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Coordination Chemistry Reviews 248 (2004) 411–427

COORDINATION CHEMISTRY REVIEWS

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Review

N-heterocyclic germylenes and related compounds

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This article is dedicated to Prof. Joachim Sieler on the ocassion of his 65th birthday

Contents

Abstract

N-heterocyclic germylenes (NHGe) are very versatile ligands and the heavier homologues of the better known N-heterocyclic carbenes (NHC). They are closely related to the Ge(II) complexes of amidinates, aminotroponiminates and β-diketiminates. The synthesis, chemistry and electronic properties of NHGe and these related compounds are reviewed and reference is made to the homologous NHC.

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Keywords: N-heterocyclic germylenes; Amidinates; Aminotroponiminates; β-Diketiminates

1. Introduction

The definition of N-heterocyclic germylenes (NHGe)[1] closely follows that for the better known homologous carbenes first reported by Arduengo et al. in 1991 (for recent reviews on NHC, see [1]). Thus, they are generally seen as derivates of 1,3,2-λ^2-diazagermole with a divalent germanium centre in the oxidation state 2+ (the valency refers to the number of bonds formed by a given atom, whereas the oxidation state refers to the number of electrons formally transferred. In this context a NHGe would be considered to be divalent and having the oxidation state 2+ for Ge, if the contribution of the lone pairs on nitrogen is not taken into account. If the NHGe acts as a Lewis base as in the metal complexes **25** or as Lewis acid as in **31**, the valency is increased without altering the oxidation state. It is profitable that both concepts are not identical, although they are usually treated as synonyms in the case of NHGe. For a definition of the two terms see [2]). In the course of this review it will be shown that the ring size can be varied from four to six and one or both of the nitrogen atoms substituted for sulphur without substantial loss of the electronic properties defining NHGe. Within the scope of this review compounds related to NHGe refers to those complexes where intramolecular complexation at germanium occurs forming a monoiminogermylene, e.g. the aminotroponiminates developed by Dias et al. (for a recent review, see [3]), β-diketiminates (for a recent review, see [4]), amidinates [5], or porphyrine-type ligands [6] (see Fig. 1). Veith's germylenes, containing a SiN_2Ge ring [7], are not discussed here, mainly because they have already been extensively reviewed [8].

Due to the stability of $GeCl_2$ in contrast to the very transient CCl_2, the corresponding acyclic diamides of Ge(II) have long been known (for recent reviews, see [9]). It appears

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[1] The acronym NHGe was introduced into the literature in close analogy to the established term NHC for the homologous N-heterocyclic carbenes.

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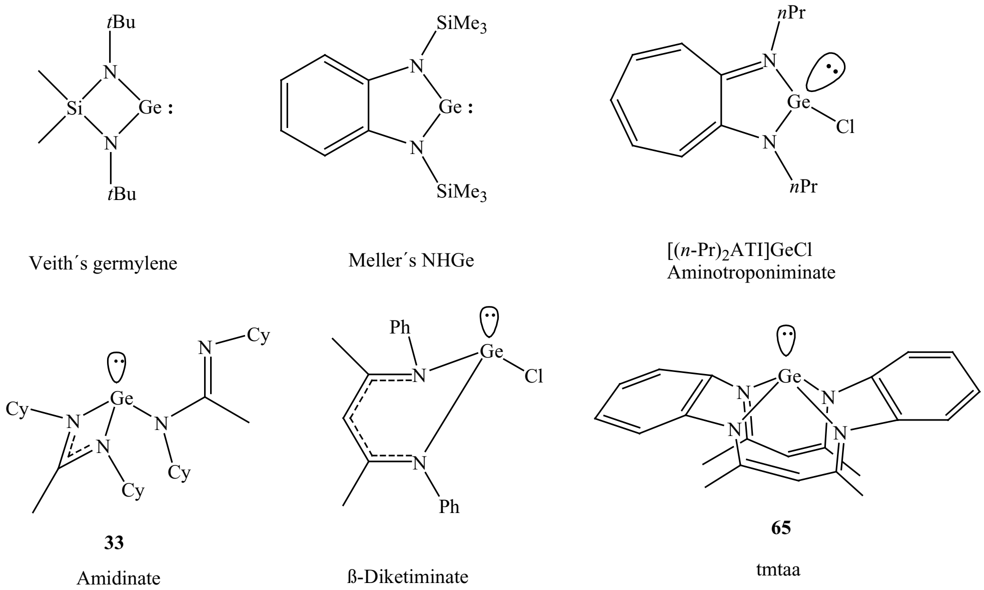
doi:10.1016/j.ccr.2003.12.004



Veith´s germylene

Meller´s NHGe

[(n-Pr)$_2$ATI]GeCl
Aminotroponiminate

33
Amidinate

ß-Diketiminate

65
tmtaa

Fig. 1. Structures of NHGe and related compounds.

that there has never been a sense of urgency to synthesise the first cyclic representative. It, therefore, comes as no surprise that when the first NHGe (Veith's germylene) [7] was published as early as 1982, its significance for the synthesis of the much sought after N-heterocyclic carbenes NHC was not noted. The first NHGe from the imidazole series was reported only 3 years later by Meller and Gräbe [10] and the first germanium analogue of Arduengo's carbene by the same group in 1989, complete with a crystal structure [11].

Around the same time the first transition metal complexes of compounds that can be regarded as intramolecularly base stabilised NHGe were reported [6,12]. The interest in these germylenes with porphyrin and porphyrin like ligands seems to come from the tumour localising ability and the cytotoxicity of the Ge(IV)-derivatives [13].

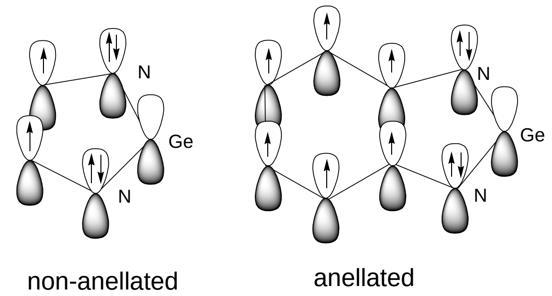
With the discovery of Arduengo et al.'s carbene in 1991 [14], interest in NHGe began in earnest, the first post-Arduengo NHGe being reported in 1992 [15]. Although the attention was focussed on NHC and their proven usefulness in catalysis [1], a very interesting and versatile chemistry of the germylenes was developed as well.

The intention of this review is to show the similarities between NHGe and their related compounds, to describe their electronic and steric properties as well as to compare them with NHC. Veith's germylene [7], although formally a NHGe and incidentally the first one to be reported in 1982, will not be discussed in this review as this class of compounds has already been described in detail elsewhere [8].

2. Theoretical studies

Unlike their NHC homologues theoretical studies of NHGe only started after their synthesis and characterisation. An earlier study by Barthelat and co-workers [16] concerning the stability of germylenes as compared to tetravalent germanium species containing double bonds predicted the greater stability of the germylene structure and attributed this to the conjugation with the heteroatom lone pair on nitrogen. In 1994, Heinemann et al. [17] conducted a more sophisticated study to explain the stability of Arduengo type NHGe and NHSi (for a recent review, see [18]) and to compare them with the NHC. Heinemann et al. essentially came to the same conclusion as Barthelat, but on a more general basis and with greater factual detail. From the N–Ge(II) single bond the later study calculated an unusually high torsional barrier for this formal single bond and attributed it to p_π–p_π electron delocalisation from the p_z lone pair on nitrogen into the empty p_z orbital on germanium. This effect is amplified by the introduction of a second amino function on germanium. The estimated effect on the Ge–N bond length was given as 8–9 pm decrease for the amino germylene and a somewhat lesser shortening for the diaminogermylene. The latter effect was attributed to averaging of the contribution from both substituents.

Having established the stabilising factors for acyclic diaminogermylenes, the study goes on to calculate the effect of cyclisation. In the case of saturated NHGe, cyclisation was estimated to be stabilising by 17.5 kcal/mol caused by an extra destabilisation of the triplet state due to the small N–Ge–N angle in the ring, an explanation based on steric factors rather than electronic factors. For unsaturated NHGe, a degree of cyclic π-electron delocalisation was evident in the theoretical calculations. There is no claim for aromaticity in NHGe in this study in contrast to the conclusions drawn by Lehmann et al. [19] who consider the aromaticity in NHGe to be much weaker than in the corresponding carbenes. To better understand the arguments for/or against aromaticity consideration should be given to the general concept. A true Hückel aromatic system possesses $(4n+2)$ π-electrons,

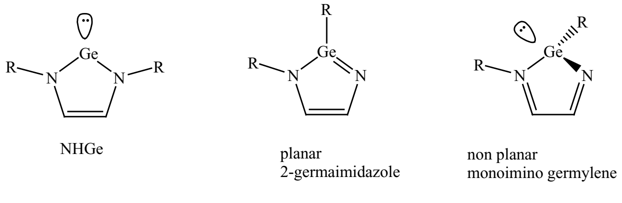


non-anellated anellated

Fig. 2. The electronic setup of the NHGe. Only the p-orbitals responsible for the delocalised π-electron system are shown.

is monocyclic and contains no heteroatoms. Whereas, the $(4n + 2)$ electron rule is only met by including two lone pairs from the nitrogen atoms, the provision regarding heteroatoms is intrinsically broken by the need for three heteroatoms in the usually five membered ring (2N and Ge). The limitation to monocyclic systems is equally violated for the anellated representatives (see Fig. 2). It is, therefore, advantageous to look at the extent of π-delocalisation before discussing aromaticity. In a study regarding group 14 substituted allyl systems Gobbi and Frenking [20] established that the bond strength of the C=E (E = C, Si, Ge, Sn, Pb) π-bond decreases rapidly going down the group and that only half of the stabilisation energy of this bond is caused by resonance stabilisation with the other half due to σ-bond and through-space electrostatic interactions. Other studies [21] use the term core contributions for the latter effects. Together with the known decrease of orbital overlap in increasing the size of the p-orbital, especially for the heavier homologues Ge, Sn and Pb, it becomes prudent to refer to the stabilisation as due to π-electron delocalisation rather than to use the term aromaticity that implies properties that cannot be fully met by NHGe.

Finally, Heinemann et al. [17] compared the stabilities of standard NHGe with hydrogen substituents on the nitrogen atoms with its 1,2-shift isomer 2-germaimidazole. The findings are very instructive. Firstly, a minimum for the planar 2-germaimidazole could not be found and, secondly, the 1,2-shift isomer actually found in symmetry relaxation calculations is a non-planar species best described as a monoiminogermylene stabilised by intramolecular coordination from an amino group (see Fig. 3). This monoiminogermylene was calculated to be 37.5 kcal/mol less stable than its cyclic diaminogermylene isomer. Derivatives are realised in the case of amidinates, aminotroponiminates and β-diketiminates of germanium(II) (see below). All these complexes realise the predicted planar[2] GeN_2C_n ($n = 1$–3) ring and an angular substituent on Ge (usually Cl, N or alkyl) with a tetrahedral geometry on germanium.



