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Hydroalumination of Oligoalkynylgermanes and -digermanes – Reactions with Heterocumulenes by Al–C or Ge–C Bond Activation and Formation of a Hexazenedialuminum Complex

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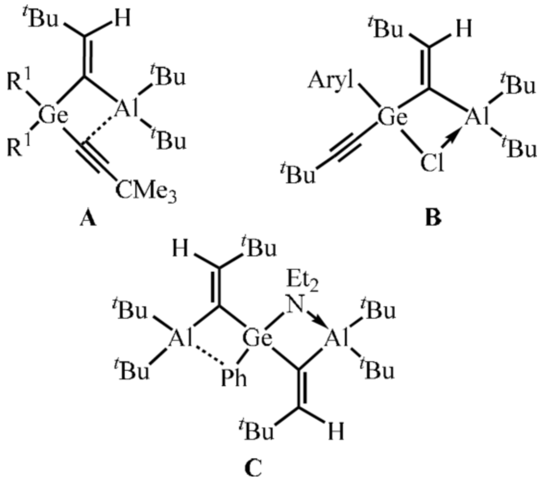
Dedicated to Prof. Alexander Filippou on the Occasion of his 60th Birthday

Abstract. Hydroalumination of the dialkynylgermane $Ph_2Ge(C{\equiv}CtBu)_2$ (**1**) and the digermanes $Ph_n(tBuC{\equiv}C)_{3-n}Ge–Ge(C{\equiv}CtBu)_{3-n}Ph_n$ (**2a**: $n = 2$; **2b**: $n = 1$) with two equivalents of $H–AltBu_2$ or $H–AlEt_2$ yielded the mixed Al/Ge compounds $Ph_2Ge[C(AltBu_2)=CH\text{-}tBu]_2$ (**3**), $[Ph_2GeC(AltBu_2)=CH\text{-}tBu]_2$ (**4a**), and $[Ph_2GeC(AlEt_2)=CH\text{-}tBu]_2$ (**4b**). Reactions of **2b** with both aluminum hydrides afforded inseparable mixtures of products. **3** reacted with heterocumulenes by retrohydroalumination. Phenyl isocyanate gave insertion of the C=N group into the resulting Ge–C(≡C–*t*Bu) bond (**5**), whereas the NCS and NCN groups of phenyl isothiocyanate and a carbodiimide inserted into $Al–C_{vinyl}$ bonds (**6** and **7**) with unaffected terminal Ge–C≡C–*t*Bu moieties. The generation of **5** represents the first example of the insertion of a heterocumulene into a Ge–C bond, which may be favored by the activation of the isocyanate group by the Lewis acidic Al atom and the increased polarity of the N=C=O fragment as determined by NBO calculations. The reactions of the digermanes **4** with heterocumulenes were unselective and afforded inseparable mixtures. Treatment of **4a** with the azide $(4\text{-}tBu)C_6H_4CH_2–N_3$ led interestingly to reductive coupling of two azide molecules, and the hexazene complex $(tBuC_6H_4CH_2N_3–N_3C_6H_4tBu)(AltBu_2)_2$ (**8**) was isolated in moderate yield. Six nitrogen atoms form a dianionic chain, which coordinated two $AltBu_2$ fragments by formation of two joint AlN_4 heterocycles.

Introduction

Functionalized alkynylsilanes and -germanes are facile starting materials for the generation of various unprecedented secondary products. They are available on simple routes and can be modified by various donors such as additional alkynyl groups,[1–6] halide atoms,[7–9] and amino substituents.[9–12] Their highly selective reactions with dialkylaluminum or -gallium hydrides afforded functionalized alkenes in which vinylic C atoms are bound in a 1,1-fashion to Al or Ga and Si or Ge atoms.[1–14] The observed regioselectivity depends on the electronegativity difference between Si or Ge and sp-hybridized alkynyl C atoms, which results in a relatively high partial negative charge at the C_α atom of the alkyne and the exclusive attack of the metal atom at this position. The concerted addition of Al–H groups to alkynes causes a high stereoselectivity and the *cis* arrangement of Al and H atoms at the resulting alkenyl groups.[1–13] *cis*/*trans*-Isomerization was observed only in rare cases and is often suppressed by steric shielding of the metal atoms or their coordinative saturation by electron donating functional groups.[5] Both effects prevent the approach of an Lewis acidic center to the C_α atom of the alkene, which was found to be crucial for the rearrangement of the kinetically favored *cis* isomer to the thermodynamically stable *trans* form.[15]

Hydrometallation of alkynylsilanes or -germanes afforded compounds with new and interesting structural motifs, which showed an exceptional reactivity. Treatment of dialkynyl derivatives with one equivalent of an aluminum or gallium hydride yielded mixed alkenyl-alkynyl compounds (**A**, Scheme 1), in which the Lewis acidic metal atoms have a close



Scheme 1. Schematic drawings of the functionalized alkenylgermanes **A** to **C**.

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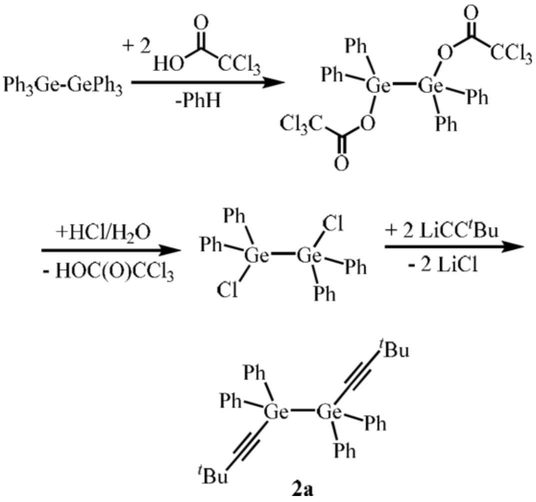
contact to the C_α atoms of the remaining alkynyl groups.[1–6,8–13,16] This interaction resulted in an activation of the *E*–C(≡C–*R*) bond (*E* = Si, Ge) and favored thermal rearrangement (1,1-carbometallation) to yield sila- or germacyclobutenes, which showed interesting fluorescence properties.[17,18] Halogen atoms attached to Si or Ge resulted in strong intramolecular Al–*X* or Ga–*X* interactions (**B**) and a significant lengthening and activation of *E*–*X* bonds (*X* = Cl, Br),[7–9] which resulted in rearrangement and exchange of halogen atoms and Al bound *tert*-butyl groups.[8,9] Similar structural motifs with N atoms in the bridging positions (Si/Ge–N–Al/Ga) are formed by hydrometallation of amino substituted silanes and germanes.[10–12,16] An activated diethylamino germane (**C**) reacted by the unprecedented elimination of an imine under mild conditions.[10] As suggested by quantum chemical calculations rearrangement and imine elimination proceeded via highly reactive silyl or germyl cations. Furthermore, the intramolecular activation of Si–*X* and Ge–*X* bonds resulted in an unusual reactivity, e.g. toward heterocumulenes.[7,19]

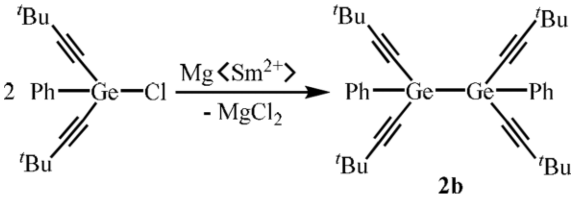
Twofold hydrometallation of dialkynylsilanes or -germanes opened facile access to chelating Lewis acids with two coordinatively unsaturated metal atoms,[1,6,10,13] which effectively coordinated halide anions in a chelating fashion.[1,10,13] Two Lewis acidic centers in a single molecule may help to activate substrates by the chelating coordination of functional groups and may result in new reactivity patterns. This manuscript describes the synthesis of a dialkynylgermane and two alkynyldigermanes containing Ge–Ge bonds, their hydroalumination reactions and the unexpected reactivity of the resulting dialuminum compounds towards various heterocumulenes and an azide.

Results and Discussion

Following a previously described procedure, the air-stable dialkynylgermane $Ph_2Ge(C{\equiv}C\text{–}tBu)_2$ (**1**) was conveniently obtained in high yield from commercially available Ph_2GeCl_2 and two equivalents of Li–C≡C–*t*Bu, which was in situ generated from H–C≡C–*t*Bu and *n*BuLi.[3] The syntheses of the digermanes **2** is less straight forward. According to a literature procedure[20] $Ph_3Ge\text{–}GePh_3$ was treated with Cl_3CCO_2H to yield the corresponding carboxylic acid ester $Ph_4Ge_2(O_2CCCl_3)_2$ (Scheme 2), which was converted to $Ph_4Ge_2Cl_2$[21] by reaction with aqueous HCl. Reaction of the dichloride with two equivalents of Li–C≡C–*t*Bu afforded by salt elimination the dialkynyldigermane **2a** in 70 % yield (Scheme 2). The tetraalkynyldigermane **2b** was obtained via treatment of $PhGeCl_3$ with two equivalents of Li–C≡C–Ph (Scheme 3). Intermediately formed $PhGeCl(C{\equiv}C\text{–}tBu)_2$[8] yielded the digermane by reductive coupling in high yield (77 %). Unselective reactions were observed with strong reducing agents such as Na or K, and only the SmI_2 mediated reduction with magnesium[22] afforded **2b**.



Scheme 2. Synthesis of **2a**.



Scheme 3. Synthesis of **2b**.

