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N-Heterocyclic Germylenes NHGe – Old Trends and New Developments

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Abstract: N-heterocyclic germylenes NHGe have recently come of age. In the last few years, they emerged as mature ligands capable of functionalisation, chirality, electronic tuning and chelating bis-NHGe ligands. The review shows the major trends and developments of the last five years.

Keywords: N-heterocyclic germylenes, transition metal complexes, ligands, carbene analogues, annelation effect, electronic properties, Meller germylenes.

INTRODUCTION

Although the chemistry of NHGe is largely developed in the shadows of the vastly more popular homologous Wanzlick-Arduengo carbenes NHC, they have actually been longer known as free ligands [1] and show a more diverse chemistry [1-4]. NHGe can change the ring size without apparent loss in stability [1], alter the oxidation state on germanium without losing their σ-donor ability [4,5] and have recently begun to discover functionalisation, a trend that was started with NHC some ten years ago [6].

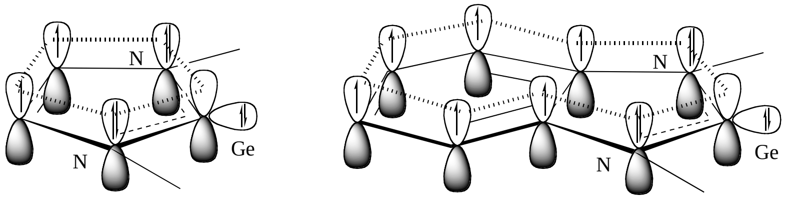
The field has focussed on several major topics, the further investigation of theoretical concepts, functionalisation of the ligand system, the development of heterosubstituted NHGe (where one or both flanking nitrogen atoms are substituted by another atom, including carbon) and an increasing number of transition metal complexes.

The fundamental differences in the properties and chemistry of six-membered NHGe and the longer known Meller germylenes still persist and are so important that the present review is ordered along these lines rather than the trends outlined above. The differences are described in a principal review published in 2004 [1] and can be summarised as Meller NHGe being neutral, electron rich and stabilised in germanium, whereas the six-membered NHGe are usually cationic, electron deficient and less stabilised in germanium. Heterosubstitution is a trend seen in both major forms of NHGe, a fact that is recognised by the allocation of a separate section.

THEORETICAL DEVELOPMENTS

Although, NHGe are generally expected to be more stable than their carbene analogues [2,6,7] and for the same reasons that $GeCl_2$ is more stable than CCl_2 [1,8], the stability and reactivity of NHGe can be significantly modified by substitution and annelation [9-11] to an extent where the reactivity is reversed and the NHGe acts as a Lewis acid [11].

Annelation withdraws electron density from the NHGe ring system to the annelated ring system [9,12] and thus destabilises the NHGe. This effect can be measured by the νCO stretching frequency of their transition metal carbene complexes [9,10,13], but also calculated via the molecular electrostatic potential MEP at germanium [9] or the addition of H_2 to the germanium centre [14] or the measurement of the N-Ge-N bond angle [15].



non-annelated annelated

Fig. (1). Depiction of the delocalised 6-π and 10-π electron systems of non-annelated and benzannelated NHGe.

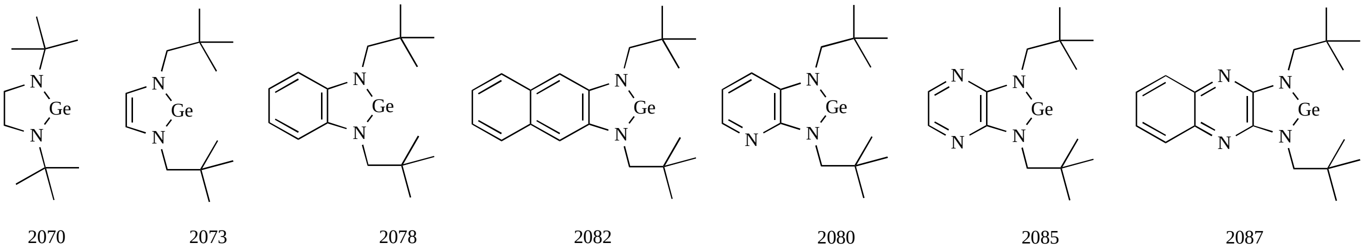


Fig. (2). Several non-annelated and annelated NHGe ligands accompanied by their Tolman Electronic Parameter TEP.

The electronic properties of the NHGe change systematically with the nature of the annelated ring system (see Fig. **1**) or the electronic influence of substituents on the C4/C5 positions of the heteroimidazole ring system. They can be calculated using the easy to compute MEP [9,10] or measured using the νCO stretching frequency of a suitable transition metal carbonyl complex of the NHGe [10,13]. Fig. (**2**) shows a number of annelated NHGe together with their Tolman Electronic Parameter TEP [16].

It has long been known that the stability of heteroannelated NHC (pyrido[b] and pyrido[c]) [1,12,17] is dependent on the sym-

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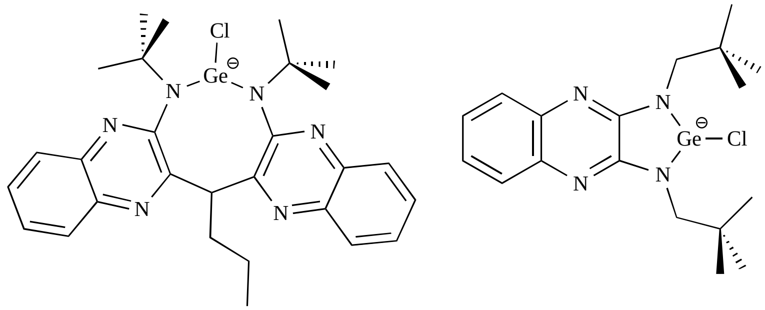


Fig. (3). Two electrophilic, chloride-stabilised NHGe. The Li(dioxane) entity, coordinated to two nitrogen atoms of the two quinoxaline systems, has been omitted for clarity.

