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Multiple ethylene activation by heteroleptic  
L(Cl)Ga-substituted germylenes†Anna Bucker,<sup>a</sup> Christoph Wolper,<sup>a</sup> Hannah Siera,<sup>b</sup> Gebhard Haberhauer<sup>b</sup> and  
Stephan Schulz<sup>b</sup> \*<sup>a,c</sup>

Ethylene insertion into the Ga–Ge bond of the L(Cl)Ga-substituted germylene LGa(μ-Cl)GeDMP **1** (L = HC(C(Me)NAr)<sub>2</sub>, Ar = 2,6-<sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; DMP = 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) at ambient temperature is followed by dimerization of the as-formed germylene to give the digermene **3**, which further reacted with ethylene in a [2 + 2] cycloaddition to give the 1,2-digermacyclobutane **4**. In marked contrast, the amino-substituted germylene L(Cl)GaGeN(SiMe<sub>3</sub>)Ar **2** reacted directly to the 1,2-digermacyclobutane **5**. Quantum chemical calculations confirmed the assumed reaction mechanism, hence demonstrating the crucial role of the substituent on the reaction mechanism.

## Introduction

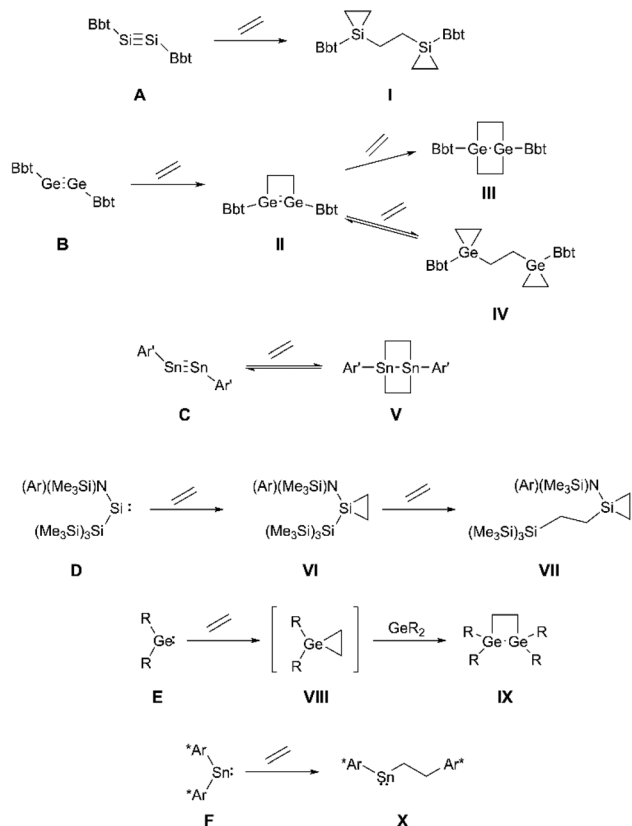
Ethylene belongs to the most important industrial feedstock chemicals, with a current production of more than 150 million tons.<sup>1</sup> It is catalytically converted into fine chemicals including polyethylene, ethylene oxide, alcohols, and aldehydes,<sup>2</sup> typically by using transition metal-based catalysts. More recently, the potential of low valent s- and p-block compounds for the activation of industrially relevant small molecules, *i.e.*, H<sub>2</sub>, CO, NH<sub>3</sub> and ethylene, has been demonstrated, and even catalytic reactions have been reported.<sup>3,4</sup> Such compounds contain a stereochemically active lone pair (donor) and an empty π-type orbital (acceptor) and thereby resemble the electronic configuration of transition-metal compounds.