NHGe planar 2-germaimidazole non planar monoimino germylene

Fig. 3. A generalised NHGe and its two most important isomers.

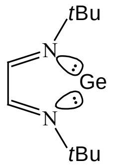


Fig. 4. Illustration of Arduengo's "chelated atom" model.

The fundamental difference to carbenes is that in the case of Ge, the divalent state is thermodynamically preferred to tetravalent isomers with formal Ge=N double bonds [17]. This is a consequence of the well-known observation that the lower oxidation state is increasingly preferred upon going down a particular main group.

Subsequent theoretical studies have combined analytical investigations with theoretical calculations so as to explain the empirical data. Among these were photoelectron spectroscopy (PES) [22,23], core excitation spectroscopy [19] and electrochemical investigations [24].

Arduengo et al. used PES to evaluate the electronic structure of NHGe [22]. Although they utilised the *tert*-butyl substituted derivative that was subsequently shown to exhibit a steric influence on the bond lengths [25], their main conclusions remain very much valid. They deduced the same electronic trends for the NHGe as Heinemann et al., but phrased it differently. In their study, they described an increase for the ionisation energy for the group 14 centre lone pair with increasing atomic number. This corresponds with an increase in s-character and thus stabilisation of the lower oxidation state in this direction [17]. On the other hand, they also stated the opposite trend for the π-3 orbital (mainly the C=C π-orbital with some out-of-phase mixing of the nitrogen lone pairs and group 14 p-orbital). In addition, they found that the contribution of the C=C backbone to the π-3 orbital diminishes accordingly. They also put forward a theory that the C_2N_2 unit of the NHGe can act as a four electron donor to the germanium atom (see Fig. 4).

Boehme and Frenking [26] again state that the main contribution for the stabilisation of NHGe comes from p_π–p_π donation of the nitrogen lone pairs into the p_z-orbital of germanium. The 6π-electron delocalisation merely provides an additional but not a necessary thermodynamic stabilisation. The study by Lehmann et al. [19], backed by core excitation spectroscopy, puts a much higher emphasis on aromaticity, but otherwise is consistent with the earlier results [17]. Stating rightly that the NHC, NHSi and NHGe formally fulfil the Hückel electron count for aromatic systems, it goes on to point out that the orbital overlap of the E=N bond (E = C,

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[2] With β-diketiminates, only the cationic species are planar, the neutral compounds possess envelope conformation.

Si, Ge) decreases with increasing atomic numbers. They also attribute the greater stability of the unsaturated species over the saturated derivatives to an aromatic and/or geometric stabilisation. For the sake of avoiding needless arguments the term aromaticity should be substituted for cyclic π-electron delocalisation.

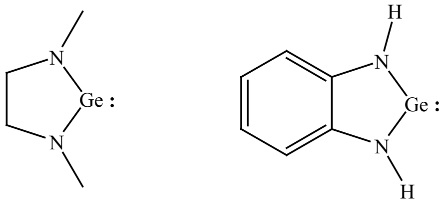
Finally, Pause et al. [24] measured and calculated the redox potentials of a number of NHC, NHSi, NHGe and NHN (N-heterocyclic nitrenes) in order to draw conclusions of the electronic structures of these compounds from the ease of reducibility. As expected, the germylenes were the easiest to reduce with the carbenes being absolutely inert under the conditions employed. Another aspect of the study carried out by Pause et al. was the influence of anellation upon the electronic structure of NHGe. Here, reduction of the non-anellated and the naphtho-anellated compounds was feasible, whereas the benzo- and pyrido-anellated species could not be reduced.

The influence of anellation was further investigated in a study by Heinicke et al. [21]. The already well-known trend for π-bond stabilisation in carbenes and stabilisation from increasing s-character of the lone pair on the heavier group 14 elements was expressed again. Although the study was mainly concerned with NHSi, the results are applicable to NHGe as well. Anellation was found to destabilise the germylene with a very pronounced effect exercised by unsymmetrical anellation. These unsymmetrically anellated germylenes are highly reactive with the reactivity considerably reduced for those species possessing a HOMO with a symmetrical charge-density distribution.

Theoretical studies concerning the reactivity of NHGe are extremely rare ([21] and for a review, see [29]). The only other very interesting study by McGuinness et al. [27] explored the possible susceptibility to oxidative addition on NHGe in catalytic processes with subsequent catalyst deactivation. This study is the first one concerned with possible catalytic applications for NHGe. Strangely, the catalytic potential of NHGe is largely unexplored especially when compared to their carbene homologues [1]. Unfortunately, it is pointed out [27] that applications involving metal-hydrocarbyl species will be prone to methyl migration and thus loss of the ligand. Therefore, in these processes, the NHGe can not be regarded as an innocent two-electron donor auxiliary ligand.

3. N-heterocyclic germylenes (NHGe)

The first stable NHGe based on the imidazole framework was published by Meller and Gräbe [10] in 1985, a full 6 years before the report of the first isolated NHC by Arduengo et al. in 1991 [14]. This, and the following two reports in 1989 [11,28], passed nearly unnoticed and it became almost universally accepted that the first report of a stable NHGe was in 1992 by Herrmann et al. [15]. It is very likely that the fact that these early reports were published in German had a good deal to do with this apparent lack of publicity.



1b **9**

Fig. 5. The structures of N-heterocyclic germylenes NHGe.

These first NHGe were the saturated diazagerma(II)cyclopentane compounds **1** and **2**. It is very interesting to note that the one is the *N*,*N*′-dimethyl and the other the *N*,*N*′-diphenyl derivative. The corresponding Wanzlick carbenes [29] were still elusive and considered to be impossible to synthesise years after Meller's original report [30]. The synthesis of **1** and **2** is fairly straightforward involving dilithiation of the appropriate diamine and subsequent reaction with $GeCl_2$(1,4-dioxane) with a yield of 27 and 67%, respectively [10] (see Scheme 1). Both compounds are remarkably stable under anaerobic conditions, but are very sensitive towards moisture. The compound **1** melts at 90 °C with slow decomposition and **2** melts without decomposition at 291–301 °C. Whereas, **1** could be purified, attempts to purify **2** by vacuum distillation failed due to the appearance of the disproportionation product **3** establishing the first reaction compound of this new class of compounds.

Some 4 years later the first crystal structure of a NHGe was reported by the same author [11]. The main concern of this publication was the oxidation of amino stabilised germylenes with azido compounds. Among the germylenes tested was the first structurally characterised and the first anellated NHGe **4** named 1,3-bis(trimethylsilyl)-1,3-diaza-2-germa(II)indane by the authors. Reaction of **4** with the silylazides **5** is facile and yields the tetraazagermoles **6** via highly reactive iminogermane[3] intermediates **7**. The second azide attacks the Ge=N bond of the iminogermane in a 1,3-dipolar addition. The unsaturated NHGe **1b** forms the hexaza-digerma-dispirododecanes **8** under similar reaction conditions. The product is formed by dimerisation of the intermediate iminogermane **7b** (see Scheme 2).

In the same year Meller and co-workers [28] published the parent compound of the benza-anellated NHGe **9** (see Fig. 5) as an impure product and reported on the first S-heterocyclic germylene SHGe **10** and the mixed NHGe **11** (see Fig. 6). The SHGe are thermally stable and could be sublimed at 120–130 °C, whereas **11** can be distilled at 125 °C without decomposition. From the distillation and sublimation residues the familiar Ge(IV) spiro-compounds were isolated.

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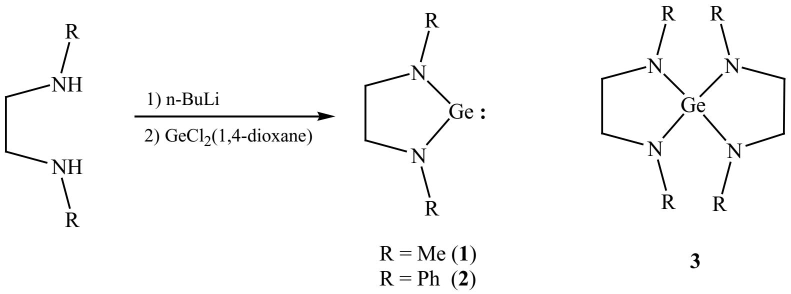
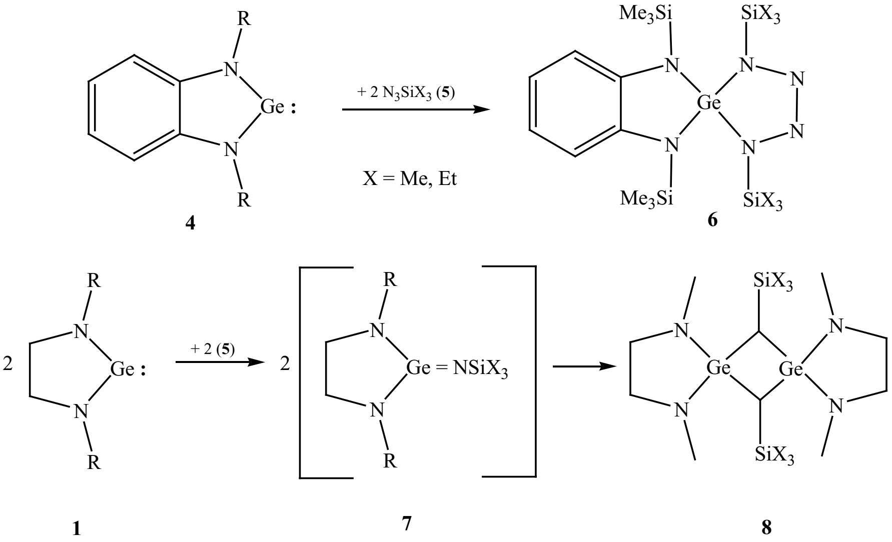
[3] The term iminogermane puts the emphasis on germanium and is the one used by Meller, a German researcher. The alternative anglosaxon term germaimine, puts the emphasis on the imine.



Scheme 1. Standard synthesis of NHGe.



Scheme 2. Reactivity of NHGe towards silylazides.

After the discovery of the first stable NHC in 1991 the interest in the analogous germylenes changed, aided by the obvious discontinuity. In 1992 Herrmann et al. published the synthesis of the saturated **12a** and unsaturated **12b** *tert*-butyl substituted analogues of **1** [15] (see Fig. 7). They are the first structurally characterised non-anellated NHGe. Whereas, **12b** is planar, the structure of **12a** displays the expected deviation from planarity for the C–C backbone. Both compounds are monomeric in all three aggregation states. That is in contrast to the assumption of Meller and Gräbe who suspected intermolecular interactions in the solid state [10]. For the first time Herrmann et al. extended the chemistry of NHGe to their coordination ability for metal complexes. Compound **12a** was reacted with $[Ni(CO)_4]$ and $[Ni(1,5\text{-}cod)_2]$ to yield the metal germylene complexes $[Ni(\mathbf{12a})_n(CO)_{4-n}]$ ($n = 1, 2$) and $[Ni(\mathbf{12a})_3]$, respectively. From the carbonyl region of the IR-spectra they deduced the π-acceptor strength of the saturated germylene **12a** by comparison with the respective PPh_3 nickel complexes. They came to the conclusion that NHGe are poor π-acceptors with a strength comparable to tertiary phosphines. This general conclusion might be premature in the light of evidence for anellated NHGe slowly unfolding some 10 years later (see below).

