



Preparation and Characterization of Organogermanes, Linear and Branched Oligogermanes

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Abstract

Recent investigations show that organo-, oligo- and polygermanes are becoming of great interest, due to their special characteristics, such as absorption in the UV region, luminescence, conductivity or thermochroism. Moreover those compounds provide interesting optical and electrochemical properties, making materials containing germanium compounds interesting for medical, biological and industrial applications. In our working group fascinating silicon, tin, phosphorus and antimony compounds were synthesized and investigated; not only for research purposes, but also towards potential use in industrial applications. Hence it was nearly inevitable to not extend our focus to the higher group 14 analogue germanium.

Oligo- and Polysilanes have been studied in a great extent and are used widely due to their material properties. Although showing many similarities to the chemistry of silicon, the analogy between silanes and germanes has been overemphasized. Germanium derivatives have not been investigated to this extent, because of difficult and cost intensive preparation of educts, wherefore the scope of this work was to get deeper insight into germanium chemistry and gain more experience, as well as give insights into preparation and characterization of organogermanes and oligogermanes.

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1. Acknowledgment

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2. Literature

In recent time the interest in organometallic chemistry of germanium has increased and has been intensely investigated. Up to the middle of the 20th century organogermanium compounds were the least understood among all of the silicon group elements. Et₄Ge, the first organogermanium compounds, was synthesized in 1887 by Winkler by reacting tetrachlorogermane and diethylzinc.¹ From that point up to 1925 no new organogermanium compound was reported, due to high prices and scarcity. Therefore, the chemistry of organogermanium compounds started to develop in the second quarter of the 20th century, when new sources of germanium were found and finally flourished in the sixties, when new chemists joined the field due to very interesting results concerning silicon and tin derivatives. Organogermanium compounds were considered as potential candidates for electronics and medical applications due to their biological activities. Germanium metal is nowadays used in semiconductors and has other industrial application, for example as an alloying agent. Certain germanium compounds have low mammalian toxicity, but marked activity against bacteria, so their use as antibacterial agents has been considered. Germanium is often regarded as being nearly identical to its lighter homologue silicon, although the band gap, electron and hole mobility and conductivity are higher in bulk elemental germanium. Organogermanium compounds have been thoroughly investigated, however are not yet widely used as intermediates or reagents in organic synthesis. For the reasons listed above, it is highly probable though, that germanium will play a more important role in the future.

Application of Grignard reagents in organometallic synthesis led to the synthesis of common aliphatic, aromatic and alicyclic germanium derivatives. Dennis and Hance were the first to produce tetralkylgermanes, namely methyl-, ethyl, propyl- and butyl derivatives back in 1925.² In 1925 Morgan, Dugald and Drew, and later Kraus and Foster, synthesized tetraphenylgermane, the first compound having an aryl- germanium bond, from GeCl₄ and PhMgBr.^{3,4}

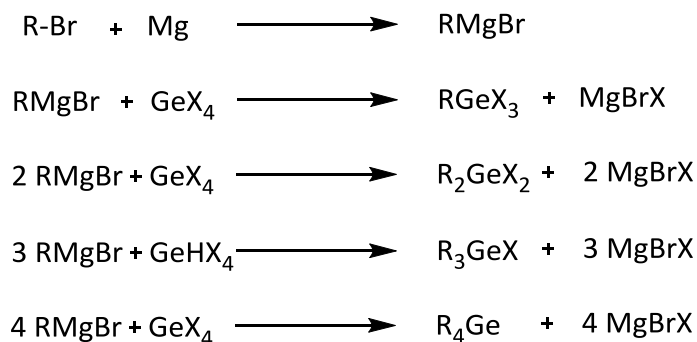


Fig. 1 Scheme Grignard reactions

The chemistry of organogermanium halides has been well established for years. Organogermanium halides have found to be helpful synthetic intermediates for the preparation of other organogermanium compounds and additionally show good thermal stability, though tend to hydrolyze easily, which demands rigorous exclusion from water. A very wide range of preparative methods is known, starting from germanium metal, other halides, alkyl- and aryl compounds, or hydrides.

Although Grignard reagents and lithium reagents have widespread use in chemistry, they are not very successful for the synthesis of organogermanium halides. Such reactions usually result in a mixture of products with mono-, di- or trihalides present, regardless of the stoichiometry. Even with an excess of Grignard or organolithium reagent, yields in excess of 80% are rare. However, lithium or magnesium reagents are recommended for introducing alkyl groups in the synthesis of very sterically- hindered molecules.^{5,6}

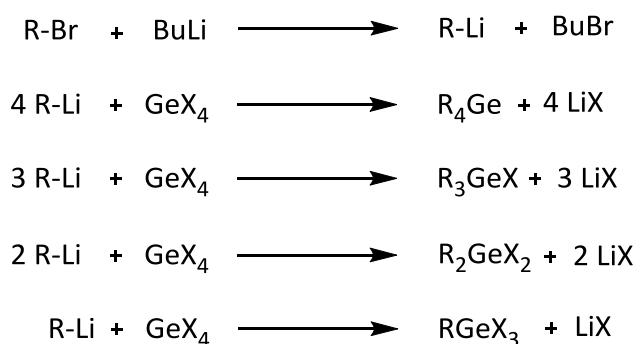


Fig. 2 Scheme organolithium reactions

Clearly, the reaction is more complex than shown in Fig. 1 and Fig. 2, being even more obvious when introducing sterically hindered ligands. A further complication is the occurrence of

halogen-metal exchange, when using educts with different halogens. Preparation of organogermanes is also known using palladium(0) mediated coupling, Barbier type reactions, insertion of dichlorogermylene. Many other alkylmetals have been used with success, notably alkylstannanes and- plumbanes, both methods giving high yields in simple procedures. The application of alkylmercury compounds is potentially useful for these preparations, however have been rarely used in practice. Substitution of the halogen in a trialkylhalogermane by a more negatively charged halogen has been used for synthesizing fluoride and chloride compounds.^{5,6,7,8}

The reaction of a halide with an organometallic reagent may be a convenient route to organogermanium halides, but better yields and control are often provided if an alkyl- or arylgermane is treated with a halogen or halogenating agent. Additionally, these starting materials have better solubility and are often easier to handle. Brominations or iodinations with bromine or iodine are commonly used, but chlorine is less convenient and chloroorganogermanes are more readily prepared from germanium(IV)chloride. When germanium tetrachloride is used, successive replacement of halogen by R groups occurs, but the reaction is difficult to control and intermediate stages of the types $RGeCl_3$, R_2GeCl_2 and R_3GeCl are very challenging to separate.

