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FACULTY OF CHEMICAL TECHNOLOGY

DEPARTMENT OF GENERAL AND INORGANIC CHEMISTRY

Jiří Böserle

Reactivity of Germylene Stabilized by a Boraguanidinate Ligand towards Unsaturated Systems

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Author: **Ing. Jiří Böserle**

Supervisor: **doc. Ing. Libor Dostál, Ph.D.**

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Candidate:

Ing. Jiří Böserle

Reviewers:

1. prof. Ing. Antonín Lyčka, DrSc.
2. prof. RNDr. Petr Hermann, Dr.
3. RNDr. Bohumír Grüner, CSc.

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Abstract

The Doctoral Dissertation is focused on the comprehensive expansion and deepening of the knowledge about the reactivity of germylenes 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. $[(i\mathrm{Pr})_2\mathrm{NB}(\mathrm{NDmp})_2]\mathrm{Ge}$:, 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, Germylenes, Unsaturated compounds, Cycloaddition reactions, Heterocyclic compounds.

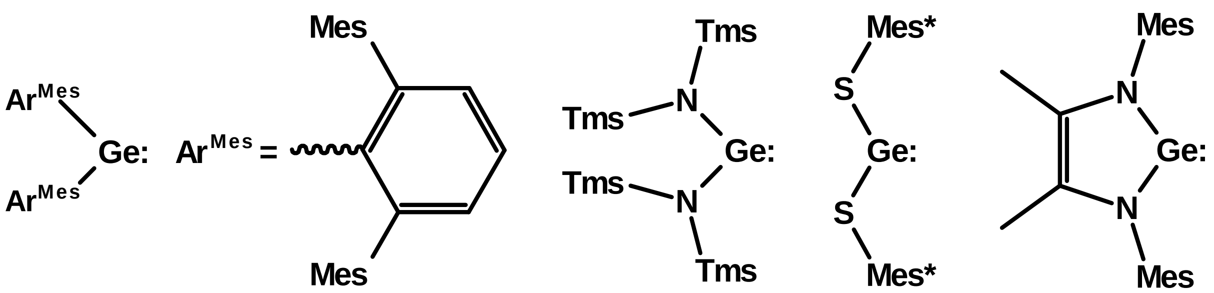
CONTENTS

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]

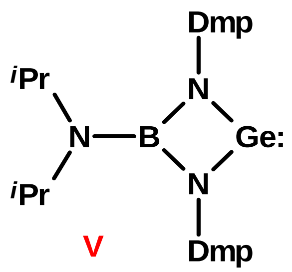
Germylenes, as members of tetrylene family, have been studied since 1950's. Unfortunately, the first germylenes were mainly obtained as undetectable and unstable species. Nevertheless, the research continued through these metastable germylenes to fully characterized germylenes stable at ambient laboratory 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]



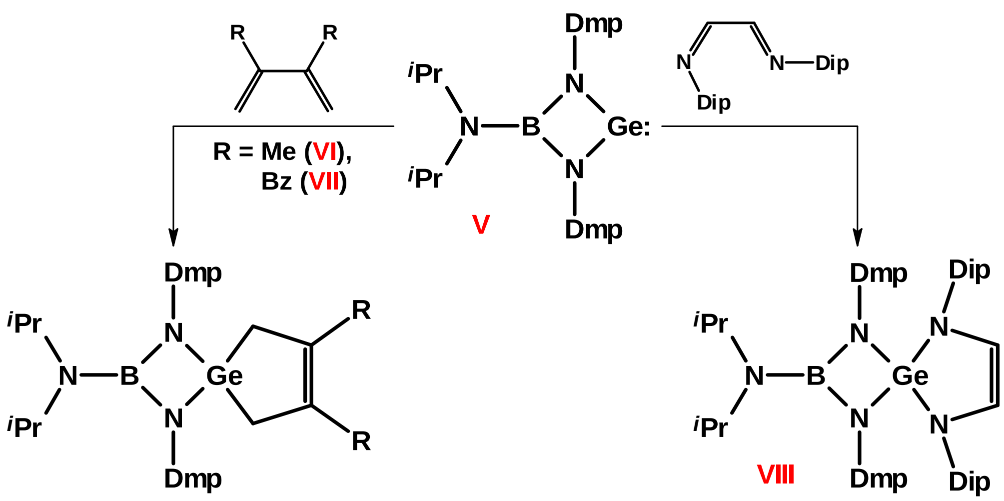
I II III IV

Scheme 1: Examples of germylenes stabilized by various types of ligands[3]



Scheme 2: Structure of the germylene V

We have recently reported a synthesis of germylene V stabilized by a boraguanidinate 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]



Scheme 3: [1+4] cycloaddition reactions of germylene V

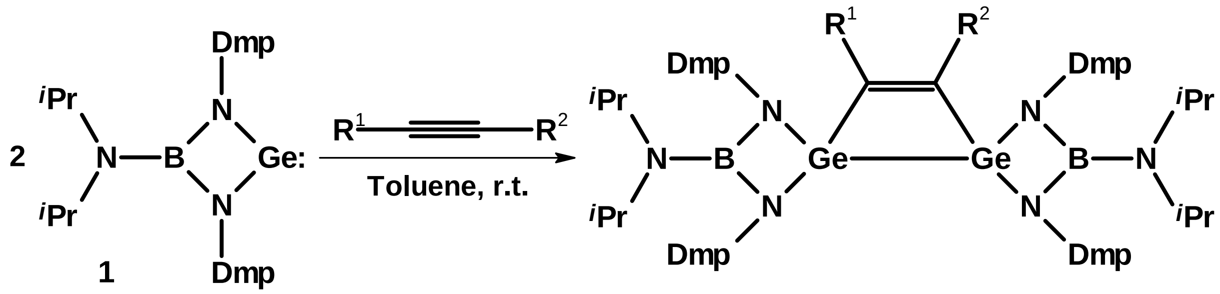
Based on these results and the literature research[1,2], the main targets and goals for this thesis were proposed. The investigation of the reactivity of V with a wide range of unsaturated systems was the main one. Necessary characterization of studied compounds and intermediates along with the investigation 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-cyclodigermabut-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-cyclodigermabut-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.



Compound	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
R^1	Me	Ph	*t*Bu	Cy	Ph	Fc	Fc	Fc	Fc
R^2	Me	Ph	H	H	H	Fc	H	Me	Ph

Scheme 4: Preparation of 1,2-cyclodigermabut-3-ene compounds **2** to **10**

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_2Ge2 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=C*H* 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_2Ge_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).