The NMR spectra of compounds **2** are similar to those of **1** with a characteristic large difference of about $\Delta\delta = 44$ between the ^{13}C NMR shifts of the C_α [$\delta = 76.7$ (**2a**), 74.7 (**2b**)] and C_β atoms [$\delta = 120.7$ (**2a**), 118.6 (**2b**)] of the alkyne. The difference between the shifts of both alkynyl carbon atoms is a measure of the polarization of the triple bond.[23] The charge on C_α is influenced by the substituents on the alkyne with *t*Bu leading to a higher negative partial charge than Ph (e.g. NBO calculations on dimesitylphosphines).[24] The slightly larger $\Delta\delta$ value in compounds **2** as compared to **1** (41.6) may result from the Ge–Ge bond and the lower oxidation state of germanium (Ge^{III}).

The molecular structure of compound **2a** is shown in Figure 1. **2a** crystallizes with a center of symmetry between the two Ge atoms resulting in an ideal staggered conformation with the alkyne substituents on opposite sides of the molecule. The arrangement is similar in **2b**, which crystallizes with two independent molecules that both adopt a staggered conformation. Bond lengths and angles are in the expected ranges with C≡C bond lengths of around 120 pm and Ge–Ge bond lengths of 241.8(1) and 240.1(av) pm, respectively.

Hydroalumination of **1** and **2a** with two equivalents of H–Al*t*Bu_2 yielded the respective hydroalumination products **3** and **4a** in 59 and 65 % yield (Scheme 4 and Scheme 5). The analogous reaction with sterically less demanding H–$AlEt_2$ was only successful with **2a** yielding **4b** in 82 % yield, while in case of **1** a mixture of unknown and inseparable products was obtained. Attempts to isolate a hydroalumination product from the reaction of compound **2b** with these aluminum hydrides failed, and

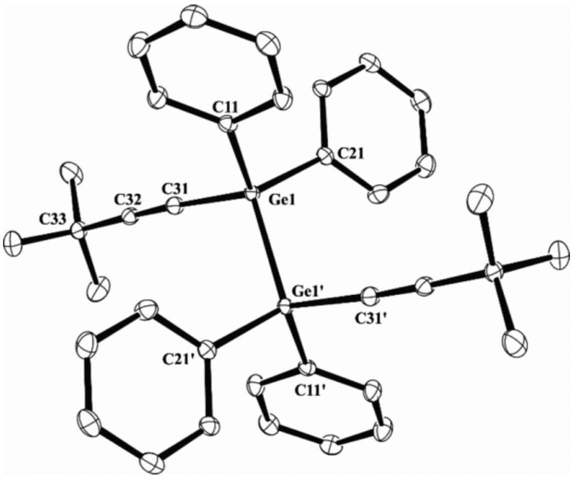
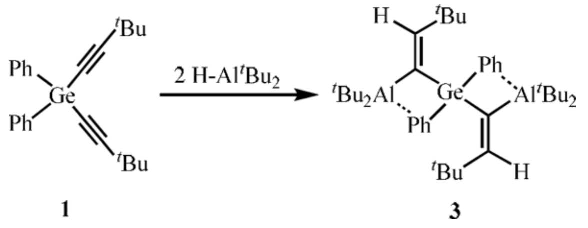
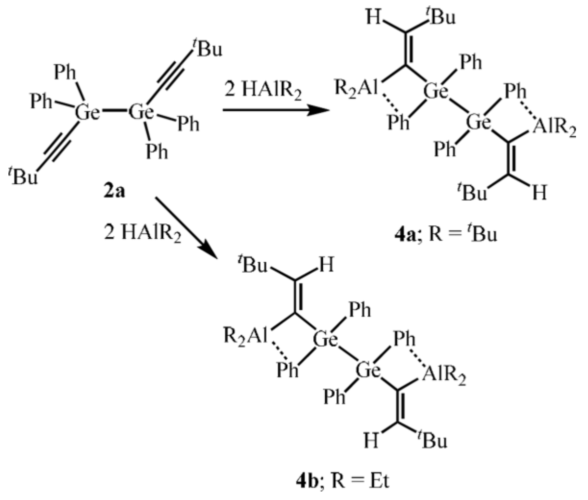


Figure 1. Molecular structure of compound **2a**. The structure of compound **2b** is similar. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms are omitted for clarity; equivalent atoms were generated by $-x + 2$, $-y + 1$, $-z + 1$. Selected bond lengths /pm and angles /° (data of compound **2b** in square brackets, average values from two independent molecules): Ge1–Ge1' 241.81(3) [240.14], Ge1–C11 194.6(1) [193.9], Ge1–C21 195.0(1), Ge1–C31 190.7(2) [189.7], C31–C32 120.5(2) [119.3]; Ge1–C31–C32 176.2(1) [171.0].

NMR spectra of the reaction mixtures gave no evidence for the formation of the expected products.



Scheme 4. Hydroalumination of dialkynylgermane **1**.



Scheme 5. Hydroalumination of dialkynyldigermane **2a**.

NMR spectra of **3** and **4** confirm hydroalumination. The ^{1}H NMR spectra show characteristic signals at $\delta = 6.89$ to 7.14 ppm for the vinylic H atoms, and signals at $\delta = 142.5$ to 146.4 ppm (C_α) and 163.1 to 169.9 ppm (C_β) in the ^{13}C NMR spectra result from vinylic C atoms. The latter may be compared to similar values found in related mono-hydroalumination products.[3] The signals of the quaternary C atoms of the alkyne bound *tert*-butyl groups are with values of $\delta = 39$ ppm considerably shifted to lower field compared to the starting materials (about $\delta = 29$ ppm). The NMR spectra of compound **4a** show broad lines at ambient temperature, which prevented the unambiguous assignment of signals in the phenyl region and indicates a dynamic behavior in solution. Despite the broadness of signals two different Al*t*Bu$_2$ groups (^{1}H, $\delta = 1.35/0.69$) are resolved, while the *t*Bu substituents at aluminum are equivalent in compounds **3** and **4b**. Different *tert*-butyl groups were recognized in the solid-state structure of **4a** (Figure 3) with one group (C41) showing a close $Me_3C\cdots HC$ contact (293 pm) to one of the phenyl substituents at Ge. While similar contacts (see discussion below) are also observed for **3** and **4b** the bulkiness of the *t*Bu groups and the presence of a second germyl fragment in **4a** may increase the rotational barrier about the C_{vinyl}–Al and all Ge–C bonds, prevent free rotation around these bonds and result in the observed broadening of signals. The strongly differing chemical shifts of the *t*Bu groups may indicate that they are in different regions of the anisotropy cone of the phenyl substituent.[25] C41 is closer to the deshielding area, C51 closer to the shielding area. The average value of the *t*Bu shifts of **4a** ($\delta = 1.02$ ppm) is close to that found for compound **3** ($\delta = 0.99$ ppm). A low temperature NMR spectrum (200 K) led to a reduction in line width but complete assignment of the signals was still not possible. The major difference being the splitting of the broad signal at $\delta = 8.15$ into two doublets at 8.42 ($^2J_{HH} = 7.3$ Hz) and 7.96 ($^2J_{HH} = 7.4$ Hz). The new signals may tentatively be assigned to the *o*-H atoms of the phenyl substituents, of which one shows a weak interaction to the Al atom and C41 (Figure 3). Hindered rotation about the Ge–C_{ipso} bond may result in two distinct H signals. Similar interactions between metal atoms such as Li, Ru or Ir and H were previously shown to cause such a hindered rotation and a high field shift of the involved *o*-H atoms.[26]

The molecular structures of compounds **3**, **4a**, and **4b** are shown in Figure 2, Figure 3, and Figure 4. Compound **3** features an approximate twofold rotation axis, which passes through the Ge atom and bisects the C11–Ge1–C21 and C31–Ge1–C41 angles. The molecule of **4a** resides on a crystallographic twofold rotation axis that passes through the center of the Ge–Ge bond, and **4b** has an inversion center located on the Ge–Ge bond. Molecular symmetry is consistent with the magnetic equivalence of the phenyl, vinyl, and Al*t*Bu$_2$ substituents in solution. Weak intramolecular contacts between the Al atoms and an *o*-C atom in **3** and **4a** [258 (**4a**) and 263 or 267 pm (**3**)] result in a deviation from planarity for the Al atoms [Al 29 (**4a**) to 32 (**3**) pm above the plane of the three directly bonded C atoms] and may help to explain the magnetic inequivalence of the two *t*Bu substituents of an Al*t*Bu$_2$ group in **4a**.

The situation is different for compound **4b**, in which the Al atom is coordinated by three C atoms (C31, C41, C43) in an essentially planar fashion (distance Al to the plane 0.3 pm) and

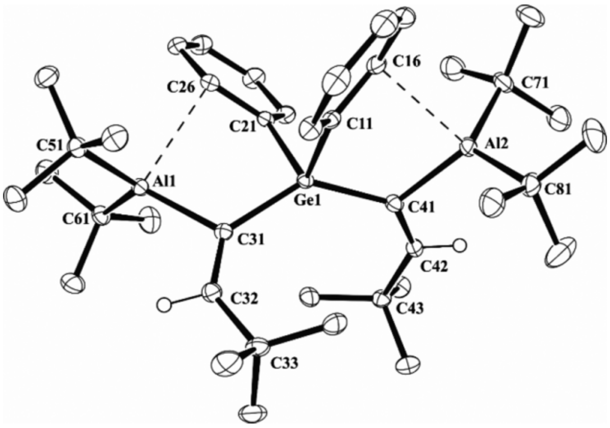


Figure 2. Molecular structure of compound **3**. Displacement ellipsoids are drawn at the 40 % level. A disordered solvent molecule (1,2-difluorobenzene) and hydrogen atoms (except H32, H42; arbitrary radius) are omitted. Selected bond lengths /pm and angles /° Ge1–C31(vinyl) 195.0(2), Ge1–C41(vinyl) 195.5(2), Ge1–C11(Ph) 197.2(2), Ge1–C21 197.5(2), C31–C32 134.4(2), C41–C42 134.7(2), Al–C(*t*Bu) 199.6(av.), Al–C_{vinyl} 198.0(av.), Al1···C26 262.7(2), Al2··C16 266.9(2), C11–Ge1–C21 103.08(7), C31–Ge1–C41 134.93(7).

