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Stabilized Germylenes Based on Diethylenetriamines and Related Diamines: Synthesis, Structures, and Chemical Properties

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A series of novel, low-valent germanium compounds **2a**–**2j** based on four diethylenetriamines **1a**–**1d**, (methyl)bis(pyrrol-2-ylmethyl)amine (**1e**), *N*,*N*′-(sulfanediyldibenzene-2,1-diyl)bis(pentafluoroaniline) (**1f**), *N*,*N*′-(oxydibenzene-2,1-diyl)bis(pentafluoroaniline) (**1g**), and (pentafluorophenyl)amines **1i** and **1j** have been obtained either by the reaction of Ge[N(SiMe$_3$)$_2$]$_2$ with various diamines (**1a**–**1e**) or by the metathesis reaction of [GeCl$_2$·dioxane] with lithium amides. The oxidative insertion (with halogenation reagents, MeI, disulfides), [1+4] cycloaddition, and oxidation reactions of the synthesized germylenes were investigated. The compositions and structures of the novel compounds were established by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, and X-ray diffraction analysis (germylenes **2b**, **2i**, **2j**, Ge^{4+} compounds **5b**, **7a**, **7b**, **8**, **10**, **11**). All the synthesized germylenes are monomeric.

Introduction

Compounds containing low-valent group 14 elements have attracted interest as models for highly important derivatives of electron-deficient carbon analogues of carbenes. In addition, the study of silylenes, germylenes, and stannylenes is also important because of their use as catalysts in organic processes such as ring-opening polymerization (ROP)[1] and as precursors for the synthesis of superconducting materials by metal-organic chemical vapor deposition (MOCVD) processes.[2] In general, these compounds are very reactive, thus additional stabilization is required. Usually, the stabilization of an electron-deficient center is realized by ligand design, balancing the inverse relationship between stability and reactivity. Two different approaches may be marked out: thermodynamic and/or kinetic stabilization of the reactive vacant p-orbital of the low-valent group 14 element. Bulky substituents in the ligand lead to kinetic stabilization, whereas thermodynamic stabilization arises from the structure of the ligand, with some groups possessing the ability to donate additional lone-pair electrons, such as a Cp ligand and neutral N and O atoms (π-donating –OR and –NR$_2$ groups). The electron stabilization may be a result of an additional transannular interaction of the metal centre with a donor group. Note that diamidogermylenes and dialkoxy(aryloxy)germylenes are sufficiently stable to be studied as "usual" molecular substances by appropriate techniques.

At the same time, germylenes of the formulae Ge(OR)$_2$ and M(NR$_2$)$_2$ are able to exist in the dimeric state with the metal atoms of one monomeric unit forming an additional bond with an O or N atom of the other unit. Typically, these dimers are less reactive than monomeric "heavier" carbenes.

Among the diamidogermanium(II) derivatives, two-coordinate Arduengo-type N-heterocyclic germylene (NHGe) compounds are widely known.[3] The reactivities of these compounds have been studied to a much greater extent than those of other diamidogermylenes. In addition, the stabilities and reactivities of NHGes are very different to those of other divalent amino-substituted derivatives of group 14 elements.

In our opinion, the dianions of diethylenetriamines, RN(CH$_2$CH$_2$N$^-$R′)$_2$, are very promising ligands for the stabilization of monomeric structures of germylenes for the following reasons: (1) the possible additional transannular interaction with the nitrogen atom of the ligand and (2) the possibility of easily designing the structures of such ligands, for example replacing the H atoms of NH groups with different substituents. The latter allows the electron properties of the central atom to be changed by varying the electron

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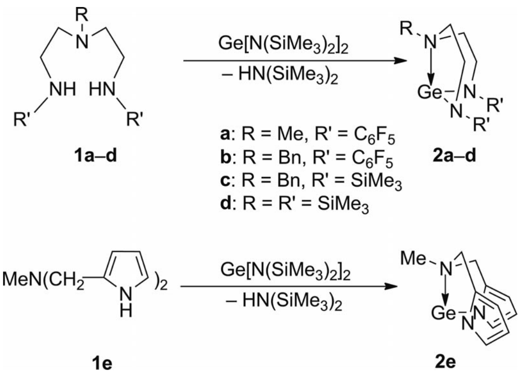
properties of these substituents. We also suppose that the stabilization of the low-valent centre bound to these ligands should be achieved not only by electronic effects but also by kinetic factors, namely due to bulky substituents at nitrogen atoms covalently bound to the atom of the group 14 elements. To date, only two divalent derivatives of group 14 elements containing diethylenetriamine as a ligand have been described. These are $MeN(CH_2CH_2NSiMe_3)_2Sn$ and $MeN(CH_2CH_2N\textit{i}Pr)_2Sn$.[4] No germanium analogues have yet been prepared. There is only one example of a germylene derivative stabilized by N_2N coordination, $[MeSi(\mu\text{-}N\textit{t}Bu)_2SiMe(\textit{t}BuN)_2]Ge$.[5]

In this paper we describe the synthesis and chemical properties of the new germylenes **2a**–**e** with N_2N coordination based on diethylenetriamine ligands **1a**–**e**, the structural determination of the compounds obtained and their structure–property correlations. Germylenes **2f**–**j** based on a set of novel chelating bis(diarylamido) ligands were prepared for comparison. This work forms a part of our studies on the synthesis and investigation of "heavy carbene" analogues stabilized by polydentate ligands.[6]

Results and Discussion

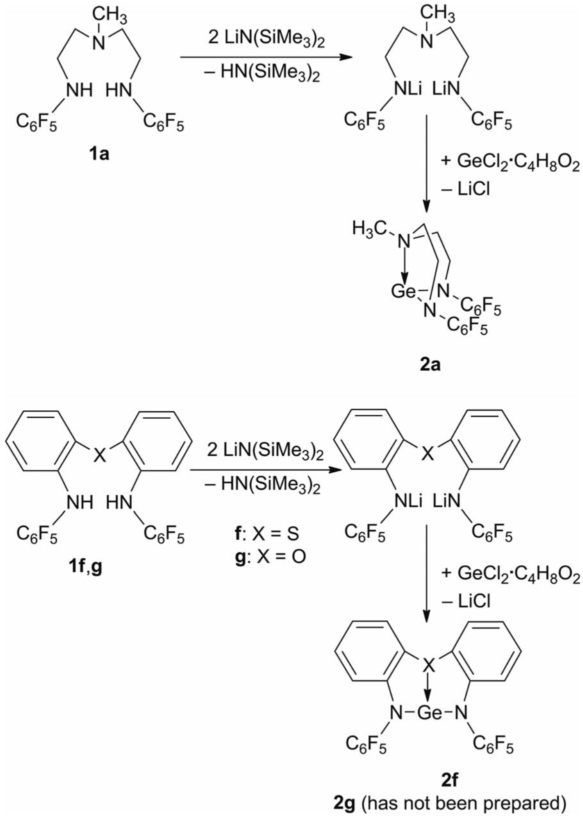
Germylene Synthesis

There are two general approaches to the preparation of the target diamidogermylenes. The first is based on the transamination of diethylenetriamine ligands with aminogermylenes such as Lappert's germylene, $Ge[N(SiMe_3)_2]_2$.[7] The second approach consists of using complexes of dihalogermylenes such as $[GeCl_2{\cdot}1,4\text{-dioxane}]$ and the dilithium salts[8] of the corresponding triamines.



Scheme 1. Synthesis of germylenes **2a**–**e** by the transamination reaction.

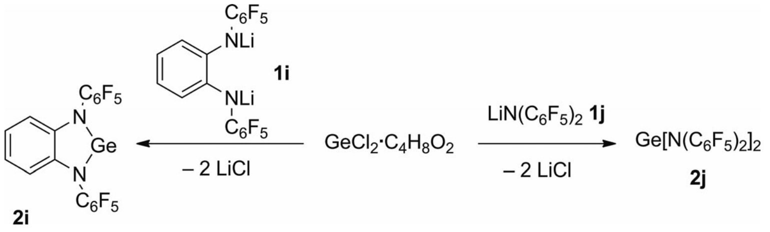
Germylenes **2a**–**e** were synthesized under mild conditions by the first method (Scheme 1). The yields of the target products were 40–60% and depended on the nature of the ligand. In addition, **2a** was obtained in 24% yield by reaction of the dilithium salt of amine **1a** and $[GeCl_2{\cdot}dioxane]$. This shorter synthetic protocol does not require the isolation of intermediates, but it gives a lower yield of **2a** (Scheme 2).



Scheme 2. Synthesis of germylenes **2a** and **2f** by using dilithium salts of the corresponding amines.

In contrast to the complexes based on the ligands **1a**–**c** and **1e**, the complex derived from *N*-silylated amine **1d** is very unstable. The generation of complex **2d** during the reaction was determined only by NMR spectroscopy (Scheme 1).

We also tested the lithium salt metathesis route for the preparation of closely related germylenes based on aromatic diamines **1f** and **1g**, which are easily prepared by the nucleo-



Scheme 3. Synthesis of germylenes **2i** and **2j** by using the lithium salts of the corresponding amines.

philic aromatic amidation of C_6F_6. Interestingly, although germylene **2f** with an additional sulfur donor group could be prepared, the corresponding germylene **2g** with an oxygen donor could not be prepared neither by the reaction of the dilithium salt of **1g** with [$GeCl_2$·dioxane] nor by transamination between $Ge[N(SiMe_3)_2]_2$ and **1g** (Scheme 2).

Furthermore, diamidogermylenes **2i** and **2j** with two-coordinate germanium atoms were synthesized by lithium salt metathesis with lithium (pentafluorophenyl)amides **1i** and **1j**, respectively (Scheme 3). The complexes **2i** and **2j** contain no additional intra- or intermolecular bonding interactions and they are sufficiently stable to study their molecular structures by XRD analysis.

Germylene Molecular Structures

The subvalent Ge^{II} centers in the two diamagnetic compounds **2i** and **2j** are stabilized by the weak π-interactions between the electron pairs of the anionic nitrogen donor atoms and the vacant orbital at the central atom. In addition, the empty orbital at Ge in **2i** should be stabilized by the electron density of the nonfluorinated aromatic system, as discussed in similar systems by Arduengo et al.[9] On the other hand, the lone pair on Ge^{II} seems to be particularly well stabilized by the highly fluorinated amide ligands with relatively high electronegativity.

To gain more insight into the bonding, the X-ray crystal structures of **2b**, **2i**, and **2j** were determined. Their molecular structures are shown in Figures 1, 2 and 3. They are all monomeric in the solid state. Compounds **2i** and **2j** each possess a two-coordinate germanium atom, as in the previously studied $Ge[N(SiMe_2R)_2]_2$ (R = Me,[10] *i*Pr[11]) and $Ge(NR^1R^2)_2$ (NR^1R^2 = 2,2,5,5-tetramethylpiperidyl, TMP).[12] The Ge–N bond lengths in **2i** and **2j** are within the range found for other Ge^{2+} amides (1.87–1.91 Å).[10–12] The N–Ge–N angle in **2j** [97.88(9)°] is larger than that in **2i** [83.45(14)°]. This can be attributed to greater steric interligand repulsion in **2j**. However, both of these angles are smaller than those [105.26(8)–111.4(5)°] observed in other Ge^{2+} amides[10–12] due to sterically less hindered ligands.

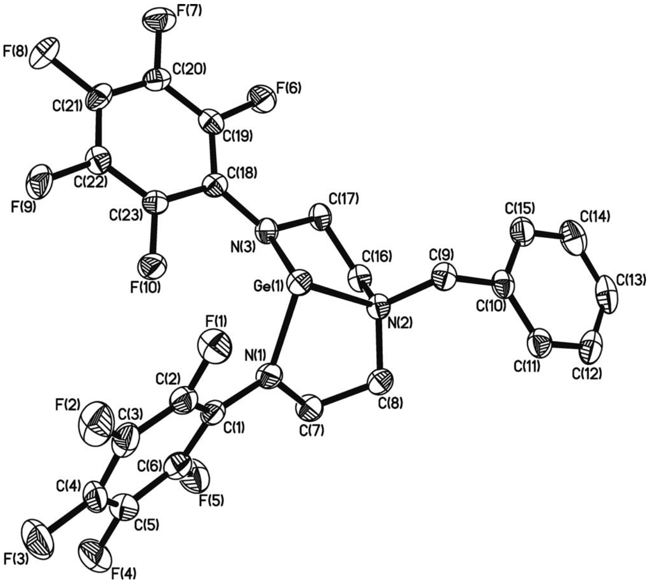


Figure 1. Molecular structure of **2b**. ORTEP diagram with elipsoids drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: N(1)–Ge 1.943(2), N(2)–Ge(1) 2.112(2), N(3)–Ge(1) 1.984(2); N(1)–Ge(1)–N(3) 102.48(10), N(1)–Ge(1)–N(2) 83.11(10), N(3)–Ge(1)–N(2) 82.36(10).