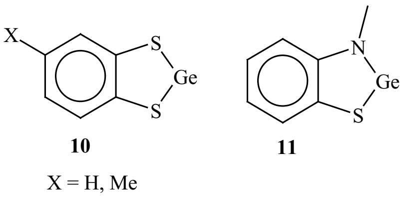


Fig. 6. The structures of S-heterocyclic germylenes SHGe.

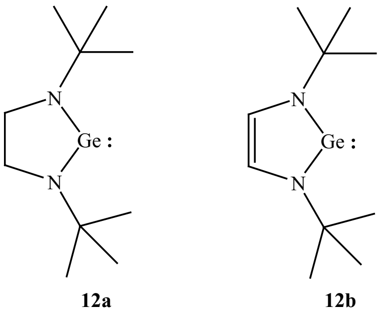
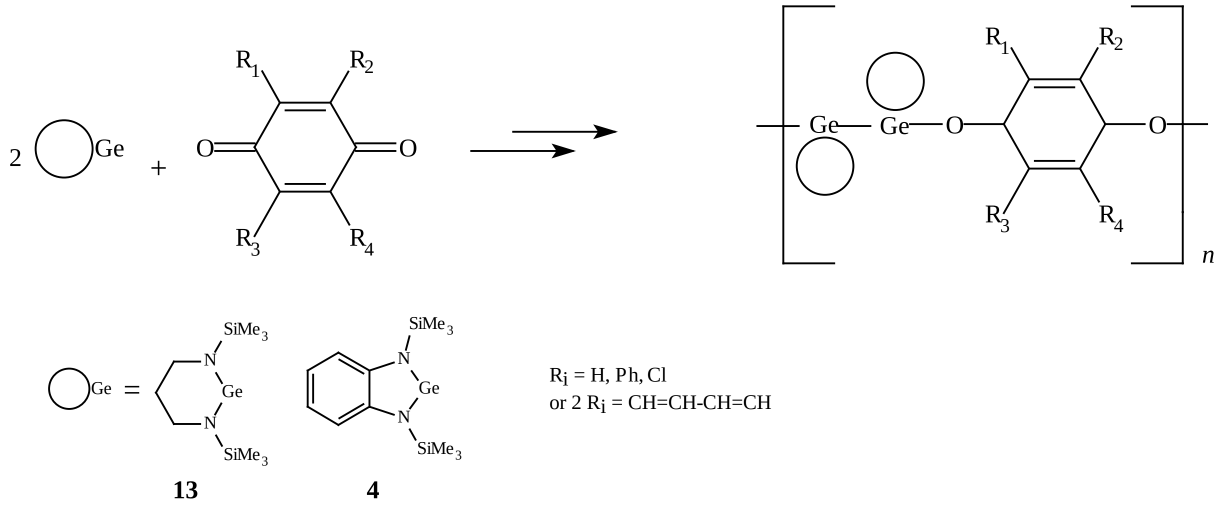


Fig. 7. The structures of Herrmann’s NHGe, the saturated and the unsaturated non-anellated NHGe.



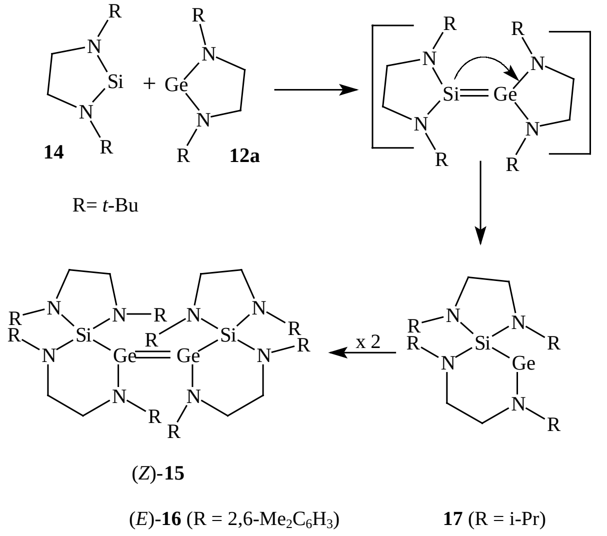
Scheme 3. The copolymerisation of NHGe with *p*-benzoquinones.

Another observation for **12a**, in particular that heating **12a** above 470 K yields **12b** by dehydrogenation, made the discovery of a chemical vapour deposition (CVD) application for **12a** and **12b** possible. Heating of **12a** or **12b** above 900 K leads to the deposition of very pure layers of Ge or Ge/GeH depending on the reaction conditions [15]. This led to various applications involving the production of thin Ge-films [31] and the deposition of pure Ge on Si-wafers [32–34].

In 1994, Kobayashi et al. reported the copolymerisation reactions of Meller's NHGe **4** and of **13** with *p*-benzoquinones [35]. The reactions were carried out without cocatalyst at very low temperatures (−78 °C) and yielded the 2:1 copolymers (Ge:quinone) with high yields and activities capitalising on the oxophilicity of Ge(II). The polymers are characterised as alternating Ge–Ge and Ge–O units, although a polymer without Ge–Ge bonds was formed in one case (see Scheme 3).

The ease of preparation of the unsaturated NHGe **12b** was utilised in the preparation of corresponding phosphenium and arsenium cations by Cowley and co-workers [36]. In 1997, they reacted **12b** with ECl_3 (E = P, As) and obtained the products in moderate yields (see Fig. 8). The fate of Ge(II) could not be fully elucidated, although some is oxidised to Ge(IV) forming the $GeCl_5^-$ counter anion. A reduction product was not reported.

In the same year, Weidenbruch and co-workers [37] studied the reaction between **12a** and the silylene analogue **14**, first reported by Denk et al. [38] and Denk and West [39] (see Scheme 4). After initial formation of a 1:1 adduct,



Scheme 4. The reactivity of the saturated NHGe **12a** with its silylene homologue.

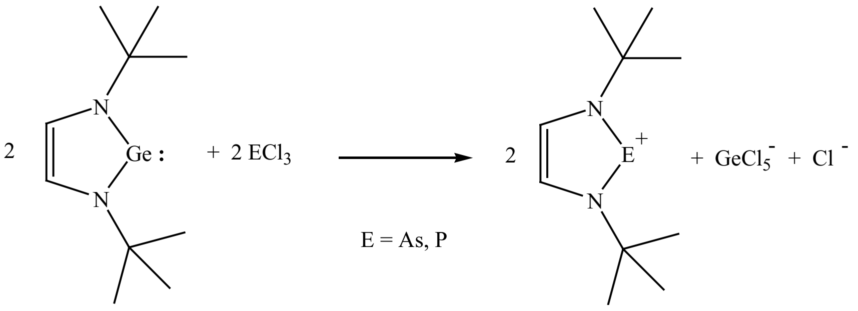
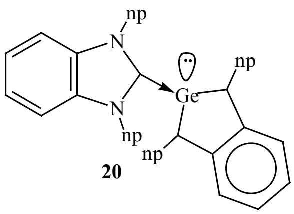


Fig. 8. The reaction of **12b** with PCl_3 and $AsCl_3$.



20

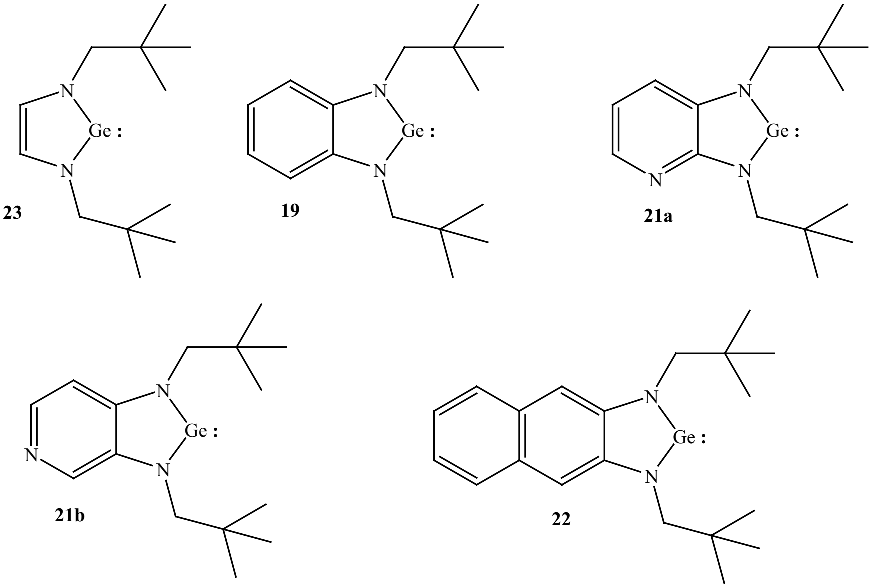
np = *neo*-pentyl

Fig. 9. The adduct between the NHGe **19** and its carbene homologue **18**.

presumably displaying a Si=Ge double bond, the silylene inserts into the Ge–N bond. The initial rearranged product dimerises to form (*Z*)-**15** possessing a very long Ge=Ge double bond of 245 pm and a large *trans*-bent angle of 45°. In a subsequent paper [40], the same authors published a report whereby they varied the N-substituents on **12a** to obtain the dimer (*E*)-**16** with the sterically less hindered NHGe (R = *i*Pr) and the monomer **17** with the sterically hindered NHGe (R = 2, 6-dimethylphenyl). The latter exhibits a short non-bonding contact of 410 pm between the two germanium atoms attributed to weak dispersive forces between the atoms.

The initial 1:1 adduct **20** was finally reported by Gehrhus and Hitchcock [41] utilising the benza-anellated carbene **18** and germylene **19**, respectively. However, in this case the silylene failed to react with the germylene again proving the greater stability of the unsaturated NHGe. The carbene/germylene adduct **20** was obtained upon mixing of benzene solutions of the two starting compounds (see Fig. 9). The structure is reminiscent of the structures of the germanium(II) aminotroponiminates [3] with the carbene acting as a neutral two electron donor to germanium instead of an anionic two electron donor as in the case of Cl^- in the aminotroponiminates. The carbene entity remains almost unchanged compared to the parent compound **18**. The planar NHC forms an angle of 105° with the likewise planar NHGe. The C–Ge–N angles (101.08 and 101.26°) in **20** compare with the N–Ge–X (X = N, Cl) angles of 95.87–100.0° in the aminotroponiminates. The C–Ge bond length is very long with 233.9 pm and is thus about 10% longer than comparable Ge–C bonds [41]. Unfortunately, no experimental details were given for the germylene **19**.

