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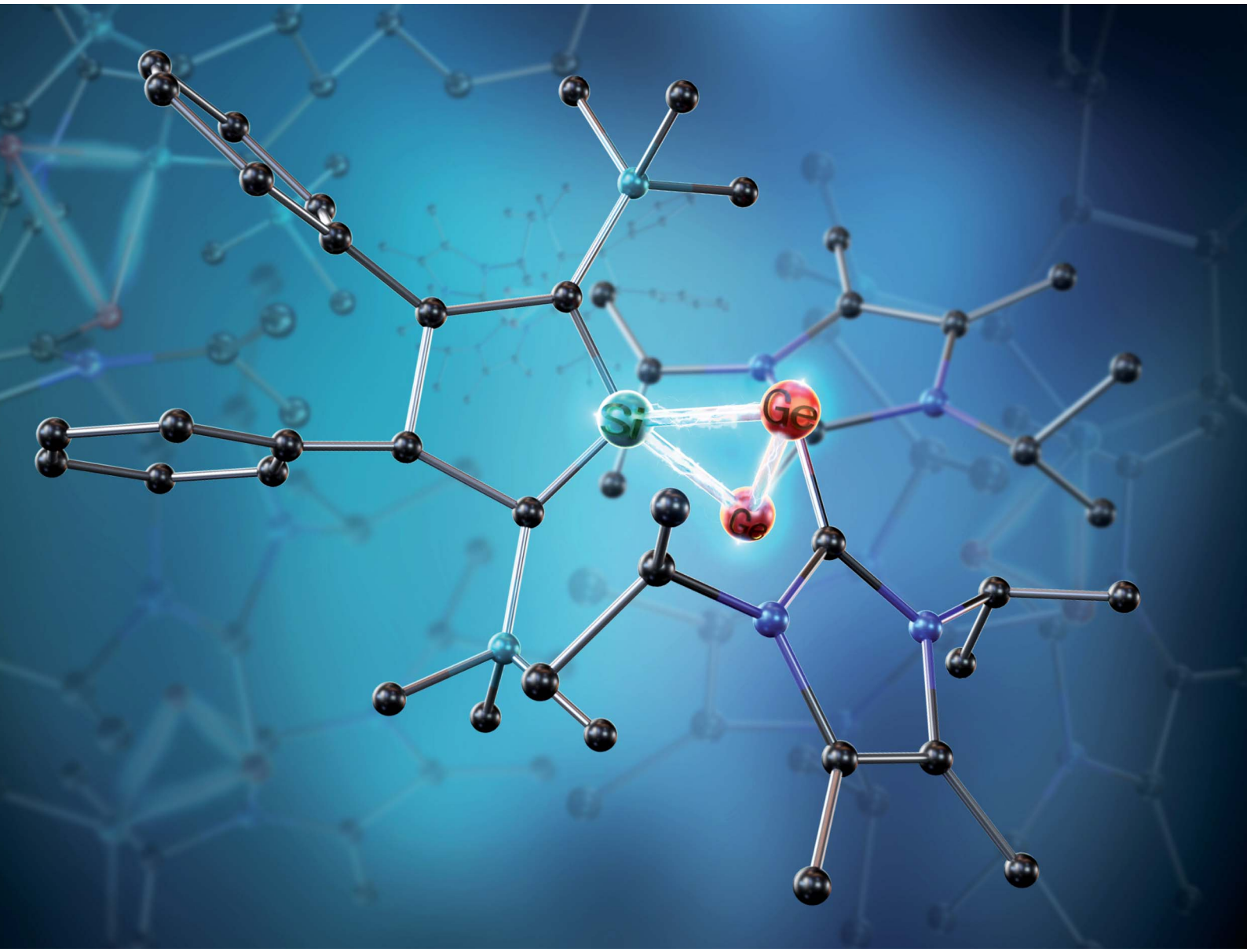

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Three-membered cyclic digermylenes stabilised by an N-heterocyclic carbene†

Zhaowen Dong, [ab] Jan Mathis Winkler,[a] Marc Schmidtmann[a] and Thomas Müller *[a]