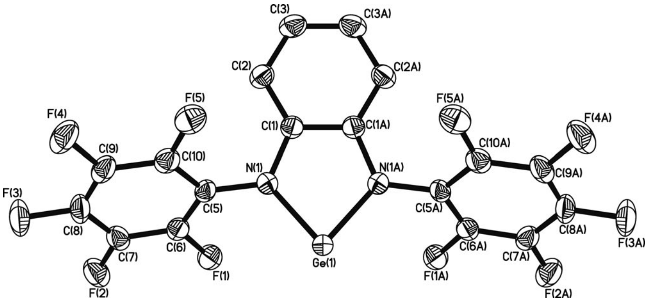


Figure 2. Molecular structure of **2i**. ORTEP diagram with elipsoids drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: N(1)–Ge 1.887(2), N(1A)–Ge(1) 1.887(2); N(1)–Ge(1)–N(1A) 83.45(14); N(1A)–Ge(1)–N(1)–C(1) –0.3(2), N(1A)–Ge(1)–N(1)–C(5) –174.94(18).

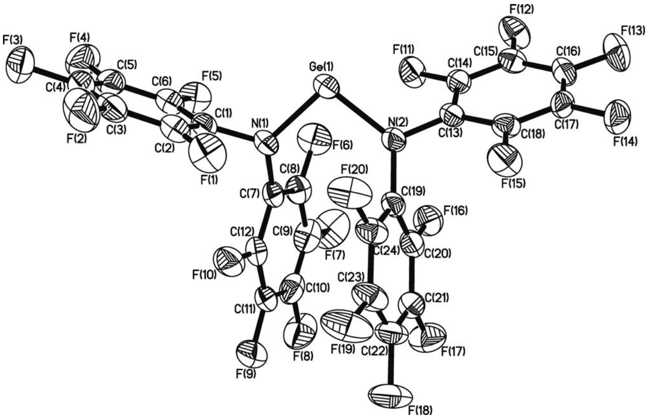


Figure 3. Molecular structure of **2j**. ORTEP diagram with elipsoids drawn at the 50% probability level. Selected interatomic distances [Å] and angles [°]: N(1)–Ge 1.871(2), N(2)–Ge(1) 1.877(2); N(1)–Ge(1)–N(2) 97.88(9).

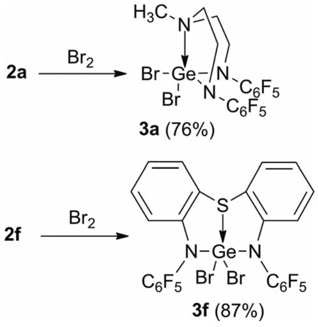
For germylene **2b**, the primary coordination environment of the Ge atom is formed by two covalently bonded nitrogen atoms and one dative-bonded nitrogen atom and may be treated as a trigonal pyramid with a lone pair in one vertex. To the best of our knowledge, this is the first example of an X-ray-studied monomeric germylene with an N_2N coordination environment. One can compare the N→Ge bond in **2b** with that in a monomeric compound with a tricoordinate germanium atom having an O_2N coordination environment, $Py(CH_2CPh_2O)(CH_2CMe_2O)Ge$.[13] The N→Ge bond length [2.112(2) Å] in **2b** is similar to that in $Py(CH_2CPh_2O)(CH_2CMe_2O)Ge$ [2.110(1) Å].[13] The covalent bonds Ge(1)–N(1) [1.943(2) Å] and Ge(1)–N(3) [1.984(2) Å] are longer than those in diamides with two-coordinate germanium atoms $Ge[N(SiMe_3)_2]_2$ [Ge–N

1.876(5) Å avg.],[10] Ge[TMP]$_2$ [Ge–N 1.89(1) Å avg.],[12] **2i**, and **2j** (see above). The elongation is caused by an additional intramolecular interaction in **2b**. The Ge(1)–N(2) bond is nearly perpendicular to the N(1)–Ge(1)–N(3) plane, which allows the ideal interaction of the nitrogen lone-pair electron with the vacant Ge orbital. The five-membered cycles –Ge(1)–N(1)–C(7)–C(8)–N(2)– and –Ge(1)–N(3)–C(17)–C(16)–N(2)– adopt "envelope" conformations, whereas the eight-membered ring –Ge(1)–N(1)–C(7)–C(8)–N(2)–C(16)–C(17)–N(3) has a "boat-chair" conformation.

Germylene Reactivity

As systematic reactivity studies of germylenes are still a focus of interest, we investigated the classic reactions of germylene chemistry, such as insertion, oxidative addition, and cycloaddition reactions, for the compounds obtained in this work.

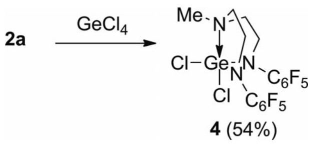
One of the best known reactions of such compounds is the oxidative halogen addition, which results in Ge^{IV} derivatives.[13,14] In this work the reactions of monomeric germylenes **2a** and **2f** with bromine were investigated (Scheme 4). Compounds **2a** and **2f** reacted with bromine at room temperature by the insertion of the germylenes into the Br–Br bond to give the expected dibromides in high yields.



Scheme 4. Halogenation of germylenes **2a** and **2f** with bromine.

The halogenation of "heavy carbenes" may be performed not only with halogens but also with other halogen-containing derivatives. Several examples of such reactions have been described.[4,14,15] MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$Sn reacts with BiCl$_3$, the tin atom abstracting two chlorine atoms from the trichloride to form MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$SnCl$_2$.[4] If PCl$_3$ was used for halogenation, the ionic complex [MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$P$^+$SnCl$_3^-$] was formed.[4] In contrast, Veith's germylene Me$_2$Si(N*t*Bu)$_2$Ge reacts with PCl$_3$ by a three-fold insertion into the P–Cl bonds to form [Me$_2$Si(N*t*Bu)$_2$Ge(Cl)]$_3$P.[14]

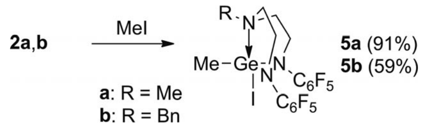
We studied for the first time the reaction of germylenes with GeCl$_4$ as halogenating reagent. The pentacoordinated germanium derivative **4** with an oxidation number 4+ was obtained (Scheme 5). The main driving force for the reaction is the formation of the insoluble polymeric [GeCl$_2$]$_n$ with the product **4** bearing a transannular interaction.



Scheme 5. Halogenation of germylene **2a** by reaction with GeCl$_4$.

Germylenes can also undergo another type of reaction by insertion into C–Hal bonds. In particular, for the characterization of "heavy carbenes" the reaction with methyl iodide is often used.[15a,16] However, in addition, a number of papers have been published concerned with a three-component reaction between germylenes, organic substrate, and RX (R = Ph, *t*Bu, Me; X = I, Br, Cl) as a novel method of C–H activation in quite inert organic substrates such as alkanes, alkenes, and alkynes and even a regioselective reaction in ethers and nitriles.[17]

The iodogermanes **5a** and **5b** were easily obtained by the oxidative addition of MeI (Scheme 6) and fully characterized by spectroscopic methods. The product **5b** was also characterized by X-ray diffraction analysis (Figure 4). Only one example of a reaction of methyl iodide and a germylene, in which the germanium atom is bonded to two nitrogen atoms, has been described,[16b] but the molecular structure of the resulting iodogermane, [HC(CMeNAr)$_2$]GeMe$_2$(I) (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$), was not studied by X-ray analysis.



Scheme 6. Oxidative addition of MeI to germylenes **2a**,**b**.

The germanium atom in **5b** is present in a distorted bipyramidal environment. The I(1)–Ge(1)–X(eq) [X = equatorial substituent N(11), N(21), C(1)] bond angles are in the range 92.99(10)–94.48(9)° and approach the idealized bipyramidal value of angles between axial and equatorial substituents (90°). The Ge–N bond lengths in germylene **2b** have an average value of 1.964(2) Å and the shorter Ge–N bond length [1.856(3) Å] in **5b** is a result of the higher oxidation state of germanium in this complex. The Ge–C bond length in **5b** is 1.940(3) Å and is typical of a Ge–C single bond, and the Ge–I bond length of 2.7599(5) Å is similar to the Ge–I bond length in (acac)GeI [acac = acetylacetonato; 2.7360(3) Å].[18] However, the Ge–I bond in **5b** is longer than the usual Ge–I bond length.[17b] This fact can be explained by the formation of a transannular interaction.

It is known that [GeBr$_2$·C$_4$H$_8$O$_2$] reacts with allyl bromide by insertion of Ge into the C–Br bond.[19] Unfortunately, our efforts to carry out the reaction between **2a** and allyl bromide failed due to unselective side-reactions.

We investigated the reactions of our germylenes with both diphenyl and diethyl disulfide (Scheme 7).[15a] It was found that the structure of the disulfide determines the behavior of the germylenes in question. Germylene **2b** reacted easily at –40 °C with diphenyl disulfide to form the corre-

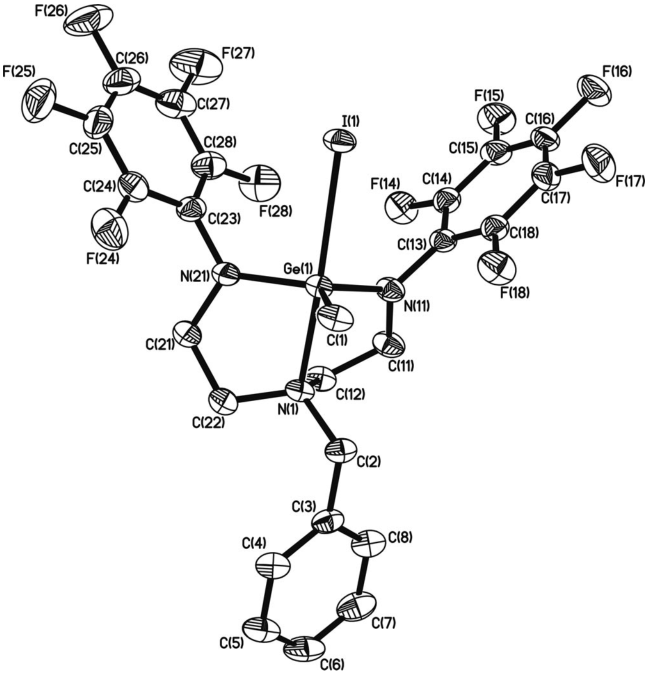
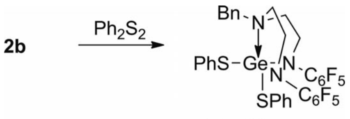


Figure 4. Molecular structure of **5b**. ORTEP diagram with elipsoids drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: N(1)–Ge(1) 2.166(3), N(11)–Ge(1) 1.858(3), N(21)–Ge(1) 1.854(3), C(1)–Ge(1) 1.940(3), I(1)–Ge(1) 2.7599(5); N(21)–Ge(1)–N(11) 121.13(14), N(21)–Ge(1)–C(1) 116.52(15), N(11)–Ge(1)–C(1) 121.03(15), N(21)–Ge(1)–N(1) 81.52(11), N(21)–Ge(1)–N(11) 121.13(14), N(11)–Ge(1)–N(1) 81.55(11), C(1)–Ge(1)–N(1) 95.80(12), N(21)–Ge(1)–I(1) 93.97(9), N(11)–Ge(1)–I(1) 94.48(9), C(1)–Ge(1)–I(1) 92.99(10), N(1)–Ge(1)–I(1) 171.18(7).