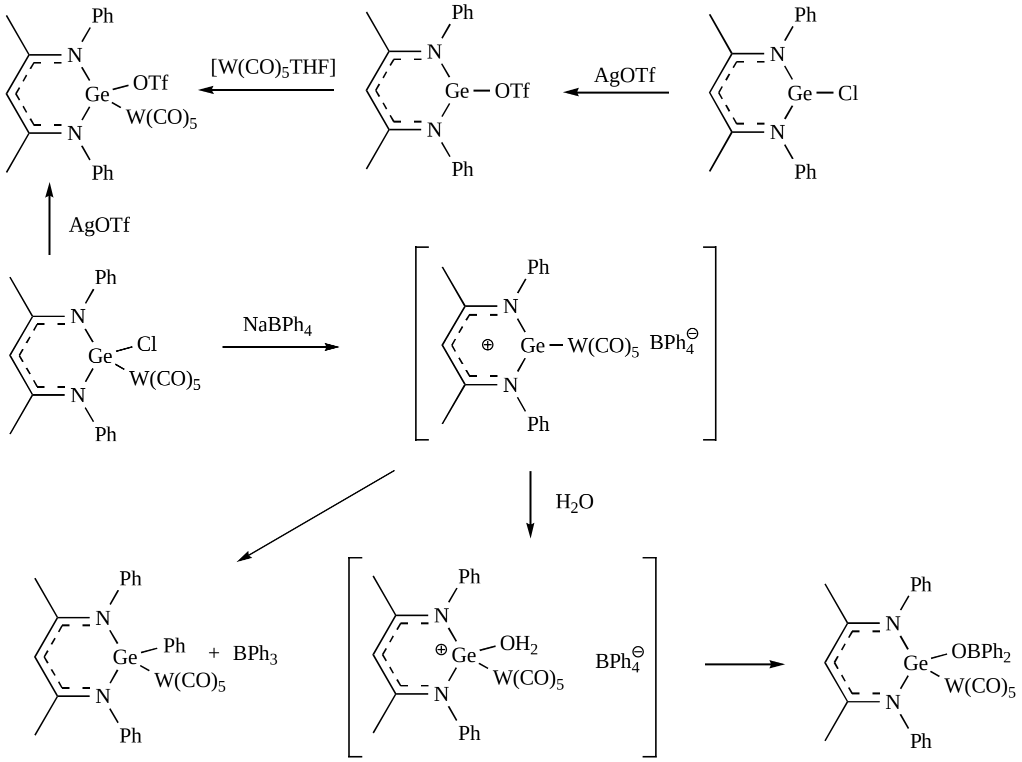


Fig. (4). Lewis acidic behaviour of cationic, six-membered NHGe.

metry of the HOMO and the location of the heteroatom relative to the nodal plane of the HOMO. This makes the pyrido[b] annelated NHGe (N-atom in the nodal plane) much more stable (and readily isolable) whereas the corresponding pyrido[c] annelated NHGe is significantly less stable and cannot be distilled without decomposition [12]. Recently, the respective pyrido[a] annelated NHGe was synthesised completing the series [18]. Not surprisingly, the pyrido[a] annelated NHGe was found to be unstable and it could not be isolated without impurities. The unsubstituted parent compound benzannelated NHGe (1-H, 3-H) is 21.88 kcal/mol more stable than the pyrido[a] annelated analogue (1-H) [18].

The matter of stability is not only influenced by the question of symmetry, and the location of a heteroatom in relation to the HOMO nodal planes, but equally so by the extent of the electronic influence of the annelated ring system on the electron density at the germanium centre. This is emphasised by two NHGe moieties, the long known eight membered NHGe with an electrophilic germanium and double quinoxaline annelation [11] and the newly synthesised quinoxaline annelated NHGe [19] (see Fig. **3**). Both compounds are unstable and act as Lewis acids towards a suitable Lewis base (chloride, PMe_3) as predicted in a recent review [4].

It is generally recognised that (4n+2)-π electron delocalisation within the NHGe ring system contributes towards the stability of the germylene [20], although it is not considered to be essential [21]. Likewise, the influence of aromaticity towards NHGe stabilisation is recognised to be much smaller than that in the lighter homologues [22]. An interesting contribution towards a quantitative determination of the aromatic stabilisation comes from a theoretical calculation by Wang and Ma [14], who investigated the addition of H_2 to the germanium centre of cyclic and acyclic germylenes. Another theoretical investigation describes the reactivities of cationic six-membered NHGe [15] (see Fig. **4**), another active area of research within the field of NHGe.

Wang and Su in their theoretical contribution determined an increasing singlet-triplet gap of these cationic six-membered ring systems going from carbene to plumbene (46, 60, 67, 72, 78 kcal/mol) making these species quite stable and not prone to dimerisation. The authors attributed this to the increasing „inert s-pair effect“ [23-25] as one goes down the group. The inert s-pair effect causes an increasing N-E-N angle, lowering of the HOMO and a reduced σ-donor ability of the ligand. In consequence, the singlet ground state is strengthened and the reactivity of the cationic NHGe

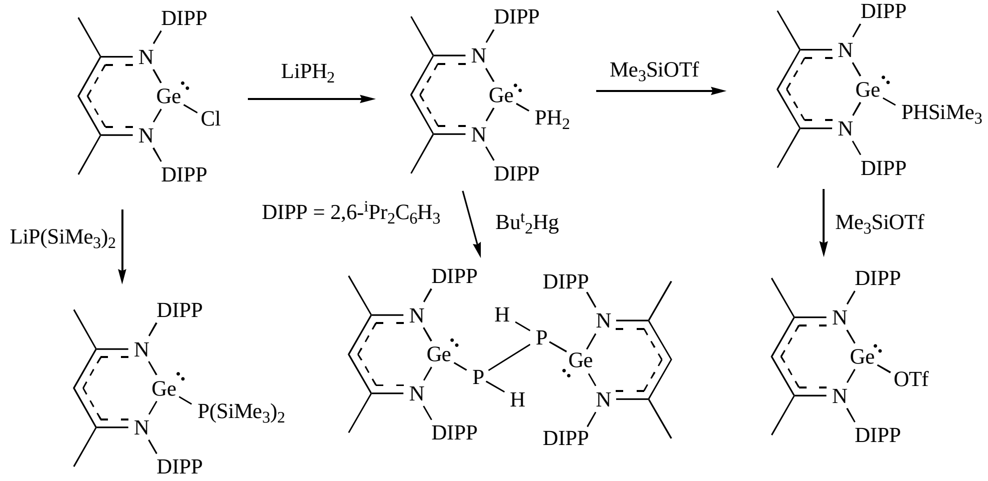


Fig. (5). Synthesis of phosphino functionalised NHGe.

is limited to insertion and addition reactions. Dimerisation becomes very unlikely.

The findings are supported by theoretical investigations on acyclic and Meller germylenes performed by Wang and Ma [14]. They calculated the reaction of molecular hydrogen H_2 with a series of germylenes. Whereas the acyclic, triplet germylenes are predicted to readily add hydrogen to form the respective Ge(IV) species, Meller germylenes (five-membered NHGe) woul not react with hydrogen in this way featuring an aromatic stabilisation that is estimated to be about 50-60% of that found in benzene [14]. For the two NHGe, addition of H_2 would be endothermic by 14 and 9 kcal/mol, respectively, with the benzannelated NHGe 5 kcal/mol less endothermic than the non-annelated NHGe. It is easy to imagine that increasing annelation would soon make this reaction exothermic and thus the corresponding NHGe unstable.

SIX-MEMBERED NHGE

Six-membered NHGe derived from ß-diketiminates are recognised as planar cationic ligands or folded neutral ligands for transition metal complexes [1,26]. In a recent review [1], Kühl pointed out that upon anionic abstraction of the exocyclic substituent on germanium, the resulting cationic ligand has an altered electronic structure. Whereas in Meller germylenes and neutral six-membered NHGe, the germanium centre is engaged in two covalent σ-bonds to its nitrogen neighbours making two π-interactions possible, the two N-Ge bonds in the cationic species are of the covalent and donor type, respectively. That leaves only one π-interaction to the remaining N-atom.

As a consequence, Barrau *et al.* found these cationic ligands always coordinated to their respective anions, even when supposedly non-coordinating anions were used [26] (see Fig. **4**). This has its reason in the electron density depleted p-orbital on germanium that causes the germanium centre to act as a Lewis acid. Apparently, the π-acceptor strength of the cationic species is rather low, although the Tolman Electronic Parameter TEP is calculated to be 2078 cm^{-1} [13,26] and thus in the region of $P(OEt)_3$ [16]. This would suggest a low σ-donor ability, not unexpected for a cationic ligand.

Further evidence for the cationic NHGe's demand for electron density can be seen in the reaction [NHGeCl{$W(CO)_5$}] with $NaBPh_4$. In the course of the reaction, the cationic NHGe-$W(CO)_5$ complex reacts with its $NaBPh_4$ anion, usually regarded as inert, under abstraction of phenyl anion and generation of BPh_3 (Fig. **4**).