Low valent group 14 compounds were found to react with ethylene in different ways.<sup>5</sup> Monovalent tetrylenes typically reacted in [2 + 2]<sup>6</sup> and [2 + 2 + 2] cycloaddition reactions<sup>7</sup> as was exemplarily shown in reactions of digermene **B**<sup>6b</sup> to compounds **II** and **III**, respectively, and of distannyne **C**<sup>7c</sup> to compound **V**. Interestingly, compound **II** reacted reversibly under kinetic control to bisgermacyclop propane **IV**.<sup>6b</sup> In contrast, the analogous bisilacyclop propane **I** was formed exclusively with disilyne **A**,<sup>8a</sup> whereas hydridotetrylenes were reported to react

with alkenes with hydrometallation,<sup>8b,8c</sup> respectively. In addition, the digermene TbbGeGeTbb (Tbb = 2,6-(CH(SiMe<sub>3</sub>)<sub>2</sub>-4-<sup>1</sup>Bu-C<sub>6</sub>H<sub>2</sub>)) served as a precatalyst in the catalytic cyclotrimerisation of terminal alkynes (Reppe reaction).<sup>9</sup> In contrast, divalent tetrylenes, which have an electron lone pair in a sp<sup>2</sup>-hybridised orbital in the plane of the molecule and a vacant p-type orbital perpendicular to the molecular plane as a result of their typically large singlet-triplet energy gap, reacted mainly with ethylene in (sometimes reversible) [2 + 1] cycloaddition reactions.<sup>10</sup> For example, the acyclic silylene **D** reacted to silirane **VI** (Scheme 1), which underwent 1,2-insertion of ethylene at 60 °C to finally give silirane **VII** as was confirmed by *in situ* <sup>1</sup>H NMR spectroscopy with C<sub>2</sub>D<sub>4</sub>.<sup>10c</sup> In contrast, Lappert's germylene **E** directly reacted to the 1,2-digermacyclobutane **IX**, most likely *via* the intermediate formation of germirane **VIII**,<sup>10g</sup> while the sterically demanding diarylgermylene (Ar')<sub>2</sub>Ge (Ar' = DMP, 2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) reacted reversibly with ethylene to the corresponding germirane.<sup>10h</sup> In contrast, the reaction of diarylstannylenes (Ar\*)<sub>2</sub>Sn **F** (Ar\* = 2,6-Ar<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-Trip<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Trip = 2,4,6-<sup>1</sup>Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>) with C<sub>2</sub>H<sub>4</sub> at 60 °C occurred with insertion into a Sn–C bond to yield stannylyne **X**.<sup>11</sup>

We are particularly interested in electron-rich tetrylenes and recently reported the synthesis of room temperature-stable silylene carbonyl complexes (L(X)Ga)<sub>2</sub>SiCO (L = HC[C(Me)N(Ar)]<sub>2</sub>; X = Br, I, Me),<sup>12</sup> which showed enhanced π-backbonding to the CO group.<sup>13</sup> In addition, heteroleptic metallasilylenes L(Cl)MSi[PhC(N-<sup>t</sup>Bu)<sub>2</sub>] (M = Al, Ga) were found to activate CO<sub>2</sub>, N<sub>2</sub>O and azides, respectively, and also reacted with white phosphorus (P<sub>4</sub>) in unprecedented [2 + 1 + 1] fragmentation reactions and with *cyclo*-E<sub>5</sub> rings of [Cp\*Fe(η<sup>5</sup>-E<sub>5</sub>)] (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>; E = P, As).<sup>14</sup> To explore the reactivity of heteroleptic tetrylenes and to investigate the influence of the group 14 element on their reactivity in more detail, we recently synthesised the L(Cl)

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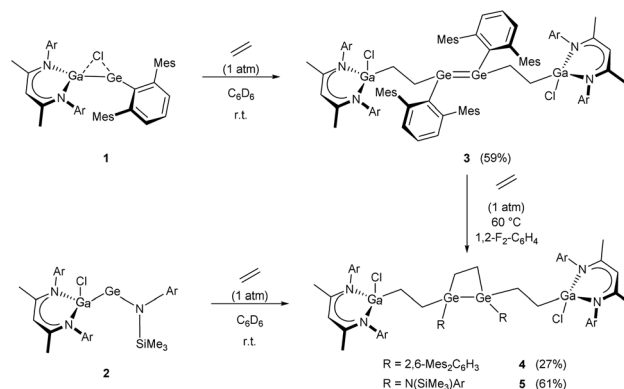