Treatment of potassium salts of silole dianions with donor stabilised germanium dichlorides gave the anticipated silagermafulvenylidenes R_2Si = Ge(Do) (R_2Si = 1-silacyclopentadiendiyl, Do = N-heterocyclic carbene (NHC)) only as transient intermediates in a side reaction. They were detected by NMR spectroscopy and, in one case, the formal dimer, 2,4-disila-1λ^3,3λ^3-digermetane, was isolated. The main products of these reactions are sila-bis-λ^3-germiranes, *i.e.* directly interconnected digermylenes that are part of a three-membered ring. The structural data, supported by the results of density functional calculations confirm the digermylene nature of these products with a long inner cyclic Ge–Ge bond that decreases the inherent high ring strain in silagermiranes.

Introduction

The unusual reactivity of compounds with low-coordinated main group elements has triggered intensive research and a great number of investigations over the last 20 years.[1,2] The addition of dihydrogen under ambient conditions to a digermyne[3] provided the blueprint for many follow-up reactivity studies on main group compounds including carbene analogues,[4–10] heteroalkenes and heteroalkynes,[11–14] and frustrated Lewis pairs.[15–18] Heavy vinylidenes **III**, as the formal fusion of carbene analogues **I** and heteroalkenes **II**, are, in view of their expected high reactivity, particularly interesting synthetic targets (Fig. 1). Several groups have recently reported the successful synthesis of selected examples of heavy vinylidenes **III** (Fig. 1) that include donor-stabilised (**V–VII**)[19–22] and not-complexed species (**IV**).[23]

Reduction of germanium(II) halides provides a synthetic route to dicoordinated digermanium compounds that are isomers of digermenylidenes **VIII**.[24–27] These germanium dimers with Ge in the formal oxidation state (+I) exist in two valence isomeric forms, digermynes **IX** and digermylenes **X** (Fig. 2).[28,29] The digermylene isomer **X** is preferred when the substituent R is a multidentate ligand.[30–39]

Following previous investigations from our laboratory,[40] we probed the potential of salt metathesis of group 14 element dianions **XI** with group 14 element dihalides **XII** followed by 1,2-elimination for the synthesis of heavy vinylidenes **III** (Fig. 3). In contrast to our expectations, two single salt metathesis reactions occurred and the isolated products after subsequent reduction by the excess dianion were cyclic ditetrylenes **XIII**.

Results and discussion

The starting materials of choice for us were silole dianions[41] and germanium dichloride stabilised by N-heterocyclic carbenes (NHC).[42,43] The reaction of dipotassium silacyclopentadiendiides K_2[**1**] with NHC-stabilised dichlorogermylene **2** gave the 3-sila-1λ^3,2λ^3-digermiranes **5** as main products (Scheme 1). Deep green crystals of siladigermiranes **5** were obtained by recrystallization from diethyl ether at −30 °C in 23% (**5a**) and 64% (**5b**) yields. Both spiro-heterocycles were characterised by NMR and UV spectroscopy, MS spectrometry and X-ray diffraction analysis (XRD) of suitable single crystals. ^{29}Si NMR data of siladigermiranes **5** are unremarkable and compare well with

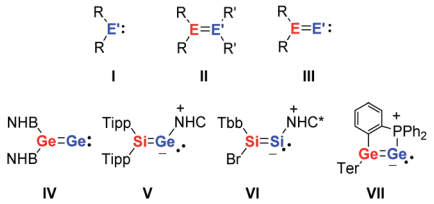

Fig. 1 Carbene analogues **I**, heteroalkenes **II**, heavy vinylidenes **III** (E, E′ = Si, Ge) and some examples of isolable sila- and germavinylidenes (**IV–VII**) (NHB = (HC(Dipp)N)$_2$B, Tipp = 2,4,6-trisopropylphenyl, NHC = (MeC(iPr)N)$_2$C, Tbb = 2,6-((Me$_3$Si)$_2$CH)$_2$-4-*tert*-butylphenyl, NHC* = (H_2C(Dipp)N)$_2$C, Ter = 2,6-bis(2,4,6-trisopropylphenyl)phenyl, and Dipp = 2,6-diisopropylphenyl).