Although anellated representatives were among the first NHGe reported, no systematic investigation of the effect anellation has on their chemistry was undertaken for a considerable period of time. This is even more surprising considering the very significant differences in the stabilisation of the anellated and non-anellated carbenes **18** [42] and **12c** [1]. Heinicke et al. investigated benzo-anellated **19** [25], pyrido-anellated **21a,b** [21] and naphtho-anellated **22** [43] NHGe and established their electronic and structural properties using NMR spectroscopy and ab initio calculations (see Fig. 10). To exclude any influence the substituents on nitrogen might have, a series of NHGe displaying *neo*-pentyl groups on the ring nitrogens were synthesised. The ^1H and ^{13}C NMR spectra display the familiar downfield shifts of the methylene groups within the *neo*-pentyl substituents due to the influence of the delocalised six π-electron system. No significant difference in chemical shifts for this substituent due to the nature of the anellated ring was observed [25]. However, the stability of the ring seems to depend on the nature of the anellation [21]. Pyrido-anellated species were found to be less stable than benzo- or naphtho-anellated analogues with pyrido[*c*]-anellation being by far the most unstable. The authors concluded that a certain degree of symmetry is required within the anellated NHGe in order to confer stability to the molecule. This condition asks for symmetry in the HOMO of the ground state rather than the atomic structure



23 **19** **21a**

21b **22**

Fig. 10. A series of *N*,*N*′-*neo*-pentyl substituted NHGe, distinguished by the anellated ring system.

Table 1
Selected bond lengths (pm) and angles (°) of a series of *N,N′*-*neo*-pentyl substituted NHGe and the *tert*-butyl substituted **31**

	Bond length (pm) (angle (°))				
	19	**21a**	**23**	**24**	**31**
N–Ge	186.1 (3) 186.6 (3)	186.0 (3) 186.6 (3)	180.8 (1)	181.9 (6)–183.7 (6)	201.6 (3) 203.1 (3)
N–C_{ring}	139.3 (5) 139.1 (5)	137.6 (4) 137.6 (4)	143.7 (3)	136.2 (8)–140.5 (10)	137.1 (4)
N–C_{chain}	145.9 (5) 145.5 (5)	146.6 (4) 146.8 (4)	145.4 (2)	142.9 (9)–147.8 (8)	151.3 (4) 152.2 (8)
C=C	141.9 (5) 138.3 (6)–139.9 (5)	142.9 (5) 133.9 (4)–138.8 (5)	138.6 (7)	132.0 (12)–134.4 (9)	145.1 (5) 146.2 (5)
N–Ge–N	84.9 (1)	84.6 (1)	87.75 (6)	85.7 (2)–86.5 (3)	105.6 (1)

of the molecule. This can best be seen in pyrido-anellation. Both the pyrido[*c*]- and the pyrido[*b*]-anellated NHGe are unsymmetric per se, but only the latter has the heteroatom in the nodal plane of the HOMO and thus is by far more stable than the former [21].

As the resolution of NMR spectra as expressed by their chemical shift values was not sufficient to detect the influence of anellation unambiguously, a study of bond lengths and bond angles of a series of NHGe was undertaken [25]. The series comprised the non-anellated **23**, benzo- **19** and pyrido[*b*]- **21a** anellated representative with *neo*-pentyl as the common substituent on nitrogen. The crystal structure determinations for the three compounds showed only a small influence of anellation, but a clear trend in the structural parameters (see Table 1). It was established that the empty p_z-orbital of germanium is in direct competition with the unsaturated backbone for the electron density of the nitrogen lone pairs. This results in an elongation of the Ge–N bonds with simultaneous shortening of the C_{ring}–N bonds in the order pyrido[*b*]- > benzo- > non-anellated.

Therefore, anellation should translate into a decrease of electron density on the germanium centre. Such an increasing electron deficiency would affect the π-acceptor properties of these ligands. As π-acceptor properties can be easily monitored by the relative position of CO-bands in the IR spectra of transition metal carbonyl complexes of these prospective ligands, Kühl and Heinicke recently published the compounds *fac*-[Mo(**23**)$_3$(CO)$_3$] **24** and *cis*-[Mo(**23**)$_2$(CO)$_4$] **25** as preliminary communication [44] (see Scheme 5). The IR spectra of these complexes indeed showed **23** to be the better π-acceptor ligand compared to the saturated NHGe **12a**. It is therefore reasonable to expect that the anellated germylenes have π-acceptor properties significantly superior to those of electron deficient phosphines. This is mirrored in the structural parameters of **23** in the structurally characterised complex **24** compared to the free ligand **23**. Upon complexation the Ge–N bond lengths increase slightly and the C_{ring}–N bonds shorten considerably as is expected if the germanium atom were indeed in competition with the unsaturated backbone for the lone pairs on nitrogen.

Finally, Laporte-Chrostowska et al. recently published a study concerning the synthesis of the sterically unprotected saturated NHGe **26** and its analysis using UV photoelectron spectroscopy [45]. The preparation involved the flash vacuum thermolysis (FVT) of the corresponding germacyclopentene (see Fig. 11). Unfortunately, the only details

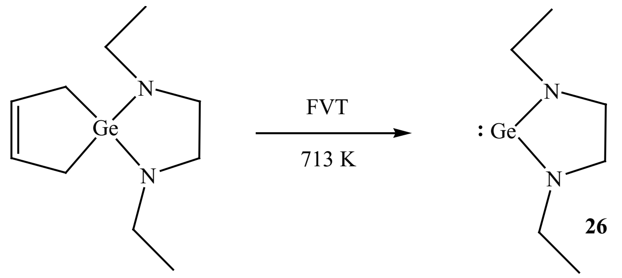
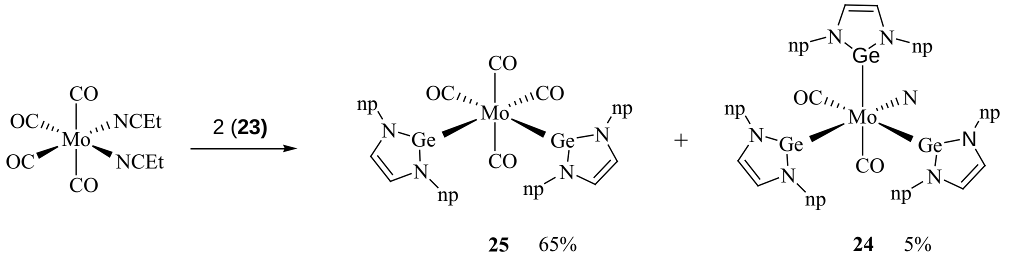
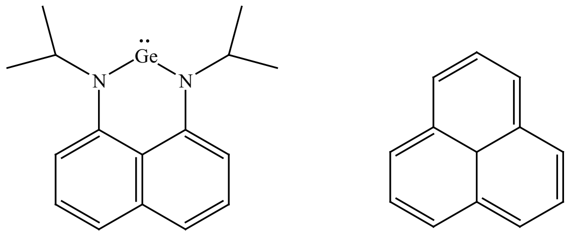


Fig. 11. The synthesis of the sterically unprotected saturated NHGe **26**.



Scheme 5. The synthesis of the molybdenum carbonyl complexes **24** and **25**.



27 perinaphtene

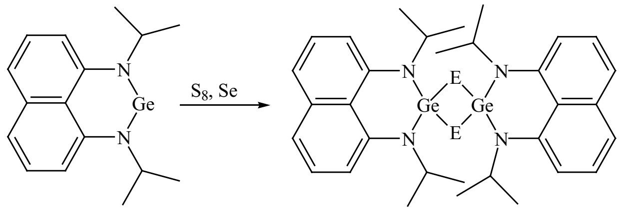
Fig. 12. The structures of the NHGe **27** and the similar hydrocarbon perinaphthene (1H-phenalene).

provided by the authors were the reaction temperature of 713 K and the ionisation potential of 7.26 eV.

Besides five membered NHGe there are a few examples with larger ring size. Richeson et al. synthesised an NHGe derived from 1,8-diaminonaphthalene [46], a ligand system already utilised for the synthesis of the homologous N-heterocyclic stannylenes NHSn [47]. The compound **27** displays rather unique electronic properties. Its germylene entity consists of a C_3N_2Ge six member ring with a delocalised seven π-electron system that makes the tricycle reminiscent of perinaphtene (1H-phenalene) (see Fig. 12). Unlike perinaphtene, **27** is planar and has a fully conjugated $(4n+2)$ π-electron system in the backbone obeying the Hückel rule. The NHGe **27** is readily coordinated to nickel forming the complex [Ni(**27**)$_4$] **28** with a distorted tetrahedral geometry on Ni. The most interesting feature of **28** is the shortening of the Ge–N bond compared to the parent germylene **27**. This would suggest poor π-acceptor properties for **27** following the arguments of Kühl et al. [44]. Such poor π-acceptor properties might be expected from an “electron rich” NHGe displaying a delocalised seven π-electron system.

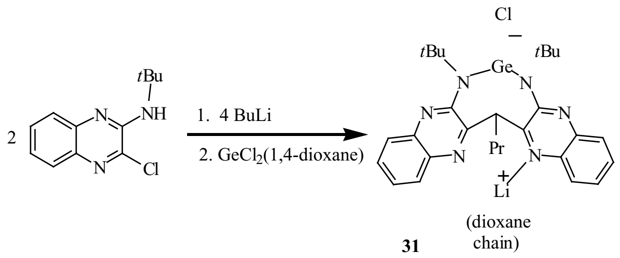
A similar observation is made for the oxidation products of **27** with the chalcogens S and Se. The respective oxidation products are the dimers **29** (E = S) and **30** (E = Se) (see Scheme 6). They too display shortened Ge–N bond lengths.

Another interesting NHGe displaying an eight membered ring was reported by Kühl et al. [48]. Germylene **31** was synthesised by a cascade reaction starting from 2-chloro-3-*tert*-butylamino-quinoxaline (see Scheme 7). In **31**, the Ge–N bond lengths are very long and are effectively single bonds without any p_π–p_π contribution from the nitrogen electron lone pairs. This is explained by the large electron pulling effect of the two quinoxaline rings. As conjugation is interrupted in the eight member ring by the presence of a sp^3-hybridised carbon atom, no additional stabilisation due to a delocalised π-electron system is possible. The result is an apparent *Umpolung* of the otherwise nucleophilic NHGe into an electrophilic one. The compound is stabilised by addition of a LiCl molecule—the chloride is coordinated to Ge and the Li atom is bonded to nitrogen atoms of the two quinoxaline rings. According to the authors, **31** can serve as an example for the diazabutadiene description of a NHGe. The reason lies in the inability of the nitrogen lone pairs to stabilise the empty p_z-orbital on Ge.



27 E = S (**29**), Se (**30**)

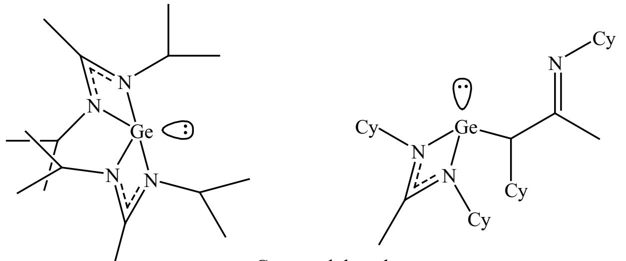
Scheme 6. The reaction of **27** with the chalcogenes sulfur and selenium.