**Scheme 1** Ethylene activation reactions by tetrylynes and tetrylenes; R = CH(SiMe<sub>3</sub>)<sub>2</sub>, Ar\* = 2,6-Dipp<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-Trip<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (Trip = 2,4,6-<sup>i</sup>Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>), Bbt = 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-4-C(SiMe<sub>3</sub>)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>, Ar' = 2,6-Dipp<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>, 2,6-Trip<sub>2</sub>-3,5-<sup>i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>.<sup>6b,7c,8a,10c,9,11</sup>

Ga-substituted germylenes LGa(μ-Cl)GeDMP **1**, which represents an intermediate of the oxidative addition reaction of DMPGeCl and LGa, in which the bridging Cl atom stabilises the empty p orbital at the Ge centre, and L(Cl)GaGeN(SiMe<sub>3</sub>)Ar **2**.<sup>15</sup> LGa(μ-Cl)GeDMP **1** was found to react with CO<sub>2</sub> with decarbonylation and with isocyanates and carbodimides with insertion into the Ga–Ge bond, demonstrating its potential for small molecule activation reactions.<sup>16</sup> We here report on (multiple) ethene activation reactions of germylenes **1** and **2** including detailed mechanistic studies (DFT calculations).

## Results and discussion

Germylene LGa(μ-Cl)GeDMP **1** reacted at ambient temperature under one atmosphere of ethylene within minutes to give the digermene **3**, which precipitated as a yellow solid in benzene during the reaction. Digermene **3** was found to further react with ethylene in 1,2-difluorobenzene in a [2 + 2] cycloaddition reaction at elevated temperature (60 °C) to give the corresponding 1,2-digermycyclobutane **4**. In marked contrast, the amido-substituted germylene L(Cl)GaGeN(SiMe<sub>3</sub>)Ar **2** reacted with ethylene at ambient temperature directly to the 1,2-digermycyclobutane **5** (Scheme 2).

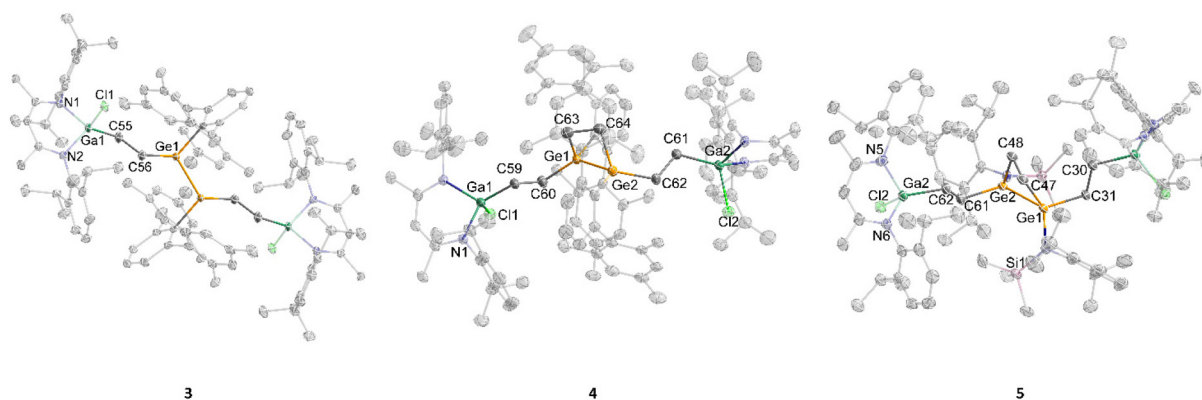


**Scheme 2** Syntheses of digermene (**3**) and 1,2-digermycyclobutanes (**4**, **5**); Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

Digermene **3** is only slightly soluble in fluorobenzene and 1,2-difluorobenzene, insoluble in benzene, toluene, THF, acetonitrile, *n*-hexane and *n*-pentane and decomposes in dichloromethane-*d*<sub>2</sub>, bromobenzene-*d*<sub>5</sub> and 1,2-dichlorobenzene-*d*<sub>4</sub> within minutes at room temperature. The <sup>1</sup>H NMR spectrum of **3** was obtained from a solution in toluene-*d*<sub>8</sub> and 1,2-difluorobenzene at 90 °C. Unfortunately, **3** was found to decompose to yet unidentified products under these conditions (Fig. S9<sup>†</sup>), hence no meaningful <sup>13</sup>C NMR spectrum was obtained. In contrast, <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4** and **5** were recorded at ambient temperature in benzene-*d*<sub>6</sub>, showing the expected resonances of the β-diketiminate and C<sub>2</sub>H<sub>4</sub> units as well as the terphenyl (**4**) and amine ligands (**5**).

