1	134402	4727,3	25140,2	138904
3859,62	30474	133952			
3877,65	30156,6	134364			
3895,7	29649,4	134631			
3913,76	29819,7	134478			
3931,82	29879,9	134570			
3949,9	29359,1	134107			
3968,01	29249	134840			
3986,11	28704,4	135488			
4004,27	28824,4	135182			
4022,34	29044,5	135214			
4040,37	28721,9	135508			
4058,52	29174,8	135618			
4076,56	29152,5	135223			
4094,61	27815,2	136194			
4112,63	27539,4	136090			
4130,8	27996,7	136154			
4148,91	28040	136133			
4166,89	28316,3	136142			
4185,02	27936	136271			
4203,16	27361,4	136782			
4221,18	26849,9	137210			
4239,28	28182,2	136310			
4257,35	27118,6	136836			
4275,41	27288,4	136479			
4293,53	27286	136957			
4311,66	27602,7	136914			
4329,67	26961,6	136993			
4347,8	27558	136778			
4365,83	26744,4	137491			
4383,94	26690,5	137599			
4401,95	26419,8	137694			
4420,08	26136,8	138139			
4438,16	26939,3	137732			
4456,24	26740,4	137563			
4474,25	26732,6	137839			
4492,35	27671,5	137070			
4510,41	26782,7	137881			
4528,49	26305,1	138182			
4546,58	25514,4	138743			
4564,72	26675,6	137929			
4582,81	26563,1	138148			
4600,91	26371,9	138487			

6.3.2 Diethylgermanium diacetate

Table 12 – Measured datas from the catalytic activity measurements MeOH = methanol ; PhIC = phenyliso cyanate

Time (s)	Integral (MeOH)	Integral(PhIC)	Time (s)	Integral (MeOH)	Integral(PhIC)
0	149728	5119,97	925,36	117266	34731,6
18,1718	149714	4970,76	943,37	116810	35357,1
36,1971	148370	6335,48	961,401	116113	35700,5
54,2803	146852	7982,89	979,536	115465	36499,1
72,373	145527	8324,48	998,617	115394	36379,2
90,5326	144494	9411,98	1016,67	114783	37448,7
108,568	144101	9674,89	1034,82	114410	37807,7
126,693	143057	10336	1052,87	113916	37858,2
144,739	142450	10494,7	1071	113585	38379,2
162,871	141546	11600,8	1089,07	113060	39396,5
180,978	140743	12179	1107,19	112620	39486,8
199,101	139303	13517,6	1125,32	112566	39741,8
217,105	138881	15186,7	1144,45	112113	40686,3
236,176	138218	14638,2	1162,48	111688	40439,2
254,257	137446	15289,6	1180,64	111685	40726,6
273,301	137018	15761,2	1198,67	110794	41614,8
291,359	136140	16034	1216,67	110284	41849,4
345,583	133965	17899,5	1234,78	109925	42457,2
363,71	133372	18864,6	1252,89	109578	42460,7
381,805	132660	19450,9	1271,03	109515	42398,5
399,837	131697	20693,9	1289,1	109331	42778,3
417,953	131761	20962,3	1307,17	108449	43774,7
436,044	130752	22123,4	1325,33	108040	44562,4
454,149	130047	22152,8	1343,4	108107	44294,3
472,242	129631	22696,7	1361,4	107253	44702,3
490,296	128960	23527,3	1379,57	107389	44961,3
508,37	125193	22944,1	1397,56	107022	44967,6
526,409	127816	24272,3	1415,62	106750	45319,5
544,489	127395	25017,4	1433,71	106735	45808,9
562,54	126334	26229,7	1451,81	105343	47251,6
580,661	126064	26082,1	1469,99	106234	45890,6
598,754	125488	26677	1488,04	105496	46888,4
616,81	124969	26601,9	1507,12	105005	47719,2
634,903	124618	27394,4	1525,22	104660	47840,4
653,022	123456	28449,6	1543,33	105017	47249,4
671,072	123475	28511,9	1561,43	103883	48725,4
689,199	122796	30024,7	1579,45	103817	49095,6
707,251	122409	29510,2	1597,65	103326	49386,8
726,355	122371	29810,8	1615,65	103431	49258,9
744,466	121272	30566,6	1633,82	103263	48904,4
762,555	120966	30815,8	1651,85	102558	49814,3
780,59	120627	31193,2	1669,92	102720	49978,7
798,721	120130	32097,8	1687,95	101910	50357,9
816,813	119957	32068,8	1706,06	101669	50246,4
834,878	119632	32265,4	1724,13	101208	51058,7
852,972	118619	33542,3	1742,17	101181	51435,9
871,068	118486	33736,2	1760,23	101046	51710,7
889,133	117871	34012,2	1778,31	100516	51612,8
907,249	117061	35230,2	1796,31	100582	51925,2