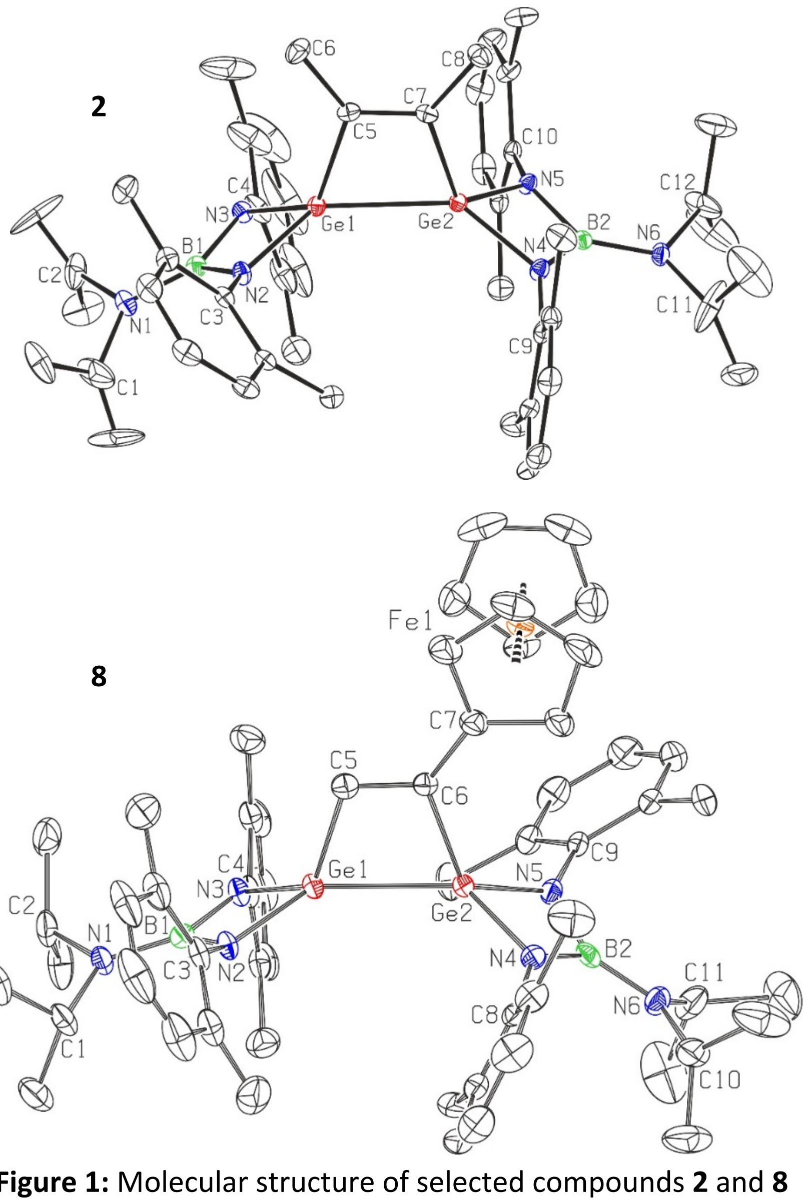
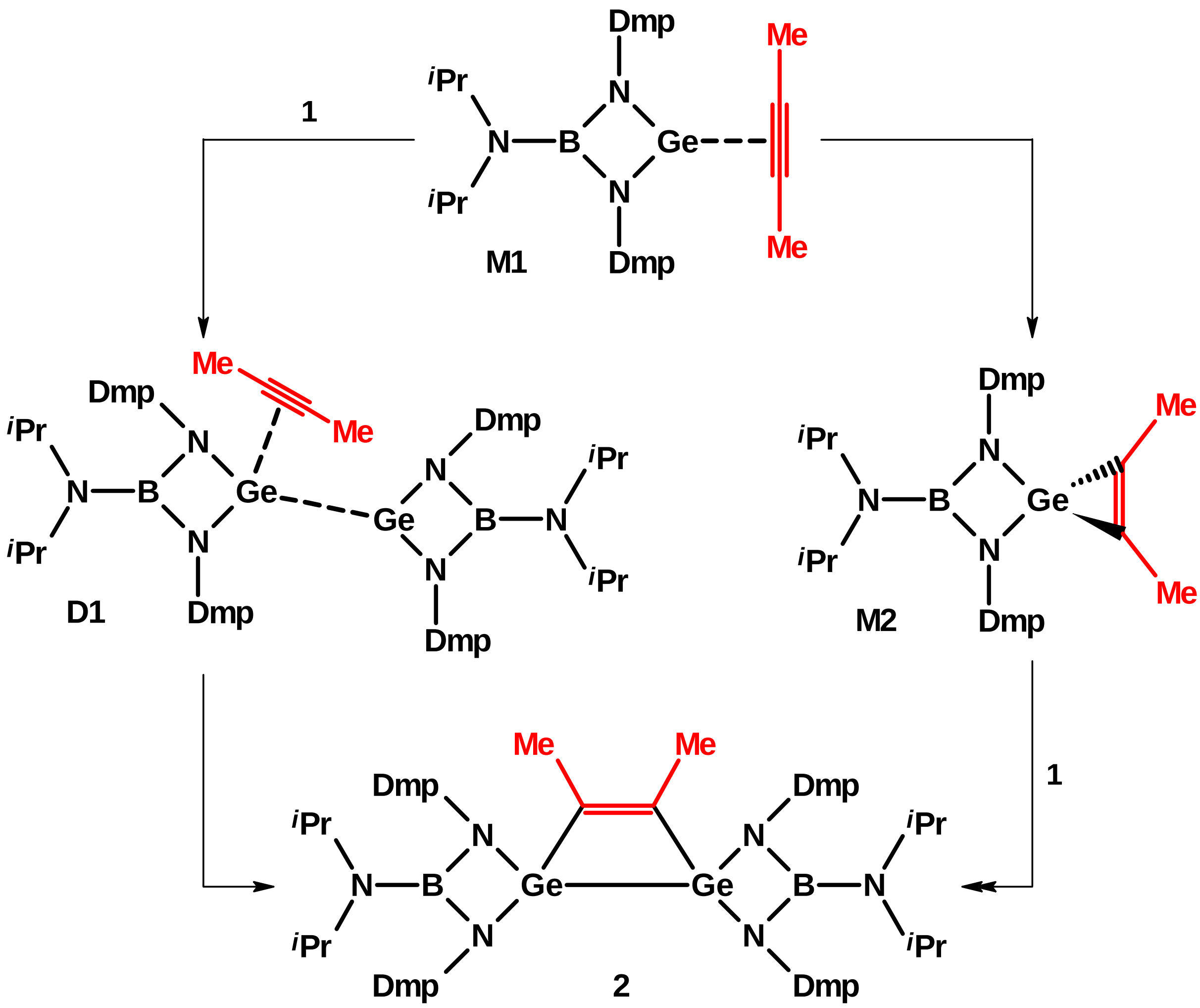


Figure 1: Molecular structure of selected compounds **2** and **8**

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.

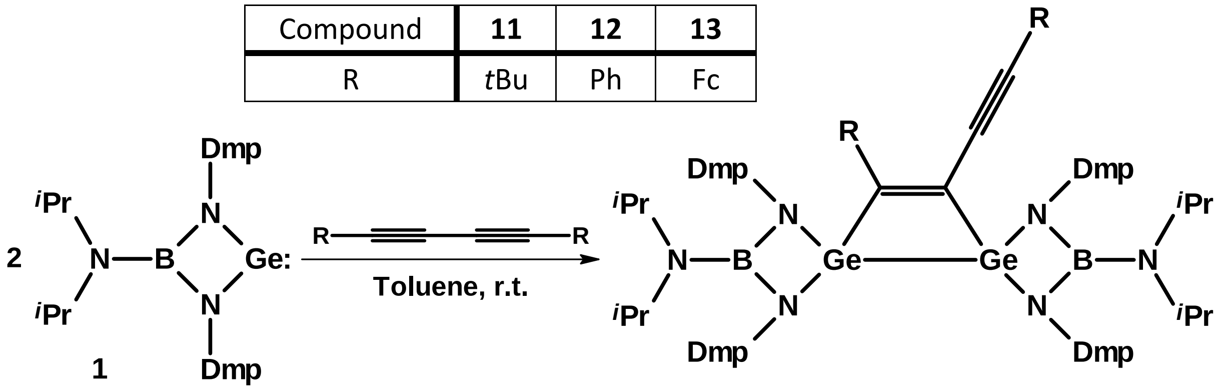


Scheme 5: Simplified mechanisms showing formation of **2**

2.2. Reactivity of compound 1 towards substituted dialkynes

Diynes with conjugated triple bonds R-C≡C-C≡C-R (R = *t*Bu, Ph or Fc) and dialkynes with molecular spacer between triple bonds ($R^1C≡C)_2R^2$ were used for reactions with germylene **1**. In the case of conjugated diynes R-C≡C-C≡C-R, only one of the triple bond was attacked by the two equivalent of germylene **1**. Therefore, these [2+2+2] cycloadition reactions led only to 1,2-cyclodigermabut-3-ene compounds **11** – **13**, while the second triple bond remained untouched (Scheme 6).

Compound	**11**	**12**	**13**
R	*t*Bu	Ph	Fc



Scheme 6: Preparation of 1,2-digermacyclobut-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 C_2Ge_2 ring can be explained by a significant steric shielding of the unreacted triple bond (Figure 2).

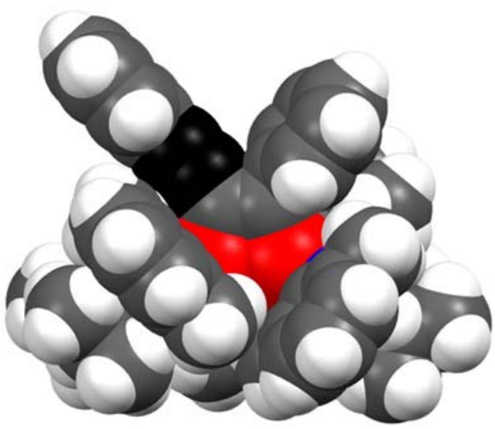
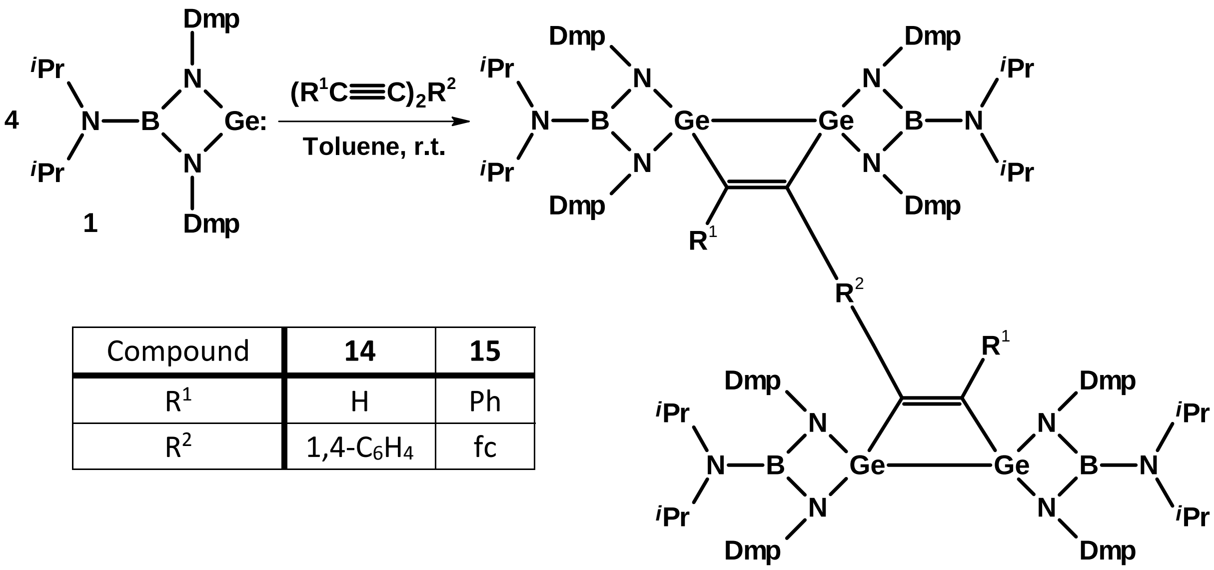


Figure 2: Space-filling model of compound **12** revealing steric hindrance of the intact C≡C bond (in black)

In contrast to conjugated diynes, dialkynes with more flexible backbone $(R^1C{\equiv}C)_2R^2$ (R^1 = H, R^2 = 1,4-C_6H_4; R^1 = Ph, R^2 = fc) provided bis(1,2-digermacyclobut-3-ene) compounds **14** and **15** when treated with four molar equivalents of the germylene **1** (Scheme 7).