Single crystals were obtained from solutions in hot fluorobenzene (**3**) and pentane (**5**) after storage at room temperature and from benzene after storage at 6 °C (**4**), respectively. Digermene **3** crystallised as bright yellow blocks in the monoclinic space group *C2/c*, 1,2-digermycyclobutane **4** as colourless plates in the triclinic space group *P* $\bar{1}$ , and 1,2-digermycyclobutane **5** as colourless blocks in the monoclinic space group *P2*<sub>1</sub>/*c* (Fig. 1). The Ge–Ge bond length in digermene **3** (2.3307(5) Å) is within the reported range for Ge–Ge double bonds (2.212–2.535<sup>17</sup>), and the substituents adopt a trans-bent orientation, which is typical for heavier dimetalenes.<sup>5f,18</sup> However, the Ge–Ge–C bond angles (Ge–Ge–C<sub>Ter</sub> 108.72(6)°; Ge–Ge–CH<sub>2</sub> 119.48(6)°) largely differ. The [2 + 2] cycloaddition of ethylene to the Ge–Ge double bond in digermene **3** causes a rearrangement of the substituents on the Ge–Ge unit from a transoid (**3**) to a cisoid orientation (**4**), and the Ge–Ge–C<sub>Ter</sub> bond angle is widened by 5° (**3** 108.72(6)°; **4** 113.77(3)°, 114.02(6)°). The Ge–Ge single bonds in the 1,2-digermycyclobutane rings (2.5440 Å **4**, 2.4607 Å **5**) are not only significantly shorter than the Ge–Ge double bond in **3**, but also largely differ by almost 8 pm. In addition, the Ge–C bonds in the 1,2-digermycyclobutane rings in **5** (2.008(2) Å, 2.010(2) Å) are slightly elongated compared to those in 1,2-digermycyclobutane **4** (1.982(2) Å, 1.973(2) Å), and the endocyclic Ge–Ge–C bond angles of **5** (73.72(7)°, 73.64(6)°) are slightly wider than those of **4** (71.42(7)°, 71.27(7)°), while the CH<sub>2</sub>–CH<sub>2</sub> bond lengths are



