Reactivity of Germylene Stabilized by a Boraguanidinate Ligand towards Unsaturated Systems

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Abstract

The Doctoral Dissertation is focused on the comprehensive expansion and deepening of the knowledge about the reactivity of germynes toward unsaturated compounds. The theoretical part of this thesis describes general electron properties of tetrylenes and selected relevant reactions of germanium(II) compounds.

The main part of this Thesis deals with the reactivity of the N,N-chelated germylene by a boraguanidinate ligand, i.e. [(iPr)_2NB(NDmp)_2]Ge:, toward alkynes, dialkynes, allenes, unsaturated compounds of nitrogen, carbonyl compounds and other substrates. All prepared compounds were characterized by multinuclear NMR spectroscopy and in most cases by infrared and Raman spectroscopy, while their molecular structures were determined by the help of X-ray diffraction analysis. Reaction mechanisms were clarified by quantum chemical calculations. The experimental part then summarizes description of the preparation of all 36 discussed compounds.

Keywords

Boraguanidinates, Germynes, Unsaturated compounds, Cycloaddition reactions, Heterocyclic compounds.
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1. Introduction

This Doctoral Dissertation is focused on the reactivity of germylenes towards various unsaturated substrates, such as alkynes, dialkynes, allenes, isonitriles, isocyanides, carbonyl compounds, etc. In general, organometallic compounds of Group 14 elements represent a rapidly developing area of modern chemistry dealing with the main group elements. Especially, low valent species with the central atom in the formal oxidation state II⁺ are more often studied nowadays. A research in this field is connected with the development in synthetical and spectroscopical techniques, theoretical knowledges and calculations methods.[1,2]

Germylenes, as members of tetrylene family, have been studied since 1950’s. Unfortunately, the first germylenes were mainly obtained as undetectable and unstable species. Nevertheless, the research continued through these metastable germylenes to fully characterized germylenes stable at ambient laboratory conditions. The most important cornerstone in this area was a clarification of the substituent influence on the ground state of the germanium atom which opened a route to exact tuning of ligand properties.[1,2]

The central germanium atom can be stabilized electronically (thermodynamically), sterically (kinetically) or by combination of both factors. Germylenes stabilized thermodynamically contain electron-donating groups in their structures. Contrarily, bulky substituents provide effective kinetic stabilization of the germylene centre. Among plenty of ligand variations, sterically demanding ligands based on alkyl chains or aryl substituents (compound I)[3a] and ligands containing Group 15 and/or 16 elements (compound II[3b] and III[3c]) play the main role (Scheme 1). Remarkable number of germylenes was also stabilized within various type of chelating ligands (compound IV in scheme 1)[3d],[1,2]
We have recently reported a synthesis of germylene $V$ stabilized by a boroguanidinate ligand (Scheme 2). This dianionic N,N-chelating ligand is derived from guanidinate by formal substitution of the carbon atom by the boron atom in former NCN backbone of the guanidinate. Moreover, basic reactivity of compound $V$ was investigated. Compound $V$ exhibited a high reactivity towards various substrates due to the presence of a vacant $p_π$ orbital and a free electron pair localized on the germanium atom. Part of this research was also aimed to the reactions with 2,3-disubstituted-1,3-butadienes and with ethane-1,2-diimine which led to preparation of spirocyclic germanium(IV) species $VI$ to $VIII$ (Scheme 3). These reactions represent the first evidence that the germylene $V$ is able to react with unsaturated systems.$[4]$

Based on these results and the literature research$^{[1,2]}$, the main targets and goals for this thesis were proposed. The investigation of the reactivity of $V$ with a wide range of unsaturated systems was the main one. Necessary characterization of studied compounds and intermediates along with the investigation of plausible reaction mechanism constitute other important points of the thesis.
2. Results and discussion

According to the structure of the substrates, this chapter is divided into seven main parts. Please note that, the germylene V commented in the previous chapter is marked as the compound 1 in next paragraphs.

2.1. Reactivity of compound 1 towards C-/Fc-substituted alkynes

Many cycloaddition reactions of germylenes with alkynes have been described in the literature. These reactions often led to germirene or 1,2-cyclogermabut-3-ene compounds.[1,2] However, to the best of our knowledge only a limited number of comprehensive studies focusing the impact the alkyne properties on the structure of the products has been performed so far. Due to the lack of such studies, germylene 1 was subjected to reactions with a set of nine symmetrically and non-symmetrically substituted alkynes in a 2:1 stoichiometric ratio (Scheme 4). These [2+2+2] cycloaddition reactions produced compounds 2 – 10 containing 1,2-cyclogermabut-3-ene ring in the structure. Based on this fact, this study showed that the structure of products is not significantly influenced by sterical and electronical properties of the used alkyne.