Compound	**14**	**15**
R^1	H	Ph
R^2	1,4-C_6H_4	fc

Scheme 7: Preparation of bis(1,2-digermacyclobut-3-ene) compounds **14** and **15**

Compounds **11** – **15** were characterized using the ^{1}H and ^{13}C{^{1}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}H and ^{13}C{^{1}H} NMR spectra were similar to those obtained for compounds **2** – **10**. Moreover, the presence of the unreacted C≡C bond in compounds **11** – **13** was confirmed by two singlets in ^{13}C{^{1}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 C≡C bond were found. Both the ^{1}H and ^{13}C{^{1}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 C_2Ge_2 cycle(s). In addition, C_2Ge_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).

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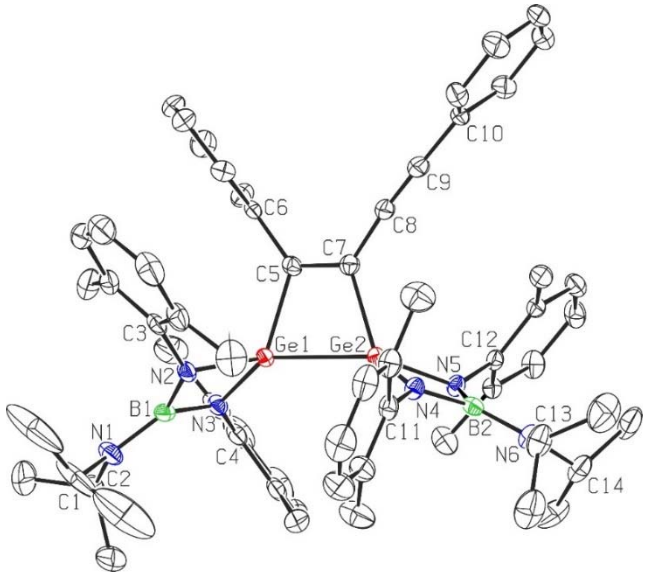

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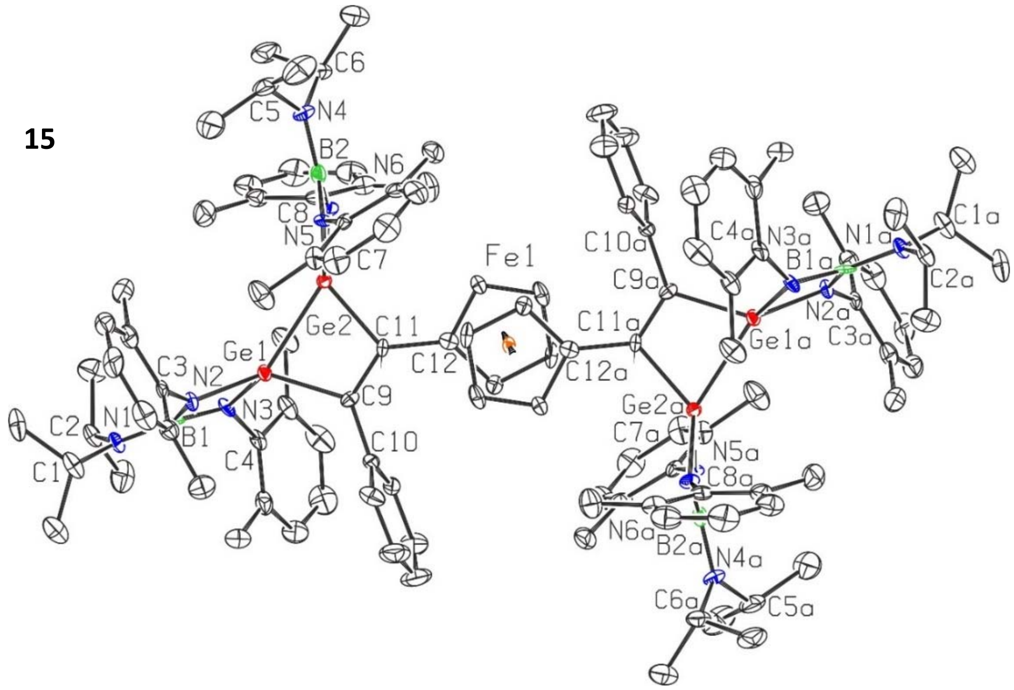
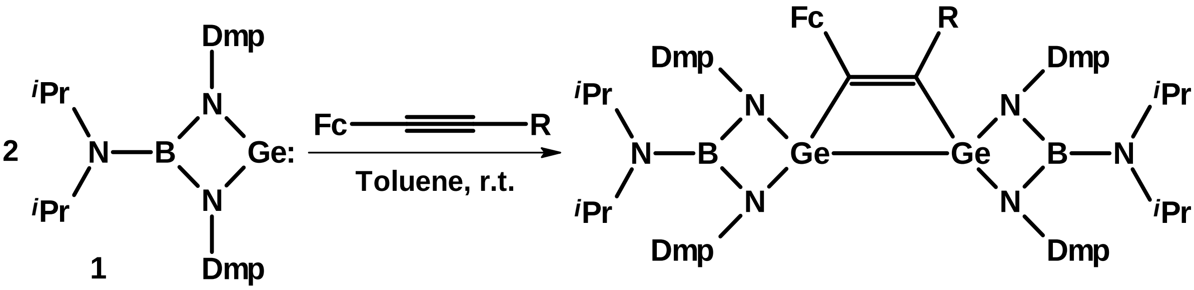


Figure 3: Molecular structure of selected compounds **12** and **15**

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_2Ge_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.



Compound	**16**	**17**	**18**
R	C(O)Me	C(O)OEt	$C(O)N(Me)_2$

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.

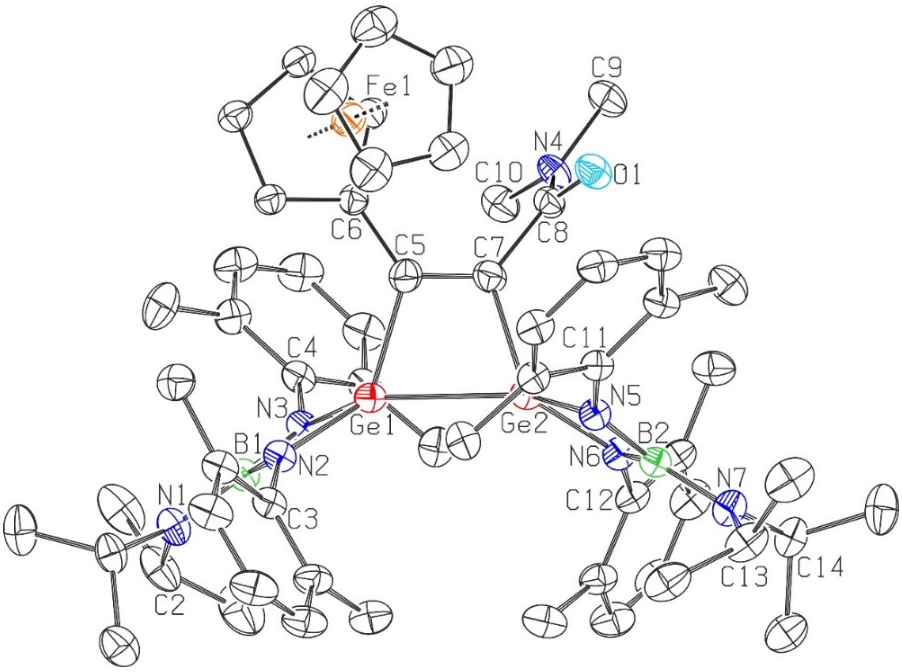
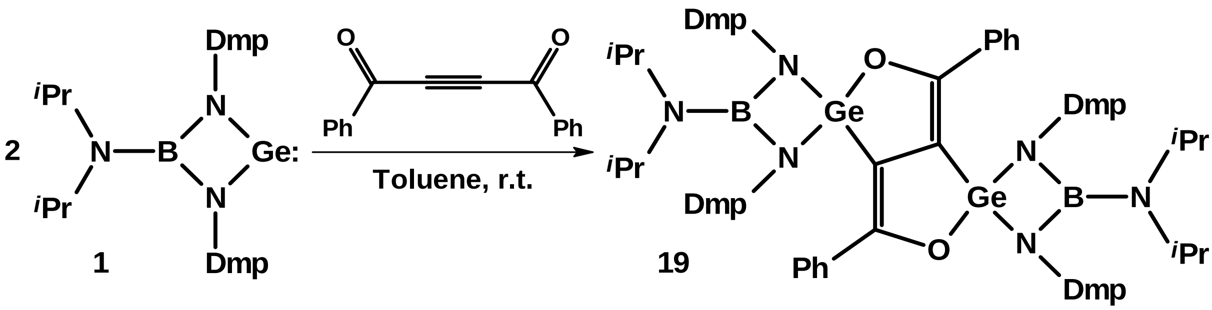


Figure 4: Molecular structure of selected compound **18**

By contrast, the reaction centre was extend to the carbonyl group only when the symmetrically substituted alkyne Ph-C(O)-C≡C-C(O)-Ph was used. In this way, the compound **19** which contains the central $C_4Ge_2O_2$ core was prepared by treating of mentioned alkyne with two molar equivalents of the germylene **1**. Thus, two five membered rings C_3GeO in the compound **19** were formed by involving oxygen atoms from carbonyl groups (Scheme 9).