Scheme 7. The synthesis of the germylene **31** starting from 2-chloro-3-*tert*-butylamino-quinoxaline.

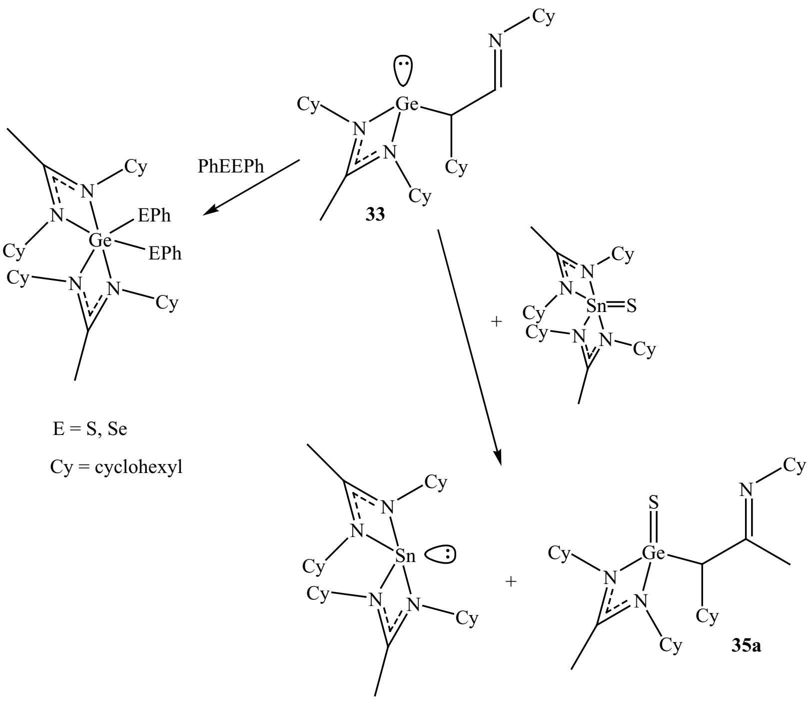
4. Amidinates

The amidinates are monoanionic ligands that form essentially planar four membered rings with Ge(II). The resulting structures can be divided into two groups, those displaying two amidinate chelate rings [5] and those with one ligand bonded in η^1-fashion [49–52] (see Fig. 13). The decisive parameter as to which structure will be realised by the complex seems to be the steric demand of the substituent on nitrogen. Whereas, **32** displaying the *iso*-propyl group has the bis-chelate structure [5], the η^1-coordination is shown by **33** possessing cyclohexyl substituents [49]. The latter can be regarded as a monoiminogermylene stabilised by intramolecular coordination from an amino group. The germylene shows the expected structure originating from the tetrahedral geometry on germanium. The structure of **32** is intermediate between trigonal bipyramidal and square pyramidal with the lone pair on germanium occupying an equatorial or apical position, respectively [5].



32 Cy = cyclohexyl **33**

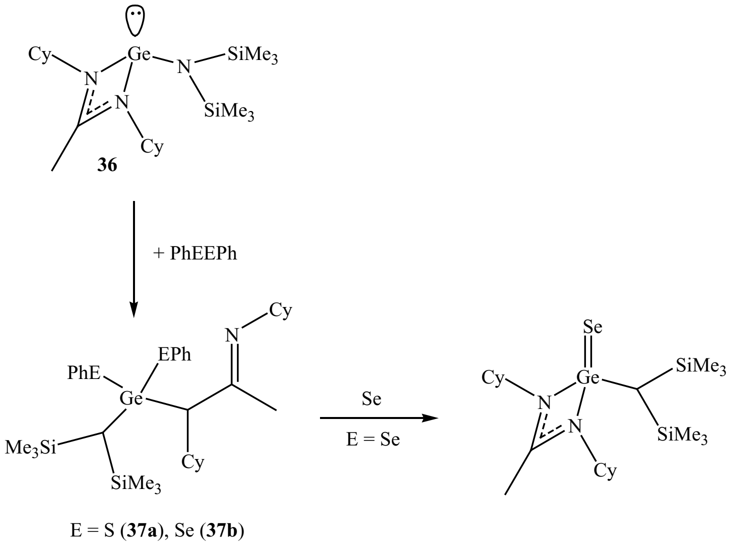
Fig. 13. The two bonding modes in germanium(II)amidinate complexes.



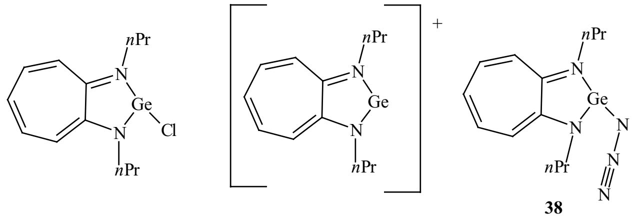
Scheme 8. The sulfur transfer reaction between **33** and the homologous Sn(IV)S compound.

The reactivity of the germanium(II) amidinate complexes was tested almost exclusively with the cyclohexyl derivative. Introduction of amido ligands onto germanium can be stepwise and the intermediate was isolated in the case of (CyNC(Bu^t)NCy)GeCl **34** [49]. No attempt to abstract the chloride by AgCl metathesis was undertaken. Oxidation by S and Se is facile and renders the germylene sulphide **35a** and selenide **35b**, where the group 16 atom occupies the position of the lone pair. The rest of the structure is virtually unchanged. Compound **35a** can also be synthesised by a sulphur transfer reaction between **33** and the homologous Sn(IV)S-compound [50] (see Scheme 8).

Another interesting experiment is the reaction of **33** with diphenyl disulphide and diselenide, respectively [51]. In both cases the product displays the hexa-coordinate germanium complex with the amidinate acting as a η^2-ligand. The mixed complex **36**, however, behaves differently (see Scheme 9) [51]. Upon reaction with the dichalcogenide oxidative addition occurs, but the η^2-bonded amidinate becomes a monodentate ligand leaving the Ge(IV) atom with a tetrahedral coordination sphere. Interestingly, reformation of the diphenyl diselenide occurs upon reaction of **37b** with elemental selenium with the product exhibiting a bidentate amidinate.



Scheme 9. The oxidation of Ge(II) amidinates with diselenides and disulfides.



[(n-Pr)$_2$ATI]GeCl [(n-Pr)$_2$ATI]Ge$^+$

Fig. 14. The structures of germanium(II)aminotroponiminates.

5. Aminotroponiminates

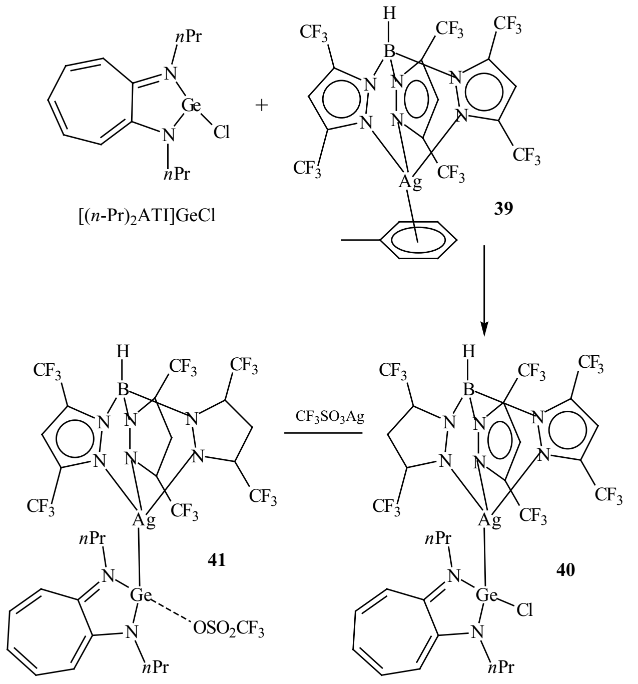
The aminotroponiminate ligand (ATI) is similar to the amidinates, but with an unsaturated carbon backbone instead of the solitary carbon atom. A review covering the synthesis and the structures of their complexes with group 14 elements has recently been published [3]. Their electronic properties and relationship to N-heterocyclic germylenes were, however, not reviewed.

ATI are monoanionic ligands with an additional amino function. Therefore, they form monoiminogermylene complexes upon reaction with GeCl$_2$(1,4-dioxane). There are two main structural differences to the NHGe. The aminotroponiminates are three-coordinate with an additional, weakly coordinated substituent, usually chloride or azide, on Ge (see Fig. 14). Secondly, the N–Ge bonds are generally significantly longer than those in NHGe. The elongation is typically around 8–9 pm and thus approximately equal to the stabilisation predicted by Heinemann et al. [17]. Abstraction of the weakly coordinated chloride atom is facile rendering a planar cation. Cation–anion interactions are usually very weak in these compounds, even in the solid state.

The chemistry of Ge(II)ATI complexes is a prime example for the thermodynamic stability of divalent cyclogermylenes compared to the 2-germaimidazole. Since the publication of the review by Dias et al. [3] the chemistry of Ge(II)ATI developed considerably with the synthesis of the azides [52] and the silver adducts of both the chlorides [53] and the azides [54].

The [ATI]Ge azides are readily accessible from the chlorides by NaCl metathesis in thf using sodium azide as the azide source [52]. They are sensitive to moisture and air and are not very stable thermally with [(n-Pr)$_2$ATI]GeN$_3$ **38** decomposing at 57 °C. The N$_{\text{ring}}$–Ge bond lengths are significantly shorter than the N$_{\text{azide}}$–Ge bond length in these complexes, again indicating a stabilising contribution from the ring nitrogen lone pairs into the empty p$_z$-orbital on germanium. The azide group itself remains linear and forms a near tetrahedral angle with the planar [ATI]Ge ring system.

Removal of chloride from [ATI]GeCl using Tp$^{\text{CF3}}$Ag (toluene) **39** failed to produce the expected [ATI]GeTp$^{\text{CF3}}$ complex and yielded the [ATI]GeCl silver adduct **40** instead (Tp$^{\text{CF3}}$ = tris-(1,3-bis-triflourmetyl)-pyrazolyl-borate) (see Scheme 10) [53]. Solutions of **40** do not eliminate AgCl even after several days. This must be due to the stabilisation of the silver atom by complexation with the tridentate Tp moiety. The chloride ion can be quantitatively removed from **40** by reaction with CF$_3$SO$_3$Ag yielding the chloride-free product Tp$^{\text{CF3}}$AgGe[(Me)$_2$ATI](OSO$_2$CF$_3$) **41** [55]. This proves that failure of AgCl metathesis is a property of **39** rather than of the [ATI]GeCl complexes.



Scheme 10. The reactivity of [(n-Pr)$_2$ATI]GeCl towards the silver complex **39**.

Silver adduct formation is equally feasible with the respective azides. The silver atom preferentially coordinates to the germanium atom even though the azide unit provides suitable donor sites [54]. The authors explain this behaviour with the Hard and Soft Acids and Bases Theory [56].

