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Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

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DOI: 10.1039/C7CC06622H

Journal Name

COMMUNICATION

Targeted Attachment of Functional Groups at Ge_9 Clusters *via* Silylation Reactions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Molecules with low-valent Ge atoms are generally synthesized from organohalogen germanes as precursors. The Zintl phase K_4Ge_9 provides reactive building blocks for a targeted synthesis of germanium-rich molecules. Silylation of chlorosilanes $ClSiR_2R'$, that carry unsaturated olefin groups R', with Ge_9 clusters leads to the introduction of olefinic side chains of variable lengths allowing for further reactions. The compounds $K[Ge_9\{Si(SiMe_3)_3\}_2(SiPh_2R')]$ (R' = $–CH=CH_2$ (1); $–(CH_2)_3CH=CH_2$ (2)) carry one such functionality, whereas $K[Ge_9(SiPh_2R')_3]$ (3, 4) offer the possibility for an interconnection of clusters due to three functional groups on the Ge_9 core. XPS measurements show that the silylated clusters are much more air-stable than the unsubstituted, bare cluster units.

Since the pioneering work of *Sekiguchi* and *Sakurai* in the synthesis of a Ge_6 prismane cage stabilized by bulky bis(trimethylsilyl)methyl groups[1] many other germane cage compounds of the general formula Ge_nR_m (n = 4, 5, 6, 8, 10, 14; $n > m$) have been isolated.[2] The synthetic protocol generally follows a reductive elimination of halogen atoms from organohalogen germanes. For n = 10 (ref. 3, 4) and 14 (ref. 5) four and nine Ge atoms, respectively, that are not connected to a ligand group, are present. [6] Bare anionic clusters Ge_n with n = 9 are easily accessible by reacting the soluble binary compounds A_4Ge_9 and $A_{12}Ge_{17}$ (A = heavier alkali metal), which then can act as building blocks in further reactions.[2, 7-10] The treatment of these units with organometallic compounds revealed a multifaceted chemistry including a large number of transition metal complexes such as $[Ge_9\text{-}Ni(CO)]^{3-}$.[11] Examples in which low oxidation states are stabilized, and which even contain an unsupported Zn−Zn bond, like in-$[Ge_9–Zn–Zn–Ge_9]^{6-}$,[12] have been realized as well as endohedrally filled clusters with deltahedral shape, $[Ni@Ge_9]^{3-}$,[11] or the non-deltahedral $[Co@Ge_{10}]^{3-}$ (ref. 13). Larger clusters such as $[Pd–Pd@Ge_{18}]^{4-}$,[14] oligomeric $[Ge_9{}^{2-}]_m$ (m = 2, 3, 4)[15-20] or pentameric $[Au_3Ge_{45}]^{9-}$ (ref. 21) are formed upon oxidation. Such interconnected Ge systems are considered as first steps in the formation of possible new Ge allotropes built up by Ge_9 clusters.[22] Only recently the link from bare anionic Zintl clusters to functionalized germane cage compounds was realized by silylation with the rather bulky $Cl\{Si(SiMe_3)_3\}_3$. The resulting $[Ge_9\{Si(SiMe_3)_3\}_3]^-$ can be obtained from K_4Ge_9 in good yields,[23] although it was for the first time synthesized using Ge(I)Br as precursor.[24] Since then a fruitful chemistry has been built up around this class of compounds. The reaction with organometallic compounds or salts leads to several complexes in which the silylated cluster acts as a ligand. With group 9 and 10 elements dimeric compounds $[M[Ge_9\{Si(SiMe_3)_3\}_3]_2]^{x-}$ (M = Zn, Cd, Hg, x = 0; M = Cu, Ag, Au, x = 1) can be obtained[25, 26], but also compounds in which the cluster replaces only one of the ligands are existent, like $[Ge_9\{Si(SiMe_3)_3\}_3Cr(CO)_5]^-$,[27] $[Ge_9\{Si(SiMe_3)_3\}_3]ZnCp^*$,[28] or the neutral Zintl cluster coinage metal *N*HC compounds $[(M–NHC)Ge_9\{Si(SiMe_3)_3\}_3]$.[29] The reaction of K_4Ge_9 with TMS-C≡C-TMS leads to the mono and bis-vinylated species $[Ge_9(CH=CH_2)]^{3-}$ and $[Ge_9(CH=CH_2)_2]^{2-}$, respectively, which can be obtained in good yields, and derivatives of this compound with different side chains as e.g. $[Ge_9(CH=CH\text{-}CH(CH_2)_2]^-$ are also known.[30-35] The linkage of two Ge_9 clusters through a conjugated π system was realized in the Zintl triade $[RGe_9–CH=CH–CH=CH–Ge_9R]^{4-}$ (R=(2Z,4E)-7-amino-5-aza-hepta-2,4-dien-2-yl),[36, 37] and also the bridging of two silylated cluster units *via* a bis-silyl group was successful, leading to the recently reported compound $K_2[\{Si(SiMe_3)_3\}_3Ge_9\text{-}SiMe_2\text{-}(C_6H_4)\text{-}SiMe_2\text{-}Ge_9\{Si(SiMe_3)_3\}_3]$.[38] The hypersilyl group $[Si(SiMe_3)_3]^+$ provides a high stability for tris-silylated compounds. With the chloro-silane derivatives $ClSiR_3$ (R = Ph, *i*Bu, *i*Pr, Et, ClSiH*t*Bu$_2$) also sterically less demanding groups can be introduced,[28, 39, 40] resulting in the bis-silylated[41] compounds $(K\text{-}18c6)_2[Ge_9\{Si(iBu)_3\}_2]$[39] and $[(CuPiPr_3)_4\{Ge_9(SiPh_3)_2\}_2]$.[28]