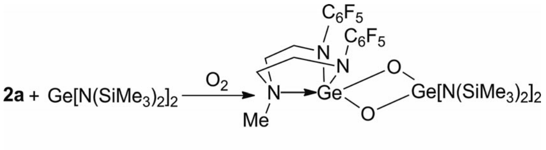
sponding disulfide adduct **6**. But this was not the case with diethyl disulfide even under irradiation with ultraviolet light. This can be attributed to the greater strength of the S–S bond in diethyl disulfide compared than in diphenyl disulfide. The relative reactivities of the germylenes based on diethylenetriamines with disulfides are similar to those found earlier for germanium(II) dialkanolamine derivatives.[6]



6 (77%)

Scheme 7. Insertion of germylene **2b** into Ph_2S_2.

Germylenes are affected by oxidants such as dioxygen and sulfur. When $(ArO)_2Ge$ reacts with sulfur, germanethione compounds with a highly dipolar “Ge=S” bond are formed, as indicated by cryoscopy.[20] The reaction of monomeric $[(Me_3Si)_2N]_2Ge$ with molecular oxygen gives rise to crystalline 1,3-digermadioxetane, $[([Me_3Si]_2N)_2Ge(\mu\text{-}O)]_2$, characterized by NMR and X-ray analysis.[21] It is supposed that the 1,3-digermadioxetane results from the germanone originally obtained. Note that in the course of the purification of **2a** from starting $Ge[N(SiMe_3)_2]_2$ we obtained a trace amount of mixed 1,3-digermadioxetane **7a** (Scheme 8), which is formed by the oxidation of a mixture of the two germylenes **2a** and $Ge[N(SiMe_3)_2]_2$ with molecular oxygen. The structure of **7a** was studied by X-ray analysis (Figure 5). The result also confirms that 1,3-digermadioxetane is formed via germanone. Instead of oxygen, trimethylamine *N*-oxide has recently been widely used.[22]



7a

Scheme 8. Formation of complex **7a**.

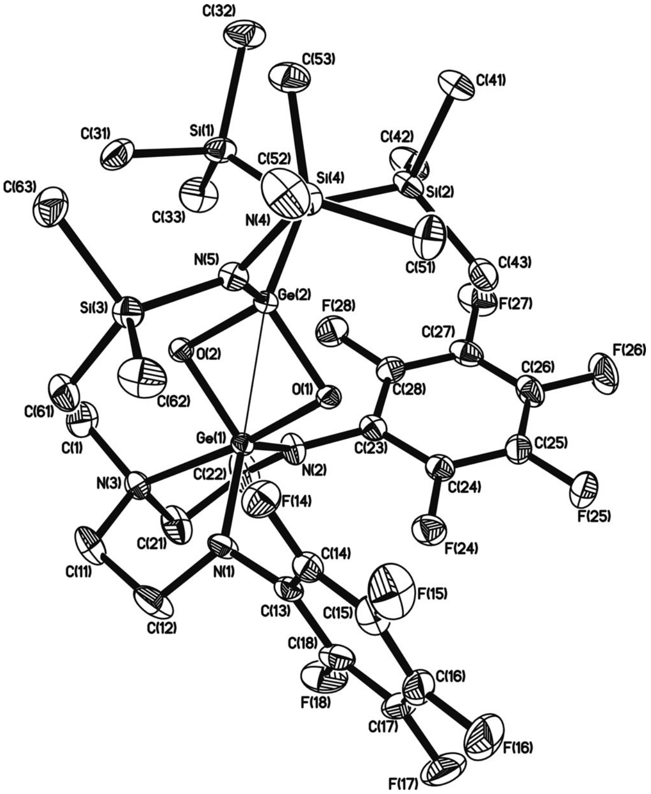
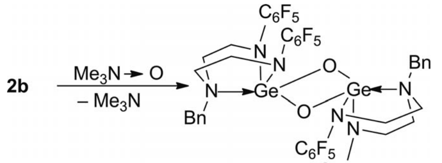


Figure 5. Molecular structure of **7a**. ORTEP diagram with elipsoids drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ge(1)–N(2) 1.8555(16), Ge(1)–N(1) 1.8485(15), Ge(1)–N(3) 2.1542(15), Ge(1)–O(1) 1.8463(12), Ge(1)–O(2) 1.8128(13), Ge(1)–Ge(2) 2.6370(3), Ge(2)–N(5) 1.8366(15), Ge(2)–N(4) 1.8411(15), Ge(2)–O(1) 1.7856(12), Ge(1)–O(2) 1.7968(12); O(2)–Ge(1)–O(1) 85.37(5), O(2)–Ge(1)–N(1) 118.71(7), O(1)–Ge(1)–N(1) 99.62(6), O(2)–Ge(1)–N(2) 119.70(7), O(1)–Ge(1)–N(2) 101.99(6), N(1)–Ge(1)–N(2) 118.66(7), O(2)–Ge(1)–N(3) 88.02(6), O(1)–Ge(1)–N(3) 173.27(6), N(1)–Ge(1)–N(3) 82.47(6), N(2)–Ge(1)–N(3) 82.40(6), N(1)–Ge(1)–Ge(2) 116.51(5), N(2)–Ge(1)–Ge(2) 118.12(5), N(3)–Ge(1)–Ge(2) 130.84(4), O(1)–Ge(2)–O(2) 87.66(6), O(1)–Ge(2)–N(5) 118.98(6), O(2)–Ge(2)–N(5) 113.65(6), O(1)–Ge(2)–N(4) 113.85(6), O(2)–Ge(2)–N(4) 108.58(6), N(5)–Ge(2)–N(4) 111.59(7), N(5)–Ge(2)–Ge(1) 128.27(5), N(4)–Ge(2)–Ge(1) 119.60(5), Ge(2)–O(1)–Ge(1) 93.10(6), Ge(2)–O(2)–Ge(1) 93.86(6).

To investigate the stabilizing effect of diethylenetriamines on the few germanium derivatives with a zwitterionic “Ge=O” bond, we carried out the reaction between germylene **2b** and $Me_3N{\rightarrow}O$ (Scheme 9). As expected, the oxidation product was obtained in 42% yield, and its structure was confirmed by X-ray diffraction analysis (Figure 6).



7b (42%)

Scheme 9. Oxidation of germylene **2b** by trimethylamine *N*-oxide.

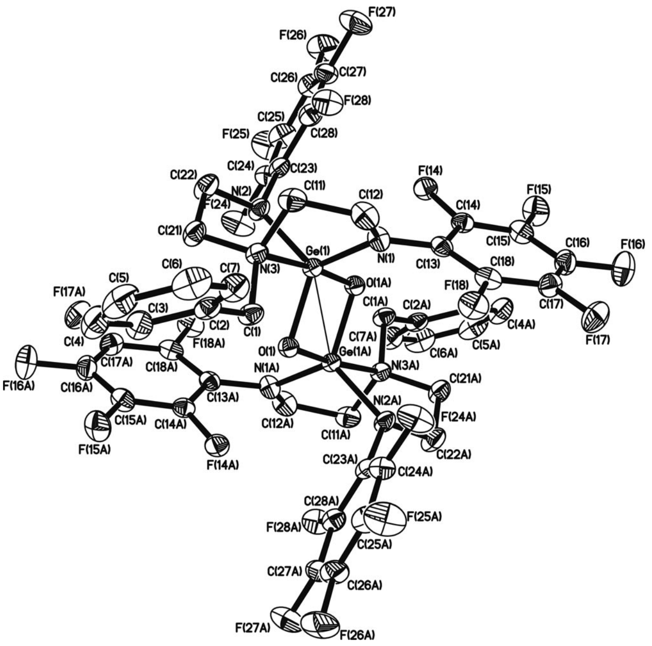
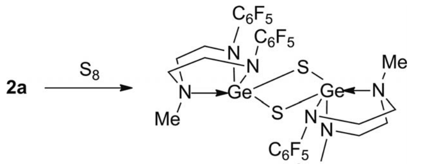


Figure 6. Molecular structure of **7b**. ORTEP diagram with elipsoids drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ge(1)–O(1) 1.7844(13), Ge(1)–O(1A) 1.8313(13), Ge(1)–N(2) 1.8519(16), Ge(1)–N(1) 1.8574(16), Ge(1)–N(3) 2.1478(17), Ge(1)–Ge(1A) 2.6524(4), O(1)–Ge(1A) 1.8313(13); O(1)–Ge(1)–O(1A) 85.64(6), O(1)–Ge(1)–N(2) 17.60(7), O(1A)–Ge(1)–N(2) 99.61(7), O(1)–Ge(1)–N(1) 122.81(7), O(1A)–Ge(1)–N(1) 100.02(7), N(2)–Ge(1)–N(1) 117.30(8), O(1)–Ge(1)–N(3) 89.54(6), O(1A)–Ge(1)–N(3) 175.18(6), N(2)–Ge(1)–N(3) 82.48(7), N(1)–Ge(1)–N(3) 82.74(7), N(2)–Ge(1)–Ge(1A) 115.27(6), N(1)–Ge(1)–Ge(1A) 118.99(6), N(3)–Ge(1)–Ge(1A) 133.05(5), Ge(1)–O(1)–Ge(1A) 94.36(6).

The reaction of **2a** with sulfur also gave the expected product (Scheme 10), the cyclodimer **8**, which was characterized by X-ray diffraction analysis (Figure 7).



8 (45%)

Scheme 10. Reaction of germylene **2a** with sulfur.

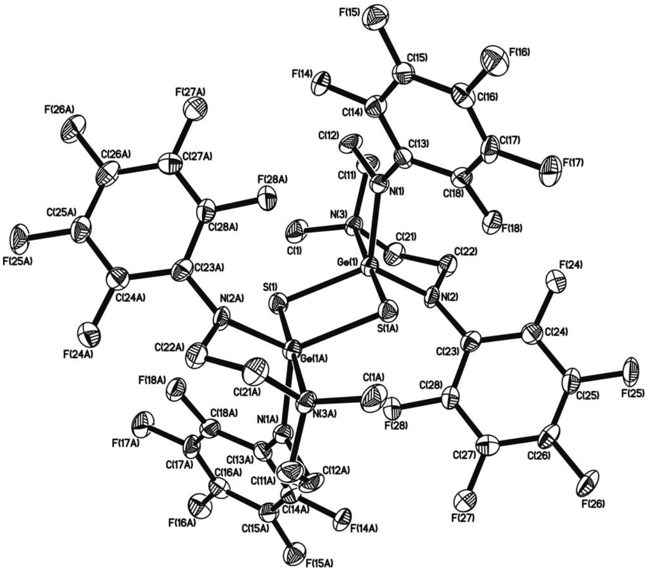


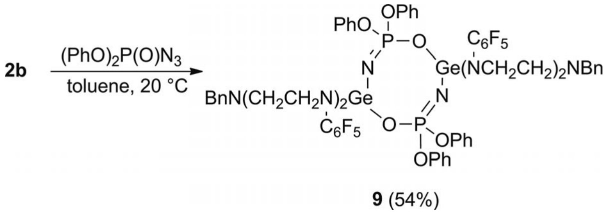
Figure 7. Molecular structure of **8**. ORTEP diagram with elipsoids drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ge(1)–S(1) 2.2062(17), Ge(1)–S(1A) 2.2875(18), Ge(1)–N(2) 1.856(5), Ge(1)–N(1) 1.869(5), Ge(1)–N(3) 2.323(5), Ge(1)–Ge(1A) 3.124; N(2)–Ge(1)–N(1) 112.7(2), N(2)–Ge(1)–S(1) 123.50(17), N(1)–Ge(1)–S(1) 118.52(16), N(2)–Ge(1)–S(1) 100.27(16), N(1)–Ge(1)–S(1) 101.32(17), S(1)–Ge(1)–S(1) 91.93(6), N(2)–Ge(1)–N(3) 78.97(19), N(1)–Ge(1)–N(3) 78.9(2), S(1)–Ge(1)–N(3) 88.63(13), S(1)–Ge(1)–N(3) 179.23(13), Ge(1)–S(1)–Ge(1) 88.07(6).

The germanium atoms in **7b** and **8** and Ge(1) in **7a** have distorted trigonal-bipyramidal geometries with N(3) and O(1) in **7a**, and N(3) and O(1a) in **7b** occupying the axial positions. N(1), N(2), and O(2) in **7a**, and N(1), N(2), and O(1) in **7b** form the equatorial plane. The coordination polyhedron of Ge(2) in **7a** is a distorted tetrahedron.