In general aryl groups are substituted by halogens more readily than alkyl ligands. Organogermanium halides can further be prepared in good yield by the halogenation of an organogermanium hydride, as the Ge-H bond is more vulnerable to substitution than a Ge-C bond. This represents a convenient route if the hydride is accessed easily. In principle, the reaction of an alkyl- or arylgermane with a germanium halide using the right stoichiometry should give the desired organogermanium halide, as it is known for analogue tin compounds.

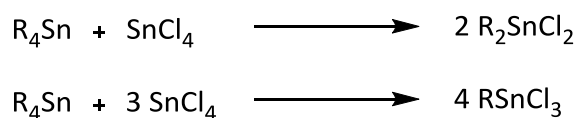


Fig. 3 Kocheshkov redistribution of tetraalkyl- or tetraaryl tin compounds with tin tetrachloride⁹

However for germanium, in practice equilibria are often set up and again a mixture of products is formed, from which it is hard to separate the desired product. Additionally those reactions require high temperatures or usage of catalyst. Reactions involving arylgermanes usually need

higher temperatures than reactions with alkylgermanes, while the latter benefit of the usage of catalysts. In few cases, with careful control of the reaction, it may be possible to obtain a quantitative yield. Separation can be achieved by using liquid chromatography or by conversion into germyl ethers, which can be separated more easily and then be reconverted into organogermanium halides.

Voegelen et al. were able to synthesize the first hydrogen compound of germanium in 1902 by reacting zinc with germanium in the presence of sulfuric acid.¹⁰ Since then the chemistry of the Ge-H bond has developed with the preparation of various germanium hydrides. It is widely accepted that the electronegativity of germanium is slightly higher than that of silicon and closest in magnitude to that of hydrogen. So in the Ge-C bond, the positive charge is on the metal. The generally low polarity of the Ge-H bond in alkylgermanes is often observed to reverse as alkyl groups are sequentially replaced by halides. Germanium hydrides can further be prepared using tetraalkyl- or arylgermanes, organogermyl alkali metals, digermanes, trialkyl- or triarylgermanium halides, reduction of germanium halides, substitution of halo(organo)germanium hydrides and hydrogermylation of C-C multiple bonds.

Oligo- and Polygermanes

Despite the many applications of germanium in physics, its chemistry is clearly underestimated. The synthesis of compounds containing Si-Si bonds has been studied in an extensive way, with methods providing good yields. In comparison closer look at germanium shows that only few routes are known, which are often accompanied by low yields or mixture of products. Compared to the already modest interest in the organometallic chemistry of germanium the field of oligo- and polygermanes is even more neglected, of course also because while the starting materials for oligosilane chemistry are relatively inexpensive, the materials or analogous oligogermanium chemistry are nearly unaffordable. Nevertheless, the promise of new optical and electronic properties of those compounds prompted persistent efforts in their preparation and characterization, since well-defined oligogermanes could not only be used for industrial applications, but compounds in the nanometer scale could give more insight into the photophysical properties of germanium nanostructures.¹¹

The concept of molecular wires or nanowires, compounds of group 14 elements with element-element bonds, has attracted a lot of interest in the last years, due to their possible application in molecular electronics and nanotechnologies. Nowadays the most common molecular conductors are carbon based, although oligomeric and polymeric silanes and stannanes have been explored as well. Germanium derivatives have not been studied as extensively, due to the absence of common synthetic approaches, as already mentioned before. However Ge-Ge bonds have been achieved by various methods, such as reductive coupling of dihalogermane or usage of germanium(II) complexes or halogermanes, but again the problem exists in generating mixture of products and low yields. The Ge-Ge single bond is considered to be stable, but weaker than the C-C or Si-Si bond. Most known oligogermanes are bearing electron donor groups, since oligogermanes bearing electron-withdrawing ligands are unstable and tend to decompose.^{12 13}

The most interesting feature of heavier group 14 analogues is their so called σ -conjugation. The effective overlap of hybridized atomic orbitals of the elements next to each other leads to the sharing of electron density along the chain. In detail, the pair of electrons in the HOMO is delocalized across the germanium-germanium backbone, making $\sigma \rightarrow \sigma^*$ electronic transitions possible, which then results in broad but distinct absorbance peaks in UV/VIS spectra and shifts of λ_{\max} to lower energy. The energy of the HOMO-LUMO gap in these compounds decreases with an increase in the number of catenated germanium atoms. Through investigations using digermanes and changing substituents it was shown, that by introduction of more inductively donating organic substituents the HOMO gets destabilized, which makes the molecule easier to oxidize. Additionally σ -delocalization leads to properties normally known for unsaturated hydrocarbons, such as absorption in the UV region, luminescence, conductivity, thermochroism as well as optical and electrochemical properties. Those properties highly depend on the nature of the substituents and the chain length.¹⁴

Oligogermanes are also electrochemically active, cyclic voltammetry and differential pulse voltammetry have shown to be useful instruments for investigating this behavior. Germanium polymers show non-linear optical properties, fluorescence and semiconductive behavior too. Those properties are even more evident than in their silicon analogues due to the smaller band gap and higher electron and hole mobility in germanium.

The first linear hexagermane $\text{Pr}^i_3\text{Ge}(\text{GePh}_2)_4\text{GePr}^i_3$ was obtained starting with the cyclic compound $\text{Ge}_4\text{Ph}_{12}$, followed by a cleavage using bromide in benzene. The $\text{Br}(\text{GePh}_2)_4\text{Br}$ chain

was then converted into the hydrate using lithiumaluminumhydride in ether. By treating the 1,4- dihydride with two equivalents of $\text{Pri}_3\text{GeNMe}_2$ in acetonitrile, this reaction is also known as a hydrogermolysis reaction, the hexagermane was obtained. According to Weinert et al. the hydrogermolysis reaction is the key step in forming Ge-Ge bonds. The organogermanes can then be converted to the corresponding chlorides and subsequently to the amides by salt metathesis with LiNMe_2 . Acetonitrile is used not only as a solvent, but also as a key synthetic reagent, because it converts the germanium amide educt R_3GeNMe_2 into the more reactive species α -germyl nitrile $\text{R}_3\text{GeCH}_2\text{CN}$.¹⁵ Germanium atoms can then be added to the chain one at a time, making use of a hydrogen protection/ deprotection strategy.