Time (s)	Integral (MeOH)	Integral(PhIC)	Time (s)	Integral (MeOH)	Integral(PhIC)
1850,51	99931,3	52415,3	2737,71	88859,6	63652,3
1868,58	99322,4	53131,5	2755,93	88269	64152,1
1887,62	98965,7	53857,4	2773,95	88542	64081,7
1905,8	98557,3	54178,3	2792,04	88228,2	64496,2
1923,85	98619,5	53705,2	2810,09	87676,1	64990,3
1941,95	97929,9	54308,5	2828,18	87487	65039,6
1960,01	98123,3	54183	2846,25	87406,1	65668,3
1978,05	98033,8	54247,3	2864,25	87302	65689,7
1996,11	97663,3	54330,9	2882,32	86859,1	66218,2
2014,14	97613	54782,3	2900,4	86652,3	66154,7
2032,24	97009	55546,1	2918,44	87292,5	65278
2050,37	96752,9	56017	2936,51	86572	66012,4
2068,37	96687,3	56151,7	2954,69	86294,7	66735,5
2086,45	96909,8	55404,9	2972,69	86566,7	66269,3
2104,54	95678,9	57076,7	2990,84	86250,8	66442
2122,61	96173,7	56148,1	3008,84	85768,4	67303,8
2140,72	96127,4	56594,9	3026,94	85847,3	66765,4
2158,85	93418,2	55227,9	3044,94	85494,9	67754,8
2176,91	94776,2	57692,2	3063,07	85915	66880,3
2195,02	95135,9	57282,7	3081,19	85044,9	67836,4
2213,1	93993,7	58467	3099,34	85308,3	67843,5
2231,25	94337,6	58001,3	3117,4	84906,8	67949,4
2249,34	94525,8	58157,9	3135,49	84018,2	68653,9
2267,4	94252,1	58273,5	3153,62	84942,4	68047,9
2285,52	93748,4	58572,1	3171,65	84556,9	68748,2
2303,54	93593,5	58857,9	3189,71	83529,8	69282,4
2321,62	94066,2	58667,1	3207,82	84041,9	68912,7
2339,66	92982,7	59756,2	3225,84	84066,5	69059,1
2357,74	92409,2	60398,4	3243,91	83677,7	69284,9
2375,87	92230,2	60667,7	3262	83633,1	69493,3
2393,85	92996,8	59708,7	3280,12	82926,1	69784,3
2411,93	92596,7	60418,3	3298,15	83445,2	69899,9
2430,05	92014,7	60538,2	3316,25	83035	69615,5
2448,12	92177,3	60852,2	3334,32	82762,1	70377,8
2466,21	91722,1	60749,7	3352,38	82714,2	70207,7
2484,29	91490,2	61548,9	3370,47	82469	70501,3
2502,42	91429,1	61446,2	3388,53	82317,4	71300,2
2520,51	91022,4	61449,7	3406,55	82183,8	70755,8
2538,59	90141,6	62451,9	3424,63	81672	71047,4
2556,69	91001,9	61957,8	3442,67	81873,9	71198,7
2574,77	90411	62054,5	3460,76	81686,6	71504,8
2592,91	90224,2	61671	3478,85	82340,6	70727,7
2611,01	89497	63546,1	3497,01	82028,8	71186,1
2629,1	89903,6	63145,3	3515,07	80541,5	72147,4
2647,22	89599,2	63190,3	3533,2	80896,7	72340,1
2665,33	89607,2	63542,9	3551,27	81135,4	71627
2683,48	89464,8	63852,6	3569,3	80694,2	72087,9
2701,51	89098	63568,5	3587,46	80193,4	72255,3
2719,65	88965,5	64129,9	3605,48	80392,4	72352,3

Time (s)	Integral (MeOH)	Integral(PhIC)	Time (s)	Integral (MeOH)	Integral(PhIC)
3641,61	80532,1	72171,1	4600,31	72441,4	77504,6
3659,79	80042,2	73001,4	4618,41	72997,5	79898,3
3677,92	79168,8	73344,9	4636,41	72410,2	80651,5
3695,91	79850,4	73188,3	4654,52	72601	80428,6
3713,99	79522,4	73595	4672,64	72748,9	80311,7
3732	78870,4	74011,7	4690,79	72160,7	80761,3
3750,13	78879,8	74256,3	4708,85	72936,3	80087,9
3768,2	79312,3	73613,3			
3786,35	79034,3	73912,5			
3804,41	78852,8	74422,2			
3822,54	78746,1	74211,3			
3840,59	78873,8	74174,6			
3858,67	78479,6	74719,1			
3876,8	78683,4	74487,8			
3894,85	77971,1	75056,6			
3912,95	78102,3	75214,1			
3930,96	78261,2	74737,9			
3949,03	77702,3	75381,5			
3967,14	77576,2	75674,9			
3985,28	76790,9	76299,1			
4003,39	77408,2	75850			
4021,51	77041,5	76110,4			
4039,55	77658,2	75500,4			
4057,66	76942,7	76028,8			
4075,73	77034,4	76140,9			
4093,75	76027,3	77067,5			
4111,88	76834,6	76264,8			
4129,97	76436,8	76260,6			
4148,07	76452,6	76585			
4166,19	75907,3	77261,8			
4184,2	76580,5	76348			
4202,25	75779,2	77239			
4220,34	76418,5	76722,6			
4239,39	75738,2	77566			
4257,44	75601,6	77443,4			
4329,06	75417,5	77833,1			
4347,07	75260,4	78401,8			
4365,14	74646,3	78533,5			
4383,27	74467,3	78520,9			
4401,4	74109,5	79201,3			
4419,51	73955	79058,5			
4437,57	73831,4	79183			
4455,66	73958,8	79073,8			
4473,79	73869,2	79338,2			
4491,89	73970,2	79192,4			
4509,99	73900,7	79570			
4528,03	73661,8	79217			
4546,11	73534,9	79633			
4564,19	73206,1	79658,6			

6.4 List of abbreviations

Abbreviation	Designation
°C	Degree celcius
DBTDA	Dibutyltin diacetate
DBTDL	Dibutyltin dilaurate
E	Ge or Sn atom
Et	Ethyl group
LAH	Lithium aluminium hydride
LDA	Lithiumdiisoproyl amine
M	Li, Na or K atom
M	mol per litere (e.g. 3M = 3 mol/L)
min	Minutes
Ph	Phenyl group
ppm	Parts per million
s	Seconds
THF	Tetrahydrofuran
μm	Micrometre

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