[a]*Institute of Chemistry, Carl von Ossietzky University of Oldenburg, Carl von Ossietzky-Str. 9-11, D-26129 Oldenburg, Federal Republic of Germany. E-mail: thomas.mueller@uni-oldenburg.de*

[b]*Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland*

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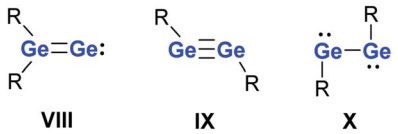


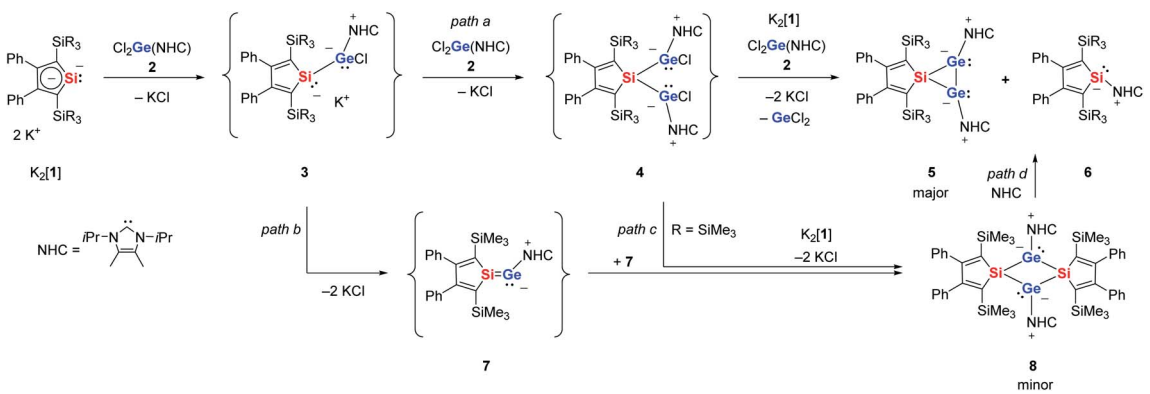
Fig. 2 Digermenylidenes VIII, digermynes IX and digermylenes X.

Fig. 3 Attempted synthesis of heavy vinylidenes by double salt metathesis and formation of cyclic ditetrylenes after salt metathesis and reduction (E, E′ = Si, Ge).

those of previously reported siladigermiranes.[44–46] The ^{13}C NMR data indicate a silole group with localized C=C double bonds (see the ESI material†). The green colour of these compounds results from broad long-wave absorptions at λ_{max} = 610 nm (**5a**) and λ_{max} = 625 nm (**5b**). During the reaction of K_2[**1a**] with dichlorogermylene **2**, the known NHC-stabilised silylene **6a** was detected by NMR spectroscopy as a by-product and was identified by comparison with literature data.[47] After isolation of compound **5a**, crystallization from diethyl ether allowed a second crop of a few dark red crystals of the tricyclic compound **8** that was identified by XRD analysis (Scheme 1). When the reaction of K_2[**1a**] and dichlorogermylene **2** was followed by NMR spectroscopy, already at −30 °C a mixture of products was detected (see ESI† for details). The ^{29}Si{^{1}H} inverse gated NMR spectra indicated the presence of the NHC-stabilised silylene **6a** (δ^{29}Si = −32.9 (SiC_4), −11.8), of the bicyclic siladigermirane **5a** (δ^{29}Si = −9.8, −7.0 (SiC_4)) and of the tricyclic disiladigermetane **8** (δ^{29}Si = +6.0 (SiC_4), −7.8). Besides these signals, there are three additional resonances at δ^{29}Si = +157.9 (SiC_4), −3.5 and −6.1 (see Fig. S1b† for details). The low field signal is in a typical region for silicon atoms involved in multiple bonds and very close to the ^{29}Si NMR chemical shift reported by the Scheschkewitz group for the NHC-stabilised silagermenylidene **9** (δ^{29}Si(**9**) = 159).[19] At reaction temperatures above −30 °C and prolonged reaction time, the intensity of these signals steadily decreased. Based on the low field ^{29}Si NMR resonance, we identified this intermediate as the NHC stabilised silagermenylidene **7**. This assignment is supported by NMR chemical shift calculations, which predict for the tricoordinated silicon atom of silagermenylidene **7** δ^{29}Si(calc) = 178, close to the experimental value (see ESI†).