A comparison of Ge–N bond lengths in [ATI]Ge complexes is very instructive to evaluate the close relationship of these compounds with NHGe. Although the Ge–N bond lengths in the cationic complexes seem to be slightly shorter than in the neutral analogues, this trend is not very pronounced (see Table 2). Dias et al. give the influence of the extended bicyclic 10 π-electron system as reason for this observation [57]. Shorter Ge–N bond lengths can be expected from cationic species as the electron deficiency on germanium will result in a greater pull on the adjacent electron lone pairs on nitrogen and thus bond shortening. However, the effect is more pronounced upon coordination on the germanium lone pair. Coordination of a Lewis acid on germanium renders the germanium centre electron deficient. This deficiency is then responsible for a stronger electron pull on the nitrogen lone pairs resulting in a decrease in the Ge–N bond length.

Table 2
Selected bond lengths (pm) of neutral and cationic [ATI]Ge complexes

Neutral compound	Cationic compound	Ge–N bond length (pm)	Reference
$[(n\text{-Pr})_2\text{ATI}]\text{GeCl}$		192.4 (2); 194.9 (2)	[52,53]
	$[(n\text{-Pr})_2\text{ATI}]\text{Ge}(\text{OSO}_2\text{CF}_3)$	193.0 (5); 191.8 (5)	[53]
40		189.4 (3); 189.8 (3)	[53,55]
$[(n\text{-Pr})_2\text{ATI}]\text{Ge}(\text{N}_3)\text{AgTp}^{\text{CF3}}$		188.2 (4); 188.4 (4)	[54]
38		194.5 (2); 195.6 (2)	[54]
$[(\text{Me})_2\text{ATI}]\text{Ge}(\text{Cl})\text{AgTp}^{\text{CF3}}$		188.5 (5); 189.6 (5)	[55]
	41	186.5 (6); 188.3 (6)	[55]
$[(\text{Me})_2\text{ATI}]\text{GeCl}$		193.7 (3); 193.8 (3)	[57]
$[(i\text{-Pr})_2\text{ATI}]\text{GeCl}$		195.6 (4)	[57]
	$[(i\text{-Pr})_2\text{ATI}]\text{Ge}(\text{OSO}_2\text{CF}_3)$	191.0 (2); 191.6 (2)	[57]
$[(\text{Me})_2\text{ATI}]\text{Ge}(\text{Ph})\text{BPh}_3$		191.3 (2); 192.0 (2)	[57]
	$[(i\text{-Pr})_2\text{ATI}]\text{Ge}$	190 (5); 191.7 (5)	[57]

6. β-Diketiminato complexes

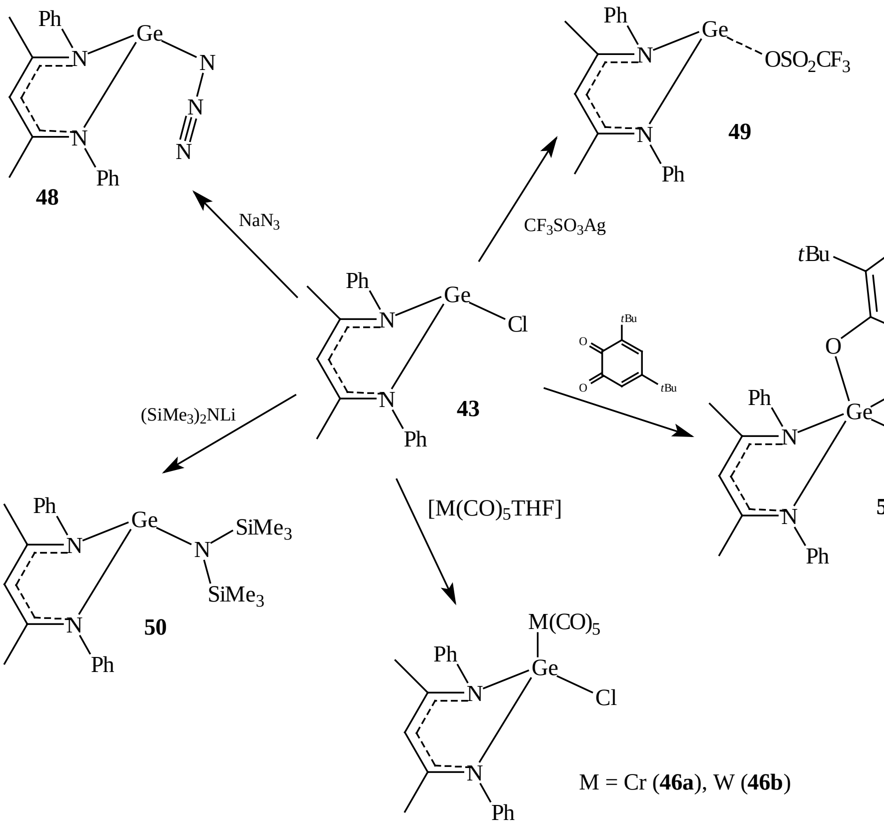
β-Diketiminates, like the amidinates and aminotroponiminates, are monoanionic ligands. While amidinates form four membered rings and ATI form five membered rings with Ge(II), the β-diketiminato-ligands display six member rings when bonded to Ge(II). Otherwise, their structures are very similar to the smaller ring systems and their chemistry resembles that of the [ATI]Ge system. The last three years saw a flurry of activity in this comparatively new field. A good description of the ligand system and its relation to amidinates is provided by reference [58], whereas a comparison to the ATI system is given in reference [59]. Dias et al. published the first report on β-diketiminato complexes of Ge(II) comparing their properties to those of the respective ATI complexes [59]. Synthesis of $[(\text{Mes})_2\text{DAP}]\text{GeCl}$ **42** ($[(\text{Mes})_2\text{DAP}] = \{\text{N}(\text{Mes})\text{C}(\text{Me})\}_2\text{CH}$ and Mes = 2,4,6-trimethylphenyl) again is facile and leads to a six member ring system with a cyclic delocalised six π-electron system that can be best described as a monoiminogermylene already familiar from the amidinato- and ATI complexes. The germanium atom does not lie in the plane of the planar C_3N_2 ligand system resulting in an envelope conformation of the Ge(II) complex. Introduction of the azide substituent follows the same procedure as for the corresponding [ATI]GeCl compounds, namely salt metathesis after reaction with sodium azide [59].

The bulk of the aryl substituent on the nitrogen atoms seems to have no influence on the synthesis of the monoiminogermylene as both the phenyl- **43** [60] and the 2,6-di-iso-propylphenyl- **44** [61] derivatives could be synthesised in rather high yields.

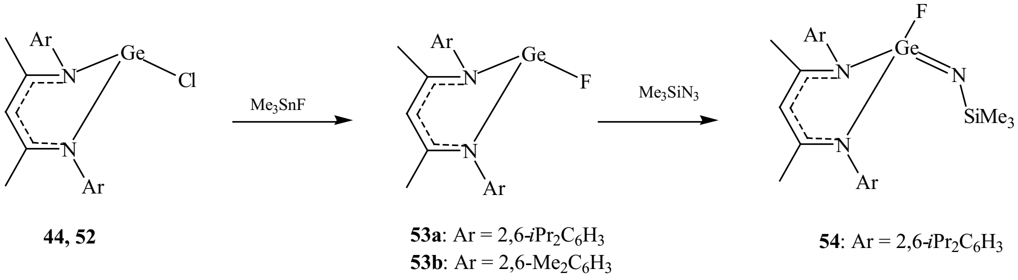
The reactivity of these compounds was investigated by Barrau and co-workers [60] independently of Dias and Roesky. Barrau points out the reactive centres on these complexes and presents experimental evidence for each. Oxidation of **43** with elemental sulfur or selenium led to the formation of the respective metallenethioacid chloride **45a** or metalleneselenaacid chloride **45b** which in contrast to the tin analogue could be fully characterised. The lone pair on germanium could also be utilised as a means to coordinate on a transition metal. Reaction of **43** with $[\text{M}(\text{CO})_5\text{THF}]$ afforded the 1:1 adducts **46a** (M = Cr) and **46b** (M = W), respectively. The IR spectra of these complexes showed νCO bands consistent with a strong σ-donor and weak π-acceptor character of the chloro-monoiminogermylene. The reactivity of the Ge–Cl bond was likewise investigated. Barrau et al. found that this bond can easily be cleaved by NaBPh_4 rendering the ionic species $[\{(\text{Ph})_2\text{DAP}\}\text{Ge}]^+\text{BPh}_4^-$ **47**. Reaction of **43** with NaN_3, $(\text{Me}_3\text{Si})_2\text{NLi}$ or $\text{CF}_3\text{SO}_3\text{Ag}$ yields in the familiar way the respective azido- **48**, triflato- **49** and amido- **50** complexes (see Scheme 11). Finally, with a *o*-benzoquinone heterocyclisation occurred yielding the cyclic product **51**. This reaction was explained by a one-electron transfer mechanism. **51** is thermally stable up to at least 150 °C.

Roesky et al. investigated the reactivity of the β-diketiminato-germanium(II) chlorides further [62]. The complexes studied were **44** and $[(\text{Me})_2\text{DAP}]\text{GeCl}$ **52**, respectively. Reaction with trimethyl tin(IV) fluoride led in a substitution reaction to the corresponding $[(\text{R})_2\text{DAP}]\text{GeF}$ **53a** ($\text{R} = i\text{Pr}$) and **53b** (R = Me) (see Scheme 12). Further reaction of the fluoride **53a** with Me_3SiN_3 in toluene yielded the expected [62] iminogermane $[(i\text{Pr})_2\text{DAP}]\text{Ge}(\text{F})\text{=NSiMe}_3$ **54**. The attempted substitution of chloride by hydride in $[(\text{R})_2\text{DAP}]\text{GeCl}$ using the complex hydride LiBH_4 did not yield the expected product $[(\text{R})_2\text{DAP}]\text{GeH}$, but the complexes $[(\text{R})_2\text{DAP}]\text{Ge}(\text{H})\text{BH}_3$ **55a,b** ($\text{R} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$: **55a**; $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$: **55b**) instead. This reaction was already observed by Dias and Wang [57] in the case of the analogous [ATI]GeCl complex with NaBPh_4 as the borane source. However, in the reaction of $[(\text{R})_2\text{DAP}]\text{GeCl}$ with LiAlH_4 at room temperature metathesis is observed and the product is the known aluminium hydride $[(\text{R})_2\text{DAP}]\text{AlH}_2$.