Scheme 9: Preparation of symmetric compound **19**

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 $C_4Ge_2O_2$ moiety is almost planar and the C5=C6 bond length is 1,362(3) Å.

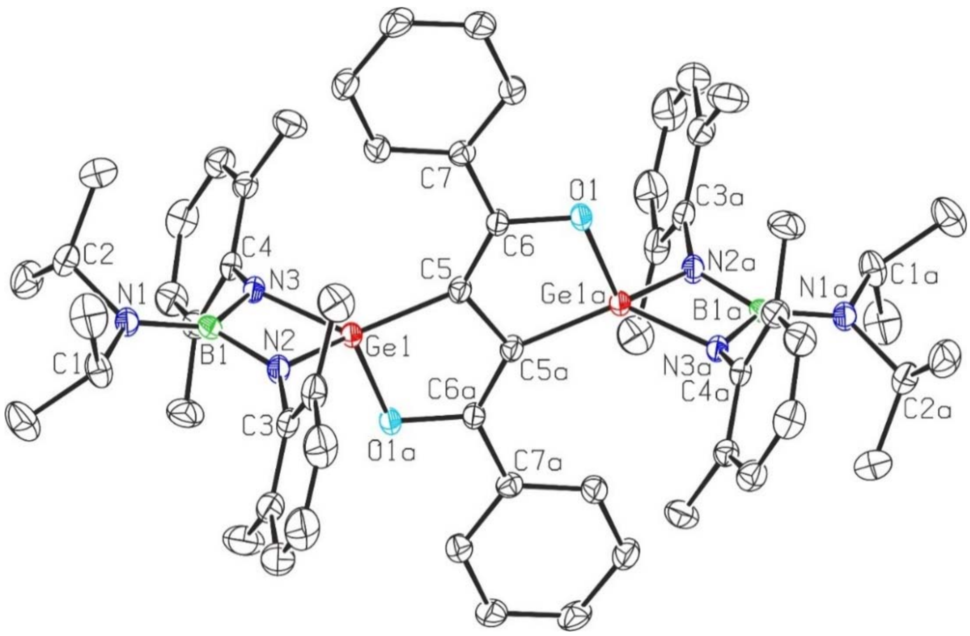
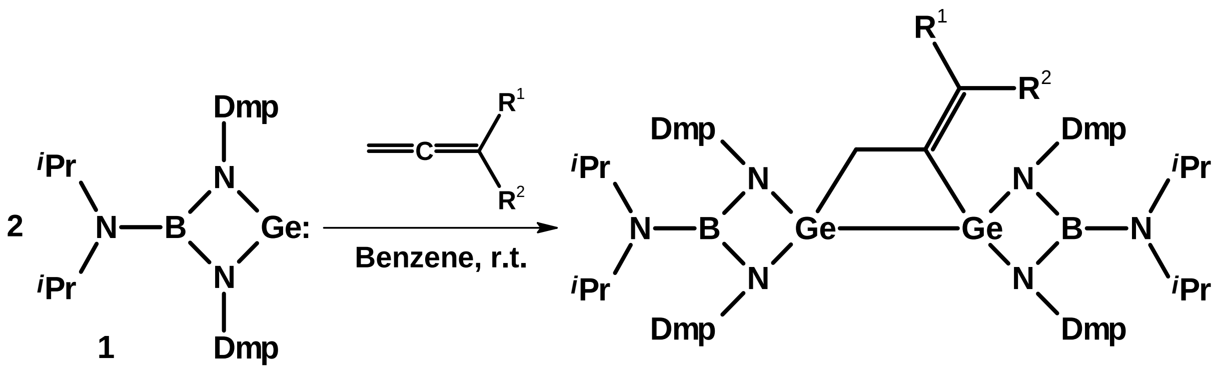


Figure 5: Molecular structure of symmetric compound **19**

2.4. Reactivity of compound 1 towards systems of cumulated double bonds

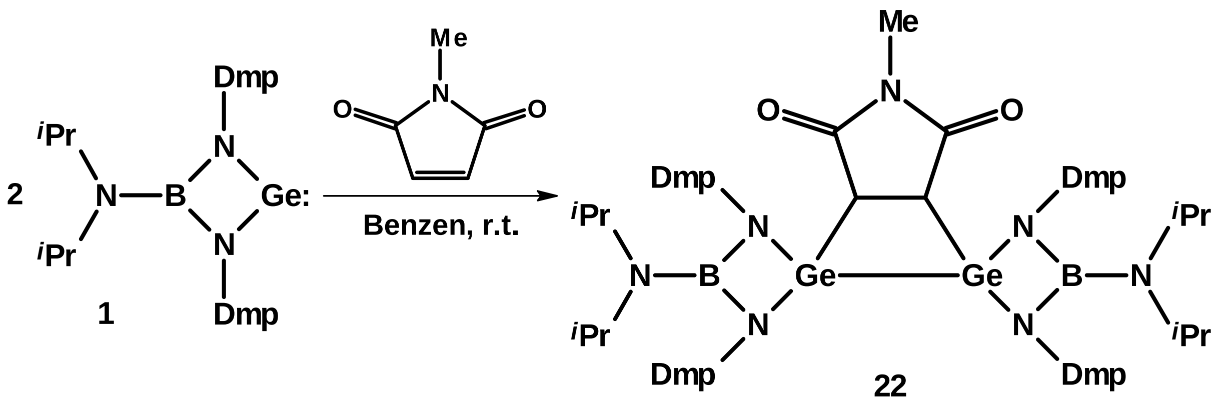
While substituted butadienes and alkynes are in the forefront of interest in the field germylene chemistry, allenes are on the opposite end of this scale.[1,2,5] Therefore, also allenes were considered and two selected examples, i.e. $H_2C{=}C{=}C(Me)_2$ and $H_2C{=}C{=}CH(OMe)$, were reacted with two molar equivalent of the germylene **1** (Scheme 10). In addition, electron deficient N-methylmaleinimide was used under the same conditions (Scheme 11).



Compound	**20**	**21**
R^1	Me	H
R^2	Me	OMe

Scheme 10: Preparation of 1,2-digermacyclobutane compounds **20** and **21**

According to the literature[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**

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*$_2$C-C=C backbone in ^{1}H 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=C*H* in the case of **21**. The ^{13}C{^{1}H} 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 ^{1}H and ^{13}C{^{1}H} NMR spectra of the compound **22** showed one signal for the *HC*-*CH* groups (^{1}H: 2.68 ppm, ^{13}C{^{1}H}: 49.2 ppm) and one signal in the ^{13}C{^{1}H} 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.

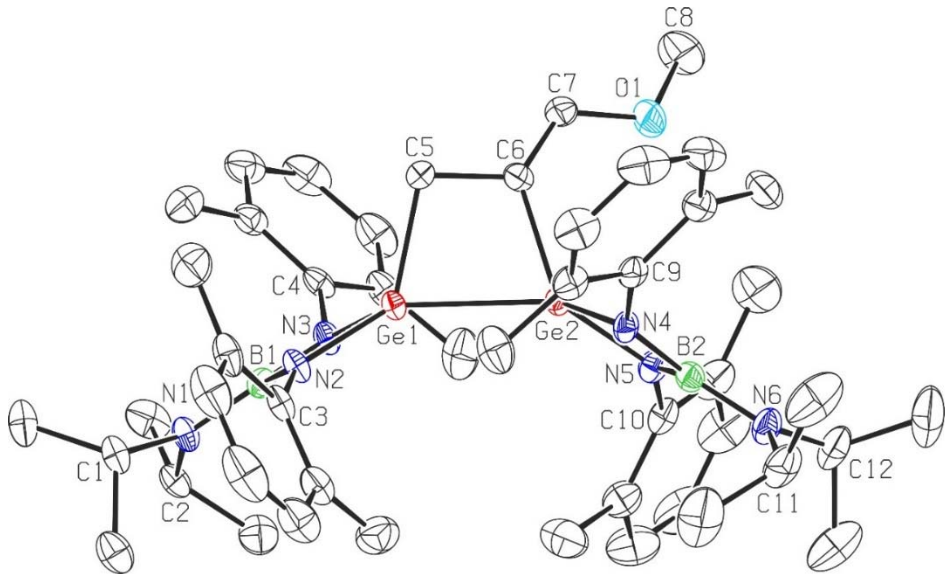


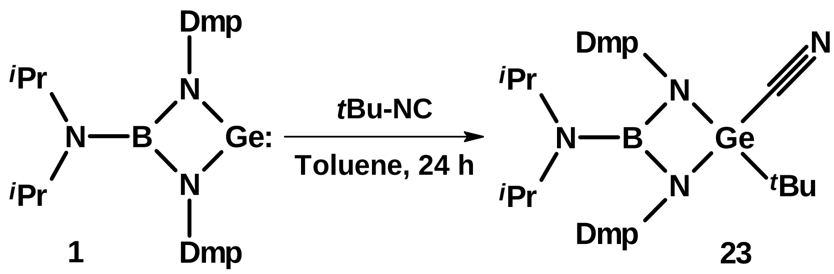
Figure 6: Molecular structure of compound **21**

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_{π} orbital of germylenes *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 *t*Bu-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**

The cyanide group was represented by one signal at 124.6 ppm in $^{13}C\{^{1}H\}$ NMR spectrum. In addition, one set of signals for the *t*Bu 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^{-1} and 2173 cm^{-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 $\Sigma r_{cov}(C,N)$ = 1,14 Å[6] for the triple bond.