Based on these experimental observations, we suggest for this complex reaction the following course (Scheme 1). The main product **5** is formed by two subsequent salt metathesis reactions *via* the germyl chlorides **3** and **4** (Scheme 1, *path a*). Such twofold salt metathesis reactions have precedence in stannole dianion chemistry.[48] The dichlorides **4** undergo a reductive dehalogenation to form the three-membered ring compounds **5**. At this point, the silole dianions **1** act as reducing agents and the NHC-stabilised silylenes **6** are obtained as by-products. The transient silagermenylidene **7** is formed by salt elimination from chloride **3a** and subsequently it dimerized to give disiladigermetane **8** (Scheme 1, *path b*). In view of the very low yield of **8**, we suggest that this is only one of several reaction channels for silagermenylidene **7**. Likewise, we cannot exclude that compound **8** is formed by double salt metathesis of digermyl chloride **4** with the starting material K_2[**1**] (Scheme 1, *path c*). Based on the result of DFT calculations, we can discard the possibility of a reversible dimerization of silagermenylidene **7**, as the dimerization is highly exothermic and exergonic (ΔE = −266 kJ mol^{-1}, ΔG = −160 kJ mol^{-1} (T = 298 K), see Fig. S7†). On the other hand, the formation of disilagermirane **5a** from disilagermetane **8** by reaction with NHC (Scheme 1, *path d*) is thermodynamically feasible as it is only slightly endothermic (ΔE = 22 kJ mol^{-1}, ΔG = 3 kJ mol^{-1} (T = 298 K), see Fig. S7†). We were not able to improve the yields of products **5** by adjusting the stoichiometry of the reaction according to the reaction course shown in Scheme 1. This suggests similar activation barriers for the competing reaction channels. Increasing the steric bulk of the N-heterocyclic carbene resulted in no reaction between the NHC-stabilised germanium dichloride and the dianion even at the temperature of boiling THF.

Deep green single crystals suitable for X-ray diffraction (XRD) analysis were obtained for both siladigermiranes **5** from



Scheme 1 Reaction of dipotassium silole dianions K_2[**1**] with NHC-stabilised dichlorogermylene **2** (a: R = Me; b: R = Et).