![Scheme 4: Preparation of 1,2-cyclogermabut-3-ene compounds 2 to 10](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>R¹</td>
<td>Me</td>
<td>Ph</td>
<td>tBu</td>
<td>Cy</td>
<td>Ph</td>
<td>Fc</td>
<td>Fc</td>
<td>Fc</td>
<td>Fc</td>
</tr>
<tr>
<td>R²</td>
<td>Me</td>
<td>Ph</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>Fc</td>
<td>H</td>
<td>Me</td>
<td>Ph</td>
</tr>
</tbody>
</table>

Compounds 2 – 10 were characterized by the \(^1\)H and \(^{13}\)C(\(^1\)H) NMR spectroscopy, infrared and Raman spectroscopy and, in case of compounds 2, 3, 6, 8 and 10, by X-Ray diffraction analysis. The reaction mechanism was investigated by means of quantum chemical calculations.
$^1$H and $^{13}$C($^1$H) NMR spectra of 2 – 10 were consistent with proposed structures. The most significant signals belonged to the carbon atoms in the C=C double bond of the central C$_2$Ge$_2$ ring that were found in the range of 150 – 190 ppm in $^{13}$C NMR spectra. In addition, sharp singlet in the range 7.85 – 8.28 ppm for C=CH proton was detected in $^1$H NMR spectra of compounds 4, 5, 6 and 8. Infrared and Raman spectra also agreed with the proposed structure of products. Finally, molecular structures of several compounds were confirmed by X-ray diffraction technique showing considerable similarity in geometrical arrangement among them. The central C$_2$Ge$_2$ ring was almost planar with single bond between atoms of germanium (2.4426(4) – 2.5029(5) Å) and double bond between carbon atoms (1.337(4) – 1.346(8) Å) (Figure 1).

Figure 1: Molecular structure of selected compounds 2 and 8
The reaction of 1 with Me-C≡C-Me leading to the formation of compound 2 was simulated and two plausible reaction mechanisms were designed using the quantum chemical calculations. The initial stage, coordination of alkyne Me-C≡C-Me to the germylene 1 was same for both mechanisms. The first one led from the adduct M1 via the formation of intermediate D1 to compound 2, while the second reaction pathway led to the product 2 via transformation of adduct M1 to germirene compound M2 (Scheme 5). Regarding to calculated energy changes of each steps and the fact that germirene compounds were not detected in the reaction mixtures, the second designed pathway seems to be only hardly probable.

Scheme 5: Simplified mechanisms showing formation of 2
2.2. Reactivity of compound 1 towards substituted dialkynes

Diynes with conjugated triple bonds R-C≡C≡C-R (R = tBu, Ph or Fc) and dialkynes with molecular spacer between triple bonds (R¹C≡C)₂R² were used for reactions with germylene 1. In the case of conjugated diynes R-C≡C≡C-R, only one of the triple bond was attacked by the two equivalent of germylene 1. Therefore, these [2+2+2] cycloaddition reactions led only to 1,2-cyclodigermbut-3-ene compounds 11 – 13, while the second triple bond remained untouched (Scheme 6).

<table>
<thead>
<tr>
<th>Compound</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>tBu</td>
<td>Ph</td>
<td>Fc</td>
</tr>
</tbody>
</table>

Scheme 6: Preparation of 1,2-digermaclobut-3-ene compounds 11 – 13

Unfortunately, preserved triple bond in these compounds 11 – 13 did not react even with an excess of germylene 1 upon heating. The failure of our attempts in the formation of second four-membered C₂Ge₂ ring can be explained by a significant steric shielding of the unreacted triple bond (Figure 2).

Figure 2: Space-filling model of compound 12 revealing steric hindrance of the intact C≡C bond (in black)
In contrast to conjugated diynes, dialkynes with more flexible backbone \((R^1\text{C}≡\text{C})_2R^2\) \((R^1 = H, R^2 = 1,4\text{C}_6\text{H}_4; \ R^1 = \text{Ph}, R^2 = \text{fc})\ provided bis(1,2-digermacyclobut-3-ene) compounds 14 and 15 when treated with four molar equivalents of the germylene 1 (Scheme 7).