The Ge–O bond lengths are similar to those of the corresponding bonds in $\{[MeSi(\mu\text{-}N\textit{t}Bu)_2SiMe(\textit{t}BuN)_2]Ge(\mu\text{-}O)\}_2$ [1.809(4) and 1.825(4) Å][5] and in $\{[P(\mu\text{-}N\textit{t}Bu)_2P(\textit{t}BuN)_2]Ge(\mu\text{-}O)\}_2$ [1.78(1) and 1.84(1) Å].[23] The Ge–X(ax) bond is, as expected, longer than the Ge–X(eq) [X = O (**7a**,**b**), X = S (**8**)] bond in the same molecule for the Ge atom in the trigonal-bipyramidal environment. This is in accordance with the hypervalent bond theory.[24] The intramolecular transannular interaction N(3)→Ge [2.1542(15) Å] in **7a** and [2.1478(17) Å] in **7b** are similar, but in **8**, N(3)→Ge [2.323(5) Å] is longer because of the lower electronegativity of S as compared with O. The transannular Ge···Ge separations in **7a** [2.6370(3) Å] and **7b** [2.6524(4) Å] are similar, but slightly longer than in $\{Ge[N(SiMe_3)_2]_2(\mu\text{-}O)\}_2$ [2.608(1) Å] and much shorter than twice the van der Waals radius of Ge^{4+} (4.30 Å). The increase in the transannular Ge···Ge separations in **8** [3.124(5) Å] can be explained by the increasing size of the bridged atoms in this case.

The reaction of germylene **2b** with water gave free ligand **1b** and germanium(II) hydroxide. Evidently, the driving force for the reaction is the formation of the precipitate of germanium(II) hydroxide. The interaction of germylenes with water does not result in the four-membered cycle –M–O–M–O–.

The reactions of germylenes with azides has been the subject of several investigations.[20] By studying the reactions of germylenes without the additional transannular interaction, it was determined that different derivatives of M^{4+} (azides, germoles, imines) might be obtained depending on the reaction conditions and the structures of the "heavy carbene" and azides. According to Barrau et al.,[20] the reaction of $(ArO)_2Ge$ [Ar = 2,4,6-$(Me_2NCH_2)_3C_6H_2$] with trimethylsilyl azide, Me_3SiN_3, yields germanimines. The reactions of germylenes with diphenylphosphoryl azide is practically unexplored.[25] We carried out this reaction with germylene **2b** and obtained the expected product **9** (Scheme 11).

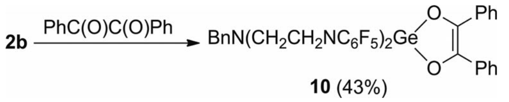


Scheme 11. Reaction of germylene **2b** with $(PhO)_2P(O)N_3$.

The similarity between the results obtained in the reactions with $(PhO)_2P(O)N_3$ and $Me_3N{\rightarrow}O$ can be explained by the analogy of the mechanisms supposed. In the case of diphenylphosphoryl azide, the intermediate might be an unstable germanimine, $(PhO)_2P(O)–N=MR_2$, that dimerizes immediately.

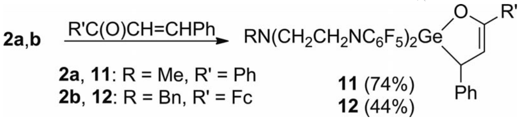
Addition to unsaturated systems is a classic reaction for "heavy carbenes", different organic substrates with conjugate double bonds having being studied. We investigated a number of similar reactions to determine the influence of organic substrate structure on the reaction.

The reactions of different M^{2+} derivatives with benzil have been studied in detail[26] and it was established that [1+4] cycloaddition products form independently of the structure of the "heavy carbene". The use of germylene **2b** in such a reaction led to the expected product **10** in moderate yield (Scheme 12).



Scheme 12. [1+4] Cycloaddition reaction of germylene **2b** with benzil.

Germylenes **2a** and **2b** reacted with chalcone and its ferrocenyl analogues to give [1+4]-cycloaddition products **11** and **12** (Scheme 13).



Scheme 13. [1+4] Cycloaddition reactions of germylene **2a** and **2b** with substituted chalcones.

The structures of **10** and **11** were confirmed by X-ray analysis (Figures 8 and 9). The coordination environment of the germanium atom in both **10** and **11** is trigonal-bipyramidal with O(1) and N(3) in **10**, and O(1) and N(3) in **11** in axial positions and O(2), N(1), and N(2) in **10**, and N(1), N(2), and C(2) in **11** in the equatorial plane. Note that in both cycloaddition products the intramolecular transannular interactions N(3)→Ge [2.089(4) Å] in **10** and [2.2566(17) Å] in **11** differ from that of the initial germylene **2b**. Moreover, this interaction is stronger, the more electronegative substituents are located at the germanium atom. This may be explained by the presence of two electronegative substituents at the germanium atom in the adduct **10** and one in the product **11**. The same trend was observed for compounds $MeN(CH_2CH_2O)_2Ge(\text{-}OCH_2CH_2O\text{-})$,[27] $HOCH_2CH_2N(CH_2CH_2O)_2Ge[\text{-}OC(O)CH_2CH_2\text{-}]$,[28] and $MeN(CH_2CH_2O)_2Ge[\text{-}OC(O)CPh_2O\text{-}]$,[29] in which N→Ge is 2.159(7), 2.149(6), and 2.080(3) Å respectively.

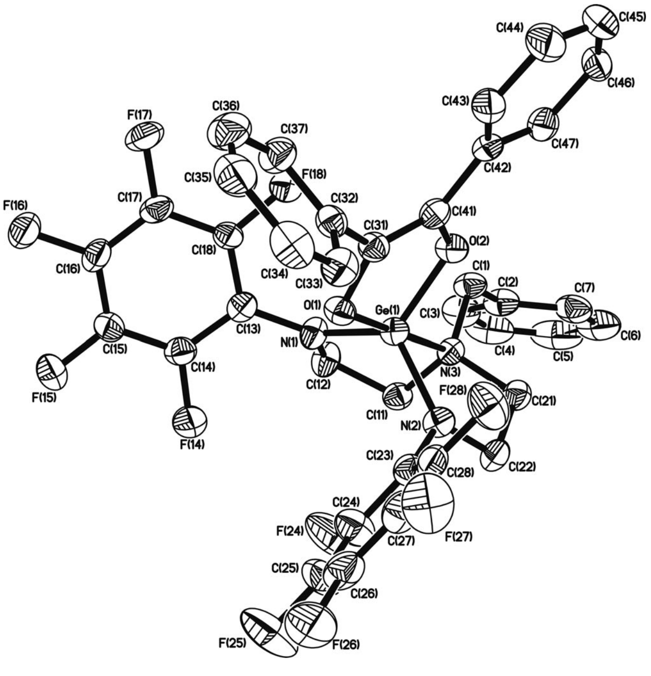


Figure 8. Molecular structure of **10**. ORTEP diagram with elipsoids drawn at the 50 % probability level; hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ge(1)–O(2) 1.796(3), Ge(1)–N(1) 1.836(4), Ge(1)–O(1) 1.838(3), Ge(1)–N(2) 1.839(4), Ge(1)–N(3) 2.089(4); O(2)–Ge(1)–N(1) 124.40(16), O(2)–Ge(1)–O(1) 89.26(14), N(1)–Ge(1)–O(1) 96.00(15), O(2)–Ge(1)–N(2) 114.40(16), N(1)–Ge(1)–N(2) 119.51(18), O(1)–Ge(1)–N(2) 97.79(15), O(2)–Ge(1)–N(3) 90.54(14), N(1)–Ge(1)–N(3) 83.40(16), O(1)–Ge(1)–N(3) 179.11(14), N(2)–Ge(1)–N(3) 83.09(15).

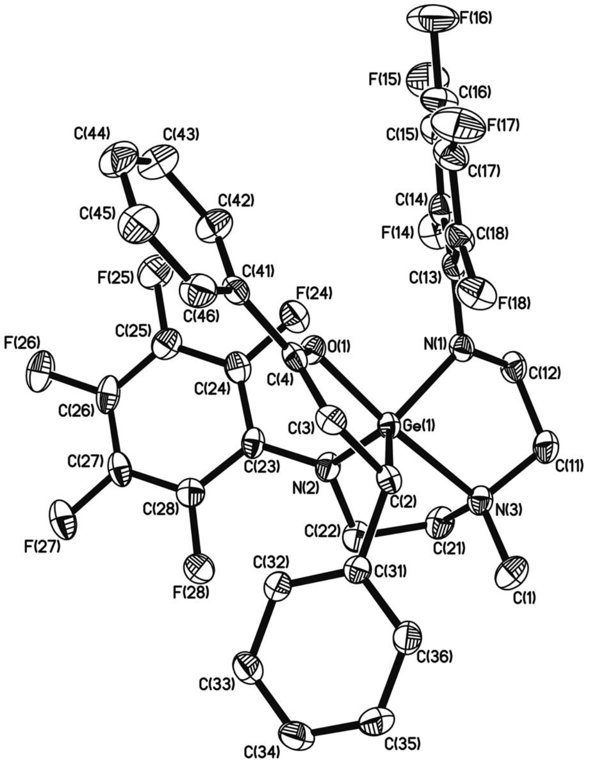


Figure 9. Molecular structure of **11**. ORTEP diagram with elipsoids drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ge(1)–N(2) 1.8596(18), Ge(1)–N(1) 1.8642(17), Ge(1)–O(1), 1.8651(14), Ge(1)–C(2) 1.996(2), Ge(1)–N(3) 2.2566(17); N(2)–Ge(1)–N(1) 117.05(8), N(2)–Ge(1)–O(1) 95.96(7), N(1)–Ge(1)–O(1) 93.04(7), N(2)–Ge(1)–C(2) 119.68(8), N(1)–Ge(1)–C(2) 122.50(8), O(1)–Ge(1)–C(2) 89.85(7), N(2)–Ge(1)–N(3) 80.90(7), N(1)–Ge(1)–N(3) 80.16(7), O(1)–Ge(1)–N(3) 170.05(6), C(2)–Ge(1)–N(3) 99.92(8).

We found that there was no reaction between monomeric germylene **2b** and 2,3-dimethylbutadiene neither at ambient temperature nor after prolonged heating. In similar reactions germanium(4+) compounds would be expected to form in which the transannular bond is weak or does not exist, because the germanium atom bonds to two donor carbon atoms.

The digermene $R_2Ge{=}GeR_2$ [R = tetrakis(2-*tert*-butyl-4,5,6-trimethylphenyl)], which dissociates into the germylene molecules R_2Ge**:** in solution, reacts with 1,4-diisopropyl-1,4-diazabuta-1,3-diene to furnish the product formed by the [4+1] cycloaddition of germylene to the nitrogen atoms.[30] Similar reactions could be expected for our germylenes, but no reaction was observed between our donor-stabilized, three-coordinate germylene **2b** and 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene.

Conclusions

A new class of two-coordinate and donor-stabilized three-coordinate germylenes based on (pentafluorophenyl)amides and diethylenetriamines have been synthesized by transamination reactions of a range of substituted amines and $Ge[N(TMS)_2]_2$ or by metathesis of lithiated ligand synthons with [$GeCl_2$·dioxane]. According to XRD studies, monomeric germylenes were obtained in all cases. Three-coordinate germylenes stabilized by an additional transannular interaction showed a reactivity similar to that of their classic two-coordinate counterparts in oxidative addition reactions with halogenation agents (bromine and $GeCl_4$), methyl iodide, diphenyl disulfide, dioxygen, sulfur, and diphenylphosphoryl azide. Although α,β-unsaturated ketones (benzil, chalcone, and its ferrocenyl analogues) led to the expected [1+4]-cycloaddition products, base-stabilized germylenes based on the diethylenetriamine backbone were found to be unreactive towards 2,3-dimethyl-1,3-butadiene and 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene.