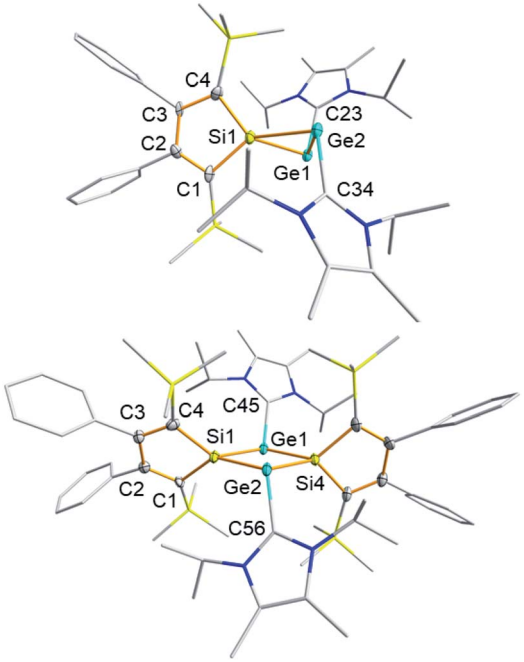


Fig. 4 Top: molecular structures of 3-sila-1λ^3,2λ^3-digermirane **5a** in the crystal (thermal ellipsoids at 50% probability, all hydrogen atoms are omitted for clarity. The NHC, Me_3Si and Ph substituents are simplified as a wireframe). Selected atomic distances [pm] and angles [°]: Ge1–Ge2 259.3(11), Si1–Ge1 244.6(2), Si1–Ge2 242.5(2), Ge1–C23 203.7(7), Ge2–C34 203.5(7), C23–Ge1–Ge2 96.59(20), C34–Ge2–Ge1 100.98(20), and $\alpha(SiC_4/SiGe_2)$ 68.3. Bottom: molecular structure of 2,3-disila-1λ^3,3λ^3-digermetane **8** in the crystal (thermal ellipsoids at 50% probability, all hydrogen atoms are omitted for clarity. NHC substituents are simplified as a wireframe). Selected atomic distances [pm] and angles [°]: Si1–Ge1 246.2(12), Si1–Ge2 245.0(16), Si4–Ge1 244.3(16), Si4–Ge2 243.1(16), Ge1···Ge2 339.8(11), Si1···Si4 352.1(20), Ge1–C45 200.2(6), Ge2–C56 201.6(5), C45–Ge1–Ge2 122.54(14), C56–Ge2–Ge1 122.74(14), and $\alpha(SiC_4/Si_2Ge_2)$ 58.3.

concentrated Et_2O solutions. Their molecular structures in the crystal are very similar and we discuss here only that of siladigermirane **5a** in detail (Fig. 4, for details on the crystal structure of siladigermirane **5b**, see ESI†). The molecule is almost C_2-symmetric and its most prominent feature is the three membered $SiGe_2$-ring with a very long Ge–Ge bond of 259.3 pm, which is longer by 7% than a regular Ge–Ge single bond (242 pm).[49] It is however shorter by 28.4 pm than what is found for the Ge–Ge separation in dianion **10** (Ge–Ge = 287.7 pm, Fig. 5)[50] and also significantly shorter than the Ge–Ge distance in the neutral germanium(I) dimer **11** (Ge–Ge = 270.9 pm).[26] In addition, the Si–Ge bonds in siladigermirane **5a** are slightly elongated compared to standard values (mean value in **5a** 243.6 pm *vs.* standard value 237 pm).[49] In summary, the metrics of the $SiGe_2$ ring are close to those reported for 3,3-di-*tert*-butyl-tetramesityl-3-siladigermirane.[45] The imidazolium substituents are oriented in a *trans*-arrangement and the Ge–C bonds (mean value 203.6 pm) are typically longer than the standard value (Ge–C = 196 pm).[43,49] The C–Ge–Ge bond angles are small (96.6° and 101.0°) and both rings of the spiro compound enclose a dihedral angle of 68.3°. The coordination environment of the germanium atoms in **5a** indicates the presence of a non-bonded electron pair at each of them. This is in agreement with the notion of siladigermiranes **5** as interconnected cyclic digermylenes, which are stabilised by the interaction with two NHCs.

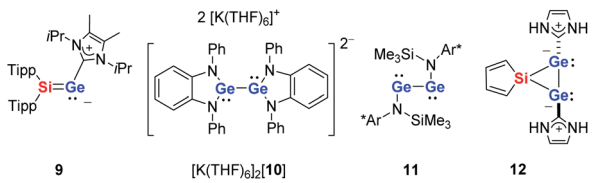


Fig. 5 Compounds that are of relevance for the discussion (Tipp: 2,4,6-triisopropylphenyl, Ar*: 2,6-bisdiphenylmethyl-4-methylphenyl).

Dark red single crystals of disiladigermetane **8** suitable for XRD analysis were obtained from the mother liquor of siladigermirane **5a** at −30 °C. The dominant feature of the molecular structure of **8** is the almost quadratic $(SiGe)_2$ four-membered ring (Fig. 3). The two silole rings are tilted by 58.3° against this central ring. The Si–Ge bonds are slightly longer (by 3–4%) than the standard value. The *trans*-cyclic Ge···Ge (339.8 pm) and Si···Si distances (352.1 pm) are smaller than the sum of the van der Waals radii (ΣvdWr(SiSi): 420 pm, ΣvdWr(GeGe): 422 pm)[51] but are longer by 40% (GeGe) and 52% (SiSi) than their respective single bonds.[49] This excludes *trans*-cyclic bonding interaction between these atoms. Similar to the siladigermiranes **5**, the NHC-substituents are arranged in a *trans* fashion at the two Ge-atoms with typically long Ge–C(NHC) bonds. The C–Ge–Ge angles are however less acute (122.5 and 122.7°) and the coordination environment around the two germanium atoms is trigonal pyramidal (sum of the bond angles around germanium, $\Sigma\alpha$(Ge) = 316.0 and 316.4°).