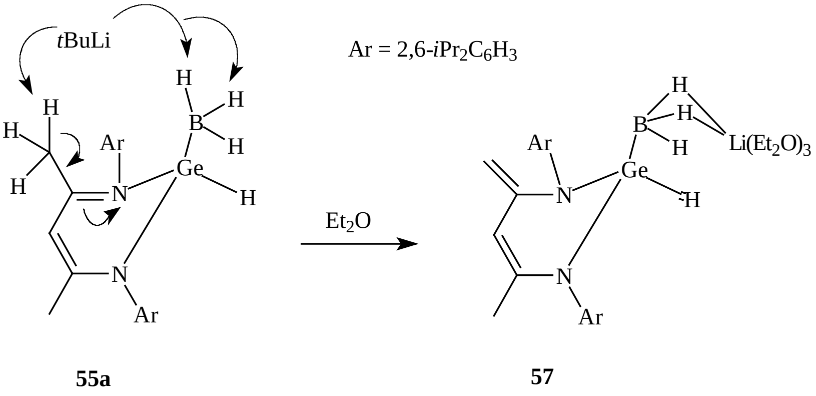
The borane adduct **55a** can be reacted further with a phosphine like PMe_3 [62]. In this reaction, the phosphine acts as a borane scavenger yielding the desired hydride $[(i\text{Pr})_2\text{DAP}]\text{GeH}$ **56**. In the reaction of **55a** with *t*BuLi a methyl proton is abstracted with the lithium ion coordinating to two B–H hydrido atoms and three ether moieties (see Scheme 13). In the resulting compound **57** the germanium



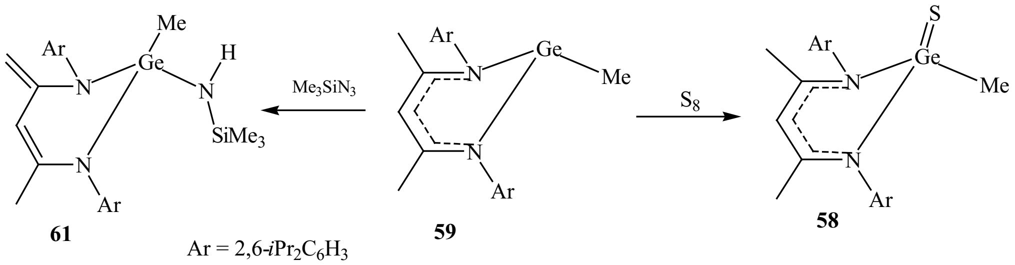
Scheme 11. The reactivity of Ge(II) β-diketiminates.



Scheme 12. The fluorination of β-diketiminates of Ge(II) and subsequent reactivity.



Scheme 13. The lithiation of **55a** with *t*-BuLi.



Scheme 14. The reactivity of the methyl derivative of a Ge(II) β-diketiminate.

is bonded to a dianionic diamido ligand instead of the monoanionic β-diketiminato.

In a further communication, Roesky and co-workers describe the oxidation of **44** and $[(i\text{Pr})_2\text{DAP}]\text{GeF}$ by elemental sulphur to the respective metallenethioacid chloride and fluoride [63] following the route shown by Barrau and co-workers [60]. However, Roesky could show that the reaction of the $[(i\text{Pr})_2\text{DAP}]\text{Ge(Cl)S}$ with MeLi renders the new Ge-methyl compound $[(i\text{Pr})_2\text{DAP}]\text{Ge(Me)S}$ **58**. Recently, this communication was followed up by a full paper [64] disclosing a whole new chemistry of these β-diketiminato germylene(II) complexes with alkyl substituents on the germanium centre. Using **44** as the starting material the study showed that the chloride atom can be substituted by the alkyl group of an alkyl-lithium reagent. A second route to complex **58** was shown by oxidation of $[(i\text{Pr})_2\text{DAP}]\text{GeMe}$ **59** with elemental sulphur (see Scheme 14). Reaction of **59** with Me_3SiN_3 does not afford the iminogermane $[(i\text{Pr})_2\text{DAP}]\text{Ge(Me)=NSiMe}_3$ **60**, but its isomer **61**. The reaction is believed to proceed in a similar fashion to that between **55a** and *t*BuLi. MeI undergoes addition to **59** to yield the compound $[(i\text{Pr})_2\text{DAP}]\text{Ge(Me)}_2\text{I}$.

Power and co-workers [65] published a study concerning bonding in the cation $[(i\text{Pr})_2\text{DAP}]\text{Ge}^+$ **62**. The authors found it surprising that the LUMO is not the “empty” germanium p_z-orbital. However, as the $[(\text{R})_2\text{DAP}]\text{GeCl}$ complexes are best described as monoiminogermylene chlorides with intramolecular N–Ge σ-donor stabilisation, the p_z-orbital on germanium is no longer empty and cannot form part of the LUMO. The study then goes on to compare the cationic $[\text{DAP}]\text{Ge}^+$ complexes with the likewise cationic $[\text{ATI}]\text{Ge}^+$ complexes underlining it with the structural determination of $[\{(i\text{Pr})_2\text{DAP}\}\text{Ge}][\text{HO}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ **63**. The similarities are as close as predicted by the theoretical studies of Heinemann et al. [17] and Boehme and Frenking [26]. The striking structural feature of the cation is its planarity as compared to the non-planar neutral complexes whereas the Ge–N bond lengths of the cationic species **62** are within the range defined by the neutral compounds (see Table 3).

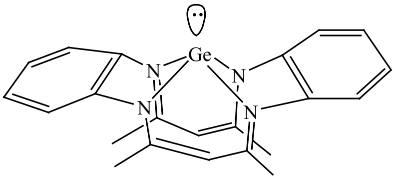
Table 3
Selected bond lengths (pm) of neutral and cationic Ge(II) β-diketiminates

Neutral compound	Cationic compound	Ge–N bond length (pm)	Reference
44		198.8 (2); 199.7 (3)	[64]
42		195.8 (2); 198.0 (2)	[59]
$[(\text{Mes})_2\text{DAP}]\text{GeN}_3$		197.2 (4); 197.5 (4)	[59]
53a		197.7 (19); 197.8 (18)	[63]
55a		191.7 (4); 193.3 (4)	[62]
57		187.5 (4); 187.9 (4)	[62]
45a		188.1 (1); 191.0 (1)	[63]
$[(i\text{Pr})_2\text{DAP}]\text{Ge(S)F}$		189.2 (2); 188.4 (2)	[63]
59		200.8 (2); 203.8 (2)	[64]
$[(i\text{Pr})_2\text{DAP}]\text{Ge}(n\text{-Bu})$		202.3 (2); 202.5 (2)	[64]
58b		193.1 (2); 194.7 (2)	[64]
	62	189.4 (2)	[65]
61		Not given	[64]

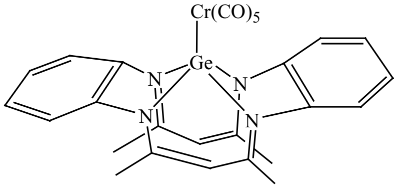
7. Macrocyclic Ge(II) compounds

At first glance, the germanium(II) complexes of such macrocycles as porphyrin, and dibenzotetramethyltetraaza[14]annulene (tmtaa) do not seem to be closely related to NHGe. However, closer inspection reveals that the Ge(II)porphyrins **64** developed by Kadish, Guilard and coworkers [6,12] are reminiscent of β-diketiminato analogues of the Ge(II)-amidinate **32**. Due to the macrocyclic nature of the ligand in **64**, the coordination sphere of germanium is square pyramidal as opposed to the intermediate structure between square pyramidal and trigonal bipyramidal observed in **32**. The Ge atom is not in the plane of the ligand which gives the whole structure a double envelope conformation (see Fig. 15).

In the tmtaa ligand system coplanarity of the β-diketiminato fragment and Ge is markedly improved. The respective compounds, reported by Cowley and coworkers [66–68], show saddle conformation displaying two planar $\text{C}_3\text{N}_2\text{Ge}$ units that stand at an angle to each other. Again the germanium atom possesses square pyramidal geometry. The Ge–N bond length is reported as 210.7 pm, clearly too long to contemplate any p_z–p_z π-electron interaction between germanium and nitrogen. An interesting reaction of this Ge(II) compound was reported by the same group. **65** was reacted with MeI at −78 °C resulting in addition of MeI to the Ge atom. In the Ge(tmtaa)(Me)I complex **66** the germanium displays a trigonal prismatic environment (see Fig. 16) [68]. The authors claimed the formation of an “inverse ylide” on the grounds that **65** were a NHC analogue. That is not true in the strict sense as Ge(tmtaa) is an intramolecular base stabilised monoiminogermylene

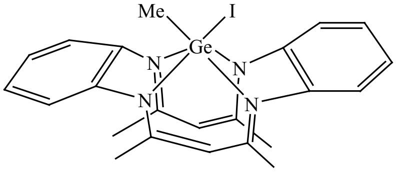


65



67

Fig. 15. The structures of the Ge(II)tmtaa complexes **65** and **67**.



66

Fig. 16. The structure of **66** displaying a trigonal prismatic coordination sphere on Ge.

amide. However, the electronic implications seem to be similar.

The same authors also published the first transition metal complex of Ge(tmtaa) **67**, synthesised by reaction of **65** with $[Cr(CO)_5THF]$ [67]. The most interesting feature is the shortening of the Ge–N bond lengths upon coordination to chromium, a feature already observed in the [ATI]Ge series. Whereas, the Ge–N bond lengths are 209.7(4) and 211.0(4) pm in the free ligand, it decreases to 201.2(7) and 202.8(7) pm in the chromium complex.

Kuchta and Parkin investigated the germanium(II) chemistry of the octamethyl derivative of Cowley's tmtaa system (Me_8taa) [69–71]. They developed the trans-chalcogenation reaction between (Me_8taa)SnS and (Me_8taa)Ge to yield (Me_8taa)GeS [69]. They also published a procedure to synthesise the full series of (Me_8taa)GeE (E = S, Se, Te) directly [70]. The Ge–N bond lengths of the chalcogenides are even shorter (196–199 pm) than in $[(tmtaa)Ge\{Cr(CO)_5\}]$.

The same authors went on to investigate the reactivity of their (Me_8taa)GeE system [71]. They found that reaction of (Me_8taa)GeE with 1,2-diiodoethane results in the formation of *trans*-(Me_8taa)GeI_2, whereas in the reaction with MeI the methyl group attacks at sulphur yielding [(Me_8taa)Ge(SMe)]I. In the reaction with thiirane both the selenide and the sulphide form the sulphide (Me_8taa)GeS.

8. Conclusion

The N-heterocyclic germylenes, developed by Veith and Meller long before their carbene homologues became known, distinguish themselves from the latter by their thermodynamic stability and their different electronic properties. Since germanium is less electronegative and larger than carbon, the corresponding NHGe possesses a weaker N–Ge p_π–p_π interaction than its carbene counterpart. Therefore, the electronic properties of the germanium centre can be more easily manipulated than the carbon centre of the NHC. Thus, anellation leads to a decrease in the π-electron density on germanium which renders the NHGe a better π-acceptor.

The increased thermodynamic stability of the divalent state for germanium, in contrast to carbon, makes the NHGe not only more easily accessible than the lighter homologue, it is also more resistant towards the electron withdrawing effects of anellation. Anellated NHC are less stable and are usually isolated as the silver complexes. Thus, despite the apparent success of the NHC, the NHGe are actually the more versatile ligands having a much greater potential for ligand diversification.

The intrinsic stability of the monoiminogermylene results in a range of related structures involving amidinate, aminotroponiminate and β-diketiminate ligands. Although the monoiminogermylene is predicted to be non-planar, the resulting germanium complexes of these ligands are mostly planar with the exception of the β-diketiminates displaying the envelope structure. Abstraction of the chloride to render the respective cationic NHGe complexes is generally facile with both the aminotroponiminate and the β-diketiminate complexes of Ge(II).