Experimental Section

General: All manipulations were performed under dry, oxygen-free argon by using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. The starting materials were synthesized according to literature procedures: $Ge[N(TMS)_2]_2$,[31] [$GeCl_2$·$C_4H_8O_2$],[32] $LiN(TMS)_2$·Et_2O,[33] $MeN(CH_2CH_2NHC_6F_5)_2$,[34] $BnN(CH_2CH_2NHC_6F_5)_2$,[24b] $BnN(CH_2CH_2NHTMS)_2$,[24b] H_2(dpma),[35] $TMSN(CH_2CH_2NHTMS)_2$,[36] FcC(O)CH=CHPh,[37] $HN(C_6F_5)_2$,[38] $LiN(C_6F_5)_2$,[38] and *N*,*N*′-bis(pentafluorophenyl)benzene-1,2-diamine (**1i**).[39] MeI (Aldrich), $GeCl_4$ (Aldrich), Et_2S_2 (Aldrich), and 2,3-dimethylbuta-1,3-diene (Aldrich) were distilled prior to use. Ph_2S_2 (Aldrich), S_8 (Merck), $N_3P(O)(OPh)_2$ (Merck), PhC(O)C(O)Ph (Aldrich), PhC(O)CH=CHPh (Aldrich), and *t*BuN=CHCH=N*t*Bu (Aldrich) were used as supplied. $Me_3N{\rightarrow}O{\cdot}2H_2O$ (Fluka) was sublimated for use. C_6D_6 was obtained from Deutero GmbH and dried with sodium. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded with a Bruker Avance 400 or ARX 200 spectrometer at room temperature. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. In ^{19}F NMR experiments, $CFCl_3$ was used as the external standard. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. Mass spectra (EI-MS, 70 eV) were recorded with a Varian CH-7a device (Philipps University Marburg, Germany). All assignments were made by reference to the most abundant isotopes. Infrared spectra were recorded with a Bruker IFS 88 FT instrument, and samples were Nujol mulls between KBr plates.

Bis{2-[(pentafluorophenyl)amino]phenyl} Thioether [$S(oC_6H_4NHC_6F_5)_2$ (1f)]: *n*BuLi (1.6 м, 83.6 mL, 0.13 mol) in hexane was added to a solution of $HN(SiMe_3)_2$ (21.6 g, 0.13 mol) in thf (70 mL) at 25 °C. After 20 min at 25 °C, a solution of bis(2-aminophenyl) thioether (6.43 g, 30.0 mmol) in thf (60 mL) was added. The mixture was cooled to –78 °C, and C_6F_6 (13.81 g, 74.0 mmol) was added within 2 min. The brownish reaction mixture was slowly warmed to 25 °C and stirred at room temp. until all the starting material had been consumed (monitored by TLC, ca. 4 h). After the addition of water (200 mL) and diethyl ether (150 mL), the raw product was extracted with diethyl ether (3 × 100 mL). The combined diethyl ether phases were dried with Na_2SO_4, and the diethyl ether was removed to give a brown oily solid, which was dissolved in CH_2Cl_2/*n*-hexane (2:1) and passed through a bed of Merck silica 60 (ca. 60 g). After further extraction with this solvent mixture, all volatiles were removed, and the residue was crystallized from hot heptane/benzene (3:1) to yield colorless crystalline needles of **1f**

(12.80 g, 78%). M.p. 178.4 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 5.74 (s, 2 H, NH), 6.37 (dd, J = 8.0 and 1.2 Hz, 2 H, C_6H_4), 6.65 (dt, J = 7.6 and 1.3 Hz, 2 H, C_6H_4), 6.91 (dt, J = 8.0 and 1.5 Hz, 2 H, C_6H_4), 7.22 (dd, J = 7.8 and 1.5 Hz, 2 H, C_6H_4) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 115.3 (s, C_6H_4), 116.9 (t, J = 13.4 Hz, C_6F_5), 120.6 (s, C_6H_4), 122.6 (s, C_6H_4), 129.7 (s, C_6H_4), 133.2 (s, C_6H_4), 138.3 (dm, J = 245.1 Hz, C_6F_5), 138.4 (dm, J = 246.0 Hz, C_6F_5), 142.4 (dm, J = 247.9 Hz, C_6F_5), 142.9 (s, C_6H_4) ppm. ^{19}F NMR (188.2 MHz, C_6D_6): δ = –163.4 (t, J = 20 Hz, 2 F, *meta*), –162.2 (t, J = 21 Hz, 1 F, *para*), –149.4 (d, J = 20 Hz, 2 F, *ortho*) ppm. MS (EI): m/z (%) = 548 (23) $[M]^+$, 365 (3) $[M - NHC_6F_5]^+$, 259 (100) $[C_6H_5NHC_6F_5]^+$. IR (Nujol): $\tilde{\nu}$ = 3385 (m, NH), 1655 (w), 1638 (w), 1524 (s), 1464 (vs), 1425 (s), 1377 (s), 1296 (s), 1232 (m), 1155 (m), 1055 (m), 981 (s), 945 (s), 866 (w), 748 (s), 735 (m), 723 (m), 671 (m), 544 (w), 434 (w) cm^{-1}. $C_{24}H_{10}F_{10}N_2S$ (548.40): calcd. C 52.56, H 1.84, N 5.11; found C 52.59, H 2.12, N 5.09.

$MeN(CH_2CH_2NC_6F_5)_2Ge$ (2a)

Method A: A solution of $MeN(CH_2CH_2NHC_6F_5)_2$ (**1a**; 0.46 g, 1.02 mmol) in toluene (5 mL) was added to a stirred solution of $Ge[N(TMS)_2]_2$ (0.40 g, 1.02 mmol) in toluene (10 mL). The mixture was stirred at room temperature for 4 d. After removal of the volatiles under vacuum, diethyl ether (10 mL) was added to the residue. The precipitate was filtered off to give **2a** (0.27 g, 51%) as a white solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.70 (s, 3 H, CH_3N), 1.77–1.90 (m, 4 H, 2 NCH_2), 2.94–3.05, 3.35–3.49 (2 m, 4 H, 2 $NCH_2C_6F_5$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 46.23 (CH_3N), 50.96 (NCH_2), 60.11 ($NCH_2C_6F_5$) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. ^{19}F NMR (376.4 MHz, C_6D_6, 25 °C): δ = –172.94 to –172.78 (m, 1 F), –165.41 to –165.26 (m, 2 F), –154.34 to –154.25 (m, 2 F) ppm. $C_{17}H_{11}F_{10}GeN_3$ (519.8835): calcd. C 39.27, H 2.13, N 8.08; found C 39.30, H 2.45, N 7.82. Prolonged standing of the mother liquor for a month led to colorless crystals of the compound $MeN(CH_2CH_2NC_6F_5)_2Ge(\mu\text{-}O)_2Ge[N(TMS)_2]_2$ (**7a**). The structure of **7a** was established by X-ray analysis.

Method B: A solution $LiN(TMS)_2{\cdot}Et_2O$ (0.88 g, 3.66 mmol) in thf (10 mL) was added dropwise at –78 °C to a stirred solution of $MeN(CH_2CH_2NHC_6F_5)_2$ (**1a**; 0.82 g, 1.83 mmol) in thf (15 mL). The reaction mixture was stirred for 1 h and then warmed to room temperature. The reaction mixture was again cooled to –78 °C, and $[GeCl_2{\cdot}C_4H_8O_2]$ (0.42 g, 1.83 mmol) in thf (15 mL) was added with stirring. After stirring at room temperature for 24 h, the volatiles were removed under vacuum. Recrystallization from toluene solution gave **2a** (0.22 g, 24%) as a white solid.

$BnN(CH_2CH_2NC_6F_5)_2Ge$ (2b): The procedure was analogous to that used for **2a** (Method A) by employing $BnN(CH_2CH_2NHC_6F_5)_2$ (**1b**; 0.81 g, 1.55 mmol) and $Ge[N(TMS)_2]_2$ (0.61 g, 1.55 mmol). Colorless crystals of **2b** (0.42 g, 46%) were obtained from a toluene solution (6 mL) at –20 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.79–1.85, 2.31–2.40 (2 m, 4 H, 2 NCH_2), 3.08–3.14 (m, 2 H, $NCH_2C_6F_5$), 3.38 (s, 2 H, NCH_2Ph), 3.41–3.50 (m, 2 H, $NCH_2C_6F_5$), 6.73–6.76, 7.00–7.07 (2 m, 5 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 51.44 (NCH_2), 56.94 ($NCH_2C_6F_5$), 62.62 ($PhCH_2$), 128.77, 129.35, 131.45, 131.51 (Ph) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. ^{19}F NMR (376.4 MHz, C_6D_6, 25 °C): δ = –172.86 to –172.65 (m, 1 F), –165.30 to –165.14 (m, 2 F), –154.21 to –154.11 (m, 2 F) ppm. MS (EI): m/z (%) = 599 (12) $[M]^+$, 390 (28) $[M - CH_2CH_2NC_6F_5]^+$, 330 (7) $[M - CH_2NC_6F_5Ge]^+$, 312 (13) $[M - CH_2Ph\ CH_2NC_6F_5]^+$.

$BnN(CH_2CH_2NSiMe_3)_2Ge$ (2c): The procedure was analogous to that used for **2a** (Method A); reaction of $BnN(CH_2CH_2NHTMS)_2$ (**1c**; 0.58 g, 1.73 mmol) with $Ge[N(TMS)_2]_2$ (0.68 g, 1.73 mmol) in toluene (15 mL) gave **2c** (0.13 g, 18%) as a yellow solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.34 (s, 3 H, $SiMe_3$), 1.97–2.02, 2.73–2.78 (2 m, 4 H, NCH_2), 3.12–3.17, 3.22–3.29 (2 m, 4 H, NCH_2), 3.69 (s, 2 H, $PhCH_2$), 6.93–6.94, 7.04–7.06, 7.30–7.32 (3 m, 5 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 1.43 ($SiMe_3$), 40.01, 49.85, 58.46, 61.01 (NCH_2), 64.50 (CH_2Ph), 127.15, 128.47, 129.19, 131.28 (Ph) ppm. $C_{17}H_{33}GeN_3Si_2$ (408.2451): calcd. C 50.01, H 8.15, N 10.29; found C 49.89, H 8.03, N 10.35.

$Me_3SiN(CH_2CH_2NSiMe_3)_2Ge$ (2d): The procedure was analogous to that used for **2a** (Method A); $Me_3SiN(CH_2CH_2NHSiMe_3)_2$ (**1d**; 0.34 g, 1.07 mmol) was treated with $Ge[N(TMS)_2]_2$ (0.42 g, 1.07 mmol) in toluene (15 mL). The reaction mixture was stirred at room temperature. After 4 d, the volatiles were removed under vacuum to give an orange oil. On the basis of the NMR spectroscopic data, the orange oil was considered to be germylene **2d**, but in view of its extreme hygroscopicity and sensitivity to oxygen our attempts to isolate **2d** in pure form failed. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.04, 0.33 (2 s, 27 H, $SiMe_3$), 1.98–2.02, 2.30–2.37, 3.17–3.21, 3.27–3.33 (4 m, 8 H, NCH_2) ppm.

Ge(dpma) (2e): The procedure was analogous to that used for **2a** (Method A); H_2(dpma) (**1e**; 0.18 g, 0.97 mmol) was treated with $Ge[N(TMS)_2]_2$ (0.38 g, 0.97 mmol) in toluene (15 mL) to give **2e** (0.09 g, 36%) as a brown solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.69 (s, 3 H, CH_3N), 2.97 and 3.48 (2 d, J = 13.6 Hz, 4 H, NCH_2), 5.96–6.13, 6.49–6.54, 6.88–6.93 (3 m, 6 H, pyrrole ring protons) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 43.15 (CH_3N), 58.52 (NCH_2), 104.75, 111.98, 121.73, 133.54 (pyrrole ring) ppm. $C_{11}H_{13}GeN_3$ (259.8511): calcd. C 50.84, H 5.04, N 16.17; found C 50.98, H 5.13, N 16.06.

$S(o\text{-}C_6H_4NC_6F_5)_2Ge$ (2f)

Method A: A solution of $LiN(SiMe_3)_2{\cdot}Et_2O$ (0.62 g, 2.60 mmol) in thf (10 mL) was added to a stirred solution of $S(o\text{-}C_6H_4NHC_6F_5)_2$ (**1f**; 0.70 g,1.30 mmol) in thf (15 mL) at –78 °C. After warming to room temperature and stirring for 1 h, the reaction mixture was again cooled to –78 °C, added to a suspension of $[GeCl_2{\cdot}C_4H_8O_2]$ (0.30 g, 1.30 mmol) in thf (15 mL), and cooled to –78 °C. The reaction mixture was stirred at room temperature overnight, and the volatiles were removed under vacuum. Recrystallization from toluene gave **2f** (0.50 g, 63%) as a white solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 6.07–6.10, 6.38–6.43, 6.76–6.82, 7.12–7.13 (4 m, 8 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 115.55, 119.50, 119.76, 132.14, 132.70, 153.26 (aromatic carbon atoms) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. ^{19}F NMR (376.4 MHz, C_6D_6, 20 °C): δ = –162.45 to –162.07 (m, 2 F), –159.86 (t, 1 F), –149.00 to –148.86 (m, 1 F), –144.43 (d, 1 F) ppm. $C_{24}H_8F_{10}GeN_2S$ (618.9938): calcd. C 46.57, H 1.30, N 4.53; found C 46.36, H 1.66, N 4.43.