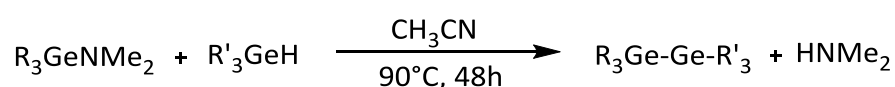


Fig. 4 Scheme hydrogermolysis¹⁶

$\text{Pr}'_3\text{Ge}(\text{GePh}_2)_4\text{GePr}'_3$ contains four central trans-coplanar germanium atoms and two terminal germanium atoms out of the plane. σ - delocalization across all 6 Ge- atoms is possible, seen also in its UV/VIS spectrum, as the λ_{max} is red shifted from those of other oligogermanes. Interestingly it can be considered to be an effective small- molecule model for larger polygermane systems because fluorescence emission is known for polygermanes, however before it was not found for oligogermanes yet. Moreover this compound shows dichroic behavior when viewed under plane- polarized light, being caused by the arrangement of the terminal germanium atoms.¹⁷ This can be considered as a validation of the assumption that discrete linear oligogermanes with enough germanium atoms might exhibit similar properties as do the polymers. Karlov et al. also used the hydrogermolysis reaction developed by the Weinert group instead of the commonly used nucleophilic substitution for the synthesis of unsymmetrical donar- acceptor oligogermanes.¹²

The Weinert group was not only able to synthesize various novel oligogermanes, but were also able to synthesize and characterize several branched organogermanes.^{18,19,20} The first organogermane, namely $(\text{Ph}_3\text{Ge})_3\text{GeH}$ and $(\text{Ph}_3\text{Ge})_3\text{GeMe}$ were synthesized in 1963 by Glockling and Hooton.²¹ Nevertheless the Weinert group were the first to structurally characterize the branched oligogermane, $(\text{Ph}_3\text{Ge})_3\text{GePh}$. Branched oligogermanes can be of usage for preparation of higher branched oligogermanes.

For oligogermanes bearing a halide atom a red shift in the absorbance maximum in the UV/Vis spectra is expected with decreasing electronegativity, since it could have been shown that more inductively electron donating groups lead to a destabilization of the HOMO in those oligogermane systems.²²

Brook et al. were able to introduce the tris(trimethylsilyl)germyl moiety and the group of Marschner et al. was later on able to synthesize $(\text{Me}_3\text{Si})_3\text{GeK}$, which shows potential for using it as single- source precursors for the synthesis of germanium nanowires containing a crystalline germanium core with a silicon oxide shell.^{15,23} In addition they were able to find an easy access to tetrakis(trimethylgermyl)germane, hexakis(trimethylgermyl)digermane and the corresponding potassium compounds.

3. Experimental

General considerations

All reactions were carried out under a nitrogen atmosphere using standard Schlenk, syringe and glovebox techniques. The reagents germane, isopropyl lithium, triphenylgermane, diphenyldichlorogermane and triphenylchlorogermane were purchased from Gelest, Inc. and were used as received. The reagents lithium dimethylamid, ^tbutyllithium and bromide were purchased from Sigma Aldrich and used as received. The reagents tetraethoxygermane, germanium dioxide, lithium aluminum hydride, magnesium, 1-bromonaphthalene, 2-bromo-p-xylene and 2-bromo-m-xylene were purchased from ABCR and used as received. The reagents potassium methoxide, hydroquinone, 1,3- butanediol and hydrochloric acid in ether were purchased from VWR and used as received. Tetrahydrofuran, ether, dichloromethane, toluene, acetonitrile and benzene were purchased from VWR and purified using a Glass Contour solvent purification system.

Unless otherwise noted ¹H and ¹³C NMR spectra were recorded using an INOVA Gemini 2000 spectrometer.

Preparation of K₂[(C₄H₆O₂)₃Ge]

2.09 g [0.02 mol] of GeO₂ were suspended in previously degassed MeOH and added slowly via syringe to a solution of 2.80 g [0.04 mol] MeOK in MeOH. A solution of 5.4 ml [0.06 mol] of 2,3-butanediol in MeOH were added slowly after 15 minutes and the cloudy solution was stirred for 1.5h. After removal of solvent and washing with Et₂O an off-white powder was obtained (90%). ¹H NMR was recorded on a Mercury 300 MHz spectrometer from Varian.

¹H NMR (CD₃OD, 25°C, 300MHz): δ 3.54 (m, 2H), 1.13 (d, 6H) ppm

Preparation of K₂[(C₆H₄O₂)₃Ge]

To a solution of 2.44 g [0.006 mol] of K₂[(C₄H₆O₂)₃Ge] in previously degassed MeOH, C₆H₆O₂ [1.97g, 0.018 mol] in MeOH was added dropwise. The cloudy, slightly pink solution was heated and kept at reflux for 2 hrs. After removal of solvent and washing with Et₂O 2.61 g [92%] of product was obtained. ¹H NMR was recorded on a Mercury 300 MHz spectrometer from Varian.

¹H NMR (CD₃OD, 25°C, 300MHz): δ 6.54-6.32 (m, 4H) ppm

Preparation of ${}^i\text{Pr}_3\text{GeCl}$

To a solution of ${}^i\text{PrLi}$ (15.8 g, 0.018 mol) in hexane, $\text{Ge}(\text{OEt})_4$ [1.8 g, 0.007 mol] was added dropwise, yielding an orange, polymeric liquid. After stirring at room temperature for 2 hours, 2M ethereal HCl was added dropwise until no white precipitate was crashing out anymore. The solution was filtered over Celite, washed with hexane and the solvent was removed, yielding an orange, oily liquid (m= 1.02 g, 64.5%).

${}^1\text{H}$ NMR (C_6D_6 , 25°C, 400MHz): δ 1.41 (m, J=7.6Hz, 1H); 1.10 (d, 18H) ppm

${}^{13}\text{C}$ NMR (C_6D_6 , 25°C, 125.7MHz): δ 19.21 (CHCH₃), 17.67 (CHCH₃) ppm

Preparation of ${}^i\text{Pr}_3\text{GeN}(\text{CH}_3)_2$

0.16 g [0.007 mol] $\text{LiN}(\text{CH}_3)_2$ were added dropwise to a solution of 0.3 g [0.001 mol] ${}^i\text{Pr}_3\text{GeCl}$ dissolved in benzene, yielding a cloudy, orange liquid. After stirring at room temperature overnight, the liquid was filtered over Celite, washed with hexane and the solvent was removed, yielding 0.15 g (48 %) of ${}^i\text{Pr}_3\text{GeN}(\text{CH}_3)_2$.