The silylated clusters being saturated and the vinyl derivatives being still highly charged did not allow - besides forming metal complexes - for a systematic development of synthetic protocols for subsequent reactions. Taking advantage of the stabilization of

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Electronic supplementary information (ESI) available: Experimental details, crystallographic details, XPS study details, ESI-MS spectra, NMR spectra, IR- and Raman spectra. CCDC 1569447 (1) 1569446 (2). See DOI: 10.1039/x0xx00000x

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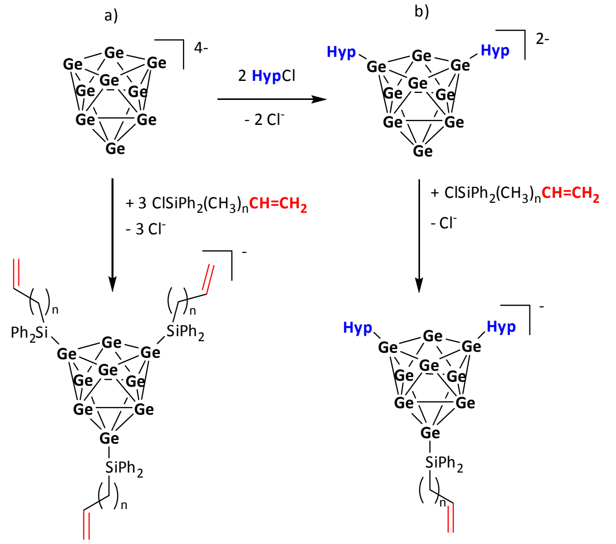
DOI: 10.1039/C7CC06622H

clusters with silyl substituents we intended now to introduce side chains with reactive double bonds *via* silylation (Scheme 1).

Here we describe the reaction of $[Ge_9]^{4-}$ and $[Ge_9\{Si(SiMe_3)_3\}_2]^{2-}$ (ref. 41) with the chlorosilanes $ClSiPh_2CH{=}CH_2$ and $ClSiPh_2(CH_2)_3CH{=}CH_2$ to afford the target molecules with functions either for cluster interconnection or for immobilization of cluster units on surfaces.