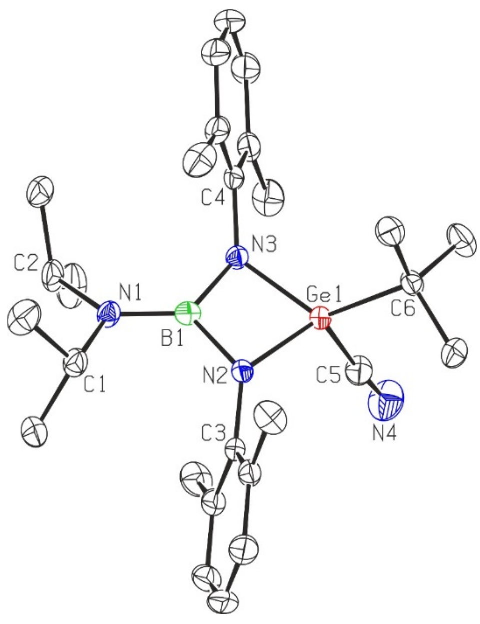
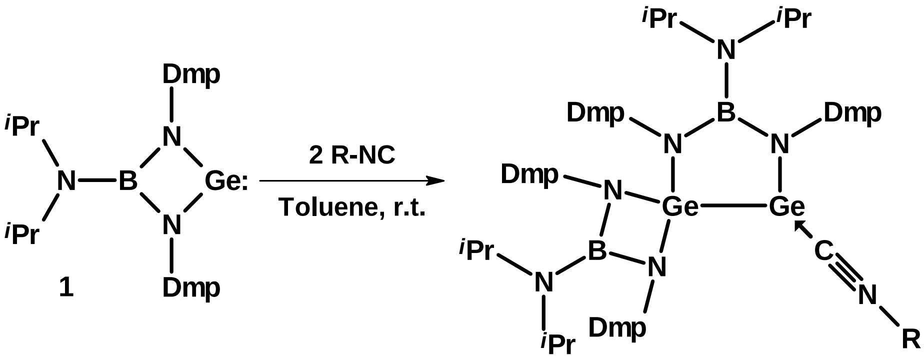


Figure 7: Molecular structure of compound **23**

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).



Compound	**24**	**25**
R	Cy	Ad

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 BGe_2N_2 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.

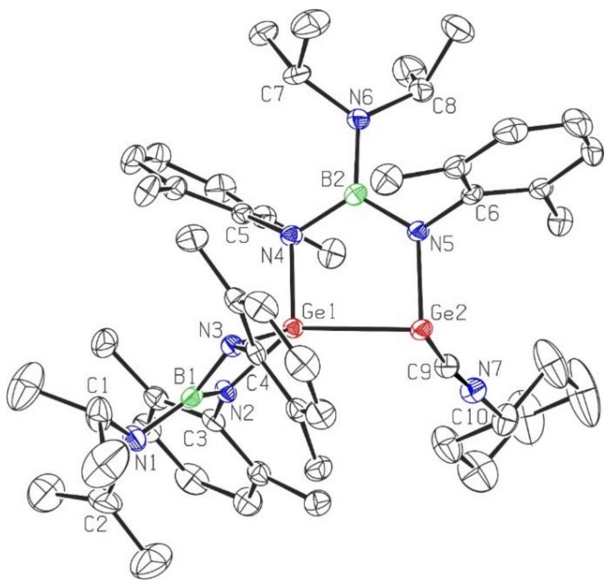
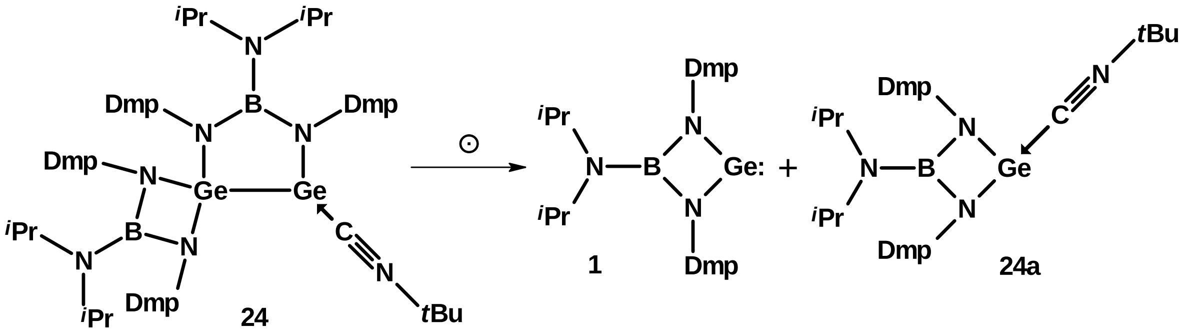


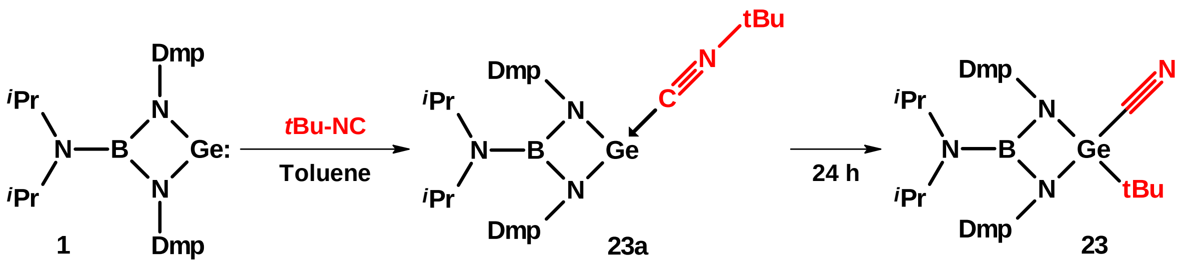
Figure 8: Molecular structure of unexpected compound **25**

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.



Scheme 14: Dissociation of selected compound **24** in solution

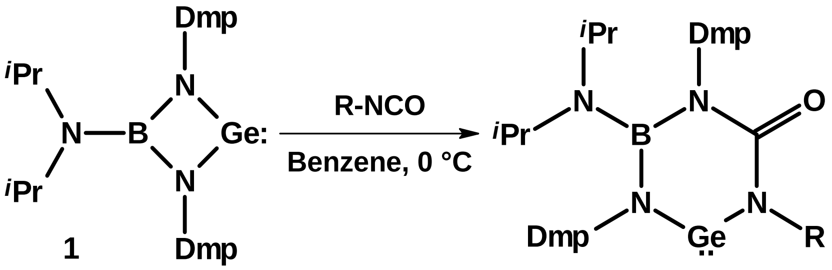
Based on this fact, the reaction between germylene **1** and *t*Bu-NC were monitored by ^{1}H NMR spectroscopy. This study also revealed the presence of the adduct **23a** (Scheme 15) showing very similar set of signals as in case of compounds **24a** and **25a** (Scheme 14). Therefore, the formation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



Scheme 15: Plausible mechanism of formation of **23**

2.5.2. Isocyanates R-NCO

The treatment of germylene **1** with isocyanates R-NCO (R = *t*Bu 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).



Compound	**26**	**27**
R	*t*Bu	Ad

Scheme 16: Preparation of new germylenes **26** and **27**

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).