${}^1\text{H}$ NMR (C_6D_6 , 25°C, 400MHz): δ 2.65 (s, 6H), 1.41 (m, J = 7.6 Hz, 3H), 1.10 (d, J = 7.6 Hz, 18H) ppm
 ${}^{13}\text{C}$ NMR (C_6D_6 , 25°C, 125.7MHz): δ 42.14 (–N(CH₃)₂), 19.58 (CH₃CHCH₃), 15.6 (CH₃CHCH₃) ppm

Preparation of ${}^i\text{Pr}_3\text{GeGePh}_3$

0.1g [0.0004 mol] of ${}^i\text{Pr}_3\text{GeN}(\text{CH}_3)_2$ and 0.13 g [0.0004 mol] Ph_3GeH were added to a Schlenk tube and dissolved in acetonitrile. The Schlenktube was closed and put into an oil bath for 48 hrs at 90°C. After removal of solvent, the solid was distilled under vacuum, yielding 0.15 g (75 %) of the desired compound.

${}^1\text{H}$ NMR (C_6D_6 , 25°C, 400MHz): δ 7.72–7.68 (m, 6H), 7.20–7.15 (m, 9H), 1.67 (m, J = 7.6 Hz, 3H), 1.18 (d, J = 7.5 Hz, 18H) ppm

${}^{13}\text{C}$ NMR (C_6D_6 , 25°C, 125.7MHz): δ 139.8 (ipso-C), 135.9 (ortho-C), 128.6 (meta-C), 128.5 (para-C), 21.3 (CH₃CHCH₃), 16.8 (CH₃CHCH₃) ppm

Treatment of ${}^i\text{Pr}_3\text{GeGePh}_3$ with $\text{CF}_3\text{SO}_3\text{H}$

A solution of $\text{CF}_3\text{SO}_3\text{H}$ in acetonitrile was added dropwise to a solution of 0.2 g [0.0003 mol] of ${}^i\text{Pr}_3\text{GeGePh}_3$ in acetonitrile and stirred at room temperature for 1 hr. After removal of solvent a light yellow solid was obtained, yielding a mixture of products.

${}^{19}\text{F}$ NMR (C_6D_6 , 25°C, 376.4MHz): δ 76.89 (s), -77.05 (s), -77.32 (s) ppm

Preparation of Ph₂GeH₂

10.01 g [0.034 mol] of Ph₂GeCl₂ were dissolved in Et₂O and LiAlH₄ [3.19 g, 0.084 mol] were added in small portions in the glovebox. The mixture was stirred at room temperature for 2 hrs, quenched dropwise with H₂O and filtered over Celite. After drying over MgSO₄, filtration and removal of solvent a colorless liquid was obtained [5.62 g, 73%]

¹H NMR (C₆D₆, 25°C, 400MHz): δ 7.48–7.15 (m, 10 H), 5.20 (s, Ge-H) ppm

¹³C NMR (C₆D₆, 25°C, 125.7MHz): δ 135.49 (ortho C), 134.20 (ipso C), 129.30 (para C), 128.66 (meta C) ppm

Preparation of H(GePh₂)₃H

A solution of 2.5 g [0.011 mol] of Ph₂GeH₂ in 8 ml Et₃N was cooled to -40°C. 7.68 ml [0.013 mol] ^tBuLi (1.7 M in hexane) was added dropwise. After stirring at -40°C for 15 minutes the yellow solution was allowed to warm to room temperature and stirred for additional 9.5 hrs. After quenching with H₂O and drying over MgSO₄ the solution was filtered over Celite, washed with hexane and the solvent removed, yielding a colorless oil, which was further recrystallized in toluene (0.25g, %)

¹H NMR (C₆D₆, 25°C, 400MHz): δ 7.59 (m, 4H, ortho C), 7.44 (m, 8H, ortho C), 7.03 (m, 18H, meta C and p-C₆H₅), 5.68 (s, 2H, GeH) ppm

¹³C NMR (C₆D₆, 25°C, 125.7MHz): δ 136.20 (C₆H₅ ipso), 135.99 (C₆H₅ ipso), 135.77 (ortho C), 135.75 (ortho C), 129.09 (meta C or para C), 129.05 (para C), 128.76 (meta C or para C), 128.64 (meta C) ppm

Preparation of ⁱPr₃Ge(GePh₂)₃GeⁱPr₃

0.25 g (0.00037mol) H(GePh₂)₃H and 0.18 (0.00074 mol) Pr₃GeNMe₂ were dissolved in acetonitrile and combined in a Schlenk tube. The Schlenktube was sealed and stirred at 90°C for 48 hours. After removal of solvent a colorless oil was obtained (0.1 g, 25 %).

Preparation of (Ph₂Ge)₄

9.34 g [0.031 mol] Ph₂GeCl₂ was dissolved in 20 ml toluene and added slowly over 35 minutes to a boiling suspension of 2.35 g [0.102 mol] of Na pieces in toluene. The reaction was kept at reflux for 1 hr, and filtered of over Celite. The product was allowed to crystallize out at room temperature. The yellow liquid was decanted via canula and the colorless crystals were dried under vacuo and recrystallized in toluene at 4°C.

^1H NMR (CDCl_3 , 25°C , 400MHz): δ 7.28 – 7.10 (m, 30 H, C_6H_5), 5.30 (s, 2H, Ge-H) ppm

^{13}C NMR (CDCl_3 , 25°C , 125.7MHz): δ 136.11 (C_6H_5 ipso), 135.57 (C_6H_5 ipso), 132.23 (ortho C), 131.32 (ortho C), 128.54 (para C), 127.80 (para C), 127.52 (meta C) 127.31 (meta C) ppm

Preparation of Br-(Ph₂Ge)₄-Br

Br_2 was dissolved in benzene and slowly added to a solution of $(\text{GePh}_2)_4$ [0.62 g, 0.0007 mol] in 20 ml of benzene until the orange color was persistent. After removal of solvent a colorless precipitate (0.54 g, 75%) was obtained.