Method B: A solution of $Ge[N(SiMe_3)_2]_2$ (0.26 g, 0.66 mmol) in toluene (10 mL) was added to a stirred solution of **1f** (0.36 g, 0.66 mmol) in toluene (10 mL). The progress of the reaction was monitored by ^{19}F NMR spectroscopy. Even after boiling the mixture for 24 h, only signals from the starting materials were detected in the spectrum.

$[o\mathrm{C_6H_4(NC_6F_5)_2}]_2\mathrm{Ge}$ (2i)

Method A: The procedure was analogous to that used for **2a** (Method B); treatment of *N*,*N′*-bis(pentafluorophenyl)benzene-1,2-diamine (**1i**; 0.57 g, 1.30 mmol) in thf (10 mL) with a solution of $\mathrm{LiN(SiMe_3)_2{\cdot}Et_2O}$ (0.62 g, 2.60 mmol) in thf (10 mL) and then $[\mathrm{GeCl_2{\cdot}C_4H_8O_2}]$ (0.30 g, 1.30 mmol) gave compound **2i** (0.44 g, 67%) from thf (5 mL) at –20 °C. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 6.51–6.58, 6.92–6.98 (2 m, 4 H, $\mathrm{C_6H_4}$) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 111.60, 121.21, 139.53 ($\mathrm{C_6H_4}$), 136.58, 139.93, 141.85, 145.24 ($\mathrm{NC_6F_5}$) ppm. ^{19}F NMR (376.4 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = –164.19 (br. t, 2 F), –159.65 (br. t, 1 F), –149.03 (d, 2 F) ppm. MS (EI): *m*/*z* (%) = 512 (100) $[\mathrm{M}]^+$.

Method B: The procedure was analogous to that used for **2a** (Method A); 1,3-bis(pentafluorophenyl)benzene-1,2-diamine (**1g**; 0.48 g, 1.10 mmol) was treated with $\mathrm{Ge[N(TMS)_2]_2}$ (0.42 g, 1.10 mmol) in toluene (15 mL). The progress of the reaction was monitored by ^{19}F NMR spectroscopy. Even after boiling the mixture for 24 h, only signals from the starting materials were detected in the spectrum.

$\mathrm{Ge[N(C_6F_5)_2]_2}$ (2j)

Method A: The procedure was analogous to that used for **2a** (Method B); treatment of bis(pentafluorophenyl)amine (**1j**; 0.96 g, 2.75 mmol) in thf (10 mL) with a solution of $\mathrm{LiN(SiMe_3)_2{\cdot}Et_2O}$ (0.66 g, 2.75 mmol) in thf (10 mL) and then $\mathrm{GeCl_2{\cdot}C_4H_8O_2}$ (0.32 g, 1.35 mmol) led to compound **2j** (0.25 g, 24%), which was crystallized from thf (6 mL) at –20 °C. ^{19}F NMR (376.4 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = –164.19 (br. t, 2 F), –159.65 (br. t, 1 F), –149.03 (d, 2 F) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling.

Method B: The procedure was analogous to that used for **2a** (Method A): bis(pentafluorophenyl)amine (**1j**; 0.77 g, 2.20 mmol) was treated with $\mathrm{Ge[N(TMS)_2]_2}$ (0.42 g, 1.10 mmol) in toluene (15 mL). The progress of the reaction was monitored by ^{19}F NMR spectroscopy. Even after boiling the mixture for 24 h, only signals from the starting materials were detected in the spectrum.

$\mathrm{MeN(CH_2CH_2NC_6F_5)_2GeBr_2}$ (3a): A solution of bromine (0.14 g, 0.87 mmol) in toluene (5 mL) was added to a stirred solution of **2a** (0.45 g, 0.87 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature for 1 d, and the volatiles were then removed under vacuum. Then diethyl ether (10 mL) was added to the residue, and the precipitate was filtered off to give **3a** (0.45 g, 76%) as a white solid. The ^{1}H and ^{13}C NMR spectra are in accord with literature data.[24b] ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 1.85 (s, 3 H, $\mathrm{NCH_3}$), 1.92–1.98, 2.14–2.20 (2 m, 4 H, 2 $\mathrm{NCH_2}$), 2.78–2.70 (m, 4 H, 2 $\mathrm{NCH_2C_6F_5}$) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 43.64 ($\mathrm{CH_3N}$), 45.27 ($\mathrm{NCH_2}$), 50.48 ($\mathrm{NCH_2C_6F_5}$) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling.

$\mathrm{S(}o\mathrm{C_6H_4NC_6F_5)_2GeBr_2}$ (3f): By applying the same experimental procedure as described above with **2f** (0.26 g, 0.42 mmol) and bromine (0.067 g, 0.42 mmol), compound **3f** (0.28 g, 87%) was obtained as a white solid. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 5.45 (s), 5.97–6.03 (m), 7.00–7.06 (dd), 7.35 (d, 8 H, aromatic protons) ppm. ^{19}F NMR (376.4 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = –163.00 to –162.79 (m, 2 F), –161.17 (t, 1 F), –149.45 (d, 2 F) ppm. $\mathrm{C_{24}H_8Br_2F_{10}GeN_2S}$ (778.802): calcd. C 37.01, H 1.04, N 3.60; found C 36.86, H 1.24, N 3.48.

$\mathrm{MeN(CH_2CH_2NC_6F_5)_2GeCl_2}$ (4): A solution of $\mathrm{GeCl_4}$ (0.21 g, 0.96 mmol) in toluene (5 mL) was added dropwise to a stirred solution of **2a** (0.50 g, 0.96 mmol) in toluene (10 mL) at 0 °C. After stirring at room temperature for 24 h, a white precipitate of $[\mathrm{GeCl_2}]_n$ was separated by filtration. The precipitate was extracted with toluene (10 mL), and the organic solutions were combined. The volatiles were removed under vacuum, and diethyl ether (10 mL) was added. A white solid was separated by filtration, washed with diethyl ether (2 × 2 mL), and dried under vacuum to give **4** (0.30 g, 54%) as a white solid. The ^{1}H and ^{13}C NMR spectra are in accord with literature data.[24b] ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 1.93 (s, 3 H, $\mathrm{NCH_3}$), 1.93–1.98, 2.20–2.25 (2 m, 4 H, 2 $\mathrm{NCH_2}$), 2.83–2.69 (m, 4 H, 2 $\mathrm{NCH_2C_6F_5}$) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 43.37 ($\mathrm{CH_3}$), 45.04 ($\mathrm{NCH_2}$), 50.99 ($\mathrm{NCH_2C_6F_5}$) ppm.

$\mathrm{MeN(CH_2CH_2NC_6F_5)_2Ge(Me)I}$ (5a): A solution of MeI (0.27 g, 1.92 mmol) in toluene (5 mL) was added to a stirred solution of **2a** (0.50 g, 0.96 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature for 4 d, and the precipitate was filtered off to give **5a** (0.58 g, 91%) as a white solid. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 1.04 (s, 3 H, $\mathrm{CH_3Ge}$), 1.47 (s, 3 H, $\mathrm{NCH_3}$), 1.61–1.71, 2.16–2.23, 2.60–2.71, 2.91–3.02 (4 m, 8 H, 2 $\mathrm{NCH_2}$ and 2 $\mathrm{NCH_2C_6F_5}$) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 22.21 ($\mathrm{GeCH_3}$), 43.05 ($\mathrm{NCH_3}$), 48.23 ($\mathrm{NCH_2}$), 56.26 ($\mathrm{NCH_2C_6F_5}$) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. $\mathrm{C_{18}H_{14}F_{10}GeIN_3}$ (611.8225): calcd. C 32.67, H 2.13, N 6.35; found C 32.43, H 2.09, N 6.44. Crystals suitable for single-crystal X-ray diffraction were grown from a concentrated toluene solution.

$\mathrm{BnN(CH_2CH_2NC_6F_5)_2Ge(Me)I}$ (5b): The procedure was analogous to that used for **5a**; reaction of **2b** (0.70 g, 1.17 mmol) with MeI (0.33 g, 2.34 mmol) in toluene (15 mL) gave **5b** (0.51 g, 59%) as a white solid. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 50 °C): δ = 1.60 (s, 3 H, $\mathrm{CH_3Ge}$), 2.19–2.36 (m, 4 H, 2 $\mathrm{NCH_2}$), 2.90–2.98, 3.03–3.11 (2 m, 4 H, 2 $\mathrm{NCH_2C_6F_5}$), 3.33 (s, 2 H, $\mathrm{PhCH_2}$), 6.70–6.74, 6.98–7.05 (2 m, 5 H, Ph) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 50 °C): δ = 23.06 ($\mathrm{GeCH_3}$), 46.42 ($\mathrm{NCH_2}$), 48.06 ($\mathrm{NCH_2C_6F_5}$), 56.78 ($\mathrm{PhCH_2}$), 127.89, 128.82, 129.13, 131.25 (Ph) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. $\mathrm{C_{24}H_{18}F_{10}GeIN_3}$ (737.9184): calcd. C 39.06, H 2.46, N 5.69; found C 39.23, H 2.40, N 5.50. Crystals suitable for single-crystal X-ray diffraction were grown from a concentrated toluene solution.

$\mathrm{BnN(CH_2CH_2NC_6F_5)_2Ge(SPh)_2}$ (6): A solution of $\mathrm{Ph_2S_2}$ (0.21 g, 0.96 mmol) in toluene (5 mL) was added dropwise at –40 °C to a stirred solution of **2b** (0.57 g, 0.96 mmol) in toluene (10 mL). The reaction mixture was stirred for 30 min and then warmed to room temperature. After stirring for 4 d, the volatiles were removed under vacuum and pentane (10 mL) was added. The precipitate was separated by filtration, washed with pentane (2 × 2 mL), and dried in vacuo to give **6** (0.60 g, 77%) as a white solid. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 2.41 (t, *J* = 5.6 Hz, 4 H, $\mathrm{NCH_2}$), 3.07 (t, *J* = 5.6 Hz, 4 H, $\mathrm{NCH_2C_6F_5}$), 4.09 (s, 3 H, $\mathrm{PhCH_2}$), 6.79–6.96, 6.98–7.06, 7.34–7.42 (3 m, 15 H, 3Ph) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 48.53, 48.95, 57.60 ($\mathrm{NCH_2}$, $\mathrm{PhCH_2}$, $\mathrm{NCH_2C_6F_5}$), 125.61, 127.28, 128.51, 128.69, 129.28, 131.14, 133.62, 136.11 (Ph) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. $\mathrm{C_{35}H_{25}F_{10}GeN_3S_2}$ (841.3193): calcd. C 51.62, H 3.09, N 5.16; found C 51.68, H 3.17, N 5.20.

Reaction of 2a with Et_2S_2: The procedure was analogous to that used for **6**; compound **2a** (0.27 g, 0.52 mmol) was treated with Et_2S_2 (0.06 g, 0.52 mmol) in toluene (15 mL). After stirring for 4 d, the volatiles were removed under vacuum to give a yellow solid (0.31 g). On the basis of the NMR spectroscopic data, only starting materials were found in the reaction mixture.