The ease with which the chloride in the six-membered NHGe ligand can be abstracted or substituted [1] can be used in synthetic strategies for the formation of functionalised NHGe. Driess *et al.* reacted NHGeCl with the lithium phosphinide $LiPH_2$ and obtained the corresponding phosphane functionalised NHGe with two vicinal σ-donor centres (see Fig. **5**) [27]. No metal complexes of this new ligand class have been reported to date, but the ligand was further diversified by altering the phosphane functionality. This can be done stepwise from the NHGe-PH_2 ligand by silylation of the phosphane or by reduction of phosphorus to the diphosphane. Alternatively, a different lithium phosphinide can be used to synthesise a phosphino functionalised NHGe.

A different approach to utilise the chloride substituent for the creation of a new NHGe family is reported by the Roesky group [28-32]. In a reaction of the NHGeCl with an Arduengo-Wanzlick carbene (1,3-dimesityl-imidazol-2-ylidene) in the presence of water, the carbene acted as auxiliary base resulting in the substitution of the chloride substituent by a OH-group [32] (see Fig. **6**).

The OH-substituted germylene NHGeOH has two functionalities, a germanium centred lone pair and a hydroxy-group. Both functional groups were successfully exploited. Oxidation with sulfur [31,33] or selenium [28] leads to carboxylic acid analogues, but with an additional donor ligand at the Ge(IV) centre. The germanium atom can act as a classical σ-donor ligand utilising its electron lone pair. Examples include the reaction with [$Fe_2(CO)_9$] and [$CpMn(CO)_3$] [34] that yield the iron(0) and manganese(I) complexes [Fe(NHGeOH)$(CO)_4$] and [CpMn(NHGeOH)$(CO)_2$], respectively. The hydroxy-group on NHGeOH is of course acidic and as such can be used as a heteroalcohol in reactions with organometallic compounds. This was done in the reaction with [Cp_2ZrMe_2] [29]. The resulting heterobimetallic oxide [NHGe-O-Zr(Me)Cp_2] not only contains an oxo-ligand bridging a low oxidation state metal centre - Ge(II) -and another in a high oxidation state - Zr(IV), but the germanium atom retains its electron lone pair and thus its ability to act as a σ-donor to another, Lewis acidic, metal centre.

Similar to Meller germylenes, six membered NHGe can be annelated. Benzannelation is obviously the most facile choice and was described by Riviere *et al.* [35] (see Fig. **7**). Synthesis follows the same route as that for the non-annelated parent compound.

Substitution of the chloro substituent with a methoxy group can be achieved by reaction of the NHGeCl compound with lithium methanolate. The electron lone pair on germanium is left intact and can in principle be used to coordinate to transition metal complexes. However, Riviere *et al.* chose to show the functionality of the lone pair by oxidising it with *o*-quinone, similar to the analogous standard reaction with λ^3-phosphane ligands [36]. Unfortunately, no transition metal carbonyl complex involving this new benzanne-

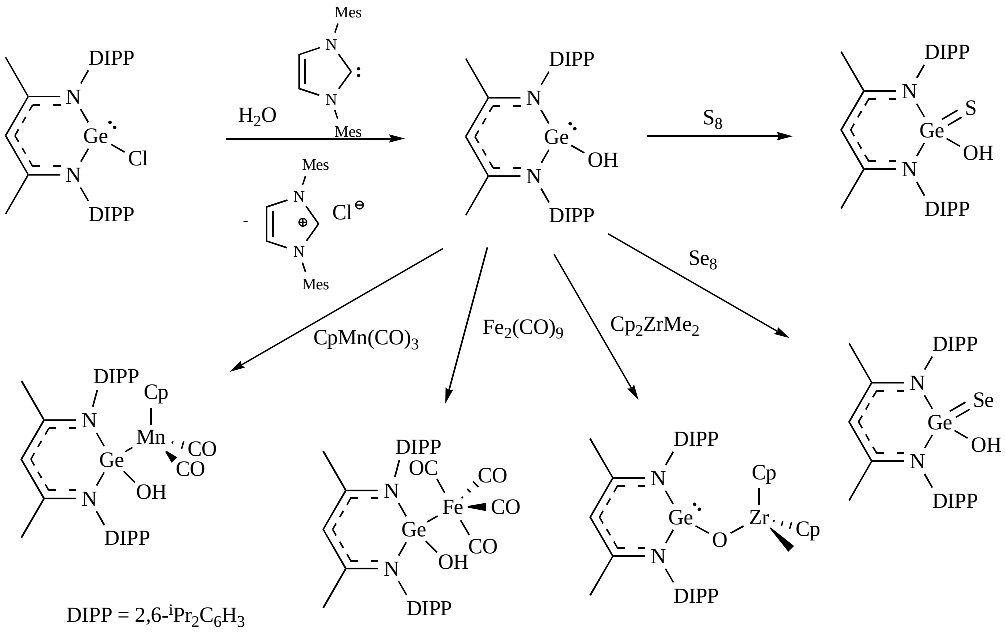


Fig. (6). Synthesis of hydroxy NHGe, oxidation and transition metal complexes thereof.

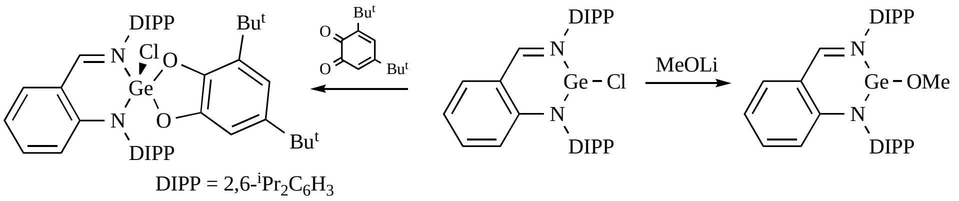


Fig. (7). Synthesis and oxidation of benzannelated, six-membered NHGe.

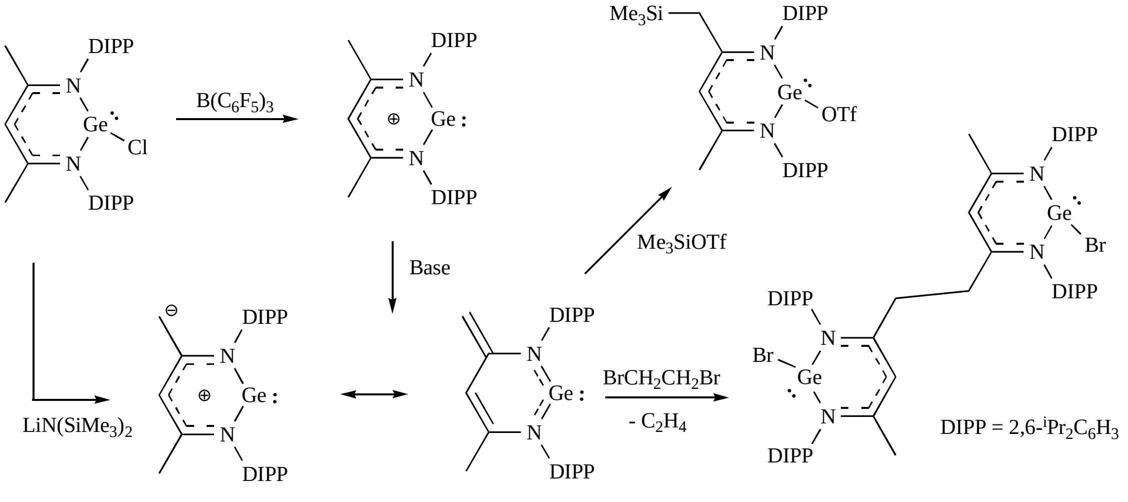


Fig. (8). Synthesis and reactivity of a NHGe with betaine structure.

lated ligand was reported and thus the influence of annelation on the electronic properties of six-membered NHGe is yet to be quantified.