^1H NMR (C_6D_6 , 25°C , 400MHz): δ 7.60 (d, $J = 7.6$ Hz, 8 H, ortho C), 7.41 (d, $J = 7.6$ Hz, 8H, ortho C), 7.06-6.90 (m, 24H, meta C and p- C_6H_5) ppm

^{13}C NMR (C_6D_6 , 25°C , 125.7MHz): δ 136.82 (C_6H_5 ipso), 134.77 (C_6H_5 ipso), 129.98 (ortho C), 129.45 (ortho C), 128.79 (meta C), 128.67 (meta C) 128.1 (para C), 127.9 (para C) ppm

Preparation of H-(GePh₂)₄-H

A solution of 0.54 g [0.0005 mol] of $\text{Br}(\text{GePh}_2)_4\text{Br}$ was treated with 0.042 g [0.0011] LiAlH_4 in Et_2O . The mixture was stirred at room temperature overnight. After removal of solvent the product was obtained as a colorless solid (0.35 g, 79 %)

^1H NMR (C_6D_6 , 25°C , 400MHz): δ 7.50 (d, $J = 7.2$ Hz, 8 H, ortho C), 7.37 (d, $J = 6.8$ Hz, 8H, ortho C), 7.05-6.96 (m, 24H, meta C and p- C_6H_5), 5.62 (s, 2H, Ge-H) ppm

^{13}C NMR (C_6D_6 , 25°C , 125.7MHz): δ 136.5 (C_6H_5 ipso), 136.0 (C_6H_5 ipso), 128.9 (ortho C), 128.8 (ortho C), 128.5 (meta C), 128.67 (meta C) 128.1 (para C), 127.7 (para C) ppm.

Preparation of Ph₃GeN(CH₃)₂

0.36 g [0.007 mol] $\text{LiN}(\text{CH}_3)_2$ were added dropwise to a solution of 2 g [0.006 mol] Ph_3GeCl dissolved in benzene, yielding a cloudy, orange liquid. After stirring at room temperature overnight, the liquid was filtered over Celite, washed with hexane and the solvent was removed, yielding 1.02 g (49 %) of $\text{Ph}_3\text{GeN}(\text{CH}_3)_2$.

^1H NMR (C_6D_6 , 25°C , 400MHz): δ 7.65 (t, 18H, m- C_6H_5), 7.24 (d, $J = 7.5$ Hz, 18H, o- C_6H_5), 6.93 (t, $J = 7.2$ Hz, 9H, p- C_6H_5), 2.71 (s, 6H, - $\text{N}(\text{CH}_3)_2$) ppm

^{13}C NMR (C_6D_6 , 25°C , 125.7MHz): δ 138.3 (ipso-C), 135.5 (o-C), 129.7 (p-C), 127.7 (m-C) ppm

Reaction of Ph₃GeNMe₂ with GeH₄ to prepare HGe(GePh₃)₃

0.037 g [0.0005 mol] of GeH₄ was condensed using an U-shaped device in liquid nitrogen and 0.037 g then added to 0.51 g [0.0015 mol] Ph₃GeN(CH₃)₂ dissolved in acetonitrile. The Schlenk was sealed and allowed to warm to room temperature, before stirring it at room temperature overnight. It was then stirred another 72 hrs at 90°C. After removal of solvent 0.2 g (41 %) of product were obtained, which were then tried to recrystallize under superheated conditions.

¹H NMR (C₆D₆, 25°C, 400MHz): δ 7.26 (d, J= 8.1 Hz, 18H, o-H ((C₆H₅)₃Ge)₃Ge(C₆H₅)), 7.15–6.92 (m, 27H, m-H and p-H), 5.85 (s, 1H, Ge-H) ppm

¹³C NMR (C₆D₆, 25°C, 125.7MHz): δ 136.5(ipso-C), 128.8 (o-C), 128.6 (p-C), 127.5 (m-C) ppm

Preparation of [C₁₀H₇]₃GeH

A solution of 1- naphthylbromide [3.91 g, 0.02 mol] in dry THF was added dropwise to 0.5 g [0.021 mol] Mg fillings in THF in order to produce the Grignard reagent. The Grignard reagent was filtered, titrated and added dropwise to a suspension of K₂[(C₆H₄O₂)₃Ge] [2 g, 0.004 mol] in THF. After stirring overnight the mixture was treated with 0.4 g [0.011 mol] LiAlH₄ and stirred for 12 hours before quenching with 10% H₂SO₄. After filtration over Celite the liquid was tried over MgSO₄ and filtered over Celite again. After removal of solvent off- white powder was obtained [0.62 g, 32.6 %] and recrystallized in dichloromethane.

¹H NMR (C₆D₆, 25°C, 400MHz): δ 7.64-7.24 (m, 10H), 6.35 (s, 1H, Ge-H) ppm

Preparation of [m-C₆H₃]₃GeH

A solution of m- xylylbromide [1.516 g, 0.008 mol] in dry THF was added dropwise to 0.22 g [0.009 mol] Mg fillings in THF in order to produce the Grignard reagent. The Grignard reagent was filtered, titrated and added dropwise to a suspension of K₂[(C₆H₄O₂)₃Ge] [1.29 g, 0.003 mol] in THF. After stirring overnight the mixture was treated with 0.26 g [0.007 mol] LiAlH₄ and stirred for 12 hours before quenching with 10% H₂SO₄. After filtration over Celite the liquid was tried over MgSO₄ and filtered over Celite again. After removal of solvent off- white powder was obtained [0.29 g, 27 %].

Preparation of [p-C₆H₉]₃GeH

A solution of p-xylylbromide [1.38 g, 0.008 mol] in dry THF was added dropwise to 0.21 g [0.009 mol] Mg filings in THF in order to produce the Grignard reagent. The Grignard reagent was filtered, titrated and added dropwise to a suspension of K₂[(C₆H₄O₂)₃Ge] [0.8 g, 0.002 mol] in THF. After stirring overnight the mixture was treated with 0.4 g [0.006 mol] LiAlH₄ and stirred for 12 hours before quenching with 10% H₂SO₄. After filtration over Celite the liquid was dried over MgSO₄ and filtered over Celite again. After removal of solvent off-white powder was obtained [0.3 g, 40 %] and recrystallized in dichloromethane.