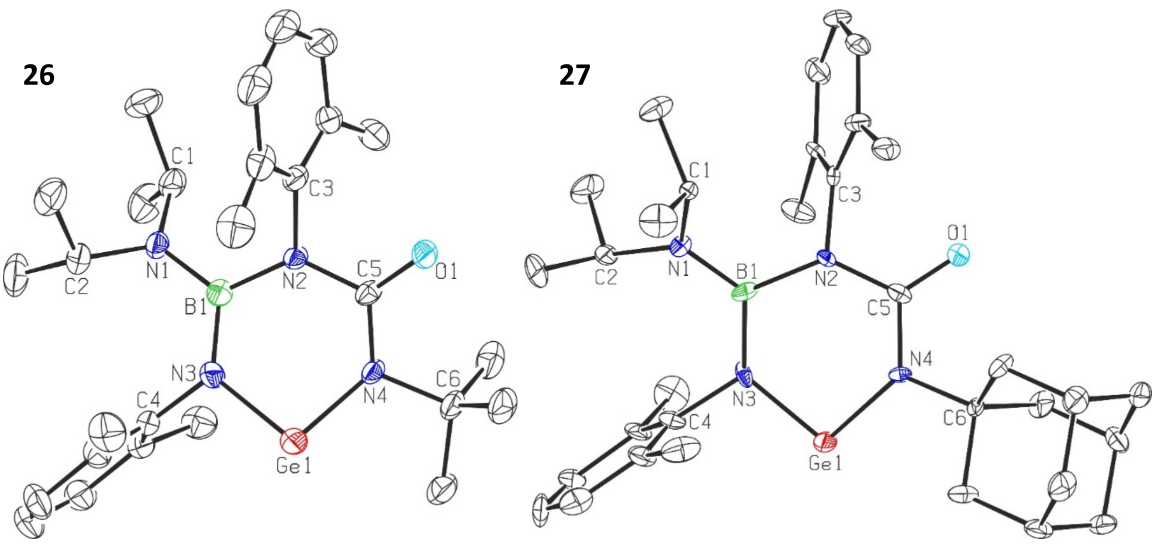
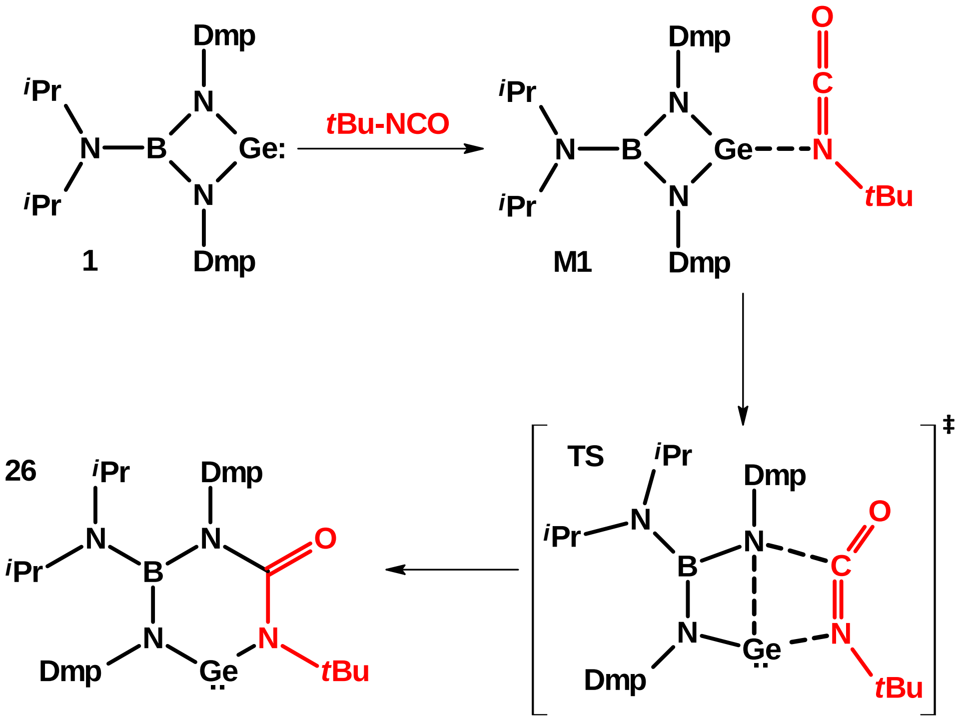


Figure 9: Molecular structure of new germylenes **26** and **27**

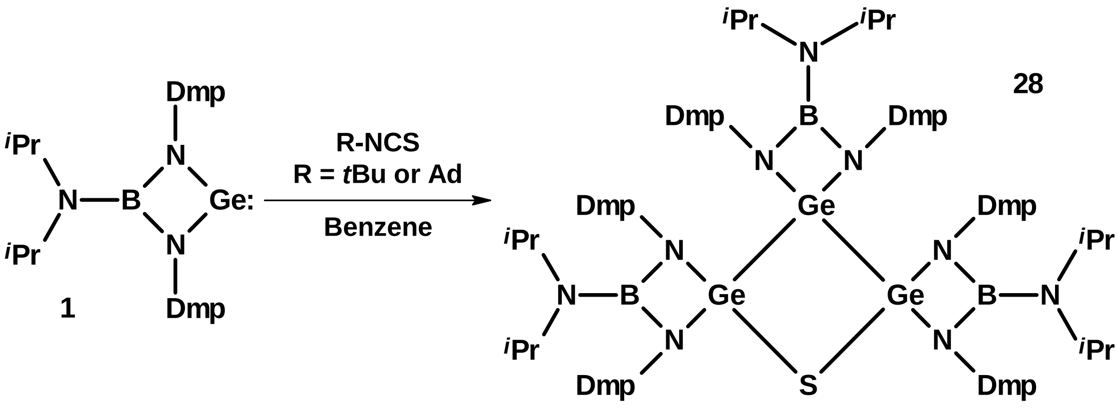
Moreover, the reaction mechanism was clarified by quantum chemical calculations. In the first step, the binding of the isocyanate moiety to germylene **1** is mediated through electron donating from the nitrogen atom to the vacant p_{π} orbital of the germylene atom (Scheme 17). The reaction mechanism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



Scheme 17: First step of reaction mechanisms leading to compound **26**

2.5.3. Isothicyanates R-NCS

The reactivity of *t*Bu-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_3S ring (Scheme 18).



Scheme 18: Preparation of unique compound **28**

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_3S ring (Figure 10).

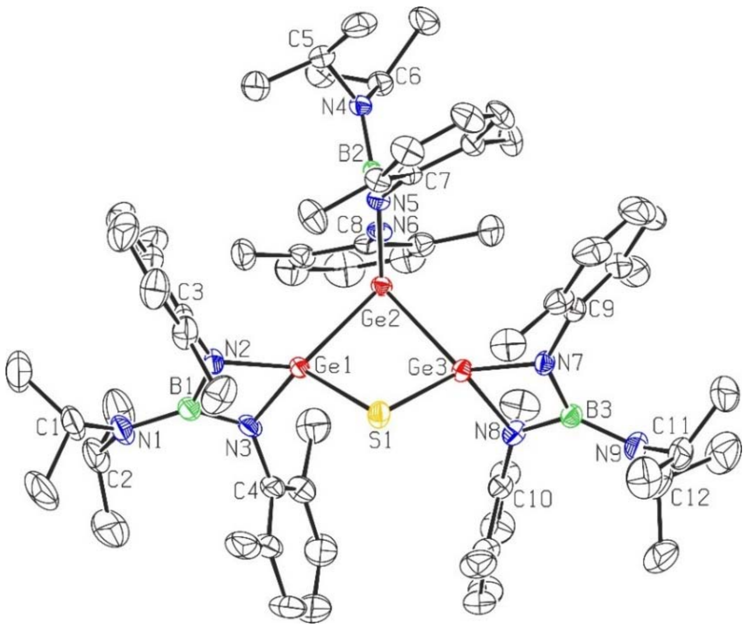
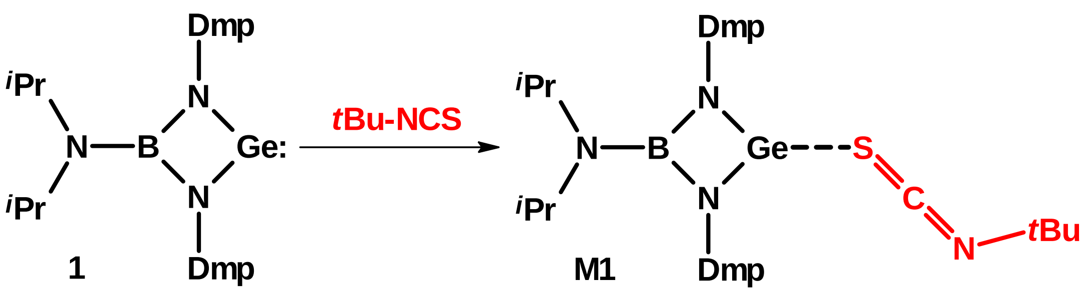


Figure 10: Molecular structure of unique compound **28**

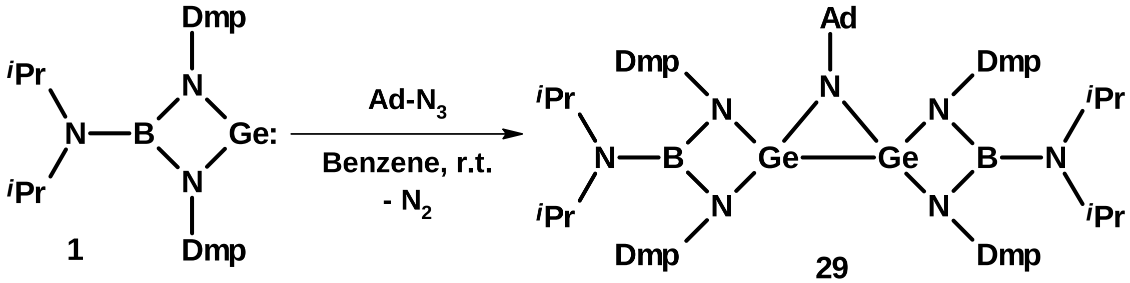
A coordination step of the reaction mechanism was simulated using the quantum chemical calculations. In contrast to isocyanate systems mentioned above (Scheme 17), isothiocyanates are coordinated to the atom of germanium *via* the sulphur atom (Scheme 19), thereby probably favouring the elimination of 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-N_3

The reaction of germylene **1** with Ad-N_3 in the stoichiometric ratio 1:1 produced an azadigermiridene compound **29**. The formation of the central three-membered Ge_2N ring was accompanied by nitrogen gas release (Scheme 20).