Chloride abstraction from NHGeCl yields a planar, cationic germylene species [1,37]. The same can be obtained when $B(C_6F_5)_3$ is used to trigger chloride abstraction [38] (see Fig. **8**). Reaction of the cationic NHGe with a base yields a zwitterionic, betain-like species that can also be obtained by reacting the NHGeCl with $LiN(SiMe_3)_2$, as the amide abstracts the proton to render the corresponding amine and the lithium cation binds the chloride in a salt metathesis reaction.

The betaine structure of this germylene could be shown by utilisation of its zwitterionic nature. Reaction with $SiMe_3OTf$ (TfO = OSO_2CF_3) yields a compound that can be regarded as deriving from a formal substitution of the $SiMe_3$-group on $SiMe_3OTf$ by the anionic end of the zwitterion and subsequent addition of the TfO- anion onto the cationic germanium atom.

On the other end, reaction of the betaine with 1,2-dibromethane results in a C-C coupling reaction of the two olefinic substituents on the six-membered ring under elimination of ethene and addition of the bromine atoms onto the Ge-atoms (see Fig. **8**).

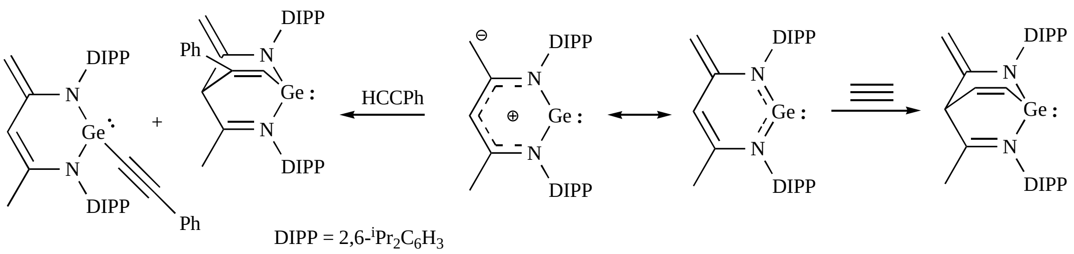


Fig. (9). Reaction of a betain-type NHGe with acetylenes.

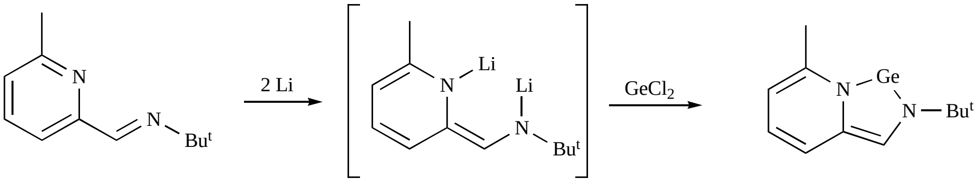


Fig. (10). Synthesis of pyrido[a] annelated NHGe.

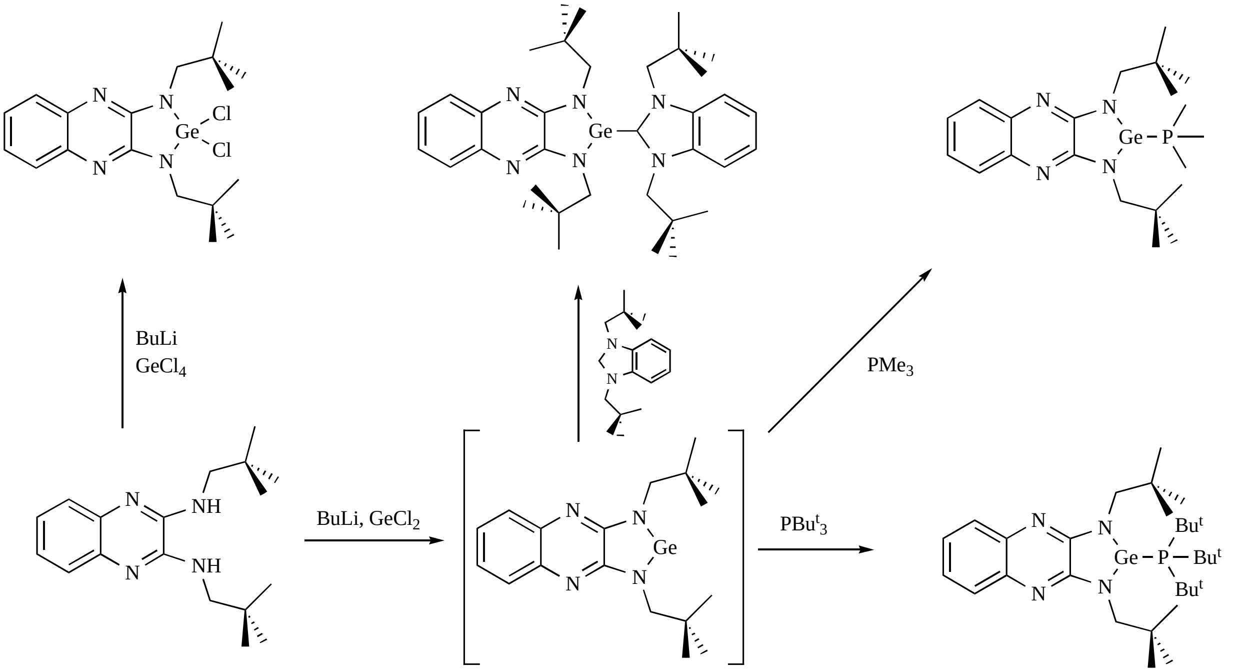


Fig. (11). Attempts to synthesise quinoxaline-annelated NHGe.

The betaine structure can also be exploited in reactions with acetylenes [39]. The acetylene adds across the six-membered ring of the germylene bonding to germanium and the *p*-carbon atom (see figure 9). Interestingly, when phenyl acetylene is used, two reaction products are obtained, the addition product, with the phenyl acetylene added across the six-membered ring, and the insertion product, whereby the germanium centre inserts into the terminal C-H bond and the proton ends up on the exocyclic olefinic carbon atom of the zwitterionic structure. The result is a germylene with an exocyclic phenyl acetylide substituent (see Fig. **9**).

Mechanistically, one might assume that the carbon carbon triple bond of the phenyl acetylene attacks the electron depleted p-orbital of the germanium atom nucleophilicly. The accompanying nucleophilic attack of the π-bond centred on the *p*-carbon atom is assisted by an electron pushing contribution of the formally negatively charged exocyclic carbon atom.

MELLER GERMYLENES [40,41]

An interesting topic in recent years has been the influence of annelation on the electronic properties of the NHGe ligand [4,9,11,12,18] and its ligating ability [10,11,42,43].

Heinicke *et al.* showed that annelation results in destabilisation of the germylene, if the heteroatom is not in the nodal plane of the NHGe's HOMO [12]. That was given as the reason why pyrido[b] annelated NHGe is far more stable than the pyrido[c] annelated isomer. For the corresponding pyrido[a] annelated NHGe (not an isomer as the second wingtip group on N is missing), destabilisation is more obvious, as the aromatic system is broken up in the initial lithiation step and cannot be fully restored in the final germylene (see Fig. **10**) [18].