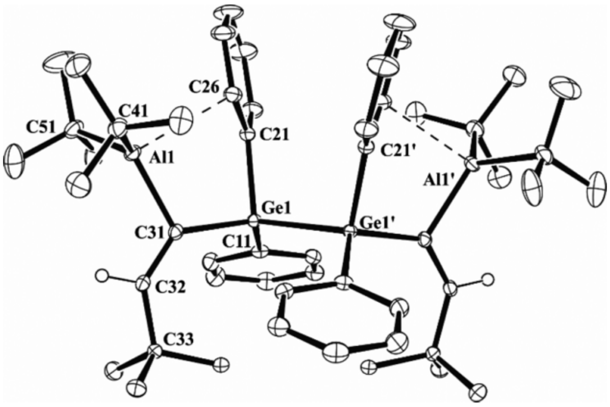


Figure 3. Molecular structure of compound **4a**. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms (except H32; arbitrary radius) are omitted; equivalent atoms were generated by $-x$, y, $-z + 1/2$. Selected bond lengths /pm and angles /° Ge1–Ge1' 246.48(3), Ge1–C11 195.6(2), Ge1–C21 197.1(1), Ge1–C31 195.7(2), C31–C32 134.2(2), Al1–C(*t*Bu) 200.3(av.), Al1–C31(vinyl) 199.0(2), Al1···C26 258.0(2), Ge1'–Ge1–C31 118.79(4), C11–Ge1–C21 102.97(6).

shows two long distances to an *o*-C atom (301 pm) and a *t*Bu group (284 pm) hereby completing the coordination environment of the Al atom to a distorted trigonal bipyramid. The unusual coordination in **4b** may be correlated to the surprising *trans*-arrangement of Al and vinylic H atoms, while in **3** and **4a** the Al and vinylic H atoms adopt the expected *cis*-positions. The isomerization of the kinetically favored *cis* product to the *trans* isomer for compound **4b** may be favored by the low steric bulk of ethyl as compared to *t*Bu groups, which allows a four-coordinate Al atom as key intermediate in the isomerization process.[15] The Al–C distances are similar to related hydroalumination products[3,4,8,13,17,19] with the Al–C_{vinyl} slightly shorter than Al–C_{alkyl} bonds. The Ge–Ge bond lengths are 4.7 (**4a**) and 1.9 pm (**4b**) longer than in the starting material **2a**.

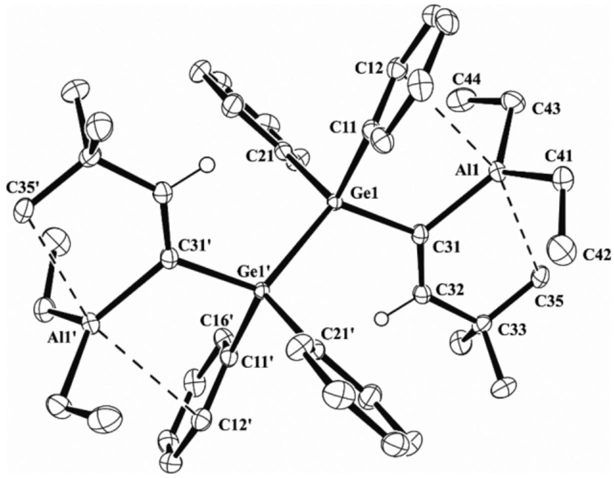
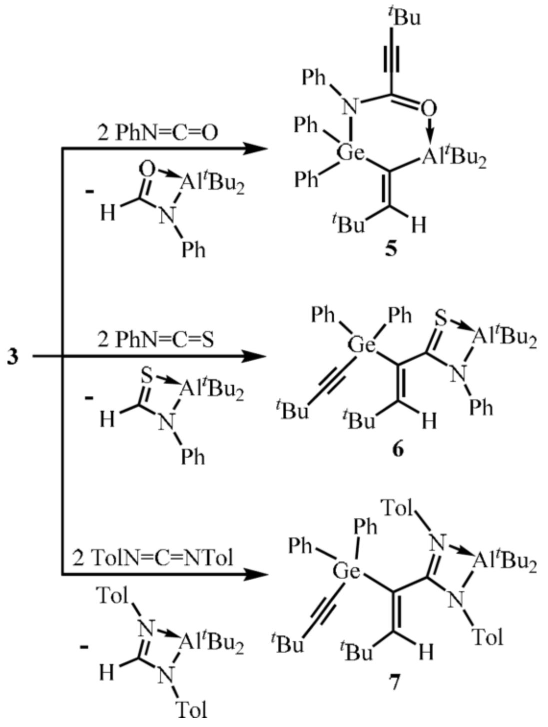


Figure 4. Molecular structure of compound **4b**. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms (except H32; arbitrary radius) are omitted; equivalent atoms were generated by $-x + 2$, $-y + 1$, $-z + 1$. Selected bond lengths /pm and angles /° Ge1–Ge1' 242.49(4), Ge1–C11 197.1(2), Ge1–C21 195.7(2), Ge1–C31 195.7(2), C31–C32 134.2(2), Al–C(Et) 196.6(av.), Al1–C31 197.5(2), Al1···C12 301, Al1···C35 284, Ge1'–Ge1–C31 116.19(5), C11–Ge1–C21 105.52(6).

The Ge–C bond lengths to those phenyl rings that show close contacts to Al are slightly longer (ca. 1.5 pm) than the other Ge–C(Ph) distances.

We studied the reactivity of the hydroalumination products **3** and **4** toward the heterocumulenes PhNCO, PhNCS, and (4-Me)$H_4C_6N=C=NC_6H_4$(4-Me). While treatment of compound **3** with two equivalents of the heterocumulenes at room temperature yielded the insertion products **5** to **7** (44 to 65 % yield; Scheme 6), the corresponding reactions of **4a** and **4b** at room



Scheme 6. Reactions of **3** with heterocumulenes (Tol = 4-MeC_6H_4).

temperature or at 50 °C led to complex mixtures of unknown compounds as determined by NMR spectroscopy. Isolation or enrichment of one of the components by recrystallization from different solvents was not successful. **5** to **7** are formed by insertion of the respective heterocumulene into the Ge–C_{vinyl} (PhNCO) or the Al–C_{vinyl} bonds [PhNCS, (4-Me)-$H_4C_6N{=}C{=}NC_6H_4$(4-Me). Retrohydroalumination occurred which may be favored by an interaction of the Lewis acidic metal atoms with the nucleophilic O, S, or N atoms.[10,27] Reaction of released H–Al*t*Bu_2 with one molecule of the heterocumulene probably afforded different hydroalumination products. One of these was unambiguously identified as PhNC(H)S–Al*t*Bu_2. Its characteristic signals [CH: $\delta(^1H)$ = 8.58; $\delta(^{13}C)$ = 185.4] were observed in NMR spectra of the crude product by comparison with spectra of a pure sample of PhNC(H)S–Al*t*Bu_2, which was independently synthesized from H–Al*t*Bu_2 and PhN=C=S. Signals of the corresponding formamide side-product (synthesis of **5**; see Experimental Section) were detected only with low intensity in the complicated NMR spectra of the reaction mixture. Both by-products could not be isolated in a solid and pure form by recrystallization. A mass spectrum of the S compound showed the mass of the dimer minus a Ph–N–C(H)–S group and a H atom and may confirm the existence of dimeric units in the solid state.

The formation of **5** is unexpected as it is the first example for the insertion of an electrophile into a Ge–C bond of a hydrometallated alkynylgermane. Amino- and aluminum-functionalized germanes showed a comparable reactivity with an insertion into activated Ge–N bonds.[12] The different reactivity of PhNCO and PhNCS may be related to charge distribution in the NCX groups. NBO calculations (TPSS/def2TZVP + GD3BJ)[28] on the adducts PhNCO→$AlMe_3$ and PhNCS→$AlMe_3$ as models for the likely first intermediate (adduct between **3** and the heterocumulene) showed a significantly larger charge separation for the NCO complex (PhNCO→$AlMe_3$: N: –0.409, C: +0.826, O: –0.542; PhNCS→$AlMe_3$: N: –0.338, C: +0.229; S: +0.034), which indicates a higher polarity in the PhNCO adduct and a much larger positive charge on the central C atom. The polarity of a Ge–C bond on the other hand is significantly lower than that of an Al–C bond due to the higher electronegativity of Ge in comparison to Al. It seems likely that the larger partial charge in case of the PhNCO adduct initiates insertion into the Ge–$C_{alkynyl}$ bond. The same reaction is energetically less favored in case of the less polarized heterocumulenes PhNCS and (4-Me)$C_6H_4N{=}C{=}NC_6H_4$(4-Me).