$[BnN(CH_2CH_2NC_6F_5)_2Ge]_2(\mu\text{-}O)_2$ (7): A solution of $Me_3N{\rightarrow}O$ (0.04 g, 0.54 mmol) in toluene (5 mL) was added to a stirred solution of **2b** (0.32 g, 0.54 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature for 4 d. The volatiles were removed under vacuum, and diethyl ether (10 mL) was added. The precipitate was filtered off to give **7** (0.14 g, 42%) as a white solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 2.16–2.32, 2.41–2.54 (2 m, 4 H, 2 NCH_2), 2.73–2.85, 3.15–3.28 (2 m, 4 H, 2 $NCH_2C_6F_5$), 3.72 (s, 2 H, $PhCH_2$), 6.79–6.90, 6.96–7.12 (5 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 43.52, 47.21 (NCH_2), 53.27 (CH_2Ph), 128.86, 128.94, 131.31, 138.65 (Ph) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. $C_{46}H_{30}F_{20}Ge_2N_6O_2$ (1223.9577): calcd. C 45.14, H 2.47, N 6.87; found C 45.30, H 2.55, N 6.90. Crystals suitable for single-crystal X-ray diffraction were grown from a concentrated toluene solution of **7**.

$[MeN(CH_2CH_2NC_6F_5)_2Ge]_2(\mu\text{-}S)_2$ (8): A solution of S_8 (0.03 g, 0.10 mmol) in thf (10 mL) was added to a stirred solution of **2a** (0.40 g, 0.77 mmol) in thf (10 mL). The reaction mixture was stirred at room temperature for 5 d and the volatiles were removed under vacuum. After recrystallization from a concentrated solution of toluene, white crystals of **8** (0.19 g, 45%) were obtained. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.67 (s, 3 H, NCH_3), 2.02–2.10, 2.34–2.43 (2 m, 4 H, 2 NCH_2), 2.73–2.83, 3.03–3.12 (2 m, 4 H, 2 $NCH_2C_6F_5$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 42.69 (NCH_3), 45.73, 50.98 (4 NCH_2) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. $C_{34}H_{22}F_{20}Ge_2N_6S_2$ (1103.899): calcd. C 36.99, H 2.01, N 7.61, S 5.81; found C 36.82, H 1.95, N 7.55, S 5.97.

$[BnN(CH_2CH_2NC_6F_5)_2GeN{=}P(OPh)_2O]_2$ (9): A solution of $N_3P(O)(OPh)_2$ (0.16 g, 0.59 mmol) in toluene (10 mL) was added to a stirred solution of **2b** (0.35 g, 0.59 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature for 4 d. The precipitate was filtered off to give **9** (0.27 g, 54%) as a white solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 2.29–2.44 (m, 4 H, 2 NCH_2), 2.89–2.97, 3.10–3.19 (2 m, 4 H, 2 $NCH_2C_6F_5$), 3.46 (s, 2 H, $PhCH_2$), 6.72–6.83, 6.96–7.01, 7.03–7.12 (3 m, 15 H, 3Ph) ppm. The ^{13}C NMR spectrum was not recorded because of the low solubility of **9**. ^{31}P NMR (161.98 MHz, C_6D_6, 25 °C): δ = –34.19 (s) ppm. $C_{70}H_{50}F_{20}Ge_2N_8O_6P_2$ (1686.3319): calcd. C 49.86, H 2.99, N 6.64; found C 49.95, H 2.91, N 6.51.

Reaction of $BnN(CH_2CH_2NC_6F_5)_2Ge$ with H_2O: H_2O (0.01 g, 0.55 mmol) was added to a stirred solution of **2b** (0.15 g, 0.25 mmol) in thf (5 mL) at room temperature. After stirring for 5 d, the volatiles were removed under vacuum. Toluene (5 mL) was added to the residue, and the precipitate was filtered. After removing all the volatiles in vacuo, a yellow oil was obtained, which corresponds to the starting amine **1b** according to the NMR spectroscopic data.[24b] ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 2.10 (t, J = 5.8 Hz, 4 H, NCH_2), 2.85–2.92 (q, 4 H, 2 $NCH_2C_6F_5$), 3.06 (s, 2 H, $PhCH_2$), 3.78 (br. s, 2 H, NHC_6F_5), 7.01–7.11 (m, 5 H, Ph) ppm.

$BnN(CH_2CH_2NC_6F_5)_2Ge$-*cyclo*-$[OC(Ph)C(Ph)O]$ (10): Solid PhC(O)C(O)Ph (0.26 g, 1.24 mmol) was added to a stirred solution of **2b** (0.74 g, 1.24 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature for 4 d, and the volatiles were removed under vacuum. Then diethyl ether (10 mL) was added to the residue, and the precipitate was filtered off to give **10** (0.43 g, 43%) as a white solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 2.18–2.23, 2.38–2.44 (2 m, 4 H, 2 NCH_2), 2.91–2.99 (m, 4 H, 2 $NCH_2C_6F_5$), 4.18 (s, 2 H,CH_2Ph), 6.70–6.72, 6.82–6.86, 6.92–6.99, 7.03–7.13, 7.25–7.27, 7.65–7.68 (6 m, 15 H, 3Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 43.51 (NCH_2), 47.79 ($NCH_2C_6F_5$), 57.07 ($PhCH_2$), 126.55, 127.06, 127.64, 128.80, 129.20, 130.87, 131.80, 135.39, 136.02, 136.55, 138.26, 139.22, 145.25, 147.72 (2 C and 3 Ph) ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. ^{19}F NMR (376.4 MHz, C_6D_6, 25 °C): δ = –148.33 to –148.17 (m, 1 F), –161.28 to –161.12 (m, 3 F), –164.98 to –164.86 (m, 1 F) ppm. $C_{37}H_{25}F_{10}GeN_3O_2$ (806.2075): calcd. C 55.12, H 3.13, N 5.21; found C 55.48, H 3.28, N 5.24.

$MeN(CH_2CH_2NC_6F_5)_2Ge$-*cyclo*-$[OC(Ph)CHCHPh]$ (11): Solid (E)-PhC(O)CH=CHPh (0.09 g, 0.42 mmol) was added to a stirred solution of **2a** (0.22 g, 0.42 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature for 7 d. The precipitate was filtered off to give **11** (0.23 g, 74%) as a white solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.45–1.52, 1.61–1.71 (2 m, 4 H, 2 NCH_2), 1.79 (s, 3 H, CH_3N), 2.61–2.89 (m, 4 H, 2 $NCH_2C_6F_5$), 3.56 (d, J = 3.3 Hz, 1 H, CHPh), 5.40 [d, J = 3.3 Hz, 1 H, CH=C(O)Ph], 6.87–6.99, 7.04–7.09, 7.20–7.30, 7.35–7.39 (4 m, 10 H, 2Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 40.03 (CHPh), 41.69 (CH_3N), 44.28, 44.71, 52.9, 53.14 (4 NCH_2), 99.35 [*C*H=C(O)Ph], 124.47, 126.01, 128.61, 128.74, 129.98, 135.48, 143.38 (2 Ph), 145.38 [Ph*C*(O)=CH] ppm. The signal of one carbon atom was not observed; the signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. $C_{32}H_{23}F_{10}GeN_3O$ (728.1387): calcd. C 52.78, H 3.18, N 5.77; found C 52.58, H 3.28, N 5.58. Crystals suitable for single-crystal X-ray diffraction were grown from a concentrated toluene solution of **11**.

$BnN(CH_2CH_2NC_6F_5)_2Ge$-*cyclo*-$[OC(Fc)CHCHPh]$ (12): Solid of (E)-FcC(O)CH=CHPh (0.08 g, 0.25 mmol) was added to a stirred solution of **2b** (0.15 g, 0.25 mmol) in toluene (15 mL). The reaction mixture was stirred at room temperature. After stirring for 7 d, the volatiles were removed under vacuum, and diethyl ether (10 mL) was added. The precipitate was separated by filtration, washed with diethyl ether (2 × 2 mL), and dried in vacuo to give **12** (0.10 g, 44%) as an orange solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.87–3.06 (m, 8 H, NCH_2), 3.64 (d, J = 2.9 Hz, 1 H, PhCH), 3.83 (s, 5 H, C_5H_5), 3.86 (s, 2 H, CH_2Ph), 3.69–3.79, 3.90–3.96, 4.01–4.05, 4.09–4.14 (4 m, 4 H, C_5H_4), 5.12 [d, J = 2.9 Hz, 1 H, CH=C(O)Fc], 6.65–6.70, 7.03–7.11, 7.20–7.27, 7.40–7.45 (4 m, 10 H, 2 Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 43.28 (CHPh), 53.21, 63.54 (NCH_2), 64.33, 67.11, 67.50 (C_5H_4), 67.90 (C_5H_5), 68.69 (CH_2Ph), 96.49 [*C*H=C(O)Fc], 125.48, 127.47, 127.86, 128.66 (Ph), 130.24 [CH=*C*(O)Fc] ppm. The ^{13}C NMR signals of the pentafluorophenyl rings were not observed under these conditions due to poor solubility and higher-order C–F coupling. $C_{42}H_{31}F_{10}FeGeN_3O$ (912.1542): calcd. C 55.30, H 3.43, N 4.61; found C 55.16, H 3.52, N 4.80.

Reaction of 2b with 2,3-Dimethylbuta-1,3-diene

Method A: A solution of 2,3-dimethylbuta-1,3-diene (0.37 g, 4.50 mmol) in toluene (5 mL) was added to a stirred solution of **2b** (0.27 g, 0.45 mmol) in toluene (10 mL). The mixture was stirred at room temperature for 4 d or heated at reflux, and the volatiles were removed under vacuum. On the basis of the NMR spectroscopic data, a mixture of unidentified compounds was obtained.

Method B: A solution 2,3-dimethylbuta-1,3-diene (0.37 g, 4.50 mmol) in toluene (5 mL) was added dropwise to a stirred solution of **2b** (0.27 g, 0.45 mmol) in toluene (10 mL) at –78 °C. The reaction mixture was stirred for 1 h and warmed to room temperature. After stirring for 4 d, the volatiles were removed under vacuum. After recrystallization from toluene, **2b** was obtained as a white solid.

Reaction of 2b with *t*BuN=C–C=N-*t*Bu: A solution of **2b** (0.31 g, 0.52 mmol) was added to a stirred solution of *t*BuN=C–C=N*t*Bu (0.09 g, 0.52 mmol) in toluene (15 mL). The reaction mixture was stirred at reflux for 12 h, and the volatiles were removed under vacuum to yield 0.39 g of a brown solid. On the basis of the NMR spectroscopic data, this was a mixture of the starting materials.

X-ray Crystallography: Crystal data and details of the X-ray analyses are given in Table 1. Experimental data sets were collected with Stoe IPDS-1 (for **2b**, **2i**, and **2j**) and Bruker SMART APEX II (for **5b**, **7a**, **7b**, **8**, **10**, and **11**) diffractometers by using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (Sir97 for **2b**, **2i**, and **2j**,[40] SHELXS[41] for **5b**, **7a**, **7b**, **8**, **10**, and **11**) and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (except solvent toluene molecules in **5b** and **10**). All hydrogen atoms were placed in calculated positions and refined by using a riding model. CCDC-854658 (for **2b**), -854659 (for **2i**), -854660 (for **2j**), -854661 (for **5b**), -854662 (for **7a**), -854663 (for **7b**), -854664 (for **8**), -854665 (for **10**), and -854666

Table 1. Crystallographic data collection parameters for **2b**, **2i**, **2j**, **5b**, **7a**, **7b**, **8**, **10**, and **11**.