![Scheme 7: Preparation of bis(1,2-digermacyclobut-3-ene) compounds 14 and 15](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R^1)</td>
<td>H</td>
<td>Ph</td>
</tr>
<tr>
<td>(R^2)</td>
<td>1,4\text{C}_6\text{H}_4</td>
<td>fc</td>
</tr>
</tbody>
</table>

Compounds 11 – 15 were characterized using the \(^1\text{H}\) and \(^{13}\text{C}[^1\text{H}]\) NMR spectroscopy, infrared and Raman spectroscopy. The molecular structures of compounds 11, 12 and 15 were determined by X-Ray diffraction analysis. The \(^1\text{H}\) and \(^{13}\text{C}[^1\text{H}]\) NMR spectra were similar to those obtained for compounds 2 – 10. Moreover, the presence of the unreacted \text{C}≡\text{C} bond in compounds 11 – 13 was confirmed by two singlets in \(^{13}\text{C}[^1\text{H}]\) NMR spectra (78.2 – 120.4 ppm) and by Raman spectroscopy where strong bands at 2175 – 2191 cm\(^{-1}\) typical for vibration of the \text{C}≡\text{C} bond were found. Both the \(^1\text{H}\) and \(^{13}\text{C}[^1\text{H}]\) NMR spectra of compounds 14 and 15 displayed two sets of signals for two magnetically non-equivalent boraguanidinate ligands. Obtained molecular structures of 11, 12 (Figure 3) and 15 (Figure 3) revealed mutual similarity in the bond arrangement of \(\text{C}_2\text{Ge}_2\) cycle(s). In addition, \(\text{C}_2\text{Ge}_2\) rings in the structure of the compound 15 exhibited parallel orientation while cyclopentadienyl ligands in the central bridging ferrocene showed staggered conformation (Figure 3).
2.3. Reactivity of compound 1 towards alkynes substituted by a functional group

In order to change a structure of the product, alkynes substituted by a carbonyl group were used. Unfortunately, reactions of two equivalents of germylene 1 with alkynes of the general formula Fc-C≡C-R (R = C(O)Me, C(O)OEt or C(O)N(Me)$_2$) again led only to the formation of C$_2$Ge$_2$ ring (Scheme 8). Obtained compounds 16 – 18 were characterized by $^1$H and $^{13}$C($^1$H) NMR spectroscopy and infrared and Raman spectroscopy. Molecular structures of compounds 17 and 18 were obtained using X-Ray diffraction analysis.
Scheme 8: Preparation of 1,2-digermacyclobut-3-ene compounds 16 – 18

The $^1$H and $^{13}$C($^1$H) NMR spectra of compounds 16 – 18 displayed expected set of signals. The presence of unreacted carbonyl groups of the respective compounds was reflected by a signal at 203.9 (16), 156.2 (17) and 160.0 ppm (18) in the $^{13}$C($^1$H) NMR spectra. This result was also confirmed by infrared and Raman spectroscopy where intensive bands around 1670 cm$^{-1}$ were detected. Structures of compounds 17 and 18 (Figure 4) were also established by X-Ray diffraction analysis, but the central core of the molecules was similar to the 1,2-digermacyclobut-3-ene compounds mentioned above.

<table>
<thead>
<tr>
<th>Compound</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>C(O)Me</td>
<td>C(O)OEt</td>
<td>C(O)N(Me)$_2$</td>
</tr>
</tbody>
</table>

Figure 4: Molecular structure of selected compound 18
By contrast, the reaction centre was extend to the carbonyl group only when the symmetrically substituted alkyne Ph-C(\(\text{O}\))-C\(\equiv\)C-C(\(\text{O}\))-Ph was used. In this way, the compound 19 which contains the central C\(_4\)Ge\(_2\)O\(_2\) core was prepared by treating of mentioned alkyne with two molar equivalents of the germylene 1. Thus, two five membered rings C\(_3\)GeO in the compound 19 were formed by involving oxygen atoms from carbonyl groups (Scheme 9).