4. Results, Discussion and Outlook

One big goal of this work was to gather more insight and experience in the field of organogermanium compounds. The working group of Weinert has extensive knowledge with germanium chemistry and the synthesis of the same. Our working group at the Technical University of Graz was not experienced with the synthesis of germanium compounds, since no conclusions can be drawn from the already established silicon, tin, phosphorus or antimony chemistry. Therefore one big goal was to learn new methods and ways of preparation, work up and characterization, supported by the knowledge of experienced scientists from the Weinert group.

As already mentioned before preparation of organogermanes is very difficult due to low yields, high cost of educts and mixture of products. A route that never really got widespread application in chemical society was the preparation of tetraorganogermanes and triorganogermanes in two steps starting from GeO_2 by preparing a hexacoordinated germanium complex and further reaction with Grignard reagents. Corriu et al. reported the hypervalent germanium complex in 1988 and also investigated the reactions of those complexes with organometallic derivatives.²⁴ This provides an alternative route for organometallic compounds, normally synthesized using GeCl_4 . The reactivity of these complexes depends on the cation, so the lithium complex for example is less reactive than the sodium or potassium complex.

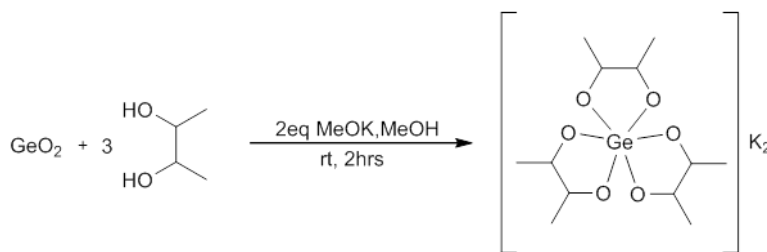
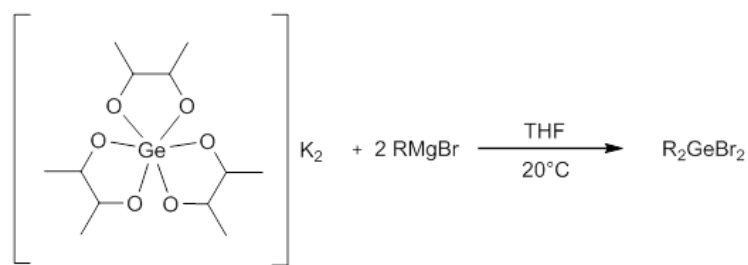


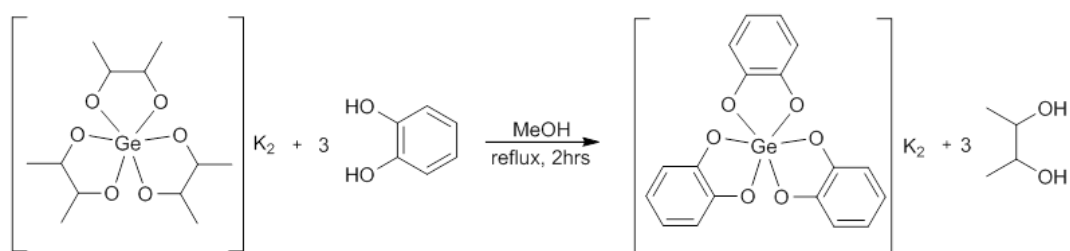
Fig. 5 Preparation of $\text{K}_2[(\text{C}_4\text{H}_6\text{O}_2)_3\text{Ge}]$

Fig. 6 Reaction of $K_2[(C_4H_6O_2)_3Ge]$ with Grignard reagents

We tried using the $K_2[(C_4H_6O_2)_3Ge]$ complex for preparing aryl substituted organogermanes, however the desired products were not formed. For that reason we decided to prepare $K_2[(C_6H_4O_2)_3Ge]$ as a precursor for the desired products. The first one to prepare the complex were Bevilard et al. in 1954 by reacting catechol and germanium dioxide in an aqueous solution.²⁵

Corriu prepared those complexes by reacting germanium dioxide with catechol in the presence of either MeOLi or MeOK, using methanol as the solvent and refluxing it for 3 days. Another route is the preparation of $K_2[(C_4H_6O_2)_3Ge]$ by reacting 2,3-butanediol with potassium methoxide in methanol as well, which provides the big advantage of shortening the reaction time to two hours. This complex can then be converted into $K_2[(C_6H_4O_2)_3Ge]$ by reacting it with catechol and an additional two hours of reflux. Those complexes are white, airstable powders.²⁶

Both complexes are known to react easily with Grignard and lithium reagents, showing more activity than its silicon analogue. Reactions with the Grignard reagents at room temperature in ether lead to the tetrasubstituted organogermanium compounds.

Fig. 7 Preparation of $K_2[(C_6H_4O_2)_3Ge]$

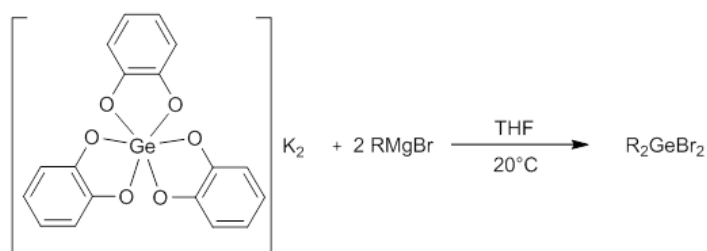


Fig. 8 Reaction of $\text{K}_2[(\text{C}_6\text{H}_4\text{O}_2)_3\text{Ge}]$ with Grignard reagents

For the reaction of the $\text{K}_2[(\text{C}_6\text{H}_4\text{O}_2)_3\text{Ge}]$ complex with naphthylmagnesiumbromide the ^1H and ^{13}C NMRs indicate that the desired product Naph_3GeH was formed, showing the characteristic hydride peak at δ 6.35 ppm in the ^1H NMR, as shown in Fig. 9. There were still byproducts, but recrystallization in toluene and dichloromethane led to the target molecule. Crystals of this compound are waiting to be analyzed via X-Ray crystallography right now, in order to confirm the structure and look into inter- or intramolecular interactions for this novel compound.