Compounds **5** to **7** show a downfield shift of the Al*t*Bu_2 resonances in the ^1H NMR spectra from δ = 0.99 in **3** to about 1.2 (**6**, **7**) or 1.63 (**5**) as a result of the increased coordination number of Al. The *t*Bu groups are equivalent in **5** (*pseudo*-mirror plane through Al and the six-membered heterocycle, Figure 5) but magnetically inequivalent in **6** (extremely broad signals; $\nu_{1/2} > 50$ Hz) and **7** (δ = 1.32, 1.08) which is likely a result of hindered rotation around the GeC–CNS (GeC–CN_2) bond (Figure 6). Compound **5** is further characterized by highfield shifts of the alkynyl C signals [$\delta(^{13}C)$ = 74.3, 108.6; **6** and **7**: ca. 80 and 119] and of the Me resonances of the attached *t*Bu group [$\delta(^1H)$ = 0.54; 1.2 for **6** and **7**], which reflects the different bonding environment of the alkynyl group in **5** (O=C–C≡C–*t*Bu) as compared to **1**, **6** or **7** (Ge–C≡C–*t*Bu). In the IR spectrum of **5** the stretching vibration ν(C≡C) is shifted to higher wave numbers as compared to **1**, **6**, or **7**. The C atoms in the heterocycles of compounds **6** and **7** show the characteristic downfield signals in the ^{13}C NMR spectra [NCS: δ = 204.2 (**6**); NCN: δ = 176.2 (**7**)].

Compound **5** (Figure 5) features a six-membered AlCGeNCO heterocycle with the atoms Al1C31Ge1N1 in a plane (largest deviation from plane 3 pm for C31) and C41 and O1 significantly below that plane (C41: 41 pm; O1: 70 pm). The C41–O1 and C41–N1 bond lengths in the heterocycle are with 127.1(2) and 132.0(2) pm between the typical values of single and double bonds and confirm delocalization of π electron density. Short distances to a *m*-H atom (GePh) of one molecule and the O and C_α atoms of the alkynyl substituent (O···H–C: 269 pm; C≡C···H–C: 284 pm) of a second molecule result in the formation of weakly bound dimers.[29]

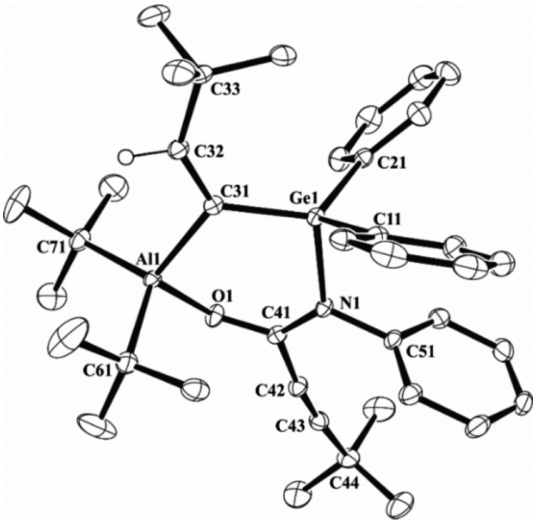


Figure 5. Molecular structure of compound **5**. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms are omitted (except H32, arbitrary radius). Selected bond lengths /pm and angles /° Ge1–C(Ph) 194.7(av.), Ge1–C31 192.0(2), Ge1–N1 198.4(1), C31–C32 134.9(2), C42–C43 118.9(2), C41–N1 132.0(2), C41–O1 127.1(2), Al1–O1 186.0(1), All–C31 199.4(2), Al1–C(*t*Bu) 200.1(av), C31–Ge1–N1 104.55(6), Ge1–N1–C41 126.7(1), N1–C41–O1 124.3(1), C41–O1–Al1 131.1(1), O1–Al1–C31 101.45(6), Al1–C31–Ge1 116.66(8).

The molecular structures of compounds **6** and **7** (Figure 6) are similar. The Al atoms are coordinated in a chelating manner by NCS or NCN ligands to form planar four-membered NCSAl or NCNAl heterocycles [largest deviation from plane for C51 (**6**: 4 pm, **7**: 3 pm)]. The vinyl group is perpendicular to that plane and on the same side as one of the *t*Bu(Al) groups, the second *t*Bu group is neighboring the $GePh_2$(C≡C*t*Bu) moiety. This structure is consistent with their magnetic inequivalence as observed in the NMR spectra of **7**, if rotation about the bond C41–C51 is slow on the NMR time scale in solution (see discussion above). The angles in the four-membered heterocycles differ considerably and are smaller than 90° at Al [72.63(8)° (**6**); 68.41(5)° (**7**)] and S [74.49(9)°] and larger than 90° for the atoms C51 [113.8(2)° **6**; 108.2(1)° (**7**)] and N1/N2 [98.7(2)° **6**; 91.6(av.)° (**7**)]. The π-electron density in the CNS or CN$_2$ groups is delocalized as evident from the bond lengths [C51–S1 173.7(4), C51–N1 131.9(4) (**6**); C51–N1 134.4(2), C51–N2 134.1(2) pm (**7**)] that are between those of standard C–N or C–S single and double bonds[30] and similar to those found in DippN=CH–NDipp(AlMe$_2$).[31] In related adducts with five- or six-coordinate metal atoms[32] bond lengths are shorter (C–N $\le$ ca. 131; C–S ca. 170 pm). The neutral ligands may formally be generated by protolytic cleavage of the Al–*X* bonds and have significantly shorter C–S distances (165–169 pm), but longer C–N bond lengths (133–135 pm) for the thio compounds and strongly differing C–N distances (ca. 128 and 137 pm) in the carbodiimide derivatives. These observations may indicate a more localized bonding situation.[33] The ligand–metal distances in these compounds are about 250 pm for Al–S and about 200 pm for Al–N bonds and longer than those in **6** [Al1–S1 234.91(1) pm; Al1–N1 195.7(3) pm], **7** [Al1–N 193.4(av.) pm] and DippN=CH–NDipp(AlMe$_2$) [Al–N 195.9(2) pm].[31]

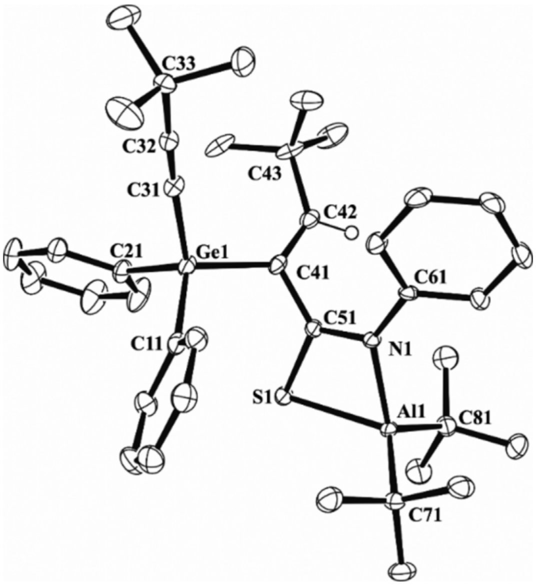
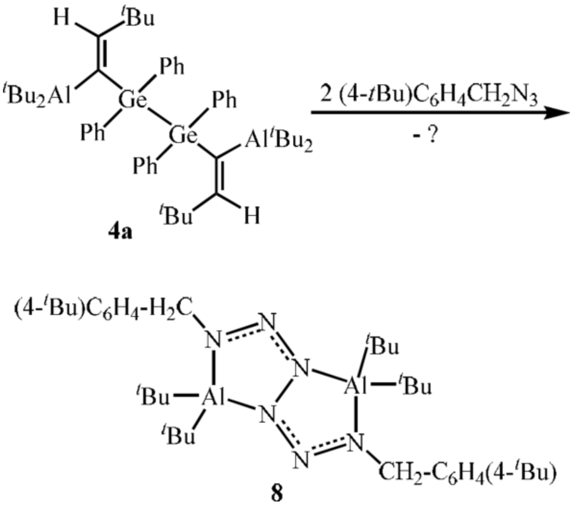


Figure 6. Molecular structure of compound **6**. Compound **7** is similar. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms are omitted (except H42; arbitrary radius). Selected bond lengths /pm (data of **7** in square brackets): Ge1–C(Ph) 194.2(av.) [194.1(av.)], Ge1–C31 190.2(3) [190.0(1)], Ge1–C41 197.5(3) [197.2(1)], C41–C42 133.3(4) [134.2(2)], C31–C32 119.0(5) [119.9(2)], C51–N1 131.9(4) [134.4(2), 134.1(2)], C51–S1 173.7(4), Al1–N1 195.7(3) [193.6(1), 193.4(1)], Al1–S1 234.9(1), Al1–C(tBu) 198.5(av.) [198.6(av.)].

Since reactions with heterocumulenes were not successful, **4a** was treated at 65 °C in *n*-hexane with the azide 4-tBuH$_4$C$_6$CH$_2$–N$_3$, which yielded via reductive coupling the coordinatively stabilized hexazene derivative **8** (Scheme 7). Ge–Ge bonds acting as reducing agents were unexpected, previously reported hexazene complexes have been obtained either by using strong reducing agents such as Zn$^{\mathrm{I}}$, Mg$^{\mathrm{I}}$, *R*Mg–H, or Fe$^{\mathrm{II}}$ [34] or recently by transmetallation with a Zn-hexazene complex as a precursor.[34,35] Purely organic hexaaza-1,5-dienes were obtained by coupling of triazenyl radicals which were in situ formed from diazoaminobenzene[36] or from diacylhydrazine and suitable diazonium salts.[37] Formally, a germaallene is eliminated in our reaction, but such a compound or any secondary product was not identified in the NMR spectra of the reaction mixture. Germallenes are highly reactive and must be kinetically protected by bulky substituents.[38] The NMR spectra of **8** are unexceptional, the EI-MS spectrum shows the molecular ion peak minus one *t*Bu group.



Scheme 7. Reaction of **4a** with 4-tBuH$_4$C$_6$N$_3$.

The structure of compound **8** (Figure 7) features a molecular plane that incorporates two five-membered N$_4$Al heterocycles. The rings are fused by a common edge (N1–N1’) to afford an unsaturated chain of six N atoms. The central N–N bond is located on a center of symmetry. The aromatic rings adopt a *trans* arrangement relative to the molecular plane. The endocyclic angles are 78.17(4)° at the Al and 114.14(9) to 117.61(7)° at the N atoms. The Al–N and Al–C bond lengths

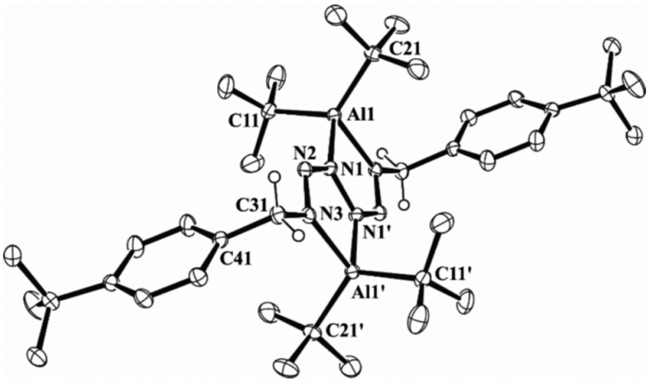


Figure 7. Molecular structure of compound **8**. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms are omitted; equivalent atoms were generated by $-x + 1$, $-y$, $-z + 1$. Selected bond lengths / pm: Al1–C(tBu) 198.3(av.), Al1–N1 193.2(1), Al1–N3’ 195.0(1), N1–N2 130.1(1), N2–N3 129.7(1), N1–N1’ 141.1(2).

are with 194.1 and 198.3 pm on average in the typical ranges of four-coordinate Al atoms. The N–N bond lengths in the hexazene backbone differ significantly and correspond to a single bond for N1–N1' [141.1(2) pm] and a delocalized π-bond for N1–N2 [130.1(1) pm] and N2–N3 [129.7(1) pm]. The hexazene ligand is formally dianionic and formed from two triazaallyl N_3^- fragments, an interpretation that has been confirmed by quantum chemical calculations.[34b] Previously reported and structurally authenticated hexazene complexes are similar to compound **8** and show the same planar backbone. With one exception the metal atoms are four-coordinate with a distorted tetrahedral coordination sphere.[34,36]

Conclusions

Hydroalumination of alkynyl germanes is a facile method for the generation of mixed aluminum-germanium compounds. Their specific reactivity depends on the activation of substrates by the Lewis-acidic Al atoms. Dual hydroalumination of mononuclear dialkynylgermanes or dinuclear dialkynyldigermanes possessing a Ge–Ge bond afforded dialuminum compounds, in which the Lewis-acids showed a weak interaction with aryl groups attached to germanium. While usually the kinetically favored *cis*-addition products were isolated, spontaneous *cis*/*trans* isomerization afforded the *trans* arrangement of Al and H atoms in the alkenyl groups for the sterically less shielded $AlEt_2$ compound **4b**. These dialuminum species are promising candidates for an application in the chelating coordination of suitable Lewis bases and may help to activate substrates by an interaction to both metal atoms. Furthermore, the Ge–Ge bond was expected to contribute to the reactivity of these compounds. Heterocumulenes such as PhNCO, PhNCS, or *R*–N=C=N–*R* were indeed activated by the coordinatively unsaturated Al atoms probably via an increased polarity of the functional groups. However, these reactions proceeded surprisingly by retrohydroalumination, elimination of a dialkylaluminum hydride molecule and reformation of one alkynyl group per formula unit. With PhNCO the activated heterocumulene was unexpectedly inserted into the Ge–C(alkynyl) bond, whereas in other cases insertion into the more polar Al–C(vinyl) bond resulted. These heterocumulenes afforded complicated reaction mixtures with the digermanium derivatives. The Ge–Ge bond was, however, involved in the remarkable reduction of an azide to a dianionic hexazene derivative via N–N bond formation. The unsaturated N_6 chain in the product was stabilized by coordination to two dialkylaluminum groups. This reaction confirms unusual reaction behavior of these new Al functionalized digermanium compounds and will stimulate further systematic investigations into their chemical properties in particular with respect to the influence of the Ge–Ge bond.

Experimental Section

General: All procedures were carried out in an atmosphere of purified argon in dried solvents (*n*-pentane, *n*-hexane over $LiAlH_4$; Et_2O and THF over Na/benzophenone, pentafluorobenzene over molecular sieves). NMR spectra (chemical shift data in δ) were recorded in C_6D_6 at ambient probe temperature using the following instruments, Bruker Avance I (^1H, 400.13; ^{13}C, 100.62; ^{15}N 40.55 MHz), BrukerAvance III (^1H, 400.03; ^{13}C, 100.59), and referenced internally to residual solvent resonances (^1H, ^{13}C). ^{13}C NMR spectra were all proton decoupled. The assignment of NMR spectra is based on HSQC, HMBC, DEPT135, HN-HMBC, and H,H-ROESY data. Elemental analyses were determined by the microanalytic laboratory of the Westfälische Wilhelms Universität Münster. IR spectra were recorded as KBr pellets with a Shimadzu Prestige 21 spectrometer, electron impact mass spectra with a Finnigan MAT 95 mass spectrometer. Commercial PhNCO and PhNCS were distilled in vacuo and stored in an argon atmosphere. H–$AlEt_2$, (4-*t*Bu)$C_6H_4N=C=NC_6H_4$(4-*t*Bu), Ph_2GeCl_2 were used as purchased. H–Al*t*Bu_2,[39] $(Ph_2GeCl)_2$,[12] PhGe(Cl)(C≡C*t*Bu)$_2$,[8] and Ph_2Ge(C≡C*t*Bu)$_2$ (**1**)[3] were synthesized according to literature procedures.

Synthesis of [$Ph_2GeC\equiv C$*t*Bu]$_2$ (2a): *n*BuLi (9.7 mL, 15.5 mmol, 1.6 M in *n*-hexane) was added at 0 °C to a solution of *t*Bu–C≡C–H (1.9 mL, 1.27 g, 15.5 mmol) in diethyl ether (25 mL). The mixture was stirred for 1 h at room temperature. $(Ph_2GeCl)_2$ (3.65 g, 6.97 mmol) was added at 0 °C, and the mixture was stirred for 16 h at room temperature. After aqueous workup (20 mL of H_2O, separation of the organic phase, further extraction of the aqueous phase with 20 mL of Et_2O), the combined organic phases were dried over $MgSO_4$. The suspension was filtered, the solvent removed in vacuo and the residue dissolved in hot *n*-hexane (5 mL). The solution was cooled to –20 °C to yield compound **2a** as a colorless, amorphous solid (3.01 g, 70 %). M.p. 145 °C (dec.). $C_{36}H_{38}Ge_2$ (615.9): C 70.2 (calcd. 70.2); H 6.2 (6.2)%. **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 7.93 (m, 8 H, *o*-H), 7.14 (m, 8 H, *m*-H), 7.08 (m, 4 H, *p*-H), 1.20 (s, 18 H, $C\equiv CCMe_3$). **^{13}C NMR** (101 MHz, C_6D_6, 300 K): δ = 136.8 (*ipso*-C), 135.1 (*o*-C), 129.3 (*p*-C), 128.6 (*m*-C), 120.7 ($C\equiv \mathit{C}CMe_3$), 76.7 ($\mathit{C}\equiv CCMe_3$), 31.1 ($C\equiv CC\mathit{Me_3}$), 28.8 ($C\equiv C\mathit{C}Me_3$). **IR** (KBr): $\tilde{\nu}$ = 3067 s, 3046 s, 3017 m, 2972 vs, 2965 vs, 2924 vs, 2897 s, 2864 s ν(CH); 2172 vs, 2139 vs $\nu(C\equiv C)$; 1981 w, 1960 w, 1904 w, 1884 w, 1823 w, 1767 w, 1653 w, 1584 w, 1568 w, 1551 w (phenyl); 1481 s, 1454 vs, 1429 vw, 1385 m, 1360 s, 1335 w, 1306 m, 1246 vs, 1240 vs δ(CH); 1204 s, 1188 s, 1159 w, 1088 vs, 1063 m, 1026 m, 995 m, 972 vw, 914 m, 852 w, 745 vs, 735 vs, 727 vs ν(CC); 694 vs, 689 vs, 671 vs (phenyl); 619 w, 548 vw, 482 vs, 451 vs, 397 vs, 368 w ν(GeC), δ(CC) cm^{-1}. **MS** (EI, 20 eV, 383 K): *m*/*z* (%): 616 (27) $[M]^+$, 560 (5) $[M - H_2C=CMe_2]^+$, 535 (6) $[M - C\equiv CCMe_3]^+$, 454 (74) $[M - 2\ C\equiv CCMe_3]^+$.

Synthesis of [PhGe(C≡C*t*Bu)$_2$]$_2$ (2b): THF (25 mL) was added to solid Mg filings (1.22 g, 50.2 mmol) and Ph(Cl)Ge(C≡C*t*Bu)$_2$ (1.27 g, 3.66 mmol). The mixture was treated with a solution of SmI_2 (2.5 mmol, 25 mL, 0.1 M in THF) and stirred for 16 h at room temperature. After aqueous work-up (20 mL of H_2O, separation of the organic phase, further extraction of the aqueous phase with 20 mL of Et_2O), the combined organic phases were dried over $MgSO_4$. Filtration, removal of the solvents in vacuo and recrystallization of the residue from *n*-hexane yielded compound **2b** as a colorless amorphous solid (1.76 g, 77 %). M.p. 155 °C (dec.). $C_{36}H_{46}Ge_2$ (624.0): C 69.3 (calcd. 69.3); H 7.4 (7.4)%. **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 8.10 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, *o*-H), 7.25 (*pseudo*-t, $^3J_{HH}$ = 7.7 Hz, 4 H, *m*-H), 7.15 (m overlap, 2 H, *p*-H), 1.14 (s, 36 H, $C\equiv CCMe_3$). **^{13}C NMR** (101 MHz, C_6D_6, 300 K): δ = 135.7 (*ipso*-C), 134.4 (*o*-C), 129.6 (*p*-C), 128.5 (*m*-C), 118.6 ($C\equiv \mathit{C}CMe_3$), 74.7 ($\mathit{C}\equiv CCMe_3$), 30.9 ($C\equiv CC\mathit{Me_3}$), 28.6 ($C\equiv C\mathit{C}Me_3$). **IR** (KBr): $\tilde{\nu}$ = 3069 s, 3049 vs, 3024 m, 2978 vs, 2961 vs, 2928 vs, 2899 vs, 2866 vs ν(CH); 2183 vs, 2144 vs $\nu(C\equiv C)$; 1950 w, 1877 w, 1813 w, 1759 w, 1645 w, 1584 m, 1545 w (phenyl); 1474 vs, 1454 vs, 1433 vs, 1391 w, 1362 vs, 1333 vw, 1304 vw, 1252 vs $\delta(CH_3)$; 1202 s, 1186 m, 1090 vs, 1065 w, 1026 m, 997 w, 920 s, 849 vw, 750 vs, 745 vs, 733 vs *ν*(CC); 694 vs, 673 s, 494 vs, 482 vs, 451 vs, 370 vs ν(GeC), δ(CC) cm^{-1}. **MS** (EI, 20 eV, 373 K): *m/z* (%): 624 (32) [M]$^+$, 609 (15) [M – Me]$^+$, 567 (23) [M – CMe$_3$]$^+$.

Synthesis of Ph$_2$Ge[C(Al*t*Bu$_2$)=CH*t*Bu]$_2$ (3): H-Al*t*Bu$_2$ (1.33 g, 9.35 mmol) was suspended in *n*-hexane (20 mL) at –78 °C. Ph$_2$Ge(C≡C*t*Bu)$_2$ (1.82 g, 4.68 mmol) was added, the cooling bath removed and the mixture stirred for 3 h at room temperature. The obtained solution was concentrated and stored at –20 °C to yield colorless crystals of compound **3** (1.85 g, 59 %). Microanalysis of the product failed although NMR spectroscopic characterization showed only a small quantity of unknown impurities (<5 %). Further purification of the product by recrystallization was not successful. M.p. 131 °C (dec.). **^{1}H NMR** (400 MHz, C$_6$D$_6$, 300 K): *δ* = 7.74 (m, 4 H, *o*-H), 7.26 (t, $^3J_{HH}$ = 7.5 Hz, 4 H, *m*-H), 7.02 (tt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.4 Hz, 2 H, *p*-H), 6.89 (s, 2 H, C=CH), 1.25 (s, 18 H, C=CCMe$_3$), 0.99 (s, 36 H, AlCMe$_3$). **^{13}C NMR** (101 MHz, C$_6$D$_6$, 300 K): *δ* = 163.1 (GeC=*C*), 152.0 (*ipso*-C), 146.4 (Ge*C*=C), 132.4 (*m*-C), 131.7 (*o*-C), 129.8 (*p*-C), 39.3 (C=C–*C*Me$_3$), 30.9 (AlC*Me$_3$*), 29.7 (C=C-C*Me$_3$*), 20.2 (s br., Al*C*Me$_3$). **IR** (KBr): ṽ = 3070 m, 3051 m, 2947 vs, 2924 vs, 2864 vs, 2828 vs, 2762 m, 2729 w, 2700 m *ν*(CH); 2148 vw, 2095 m; 1965 w, 1883 vw, 1830 vw, 1769 vw, 1703 vw, 1651 vw, 1601 m, 1558 vs *ν*(C=C), phenyl; 1462 vs, 1431 s, 1385 m, 1360 s, 1306 w, 1246 s *δ*(CH$_3$); 1198 s, 1159 sh w, 1086 s, 1051 m, 1026 m, 999 s, 935 m, 918 w, 893 w, 876 w, 810 vs, 735 vs, 718 vs *ν*(CC); 698 vs, 667 w, 637 m (phenyl); 583 vs, 538 w, 503 m, 459 s, 415 s, 388 vw ν(GeC), ν(AlC), δ(CC) cm^{-1}.

Synthesis of [Ph$_2$GeC(Al*t*Bu$_2$)=CH*t*Bu]$_2$ (4a): H-Al*t*Bu$_2$ (0.41 g, 2.90 mmol) was suspended in *n*-hexane (15 mL) at –78 °C. (Ph$_2$GeC≡C*t*Bu)$_2$ (**2a**) (0.80 g, 1.30 mmol) was added, the cooling bath removed, and the reaction mixture stirred for 16 h at room temperature. The solution was concentrated and stored at –20 °C to yield colorless crystals of compound **4a** (0.76 g, 65 %). The signals in the phenyl region of the NMR spectra were comparatively broad, which prevented a complete assignment of the resonances. M.p. 156 °C (dec.). C$_{52}$H$_{76}$Al$_2$Ge$_2$ (900.4): C 69.8 (calcd. 69.4); H 8.8 (8.5)%. **^{1}H NMR** (400 MHz, C$_6$D$_6$, 300 K): *δ* = 8.15 (s br., ca. 4 H, Ph), 7.32 (s br., ca. 4 H, Ph), 7.14 (s, 2 H, C=CH), 6.83 (s br., ca. 12 H, Ph), 1.35 (s br., 18 H, AlCMe$_3$), 1.07 (s, 18 H, C=CHC*Me$_3$*), 0.69 (s br., 18 H, AlCMe$_3$). **^{13}C NMR** (101 MHz, C$_6$D$_6$, 300 K): *δ* = 167.2 (GeC=*C*), 142.5 (Ge*C*=C), ca. 137 (Ph), ca. 128 (Ph), 39.7 (C=C*C*Me$_3$), 31.7 and 30.6 (AlC*Me$_3$*), 28.9 (C=CC*Me$_3$*), 20.0 (s br., Al*C*Me$_3$). **IR** (KBr): ṽ = 3067 s, 3049 s, 2953 vs, 2926 vs, 2907 vs, 2864 vs, 2830 vs *ν*(CH); 1954 w, 1896 vw, 1877 vw, 1823 w, 1773 w, 1651 vw, 1593 m, 1554 s *ν*(C=C), phenyl; 1462 vs, 1429 vs, 1385 m, 1358 s, 1307 m, 1246 s *δ*(CH$_3$); 1200 s, 1157 m, 1084 s, 1065 w, 1024 m, 999 s, 966 w, 934 w, 910 w, 891 w, 874 w, 810 s, 733 vs, 700 vs *ν*(CC); 667 w, 640 w, 625 w (phenyl), 577 s, 501 w, 465 s ν(GeC), ν(AlC), δ(CC) cm^{-1}. **MS** (EI, 20 eV, 413 K): *m/z* (%): 701 (2) [M – CMe$_3$ – HAl(CMe$_3$)$_2$]$^+$, 618 (4) [M – 2 Al(CMe$_3$)$_2$]$^+$.

Synthesis of [Ph$_2$GeC(AlEt$_2$)=CH*t*Bu]$_2$ (4b): (Ph$_2$GeC≡C*t*Bu)$_2$ (**2a**) (1.00 g, 1.62 mmol) was suspended in *n*-pentane (30 mL), and H–AlEt$_2$ (350 µL, 0.28 g, 3.26 mmol) was added at –78 °C. The cooling bath was removed and the mixture stirred for 3 h at room temperature. The solution was concentrated in vacuo and stored at –45 °C to yield compound **4b** as colorless crystals (1.06 g, 82 %). M.p. 140 °C (dec.). C$_{44}$H$_{60}$Al$_2$Ge$_2$ (788.2): C 66.7 (calcd. 67.1); H 7.6 (7.7)%. **^{1}H NMR** (400 MHz, C$_6$D$_6$, 300 K): *δ* = 7.76 (m, 8 H, *o*-H), 7.16 (m overlap, 8 H, *m*-H), 7.10 (t, $^3J_{HH}$ = 7.2 Hz, 4 H, *p*-H), 7.03 (s, 2 H, C=CH), 1.05 (t, $^3J_{HH}$ = 8.1 Hz, 12 H, AlCH$_2$*Me*), 1.02 (s, 18 H, C=CC*Me$_3$*), 0.00 (q, $^3J_{HH}$ = 8.1, 8 H, AlCH$_2$). **^{13}C NMR** (101 MHz, C$_6$D$_6$, 300 K): *δ* = 169.9 (GeC=*C*), 142.7 (Ge*C*=C), 141.0 (*ipso*-C), 135.5 (*o*-C), 129.3 (*p*-C), 129.1 (*m*-C), 38.7 (C=C*C*Me$_3$), 28.7 (C=CC*Me$_3$*), 9.4 (AlCH$_2$*Me*), 3.7 (AlCH$_2$). **IR** (KBr): ṽ = 3065 s, 3049 s, 3019 m, 2992 m, 2949 vs, 2899 vs, 2862 vs, 2781 m, 2725 w ν(CH); 1956 w, 1884 w, 1821 w, 1775 w, 1701 vw, 1651 vw,1599 m, 1582 m, 1558 vs, 1512 w ν(C=C), phenyl; 1479 vs, 1460 s, 1427 vs, 1400 m, 1375 m, 1354 s, 1331 w, 1304 w, 1250 s δ(CH$_3$), δ(CH$_2$); 1227 m, 1188 s, 1157 w, 1082 vs, 1063 w, 1024 m, 955 vs, 949 m, 935 m, 916 m, 905 s, 893 s, 856 w, 796 vs, 733 vs, 700 vs *ν*(CC); 642 vs, 617 vs (phenyl); 596 vs, 521 m, 461 vs, 399 s ν(GeC), ν(AlC), δ(CC) cm^{-1}. **MS** (EI, 25 eV, 298 K): *m/z* (%): 674 (32) [M – 2 CMe$_3$]$^+$, 645 (21) [M – 2 CMe$_3$ – Et], 617 (24) [M – AlEt$_2$ – CMe$_3$ – Et]$^+$.

Synthesis of Ph$_2$Ge[C(Al*t*Bu$_2$)=CH*t*Bu][N(Ph)C(O)C≡C*t*Bu] (5): PhNCO (100 µL, 0.11 g, 0.92 mmol) was added at room temperature to a solution of compound **3** (0.30 g, 0.45 mmol) in *n*-hexane (10 mL). The solution was stirred for 16 h, concentrated and stored at –45 °C to yield colorless crystals of compound **5** (0.13 g, 44 %). M.p. 186 °C (dec.). C$_{39}$H$_{52}$AlGeNO (650.5): C 71.9 (calcd. 72.0); H 8.1 (8.1); N 2.5 (calcd. 2.2)%. **^{1}H NMR** (400 MHz, C$_6$D$_6$, 300 K): *δ* = 7.66 [m, 4 H, *o*-H(GePh)], 7.51 (s, 1 H, GeC=CH), 7.07 [m overlap, 2 H, *p*-H(GePh)], 7.06 [m overlap, 4 H, *m*-H(GePh)], 6.72 [tt, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.1 Hz, 1 H, *p*-H(NPh)], 6.60 [*pseudo*-t, $^3J_{HH}$ = 7.7 Hz, 2 H, *m*-H(NPh)], 6.41 [m, 2 H, *o*-H(NPh)], 1.63 (s, 18 H, AlCMe$_3$), 0.92 (s, 9 H, C=CC*Me$_3$*), 0.56 (s, 9 H, C≡CCMe$_3$). **^{13}C NMR** (101 MHz, C$_6$D$_6$, 300 K): *δ* = 169.4 (GeC=*C*), 163.2 (NCO), 142.8 [*ipso*-C(NPh)], 137.9 [*ipso*-C(GePh)], 137.5 (s br., Ge*C*=CH), 135.2 [*o*-C(GePh)], 130.1 [*p*-C(GePh)], 128.6 [*m*-C(GePh) and *o*-C(NPh)], 128.4 [*m*-C(NPh)], 127.2 [*p*-C(NPh)], 108.6 (C≡*C*CMe$_3$), 74.3 (*C*≡CCMe$_3$), 39.8 (C=C*C*Me$_3$), 32.0 (AlC*Me$_3$*), 29.7 (C=CC*Me$_3$*), 29.1 (C≡CC*Me$_3$*) 27.5 (C≡C*C*Me$_3$), 17.1 (br., Al*C*Me$_3$). **IR** (KBr): ṽ = 3071 s, 3053 s, 3028 m, 2972 vs, 2938 vs, 2922 vs, 2905 vs, 2864 vs, 2818 vs, 2750 s, 2718 m, 2689 s ν(CH); 2278 w; 2218 vs ν(C≡C); 1969 w, 1954 w, 1896 vw, 1884 vw, 1830 vw, 1717 sh, 1668 m, 1651 m, 1593 vs, 1553 vs, 1528 vs ν(C=N), phenyl, ν(C=C); 1487 vs, 1460 vs, 1420 vs, 1414 vs, 1408 vs, 1381 vs, 1360 vs, 1308 s, 1287 m, 1258 vs, 1248 sh δ(CH); 1223 vs, 1198 vs, 1088 vs, 1072 w, 1020 m, 999 s, 928 s, 899 s, 887 m, 810 vs, 769 s, 733 vs, 719 s ν(CC), ν(CN); 694 vs, 679 sh (phenyl); 598 vs, 586 sh, 540 s, 513 s, 474 vs, 428 s, 413 vs ν(GeN), ν(GeC), ν(AlO), ν(AlC), δ(CC) cm^{-1}. **MS** (EI, 20 eV, 298 K): *m/z* (%): 594 (100) [M – CMe$_3$]$^+$, 538 (4) [M – CMe$_3$ – butene]$^+$.

Synthesis of Ph$_2$Ge[C≡C*t*Bu][C(=CH*t*Bu)(C(=S)N(Ph)Al*t*Bu$_2$)] (6): PhNCS (133 µL, 0.15 g, 1.11 mmol) was added at room temperature to a solution of compound **3** (0.37 g, 5.50 mmol) in *n*-hexane (15 mL). The mixture was stirred for 16 h. Concentration in vacuo and storage of the solution at -45 °C yielded colorless crystals of compound **6** (0.24 g, 65 %). The product was contaminated with small quantities of impurities (<5 %) which could not be removed by recrystallization and led to unsatisfactory results for microanalysis. M.p. 104 °C (dec.). **^{1}H NMR** (400 MHz, C$_6$D$_6$, 300 K): *δ* = 7.93 [s br., 4 H, *o*-H(GePh)], 7.32 [m, 2 H, *o*-H(NPh)], 7.19 [m overlap, 2 H, *m*-H(NPh)], 7.16 [s br., 4 H, *m*-H(GePh)], 7.10 [m overlap, 2 H, *p*-H(GePh)], 6.95 [tt, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1 Hz, 1 H, *p*-H(NPh)], 6.54 (s, 1 H, C=CH), 1.22 (s, 9 H, C≡CCMe$_3$), 1.17 (s br., 18 H, AlCMe$_3$), 0.99 (s, 9 H, C=CCMe$_3$). **^{13}C NMR** (101 MHz, C$_6$D$_6$, 300 K): *δ* = 204.2 (NCS), 159.4 (GeC=*C*), 144.0 [*ipso*-C(NPh)], 136.8 [br., *ipso*-C(GePh)], 135.7 (br., Ge*C*=CH), 135.3 [*o*-C(GePh)], 129.8 [*p*-C(GePh)], 129.3 [*m*-C(NPh)], 128.6 [*m*-C(GePh)], 126.0 [*p*-C(NPh)], 124.5 [*o*-C(NPh)], 119.4 (C≡*C*CMe$_3$), 78.9 (*C*≡CCMe$_3$), 36.2 (C=C*C*Me$_3$), 30.8 (C≡CC*Me$_3$*), 30.3 (AlC*Me$_3$*), 29.8 (C=CC*Me$_3$*), 28.7 (C≡C*C*Me$_3$), 16.9 (br., Al*C*Me$_3$). **IR** (KBr): ṽ = 3069 s, 3049 m, 3026 m, 2961 vs, 2938 vs, 2920 vs, 2907 vs, 2866 vs, 2830 vs, 2760 m, 2729 w, 2700 m *ν*(CH); 2178 m, 2145 s ν(C≡C); 2112 sh, 2066 w; 1967 vw, 1952 w, 1933 vw, 1896 vw, 1879 w, 1856 vw, 1815 w, 1776 w, 1763 vw, 1721 vw, 1686 vw, 1651 w, 1584 s ν(C=N), phenyl, ν(C=C); 1493 vs, 1462 vs, 1447 sh vs, 1433 vs, 1385 w, 1362 vs, 1331 w, 1308 w, 1252 vs δ(CH); 1233 s, 1204 s, 1173 w, 1155 w, 1119 s, 1090 s, 1028 w, 999 m, 934 m, 918 m, 874 m, 839 m, 810 vs, 750 vs, 735 vs ν(CC); 694 vs, 673 s, 638 s phenyl; 596 s, 546 m, 492 m, 467 s, 417 s, 387 vw ν(GeC), ν(AlO), ν(AlS), ν(AlC), δ(CC) cm^{-1}. **MS** (EI, 20 eV, 413 K): *m/z* (%): 610 (5) $[\mathrm{M - CMe_3}]^+$, 526 (9) $[\mathrm{M - Al}t\mathrm{Bu_2}]^+$, 470 (37) $[\mathrm{M - Al}t\mathrm{Bu_2}$ – butene$]^+$.

Synthesis of $\mathrm{Ph_2Ge[C{\equiv}C}t\mathrm{Bu][C(=CH}t\mathrm{Bu)\{C(NC_6H_4Me)_2(Al}t\mathrm{Bu_2)\}]}$ (7): $\mathrm{[4\text{-}MeC_6H_4N{=}]_2C}$ (0.20 g, 0.90 mmol) was added at room temperature to a solution of compound **3** (0.60 g, 0.89 mmol) in *n*-hexane (10 mL). The mixture was stirred for 16 h and heated for further 16 h to 65 °C. The solvent was removed in vacuo, and the residue recrystallized from pentafluorobenzene (6 mL) at –45 °C to yield colorless crystals of compound **7** (0.35 g, 52 %). The product was contaminated with small quantities of impurities (<5 %) which could not be removed by recrystallization and led to unsatisfactory results for microanalysis. M.p. 217 °C (dec.). **^{1}H NMR** (400 MHz, $\mathrm{C_6D_6}$, 300 K): δ = 7.36 [m, 4 H, *o*-H(GePh)], 7.29 [d, $^3J_{\mathrm{HH}}$ = 8.3 Hz, 4 H, *o*-H(NTol)], 7.09 [m overlap, 4 H, *m*-H(NTol)], 7.07 [m overlap, 4 H, *m*-H(GePh)], 7.06 [m overlap, 2 H, *p*-H(GePh)], 6.80 (s, 1 H, C=CH), 2.21 (s, 6 H, $\mathrm{CH_3}$), 1.32 (s, 9 H, $\mathrm{AlCMe_3}$), 1.24 (s, 9 H, $\mathrm{C{\equiv}CCMe_3}$), 1.08 (s, 9 H, $\mathrm{AlCMe_3}$), 1.05 (s, 9 H, $\mathrm{C{=}CCMe_3}$). **^{13}C NMR** (101 MHz, $\mathrm{C_6D_6}$, 300 K): δ = 176.2 (NCN), 164.4 (GeC=*C*), 141.1 [*ipso*-C(NTol)], 136.8 [*ipso*-C(GePh)], 135.0 [*o*-C(GePh)], 133.0 [*p*-C(NTol)], 129.8 [*m*-C(NTol)], 129.6 [*p*-C(GePh), 128.4 [*m*-C(GePh)], 125.8 [*o*-C(NTol)], 126.0 (Ge*C*=C), 118.7 (C≡*C*CMe$_3$), 80.0 (*C*≡CCMe$_3$), 37.2 (C=*C*CMe$_3$), 30.9 (C≡CC*Me$_3$*), 30.8 and 30.5 (AlC*Me$_3$*), 29.6 (C=CC*Me$_3$*), 28.7 (C≡C*C*Me$_3$), 20.9 (Me), 16.8 and 15.7 (s br., Al*C*Me$_3$). **^{15}N NMR** (41 MHz, $\mathrm{C_6D_6}$, 300 K): δ = 163 (C=N). **IR** (KBr): $\tilde{\nu}$ = 3069 m, 3053 s, 3017 m, 2967 vs, 2938 vs, 2918 vs, 2905 vs, 2862 vs, 2824 vs, 2758 w, 2727 w, 2696 w ν(CH); 2187 m, 2153 m ν(C≡C); 1960 vw, 1886 w, 1827 vw, 1773 vw, 1651 sh, 1634 m, 1591 vs, 1574 m, 1506 vs ν(C=N), phenyl, ν(C=C); 1462 vs, 1412 vs, 1379 sh, 1360 vs, 1319 vs, 1300 s, 1252 vs δ(CH); 1202 s, 1155 w, 1123 w, 1109 w, 1090 s, 1069 vw, 1024 w, 1001 m, 986 w, 937 w, 916 s, 903 m, 847 w, 814 vs, 787 w, 768 w, 737 vs ν(CC), ν(CN); 698 vs, 673 m, 646 w, 610 s (phenyl); 598 sh, 548 m, 513 m, 498 s, 473 s, 459 s, 442 s ν(GeC), ν(AlN), ν(AlC), δ(CC) cm^{-1}. **MS** (EI, 20 eV, 413 K): *m/z* (%): 697 (100) $[\mathrm{M - CMe_3}]^+$, 613 (15) $[\mathrm{M - Al(CMe_3)_2}]^+$, 557 (91) $[\mathrm{M - Al(CMe_3)_2}$ – butene$]^+$.

Synthesis of $[t\mathrm{BuC_6H_4CH_2N_3(Al}t\mathrm{Bu_2)\text{-}]_2}$ (8): A solution of compound **4a** (0.26 g, 0.29 mmol) in *n*-hexane (10 mL) was treated at room temperature with solid 4-$t\mathrm{BuC_6H_4CH_2N_3}$ (0.11 g, 0.58 mmol). The mixture was heated to 65 °C and stirred for 16 h. The solution was concentrated in vacuo and stored at -15 °C to afford colorless crystals of compound **8** (0.13 g, 68 %). Many unknown by-products were formed, which could not be removed completely (<5 %) be removed by repeated recrystallization. Excess azide was identified as one impurity by IR spectroscopy. Microanalysis gave, therefore, insufficient results, and we do not present the data of the IR spectrum. M.p. 95 °C (dec.). **^{1}H NMR** (400 MHz, $\mathrm{C_6D_6}$, 300 K): δ = 7.21 (s, 4 H, *o*-H), 7.20 (s, 4 H, *m*-H), 4.68 (s, 4 H, $\mathrm{NCH_2}$), 1.16 (s, 18 H, 4-$\mathrm{CMe_3}$), 1.05 (s, 36 H, $\mathrm{AlCMe_3}$).**^{13}C NMR** (101 MHz, $\mathrm{C_6D_6}$, 300 K): δ = 152.0 (*p*-C), 133.0 (*ipso*-C), 129.5 (*o*-C), 126.2 (*m*-C), 59.7 ($\mathrm{NCH_2}$), 34.6 (4-*C*Me$_3$), 31.3 (4-C*Me$_3$*), 29.7 (AlC*Me$_3$*), 15.5 (s br., Al*C*Me$_3$). **MS** (EI, 20 eV, 413 K): *m/z* (%): 603 (100) $[\mathrm{M - CMe_3}]^+$.

Synthesis of $\mathrm{PhNC(H)O(Al}t\mathrm{Bu_2)}$: In an NMR experiment PhNCO and H-Al*t*Bu$_2$ were combined in a molar ratio of 1:1. **^{1}H NMR** (400 MHz, $\mathrm{C_6D_6}$, 300 K): δ = 7.68 (s, 1 H, HCO), 7.09 (m, 2 H, *o*-H), 7.01 (m, 2 H, *m*-H), 6.95 (m, 1 H, *p*-H), 1.13 (s, 18 H, $\mathrm{AlCMe_3}$). **^{13}C NMR** (101 MHz, $\mathrm{C_6D_6}$, 300 K): δ = 170.2 ($^1J_{\mathrm{CH}}$ = 196.7 Hz, NCO), 142.6 (*ipso*-C), 125.5 (*o*-C), 127.4 (*p*-C), 129.7 (*m*-C), 30.8 (AlC*Me$_3$*), 15.3 (s br., Al*C*Me$_3$). **^{15}N NMR** (41 MHz, $\mathrm{C_6D_6}$, 300 K): δ = 195.

Synthesis of $\mathrm{PhNC(H)S(Al}t\mathrm{Bu_2)}$: PhNCS (0.53 g, 3.93 mmol) was added at 0 °C by a syringe to a solution of H-Al*t*Bu$_2$ (0.51 g, 3.59 mmol) in *n*-hexane (20 mL). The mixture was stirred at room temperature overnight, the solvent was removed in vacuo and the residue recrystallized from *n*-pentane (10 mL) to yield colorless crystals of $\mathrm{PhNC(H)S(Al}t\mathrm{Bu_2)}$ (0.69 g, 69 %). **^{1}H NMR** (400 MHz, $\mathrm{C_6D_6}$, 300 K): δ = 8.58 (s, 1 H, CHS), 6.91 (m, 2 H, *m*-H), 6.85 (m, 1 H, *p*-H), 6.66 (d, $^2J_{\mathrm{HH}}$ = 7.7 Hz, 2 H, *o*-H), 1.24 (s, 18 H, $\mathrm{AlCMe_3}$). **^{13}C NMR** (101 MHz, $\mathrm{C_6D_6}$, 300 K): δ = 185.4 ($^1J_{\mathrm{CH}}$ = 181.0 Hz, CHS), 143.2 (*ipso*-C), 129.9 (*m*-C), 127.1 (*p*-C), 119.6 (*o*-C), 29.8 (AlC*Me$_3$*), 16.8 (s br., Al*C*Me$_3$). **MS** (EI, 20 eV, 353 K): *m/z* = 417 (21) [M(dimer) – Ph-N-C(H)-S – H]$^+$, 137 (100) [Ph-N-C(H)-SH]$^+$, 136 (75) [Ph-NC(H)-S]$^+$.

X-ray Crystallography: Crystals suitable for X-ray crystallography were obtained by recrystallization from *n*-hexane at room temperature (**2a**, **2b**) or –45 °C (**5**, **6**, **8**), 1,2-difluorobenzene (–30 °C, **3**) or pentafluorobenzene (–20 °C: **4a**; –45 °C: **4b** and **7**). Intensity data was collected with Bruker Venture or Bruker Quazar (**6**) diffractometers with multilayer optics and Mo-K_α radiation. Data reduction was carried out using the program SAINT+.[40] The crystal structures were solved by direct methods using SHELXTL.[41] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on F^2 using SHELXTL.[41] The hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. The molecule of **2a** was located on an inversion center. Compound **2b** crystallized with two molecules in the asymmetric unit, two *t*Bu groups (molecule 1) and a central Ge–Ge unit (molecule 2) were disordered and refined on split positions [0.67:0.33 (C43); 0.73:0.27 (C63); 0.95:0.05 (Ge3–Ge4)]. Compound **3** crystallized with half a molecule of 1,2-difluorobenzene per formula unit, which was disordered over an inversion center. The structure of **4b** contained a disordered Ge–Ge bond (0.94:0.06). The *t*Bu groups of the vinyl and alkynyl substituents of compound **6** were rotationally disordered and refined on split positions [0.83:0.17 (C33); 0.71:0.29 (C43)]. The molecules of **8** reside on a center of symmetry.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1836910 (**2a**), CCDC-1836911 (**2b**), CCDC-1836912 (**3**), CCDC-1836913 (**4a**), CCDC-1836914 (**4b**), CCDC-1836915 (**5**), CCDC-1836916 (**6**), CCDC-1836917 (**7**), and CCDC-1836918 (**8**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

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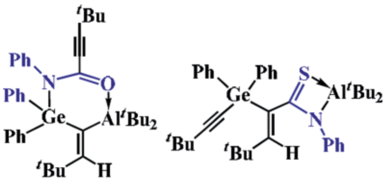
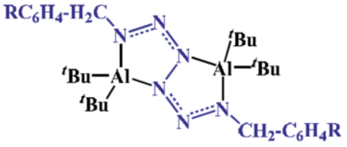
Hydroalumination of Oligoalkynylgermanes and -digermanes – Reactions with Heterocumulenes by Al–C or Ge–C Bond Activation and Formation of a Hexazenedialuminum Complex



Ge-C vs. Al-C Insertion



Ge-Ge Bond as a Reductant