In quinoxaline annelated NHGe, the cause for destabilisation is different. Here, the electron withdrawing effect of the quinoxaline ring system results in the depletion of the N-Ge π-bonds, the stabilising factor in Meller germylenes [9]. As a result, Lewis acidic behaviour can be expected [4].

The quinoxaline annelated NHGe is in itself unstable and decomposes before it can be isolated and fully characterised [19]. Stabilisation can be achieved by addition of LiCl similar to a recently reported eight-membered NHGe [11], although the chloride stabilised NHGe-Cl adduct could not be isolated. Similarly, addi-

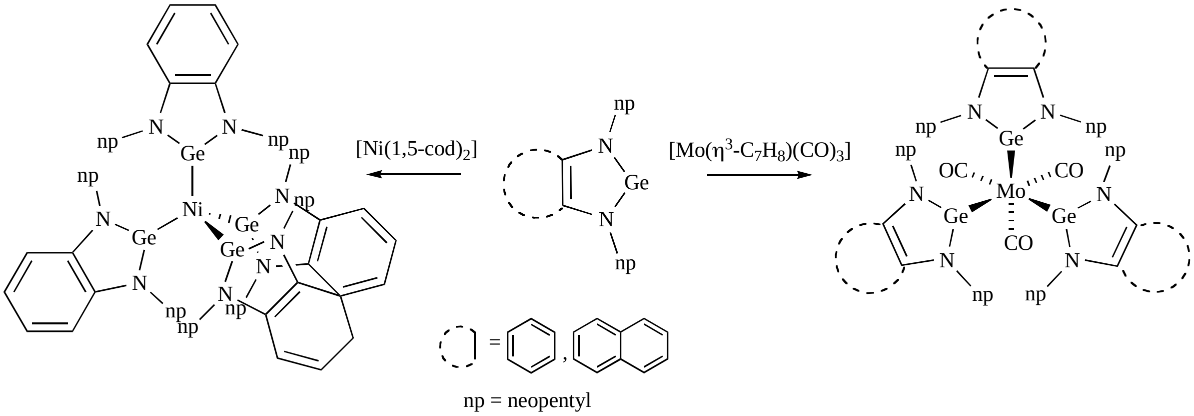
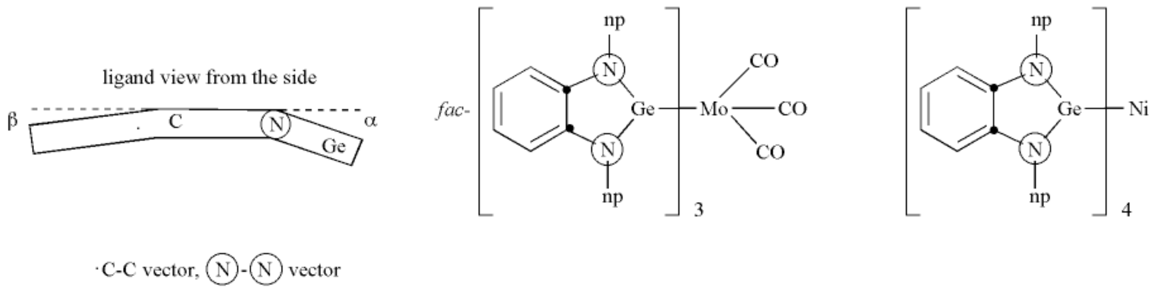


Fig. (12). Transition metal complexes of annelated NHGe.



	2b		2c	
	α	β	α	β
Ligand 1	8.30° (0.16)	3.64° (0.17)	8.55° (0.17)	1.26° (0.17)
Ligand 2	6.62° (0.11)	3.79° (0.11)	7.87° (0.17)	2.17° (0.16)
Ligand 3	7.75° (0.11)	3.34° (0.12)	8.83° (0.13)	0.90° (0.13)
Ligand 4	-	-	7.78° (0.14)	1.06° (0.13)
Average	7.56°	3.59°	8.26°	1.35°

Fig. (13). Folding within NHGe ligands of transition metal NHGe ligands.

tion of a phosphane results in stabilisation of the NHGe by a σ-donor interaction of the phosphane into the partially empty p-orbital on germanium (see Fig. **11**). Unfortunately, the phosphane adducts are only stable in solution and decomposition occurs during attempted isolation of the complexes. The existence of the adducts in solution could be established through the phosphorus chemical shift values using ^{31}P-NMR spectroscopy [7,19]. A similar stabilisation can be achieved by addition of a Wanzlick-Arduengo carbene.

Benzo- and naphtho annelated NHGe are more stable and can be isolated and structurally characterised [9,17,44]. Transition metal complexes of any NHGe are, however, rare [2,10,42,45]. Very recently, Heinicke *et al.* published some molybdenum(0) and nickel(0) complexes of annelated NHGe ligands that gave some interesting insights into the electronic properties of these ligands [10] (see Fig. **12**).

The synthesis of these transition metal complexes is rather facile starting from a suitable metal precursor ([Mo(η^3-C_7H_8)(CO)$_3$] or [Ni(1,5-cod)$_2$]) and the appropriate annelated NHGe ligand. The structures are fac-octahedral for the molybdenum and tetrahedral for the nickel complex, respectively. The most interesting feature of these transition metal complexes is the non-planarity of the NHGe ligands. Whereas normally, the annelated ring system and the five-membered ring of the Meller germylene are coplanar, the structure of the NHGe ligand is significantly different in these transition metal complexes.

The annelated NHGe ligand folds along two vectors, the N-N vector and the C-C vector of the annelation bridge bond (see Fig. **13**). The folding enables the minimisation of steric hindrance and maximum approach of the germanium atoms to the molybdenum centre. It is made possible by a considerably reduced stabilisation energy of the delocalised 10-π-electron system owing to the electron pulling effect of the annelated ring system on the nitrogen lone pairs and subsequent depletion of the N-Ge π-bonds. The latter can be seen by the νCO stretching frequency of the corresponding transition metal carbonyl complexes that increase in the order non-annelated < benzo < naphtho [9,10,13,42].

Modification of the classical Meller germylene framework is not limited to annelation, but can extent to other properties in close analogy to the design of NHC ligands [2,6]. The introduction of chirality [46,47] can be achieved by using chiral diamines that can be obtained by modification of chiral precursor compounds or from achiral diimines [48] (see Fig. **14**). The synthesis follows established synthetic routes [1], but deviates slightly by employing $GeCl_4$ instead of the more familiar and direct $GeCl_2$ option. This makes a reduction step to the Ge(II) NHGe necessary. Lithium as choice for the reducing agent is somewhat remarkable, but has its advantages compared to the more potent standard alternatives potassium and KC_8.

Partial unsaturation, and thus the introduction of chirality, can also be achieved by protonation of the ligand backbone using $[H(OEt_2)_2][B(C_6F_5)_4]$ [49].