![Scheme 9: Preparation of symmetric compound 19](image)

The structure of the compound 19 was established by the \(^1\)H and \(^{13}\)C\({}^{1}\)H\) NMR spectroscopy where one set of signals for both equivalent boraguanidinate ligands was found. In addition, singlets at 105.6 and 163.8 ppm, respectively, in the \(^{13}\)C\({}^{1}\)H\) NMR spectrum were assigned to atoms of C=C bond within the central framework. The presence of these double bonds was confirmed by infrared and Raman spectroscopy as well. The structure of the compound 19 was unambiguously determined by X-Ray diffraction analysis (Figure 5). The central C\(_4\)Ge\(_2\)O\(_2\) moiety is almost planar and the C5=C6 bond length is 1,362(3) \(\text{Å}\).

![Figure 5: Molecular structure of symmetric compound 19](image)
2.4. Reactivity of compound 1 towards systems of cumulated double bonds

While substituted butadienes and alkynes are in the forefront of interest in the field of germylene chemistry, allenes are on the opposite end of this scale.\cite{1,2,5} Therefore, also allenes were considered and two selected examples, i.e. $\text{H} \equiv \text{C} \equiv \text{C} \text{(Me)}_2$ and $\text{H} \equiv \text{C} \equiv \text{C} \equiv \text{C(OMe)}$, were reacted with two molar equivalent of the germylene 1 (Scheme 10). In addition, electron deficient N-methylmaleinimide was used under the same conditions (Scheme 11).

![Scheme 10: Preparation of 1,2-digermacyclobutane compounds 20 and 21](image)

According to the literature\cite{5}, only the terminal double bond in allenes is attacked by the germylene 1 to form a 1,2-digermacyclobutane compounds 20 and 21, while the second C=C bond is preserved as exocyclic double bond in prepared compounds (Scheme 10). The formation of the 1,2-digermacyclobutane ring was also observed in the case of the use of N-methylmaleinimide (Scheme 11).

![Scheme 11: Preparation of 1,2-digermacyclobutane compounds 22](image)
The presence of unreacted double C=C and C=O bonds in compounds 20 – 22, respectively, was confirmed by multinuclear NMR spectroscopy. The central $H_2C-C=C$ backbone in $^1H$ NMR spectra of compounds 20 and 21 was represented by the signal at 2.14 and 2.06 ppm, respectively. In addition, triplet found at 5.60 ppm belonged to the proton on the double bond C-C=CH in the case of 21. The $^{13}C(^1H)$ NMR spectra of compounds 20 and 21 were also measured and revealed a set of three signals for C-C=C linkage in all cases. The $^1H$ and $^{13}C(^1H)$ NMR spectra of the compound 22 showed one signal for the H-C-CH groups ($^1H$: 2.68 ppm, $^{13}C(^1H)$: 49.2 ppm) and one signal in the $^{13}C(^1H)$ NMR spectrum at 172.5 ppm for C=O groups. Infrared and Raman spectra corroborated the presence of C=C and C=O bonds by intensive bands around 1626 cm$^{-1}$ (C=C) and 1758 cm$^{-1}$ (C=O), respectively. The molecular structure of the compound 21 was established by X-Ray diffraction analysis (Figure 6). Although the central $C_2Ge_2$ ring is still trapezoid, it exhibited a significant deviation from planarity in comparison with the structure of 1,2-digermacyclobut-3-ene compounds discussed above.

![Figure 6: Molecular structure of compound 21](image)

2.5. Reactivity of compound 1 towards unsaturated compounds of nitrogen

This chapter is divided into four parts dealing with isonitriles R-NC and compounds containing a system of cumulated multiple bonds in their structures (i.e. isocyanates R-NCO, isothiocyanates R-NCS and organic azide R-N$_3$).
2.5.1. Isonitriles R-NC

According to the literature research, isonitriles R-NC smoothly interact with the vacant $p_{\pi}$ orbital of germynes via their free electron pair localized on the carbon atom often leading to the activation of the C-N bond in corresponding isonitrile. Accordingly, the treatment of germylene 1 with one molar equivalent of tBu-NC yielded germanium(IV) compound 23 as a product of oxidative addition of isonitrile to the germylene 1 (Scheme 12).

![Scheme 12: Preparation of compound 23](image)

The cyanide group was represented by one signal at 124.6 ppm in $^{13}$C{\textsuperscript{1}H} NMR spectrum. In addition, one set of signals for the tBu moiety was found. The presence of CN group was also verified by the observation of the band in corresponding infrared and Raman spectra at 2170 cm\textsuperscript{-1} and 2173 cm\textsuperscript{-1}, respectively. Finally, the structure of the compound 23 was unambiguously determined by X-Ray diffraction analysis (Figure 7). The C5≡N4 bond length (1.129(3) Å) corresponds to the $\Sigma_{\text{cov}}$(C,N) = 1,14 Å\textsuperscript{[6]} for the triple bond.