Scheme 20: Preparation of azadigermiridene **29**

The ^{1}H and $^{13}C\{^{1}H\}$ 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).

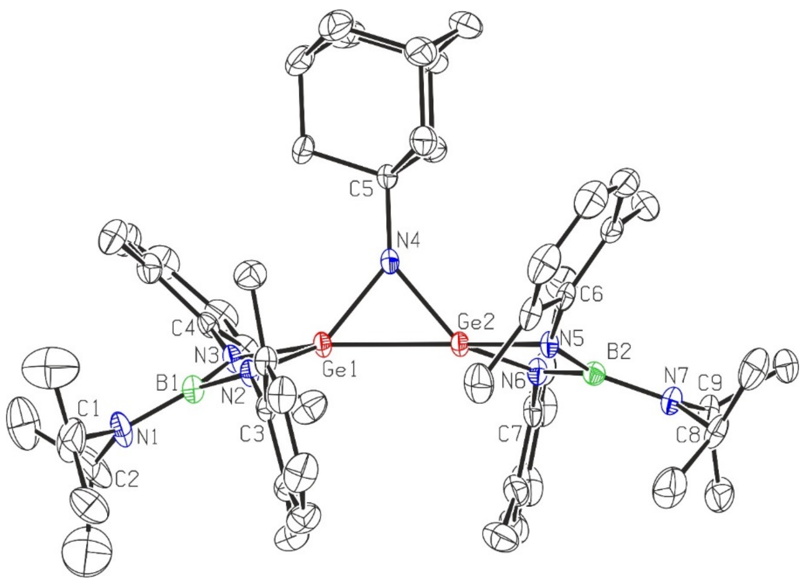
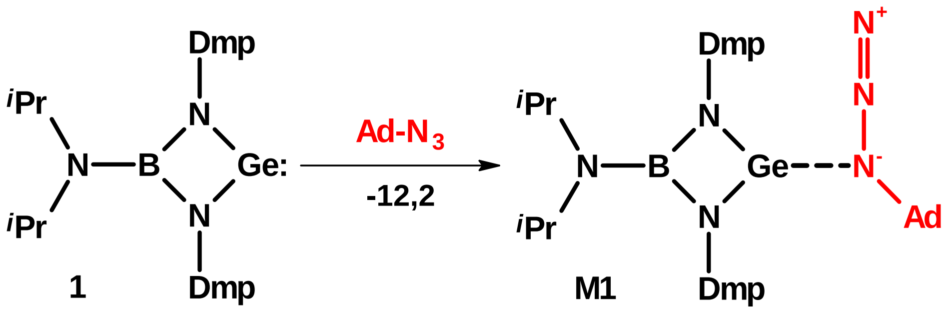


Figure 11: Molecular structure of azadigermiridene **29**

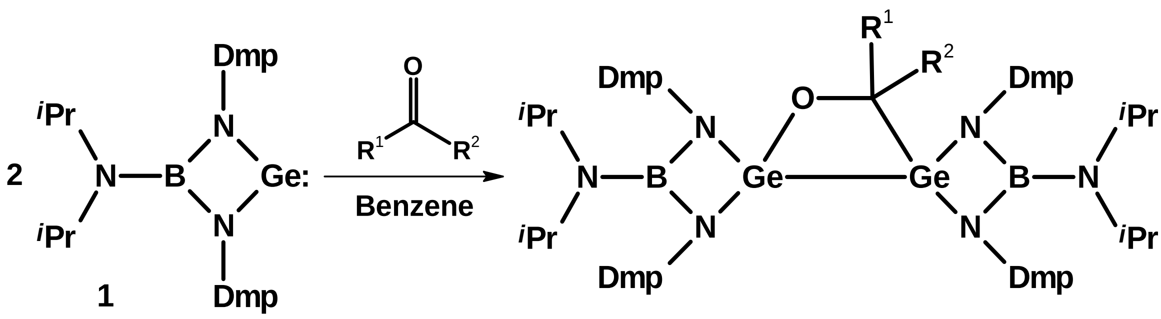
According to the reactions mentioned above in this chapter, the first step of the reaction mechanism leading to the compound **29** was optimized by quantum chemical calculations. Obtained results showed coordination of the N_3 moiety to the germanium atom through the nitrogen atom with a partial negative 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**

2.6. Reactivity of compound 1 towards fluorinated carbonyl compounds

Reactions of germylene **1** with benzaldehyde, acetone, acetophenone 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 C_6F_5-CHO and Ph-C(O)-CF_3 led to the formation of compounds **30** and **31** containing the central CGe_2O 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).

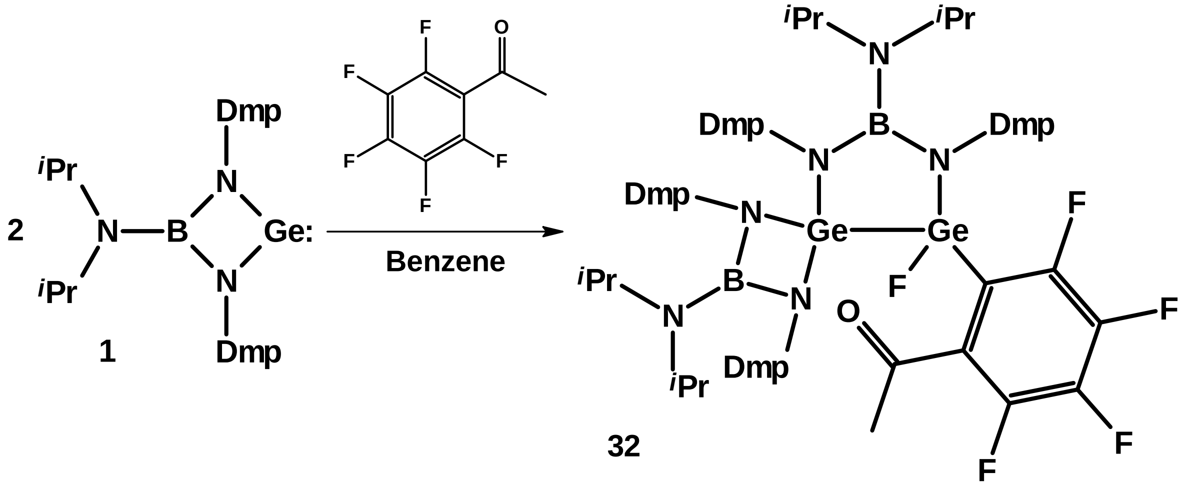


Compound	**30**	**31**
R^1	C_6F_5	Ph
R^2	H	CF_3

Scheme 22: Preparation of compounds **30** and **31** containing the central CGe_2O ring

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_6F_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_2O ring was reflected in the $^{13}C\{^1H\}$ 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_6F_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_2N_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

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 $^{13}C\{^1H\}$ 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 (Σ_{rcov}(Ge,O) = 1.84 Å)[6] was found in the molecular structure obtained by X-Ray diffraction analysis (Figure 12).

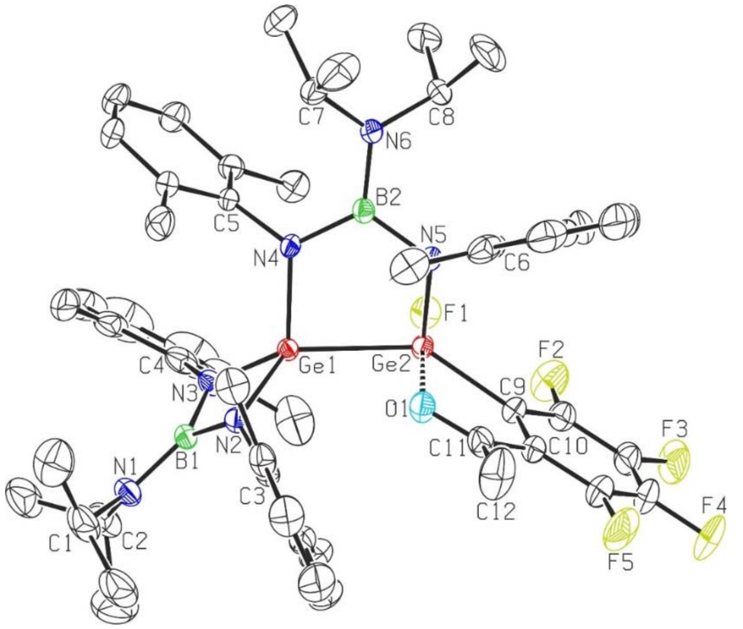
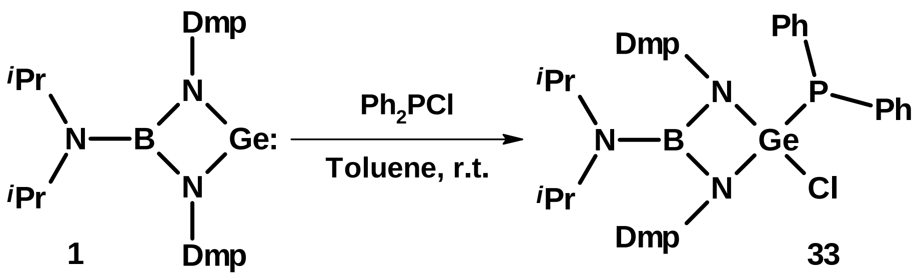