The reaction of the bis-silylated cluster $[Ge_9\{Si(SiMe_3)_3\}_2]^{2-}$ with $ClSiPh_2CH{=}CH_2$ in tetrahydrofuran (thf) or acetonitrile (acn) leads to the formation of a mixed silylated cluster[41] $K[Ge_9\{Si(SiMe_3)_3\}_2(SiPh_2CH{=}CH_2)]$ (**1**) with two hypersilyl groups and one vinylated silyl group. NMR investigations showed that the reaction is stoichiometric and proceeds quantitatively.

ESI-MS, Raman- and IR spectroscopy (Supporting Information) confirmed the composition of the product (**1**), and yellow needle-shaped crystals of **1**$\cdot(Tol)_{1.23}$ have been obtained from toluene. The crystals contain two crystallographically independent cluster units, with only slightly different bond lengths and angles. Both Ge_9 cluster cores possess slightly distorted C_s symmetry,[42] as shown by three very different prism heights (average values for both clusters: h_1 = 3.07 Å, h_2 = 3.30 Å, h_3 = 3.79 Å). However, a relation to C_{2v} symmetry is still existing, since there is a "square base" with a smaller α_1 angle (average value: 16.2°). Interestingly, this side is not located between the two hypersilyl groups like in the bis-silylated precursor,[41] but lies between one hypersilyl group and the vinylated silyl substituent. The Ge–Si bond lengths are unaffected by the substituents and range from 2.372(2) to 2.395(2) Å. The C-C double bonds with 1.289(12) Å resp. 1.307(13) Å are in the normal range. For instance, the vinyl groups of the bis-vinylated clusters range between 1.21–1.34 Å.[30]



Scheme 1: Reaction pathways for the attachment of olefin functionalities at Ge_9 clusters by reaction with with $ClSiR_2R'$ [R' = $-CH{=}CH_2$; $-(CH_2)_3CH{=}CH_2$] chloro-silanes a) Silylation of $[Ge_9]^{4-}$ with three $ClSiR_2R'$ groups under formation of a tris-functionalized species. b) Silylation step on $[Ge_9\{Si(SiMe_3)_3\}_2]^{2-}$ resulting in a mixed tris-silylated Ge_9 species with the olefin functionality on one silyl group group (Hyp = $[Si(SiMe_3)_3]$).

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Furthermore, the structure shows that the vinyl group at the silyl substituent should be accessible for further reactions despite the presence of the bulky hypersilyl groups (Figure 1a). However, to improve the accessibility of the double bond, a longer alkenyl group should be advantageous. Therefore, a pentenyl rest was attached on the silyl group. The reaction of the chloro-silane $ClSiPh_2(CH_2)_3CH{=}CH_2$ with the bis-silylated cluster in thf or acn leads to the formation of $K[Ge_9\{Si(SiMe_3)_3\}_2(SiPh_2(CH_2)_3CH{=}CH_2)]$ (**2**). The product was characterized by ESI-MS, NMR, Raman and IR spectroscopy (Supporting Information). Red plate-shaped crystals of the composition **2**$\cdot$(thf) were obtained from a toluene solution (Figure 1b). The symmetry of the Ge_9 cluster core is again C_s, but with a stronger relation to C_{2v} than in compound **1**, since the two regarding prism heights are more similar (h_1 = 3.146(1) Å, h_2 = 3.249(1) Å, h_3 = 3.733(1) Å); the "square base" with the lowest α_1 angle (17.0°) is again situated between one hypersilyl and the new silyl group. The Ge−Si bond of the pentenyl silyl group is slightly shorter than that of the hypersilyl groups: 2.367(2) Å vs. 2.372(2) Å and 2.373(2) Å, respectively. The double bond of the pentenyl substituent is with 1.206(17) Å quite short, probably as a result of the relatively large displacement ellipsoid of the "dangling", end-standing C atom.

In the crystal structures of **1** and **2** (for details see Supporting Information) the functionalized clusters are arranged in one-dimensional strands: The clusters are connected *via* the counter ion K, which also coordinates to one phenyl ring of the functionalized silyl group and to a solvent molecule.