![Figure 7: Molecular structure of compound 23](image)
In sharp contrast to previous, the reaction of germylene 1 with two equivalents of Cy-NC or Ad-NC led to the formation of unexpected compounds 24 and 25, respectively, containing a coordinated isonitrile moiety and two germanium atoms formally in different oxidation state II+ and IV+ (Scheme 13).

\[
\begin{array}{c}
\text{N-B-Ge-Ge-B} \\
\text{iPr} \\
\text{Dmp}
\end{array}
\quad \xrightarrow{2 \text{ R-NC}} \\
\text{Toluene, r.t.}
\begin{array}{c}
\text{N-B-Ge-Ge-B} \\
\text{iPr} \\
\text{Dmp}
\end{array}
\]

### Scheme 13: Preparation of unexpected compounds 24 and 25

Obtained molecular structures of compounds 24 and 25 (Figure 8) showed nearly planar central five-membered BGe₂N₂ ring with the Ge₁ atom N,N-chelated by the boraguanidinate ligand. The second ligand forms a bridge between both germanium atoms. The isonitrile molecule is only coordinated to the germanium(II) atom in both compounds, whereas C≡N bond lengths were 1.146(4) and 1.157(8) Å, respectively, and N-Ge-C bond angles were 91.22(10) and 90.33(16)°, respectively.

![Figure 8: Molecular structure of unexpected compound 25](image-url)
Surprisingly, our attempt to characterize compounds 24 and 25 in the solution using the $^1$H and $^{13}$C($^1$H) NMR spectroscopy led to the observation of two sets of signals. One set of signals was assigned to the free germylene 1, while the second one was identified as an adduct 24a and 25a, respectively, of germylene 1 with corresponding isonitrile (Scheme 14). In addition, a performed study in these solutions by $^1$H - $^1$H EXSY NMR showed dynamical equilibrium between both species.

Based on this fact, the reaction between germylene 1 and tBu-NC were monitored by $^1$H NMR spectroscopy. This study also revealed the presence of the adduct 23a (Scheme 15) showing very similar set of signals as in case of compounds 24a and 25a (Scheme 14). Therefore, the formation of the adduct 23a is expected, that then spontaneously converts to the final product 23 (Scheme 15).

2.5.2. Isocyanates R-NCO

The treatment of germylene 1 with isocyanates R-NCO (R = tBu or Ad) in 1:1 molar ratio produced new heterocyclic products as a results of the isocyanate insertion into one Ge-N bond, i.e., compounds 26 and 27. Thus, the original four-membered BGeN$_2$ ring of germylene 1 was expanded to the six-membered one (CBGeN$_3$). With regard to the course of the reaction, germanium atom is still in oxidation state II+ here (Scheme 16).
Structures of both products 26 and 27 were determined by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy where an expected set of signals was found. The sharp singlets at 159.1 and 158.6 ppm, respectively, in the $^{13}$C{$^1$H} NMR spectra were assigned to the carbon atom in present C=O groups. Infrared and Raman spectra of both compounds 26 and 27 reported the intense band around 1638 cm$^{-1}$ due to carbonyl group stretching vibration. Molecular structures of both compounds were obtained by X-Ray diffraction analysis (Figure 9).

Moreover, the reaction mechanism was clarified by quantum chemical calculations. In the first step, the binding of the isocyanate moiety to germylene 1 is mediated through electron donating from the nitrogen atom to the vacant $p_\pi$ orbital of the germylene atom (Scheme 17). The reaction mechanism continues from this adduct M1 via the formation of bicyclic intermediate TS to compound 26 (Scheme 17).
2.5.3. Isothiocyanates R-NCS

The reactivity of \textit{tBu}-NCS and Ad-NCS with 1 was also studied. In contrast to the formation of 26 and 27, the treatment of both isothiocyanates with one equivalent of the germylene 1 reproducibly led to the formation of the compound 28 containing the central Ge$_3$S ring (Scheme 18).

\begin{center}
\textbf{Scheme 17:} First step of reaction mechanisms leading to compound 26
\end{center}

\begin{center}
\textbf{Scheme 18:} Preparation of unique compound 28
\end{center}
Structure of the compound 28 was established using the $^1$H and $^{13}$C($^1$H) NMR spectroscopy where two sets of signals for non-equivalent boraguanidinate ligands in 1:2 mutual integral ratio were obtained. The molecular structure obtained by X-Ray diffraction analysis showed a quite puckered Ge$_3$S ring (Figure 10).