The stability of Meller germylenes is a question of considerable interest. Herrmann *et al.* reported the thermal decomposition of Meller germylenes as a source for germanium and germanium hy-

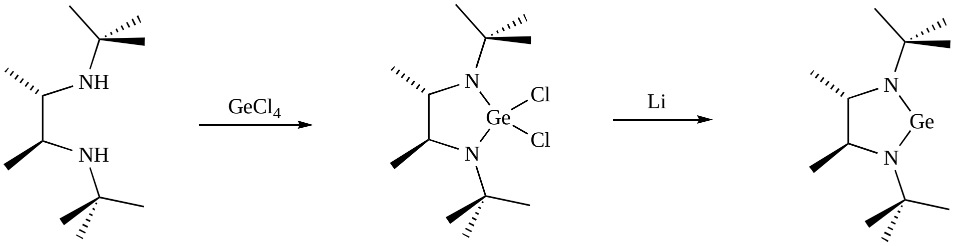


Fig. (14). Synthesis of chiral Meller NHGe.

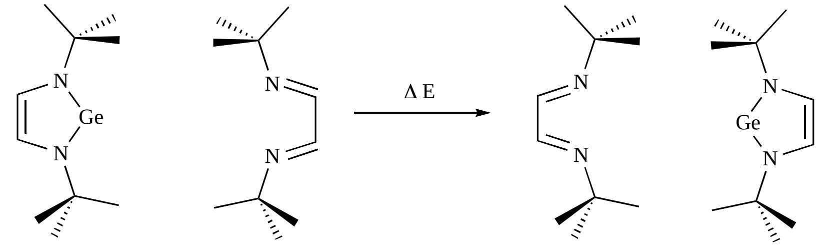


Fig. (15). Germanium transfer of Meller NHGe.

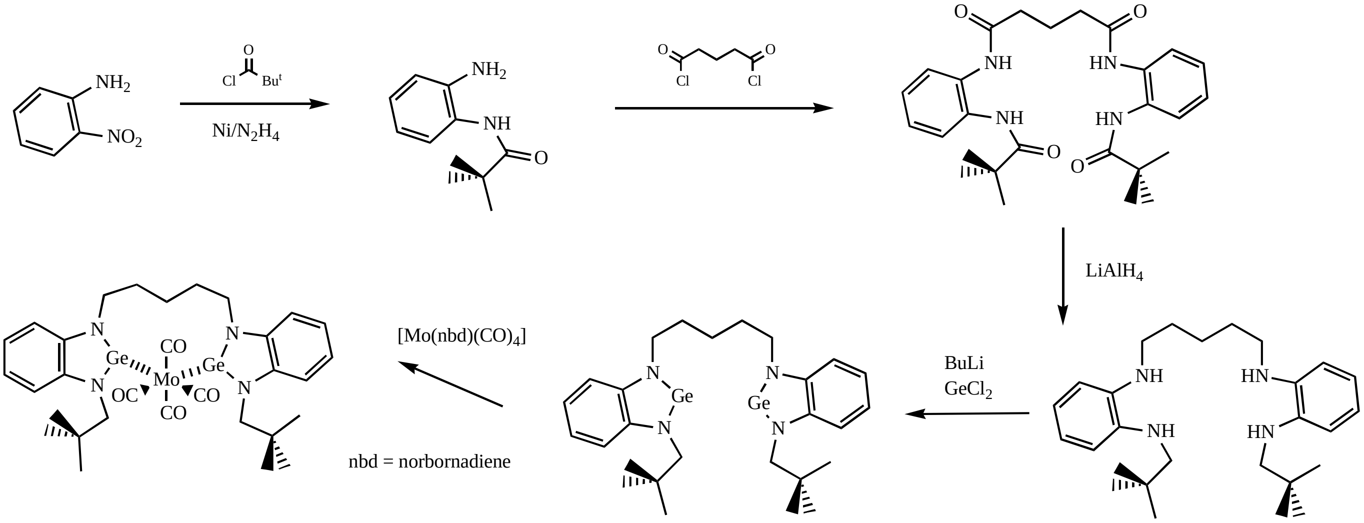


Fig. (16). Synthesis of *bis*-NHGe ligands and their Mo(0) complexes.

dride in chemical vapour deposition applications [43]. Consequently, the reaction between a suitable diimine and $GeCl_2$, $GeCl_4$ or a Meller germylene (see Fig. **15**) has received some attention recently.

Jones *et al.* have shown that a diimine can react with $GeCl_2$ in an addition reaction to the corresponding Ge(IV) species [50]. Prior lithiation of the diimine and subsequent reaction with $GeCl_2$ yields the corresponding Meller germylene. Reaction of a diimine with a Meller germylene results in diimine exchange on germanium, or from a different perspective in germanium transfer from one diimine to the other [51] (see Fig. **15**).

Another predictable trend is the diversification towards *bis*-NHGe ligands in analogy to *bis*-NHC ligands [7,52]. Hahn *et al.* introduced a range of different bis-NHGe mounted on aromatic [53-55], heteroaromatic [53] and aliphatic [54,56] scaffolds [55].

The synthesis of *bis*-NHGe ligands follows largely the protocols of their mono-NHGe analogues, except that two binding sites for the germanium atoms have to be provided (see Fig. **16**). Thus, a stepwise protocol may be employed whereby not the diamine, but an ortho-nitroaminobenzene is acylated with pivaloyl chloride, the nitro-group reduced to the amine, two units coupled with a dicarboxylic acid dichloride, followed by reduction to the tetraamine with $LiAlH_4$ and finally lithiation with BuLi and reaction with germanium(II) chloride. The *bis*-NHGe ligand can then be used in the synthesis of transition metal chelate complexes, e.g. reaction with $[Mo(nbd)(CO)_4]$ (nbd = norbornadiene).

Variations to the general protocol include the choice of reducing agent ($LiAlH_4$, AlH_3, Ni/N_2H_4) or source of germanium ($BuLi/GeCl_2$, $Ge(N(SiMe_3)_2)$). The transition metal precursor remained surprisingly invariant with $[Mo(nbd)(CO)_4]$ as the only example. This is a reflection on the entire transition metal chemistry of NHGe ligands to date that has been limited to *cis*-$[Mo(NHGe)_2(CO)_4]$ [42,54,56], *fac*-$[Mo(NHGe)_3(CO)_3]$ [10,42], $[Ni(NHGe)_2(CO)_2]$ [43] and $[Ni(NHGe)_4]$ [10,45] complexes [1,55].

HETEROSUBSTITUTED NHGe

Although NHGe obtained their name because they are the germanium analogues of N-heterocyclic carbenes NHC [1] and thus are taken to feature two amino substituents on the germanium centre, that does not necessarily have to be the case. Strictly speaking, one amino substituent would suffice, but even with both nitrogen atoms substituted by another heteroatom, the general structure would be preserved and the stabilising effect of N-substitution only

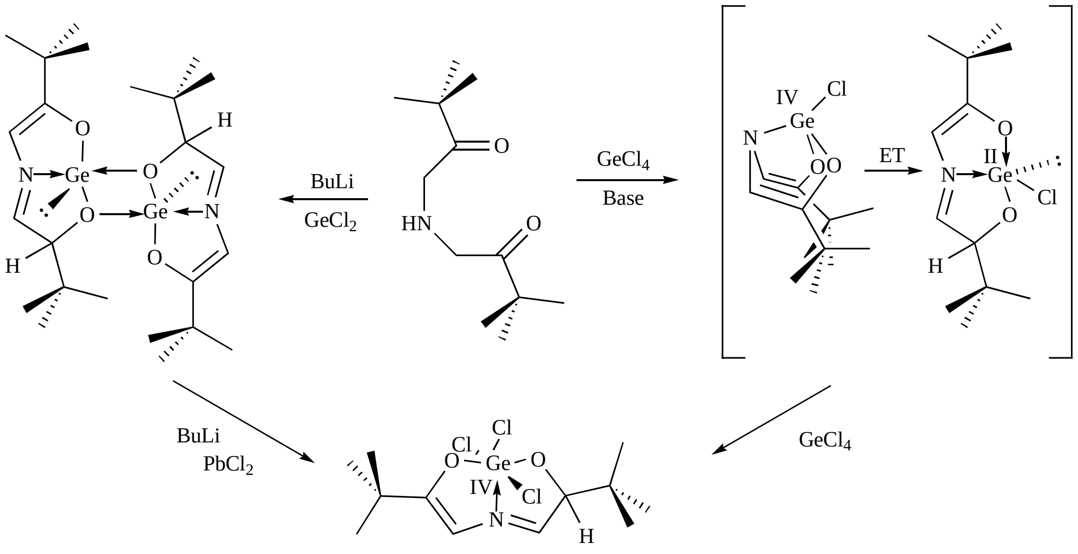


Fig. (17). An amino substituted diketone as scaffold for NHGe compounds.