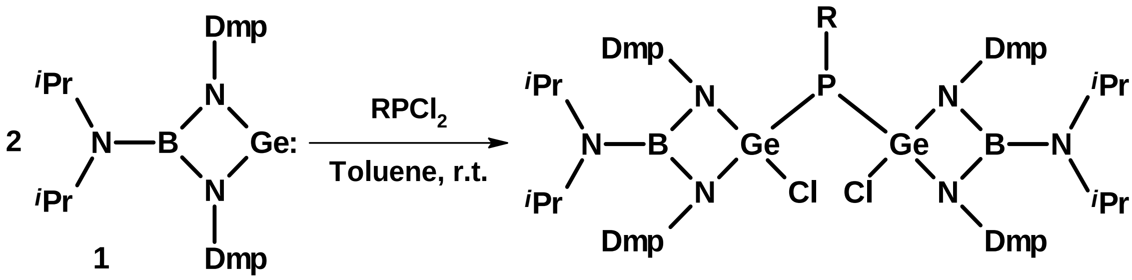
Figure 12: Molecular structure of unexpected compound **32**

2.7. Reactivity of compound 1 towards substituted chlorophosphines

Base on the previous results proving that germylenes are able to insert toward various element-halogen or element-hydrogen bonds, germylene **1** was treated with a variety of compounds containing B-H ($H_3B.S(Me)_2$), B-Cl ($PhBCl_2$), Al-Cl ($EtAlCl_2$), Si-H (Ph_3SiH, Ph_2SiH_2), Si-Cl (Me_2SiCl_2), Sn-Cl (Me_2SnCl_2), P-Cl (PH_2PCl, $RPCl_2$ a PCl_3) or N-H (NH_3) bond. However, only reactions of germylene **1** with Ph_2PCl (Scheme 24) or $RPCl_2$ (R = *t*Bu 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).



Scheme 24: Preparation of insertion product **33**



Compound	**34**	**35**
R	*t*Bu	Ph

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

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.

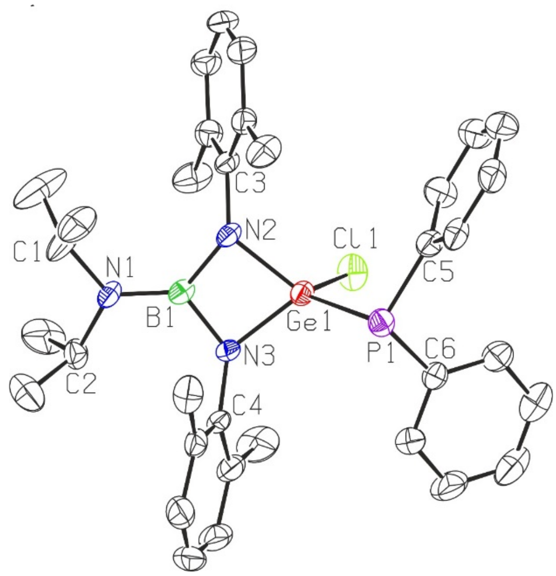


Figure 13: Molecular structure of compound **33**

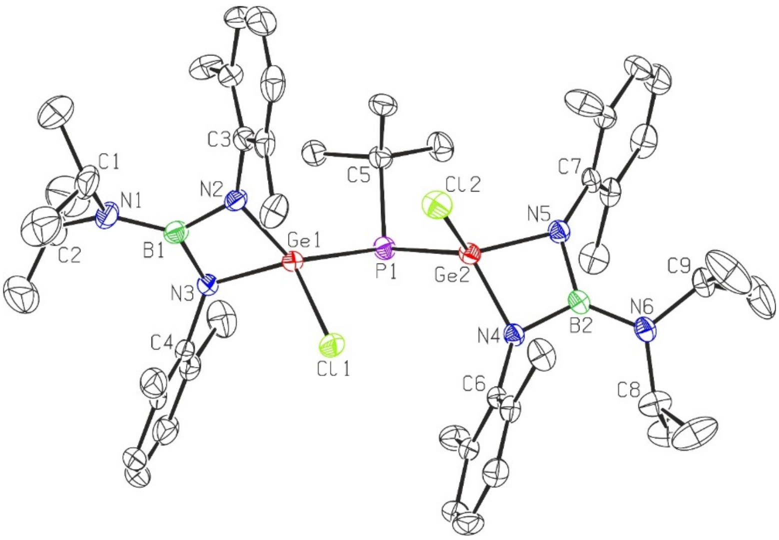


Figure 14: Molecular structure of compound **34**

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.

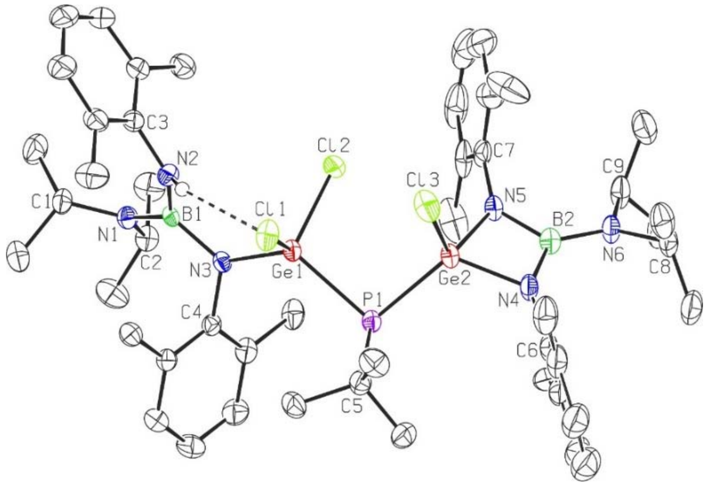
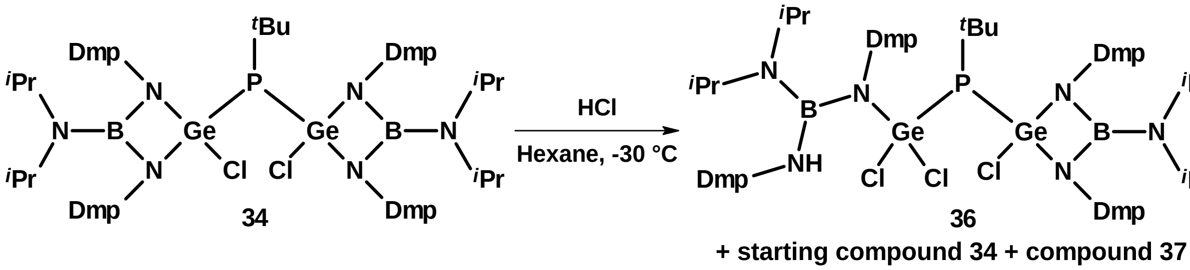


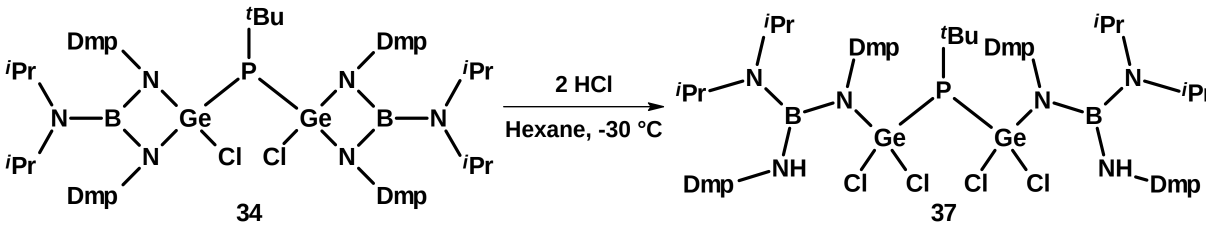
Figure 15: Molecular structure of unexpected compound **36**

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}H NMR spectra. The formation of the compound **37** was recognized by the signal at 17.6 ppm in ^{31}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 cased 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-N_3 was obtained producing also new types of germylenes **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 germylenes 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

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5. Published Works

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

A. Böserle J., Zhigulin G., Štěpnička P., Horký F., Erben M., Jambor R., Růžička A., Ketkov S., Dostál L.; Facile Activation of Alkynes with a Boraguanidinato-Stabilized Germylene: combined Experimental and Theoretical Study, *Dalton Trans.*, **2017**, 46, 12339.

B. Böserle J., Jambor R., Erben M., Horký F., Štěpnička P., Růžička A., Dostál L.; Reactivit of an N,N-chelated germylene toward substituted alkynes, alkenes and allenes, to be submitted to *Eur. J. Inorg. Chem.*

C. Böserle J., Zhigulin G., Ketkov S., Jambor R., Růžička A., Dostál L.; Diverse Reactivity of a Boraguanidinato Germylene toward Organic Pseudohalogens, under revision in *Dalton Trans.*

D. Böserle J., Jambor R., Růžička A., Dostál L.; Insertion of the N,B,N-chelated Germylene into P-Cl Bond(s) in Selected Chlorophosphines, *J. Organomet. Chem.*, **2018**, 855, 44.