**Figure 10:** Molecular structure of unique compound 28

A coordination step of the reaction mechanism was simulated using the quantum chemical calculations. In contrast to isocyanate systems mentioned above (Scheme 17), isothiocyanates are coordinated to the atom of germanium via the sulphur atom (Scheme 19), thereby probably favouring the elimination of R-NC molecule and formation of 28.

**Scheme 19:** First step of reaction mechanisms leading to the compound 28
2.5.4. Organic azide Ad-N₃

The reaction of germylene 1 with Ad-N₃ in the stoichiometric ratio 1:1 produced an azadigermiridene compound 29. The formation of the central three-membered Ge₂N ring was accompanied by nitrogen gas release (Scheme 20).

Scheme 20: Preparation of azadigermiridene 29

The ¹H and ¹³C{¹H} NMR spectra of the symmetric compound 29 revealed expected three signals for the adamantyl substituent and one set of signals for both equivalent boraguanidinate ligands. These signals were found in the expected 1:2 mutual integral ratio. The molecular structure of the compound 29 was determined by X-Ray diffraction analysis (Figure 11).

Figure 11: Molecular structure of azadigermiridene 29
According to the reactions mentioned above in this chapter, the first step of the reaction mechanism leading to the compound 29 was optimized by quantum chemical calculations. Obtained results showed coordination of the N₃ moiety to the germanium atom through the nitrogen atom with a partial negative charge (Scheme 21). The final step is than obviously the release of dinitrogen.

![Scheme 21: The first step of reaction mechanisms leading to compound 29](image)

**2.6. Reactivity of compound 1 towards fluorinated carbonyl compounds**

Reactions of germylene 1 with benzaldehyde, acetone, acetonitrile or benzophenone in various stoichiometric ratio were tested. However, mixtures of non-isolable products were usually obtained, or starting compound were isolated. Contrarily, treatment of two equivalent of germylene 1 with fluorinated carbonyl compounds C₆F₅-CHO and Ph-C(O)-CF₃ led to the formation of compounds 30 and 31 containing the central CGe₂O ring. These heterocyclic analogues of 1,2-digermacyclobutane compounds were evidently formed by [2+2+2] cycloaddition reactions similarly to above described alkynes (Scheme 22).

![Scheme 22: Preparation of compounds 30 and 31 containing the central CGe₂O ring](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>30</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>R¹</td>
<td>C₆F₅</td>
<td>Ph</td>
</tr>
<tr>
<td>R²</td>
<td>H</td>
<td>CF₃</td>
</tr>
</tbody>
</table>
Structures of prepared compounds were determined using the multinuclear NMR spectroscopy. The $^{19}$F NMR spectra of the compound 30 showed three signals for C$_6$F$_5$ fragment, while one signal was found for CF$_3$ group in the corresponding $^{19}$F NMR spectrum of 31. The formation of the central CGe$_2$O ring was reflected in the $^{13}$C$^{[1]}$H NMR spectra of both compounds by a singlet at 73.3 ppm (30) and a quartet at 93.2 ppm (31), respectively.

Surprisingly, the reaction of germylene 1 with 2',3',4',5',6'-pentafluoroacetophenone (C$_6$F$_5$-C(O)-Me) in 2:1 molar ratio produced an unexpected compound 32 where germylene 1 was inserted into the C-F bond. In a central five-membered BGe$_2$N$_2$ ring, both germanium atoms are in the same oxidation state IV+ and one boraguanidinate ligand forms a bridge between them (Scheme 23).