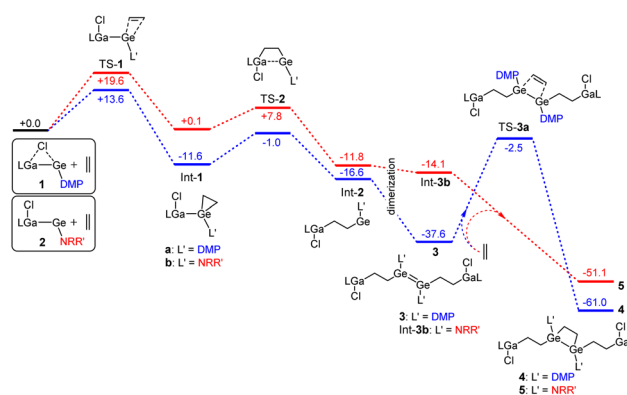


**Fig. 1** Solid state structures of **3–5** with thermal ellipsoid (50%); H atoms omitted for clarity. Selected average bond lengths [Å] and bond angles [°]: compound **3**: Ge1–Ge#1 2.3307(5), Ge1–C56 1.993(2), Ga1–C55 1.970(2), C55–C56 1.535(3), C30–Ge1–Ge#1 108.72(6), C56–Ge1–Ge#1 119.48(6), Ga1–C55–C56 115.52(14), Ge1–C56–C55 113.93(14); compound **4**: Ge1–Ge2 2.5440(3), Ge1–C63 1.982(2), Ge1–C60 1.986(2), Ge2–C64 1.973(2), Ge2–C62 1.982(2), Ga1–C59 1.977(2), Ga2–C61 1.990(2), C59–C60 1.537(3), C61–C62 1.535(3), C63–C64 1.551(3), Ge1–Ge2–C64 71.42(7), Ge2–Ge1–C63 71.27(7), Ge2–Ge1–C60 132.38(7), Ge1–Ge2–C62 130.68(6), Ge1–Ge2–C010 114.02(6), Ge2–Ge1–C65 113.77(3), Ga1–C59–C60 112.29(14), Ga2–C61–C62 112.12(14), Ge1–C60–C59 115.47(15), Ge2–C62–C61 117.24(14); compound **5**: Ge1–Ge2 2.4607(3), Ge1–C31 1.987(2), Ge1–C47 2.008(2), Ge2–C48 2.010(2), Ge2–C61 1.986(2), Ga1–C30 1.966(2), Ga2–C62 1.963(2), C30–C31 1.536(3), C47–C48 1.548(3), C61–C62 1.532(3), Ge1–Ge2–C48 73.77(7), Ge2–Ge1–C47 73.64(6), Ge2–Ge1–C31 121.99(7), Ge1–Ge2–C61 120.91(7), Ge1–Ge2–N4 122.51(6), Ge2–Ge1–N3 123.00(6), Ga1–C30–C31 116.37(15), Ga2–C62–C61 116.38(15), Ge1–C31–C30 113.69(15), Ge2–C61–C62 114.19(14).

almost identical (1.551(3) Å **4**; 1.548(3) Å **5**), respectively. These results are most likely due to the sterically more demanding terphenyl substituent compared to the amido substituent as is proven by comparing the calculated buried volumes  $V_{\text{bur}}$ <sup>19</sup> of 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (36.8%) vs. N(SiMe<sub>3</sub>)(Ar) (34.5%).<sup>20</sup> The exocyclic ethane units in **3–5** have identical CH<sub>2</sub>–CH<sub>2</sub> (1.532(3)–1.537(3) Å), Ge–CH<sub>2</sub> (1.982(2)–1.993(2) Å) and Ga–CH<sub>2</sub> (1.963(2)–1.990(2) Å) bond lengths, as is expected from the comparable atomic radii of Ga (124 pm) and Ge (121 pm).<sup>21</sup>

Recently, regioselective and stereoselective insertion reactions of phenylacetylene into the tetrel–tetrylene linkage of germylstannylene, germylplumbylene and stannylplumbylene as well as the silylated germylene [(Me<sub>3</sub>Si)<sub>3</sub>Si]<sub>2</sub>Ge have been reported.<sup>22</sup> In addition, 1,2-insertion reactions of alkynes into Ge–C bonds of dibromodigermenes were found to give bromovinylgermylenes,<sup>23</sup> while silylenes containing a sterically demanding, electropositive hypersilyl (Si(SiMe<sub>3</sub>)<sub>3</sub>) ligand reacted with ethylene to the corresponding silirane.<sup>10c–e</sup> Moreover, trimethylstannyl-substituted silylenes reversibly inserted ethylene into the Si–Sn bond.<sup>24</sup> However, to the best of our knowledge, we report here for the first time the multiple activation of ethylene using germylenes containing a bulky, electropositive main group metal-substituent.

The mechanism of the reaction was subsequently investigated by quantum chemical calculations. In addition to the reaction of **1** and **2** with ethylene (Fig. 2), the addition of C<sub>2</sub>H<sub>4</sub> to reference systems with sterically less demanding substituents as well as substituents without a Ga centre was computed (Fig. S10–S12†). While the barrier for cycloaddition of germylenes to the C–C double bond of ethylene has been found to be close to zero in gas-phase kinetic studies<sup>25</sup> and quantum chemical calculations<sup>26</sup> (see also Fig. S10–S12†), activation barriers of 13.6 and 19.6 kcal mol<sup>−1</sup> are found for germylenes **1**