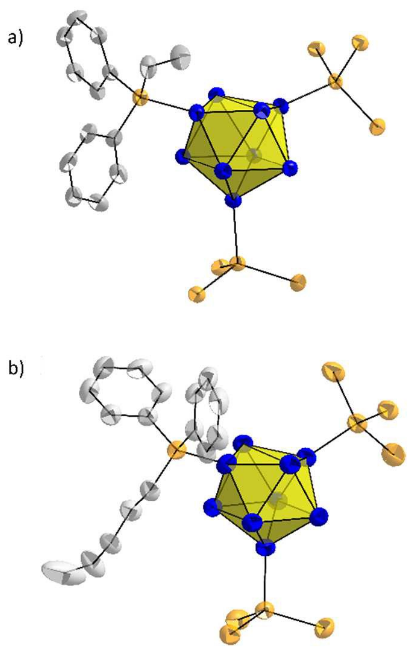

Figure 1: Molecular structures of the cluster anions of compound **1** (a) and **2** (b). Ge atoms are in blue, Si atoms in orange and C atoms in grey, displacement ellipsoids are shown at a probability level of 50%. $[Ge_9]$ is shown as polyhedron. For reasons of clarity H atoms and methyl groups at the hypersilyl units are omitted.

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We performed X-ray photoelectron spectroscopy (XPS) studies on **1** and **2**, i.a. in order to get an idea about the air sensitivity of these compounds (for data of 2 see Supporting Information). As a reference, we used the rather sensitive K_4Ge_9. Both species, the silylated cluster and the bare cluster compound, were sputtered with Ar^+ before the first XPS measurement. K_4Ge_9 is characterized by a Ge $2p_{3/2}$ core level peak that still shows conspicuous components related to oxidized Ge (Ge^{II}, Ge^{IV}), while the main peak component of the silylated compounds is related to non-oxidized Ge. We conclude that the compounds mainly consist of Ge^0 with only small amounts of germanium oxides (for the ratios of all species see Supporting Information). After an exposition of the cluster compounds to air for 30 min the Ge signals of K_4Ge_9 had disappeared, accompanied by an increase of the K and the O signals; this hints for a complete oxidation and decomposition of the compound and a dense potassium oxide layer covering the surface. The silylated compounds, however, are significantly more air-stable. The oxide fractions increased slightly, but the main species is still Ge^0 (Figure 2). This points out that the silylated compounds have an enhanced stability on air than the bare Ge_9 clusters, which raises their potential as candidates for further applications even in oxygen- and moisture-containing environments.

The longer pentenyl group of compound **2** promises a better accessibility of the double bond at the cluster, but the introduction of smaller substituents than phenyl at the silyl groups would be a step in the same direction. Therefore, $[Ge_9\{Si(SiMe_3)_3\}_2]^{2-}$ was treated with $ClSiMe_2CH{=}CH_{2,}$ and we obtained $K[Ge_9\{Si(SiMe_3)_3\}_2(SiMe_2CH{=}CH_2)]$ with sterically less demanding methyl groups on the vinylated silyl substituent. (see Supporting Information) The formation of the product proceeds analogously to **1** and **2**, as shown by ESI-MS and NMR experiments, whereas the crystallization of the product has not been successful so far. Further, less bulky substituents than hypersilyl at the cluster could also enhance the accessibility of the double bond. The reaction of a bis-silylated cluster equipped with tri-phenyl-silyl groups, $[Ge_9\{SiPh_3\}_2]^{2-}$,[28] with $ClSiPh_2CH{=}CH_2$ leads to the formation of the mixed cluster $K[Ge_9(SiPh_3)_2(SiPh_2CH{=}CH_2)]$, indicating that this type of reaction is not limited to the sterically demanding hypersilyl groups. The anion was characterized by ESI-MS, and as a side product the tris-silylated clusters $[Ge_9\{SiPh_3\}_3]^-$ and $[Ge_9(SiPh_3)(SiPh_2CH{=}CH_2)_2]^-$ were observed.