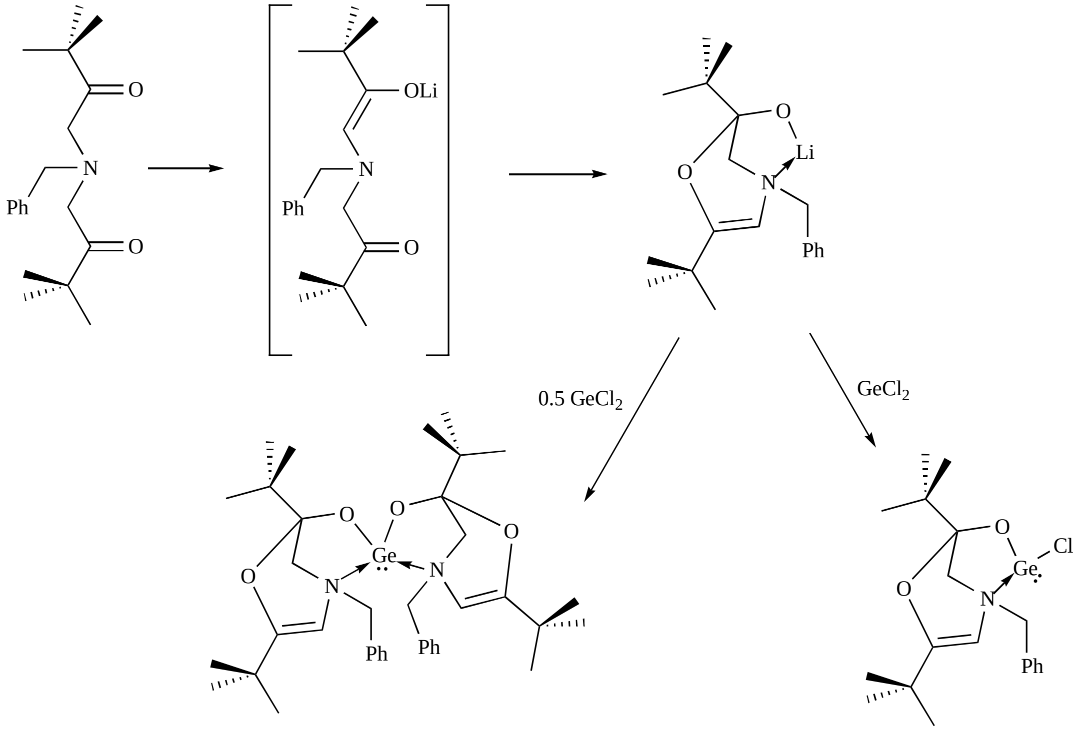


Fig. (18). The influence of substitution on the amino functionality.

mitigated. The extent of destabilisation needs to be evaluated for each individual system.

Bettermann and Arduengo [57] have used an amino substituted diketone [58] to synthesise hypervalent main group compounds [59]. Driess *et al.* extended this concept to synthesise the corresponding Ge(II) and Ge(IV) compounds [60] (see Fig. **17**). Reaction of the diketone with GeCl$_4$ results in the "normal" Ge(IV) 4–Ge–8 compound [61] that rearranges into the hypervalent 4–Ge-10 Ge(II) compound via an intramolecular metal to ligand electron transfer ET process. The latter can be oxidised to the corresponding hypervalent 6-Ge-12 Ge(IV) compound upon reaction with GeCl$_4$ and generation of GeCl$_2$ as the reduced species.

Reaction of the diketone with BuLi and GeCl$_2$ renders a Ge(II) complex of the ligand that features a dimeric structure and an acidic proton in one of the two metallacycles of the monomer (see Fig. **17**). Upon deprotonation (with BuLi) and oxidation (with PbCl$_2$), the same hypervalent 6-Ge-12 Ge(IV) species as above is obtained. Arduengo used the corresponding phosphorus compounds as ligands for (transition) metal complexes and found that the hypervalent structure of the ligand was only preserved in the case of silver(I). For all other central atoms, the phosphorus ligand reverts back to the 4-P-8 structure [59]. Unfortunately, no transition metal complexes were reported for the germanium analogues and thus the influence of germanium on the ligand structure cannot be shown.

Substitution of the NH functionality on the diketone to a NR (CH$_2$Ph) functionality results in a completely different ligand behaviour and different germylene ligands (see Fig. **18**) [62]. Now, the ligand is no longer tridentate in nature, as the enolate end of the

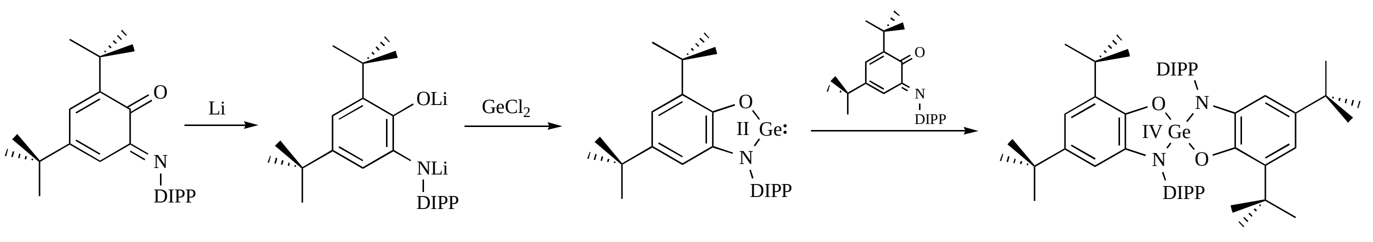


Fig. (19). Synthesis of NHGe from monoimino *o*-quinone. DIPP = 2,6-diisopropylphenyl.

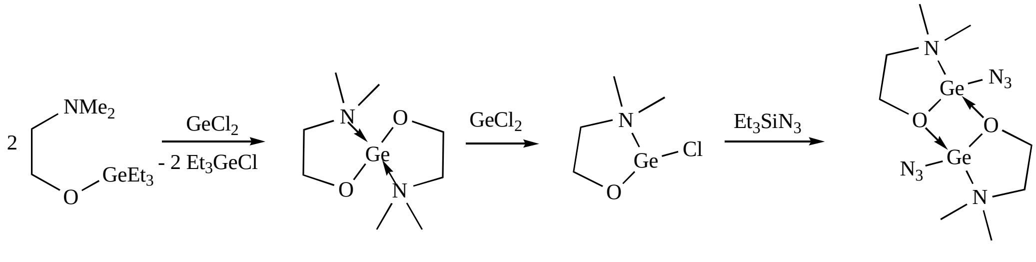


Fig. (20). Synthesis of N,O substituted NHGe.