**Fig. 2** Gibbs energies for the reaction of germylenes **1** and **2** with ethylene yielding the 1,2-digermacyclobutanes **4** and **5** calculated by means of PBE0–D3BJ. The values are given in kcal mol<sup>−1</sup>. L = HC(C(Me)NAr)<sub>2</sub>, Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; DMP = 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; NRR' = N(SiMe<sub>3</sub>)(Ar).

and **2** as a result of the sterically demanding substituents. The higher barrier for **2** agrees with previous quantum chemical calculations, which showed that electron-withdrawing groups on the germylene hinder the cycloaddition.<sup>27</sup> As-formed germiranes Int-1 then undergo 1,2-migration of the C<sub>2</sub>H<sub>4</sub> unit into the Ge–Ga bonds to give germylenes Int-2, which dimerise to digermenes as demonstrated by the isolation of **3** (Fig. 2). A comparison with the reference systems shows that the driving force of the 1,2-migration is essentially the reduction of steric interactions.

Insertion of a C<sub>2</sub>H<sub>4</sub> unit into a tetrel–ligand bond was previously observed by Power *et al.* in the reactions of sterically hindered stannylenes with C<sub>2</sub>H<sub>4</sub>,<sup>11</sup> whereas, to the best of our



knowledge, it is without precedent in germylene chemistry except for the C<sub>2</sub>H<sub>4</sub> insertion into the Ge–Ge double bond of 1,2-cyclodigermene **II**, which occurred under kinetic control to give the bisgermacyclopropane **IV**.<sup>6b</sup> The digermenes **3** and Int-**3b** then react with another equivalent of ethylene in [2 + 2] cycloaddition to give the corresponding 1,2-digermacyclobutanes **4** and **5**, respectively. The calculations reveal that the addition of ethylene to Int-**3b** is barrier free (Fig. S13†), whereas an activation energy of 35.1 kcal mol<sup>-1</sup> is found for the addition of C<sub>2</sub>H<sub>4</sub> to **3**, which is due to the sterically very demanding DMP ligands (Fig. 2 and S13†). The calculations clearly explain why digermene **3** can be isolated in marked contrast to Int-**3b**.

## Experimental

### Synthetic procedures

All experiments were performed either in a glovebox and using standard Schlenk line techniques under argon atmosphere. Toluene and *n*-hexane were dried using a mBraun solvent purification system (SPS), degassed and stored in Schlenk flasks under argon atmosphere. Deuterated solvents were stored over molecular sieves (4 Å) and degassed prior to use. The anhydrous nature of the solvents was verified by Karl Fischer titration. LGa(μ-Cl)GeDMP (**1**) and L(Cl)GaGeN(SiMe<sub>3</sub>)Ar (**2**) were synthesized according to literature procedures.<sup>15</sup> Microanalysis was performed at the Elemental Laboratory for Microanalysis of the University of Duisburg-Essen. The melting points were measured using a Thermo Scientific 9300 apparatus.

### Spectroscopic methods

NMR spectra were either recorded using a Ascend™ 400 spectrometer (<sup>1</sup>H NMR, 400 MHz; <sup>13</sup>C{<sup>1</sup>H} NMR, 100 MHz) or a Bruker Avance DPX-300 spectrometer (<sup>1</sup>H NMR, 300 MHz). The spectra were referenced to internal C<sub>6</sub>D<sub>5</sub>H (<sup>1</sup>H: δ = 7.16, C<sub>6</sub>D<sub>6</sub>) and toluene-*d*<sub>7</sub> (<sup>1</sup>H: δ = 2.08, toluene-*d*<sub>8</sub>) or to natural-abundance carbon resonances C<sub>6</sub>D<sub>6</sub> (<sup>13</sup>C: δ = 128.06, C<sub>6</sub>D<sub>6</sub>) and toluene-*d*<sub>8</sub> (<sup>13</sup>C: δ = 20.43, toluene-*d*<sub>8</sub>). IR spectra were recorded with an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The IR spectrometer was placed in a glovebox to guarantee measurements under inert gas conditions.