The formation of compounds **1** and **2** show that a targeted introduction of one or two functional groups on the Ge_9 clusters is possible which opens the possibility for immobilization of such units on surfaces or to interconnect such clusters. To build up three-dimensional Ge_9 networks, however, more functional groups would be useful. For this reason, we synthesized clusters with a double bond at each of the three silyl groups of the tris-silylated cluster. The reaction of three equivalents of $ClSiPh_2CH{=}CH_2$ or $ClSiPh_2(CH_2)_3CH{=}CH_2$ with K_4Ge_9 in acn or thf led to the formation of red solutions, and the tris-silylated clusters in $K[Ge_9(SiPh_2CH{=}CH_2)_3]$ (**3**) and $K[Ge_9(SiPh_2(CH_2)_3CH{=}CH_2)_3]$ (**4**) could be identified *via* ESI-MS (Figure 3).

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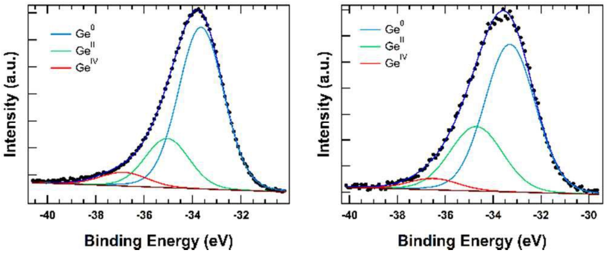

Figure 2: XP spectra in the Ge 3d region of compound **1** after sputtering (left) and after exposure to air for 30 min (right).

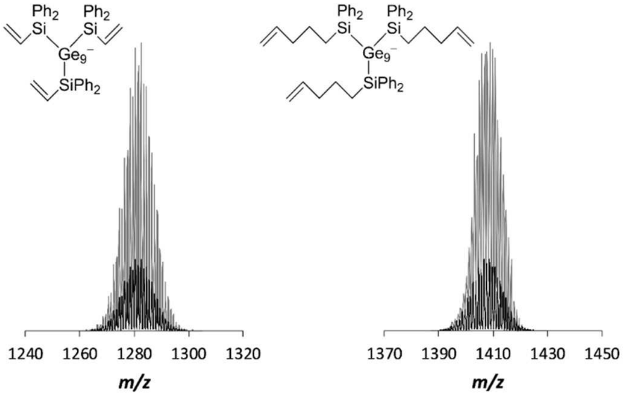

Figure 3: ESI-MS spectra of solutions of **3** (left, *m/z* = 1282 $[Ge_9(SiPh_2CH{=}CH_2)_3]^-$) and **4** (right, *m/z* = 1408 $[Ge_9\{SiPh_2(CH_3)_3CH{=}CH_2\}_3]^-$).

NMR spectroscopy showed that the reactions proceeded quantitatively, no side products were detected. The obtained products are stable in solution, however, the crystallization of the compounds has not been successful as yet. Since there is only one set of signals for the silyl groups in the NMR spectra, indicative for three magnetically identical groups, a similar structure as found for other tris-silylated clusters with the three groups attached at the caps of the trigonal prism can be assumed.

The presented compounds fulfill many demands for various applications. They allow access to clusters with a localized double bond (compound **1** and **2**) by adding functionalized silyl groups with side chains of different lengths on a bis-silylated cluster. Those cluster species are ideal for controlled reactions with one double bond or for an immobilization of the clusters on surfaces. Especially the enhanced air-stability qualifies them to test them for further applications. Moreover, the compounds **3** and **4** with three functional groups on one cluster can be obtained. They are perfect for the potentially formation of Ge_9 cluster networks. In order to further improve the accessibility of the olefin chains, first strategies to decrease the steric demand of the olefin chains are presented.

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DOI: 10.1039/C7CC06622H

Acknowledgement. Supported by Deutsche Forschungsgemeinschaft (DFG) within the International Research Training Group 2022 (ATUMS), the TUM International Graduate School of Science and Engineering (IGSSE). The authors thank Dr. Wilhelm Klein for support in crystallographic questions, Sebastian Geier for Raman and David Mayer for IR measurements.

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