Complex	**2b**	**2i**	**2j**	**5b**	**7a**	**7b**	**8**	**10**	**11**
Formula	$C_{23}H_{15}F_{10}GeN_3$	$C_{18}H_4F_{10}GeN_2$	$C_{24}F_{20}GeN_2$	$C_{31}H_{26}F_{10}GeIN_3$	$C_{29}H_{47}F_{10}Ge_2N_5O_2Si_4$	$C_{70}H_{54}F_{20}Ge_2N_6O_2$	$C_{34}H_{22}F_{20}Ge_2N_6S_2$	$C_{48.67}H_{38.33}F_{10}GeN_3O_2$	$C_{35}H_{26}F_{10}GeN_3O$
M_r	595.97	510.84	768.85	830.04	945.26	1536.37	1103.88	959.75	767.18
Crystal system	triclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic	triclinic	triclinic	trigonal	triclinic
Space group	$P\bar{1}$	$Pnma$	$Pbca$	$Pbca$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
Z	2	4	8	8	4	1	1	18	2
T [K]	293(2)	293(2)	293(2)	180(2)	150(2)	150(2)	150(2)	150(2)	150(2)
a [Å]	7.693(5)	6.1666(12)	14.120(5)	12.8050(18)	11.0262(8)	11.8540(11)	9.330(3)	44.999(3)	11.0951(6)
b [Å]	8.601(5)	20.818(4)	14.123(5)	21.427(3)	34.270(2)	11.9205(12)	10.952(3)	44.999(3)	11.7015(6)
c [Å]	17.731(5)	15.324(3)	24.455(5)	22.556(3)	11.2722(8)	13.3564(13)	11.206(3)	11.6920(18)	12.7451(6)
α [°]	84.663(5)	90	90	90	90	68.806(2)	63.389(4)	90	93.032(1)
β [°]	80.985(5)	90	90	90	111.592(1)	75.749(2)	71.037(4)	90	106.189(1)
γ [°]	75.536(5)	90	90	90	90	64.895(1)	66.982(4)	120	92.008(1)
V [Å^3]	1120.2(10)	1967.2(7)	4877(3)	6188.8(15)	3960.5(5)	1583.8(3)	926.5(5)	20503(4)	1584.71(14)
$\rho_{calcd.}$ [g cm^{-3}]	1.767	1.725	2.094	1.782	1.585	1.611	1.978	1.399	1.608
μ [mm^{-1}]	1.469	1.656	1.431	2.076	1.721	1.061	1.875	0.755	1.061
Total reflections	9827	14500	32864	56717	40700	13431	5872	58502	15281
Unique reflections (R_{int})	4096 (0.0588)	1981 (0.0612)	4772 (0.0628)	6747 (0.0655)	9567 (0.0317)	6753 (0.0277)	3472 (0.0438)	8487 (0.1260)	6909 (0.0352)
No. of variables	334	143	424	382	482	451	290	515	452
Restraints	0	0	0	0	0	0	0	10	0
R_1 [$I > 2\sigma(I)$]	0.0342	0.0387	0.0313	0.0358	0.0282	0.0346	0.0627	0.0630	0.0375
wR_2 (all data)	0.0809	0.1319	0.0715	0.0907	0.0682	0.0795	0.1621	0.1876	0.0851
Largest diff. peak/hole [e Å^{-3}]	0.615/–0.792	0.363/–1.175	0.364/–0.232	1.654/–0.782	0.490/–0.399	0.438/–0.317	1.770/–1.709	0.686/–0.526	0.508/–0.455

(for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) T. Szymańska-Buzar, *Coord. Chem. Rev.* **2005**, *249*, 2195–2202; b) M. Górski, A. Kochel, T. Szymańska-Buzar, *J. Organomet. Chem.* **2006**, *691*, 3708–3714.

[2] a) T. Chen, W. Hunks, P. S. Chen, G. T. Stauf, T. M. Cameron, C. Xu, A. G. DiPasquale, A. L. Rheingold, *Eur. J. Inorg. Chem.* **2009**, 2047–2049; b) M. A. Malik, M. Afzaal, P. O'Brien, *Chem. Rev.* **2010**, *110*, 4417–4446.

[3] M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354–396.

[4] J.-L. Fauré, H. Gornitzka, R. Réau, D. Stalke, G. Bertrand, *Eur. J. Inorg. Chem.* **1999**, 2295–2299.

[5] M. Veith, S. Becker, V. Huch, *Angew. Chem.* **1989**, *101*, 1287; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1237–1238.

[6] M. Huang, M. M. Kireenko, K. V. Zaitsev, Y. F. Oprunenko, A. V. Churakov, J. A. K. Howard, M. V. Zabalov, E. Kh. Lermontova, J. Sundermeyer, T. Linder, S. S. Karlov, G. S. Zaitseva, *J. Organomet. Chem.* **2012**, *706–707*, 66–83.

[7] a) F. E. Hahn, A. V. Zabula, T. Pape, A. Hepp, *Eur. J. Inorg. Chem.* **2007**, 2405–2408; b) T. Gans-Eichler, D. Gudat, K. Nattinen, M. Nieger, *Chem. Eur. J.* **2006**, *12*, 1162–1173.

[8] a) D. Matioszek, N. Katir, N. Saffon, A. Castel, *Organometallics* **2010**, *29*, 3039–3046; b) A. McHeik, N. Katir, A. Castel, H. Gornitzka, S. Massou, P. Riviere, T. Hamieh, *Eur. J. Inorg. Chem.* **2008**, 5397–5403.

[9] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

[10] R. W. Chorley, P. B. Hitchcock, M. F. Lappert, W. P. Leung, P. P. Power, M. M. Olmstead, *Inorg. Chim. Acta* **1992**, *198*, 203–209.

[11] A. Schnepf, *Z. Anorg. Allg. Chem.* **2006**, *632*, 935–938.

[12] M. Veith, A. Rammo, *Z. Anorg. Allg. Chem.* **2001**, *627*, 662–668.

[13] M. Huang, E. Kh. Lermontova, K. V. Zaitsev, A. V. Churakov, Y. F. Oprunenko, J. A. K. Howard, S. S. Karlov, G. S. Zaitseva, *J. Organomet. Chem.* **2009**, *694*, 3828–3832.

[14] M. Veith, M. Grosser, V. Huch, *Z. Anorg. Allg. Chem.* **1984**, *513*, 89–102.

[15] a) E. Bonnefille, S. Mazires, N. El Hawi, H. Gornitzka, C. Couret, *J. Organomet. Chem.* **2006**, *691*, 5619–5625; b) A. Tzschach, M. Scheer, K. Jurkschat, *Z. Anorg. Allg. Chem.* **1984**, *512*, 177–180.

[16] a) L. D. Silverman, M. Zeldin, *Inorg. Chem.* **1980**, *19*, 270–272; b) Y. Ding, Q. Ma, H. W. Roesky, R. Herbst-Irmer, I. Usón, M. Noltemeyer, H.-G. Schmidt, *Organometallics* **2002**, *21*, 5216–5220; c) C. S. Weinert, A. E. Fenwick, P. E. Fanwick, I. P. Rothwell, *Dalton Trans.* **2003**, 532–539.

[17] a) K. A. Miller, J. M. Bartolin, R. M. O'Neill, R. D. Sweeder, T. M. Owens, J. W. Kampf, M. M. B. Holl, N. J. Wells, *J. Am. Chem. Soc.* **2003**, *125*, 8986–8987; b) A. E. Wetherby, C. R. Samanamu, A. C. Schrick, A. DiPasquale, J. A. Golen, A. L. Rheingold, C. S. Weinert, *Inorg. Chim. Acta* **2010**, *364*, 89–95.

[18] S. R. Stobart, M. R. Churchill, F. J. Hollander, W. J. Youngs, *J. Chem. Soc., Chem. Commun.* **1979**, 911–912.

[19] N. A. Victorov, T. K. Gar, I. S. Nikishina, V. M. Nosova, D. A. Ivaschenko, V. F. Mironov, *Russ. J. Gen. Chem.* **1986**, *56*, 1535–1539.

[20] J. Barrau, G. Rima, T. E. Amraoui, *J. Organomet. Chem.* **1998**, *570*, 163–174.

[21] D. Ellis, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1992**, 3397–3398.

[22] P. Jutzi, H. Schmidt, B. Neumann, H. G. Stammler, *Organometallics* **1996**, *15*, 741–746.

[23] I. Schranz, L. Grocholl, C. J. Carrow, L. Stahl, R. J. Staples, *J. Organomet. Chem.* **2008**, *693*, 1081–1095.

[24] a) Y. I. Baukov, S. N. Tandura in *The chemistry of organic germanium, tin and lead compounds* (Ed.: Z. Rappoport), Wiley, Chichester, **2002**, vol. 2, pp. 1036–1072; b) E. Kh. Lermontova, M. Huan, A. V. Churakov, J. A. K. Howard, M. V. Zabalov, S. S. Karlov, G. S. Zaitseva, *Dalton Trans.* **2009**, 4695–4702.

[25] A. Meller, G. Ossig, W. Maringgele, M. Noltemeyer, D. Stalke, R. Herbstirmer, S. Freitag, G. M. Sheldrick, *Z. Naturforsch. B* **1992**, *47*, 162–170.

[26] a) N. Tokitoh, K. Manmaru, R. Okazaki, *Organometallics* **1994**, *13*, 167–171; b) G. Billeb, K. Bootz, W. P. Neumann, G. Steinhoff, *J. Organomet. Chem.* **1991**, *406*, 303–308.

[27] S. N. Gurkova, A. I. Gusev, N. V. Alekseev, T. K. Gar, N. A. Viktorov, *J. Struct. Chem.* **1991**, *31*, 833–835.

[28] a) N. V. Alekseev, S. N. Gurkova, A. I. Gusev, S. N. Tandura, T. K. Gar, N. Y. Khromova, N. A. Viktorov, V. F. Mironov, *Zh. Obshch. Khim.* **1982**, *52*, 2136–2137; b) S. N. Gurkova, A. I. Gusev, N. V. Alekseev, T. K. Gar, N. Y. Khromova, N. A. Viktorov, *J. Struct. Chem.* **1984**, *25*, 458–462.

[29] D. H. Chen, H. C. Chiang, *J. Chin. Chem. Soc.* **1993**, *40*, 373–377.

[30] A. Arndt, H. Schafer, W. Saak, M. Weidenbruch, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1341–1342.

[31] M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Riviere, M. Riviere-Baudet, *J. Chem. Soc., Dalton Trans.* **1977**, 2004–2009.

[32] S. P. Kolesnikov, I. S. Rogozhin, O. M. Nefedov, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1974**, *23*, 2297–2298.

[33] U. Wannagat, H. Niederprum, *Chem. Ber.* **1961**, *94*, 1540–1547.

[34] R. R. Schrock, J. Lee, L.-C. Liang, W. M. Davis, *Inorg. Chim. Acta* **1998**, *270*, 353–362.

[35] Y. Li, A. Turnas, J. T. Ciszewski, A. L. Odom, *Inorg. Chem.* **2002**, *41*, 6298–6306.

[36] H. C. S. Clark, G. N. Cloke, P. B. Hitchcock, J. B. Love, A. P. Wainwright, *J. Organomet. Chem.* **1995**, *501*, 333–340.

[37] C. R. Hauser, J. K. Lindsay, *J. Org. Chem.* **1957**, *22*, 482–485.

[38] a) R. Koppang, *Acta Chem. Scand.* **1971**, *25*, 3067–3071; b) A. Khvorost, P. L. Shutov, K. Harms, J. Lorberth, J. Sundermeyer, S. S. Karlov, G. S. Zaitseva, *Z. Anorg. Allg. Chem.* **2004**, *630*, 885–889.

[39] M. M. Khusniyarov, E. Bill, Th. Weyhermüller, E. Bothe, K. Harms, J. Sundermeyer, K. Wieghardt, *Chem. Eur. J.* **2008**, *14*, 7608–7622. This ligand was first obtained in 20% yield, see: A. Khvorost, Ph. D. Thesis, Philipps-Universität Marburg, **2003**. The refined synthetic procedure and other ligand syntheses by nucleophilic amidation of C_6F_6 were developed later, see: A. Sorokin, Ph. D. Thesis, Philipps-Universität Marburg, **2006**.

[40] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[41] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, **1997**.

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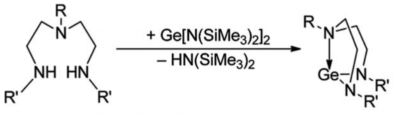
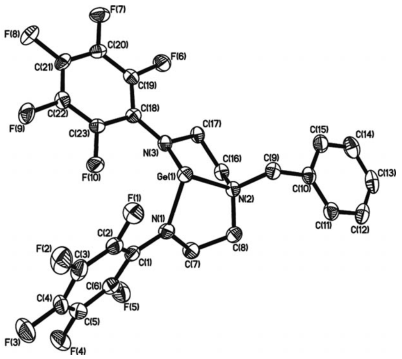
Germylenes





A series of novel, low-valent germanium compounds have been obtained by the reaction of Ge[N(SiMe$_3$)$_2$]$_2$ with various diamines or by the metathesis reaction of [GeCl$_2$·dioxane] with lithium amides. The oxidative insertion, [1+4] cycloaddition, and oxidation reactions of the synthesized germylenes were investigated. All the synthesized germylenes are monomeric.

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Stabilized Germylenes Based on Diethylenetriamines and Related Diamines: Synthesis, Structures, and Chemical Properties

Keywords: Germanium / N-ligands / X-ray diffraction / Amines / Lithium