![Scheme 23: Insertion of germylene 1 into the C-F bond](image)

The compound 32 was characterized by multinuclear NMR analysis. The $^{19}$F NMR spectra revealed five signals in the range -147.6 to -120.4 ppm. The presence of the C=O group was confirmed by $^{13}$C$^{[1]}$H NMR spectroscopy (signal at 193.7 ppm) and infrared and Raman spectroscopy (band around 1668 cm$^{-1}$). Nevertheless, the weak interaction O1-Ge2 with length 2.369(2) Å ($\Sigma_{\text{cov}}$(Ge,O) = 1.84 Å)$^6$ was found in the molecular structure obtained by X-Ray diffraction analysis (Figure 12).
2.7. Reactivity of compound 1 towards substituted chlorophosphines

Based on the previous results proving that germynes are able to insert toward various element-halogen or element-hydrogen bonds, germylene 1 was treated with a variety of compounds containing B-H (H₃B.S(Me)₂), B-Cl (PhBCl₂), Al-Cl (EtAlCl₂), Si-H (Ph₃SiH, Ph₂SiH₃), Si-Cl (Me₂SiCl₂), Sn-Cl (Me₂SnCl₂), P-Cl (PH₂PCI, RPCl₂ a PCl₃) or N-H (NH₃) bond. However, only reactions of germylene 1 with Ph₂PCI (Scheme 24) or RPCl₂ (R = tBu or Ph) (Scheme 25) in 1:1 and 2:1 stoichiometric ratio, respectively, produced isolable compounds 33 – 35. The P-Ge-Cl linkage was found in these products of insertion of germylene 1 into the P-Cl bond(s).
Structures of compounds 33 – 35 were established using the multinuclear NMR spectroscopy, whereas the course of the reaction was monitored by the $^{31}$P NMR spectroscopy. Compounds 33 – 35 were identified in the $^{31}$P NMR spectra by the signal at -10.4 (33), -34.4 (34) and 44.5 ppm (35), respectively. Molecular structures of products 33 (Figure 13) and 34 (Figure 14) obtained by X-Ray diffraction analysis, confirmed the presence of P-Ge-Cl backbone.

### Scheme 25: Preparation of compounds 34 and 35

<table>
<thead>
<tr>
<th>Compound</th>
<th>34</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>tBu</td>
<td>Ph</td>
</tr>
</tbody>
</table>

**Figure 13:** Molecular structure of compound 33
During initial attempts to measure single-crystals of compound 34 by X-Ray diffraction analysis, molecular structure of the compound 36 was fortuitously obtained (Figure 15). This compound was characterized as a formal product of the reaction between compound 34 and one equivalent of HCl where Ge-N bond was cleaved. The signal at 23.1 ppm was obtained for this compound in $^{31}$P NMR spectrum.

The compound 36 was prepared by the reaction of compound 34 with HCl in 1:1 molar ratio (Scheme 26). Unfortunately, this reaction was not so straightforward. Thus, the required compound 36 was obtained by fractional crystallization from the reaction mixture containing also an unexpected by-product 37.
Scheme 26: Reaction targeting to preparation of compound 36

The structure of compounds 36 and 37 were particularly characterized by infrared and Raman spectroscopy where the significant band for NH group around 3396 cm\(^{-1}\) was found. In addition, the signal at 5.28 and 5.42 ppm, respectively were assigned to the NH group in the \(^1\text{H}\) NMR spectra. The formation of the compound 37 was recognized by the signal at 17.6 ppm in \(^{31}\text{P}\) NMR spectra of reaction mixtures. Moreover, the compound 37 was prepared by the reaction of the compound 34 with two equivalents of HCl (Scheme 27).

Scheme 27: Preparation of compound 37
3. Summary

To conclude, 36 original compounds were prepared and characterized by multinuclear NMR analysis, infrared spectroscopy, Raman spectroscopy and X-Ray diffraction analysis.

The remarkable potential of 1 to react with a variety of unsaturated substrates was clearly demonstrated. These reactions in most cases produced novel heterocyclic compounds and some of them can be considered as unique.

On several occasions, a diverse reactivity depending on the substrate, e.g. R-NC vs. R-NCO vs. R-NCS vs. R-N₃ was obtained producing also new types of germynes 26 and 27, with some potential for future studies. Similarly the carbonyl compounds reacted with the germylene 1 either at the C=O bond or via C-F activation producing different product. This field seems to interesting target point for further investigation.

In conclusion, the reactivity of 1 with unsaturated systems was investigated and obtained results opened new ways for future research. The modification of the boraguanidinate backbone in related germynes is also of future interest, e.g. by increasing the steric bulk or incorporation of other reactive centres, next to germylene one, such as H-B bond.
4. References


5. Published Works

List of papers published by the author in the topic belonging to the Doctoral Dissertation:


