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Functionalized Alkynyl-chlorogermanes: Hydrometallation, Ge-Cl Bond Activation, Ge-H Bond Formation and Chlorine*tert*-Butyl Exchange *via* a Transient Germyl Cation[†]

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Treatment of alkynyl-arylchlorogermanes $\operatorname{Aryl_nGe}(\operatorname{Cl})(\operatorname{C}=\operatorname{C-}^t\operatorname{Bu})_{3-n}$ (n = 1, 2) with $\operatorname{HM}^t\operatorname{Bu_2}(M = \operatorname{Al}, \operatorname{Ga})$ yielded mixed Al or Ga alkenyl-alkynylchlorogermanes *via* hydrometallation reactions. Intramolecular interactions between the Lewis-basic Cl atoms and the Lewis-acidic Al or Ga atoms afforded MCGeCl heterocycles. The endocyclic M-Cl distances were significantly lengthened compared to the starting compounds and indicated Ge-Cl bond activation. Dual hydrometallation succeeded only with HGa'Bu₂. One Ga atom of the product was involved in a Ga-Cl bond, while the second one had an

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interaction to a C-H bond of a phenyl group. In two cases treatment of chlorogermanes with two equivalents of HAl^{*t*}Bu₂ resulted in hydroalumination of one alkynyl group and formation of unprecedented Ge-H functionalized germanes, Aryl-Ge(H)(C=C-^{*t*}Bu[C(Al^{*t*}Bu₂)=C(H)-^{*t*}Bu] (Aryl = mesityl, triisopropylphenyl). The Al atoms of these compounds interacted with the α -C atoms of the alkynyl groups. Ph(Cl)Ge(C=C-^{*t*}Bu)[C(Al^{*t*}Bu₂}=C(H)-^{*t*}Bu] reacted in an unusual Cl/^{*t*}Bu exchange to yield the *tert*butylgermane Ph(^{*t*}Bu)Ge(C=C-^{*t*}Bu)[C{Al(^{*t*}Bu)(Cl)}=C(H)-^{*t*}Bu]. Quantum chemical calculations suggested the formation of a germyl cation as a transient intermediate.

Introduction

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Hydroalumination and hydrogallation of donor functionalized alkynylsilanes and – germanes afford unique compounds, in which intramolecular interactions between the Lewis-acidic and –basic constituents result in an activation of the bonds between the Group 14 elements and the donor groups. These compounds are active Lewis pairs that after cleavage of the M-donor bonds (M = Al, Ga) are able to activate or coordinate molecules and show a reactivity comparable to that of frustrated Lewis pairs.¹ Treatment of a pyrrolidyl-trialkynylsilane, for instance, with equimolar quantities of HAl'Bu₂ or HGa'Bu₂ yielded alkenyl-dialkynylsilanes with the Al or Ga atoms geminal to silicon (**A**, Chart 1).² Strong intramolecular M-NR₂ interactions afforded four-membered Si-CAlN heterocycles with a significantly lengthened Si-N bond. Similar compounds were obtained by hydrometallation of diethylamino-ethynylgermanes (**B**).³ The activation and

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weakening of the Si-N and Ge-N bonds was confirmed by decreased Wiberg bond indices.³ A germane reacted as an active Lewis pair which after cleavage of the endocyclic Ga-N bond activated the C-H bond of a terminal alkyne and initiated an alkynyl-amine exchange with the release of diethylamine.³ Phenyl isocyanate was inserted into an activated Ge-N bond at room temperature, while isothiocyanates required more drastic reaction conditions.³ Dual hydrometallation afforded dialuminium and digallium compounds which have been applied as chelating Lewis acids for the effective coordination of donors.⁴ Addition of chloride anions to a diethylaminodialuminium germane resulted in the unique elimination of an imine, Me-C(H)=N-Et, by formation of a Ge-H bond.⁵ The remaining GeAl₂ compound coordinated the chloride anion in a chelating manner (C). Quantum-chemical calculations suggested an unprecedented mechanism, in which imine formation under unexpectedly mild conditions is favoured by the intermediate generation of a germyl cation.⁵ Cl atoms as donor substituents have been applied in a single case. Hydrometallation of a chloro-triethynylsilane⁶ gave Si/M compounds which had strong M-Cl bonding interactions and lengthened Si-Cl bonds. Dual hydrogallation yielded the expected digalliumsilane in which one Ga atom was coordinated to the Cl atom, while the other showed an interaction to the α -C atom of the remaining alkynyl group. Dual hydroalumination led to a remarkable Cl/[/]Bu exchange with a ¹Bu group migrating from Al to Si and the Cl atom from Si to Al (formal 1,3-dyotropic rearrangement, \mathbf{D}).⁶ According to quantum chemical calculations this exchange is initiated by an interaction of the Cl atom with Al and proceeds via a silvl cation, a revised version of the unprecedented mechanism is included in this article. These examples clearly demonstrate that hydrometallated and donor functionalized alkynylsilanes and -germanes form a fascinating new class of compounds which enable secondary reactions as active Lewis

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pairs or show interesting intramolecular transformations. In this article we report on the synthesis of the first chlorine functionalized alkynylgermanes and present some preliminary aspects of their reactivity.



Chart 1. Compounds obtained from functionalized silanes and germanes

Results and Discussion

Synthesis of chlorine functionalized alkynylgermanes

The aryl-substituted alkynyl(chloro)germanes **1a** to **1d** were readily obtained in moderate (Ar = Mes, Trip) to high yields (Ar = Ph) by lithiation of H-C=C-^{*t*}Bu with ^{*n*}BuLi and reaction of the *in-situ* generated alkynide with Ar_{*n*}GeCl_{4-*n*} (Scheme 1). The commercially not available precursors MesGeCl₃⁷ and TripGeCl₃⁸ were synthesized on new routes from Mes₂Mg or Trip₂Mg and an excess of GeCl₄. The alkynyl C atoms of **1a** to **1d** showed ¹³C NMR resonances in the expected ranges of δ = 75.7 to 80.6 (Ge-C=C) and

115.9 to 120.1 (Ge-C=C). The differences between the shifts of both C atoms are larger $(\Delta \delta = 43.4)$ for the phenyl derivatives (1a, 1b) as compared to the sterically better shielded mesityl or triisopropylphenyl compounds 1c and 1d ($\Delta \delta = 35.9$). Such differences have been correlated to the charge distribution in the alkynyl groups and the chemical reactivity.^{4a,9} Two absorptions of the C=C stretching vibrations were observed in the IR spectra in narrow ranges at 2185 and 2155 cm⁻¹.

 $Ar_nGeCl_{4-n} \xrightarrow{+ x \text{ LiC}=C^{-t}Bu} Ar_n(Cl)Ge(C=C^{-t}Bu)_{3-n}$ Ar = Ph, n = 2 Ar = Ph, n = 1 Ar = Mes, n = 1 Ar = Mes, n = 1 Ar = Trip, n = 1 Ie: Ar = Mes, n = 1 Ie: Ar = Mes, n = 1 Ie: Ar = Trip, n = 1

Scheme 1. Syntheses of chlorine functionalized alkynylgermanes [x = 3-n; Mes = 2,4,6-Me₃C₆H₂; Trip = 2,4,6-(Me₂CH)₃C₆H₂].



Figure 1. Molecular structure and atomic numbering scheme of compound 1a (com-

pounds **1b** and **1c** are similar). Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms have been omitted for clarity. X-Ray crystal structure determinations of **1a** to **1c** (Fig. 1) revealed the distorted tetrahedral coordination of the Ge atoms, and C=C triple bond lengths in the normal range (119.4 pm on average). The Ge-Cl distances correspond to standard values of terminal Ge-Cl groups¹⁰ [215.9(5) to 220.8(1) pm; Table 1]. The Ge-C distances depend on the hybridization of the C atoms. The shortest bonds were accordingly observed to the alkynyl groups [188.1(2) to 189.3(4) Å *vs.* 192.1(1) to 195.0(4) Å].

Hydrometallation and activation of Ge-Cl bonds

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Treatment of the alkynylgermanes **1a** to **1d** with one equivalent of dialkylaluminum or –gallium hydrides, HM'Bu₂ (M = Al, Ga), at -78 °C and stirring for 3 to 16 h at room temperature yielded the *cis*-hydrometallation products **2** (*cis* refers to the relative orientation of Al or Ga to H in the resulting alkenyl groups).¹¹ Concentration and cooling of the mixtures or recrystallization of the crude products from 1,2-difluorobenzene afforded colourless solids in yields of 55 (**2c**) to 91% (**2e**) (Scheme 2). The reactions were highly regioselective with respect to the addition of the electropositive metal atoms to the C atoms bound to Ge. These C atoms carry a relatively high negative partial charge due to the electronegativity difference between Ge and the sp-hybridized C atoms. The Cl atoms coordinate with a lone pair of electrons to the metal atoms hereby forming four-membered GeCMCl heterocycles (see below, Fig. 2). In the absence of Lewis basic substituents such as Cl or NR₂ the alkynyl groups were also found to interact with the

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Lewis acidic metal atoms.^{9,12,13} This was typically associated with a shift of the stretching vibrations $v_{C=C}$ in the IR spectrum to lower wave numbers (by about 50 cm⁻¹) and a comparably large difference $\Delta\delta$ between the ¹³C NMR signals of the ethynyl C atoms. The essentially identical values of $v_{C=C}$ in the IR spectra (2180 and 2150 cm⁻¹) and the almost unchanged $\Delta\delta$ values (35 to 45 ppm) in the ¹³C NMR spectra of the free alkynes 1 and the hydrometallation products 2 confirm the absence of interactions between the respective C and metal atoms in compounds 2b to 2e. There was no evidence for an isomerization of the kinetically favored cis-hydrometallation products into the thermodynamically favored *trans*-isomers.¹¹ This isomerisation was previously found to proceed *via* an intermolecular activation step in which the alkenvl functionality adopts a bridging position between two metal atoms. Compounds 2 show characteristic signals at $\delta = 6.7$ to 7.1 for the vinylic H atoms in the ¹H NMR and at around $\delta = 145$ (Ge-C=C) and 165 (Ge-C=C) for the vinylic C atoms in the 13 C NMR spectra. The *tert*-butyl groups bound to Al or Ga are diastereotopic for 2b to 2e and give two different sets of signals as a consequence of the chiral coordination of the Ge atom. Equilibration by fast rotation about the M-C(vinyl) bond is prevented by the intramolecular M-Cl interaction.



Scheme 2. Hydrometallation of alkynylgermanes; if not stated otherwise $R^2 = -C \equiv C$ -^{*i*}Bu.

A representative example (2a) of the structures of the hydrometallation products 2 is shown in Fig. 2, selected bond lengths of 2a to 2e are summarized in Table 1. Compounds **2b** to **2e** feature a chiral coordination sphere at the Ge atoms and crystallize as racemic mixtures in centrosymmetric space groups $(P\overline{1}, P2_1/c)$. Strong intramolecular interactions of the Cl atoms bound to Ge with the Al or Ga atoms result in the formation of unprecedented almost planar four-membered MCGeCl heterocycles (largest deviation from the idealized plane through the four atoms is <8 pm for C; c.f. Table 1). This interaction leads to a significant increase of the Ge-Cl distances from about 218 pm in compounds 1 to 232.85(3) to 237.89(5) pm in the hydrometallation products 2 (the longest distance is observed for the sterically most shielded triisopropylphenyl derivative 2d). The shorter Ge-Cl distance of 227.34(3) pm in the Ga compound 2e reflects the relatively weak acceptor strength of Ga compared to Al atoms. The associated Al-Cl and Ga-Cl distances of 241.50(6) (2a) and 243.58(7) (2d) pm and 263.01(4) pm (2e; M = Ga), respectively, are on the longer side of bond lengths observed for typical metal-halogen bridges.^{4,14} The increase in Ge-Cl bond lengths is associated with a distortion of the tetrahedral coordination sphere of the Ge atom. Krossing *et al.* used the sum of angles at a Si atom to the directly bonded C atoms (Σ anglesSiC₂) as an indicator for the charge separation between Si and F.¹⁵ The sum of angles was correlated with the bond classification following the sequence 329° (covalent) $< 345 - 354^{\circ}$ (significant ionic character) $< 360^{\circ}$ (ionic). According to this classification compounds 2 all show a significant ionic character of the activated Ge-Cl bonds (Σ anglesGeC₂ = 353 to 356°). The heterocycles may be described as irregular rectangles resembling a kite with endocyclic angles that are obtuse at the C atom [103.35(7) (2a) to $106.19(6)^{\circ} (2e)]$, almost ideally 90° at Ge $[93.37(4)^{\circ}$ in **2e**], acute at Cl (*ca.* 80°) and Al (*ca.* 85°); a slightly smaller endocyclic

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angle [81.30(4)°] resulted at the Ga atom of **2e**. Ge-C distances increase from Ge-C=C to Ge-C=CH and Ge-C(Ar) in intervals of about 4 and 1 pm. Compound **2a** forms loosely bonded dimers in the solid state *via* an interaction between a Cl atom of one molecule and an *o*-H atom of a second molecule (Cl···H16 288 pm, Cl···C16 383 pm, angle Cl-H-C 175°).



Figure 2. Molecular structure and atomic numbering scheme of compound **2a** (compounds **2b** to **2e** are similar). Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H32, arbitrary radius) have been omitted for clarity.

It was shown in previous experiments that dual hydrometallation of Si or Ge centered bis- and trisalkynes $R_2E(C=CR')_2$ and $RE(C=C-R')_3$ (R = alkyl, aryl; E = Si, Ge) affords silanes and germanes that carry two Lewis acidic metal functionalities in a molecule and are able to coordinate Lewis bases such as Cl⁻ anions in a chelating manner.⁴ It was therefore hoped that double hydrometallation of compounds 1 may lead to a further weakening and activation or even a complete cleavage of the Ge-Cl bond.

Reaction of **1b** with two equivalents of HAl^{*t*}Bu₂ produced an inseparable mixture of compounds. HGa^{*t*}Bu₂ in contrast afforded after prolonged stirring (48 h) the bishydro-

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gallation product **3** in 74% yield (Scheme 3). The analogous reaction of **1d** yielded an unidentifiable mixture, while H-Cl exchange was observed upon treatment of 1c with two equivalents of HAl^tBu₂ (see below, Scheme 4). The ¹H NMR spectrum of the Ga_2Ge compound **3** at room temperature was deceptively simple. It showed two broad singlets of different ^tBu groups of the Ga^tBu₂ substituents and only one signal for the vinylic H atom and the 'Bu group of the C=CH-'Bu moieties. This is consistent with a dynamic behaviour of **3** in solution, and each of the $Ga^{t}Bu_{2}$ units may alternately coordinate in a fast exchange process to the Cl atom (c.f. solid state structure, Fig. 3). Variable temperature NMR studies demonstrated that at 190 K the structure in solution resembles that in the solid state as indicated by the magnetic inequivalence of all six ^tBu groups and the two vinylic H atoms as well as a broadening of the resonance of the o-H atoms. This is consistent with one Ga atom being coordinated to the Cl atom and the second interacting with an o-C atom of the phenyl group, which in turn results in a hindered rotation of the phenyl substituent about the Ge-C bond. The energy for the exchange process was estimated to $\Delta G^{\neq} = 44 \text{ kJ/mol based on a coalescence temperature}$ of 210 K.



Scheme 3. Dual hydrogallation of 1b and formation of 3.

One half of the molecular structure of **3** (Fig. 3) is strongly related to that of the mono-hydrometallation product **2e**. A four-membered GeCGaCl heterocycle is formed by an interaction of the Cl with one of the Ga atoms. The Ga2-Cl1 distance [265.08(8)

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pm, Table 1] is in the longer range of typical M-CI-Ga bridges,¹⁴ and the Ge(1)-Cl(1) bond [229.60(8) pm] is significantly lengthened compared to the starting compound **1b** [215.93(5) pm]. Hydrogallation of the second alkynyl group resulted in the formation of a divinyl compound with two Ga atoms in a single molecule. The second Ga atom is not bonded to the Cl atom (Ga1…Cl1 441 pm), instead there is a relatively short contact (Ga1…C32 281 pm; Ga1…H32 240 pm]) to an *o*-C-H bond of the phenyl group resulting in a pyramidalization of the Ga atom (Ga1…C₃-plane 29 pm). Such weak aluminum- or gallium-phenyl interactions have also been observed in the related compound Ph(Et₂N)Ge[C(Al'Bu₂)=CH-^tBu]₂³ (Al…*o*-C distance 260 pm) which shows a fascinating chemical behavior (see Introduction). The longer M…C distance in **3** reflects the weaker Lewis-acidity of the Ga atoms.



Figure 3. Molecular structure and atomic numbering scheme of compound **3**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H12 and H22, arbitrary radius) have been omitted for clarity.

Generation of Ge-H bonds by chlorine-hydrogen transfer

In attempts to obtain double hydroaluminated compounds analogous to **3** (Scheme 3) we treated the dialkynylgermane **1c** with two equivalents and the monohydroaluminated species **2d** with equimolar quantities of HAl^{*t*}Bu₂ (Scheme 4). However, instead of the doubly reduced divinyl compounds we obtained Ge-H functionalized germanes. $ClAl^{t-}$ Bu₂¹⁶ was identified as a by-product by its characteristic NMR data.



Scheme 4. Hydroalumination of compounds 1c and 2d and Cl-H exchange.

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¹H NMR spectra of the reaction mixtures after 90 min at room temperature showed only the signals of ClAl'Bu₂ and the germanes **4**. Removal of ClAl'Bu₂ by sublimation in vacuum afforded residues which were recrystallized from 1,2-difluorobenzene to yield **4a** and **4b** in almost quantitative yields. The Ge-H bonds of compounds **4a** and **4b** were identified by characteristic strong absorptions in the IR spectra (ν GeH = 2066 and 2058 cm⁻¹)¹⁷ and by resonances in the ¹H NMR spectra at δ = 6.5. Two absorptions in the IR spectra with comparatively low wave numbers of about 2150 and 2107 cm⁻¹ for the stretching vibrations of the C=C bonds (compare 2180 and 2150 cm⁻¹ for **2b** to **2e**) and increased $\Delta\delta$ values of 51.1 and 59.0 ppm between the resonances of the ethynyl C atoms in the ¹³C NMR spectra (35 to 45 ppm for **2b** to **2e**; see above) were indicative of

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an interaction between the α -C atom of the C=C triple bond (bearing a relatively high negative partial charge) and the Lewis acidic Al atom.^{12,13} The observed H-Cl exchange (Scheme 4) by treatment with an aluminum hydride is well documented in the literature, and LiAlH₄ or related hydrides have been used for the generation of Ge-H bonds from the respective halogen precursors.¹⁸ The selective hydroalumination of the first alkynyl group verifies that the reduction of the C=C triple bond is actually the preferred reaction. Steric shielding may hinder the second hydoalumination step and favor H-Cl exchange. The different reactivity of HGa'Bu₂ and HAl'Bu₂ may result from the higher polarity of the Al-H compared to the Ga-H bond.

The molecular structure of **4b** (Fig. 4) revealed a distorted tetrahedral coordination sphere for the Ge atom with four different substituents: an H atom, alkynyl, aryl and alkenyl groups (sum of the angles C-Ge-C = 327.4°; H-Ge-C with C21 and C31: 348.1°; Table 1). The most interesting feature is the intramolecular contact of the α -C atom of the alkynyl group to the Al atom which has been predicted by spectroscopic observations. The Al1…C11 distance is with 250.8(2) pm comparable to related monomeric species such as Me₂(PhC=C)Ge[(Al'Bu₂)=C(H)-Ph] or Ph₂(PhC=C)Ge[(Al'Bu₂)=C(H)-Ph] (240 to 255 pm).^{5,12,13} These interactions result in an activation of the Ge-C(alkynyl) bonds and selective rearrangement reactions with the formation of germacyclobutenes in the melt.⁹ Caused by this Al…C interaction the Ge-C(alkynyl) bond of **4b** [197.0(2) pm] is lengthened by about 10 pm compared to compounds **2b** to **2e** which have exclusively terminal alkynyl groups. Further indicative for this interaction are the formation of an almost planar AlC₂Ge heterocycle (torsion angle Al1-C31-Ge1-C11 = 15.9°), an acute angle C11-Ge1-C31 of 93.98(7)° and the large deviation of the Al atom (37.2 pm) from the plane of the directly bonded C atoms (C31, C41, C51). The C=C bond length is almost unaffected [C11-C12 120.9(3) pm; 119.4 pm on average in **2b** to **2e**], and the Ge-C=C group deviates only slightly from linearity $[172.4(2)^{\circ}]$. The Ge-H bond length $[142(2) \text{ pm}]^{19}$ and other molecular parameters are unexceptional.



Fig. 4. Molecular structure and atomic numbering scheme of compound 4. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H1 and H32, arbitrary radius) have been omitted for clarity.

Intramolecular chlorine-tert-butyl exchange

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Heating compound **2b** for 2 d at 50 °C resulted in its conversion to compound **5** by transfer of the bridging Cl atom from Ge to Al (Scheme 5) and a simultaneous ^{*t*}Bu migration from Al to Ge (1,3-dyotropic rearrangement⁶). The related gallium compound **2e** showed under similar conditions no reactivity and was recovered almost quantitatively. Compared to the ¹H NMR spectrum of **2b** there is a small shift for the relevant signals of the ^{*t*}Bu groups from $\delta = 1.36$ and 1.44 (Al^{*t*}Bu)₂ to 1.38 and 1.39 (Al^{*t*}Bu, Ge^{*t*}Bu), respectively, and the C=CH signal is shifted from $\delta = 7.00$ to 7.33. The most significant

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change is found in the ¹³C NMR spectrum for the C_β atom of the alkynyl substituent which is shifted from $\delta = 122.9$ in **2b** to $\delta = 140.7$ in **5**. With only a small change in the chemical shift for the corresponding C_a atom ($\delta = 78.0$ vs. 84.1) the difference $\Delta \delta_{CC}$ increases from 44.9 to 56.6. Large differences $\Delta \delta_{CC}$ are indicative of an interaction between the Lewis acidic Al atom and the alkynyl group (see above).^{12,13} The observed value therefore suggests that in contrast to the solid state (see below) compound **5** may be monomeric in solution with an Al-alkynyl interaction similar to **4a** and **4b**.



Scheme 5. Thermal rearrangement of compound 2b

The molecular structure of **5** in the solid state consists of a centrosymmetric dimer (Fig. 5) with a central Al₂Cl₂ heterocycle. It verifies the remarkable Cl/^tBu exchange with the Cl atom bonded to Al and a ^tBu group attached to Ge. The Ge atom has a chiral coordination sphere and is bonded to four C atoms of four different substituents. The Al-Cl distances are in the normal range of typical Al-Cl-Al bridges,¹⁴ but they differ considerably [227.41(7) and 236.80(6) pm] and reflect an unsymmetric bonding situation. The distance between Al and the α -C atom of the alkynyl group (Al1…C11) is

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with 309 pm too long for a strong intramolecular Al \cdots C=C bonding interaction, but it is shorter than the sum of the van der Waals radii (354 pm¹⁹). The molecular conformation seems to support a weak interaction between these atoms. The dimeric molecules are perfectly preorganized to facilitate monomerisation. The Ge-C(alkynyl) and AlC(vinyl) bonds are parallel to each other as evident from the small All-C31-Ge1-C11 torsion angle (1.6°). The α -C atom of the alkynyl group approaches the Al atom from the opposite side of the longer endocyclic Al-Cl bond (angle C11...Al1-Cl1' 157.9°) which results in a surprisingly large C31-Al1-C51 angle of 125.01(8). The coordination sphere of the Al atom may be described by a distorted trigonal bipyramide with the atoms C31, C51 and C11 in the equatorial plane (deviation of the Al atom from that plane 31 pm). One axial position is occupied by Cl1', the other by the alkynyl C atom Cl1 with a weak Al...C interaction. Dissociation may be supported by gradual strengthening of the Al…C interaction and concomitant weakening of the Al1-Cl1' bond, and in solution a situation similar to 4a and 4b with an intramolecular Al-alkynyl interaction may help to stabilize the monomeric formula units. This may be interpreted in terms of a small preference of the Al…Cl over the Al…C(alkynyl) interaction in the solid state.

A similar Cl/⁴Bu exchange has previously been observed for an Al₂Si compound.⁶ In contrast to the rearrangement of the GeAl compound **2b** (Scheme 5) it proceeded under mild conditions (room temperature) and much faster (<2 h). A revised version of the calculated mechanism is shown below. Chelating coordination of the Cl atom by both Al atoms and the intermediate formation of a silyl cation are the key steps to facilitate this reaction. A higher reaction temperature and a longer reaction time is required for the formation of the monoaluminium compound **5**. A conceivable reaction mechanism is discussed below.



Figure 5. Molecular structure and atomic numbering scheme of compound **5**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H32, arbitrary radius) have been omitted for clarity. Equivalent atoms are generated by -x, -y, -z.

Quantum-chemical calculations on the rearrangement mechanisms

To understand the mechanism of the Cl/⁴Bu exchange of the GeAl compound **2b**, stateof-the-art dispersion-corrected DFT calculations were performed at the PW6B95-D3/def2-QZVP//TPSS-D3/def2-TZVP + COSMO-RS(toluene) level of theory (simply PW6B95 later on). Scheme 6 summarizes the most feasible free energy path, while detailed energies and geometries of various intermediates and transition structures are included in the Supporting Information (SI).



Scheme 6. The PW6B95-D3 predicted free energy path (in kcal/mol; $R = {}^{t}Bu$) for the thermal Cl/^tBu exchange of the Ge/Al compound **2b**.

As shown in Scheme 6, heterolytic cleavage of the Ge-Cl bond of **2b** and rotation about an Al-C bond leads to the zwitterionic intermediate **a** in an endergonic step (20.0 kcal/mol). The acyclic intermediate **a** contains an anionic alanate moiety with Cl bonded to Al and a nearly planar coordinated cationic Ge atom,²⁰ the latter being stabilized by loose Ge…H interactions (209.7 pm) with an Al bound 'Bu group. From the metastable intermediate **a**, a 'Bu shift from the alanate part to the cationic Ge atom requires a free energy barrier of only 7.9 kcal/mol, leading to the less polar molecule **b** in an exergonic step [-9.3 kcal/mol]. Molecule **b** contains two neutral centers with Ge and Al bonded to the respective 'Bu and Cl groups and the Lewis-acidic Al atom being stabilized by weak Al…H interactions (209.2 pm to the Ge-'Bu group). Intramolecular rotation about the Ge-C(alkenyl) bond of the acyclic molecule **b** affords the final product **5**

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(monomeric in solution), which is further stabilized by 9.4 kcal/mol *via* an A1····alkynyl interaction. The dimeric form (5)₂ is formed *via* two stronger Al-Cl-Al bridges. It is however 2.9 kcal/mol higher in free energy in solution than two monomeric formula units of 5 mainly due to unfavorable entropy ($T \cdot \Delta S = 19.5$ kcal/mol) and solvation effects (3.8 kcal/mol). The overall Cl/^tBu exchange reaction involving the zwitterionic molecule **a** as key intermediate is thus exergonic by 18.7 kcal/mol with a moderate free energy barrier of 27.9 kcal/mol which is consistent with the observed experimental conditions (heating for 2 d at 50 °C).

A similar Cl/⁴Bu exchange has previously been reported for an Al₂Si compound (labeled **E** in Scheme 7). The reaction occurred under surprisingly mild conditions (below 2 h at room temperature) although a stronger Si-Cl instead of a Ge-Cl bond is involved.⁶ Based on early DFT calculations, a zwitterionic mechanism similar to that in Scheme 6 was proposed for the Cl/⁴Bu exchange between one Si and one (rather than two) Al atom, which however encounters a unreasonably high potential barrier of 37.7 kcal/mol that is almost insurmountable under ambient conditions.⁶ The predicted ~10 kcal/mol higher barrier for the Cl/⁴Bu exchange involving a single Al atom is consistent with the stronger Si-Cl compared to a Ge-Cl bond. This strongly suggested that the additional Lewis-acidic Al atom in the Al₂Si compound **E** could act in a cooperative way to reduce the Cl/⁴Bu exchange activation barrier, as corroborated by the revised mechanism based on new DFT calculations (Scheme 7).

As shown in Scheme 7, rotation about the Si-C bond over low free energy barrier led to the cleavage of the Al \cdots alkynyl interaction in compound **E** and the formation of molecule **F** with the Cl atom coordinated by both Al atoms in a chelating manner. The chelating coordination of the Cl atom helps to facilitate the heterolytic cleavage of the

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Si-Cl bond, to generate a silyl cation²⁰ and to stabilize the Cl⁻ anion within the key transition structure **TSFG**. As a result, the free energy barrier required for the ^{*t*}Bu shift from Al to the cationic Si atom is significantly reduced from 39.2 kcal/mol (*via* **TSFG'**, see SI) to 29.4 kcal/mol for the respective cases involving one or two Al atoms. After the Cl/^{*t*}Bu exchange, rotation about two Si-C bonds results in cleavage of the Al-Cl-Al bridge with one of the Al atoms being stabilized by a newly formed Al⁺⁺alkynyl interaction in the final products **H** and **D**. Consistent with experimental NMR data,⁶ our DFT calculations suggest that the isomer **D** (Chart 1) is about 1.9 kcal/mol lower in free energy (compared with 0.9 kcal/mol derived from the **H** : **D** ratio of 18 : 82 in the NMR spectra⁶) with a very low inter-conversion barrier to the isomer **H**. The overall Cl/⁴Bu exchange with one Si and two Al atoms interacting in a cooperative way is exergonic by 16.8 kcal/mol over a moderate free energy barrier of 29.4 kcal/mol, which is comparable with that calculated for the Cl/⁴Bu exchange of the Ge/Al compound **2b**. The similar barriers underscore the efficiency of the chelating coordination of the Cl atom in **F** which facilitates Si-Cl bond cleavage despite the relatively high Si-Cl bond energy.

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Scheme 7. The TPSS-D3 predicted free energy path (in kcal/mol; $R = {}^{t}Bu$) for the rearrangement of the chlorine functionalized Al₂Si compound **E**.

Conclusion

The new functionalized chlorogermanes $ArylGe(Cl)(C=C-^{I}Bu)_{2}$ (**1a** to **1d**; Aryl = Ph, Mes, Trip) are valuable starting materials for a variety of secondary reactions, but this article is focused on hydrometallation as an important aspect of their chemical behaviour. Treatment with equimolar quantities of HAl'Bu₂ or HGa'Bu₂ afforded by reduction of one C=C bond selectively alkenylgermanes (**2a** to **2e**) in which the Ge and Al/Ga atoms (M) adopted geminal positions at the resulting vinyl groups. Intramolecular Al-Cl or Ga-Cl interactions resulted in the formation of MCGeCl heterocycles and compared to the starting compounds significantly lengthened Ge-Cl bonds. A similar lengthening of Si/Ge-N bonds has been observed previously for corresponding amino functionalized silanes and germanes.^{2,3} It correlates to a decrease of the calculated Wiberg bond indices and an increased reactivity with the facile insertion of heterocumulenes.³ A similar behaviour is expected for the Cl-Ge compounds **2a** to **2e** reported in this article with the formation of interesting halogenated species of suitable substrates.

Dual hydrometallation of the Cl functionalized compounds was successful only on one occasion (**3**) with HGa^{*t*}Bu₂ as the reductant. HAl^{*t*}Bu₂ led to Cl-H exchange and the formation of Ge-H functionalized compounds, ArylGe(H)(C=C-^{*t*}Bu)[C(Al^{*t*}Bu₂)=C(H)-^{*t*}Bu] (**4a**, **4b**). Hydroalumination of the first triple bond seems to be favoured in these

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reactions, while steric shielding may facilitate Cl-H exchange. The germanes 4 show an intramolecular interaction between the Lewis acidic Al and the α -C atoms of the intact alkynyl groups which has been recognized as an essential step in bond activation and cyclisation reactions.⁹ An interesting challenge for future investigations is the observation of an interaction of the Al atom to the Ge bound H atom. However, the polarity of the Ge-H bond and the charge at H seem to be too low to favour such a unique structural motif in competition to any other donor. The presence of the Lewis acidic Al atom in the same molecule may help to facilitate insertion reactions into the Ge-H bond.

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Thermally initiated rearrangement of **2b** with Cl/^{*t*}Bu exchange afforded the compound Ph(^{*t*}Bu)Ge(C=C-^{*t*}Bu)[C{Al(^{*t*}Bu)(Cl)}=C(H)-^{*t*}Bu] (**5**) in which the Cl atom is bonded to Al and a ^{*t*}Bu group is attached to Ge. This process formally corresponds to a 1,3dyotropic rearrangement.^{6,21} Quantum chemical calculations corroborate a unique reaction mechanism in which a germyl cation is formed as a reactive intermediate. A revised mechanism for a similar rearrangement with an Al₂Si compound confirmed the formation of a silyl cation and the activation of the Si-Cl bond by the chelating coordination of the Cl atom by two Lewis acids. The higher Si-Cl bond energy compared to Ge-Cl is compensated by this specific interaction. **5** is dimeric in the solid state *via* Al-Cl-Al bridges. Results of spectroscopic investigations verify its dissociation to yield the monomeric fragments in solution in which the remaining alkynyl group interacts with the Al atom similar to the molecular structures of **4a** and **4b**.

These silanes and germanes functionalized by Al or Ga atoms and donor substituents are accessible on facile routes and are highly promising materials as active Lewis pairs in the coordination, activation and insertion of substrates,³ for intramolecular rearrangement reactions,⁵ for the formation of sila- and germacyclobutenes^{9a} or the genera-

tion of silyl and germyl cations²⁰ by a complete transfer of the Lewis base from Si or Ge to the Lewis acidic centers. They will find wide application in future investigations.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-pentane, cyclopentane, *n*-hexane with LiAlH₄; Et₂O, THF, toluene with Na/benzophenone; 1,2-difluorobenzene, pentafluorobenzene with molecular sieves). Microanalyses were carried out by the microanalytical laboratory of the Westfälische Wilhelms-Universität Münster. NMR spectra were recorded in C_6D_6 or C_6D_{12} at ambient probe temperature using the following Bruker instruments: Avance I (¹H, 400.13; ¹³C, 100.62 MHz) or Avance III (¹H, 400.03; ¹³C, 100.59 MHz) and referenced internally to residual solvent resonances (chemical shift data in δ). ¹³C NMR spectra were all proton decoupled. IR spectra were recorded as paraffin mulls between CsI or KBr plates on a Shimadzu Prestige 21 spectrometer. MesGeCl₃⁷ and TripGeCl₃⁸ have been reported in the literature previously, we synthesized these trichlorides on different routes and isolated them in 68% yield (see synthesis of 1c and 1d). $HAl^tBu_2^{22}$ and $HGa^tBu_2^{22}$ were obtained according to literature procedures. H-C= $C^{-1}Bu$, GeCl₄, PhGeCl₃, Ph₂GeCl₂ and ^{*n*}BuLi were used as purchased. The assignment of NMR spectra is based on HMBC. H,H-ROESY, HSQC and DEPT135 data. Only the most intensive mass of each fragment is given in the documentation of the mass spectra; the complete isotopic patterns agree with the calculated ones.

Synthesis of Ph₂Ge(Cl)C≡C-^tBu 1a

A solution of ^{*n*}BuLi (5.90 mL, 9.44 mmol, 1.6 M in *n*-hexane) was added at room temperature to a solution of H-C=C-^tBu (1.20 mL, 0.80 g, 9.76 mmol) in Et₂O (50 mL). After stirring for 16 h at room temperature the pale yellow mixture was added dropwise at -78 °C to a solution of Ph₂GeCl₂ (2.00 mL, 2.83 g, 9.51 mmol) in Et₂O (50 mL). The mixture was slowly warmed to room temperature and stirred for 16 h. Distilled water (20 mL) was added and the organic layer was separated. The aqueous layer was extracted three times with Et₂O (3 x 20 mL). The combined organic layers were dried over MgSO₄ and filtered. All volatiles of the filtrate were removed under reduced pressure, and the residue was recrystallized from *n*-hexane to afford **1a** as a colorless solid. Yield: 3.15 g (97%). M.p. (argon, sealed capillary): 53 °C. Microanalysis: found C 62.8, H 5.6%; [C₁₈H₁₉ClGe (343.39)] requires C 63.0, H 5.6%. ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 1.11$ (s, 18 H, ^tBu), 7.11 (m, overlap, 4H, *m*-H), 7.13 (m, overlap, 2H, *p*-H), 7.79 (dd, ${}^{3}J_{HH} = 6.5$ Hz, ${}^{4}J_{HH} = 3.0$ Hz, 4H, o-H). ${}^{13}C$ NMR (C₆D₆, 101 MHz, 300 K): $\delta =$ 28.6 (CMe₃), 30.6 (CMe₃), 75.9 (GeC=C), 120.1 (GeC=C), 129.0 (m-C), 130.9 (p-C), 133.6 (o-C), 135.3 (*ipso-C*). IR (KBr plates, paraffin, cm⁻¹): 2181 vs, 2151 vs v(C=C); 1962 w, 1892 w, 1817 w, 1771 w, 1653 vw, 1582 w (phenyl); 1447 vs, 1439 vs, 1371 vs (paraffin); 1337 w, 1306 m, 1250 vs & (CH₃); 1204 m, 1194 m, 1159 vw, 1094 s, 1069 w, 1026 w, 995 w, 968 vw, 922 m, 849 w v(CC); 743 vs (paraffin); 694 vs (phenyl); 617 vw, 550 vw, 490 s, 459 vs, 390 vs v(GeC), v(GeCl). Mass spectrum (EI+, 20 eV, 298 K): m/z (%) = 344 (4) [M]⁺, 309 (1) [M - C1]⁺, 287 (8) [M - ^tBu]⁺, 263 (15) [M - C=C- $^{t}Bu]^{+}$.

Synthesis of PhGe(Cl)(C≡C-^tBu)₂ 1b

Compound **1b** was obtained in an analogous manner to compound **1a** from two equivalents of ^{*n*}BuLi (15.5 mL, 24.8 mmol, 1.6 M in *n*-hexane), two equivalents of H-C=C-^{*t*}Bu (3.00 mL, 2.00 g, 24.4 mmol) and one equivalent of PhGeCl₃ (2.00 mL, 3.17 g, 12.4 mmol). Yield: 3.97 g (92%). M.p.: 51 °C (Ar, sealed capillary). Microanalysis: found C 62.4, H 6.7%; [C₁₈H₂₃ClGe (347.43)] requires C 62.2, H 6.7%. ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 1.04$ (s, 18H, ^tBu), 7.10 (m, overlap, 1H, *p*-H), 7.12 (m, overlap, 2H, *m*-H), 7.92 (dd, ${}^{3}J_{\text{HH}} = 7.6$ Hz, ${}^{4}J_{\text{HH}} = 1.7$ Hz, 2H, *o*-H). 13 C NMR (C₆D₆, 101 MHz, 300 K): $\delta = 28.5$ (CMe₃), 30.3 (CMe₃), 75.7 (GeC=C), 118.4 (GeC=C), 129.0 (m-C), 131.2 (p-C), 132.9 (o-Ph), 135.4 (ipso-C). IR (CsI plates, paraffin, cm⁻¹): 2190 vs, 2155 vs v(C≡C); 2059 vw, 1983 vw, 1966 w, 1910 vw, 1892 w, 1841 vw, 1825 w, 1774 w, 1661 w, 1657 sh, 1590 w (phenyl); 1462 vs, 1377 vs (paraffin); 1337 s, 1310 vs, 1253 vs δ(CH₃); 1204 s, 1187 s, 1172 m, 1159 m, 1097 vs, 1068 w, 1027 s, 997 m, 985 w, 972 w, 923 vs, 890 m, 863 m, 854 m, 755 vs, 736 vs v(CC); 723 vs (paraffin); 694 vs, 679 s (phenyl); 617 vw, 554 w, 499 vs, 488 vs, 462 vs vGeC, δ (CC), v(GeCl). Mass spectrum (EI+, 20 eV, 298 K): m/z (%): 348 (6) $[M]^+$, 333 (6) $[M - CH_3]^+$, 313 (4) $[M - CI]^+$, 291 $(11) [M - {}^{t}Bu]^{+}, 267 (36) [M - C \equiv C - {}^{t}Bu]^{+}.$

Synthesis of Mes(Cl)Ge(C \equiv C^{-t}Bu)₂ 1c

A solution of MesBr (5.40 mL, 6.98 g, 35.1 mmol) in THF (40 mL) was added dropwise at 50 °C to Mg turnings (1.00 g, 41.1 mmol). After completion the mixture was heated for 5 min under reflux conditions. The mixture was allowed to cool to room temperature, 1,4-dioxane (10.0 mL, 10.3 g, 117 mmol) was added. The resulting suspension was heated under reflux for 5 min, cooled to room temperature and allowed to

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settle. The supernatant solution was decanted and the solid MgBr₂(dioxane) was washed with THF (20 mL). The decanted solution can be used directly for further transformations (preferred method). Alternatively, the THF fractions were combined and the solvent was removed *in vacuo*. The remaining solid (Mes₂Mg²³) was washed three times with Et₂O (10 mL) and then treated with THF (100 mL). The mixture was filtered, and the filtrate was added dropwise at -78 °C to a solution of GeCl₄ (5.00 mL, 9.40 g, 43.8 mmol) in THF (100 mL). The mixture was allowed to warm to room temperature, stirred overnight and then heated under reflux for 5 min. The solvent was removed *in vacuo* at room temperature, and the remaining residue was treated with *n*-pentane (3 x 20 mL). After filtration the filtate was concentrated *in vacuo* until the product started to precipitate (~4 mL). The solvent was removed with a pipette and the obtained product was dried *in vacuo* to yield MesGeCl₃ as a pale yellow powder. Yield: 7.10 g (68% based on MesBr; ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 1.87$ (s, 3H, *p*-Me), 2.40 (s, 6H, *o*-Me), 6.41 (s, 2H, *m*-H). ¹³C NMR (C₆D₆, 101 MHz, 300 K): $\delta = 20.8$ (*p*-Me), 23.8 (*o*-Me), 130.8 (*m*-C), 130.9 (*ipso*-C), 142.7 (*o*-C), 143.0 (*p*-C)).

A solution of H-C=C-^{*t*}Bu (1.20 mL, 0.80 g, 9.76 mmol) in Et₂O (50 mL) was treated with ^{*n*}BuLi (6.10 mL, 9.76 mmol, 1.6 M in *n*-hexane) at room temperature and the mixture was stirred overnight. It was added dropwise at -78 °C to a solution of MesGeCl₃ (1.46 g, 4.90 mmol) in Et₂O (50 mL). The mixture was slowly warmed to room temperature and stirred for 16 h. Distilled water (20 mL) was added, and the organic layer was separated. The aqueous layer was extracted three times with Et₂O (3 x 20 mL). The combined organic layers were dried over MgSO₄ and filtered. All volatiles of the filtrate were removed under reduced pressure, and the residue was recrystallized from *n*-hexane (-30 °C) to yield **1c** as a colorless solid. Yield: 1.20 g (63%). M.p.: 92 °C. Microanaly-

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sis: found C 64.7, H 7.5%; [C₂₁H₂₉ClGe (389.51)] requires C 64.8, H 7.5%. ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 1.06$ (s, 18H, C=C-CMe₃), 2.02 (s, 3H, *p*-Me), 2.84 (s, 6H, *o*-Me), 6.67 (s, 2H, *m*-H). ¹³C NMR (C₆D₆, 101 MHz, 300 K): $\delta = 21.0$ (*p*-Me), 24.0 (*o*-Me), 28.4 (CMe₃), 30.1 (CMe₃), 80.4 (GeC=C), 116.9 (GeC=C), 129.2 (*ipso*-C), 130.1 (*m*-C), 141.0 (*p*-C), 144.0 (*o*-C). IR (KBr plates, paraffin, cm⁻¹): 2189 vs, 2154 vs v(C=C); 2008 vw, 1946 vw, 1906 vw, 1879 vw, 1749 vw, 1717 vw, 1601 m, 1555 s (aromatic ring); 1470 vs, 1377 vs (paraffin); 1296 s, 1252 vs δ (CH₃); 1202 s, 1103 w, 1028 m, 924 s, 845 s, 750 vs v(CC); 725 s (paraffin); 590 m, 542 s, 492 vs v(GeC), δ (CC), v(GeCl). Mass spectrum (EI+, 20 eV, 323 K): m/z (%) = 390 (2) [M]⁺, 375 (2) [M – Me]⁺, 354 (19) [M – HCl], 308 (39) [M – H-C=C-^{*t*}Bu]⁺.

Synthesis of [2,4,6-(Me₂CH)₃C₆H₂]Ge(Cl)(C≡C-^{*t*}Bu)₂ 1d

A solution of 2,4,6-(Me₂CH)₃C₆H₂Br (7.83 g, 7 mL, 27.7 mmol) in THF (50 mL) was added dropwise to Mg turnings (1.00 g, 41.1 mmol). The mixture was heated under reflux conditions for 2.5 h. 1,4-dioxane (10.0 mL, 10.3 g, 117 mmol) was added at room temperature. The resulting suspension was heated under reflux for 5 min and cooled to room temperature. MgBr₂(dioxane) precipitated as a colourless solid which was allowed to settle overnight. The supernatant solution was decanted and added dropwise at -78 °C to a solution of GeCl₄ (7.52 g, 4.00 mL, 35.1 mmol) in THF (50 mL). The mixture was warmed to room temperature and heated under reflux conditions (5 min). The solvent was removed *in vacuo*, and the residue was extracted with *n*-pentane (3 x 20 mL). The combined extracts were concentrated until the product started to precipitate (~4 mL). The remaining solvent was removed by a pipette, and the remaining solid was dried *in vacuo* to yield 2,4,6-(Me₂CH)₃C₆H₂GeCl₃ as a pale yellow solid. Yield: 8.40 g (79% based on aryl bromide; ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 1.15$ (d, ³*J*_{HH} = 7.0 Hz, 6H, *p*-CH*Me*₂), 1.25 (d, ³*J*_{HH} = 6.6 Hz, 12H, *o*-CH*Me*₂), 2.68 (hept, ³*J*_{HH} = 7.0 Hz, 1H, *p*-CHMe₂), 3.94 (hept, ³*J*_{HH} = 6.6 Hz, 2H, *p*-CHMe₂), 7.11 (s, 2H, *m*-H)).

A solution of H-C=C-^{*t*}Bu (1.80 g, 21.9 mmol) in Et₂O (50 mL) was treated at room temperature with a solution of ^{*n*}BuLi (13.5 mL, 21.6 mmol, 1.6 M in *n*-hexane). The mixture was stirred for 3 h and added at -78 °C to a solution of [2,4,6-

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 $(Me_2CH)_3C_6H_2$ GeCl₃ (4.13 g, 10.8 mmol) in Et₂O (50 mL). The mixture was stirred for 2 h at -78 °C, allowed to warm to room temperature over a period of 16 h and treated with distilled water (20 mL). The phases were separated, and the aqueous phase was extracted two times with Et₂O (2 x 10 mL). The combined organic phases were dried over MgSO₄ and filtered. The solvent of the filtrate was removed *in vacuo*, and the solid residue was recrystallized from *n*-hexane (-40 °C) to afford compound 1d as colourless crystals. Yield: 3.75 g (73%). M.p.: 96 °C. Microanalysis: found C 68.3, H 8.8%; $[C_{27}H_{41}ClGe (473.67)]$ requires C 68.5, H 8.7%. ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta =$ 1.08 (s, 18H, CMe₃), 1.20 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6H, p-CHMe₂), 1.39 (d, ${}^{3}J_{HH} = 6.7$ Hz, 12H, o-CHMe₂), 2.75 (hept, ${}^{3}J_{HH} = 6.8$ Hz, 1H, p-CHMe₂), 4.40 (hept, ${}^{3}J_{HH} = 6.7$ Hz, 2H, o-CHMe₂), 7.17 (s, 2H, m-H). ¹³C NMR (C₆D₆, 101 MHz, 300 K): $\delta = 24.0$ (p-CHMe2), 25.4 (o-CHMe2), 28.5 (CMe3), 30.4 (CMe3), 33.1 (o-CHMe2), 34.7 (p- $CHMe_2$, 80.6 (GeC=C), 115.9 (GeC=C), 122.8 (*m*-C), 128.8 (*ipso*-C), 152.4 (*p*-C), 153.4 (o-C). IR (CsI plates, paraffin, cm⁻¹): 2187 s, 2155 s v(C=C); 1763 vw, 1690 vw, 1599 s, 1558 m (aromatic ring); 1466 vs, 1379 vs (paraffin); 1319 s, 1304 sh, 1252 vs δ(CH₃); 1202 s, 1165 s, 1136 m, 1103 s, 1070 m, 1059 m, 1032 m, 1016 m, 957 m, 922 vs, 878 vs, 839 m, 752 vs v(CC); 723 vs (paraffin); 648 w, 611 w, 569 vw, 554 w, 515 m, 486 vs v(GeC), ∂ (CC), v(GeCl). Mass spectrum (EI+, 20 eV, 298 K): m/z (%): 474

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(1) $[M]^+$, 439 (5) $[M - Cl]^+$, 438 (5) $[M - HCl]^+$, 417 (8) $[M - {}^tBu]^+$, 392 (10) $[M - H-C=C-{}^tBu]^+$, 381 (7) $[M - HCl - {}^tBu]^+$, 357 (22) $[M - HCl - C=C-{}^tBu]$.

Synthesis of Ph₂Ge(Cl)[C(Al^tBu₂)=C(H)-^tBu] 2a

A solution of compound 1a (1.00 g, 2.91 mmol) in n-pentane (10 mL) was slowly added at -78 °C to a suspension of HAl¹Bu₂ (0.42 g, 2.96 mmol) in *n*-pentane (15 mL). The mixture was allowed to warm to room temperature and stirred for 16 h. The solution was concentrated and stored at -30 °C to yield **2a** as colourless crystals. Yield: 0.89 g (63%). M.p.: 108 °C (Ar, sealed capillary). Microanalysis: found C 64.6, H 8.0%; [C₂₆H₃₈AlClGe (485.61)] requires C 64.3, H 7.9%. ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 0.86$ (s, 9H, C=C-CMe₃), 1.35 (s, 18H, AlCMe₃), 7.10 (m, overlap, 2H, p-H), 7.11 (m, overlap, 4H, *m*-H), 7.12 (s overlap, 1H, C=CH), 7.76 (m, 4H, *o*-H). ¹³C NMR $(C_6D_6, 101 \text{ MHz}, 300 \text{ K}): \delta = 17.5 (\text{br., Al}CMe_3), 29.2 (C=CH-CMe_3), 30.7 (AlCMe_3),$ 38.7 (C=CH-CMe₃), 129.1 (m-C), 131.2 (p-C), 134.8 (o-C), 137.1 (ipso-C), 140.7 (br., GeC=C), 167.6 (GeC=C). IR (KBr plates, paraffin, cm⁻¹): 1956 vw, 1884 vw, 1815 vw, 1767 vw, 1682 vw, 1653 vw, 1593 m, 1562 m (phenyl); 1437 vs, 1379 vs (paraffin); 1337 sh, 1306 m, 1250 m & (CH₃); 1192 m, 1157 w, 1088 s, 1067 w, 1050 w, 1022 m, 1001 m, 970 w, 937 m, 887 m, 847 w, 810 vs, 787 s v(CC); 731 vs (paraffin; 696 vs, 675 m (phenyl); 581 s, 542 m, 501 m, 455 m, 412 s v(AlC), v(GeC), δ(CC), v(GeCl). Mass spectrum (EI+, 25 eV, 298 K): m/z (%): 429 (52) $[M - {}^{t}Bu]^{+}$.

Synthesis of Ph(Cl)Ge(C=C-^tBu)[C(Al^tBu₂)=C(H)-^tBu] 2b

A solution of compound **1b** (2.47 g, 7.11 mmol) in *n*-pentane (10 mL) was slowly added at -78 °C to a suspension of HAl'Bu₂ (1.01 g, 7.11 mmol) in *n*-pentane (40 mL). The

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mixture was allowed to warm to room temperature and stirred for 16 h. The solution was concentrated and stored at -30 °C to yield colourless crystals of **2b**. Yield: 2.00 g (57%). M.p.: 114 °C (Ar, sealed capillary). Microanalysis: found C 63.2, H 8.5%; [C₂₆H₄₂AlClGe (489.65)] requires C 63.8, H 8.6%. ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 0.95$ (s, 9H, C=CH-CMe₃), 1.13 (s, 9H, C=C-CMe₃), 1.36 and 1.44 (each s, 9H, AlCMe₃), 7.00 (s, 1H, C=CH), 7.06 (m, 1H, p-H), 7.11 (m, 2H, m-H), 7.97 (d, 2H, ³J_{HH}) = 7.2 Hz, o-H). ¹³C NMR (C₆D₆, 101 MHz, 300 K): δ = 17.0 and 17.5 (br., AlCMe₃), 28.7 (C=C-CMe₃), 29.2 (C=C-CMe₃), 30.3 (C=C-CMe₃), 30.3 and 30.5 (AlCMe₃), 39.3 $(C=C-CMe_3)$, 78.0 (GeC=C), 122.9 (GeC=C), 129.3 (m-C), 131.8 (p-C), 133.3 (o-C), 137.9 (*ipso*-C), 141.6 (GeC=C), 168.0 (GeC=C). IR (CsI plates, paraffin, cm^{-1}): 2183 s. $2151 \text{ s}, 2118 \text{ sh } v(C \equiv C); 1975 \text{ vw}, 1960 \text{ vw}, 1908 \text{ vw}, 1888 \text{ vw}, 1836 \text{ vw}, 1821 \text{ vw},$ 1773 vw, 1682 vw, 1653 vw, 1601 s, 1568 m, 1506 m v(C=C), (phenyl); 1468 vs, 1379vs. 1362 vs (paraffin); 1335 m, 1306 m, 1252 s δ (CH₃); 1200 m, 1090 m, 1065 w, 1024 m, 1001 m, 972 vw, 935 m, 924 sh, 891 m, 812 vs, 789 s, 750 s, 733 s v(CC); 721 s (paraffin); 696 s, 679 m (phenyl); 631 vw, 586 s, 544 w, 503 m, 469 s, 413s, 395 s $v(GeC), v(AlC), v(GeCl), \delta(CC)$. Mass spectrum (EI+, 20eV, 323 K): m/z (%): 433 $(100) [M - {}^{t}Bu]^{+}.$

Synthesis of $Mes(Cl)Ge(C \equiv C^{-t}Bu)[C(Al^{t}Bu_{2})=C(H)^{-t}Bu]$ 2c

A solution of compound 1c (0.76 g, 1.95 mmol) in *n*-hexane (5 mL) was slowly added at -78 °C to a suspension of HAl'Bu₂ (0.276 g, 1.94 mmol) in *n*-hexane (10 mL). The cooling bath was removed and the mixture was stirred for 3 h at room temperature. Concentrating the solution and storing at -30 °C yielded compound 2c as colourless crystals. Yield: 0.57 g (55%). M.p.: 134 °C (Ar, sealed capillary). Microanalysis: found

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C 65.5, H 9.1%; $[C_{29}H_{48}AlClGe (531.73)]$ requires C 65.5, H 9.1%. ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 1.08$ (s, 9H, C=CH-CMe₃), 1.10 (s, 9H, C=C-CMe₃), 1.32 and 1.44 (each s, 9H, AlCMe₃), 1.98 (s, 3H, *p*-Me), 2.74 (s, 6H, *o*-Me), 6.63 (s, 2H, *m*-H), 6.73 (s, 1H, C=CH). ¹³C NMR (C₆D₆, 101 MHz, 300 K): $\delta = 16.9$ and 17.2 (br., AlC-Me₃), 21.0 (*p*-Me), 24.2 (*o*-Me), 28.4 (C=CH-CMe₃), 28.7 (C=C-CMe₃), 30.0 (C=C-CMe₃), 30.6 and 30.7 (AlCMe₃), 39.3 (C=CH-CMe₃), 84.1 (GeC=C), 121.0 (GeC=C), 130.3 (*m*-C), 132.1 (*ipso*-C), 141.7 (*p*-C), 144.2 (*o*-C), 149.1 (GeC=C), 163.1 (GeC=C). IR (KBr plates, paraffin, cm⁻¹): 2185 vs, 2151 vs, 2116 sh v(C=C); 1767 vw, 1734 vw, 1599 vs, 1557 s v(C=C), (aromatic ring); 1468 vs, 1410 vs, 1379 vs, 1360 vs (paraffin); 1292 s, 1250 vs δ (CH₃); 1198 s, 1028 s, 1003 s, 935 m, 883 m, 851 s, 810 vs, 783 vs, 748 vs v(CC); 718 vs (paraffin); 592 vs, 542 s, 509 s, 490 s, 467 m, 419 vs, 393 s v(GeC), v(AlC), v(GeCl), δ (CC). Mass spectrum (EI+, 20eV, 373 K): *m/z* (%): 475 (69) [M – 'Bu]⁺, 419 (11) [M – 'Bu – butene]⁺; 355 (100) [M – Mes – H'Bu]⁺.

Synthesis of [2,4,6-(Me₂CH)₃C₆H₂]Ge(Cl)(C≡C-^tBu)[C(Al^tBu₂)=C(H)-^tBu] 2d

Compound **1d** (0.35 g, 0.74 mmol) was added at -60 °C to a suspension of HAl^{*t*}Bu₂ (0.11 g, 0.77 mmol) in *n*-pentane (20 mL). The cooling bath was removed and the solution was stirred for 3 h at room temperature. All volatiles were removed *in vacuo* and the microcrystalline residue was recrystallized at -30 °C from 1,2-difluorobenzene to afford colourless crystals of compound **2d**. Yield: 0.32 g (70%). The compound decomposes slowly at room temperature in C₆D₆. M.p.: 87 °C (decomp.). Microanalysis: found C 68.4, H 9.8%; [C₃₅H₆₀AlClGe (615.89)] requires C 68.3, H 9.8%. ¹H NMR (C₆D₆, 400 MHz, 300 K): δ = 1.08 (s, 9H, C=CH-CMe₃), 1.13 (s, 9H, C=C-CMe₃), 1.15 (d, ³J_{HH} = 7.0 Hz, 6H, *p*-CHMe₂), 1.31 (d, ³J_{HH} = 6.6 Hz, 6H, *o*-CHMe), 1.33 (s, 9H, AlC-

Me₃), 1.39 (s, br., 6H, *o*-CH*Me*), 1.46 (s, 9H, AlCMe₃), 2.70 (hept, ${}^{3}J_{HH} = 7.0$ Hz, 1H, *p*-CHMe), 4.00 (s, br., 2H, *o*-CHMe), 6.75 (s, 1H, C=CH), 7.17 (overlap, 2H, *m*-H). ¹³C NMR (C₆D₆, 101 MHz, 300 K); $\delta = 16.9$ and 17.4 (AlCMe₃), 23.8 (*p*-CHMe), 25.3 and 26.4 (br., o-CHMe), 28.6 (C=C-CMe₃), 28.8 (C=CH-CMe₃), 30.2 (C=C-CMe₃), 31.0 $(AlCMe_3)$, 33.4 (br., o-CHMe), 34.6 (p-CHMe), 39.0 (C=CH-CMe_3), 85.0 (GeC=C), 119.9 (GeC=C), 123.6 (br., m-C), 131.7 (ipso-C), 149.5 (GeC=C), 153.1 (p-C), 155.7 (o-C), 163.5 (GeC=C). ¹H NMR (C₆D₁₂, 400 MHz, 300 K): $\delta = 1.00$ and 1.08 (each s, 9H, AlCMe₃), 1.13 (s, 9H, C=CH-CMe₃), 1.22 (s, 9H, C=C-CMe₃), 1.24 (m, br., 18H, o- and p-CHMe₂), 2.83 (m, br., 3H, o- and p-CHMe₂), 6.62 (s, 1H, C=CH), 7.06 (br., 2H, m-H). ¹³C NMR (C₆D₁₂, 101 MHz, 300 K): δ = 17.0 and 17.5 (AlCMe₃), 24.1 (p-CHMe), 25.5 (o-CHMe), 29.1 (C≡C-CMe₃), 29.3 (C=CH-CMe₃), 30.7 (C≡C-CMe₃), 30.9 and 31.0 (AlCMe₃), 33.7 (o-CHMe), 35.3 (p-CHMe), 39.5 (C=CH-CMe₃), 85.6 $(GeC \equiv C)$, 119.5 $(GeC \equiv C)$, 124.0 (m-C), 132.0 (ipso-C), 150.5 (GeC = C), 152.9 (p-C), 155.8 (o-C), 163.3 (GeC=C). IR (CsI plates, paraffin, cm⁻¹): 2181 m, 2149 m v(C=C); 1771 vw, 1597 m, 1558 m, 1506 m v(C=C), (aromatic ring); 1452 vs, 1379 vs (paraffin); 1308 m, 1269 m, 1252 s δ (CH₃); 1202 w, 1167 w, 1334 vw, 1099 w, 1069 vw, 1055 w, 1026 w, 1003 w, 957 vw, 935 m, 881 m, 841 w, 812 m 785 w, 750 s v(CC); 721 s (paraffin); 648 vw, 615 vw, 579 m, 544 vw, 519 vw, 486 vw, 467 vw v(GeC), δ(CC), ν(AlC), ν(GeCl). Mass spectrum (EI+, 25 eV, 323 K): m/z (%): 560 (26) [M – butene]⁺.

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Synthesis of $Ph(Cl)Ge(C \equiv C^{-t}Bu)[C(Ga^{t}Bu_{2}) = C(H)^{-t}Bu]$ 2e

A solution of HGa^tBu₂ (0.20 g, 1.08 mmol) in toluene (25 mL) was treated at room temperature with compound **1b** (0.35 g, 1.01 mmol) and stirred for 16 h. The volatiles

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were removed in vacuo, and the residue was recrystallized from 1.2-difluorobenzene to yield colourless crystals of compound 2e. Yield: 0.49 g (91%, based on 1b). M.p.: 109 °C (Ar, sealed capillary). Microanalysis: found C 58.6, H 8.0%; [C₂₆H₄₂ClGaGe (532.39)] requires C 58.7, H 8.0%. ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 1.00$ (s, 9H, $C=CH-CMe_3$, 1.15 (s, 9H, $C=C-CMe_3$), 1.40 and 1.47 (each s, 9H, GaCMe_3), 6.67 (s, 1H, C=CH), 7.07 (t, 1H, ${}^{3}J_{HH} = 7.3$ Hz, p-H), 7.13 (pseudo-t, 2H, ${}^{3}J_{HH} = 7.3$ Hz m-H), 7.98 (d, 2H, ${}^{3}J_{HH} = 6.8$ Hz, o-H). ${}^{13}C$ NMR (C₆D₆, 101 MHz, 300 K): $\delta = 26.5$ and 27.1 (GaCMe₃), 28.7 (C=C-CMe₃), 29.5 (C=CH-CMe₃), 30.4 (C=C-CMe₃), 30.5 and 30.7 $(GaCMe_3)$, 39.2 (C=CH-CMe_3), 78.4 (GeC=C), 121.2 (GeC=C), 129.1 (m-C), 131.2 (p-C)) C), 133.2 (o-C), 138.8 (ipso-C), 144.4 (GeC=C), 165.1 (GeC=C). IR (CsI plates, paraffin, cm⁻¹): 2185 s, 2151 s v(C=C); 1973 vw, 1956 vw, 1904 vw, 1888 vw, 1834 vw, 1819 vw, 1771 vw, 1684 vw, 1655 vw, 1599 m, 1566 m v(C=C), (phenyl); 1454 vs, 1692 m, 11379 vs (paraffin); 1306 s, 1252 vs & (CH₃); 1200 s, 1175 s, 1092 s, 1089 m, 1011 m, 970 m. 937 s. 922 m. 889 m. 847 w. 810 s. 789 m. 750 s. 735 vs v(CC); 718 s (paraffin); 696 s, 677 w (phenyl); 619 vw, 586 m, 538 w, 500 m, 461 m v(GeC), v(GeCl), v(GaC), δ (CC). Mass spectrum (EI+, 20eV, 298 K): m/z (%): 475 (100) [M – ^tBu]⁺.

Synthesis of Ph(Cl)Ge[C(Ga^tBu₂)=C(H)-^tBu]₂ 3

A solution of HGa^{*t*}Bu₂ (0.48 g, 2.60 mmol, excess) in toluene (25 mL) was treated at room temperature with compound **1b** (0.41 g, 1.18 mmol). The mixture was stirred for 48 h. The volatiles were removed *in vacuo*, and the residue was recrystallized from pentafluorobenzene to yield colourless crystals of compound **3**. Yield: 0.63 g (74%). The limited stability of the compound prevented the acquirement of an IR spectrum and microanalysis and caused impurities in the NMR spectra. M.p.: 112 °C (decomp., Ar, sealed capillary). ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 0.92$ (s br., 18H, GaC*Me*₃), 1.19 (s, 18H, C=CH-C*Me*₃), 1.39 (s br., 18H, GaC*Me*₃), 6.49 (s, 2H, C=CH), 7.00 (t, 1H, ³J_{HH} = 7.5 Hz, *p*-H), 7.16 (m, 2H, *m*-H), 7.77 (d, 2H, ³J_{HH} = 6.5 Hz, *o*-H). ¹H NMR (toluene-d₈, 400 MHz, 190 K): $\delta = 0.75$ and 1.09 (each s br., 9H, GaC*Me*₃), 1.19 and 1.24 (each s, 9H, C=CH-C*Me*₃), 1.42 and 1.54 (each, s br., 9H, GaC*Me*₃), 6.34 and 6.54 (each s, 1H, C=CH), 6.87 (s br., 1H, *p*-H), 7.02 (overlap, 2H, *m*-H), 7.69 (s br., 2H, *o*-H). ¹³C NMR (C₆D₆, 101 MHz, 300 K): $\delta = 28.4$ and 28.6 (GaCMe₃), 29.8 (C=CH-C*Me*₃), 30.6 and 31.3 (GaC*Me*₃), 38.7 (C=CH-CMe₃), 130.8 (*p*-C), 131.1 (*m*-C), 131.3 (*o*-C), 147.2 (*ipso*-C), 149.9 (GeC=C), 161.3 (GeC=C). Mass spectrum (EI+, 20eV, 303 K): *m/z* (%): 661 (8) [M - ^{*i*}Bu]⁺, 441 (57) [M - ClGa^{*i*}Bu₂ - ^{*i*}Bu]⁺.

Synthesis of MesGe(H)(C=C-^tBu)[C(Al^tBu₂)=C(H)-^tBu] 4a

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Solid Mes(Cl)Ge(C=C-^{*t*}Bu)₂ (**1c**, 0.36 g, 0.92 mmol) was added at -78 °C to a solution of HAl^{*t*}Bu₂ (0.26 g, 1.83 mmol) in *n*-hexane (10 mL). The mixture was stirred for 5 min. The cooling bath was removed and the mixture stirred for 2 h while warming up to room temperature. The solvent was removed *in vacuo* and the residue heated to 60 °C (10^{-3} Torr, 1 h) to remove the by-product ClAl^{*t*}Bu₂ by sublimation. It was collected at a cool finger which was cooled with solid CO₂. Recrystallisation of the residue from 1,2-difluorobenzene (1 mL) at -30 °C yielded colourless crystals of **4a**. Yield: 0.40 g (87% based on **1c**). M.p.: 111 °C. Microanalysis: found C 69.5, H 9.8%; [C₂₉H₄₉AlGe (497.28)] requires C 70.0, H 9.9%. ¹H NMR (C₆D₆, 400 MHz, 300 K): δ = 0.95 (s, 9H, C=CH-CMe₃), 1.02 (s, 9H, C=C-CMe₃), 1.43 (s, 18H, AlCMe₃), 2.03 (s, 3H, *p*-Me), 2.59 (s, 6H, *o*-Me), 6.41 (s, 1H, GeH), 6.73 (s, 2H, *m*-H), 7.00 (s, 1H, C=CH). ¹³C NMR (C₆D₆, 101 MHz, 300 K): δ = 18.3 (br., AlCMe₃), 21.0 (*p*-Me), 24.7 (*o*-Me), 29.0

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(C=CH-CMe₃), 29.4 (C=C-CMe₃), 30.6 (C=C-CMe₃), 31.0 (br., AlCMe₃), 39.1 (C=CH-CMe₃), 79.8 (GeC=C), 129.3 (*m*-C), 130.9 (br., GeC=C), 134.4 (*ipso*-C), 139.5 (*p*-C), 139.9 (br., GeC=C), 143.2 (*o*-C), 163.9 (GeC=C). IR (KBr plates, paraffin, cm⁻¹): 2151 s, 2108 s v(C=C); 2066 s v(GeH); 1715 w, 1603 vs, 1570 m v(C=C), (aromatic ring); 1445 vs, 1375 vs (paraffin); 1294 s, 1246 vs δ (CH₃); 1200 vs, 1026 vs, 1001 s, 934 s, 899 m, 868 m, 845 s, 806 vs, 775 vs v(CC); 725 vs (paraffin); 586 vs, 546 s, 500 w, 469 s, 413 s v(GeC), v(AlC), δ (CC). Mass spectrum (EI+, 20eV, 298 K): m/z (%): 440 (2) [M – H^tBu]⁺, 357 (65) [M – Al^tBu₂]⁺.

Synthesis of [2,4,6-(Me₂CH)₃C₆H₂]Ge(H)(C≡C-^tBu)[C(Al^tBu₂)=C(H)-^tBu] 4b

A mixture of $[2,4,6-(Me_2CH)_3C_6H_2]Ge(CI)(C\equiv C-^{1}Bu)[C {Al(CMe_3)_2}=C(H)-^{1}Bu]$ (2d, 0.29 g, 0.47 mmol) and HAl'Bu₂ (0.067 g, 0.47 mmol) was treated at -78 °C with *n*hexane (10 mL) and stirred for 5 min. The cooling bath was removed, the mixture was allowed to warm to room temperature and stirred for 90 min to give a pale yellow solution. The solvent was removed *in vacuo* and the residue heated to 60 °C (10⁻³ Torr, 1 h) to remove the by-product ClAl'Bu₂ by sublimation. It was collected at a cool finger which was cooled with solid CO₂. The residue was recrystallized from 1,2difluorobenzene (1 mL) at -45 °C to yield colourless crystals of compound **4b**. Yield: 0.26 g (95% based on **2d**). M.p.: 111 °C. Microanalysis: found C 70.5, H 9.5%; [C₃₅H₆₁AlGe·C₆H₄F₂ (581.48+114.09)] requires C 70.8, H 9.4%. ¹H NMR (C₆D₆, 400 MHz, 300 K): $\delta = 0.91$ (s, 9H, C=CH-CMe₃), 1.02 (s, 9H, C=C-CMe₃), 1.15 (dd, 6H, ³J_{HH} = 6.9 Hz, ⁵J_{HH} = 2.5 Hz, *p*-CHMe₂, both resonances coincide), 1.36 and 1.41 (each d, ³J_{HH} = 6.7 Hz, 6H, *o*-CHMe₂), 1.43 (s, 18H, AlCMe₃), 2.73 (sep, 1H, ³J_{HH} = 6.9 Hz, *p*-CH), 3.58 (m br., 2H, *o*-CH), 6.50 (s, 1H, GeH), 6.96 (s, 1H, C=CH), 7.17 (s, 2H, *m*- H). ¹³C NMR (C₆D₆, 101 MHz, 300 K): $\delta = 18.4$ and 19.3 (br., AlCMe₃), 23.98 and 24.01 (*p*-CH*Me*₂), 24.7 and 25.4 (br., *o*-CH*Me*₂), 29.3 (C=C-CMe₃), 29.4 (C=CH-C*Me*₃), 30.8 (C=C-C*Me*₃), 31.0 (AlC*Me*₃), 34.6 (*p*-CH), 35.0 (br., *o*-CH), 39.1 (C=CH-CMe₃), 81.2 (GeC=C), 122.2 (*m*-C), 129.5 (br., C=C-CMe₃), 134.2 (*ipso*-C), 140.2 (GeC=C), 151.0 (*p*-C), 154.2 (*o*-C), 163.8 (GeC=C). IR (KBr plates, paraffin, cm⁻¹): 2149 m, 2106 s v(C=C); 2058 vs vGeH; 1599 vs, 1562 s v(C=C), (aromatic ring); 1464 vs, 1375 vs (paraffin); 1310 w, 1264 vs δ (CH₃); 1198 m, 1163 w, 1101 w, 1063 vw, 1028 vw, 999 w, 935 s, 880 m, 840 vw, 802 vs, 752 vs v(CC); 710 sh (paraffin); 648 w, 581 s, 521 vw, 469 m, 413 s v(GeC), v(AlC), δ (CC). Mass spectrum (EI+, 20eV, 298 K): *m/z* (%): 526 (38) [M – H₂C=CMe₂]⁺; 440 (7) [M – HAl^tBu₂]⁺.

Synthesis of Ph(^tBu)Ge(C=C-^tBu)[C{Al(^tBu)(Cl)}=C(H)-^tBu] 5

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A solution of Ph(Cl)Ge(C=C-^{*i*}Bu)[C(Al^{*i*}Bu₂)=C(H)-^{*i*}Bu] (**2b**, 0.32 g, 0.65 mmol) in toluene (15 mL) was stirred for 48 h at 50 °C. The solvent was removed *in vacuo* and the residue was recrystallized from 1,2-difluorobenzene (0.5 mL) at -45 °C to give colourless crystals of compound **5**. Yield: 0.22 g (69%). M.p.: 115 °C. Microanalysis: found C 63.8, H 8.6%; [C₂₆H₄₂AlClGe (489.65)] requires C 63.8, H 8.7%. ¹H NMR (C₆D₆, 400 MHz, 300 K): δ = 0.95 (s, 9H, C=CH-C*Me*₃), 1.12 (s, 9H, C=C-C*Me*₃), 1.38 (s, 9H, AlC*Me*₃), 1.39 (s, 9H, GeC*Me*₃), 7.09 (m, 1H, *p*-H), 7.17 (m, overlap, 2H, *m*-H), 7.33 (s, 1H, C=CH), 7.82 (d, 2H, ³*J*_{HH} = 7.3 Hz, *o*-H). ¹³C NMR (C₆D₆, 101 MHz, 300 K): δ = 18.1 (br., AlCMe₃), 29.3 (C=CH-C*Me*₃), 29.6 (GeC*Me*₃), 29.9 (C=C-C*Me*₃), 30 (difficult to assign unambiguously, GeCMe₃), 30.1 (C=C-CMe₃ and AlC*Me*₃), 37.5 (C=CH-CMe₃), 84.1 (GeC=C), 128.8 (*m*-C), 129.7 (*p*-C), 134.8 (*o*-C), 135.7 (GeC=C), 138.7 (*ipso*-C), 140.7 (GeC=C), 168.0 (GeC=C). IR (KBr plates, paraffin, cm⁻¹): 2158

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s, 2133 s v(C=C); 1948 w, 1881 w, 1813 w, 1759 vw, 1719 vw, 1645 w, 1601 w, 1557 s, 1506 m v(C=C), (phenyl); 1458 vs, 1369 vs (paraffin); 1303 w, 1250 vs $\partial(CH_3)$; 1198 vs, 1180 vs, 1088 s, 1007 s, 935 s, 891 s, 818 vs v(CC); 729 vs (paraffin); 698 vs, 671 s (phenyl); 581 vs, 469 s, 417 s v(GeC), v(AlC), v(AlCl), $\partial(CC)$. Mass spectrum (EI+, 20eV, 323 K): m/z (%): 315 (100) [M – ClAl^tBu₂ + H]⁺.

X-Ray crystallography

Crystals suitable for X-ray crystallography were obtained from cyclopentane (2a, 3), *n*hexane (1a, 1d, 2c), ethanol (99.6% without further purification; 1a) or 1,2difluorobenzene (1b, 2b, 2d, 2e, 5). Intensity data was collected on Bruker Quazar or D8-Venture diffractometers with monochromated Mo K_{α} radiation. The collection method involved ω scans. Data reduction was carried out using the program SAINT+.²⁴ The crystal structures were solved by Direct Methods using SHELXTL.^{25,26} Nonhydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on F^2 using SHELXTL.^{25,26} Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Molecular structures were drawn with the DIAMOND program package.²⁷ The crystals of 2a enclosed half a cyclopentane molecule per formula unit, which was disordered across a center of symmetry. The atoms were refined with occupancy factors of 0.5. A t Bu group (C51) of 2c was disordered; the atoms were refined on split positions (0.82 : 0.18). 2d crystallized with half a 1,2-difluorobenzene molecule per formula unit. It was disordered across a center of symmetry, and the fluorine atoms were refined with occupancy factors of 0.5. Two ^tBu groups of **3** were disordered (C02, C04) and refined on

Crystal data for Ph₂Ge(Cl)C=C-^{*t*}Bu **1a**: C₁₈H₁₉ClGe, M = 343.37, triclinic, a = 917.91(4) pm, b = 989.48(4) pm, c = 1028.82(4) pm, $\alpha = 79.784(1)^{\circ}$, $\beta = 66.568(1)^{\circ}$, $\gamma = 87.376(1)^{\circ}$, V = 0.84346(6) nm³, T = 153(2) K, space group $P\bar{1}$, Z = 2, μ (MoK α) = 1.963 mm⁻¹, 13810 reflections measured, 5002 independent reflections ($R_{int} = 0.023$). The final *R* values were $R_1 = 0.0266$ ($I > 2\sigma(I)$; 4488) and w $R(F^2) = 0.0654$ (all data). The goodness of fit on $F^2 = 1.081$.

Crystal data for PhGe(Cl)(C=C-^{*t*}Bu)₂ **1b**: C₁₈H₂₃ClGe, M = 347.40, monoclinic, a = 957.84(4) pm, b = 1280.35(6) pm, c = 1499.70(7) pm, $\beta = 90.530(3)^{\circ}$, V = 1.8391(1) nm³, T = 153(2) K, space group $P2_1/n$, Z = 4, μ (MoK α) = 1.801 mm⁻¹, 29822 reflections measured, 5146 independent reflections ($R_{int} = 0.044$). The final R values were $R_1 = 0.0307$ ($I > 2\sigma(I)$; 4218) and w $R(F^2) = 0.0755$ (all data). The goodness of fit on $F^2 = 1.057$.

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Crystal data for MesGe(Cl)(C=C-^{*t*}Bu)₂ **1c**: C₂₁H₂₉ClGe, M = 389.48, monclinic, a = 957.61(3) pm, b = 1248.25(5) pm, c = 1798.69(6) pm, $\beta = 91.0378(8)^{\circ}$, V = 2.1497(1) nm³, T = 153(2) K, space group $P2_1/n$, Z = 4, μ (MoK α) = 1.548 mm⁻¹, 30071 reflections measured, 5349 independent reflections ($R_{int} = 0.020$). The final R values were $R_1 = 0.0314$ ($I > 2\sigma(I)$; 4861) and w $R(F^2) = 0.0881$ (all data). The goodness of fit on $F^2 = 1.078$.

Crystal data for **2a**: C₂₆H₃₈AlClGe·0.5C₅H₁₀, M = 520.65, triclinic, a = 1132.57(5)pm, b = 1144.65(5) pm, c = 1290.22(6) pm, $\alpha = 86.604(1)^{\circ}$, $\beta = 72.707(1)^{\circ}$, $\gamma = 65.513(1)^{\circ}$, V = 1.4494(1) nm³, T = 100(2) K, space group $P\bar{1}$, Z = 2, μ (MoK α) = 1.192 mm⁻¹, 22581 reflections measured, 8364 independent reflections ($R_{int} = 0.026$). The

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final *R* values were $R_1 = 0.0312$ ($I > 2\sigma(I)$; 7168) and w $R(F^2) = 0.0770$ (all data). The goodness of fit on $F^2 = 1.059$.

Crystal data for **2b**: C₂₆H₄₂AlClGe, M = 489.61, triclinic, a = 1017.63(5) pm, b = 1072.59(5) pm, c = 1395.37(6) pm, $\alpha = 80.891(1)^{\circ}$, $\beta = 74.815(1)^{\circ}$, $\gamma = 89.831(1)^{\circ}$, V = 1.4502(1) nm³, T = 153(2) K, space group $P\bar{1}$, Z = 2, μ (MoK α) = 1.188 mm⁻¹, 20227 reflections measured, 7696 independent reflections ($R_{int} = 0.018$). The final R values were $R_1 = 0.0263$ ($I > 2\sigma(I)$; 7138) and w $R(F^2) = 0.0717$ (all data). The goodness of fit on $F^2 = 1.059$.

Crystal data for **2c**: C₂₉H₄₈AlClGe, M = 531.69, monoclinic, a = 1245.23(6) pm, b = 1597.02(8) pm, c = 1567.57(8) pm, $\beta = 90.140(2)^{\circ}$, V = 3.1174(3) nm³, T = 100(2) K, space group $P2_1/c$, Z = 4, μ (MoK α) = 1.110 mm⁻¹, 44968 reflections measured, 9122 independent reflections ($R_{int} = 0.200$). The final *R* values were $R_1 = 0.0458$ ($I > 2\sigma(I)$; 7750) and w $R(F^2) = 0.1374$ (all data). The goodness of fit on $F^2 = 1.061$.

Crystal data for **2d**: C₃₅H₆₀AlClGe·0.5C₆H₄F₂, M = 672.89, monoclinic, a = 944.42(4)pm, b = 2359.7(1) pm, c = 1770.27(8) pm, $\beta = 96.808(2)^{\circ}$, V = 3.9173(3) nm³, T = 153(2) K, space group $P2_1/c$, Z = 4, μ (MoK α) = 0.900 mm⁻¹, 57482 reflections measured, 9331 independent reflections ($R_{int} = 0.054$). The final R values were $R_1 = 0.0340$ ($I > 2\sigma(I)$; 7742) and w $R(F^2) = 0.0864$ (all data). The goodness of fit on $F^2 = 1.028$.

Crystal data for **2e**: C₂₆H₄₂ClGaGe, M = 532.35, triclinic, a = 1013.87(4) pm, b = 1068.16(4) pm, c = 1403.20(5) pm, $\alpha = 81.233(1)^{\circ}$, $\beta = 75.177(1)^{\circ}$, $\gamma = 89.661(1)^{\circ}$, V = 1.45103(9) nm³, T = 153(2) K, space group $P\bar{1}$, Z = 2, μ (MoK α) = 2.065 mm⁻¹, 23115 reflections measured, 9121 independent reflections ($R_{int} = 0.019$). The final R values

were $R_1 = 0.0265$ ($I > 2\sigma(I)$; 7706) and w $R(F^2) = 0.0707$ (all data). The goodness of fit on $F^2 = 1.041$.

Crystal data for **3**: C₄₄H₈₁ClGa₂Ge, M = 857.56, triclinic, a = 922.69 (9) pm, b = 1570.8(2) pm, c = 1690.8(2) pm, $\alpha = 89.192(3)^{\circ}$, $\beta = 79.211(3)^{\circ}$, $\gamma = 78.593(3)^{\circ}$, V = 2.3590(4) nm³, T = 153(2) K, space group $P\bar{1}$, Z = 2, μ (MoK α) = 1.849 mm⁻¹, 33665 reflections measured, 13669 independent reflections ($R_{int} = 0.036$). The final R values were $R_1 = 0.0476$ ($I > 2\sigma(I)$; 9327) and w $R(F^2) = 0.1222$ (all data). The goodness of fit on $F^2 = 1.010$.

Crystal data for **4b**: C₃₅H₆₁AlGe·0.5C₆H₄F₂, M = 638.45, triclinic, a = 1029.46(2) pm, b = 1123.23(2) pm, c = 1778.22(3) pm, a = 103.385(1), $\beta = 104.904(1)^{\circ}$, $\gamma = 94.404(1)$, V = 1.91261(6) nm³, T = 120(2) K, space group $P\bar{1}$, Z = 2, μ (MoK α) = 0.851 mm⁻¹, 30166 reflections measured, 9462 independent reflections ($R_{int} = 0.034$). The final Rvalues were $R_1 = 0.0382$ ($I > 2\sigma(I)$; 8255) and w $R(F^2) = 0.0985$ (all data). The goodness of fit on $F^2 = 1.033$.

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Crystal data for **5**: $C_{52}H_{84}Al_2Cl_2Ge_2$, M = 979.23, triclinic, a = 915.20(3) pm, b = 1122.50(4) pm, c = 1505.49(5) pm, $\alpha = 109.175(2)^\circ$, $\beta = 96.345(2)^\circ$, $\gamma = 100.563(2)^\circ$, V = 1.41156(9) nm³, T = 153(2) K, space group $P\bar{1}$, Z = 1, μ (MoK α) = 1.220 mm⁻¹, 17869 reflections measured, 8159 independent reflections ($R_{int} = 0.029$). The final R values were $R_1 = 0.0384$ ($I > 2\sigma(I)$; 6640) and w $R(F^2) = 0.0891$ (all data). The goodness of fit on $F^2 = 1.052$.

Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC– 1428775 to 1428785 (1a, – 1c, 2a – 2e, 3, 4a, 5).

Computational methods

The quantum chemical DFT calculations have been performed with the TURBOMOLE suite of programs.^{28,29} The structures are fully optimized at the TPSS-D3/def2-TZVP level of theory, which combines the accurate TPSS meta-GGA density functional³⁰ with the BJ-damped D3 dispersion correction 31,32 and the def2-TZVP basis set $^{33-35}$, using the density-fitting RI-J approach^{36,37} to accelerate the calculations. The optimized structures are characterized by frequency analysis at the same level of theory to identify the nature of located stationary points (no imaginary frequency for true minima and only one imaginary frequency for transition state) and to provide thermal corrections according to the modified ideal gas-rigid rotor-harmonic oscillator model.³⁸ Using the fully optimized geometries, the solvation free energies in toluene solvent are computed by the COSMO-RS solvation model in the COSMOtherm program package using the BP TZVP C30 1201.ctd parameter file,³⁹ while more reliable total electronic energies are computed at the TPSS-D3 and higher hybrid-meta PW6B95-D3⁴⁰ levels of theory together with the large def2-QZVP basis set.⁴¹ As expected, the TPSS-D3 method tends to slightly underestimate the reaction barriers but still shows very good agreement (mostly within 2 kcal mol) with the PW6B95-D3 methods for the relative energies. The final Gibbs free energies (ΔG) in toluene solvent are determined from the total electronic energies plus thermal corrections and COSMO-RS solvation free energies. In our discussion, the TPSS-D3 Gibbs free energies (in kcal mol⁻¹, at 298.15 K and 1 atm) will be used unless specified otherwise.

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Notes and references

Published on 19 November 2015. Downloaded by Washington University in St. Louis on 21/11/2015 20:10:47.

- (a) Frustrated Lewis Pairs, vol. I and II, in *Topics in Current Chemistry*, ed. G.
 Erker and D. W. Stephan, Springer, Heidelberg, Germany, 2013; (b) G. C.
 Welch, R. R. San Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124-1126; (c) D. W. Stephan and G. Erker, *Angew. Chem.*, 2010, **122**, 50-81, (*Angew. Chem. Int. Ed.*, 2010, **49**, 46-76).
- W. Uhl, J. Bohnemann, B. Kappelt, A. Hepp and M. Layh, *Dalton Trans.*, 2014,
 43, 14386-14398.
- W. Uhl, J. Tannert, M. Layh, A. Hepp, S. Grimme and T. Risthaus, *Organometallics* 2013, **32**, 6770-6779.
- 4 (a) W. Uhl, D. Heller, J. Kösters, E.-U. Würthwein and N. Ghavtadze, *Eur. J. Inorg. Chem.*, 2012, 1359-1368; (b) W. Uhl, D. Heller, M. Rohling and J.
 Kösters, *Inorg. Chim. Acta*, 2011, **374**, 359-365.
- 5 W. Uhl, J. Tannert, C. Honacker, M. Layh, Z.-W. Qu, T. Risthaus and S. Grimme, *Chem. Eur. J.*, 2015, **21**, 2638-2650.
- W. Uhl, J. Bohnemann, M. Layh and E.-U. Würthwein, *Chem. Eur. J.*, 2014, 20, 8771-8781.
- P. Riviere and M. Riviere-Baudet, in *Organometallic Synthesis* (ed. R. B. King, J. J. Eisch) Vol. 4, Elsevier, 1988.

- M. A. Chaubon, B. Dittrich, J. Escudié, H. Ramdane, H. Ranaivonjatovoo and J. Satgé, Synth. React. Inorg. Met.-Org. Chem., 1997, 27, 519-533.
- (a) W. Uhl, S. Pelties, J. Tannert, B. J. Ravoo and E.-U. Würthwein, *Chem. Eur. J.*, 2015, 21, 2629-2637; (b) W. Uhl, M. Rohling, E.-U. Würthwein, N.
 Ghavtadze and K. Bergander, *Organometallics*, 2010, 29, 5236-5240; (c) P. D.
 Ortiz, R. Suardiaz, L. de Vega, G. Hennrich and P. J. Ortiz, *J. Phys. Chem. A*, 2010, 114, 2939-2944; (d) E. Kleinpeter and A. Frank, *Terahedron*, 2009, 65, 4418-4421; (e) E. Kleinpeter and A. Schulenburg, *J. Org. Chem.*, 2006, 71, 3869-3875.
- Some arylgermanium derivatives for comparison: (a) K. V. Zaitsev, A. A.
 Kapranov, A. V. Churakov, O. Kh. Poleshchuk, Y. F. Oprunenko, B. N. Tarasevich, G. S. Zaitseva and S. S. Karlov, Organometallics, 2013, 32, 6500-6510; (b)
 R. D. Sweeder, K. A. Miller, F. A. Edwards, J. Wang, M. M. Banaszak Holl and
 J. W. Kampf, Organometallics, 2003, 22, 5054-5062; (c) C. R. Samanamu, C. R.
 Anderson, J. A. Golen, C. E. Moore, A. L. Rheingold and C. S. Weinert, J. Organomet. Chem., 2011, 696, 2993-2999; (d) D. Dakternieks, A. E. K. Lim, B.
 Zobel and E. R. T. Tiekink, Main Group Met. Chem., 2000, 23, 789-790; (e) Y.
 Sugiyama, T. Matsumoto, H. Yamamoto, M. Nishikawa, M. Kinoshita, T. Takei,
 W. Mori and Y. Takeuchi, Tetrahedron, 2003, 59, 8689-8696.
- W. Uhl, H. R. Bock, M. Claesener, M. Layh, I. Tiesmeyer and E.-U. Würthwein, *Chem. Eur. J.*, 2008, 14, 11557-11565.
- (*a*) W. Uhl, M. Rohling and J. Kösters, *New. J. Chem.*, 2010, **34**, 1630-1636; *(b)* W. Uhl, J. Bohnemann, B. Kappelt, K. Malessa, M. Rohling, J. Tannert, M.

Layh and A. Hepp, *Z. Naturforsch.*, 2014, **69b**, 1333-1347; *(c)* W. Uhl and J. Tannert, *Z. Naturforsch.*, 2015, **70b**, 115-118; references therein.

- W. Uhl, S. Pelties, M. Rohling and J. Tannert, *Eur. J. Inorg. Chem.*, 2014, 2809-2818.
- Few recent examples: Al-Cl-Al: (a) P. Henke and H. Schnöckel, Chem. Eur. J., 14 2009, **15**, 13391-13398; (b) A. Del Grosso, R. G. Pritchard, C. A. Muryn and M. J. Ingleson, Organometallics, 2010, 29, 241-249; (c) A. Hernán-Gómez, A. Martin, M. Mena and C. Santamaria, Inorg. Chem., 2010, 49, 8401-8410; Ga-Cl-Ga: (d) W. Uhl, M. Claesener, D. Kovert, A. Hepp, E.-U. Würthwein and N. Ghavtadse, Organometallics, 2011, 30, 3075-3082; (e) X. Tian, R. Fröhlich and N. W. Mitzel, Dalton Trans., 2005, 380-384; (f) S. M. Kilyanek, X. Fang, R. F. Jordan, Organometallics, 2009, 28, 300-305; Al-Cl-M: (g) K. Albahili, S. Gambarotta and R. Duchateau, Organometallics, 2011, **30**, 4655-4664; (h) I. Thapa, S. Gambarotta, I. Korobkov, R. Duchateau, S. V. Kulangara and R. Chevalier, Organometallics, 2010, 29, 4080-4089; (i) M. Ohashi, M. Ikawa and S. Ogoshi, *Organometallics*, 2011, **30**, 2765-2774; **Ga-Cl-M**: (*j*) H.-W. Lerner, I. Sänger, F. Schödel, M. Bolte and M. Wagner, Z. Naturforsch., 2011, 66b, 695-699; (k) C. J. Durango-Garcia, J. O. C. Jimenez-Halla, M. Lopez-Cardoso, V. Montiel-Palma, M. A. Munoz-Hernandez and G. Merino, Dalton Trans., 2010, 10588-10589; (1) T. Adamczyk, G.-M. Li, G. Linti, H. Pritzkow, A. Seifert and T. Zessin, Eur. J. Inorg. Chem., 2011, 3480-3492; Si-Cl-Al: (m) U. Klingebiel, M. Noltemeyer, H.-G. Schmidt and D. Schmidt-Bäse, Chem. Ber./Recueil, 1997, 130, 753-755; (n) J. Niesmann, U. Klingebiel, C. Röpken, M. Noltemeyer and R. Herbst-Irmer, Main Group Chemistry, 1998, 2, 297-308.

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- M. Rohde, L. O. Müller, D. Himmel, H. Scherer and I. Krossing, *Chem. Eur. J.*,
 2014, 20, 1218-1222.
- 16 W. Uhl, Z. Anorg. Allg. Chem., 1989, 570, 37-53.
- (a) D. C. McKean, M. W. McKenzie and A. R. Morrison, J. Mol. Struct., 1984,
 116, 331-344; (b) X. Wang, L. Andrews and G. P. Kushto, J. Phys. Chem. A,
 2002, 106, 5809-5816; (c) P. Lepage, J.-P. Champion and A. G. Robiette, J.
 Mol. Spectrosc., 1981, 89, 440-448; (d) A. E. Tomosada, S. Kim, Y. Osamura,
 S. W. Yang, A. H. H. Chang and R. I. Kaiser, Chem. Phys., 2012, 409, 49-60;
 (e) N. W. Mitzel, U. Losehand, S. L. Hinchley and D. W. H. Rankin, Inorg.
 Chem., 2001, 40, 661-666.
- Synthesis and few structures of Ge-H compounds: (a) J. A. Cooke, C. E. Dixon, M. R. Netherton, G. M. Kolleger and K. M. Baines, Synth. React. Inorg. Met.-Org. Chem., 1996, 26, 1205-1217; (b) K. Oshima, in Houben Weyl, 5 (ed. M. G. Moloney), Science of Synthesis, Organometallics, Compounds of Group 14, Thieme Verlag, 2003; (c) J. B. Lambert, C. L. Stern, Y. Zhao, W. C. Tse, C. E. Shawl, K. T. Lentz and L. Kania, J. Organomet. Chem., 1998, 568, 21-31; (d) C. H. Yoder, T. M. Agee, A. K. Griffith, C. D. Schaeffer (Jr.), M. J. Carroll, A. S. DeToma, A. J. Fleisher, C. J. Gettel and A. L. Rheingold, Organometallics, 2010, 29, 582-590; (e) Z. D. Brown, P. Vasko, J. C. Fettinger, H. M. Tuononen and P. P. Power, J. Am. Chem. Soc., 2012, 134, 4045-4048; (f) A. Kawachi, Y. Tanaka and K. Tamao, Organometallics, 1997, 16, 5102-5107; (g) C. R. Samanamu, C. R. Anderson, J. A. Golen, C. E. Moore, A. L. Rheingold and C. S. Weinert, J. Organomet. Chem., 2011, 696, 2993-2999; (h) G. S. McGrady, M. Odlyha, P. D. Prince and J. W. Steed, CrystEngComm., 2002, 4, 271-276.

Dalton Transactions Accepted Manuscript

- M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer and D. G. Truhlar, J.
 Phys. Chem. A, 2009, **113**, 5806-5812.
- Silyl or germyl cations are highly reactive; persistent compounds have been reported in few cases; selected references: (a) T. Müller, Adv. Organomet. Chem., 2005, 53, 155-215; (b) H. F. T. Klare and M. Oestreich, Dalton Trans., 2010, 39, 9176-9184; (c) J. B. Lambert, Y. Zhao, H. Wu, W. C. Tse and B. Kuhlmann, J. Am. Chem. Soc., 1999, 121, 5001-5008; (d) A. Schäfer, M. Reißmann, S. Jung, A. Schäfer, W. Saak, E. Brendler and T. Müller, Organometallics, 2013, 32, 4713-4722; (e) M. Reißmann, A. Schäfer, S. Jung and T. Müller, Organometallics, 2013, 32, 6736-6744; (f) Y. Xiong, S. Yao, S. Inoue, J. D. Epping and M. Driess, Angew. Chem., 2013, 125, 7287-7291; (Angew. Chem. Int. Ed., 2013, 52, 7147-7150); (g) C. Schenk, C. Drost and A. Schnepf, Dalton Trans., 2009, 173-776; (h) A. Schäfer, W. Saak, D. Haase and T. Müller, Chem. Eur. J., 2009, 15, 3945-3950; (i) donor stabilized germyl cations: V. N. Khrustalev, I. A. Portnyagin, I. V. Borisova, N. N. Zemlyansky, Y. A. Ustynyuk, M. Yu. Antipin, M. S. Nechaev, Organometallics, 2006, 25, 2501-2504.
- (a) M. T. Reetz, Angew. Chem., 1972, 84, 161-162, (Angew. Chem. Int. Ed. Engl., 1972, 11, 129-130); (b) I. Fernandez, F. P. Cossio and M. A. Sierra, Chem. Rev., 2009, 109, 6687-6711; (c) M. F. Croisant, R. van Hoveln and J. M. Schomaker, Eur. J. Org. Chem., 2015, 5897-5907.
- W. Uhl, L. Cuypers, R. Gaupner, J. Molter, A. Vester and B. Neumüller, Z.
 Anorg. Allg. Chem., 2001, 627, 607-614.
- (a) W. Seidel and I. Bürger, Z. Anorg. Allg. Chem., 1978, 447, 195-198; (b) W. J.
 Kerr, A. J. B. Watson and D. Hayes, Org. Biomol. Chem., 2008, 6, 1238-1243;

(c) J. Langer, S. Krieck, R. Fischer, H. Görls, D. Walther and M. Westerhausen, Organometallics, 2009, 28, 5814-5820.

- 24 (a) Saint+; Version 6.02 (includes Xprep and Sadabs), Bruker AXS INC., Madison, Wisconsin, USA, 1999; (b) G. M. Sheldrick, SADABS, University of Göttingen, Germany, 1996.
- 25 (a) Shelxtl-Plus, REL. 4.1; Siemens Analytical X-RAY Instruments Inc.: Madison, WI, 1990; (b) G. M. Sheldrick, SHEXL-97 and SHELXL-2013, Program for the Refinement of Structures; Universität Göttingen, Germany, 1997 and 2013.
- 26 G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122.
- K. Brandenburg, H. Putz and M. Berndt, DIAMOND 3.2i, Crystal Impact GbR, Bonn, 1999.
- 28 R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel, *Chem. Phys. Lett.* 1989, 162, 165-169.
- R. Ahlrichs, M. K. Armbruster, R. A. Bachorz, M. Bär, H.-P. Baron, R.
 Bauernschmitt, F. A. Bischoff, S. Böcker, N. Crawford, P. Deglmann, F. D.
 Sala, M. Diedenhofen, M. Ehrig, K. Eichkorn, S. Elliott, F. Furche, A. Glöß, F.
 Haase, M. Häser, C. Hättig, A. Hellweg, S. Höfener, H. Horn, C. Huber, U.
 Huniar, M. Kattannek, W. Klopper, A. Köhn, C. Kölmel, M. Kollwitz, K. May,
 P. Nava, C. Ochsenfeld, H. Öhm, M. Pabst, H. Patzelt, D. Rappoport, O. Rubner,
 A. Schäfer, U. Schneider, M. Sierka, D. P. Tew, O. Treutler, B. Unterreiner, M.
 von Arnim, F. Weigend, P. Weis, H. Weiss, and N. Winter, *TURBOMOLE v6.4*,

- J. M. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*,
 2003, **91**, 146401.
- S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. 2010, 132, 154104.
- 32 S. Grimme and L. Goerigk, J. Comput. Chem., 2011, **32**, 1456-1465.
- 33 F. Weigend, Phys. Chem. Chem. Phys., 2006, 8, 1057.
- 34 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297-3305.
- A. Klamt and G. Schüürmann, J. Chem. Soc. Perkin Trans., 1993, 2, 799.
- 36 K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, 97, 119.
- P. Deglmann, K. May, F. Furche and R. Ahlrichs, *Chem. Phys. Lett.*, 2004, 384, 103.
- 38 S. Grimme, *Chem. Eur. J.*, 2012, **18**, 9955.

- F. Eckert and A. Klamt, *COSMOtherm*, Version C3.0, Release 14.01;
 COSMOlogic GmbH & Co. KG, Leverkusen, Germany, 2013.
- 40 Y. Zhao and D.G. Truhlar, J. Phys. Chem. A, 2005, 109, 5656.
- 41 F. Weigend, F. Furche and R. Ahlrichs, J. Chem. Phys., 2003, 119, 12753.

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Table 1. Selected bolid lengths (pii) and angles () of compounds $1 = 3$.											
	1 a	1b	1c	2a	2b	2c	2d	2e	3	4b	5
Ge-Cl	217.15(4)	215.93(5)	218.13(5)	233.13(4)	232.85(3)	234.00(5)	237.89(5)	227.34(3)	229.60(8)	_	_
Ge-C(≡C)	188.2(1)	188.1(av)	188.4(av)	-	187.6(1)	188.8(2)	189.1(2)	188.2(1)	-	197.0(2)	194.1(2)
Ge-C(Ar)	192.4(1)	192.8(2)	193.8(2)	193.2(av)	192.0(1)	194.2(2)	195.8(2)	192.5(1)	195.1(3)	196.7(2)	195.5(2)
Ge-C(=C)	_	-	-	192.3(1)	191.2(1)	192.7(2)	192.8(2)	191.3(1)	193.9(3)	193.9(2)	196.1(2)
M-Cl	_	_	_	241.50(6)	243.25(5)	243.14(7)	243.58(7)	263.01(4)	265.08(8)	_	227.41(7) 236.80(6)
C-Ge-Cl ^a	_	-	-	89.89(4)	90.17(4)	89.65(5)	89.03(6)	93.37(4)	92.27(9)	-	_
C-M-Cl ^a	_	-	-	85.82(4)	85.30(4)	85.27(6)	85.84(5)	81.30(4)	80.89(8)	-	_
M-C-Ge ^a	_	-	-	103.35(7)	103.92(6)	103.83(8)	104.44(9)	106.19(6)	106.8(1)	100.81(8)	113.25(9)
M-Cl-Ga ^a	_	-	-	80.74(2)	80.54(1)	80.91(2)	80.27(2)	79.05(1)	79.20(2)	-	—
d ^b	_	-	-	4(C)	2(C)	5(C)	5(C)	3(C)	8(C)	13(C)	—
$Ge \cdots C_3^{\ c}$	58	54	48	23	24	24	24	30	29	64	_
$\sum \text{GeC}_2^d$	333.5	336.9	341.7	355.6	355.3	355.2	355.4	352.6	353.1	327.4	_

Table 1. Selected bond lengths (pm) and angles (°) of compounds 1-5

^aGeCIMC heterocycle; endocyclic angles ^bmaximum distance of an atom from the average GeCIMC plane ^cdistance of the Ge atom from the average plane of the directly bonded C atoms

^dsum of the angles C-Ge-C

Graphical Abstract:

Functionalized Alkynyl-chlorogermanes: Hydrometallation, Ge-Cl Bond Activation, Ge-H Bond Formation and Chlorine-*tert*-Butyl Exchange *via* a Transient Germyl Cation

Christian Honacker, Zheng-Wang Qu, Jens Tannert, Marcus Layh, Alexander Hepp, Stefan Grimme, and Werner Uhl

Hydroalumination of an alkynyl-chlorogermane afforded an alkenylgermane in which the Ge-Cl bond is activated by an Al-Cl interaction. Heating resulted in a ^{*t*}Bu/Cl exchange and the formation of an Al-Cl species *via* a transient germyl cation.

'Bu 'Bu н ∕Bu **Ge-Cl** activation germyl cation solution DFI