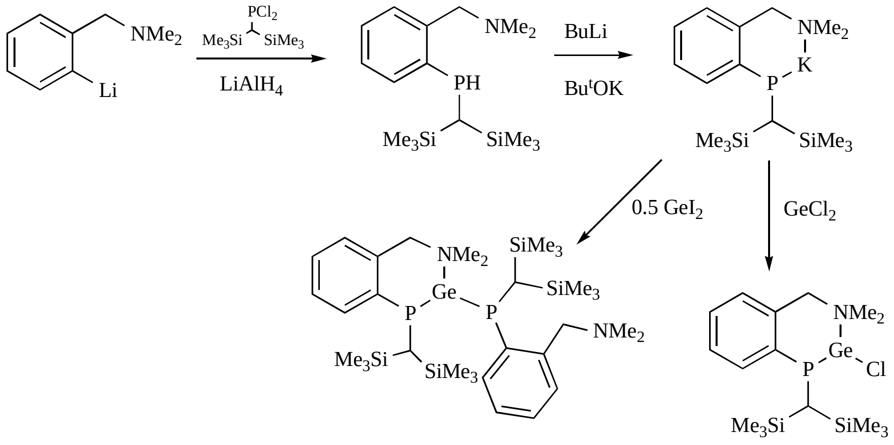


Fig. (21). Synthesis of N,P substituted NHGe.

lithiated ligand engages in a carbonyl reaction on the carbonyl terminus of the ligand resulting in ring closure and an essentially bidentate anionic N,O ligand as a lithium salt. This new ligand can now be used in the synthesis of new germylene compounds. Both, a 1:1 3-Ge-8 and a 2:1 hypervalent 4-Ge-10 compound were synthesised, both retaining an electron lone pair that can potentially be used to form transition metal complexes.

A different approach to synthesise N,O substituted NHGe was reported by Piskunov *et al.* [63]. They lithiated a monoimino *o*-quinone species and subsequently reacted it with $GeCl_2$ to obtain the corresponding benzannelated N,O substituted NHGe (see Fig. **19**). The electron lone pair on Ge(II) can be oxidised by a second equivalent of the starting monoimino *o*-quinone to yield the corresponding spiro-Ge(IV) species. The oxidation is a modification of the usual method using *o*-chloranil as the oxidising agent.

The synthesis of N,O substituted NHGe can be achieved using simple N,N-substituted aminoethanolate ligands [64-67]. Reaction of $GeCl_2$ with the aminoethanolate-$GeEt_3$ compound yields the spiro-Ge(II)L_2 complex in a ligand exchange reaction (see Fig. **20**). Reaction of the spiro-germylene with $GeCl_2$ renders a saturated, five-membered, non-planar N,O NHGeCl. The chloro substituent can be exchanged to an azide upon reaction with Et_3SiN_3 resulting in a dimeric NHGe species. Dimerisation probably occurs owing to insufficient electron density transfer into the germanium p-orbital from the neighbouring O-substituent [68, 69].

Returning back to the fifth main group, we note Izod's synthesis of a benzannelated, N,P substituted six-membered NHGe [70,71]. The reaction starts from o-lithiated dimethylbenzylamine and silylated dichlorophosphane (see Fig. **21**). Reduction with $LiAlH_4$ yields the corresponding aminophosphane that can be lithiated with BuLi. The lithium compound proved to be unsuitable for the introduction of germanium and was exchanged with potassium upon reaction with Bu^tOK.

Reaction with one equivalent of $GeCl_2$ yields the respective N,P substituted NHGeCl whereas reaction with half an equivalent of GeI_2 yields the same NHGe, but with the chloro ligand substituted for the phosphane moiety.

An interesting reaction occurs when the six-membered NHGeCl is reduced with potassium [72]. After reduction, ring contraction results in a five-membered, exocyclic amino substitued N,C NHGe (see Fig. **22**) that reacts with a second molecule of NHGeCl. This amino-bridged bis-germylene is then cleaved by potassium to yield an exocyclic amino substituted six-membered NHGe and the potassium "salt" of an aza-germa-cylopentadienide that could be structurally characterised and was found to be a dimer with K---Ge in-

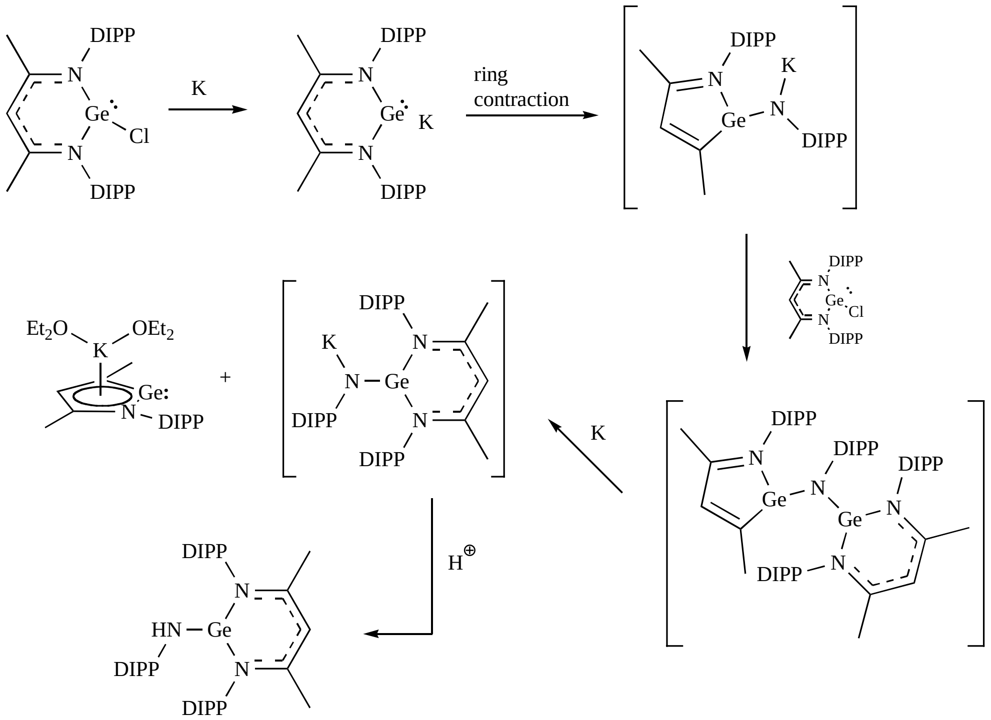


Fig. (22). Synthesis of a germa-cyclopentadienide analogue from a six-membered NHGe.

teractions [72]. Unfortunately, no complexes of this fascinating ligand system have been reported to date.

CONCLUSION

Recent years have seen a concentration onto well defined development lines within the field of N-heterocyclic germylenes: functionalisation, Meller germylenes, six-membered NHGe and heterosubstituted NHGe. Functionalisation is clearly still in its infancy with leading examples being the introduction of a reactive functional group (OH, PH, NH) as exocyclic substituent on germanium, chirality in the ligand backbone, *bis*-NHGe ligands and annelation of the ring system. Heterosubstitution modifies the electronic stability of the NHGe and determines its steric demand as a ligand (via the possible substitution pattern on the heteroatom). In future we will probably see an increase in the scope and diversity of functional groups, rising amounts of transition metal NHGe complexes (and not only those with a M(0) centre) and possibly the exploitation of the chelate effect.

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