Quantum mechanical calculations at the density functional M06-2X/Def2-TZVP for **5a** and for the model siladigermirane **12** were used to investigate the electronic nature of the spiro compounds **5** (see ESI†). The molecular structures optimized for **5a** and **12** at this level of theory agree well with the experimental structures that are obtained from XRD analysis. The largest deviation in bond lengths is found for the Ge–C(NHC) linkage showing germanium carbon distances that are elongated by 2% (**5a**) and by 1% (**12**) compared to the experimental structure of **5a** (see Table S4†). The mean bond dissociation energy (BDE) of the Ge–C(NHC) bond calculated for model compound **12** is substantial (BDE(mean) = 251 kJ mol^{-1}). This indicates the strong stabilization of the siladigermirane by the two NHC substituents at the low coordinated germanium centres. The HOMO of compound **12** is almost exclusively the Ge–Ge σ-bond which is a combination of the atomic Ge(4p) orbitals that are oriented perpendicular to the respective Ge–Si vector. Consequently, the HOMO is slightly bent away from the centre of the three membered ring (Fig. 6). The atomic Ge(4s) orbitals dominate the HOMO−2. The shapes of the HOMO−1 and the LUMO indicate the cross-hyperconjugation between the silole ring and the Ge–Si σ-bonds of the three membered ring (Fig. 6).[52,53] A population analysis in the framework of natural bond orbital (NBO) theory[54] suggests that the Ge–Ge σ-bond is

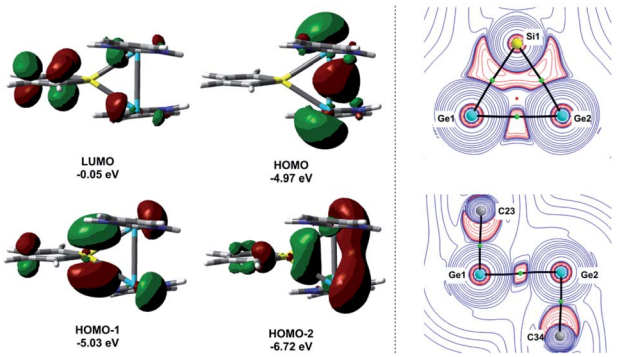
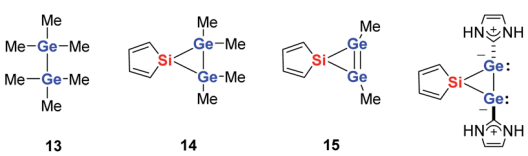


Fig. 6 Left: calculated surface diagrams of the frontier molecular orbitals of siladigermirane **12** (isodensity value 0.04, at M06-2X/Def2/TZVP). Right: 2D contour plots of the calculated Laplacian of the electron density, $\nabla^2\rho(r)$, in the Ge1–Si1–Ge2 plane (top) and in the Ge1–Ge2–C34 plane (bottom) of model compound **12**. The molecular graph of model **12** is projected onto the respective contour plot. Solid black lines show the bond paths, which follow the line of maximum electron density between bonded atoms. The corresponding bond critical points (bcp's) are shown as green circles, and ring critical points as red spheres. Red contours indicate regions of local charge accumulation ($\nabla^2\rho(r) < 0$); blue contours indicate regions of local charge depletion ($\nabla^2\rho(r) > 0$).

composed of almost exclusively Ge(4p) orbitals (94% p-orbital contribution, Fig. S9†). The lone pairs at both germanium atoms show large contributions of the 4s(Ge) atomic orbitals (79% s-, 21% p-orbital contribution). The calculated Wiberg bond index (WBI) of the Ge–Ge bond in **12** is very close to that of typical Ge–Ge single bonds (WBI = 0.84 (**12**) *vs.* 0.89 (**13**) and 0.92 (**14**), Table 1).[55] From the wavefunction-based analysis, it is apparent that the long Ge–Ge bond in model compound **12** and likewise in siladigermiranes **5** is the result of the almost pure p-orbital contributions. The complementary analysis of the calculated electron density (quantum theory of atoms in molecules, QTAIM) identifies the Ge–Ge bond in **12** by its properties at the bond critical point (bcp) as being non-polar and covalent

Table 1 Calculated properties of the Ge–Ge bond according to NBO analysis and QTAIM analysis of the calculated electron density in model siladigermirane **12** and related compounds **13–15** (M06-2X/Def2-TZVP)



Ge–Ge [pm]	245.9	245.2	224.2	261.8
WBI	0.89	0.92	1.77	0.84
ρ [a.u.]	0.086	0.077	0.091	0.057
$\nabla^2(\rho)$ [a.u.]	−0.104	−0.063	−0.044	−0.015
H [a.u.]	−0.041	−0.036	−0.050	−0.020
ε	0.000	0.375	0.235	0.836

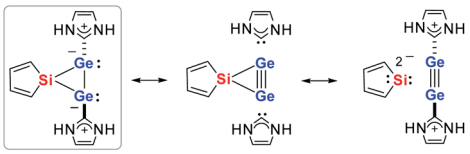


Fig. 7 Possible resonance structures of 3-sila-1λ^3,2λ^3-digermirane **12**.

(significant electron density ρ, negative Laplacian $\nabla^2\rho$, negative total energy density H, see Table 1 and ESI†).[56] The electron density at the bcp is however small compared to that calculated for the typical Ge–Ge bond in hexamethyl digermane, **13**, and for the Ge–Ge bond in siladigermirane **14**. Noticeable is the non-spherical electron distribution at the bcp as expressed by the large ellipticity ε of the electron density at the bcp. It is larger than calculated for the π-bond in siladigermirene **15** and the accumulation of charge extends into an area in the plane of the three-membered ring and directed away from its centre in agreement with the shape of the σ-Ge–Ge bond (Fig. 5). Consistent with the analysis of the experimental structure, the computational results indicate the digermylene nature of compounds **5** and **12** with the two germylene centres interconnected by a Ge–Ge σ-bond as represented by the canonical structure **12A** (Fig. 7). Contributions of resonance structures with multiple bonds between the germanium atoms (*i.e.* **12B** and **12C**) are negligible.

As the ring strain in heavy cyclopropanes (E_3H_6, E = Si, Ge) is considerably higher than that of cyclopropane (162–165 kJ mol^{-1} *vs.* 124 kJ mol^{-1} for C_3H_6),[57,58] we studied the influence of the integration of the Ge_2 unit in a three-membered ring using a set of isodesmic reactions. We found that the long Ge–Ge bond reduces the ring strain in siladigermirane **12** by 32 kJ mol^{-1} compared to a related siladigermirane (see ESI† for details). This factor contributes to the thermodynamic stability of this unusual $SiGe_2$ cycle.

Conclusions

The reaction of K_2[**1**] with NHC stabilised germanium dichloride yields 3-sila-1λ^3,2λ^3-digermiranes **5** as main products. The targeted silagermylidene **7** was detected only as an intermediate in a side reaction by NMR spectroscopy. Based on the analysis of the structural and computational data the three-membered ring compounds **5** are directly interconnected digermylenes that are stabilised by NHCs.

Author contributions

Z. D. was responsible for experimental investigations and formal analysis (lead), computational investigation and visualization, data presentation and writing original draft (equal with T. M.), methodology and conceptualization (supportive). J. M. W. was responsible for experimental investigations (supportive) and validation. M. S. collected the X-ray data and solved the

crystal structures. T. M. was in charge for methodology and conceptualization, computational investigations, review and editing of the manuscript (lead), project administration and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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