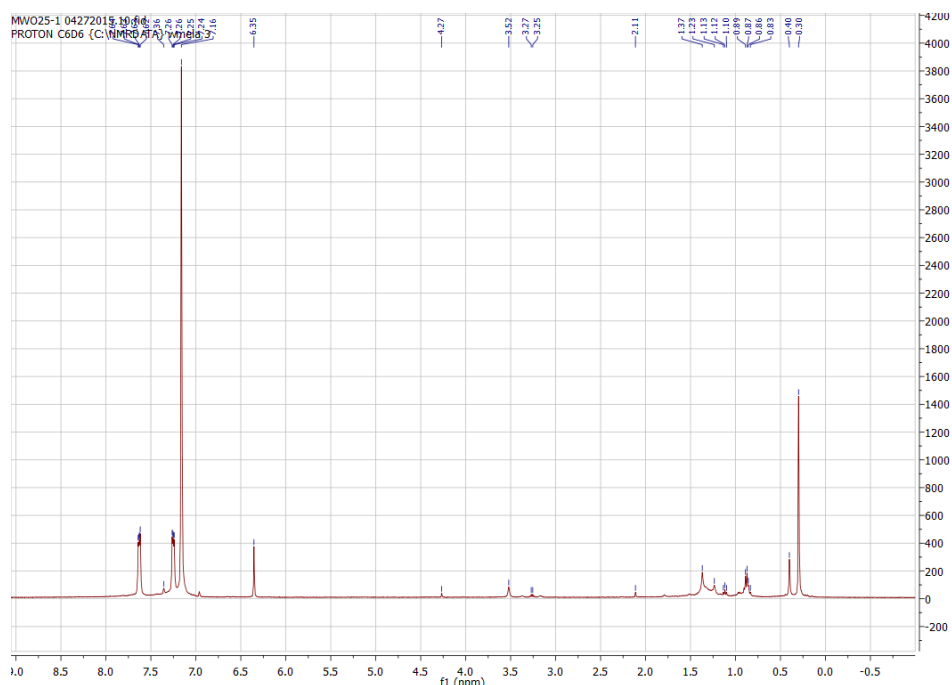


Fig. 9 ^1H NMR of $[\text{C}_{10}\text{H}_7]_3\text{GeH}$

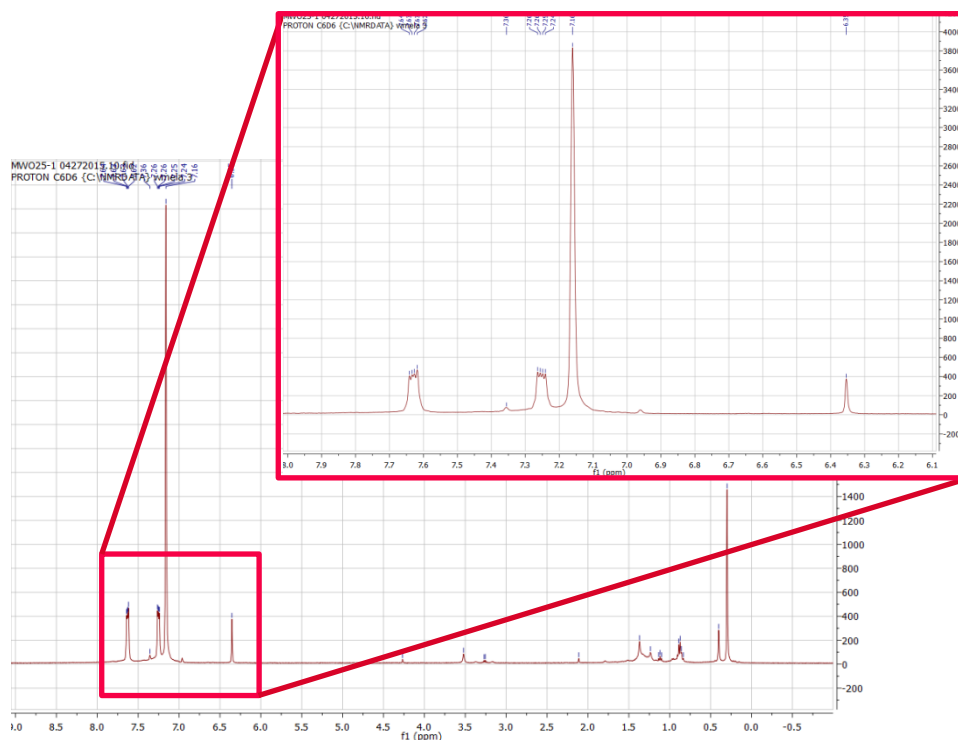


Fig. 10 ^1H NMR of $[\text{C}_{10}\text{H}_7]_3\text{GeH}$

Several reactions were carried out using different aryl substituents. However, in the case of xylene substituents no main product was formed and several byproducts were obtained. Furthermore, still starting material was present in the reaction solution. Although changing the reaction conditions, namely temperature, solvents, stoichiometry and steps, the target molecules could not be synthesized by these methods. This furthermore proves the difficulty of finding a universal applicable route to prepare organogermanes. No time was left to perform another reaction, however due to the new insights of this reaction the project will be continued both at the home university, as well as Oklahoma State University.

As mentioned in the beginning, oligogermanes are becoming of great interest, because of their unique properties and their use thereof. Although the Weinert group developed and studied the hydrogermylation reaction in an extensive way, it is limited as well. Since several of those reactions are already known in literature, they will not be further discussed within the scope of this work. Uhlig already showed 1991 that by reaction of a phenyl derivative with $\text{CF}_3\text{SO}_3\text{H}$, the trifluoromethane sulfonate of germanium was obtained, as was already known for the silicon derivatives.²⁷ Introduction of HOTf leads to electrophilic substitution of one aryl group. The triflate group can then be subsequently substituted by nucleophilic substitution, as for example chloride, in order to gain the halide compounds. In 2012 Zaitseva et al. were able to isolate

various germanium triflates.²⁸ They assumed, that because of the triflate group being a strong electron acceptor, various structural parameters may be different. When using Ph_4Ge no matter the conditions, only one phenyl group was substituted. According to Zaitsev et al. the introduction of two triflate groups to one Ge atom is impossible due to electron acceptor ability of OTf that complicates sequential electrophilic substitution. In the scope of this work, a very similar reaction was carried out when reacting $^i\text{Pr}_3\text{GeGePh}_3$ with $\text{CF}_3\text{SO}_3\text{H}$, in order to gain the desired compound $^i\text{Pr}_3\text{GeGePh}_2\text{OTf}$. However, in contrast to the previous mentioned work, we encountered similar problems as Zaitsev et al. did when examined the compound $\text{Ph}_3\text{GeGeMe}_3$; a mixture of products was formed, making a separation and identification of the products impossible. There might have been several reaction routes, leading to various products, as is confirmed by the ^{19}F NMR. For similar tin compounds, it is known that not only the phenyl group, but also the methyl groups in the presence of geometrically strained aryl groups can be substituted.²⁹