The ligating properties of the NHGe and their related compounds have been explored to some extend. The transition metals utilised were mostly nickel, silver and the group 6 metals. No systematic study concerning the use of these Ge(II) ligand systems as ligands for transition metals has been performed up to date. However, from the evidence available it seems to be clear that the ligating properties of NHGe are strongly dependent on the electronic influence exerted by the substituents on the heterocyclic ring.

The amidinate and β-diketiminate complexes of Ge(II) could easily be oxidised by the chalcogenides sulphur and selenium. Oxidation invariably took place on the germanium lone pair without altering the structure of the molecule. This behaviour is reminiscent of the phosphines, a class of compounds likened to the NHC, the lighter homologues of NHGe. As oxidation of the Ge(II) centre by the chalcogenide reduces the electron density on the germanium atom, the N–Ge bond lengths decrease and the bond order increases in order to counterbalance this.

Acknowledgements

Part of this review was written while visiting Prof. Evamarie Hey-Hawkins' research group in Leipzig. I thank Prof. Joachim Heinicke for many fruitful discussions. Some very helpful comments by anonymous referees are gratefully acknowledged.

References

[1] W.A. Herrmann, Angew, Chem., Int. Ed. Engl. 41 (2002) 1290;
W.A. Herrmann, C. Kocher, Angew. Chem., Int. Ed. Engl. 36 (1997) 2162;
A.H. Cowley, J. Organomet. Chem. 617 (8) (2001) 105;
T. Westkamp, V.P.W. Böhm, W.A. Herrmann, J. Organomet. Chem. 600 (2000) 12.

[2] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1989, p. 31.

[3] H.V.R. Dias, Z. Wang, W. Jin, Coord. Chem. Rev. 176 (1998) 67.

[4] L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031.

[5] H.H. Karsch, P.A. Schlüter, M. Reisky, Eur. J. Inorg. Chem. (1998) 433.

[6] K.M. Kadish, B. Boisselier-Cocolios, C. Swistak, J.M. Barbe, R. Guilard, Inorg. Chem. 25 (1986) 122.

[7] M. Veith, M. Grosser, Z. Naturforsch. 37b (1982) 1375.

[8] M. Veith, Angew. Chem. 99 (1987) 1;
M. Veith, Angew, Chem., Int. Ed. Engl. 26 (1987) 1;

M. Veith, Metal Clusters Chem. 1 (1999) 73.

[9] J. Barrau, G. Rima, Coord. Chem. Rev. 178 (80) (1998) 593;
N. Tokitoh, R. Okazaki, Coord. Chem. Rev. 210 (2000) 251.

[10] A. Meller, C.-P. Gräbe, Chem. Ber. 118 (1985) 2020.

[11] J. Pfeiffer, W. Maringgele, M. Noltemeyer, A. Meller, Chem. Ber. 122 (1989) 245.

[12] K.M. Kadish, C. Swistak, B. Boisselier-Cocolios, J.M. Barbe, R. Guilard, Inorg. Chem. 25 (1986) 4336.

[13] S. Nakajima, H. Hayashi, Y. Omote, Y. Yamazaki, S. Hirata, T. Maeda, Y. Kubo, T. Takemura, Y. Kakiuchi, Y. Shindo, K. Koshimizu, I. Sakata, J. Photochem. Photobiol., B. 7 (1990) 189.

[14] A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[15] W.A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, Angew. Chem. 104 (1992) 1489;
W.A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, Angew. Chem. Int. Ed. Engl. 31 (1992) 1485.

[16] G. Trinquier, J.-C. Barthelat, J. Satge, J. Am. Chem. Soc. 104 (1982) 5931.

[17] C. Heinemann, W.A. Herrmann, W. Thiel, J. Organomet. Chem. 475 (1994) 73.

[18] B. Gehrhus, M.F. Lappert, J. Organomet. Chem. 617 (8) (2001) 209.

[19] J.F. Lehmann, S.G. Urquhart, L.E. Ennis, A.P. Hitchcock, K. Hatano, S. Gupta, M.K. Denk, Organometallics 18 (1999) 1862.

[20] Gobbi, G. Frenking, J. Am. Chem. Soc. 116 (1994) 9287.

[21] J. Heinicke, A. Oprea, M.K. Kindermann, T. Karpáti, L. Nyulászi, T. Veszprémi, Chem. Eur. J. 4 (1998) 541.

[22] A.J. Arduengo III, H. Bock, H. Chen, M. Denk, D.A. Dixon, J.C. Green, W.A. Herrmann, N.L. Jones, M. Wagner, R. West, J. Am. Chem. Soc. 116 (1994) 6641.

[23] M. Denk, J.C. Green, N. Metzler, M. Wagner, Dalton Trans. (1994) 2405.

[24] L. Pause, M. Robert, J. Heinicke, O. Kühl, Perkin Trans. 2 (2001) 1383.

[25] O. Kühl, P. Lönnecke, J. Heinicke, Polyhedron 20 (2001) 2215.

[26] C. Boehme, G. Frenking, J. Am. Chem. Soc. 118 (1996) 2039.

[27] D.S. McGuinness, B.F. Yates, K.J. Cavell, Organometallics 21 (2002) 5408.

[28] J. Pfeiffer, M. Noltemeyer, A. Meller, Z. Anorg. Allg. Chem. 572 (1989) 145.

[29] A.J. Arduengo III, Acc. Chem. Res. 32 (1999) 313.

[30] A.J. Arduengo, III, personal communication.

[31] R. Prokop, R. Merica, F. Glatz, S. Veprek, F.-R. Klingan, W.A. Herrmann, Organosilicon Chem. II (Münch. Silicontage), 1996, pp. 815–820 (Meeting date 1994).

[32] S. Veprek, R. Prokop, R. Merica, F. Glatz, F.-R. Klingan, W.A. Herrmann, Proc. -Electrochem. Soc. 96 (5) (1996) 247.

[33] R. Prokop, R. Merica, F. Glatz, S. Veprek, F.-R. Klingan, W.A. Herrmann, J. Non-Cryst. Solids (1996) 198.

[34] S. Veprek, R. Prokop, R. Merica, F. Glatz, F.-R. Klingan, W.A. Herrmann, Chem. Mater. 8 (1996) 825.

[35] S. Kobayashi, S. Iwata, M. Hiraishi, J. Am. Chem. Soc. 116 (1994) 6047.

[36] C.J. Carmalt, V. Lomeli, B.G. McBurnett, A.H. Cowley, Chem. Commun. (1997) 2095.

[37] A. Schäfer, W. Saak, M. Weidenbruch, H. Marsmann, G. Henkel, Chem. Ber./Recueil. 130 (1997) 1733.

[38] M. Denk, J.C. Greene, N. Metzler, M. Wagner, Dalton Trans. (1994) 2405.

[39] R. West, M. Denk, Pure Appl. Chem. 68 (1996) 785;
M. Denk, R.K. Hayashi, R. West, Chem. Commun. (1994) 33.

[40] A. Schäfer, W. Saak, M. Weidenbruch, Z. Anorg. Allg. Chem. 624 (1998) 1405.

[41] B. Gehrhus, P.B. Hitchcock, M. F. Lappert, Dalton Trans. (2000) 3094.

[42] F.E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, Chem. Eur. J. 5 (1999) 1931.

[43] J. Heinicke, A. Oprea, Heteroatom. Chem. 9 (1998) 439.

[44] O. Kühl, P. Lönnecke, J. Heinicke, Inorg. Chem. 42 (2003) 2836.

[45] A. Laporte-Chrostowska, S. Foucat, T. Pigot, V. Lemierre, G. Pfister-Guillouzo, Main Group Met. Chem. 25 (2002) 55.

[46] P. Bazinet, G.P.A. Yap, D.S. Richeson, J. Am. Chem. Soc. 123 (2001) 11162.

[47] C. Drost, P.B. Hitchcock, M.F. Lappert, Angew. Chem., Int. Ed. Engl. 38 (1999) 1113.

[48] O. Kühl, P. Lönnecke, J. Heinicke, New J. Chem. 26 (2002) 1304.

[49] S.R. Foley, C. Bensimon, D.S. Richeson, J. Am. Chem. Soc. 119 (1997) 10359.

[50] S.R. Foley, D.S. Richeson, Chem. Commun. (2000) 1391.

[51] S.R. Foley, G.P.A. Yap, D.S. Richeson, Dalton Trans. (2000) 1663.

[52] A.E. Ayers, D.S. Marynick, H.V.R. Dias, Inorg. Chem. 39 (2000) 4147.

[53] A.E. Ayers, H.V.R. Dias, Inorg. Chem. 41 (2002) 3259.

[54] H.V.R. Dias, A.E. Ayers, Polyhedron 21 (2002) 611.

[55] H.V.R. Dias, Z. Wang, Inorg. Chem. 39 (2000) 3890.

[56] R.G. Pearson, Survey Prog. Chem. 5 (1969) 1;
R.G. Pearson (Ed.), Hard and Soft Bases and Acids, Dordon/Hutchinson/Ross, Stroudsburg, PA, 1973.

[57] H.V.R. Dias, Z. Wang, J. Am. Chem. Soc. 119 (1997) 4650.

[58] P.B. Hitchcock, M.F. Lappert, M. Layh, D.-S. Liu, R. Sablong, T. Shun, Dalton Trans. (2000) 2301.

[59] A.E. Ayers, T. Klapötke, H.V.R. Dias, Inorg. Chem. 40 (2001) 1000.

[60] A. Akkari, J.J. Byrne, I. Saur, G. Rima, H. Gornitzka, J. Barrau, J. Organomet. Chem. 622 (2001) 190.

[61] Y. Ding, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, P.P. Power, Organometallics 20 (2001) 1190.

[62] Y. Ding, H. Hao, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Organometallics 20 (2001) 4806.

[63] Y. Ding, Q. Ma, H.W. Roesky, I. Usón, M. Noltemeyer, H.-G. Schmidt, J. Am. Chem. Soc. 124 (2002) 8542.
[64] Y. Ding, Q. Ma, H.W. Roesky, R. Herbst-Irmer, I. Usón, M. Noltemeyer, H.-G. Schmidt, Organometallics 21 (2002) 5216.
[65] M. Stender, A.D. Phillips, P.P. Power, Inorg. Chem. 40 (2001) 5314.
[66] D.A. Atwood, V.O. Atwood, A.H. Cowley, J.L. Atwood, E. Román, Inorg. Chem. 31 (1992) 3871.
[67] D.A. Atwood, V.O. Atwood, A.H. Cowley, H.A. Gobran, J.L. Atwood, Inorg. Chem. 32 (1993) 4671.
[68] D.A. Atwood, V.O. Atwood, A.H. Cowley, H.R. Gobran, Polyhedron 12 (1993) 2073.
[69] M.C. Kuchta, G. Parkin, J. Am. Chem. Soc. 116 (1994) 8372.
[70] M.C. Kuchta, G. Parkin, Chem. Commun. (1994) 1351.
[71] M.C. Kuchta, G. Parkin, Chem. Commun. (1996) 1669.