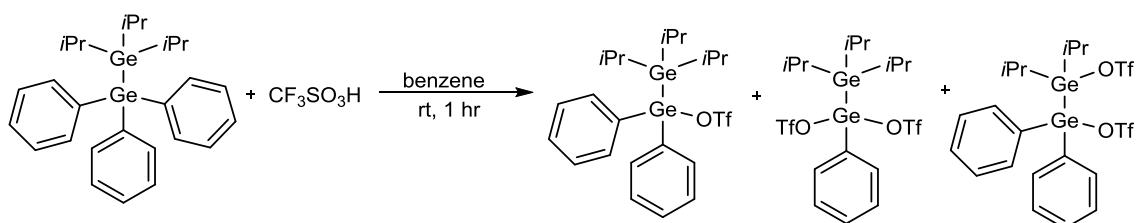


Fig. 11 Possible products when reacting $^i\text{Pr}_3\text{GeGePh}_3$ with $\text{CF}_3\text{SO}_3\text{H}$

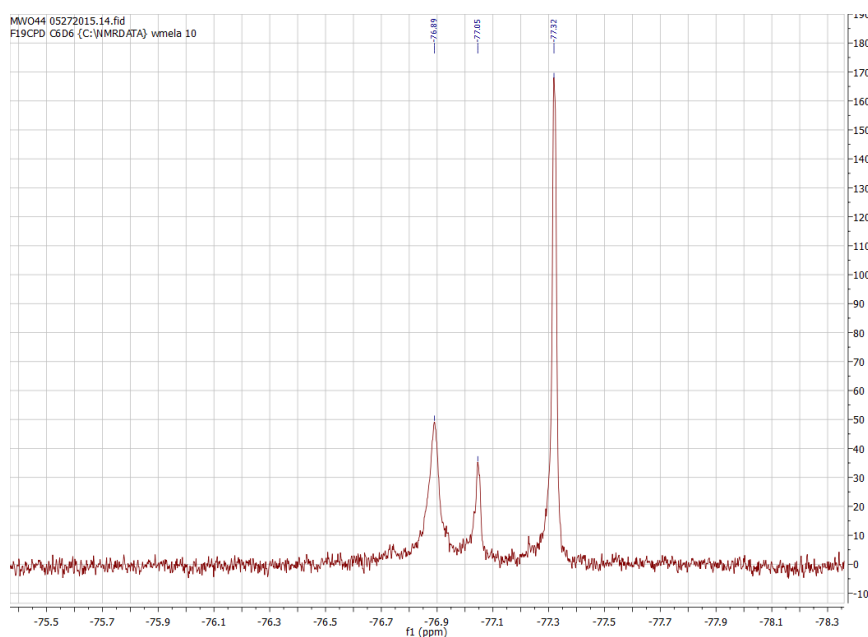


Fig. 12 ^{19}F NMR, reaction of $^i\text{Pr}_3\text{GeGePh}_3$ with $\text{CF}_3\text{SO}_3\text{H}$

Another possible method for preparing organogermanium compounds or polymers might be the usage of samarium (II) diiodide, a mild one- electron reducing reagent, as was proposed by Mochida et al. in 2005.³⁰ This reaction will be performed in the future at the home institution.

As already mentioned before, germanium has a smaller band gap, which can be even further reduced upon attaching larger-sized substituents to the side chains or applying strain, a higher electron and hole mobility and a bigger Bohr radius ($R_b=11.5$ nm), making compounds very interesting due to their unique properties.^{31,32,33} In addition germanium nanoparticles are expected to function as direct band gap materials. The critical step in the preparation of nanoparticles is always the control of size and their morphology.

Since semiconductor nanoparticles show unique size- and shape dependent electronic and optical properties they have gained interest in the past.³⁴ However the lack of simple synthetic pathways for preparing Ge nanoparticles, which mainly consist of thin film or physical methods, has made using germanium nanoparticles in a larger set up difficult, although being reasonable cheap and providing easy scale-up options. Additionally, high temperatures or strong reducing agents are normally required, entailing problems with either contamination and difficult work up or high energy uptake. Delpech et al. could show that the conditions required for preparing nanoparticles are highly dependent on the nature of the ligand used, giving more insight into the chemistry of main group metal nanoparticles and possible leading to future low temperature thermolysis pathways.^{35,36,37,38,39,40,41} Weinert et al. were able to synthesize germanium nanoparticles starting from linear and branched oligogermanes and were able to show that the size of the nanoparticles is highly dependent on the number of catenated germanium atoms. Moreover their nanoparticles showed fluorescence.⁴² Tilley et al. synthesized germanium nanocrystals via hydride reduction, using lithium aluminum hydride, lithium triethyl borohydride, lithium borohydride or sodium borohydride, of germanium tetrachloride in inverse micelles.⁴³ Before that metal hydride reduction of nonpolar solutions of cetyl trimethylammonium bromide and GeI_4 or sodium naphthalide reduction of $GeCl_4$, or reduction of GeI_4 by $LiAlH_4$, as well as supercritical solvents have proved to be successful routes to synthesize germanium nanocrystals.^{44,45,46,47,48,49} These nanocrystals showed strong blue luminescence, making the compounds interesting for application as optical probes, since quantum dots are becoming more popular as replacements for fluorescent dyes in biological fluorescence imaging, due to their resistance to photobleaching.

In the past germanium has been considered as Li- alloying anode material for next generation lithium ion batteries, possibly improving the capacity compared to standard graphite anodes. The biggest problem to face is the poor cycling stability and the rapid capacity loss. To prevent the agglomeration of nanoparticles, which normally leads to limitation of the lithium ion diffusion pathway, Wang et al. prepared Ge nanoparticles under the aid of in situ grown graphene, creating hybrid nanostructures, showing promising results towards improving cyclability, but also eliminating particle agglomeration and pulverization.⁵⁰

On that note, this collaboration is the beginning of interesting future experiments, including the synthesis and characterization of novel organogermanium derivatives and their potential in industrial applications as for example high performance lithium ion batteries.

Moreover this project may lead to close cooperation with the Elettra Synchrotrone in Trieste, opening new ways related to material science. Our working group was already successful in getting more insight into these fields with various organotin and organosilicon compounds.

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