### Crystallography

The crystals were mounted on nylon loops in inert oil. Data of **3** were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (monochromated MoK<sub>α</sub> radiation, λ = 0.71073 Å) and data of **4** and **5** were collected on a Bruker AXS D8 Venture diffractometer with photon II detector (monochromated CuK<sub>α</sub> radiation, λ = 1.54178 Å, microfocus source) at 100 (2) K. Structures were solved by direct methods (SHELXS-2013)<sup>28</sup> and refined anisotropically by full-matrix least-squares on F<sup>2</sup> (SHELXL-2017).<sup>29,30</sup> Absorption corrections were performed semi-empirically from equivalent reflections on the basis of multi-scans (Bruker AXS APEX3). Hydrogen

atoms were refined using a riding model or rigid methyl groups.

Two solvent molecules are disordered in **3** over a two-fold rotational axis. The local symmetry was ignored in the refinement (negative PART) and all bond lengths and angles of the solvent molecules were restrained to be equal (SADI). In addition, the atoms were restrained to lie on a common plane (FLAT). RIGU and SIMU restraints were applied to the displacement parameters.

**4** contains four highly disordered benzene molecules and **5** two highly disordered *n*-pentane molecules, respectively. The final refinements were done with solvent free datasets from a PLATON/SQUEEZE run.<sup>31</sup> The molecules were included in the sum formulas for completeness.

The bond lengths and angles of the solvent molecule in **5** were restrained to be equal (SADI).

CCDC 2250957 (**3**), 2250958 (**4**) and, 2250959 (**5**) contain the supplementary crystallographic data for this paper.

### Computations

All calculations were performed by using the program package Gaussian 16.<sup>32</sup> The geometrical parameters of all stationary points were optimized by means of PBE0<sup>33</sup> with additional dispersion correction with Becke–Johnson damping.<sup>34</sup> The basis set def2-SVP<sup>35,36</sup> was employed. For all stationary points no symmetry restriction was applied. Frequency calculations were carried out at each of the structures to verify the nature of the stationary point. It turned out that all transition states have exactly one imaginary frequency, whereas all other structures have none.

Furthermore, the energies of the stationary points were calculated using the density functionals PBE0-D3BJ and the basis set def2-TZVP.<sup>35,36</sup> To take solvent effects into account, the solvent model SMD<sup>37</sup> (benzene as solvent) was used for the single point calculations.

**Synthesis of compound 3.** A degassed red solution of germylene LGa(μ-Cl)GeDMP **1** (65 mg, 0.071 mmol) in 1 mL of 1,2-difluorobenzene under an ethene atmosphere (1 atm) was stirred for 5 minutes, upon which a yellow participate was formed. The ethene atmosphere was removed and replaced by an argon atmosphere. The solid was dissolved in hot 1,2-difluorobenzene (2 mL) and stored at ambient temperature to give yellow crystals of digermene **3**. Yield: 39 mg (0.021 mmol, 59%), m.p. 128 °C decomp. Anal. Calcd for C<sub>110</sub>H<sub>140</sub>Cl<sub>2</sub>Ga<sub>2</sub>Ge<sub>2</sub>N<sub>4</sub>: C 70.50, N 2.99, H 7.53; found: C 69.30, N 2.70, H 7.24. <sup>1</sup>H NMR (300 MHz, Tol-*d*<sub>8</sub> with 1,2-F<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 363 K): δ [ppm] = 7.30–6.10 (m, ArH, overlapping with solvent) 4.83 (s, 2H, γ-CH), 3.49 (sept, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.83 (sept, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.33 (s, 10H, CH<sub>3</sub>), 1.44 (s, 12H, CH<sub>3</sub>), 1.37 (s, 6H, CH<sub>3</sub>), 1.09 (m, 52H), 0.87 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.81 (m, 4H), 0.70 (m, 6H). It is not possible to assign every signal due to the unsatisfactory resolution of the spectrum. Due to the insolubility and instability of digermene **3** in common solvents it was not possible to measure <sup>13</sup>C NMR spectra or 2D spectra. IR(ATR): ν [cm<sup>-1</sup>] = 2958, 2914, 2861, 1596, 1529, 1438, 1385, 1308, 1266,



1223, 1180, 1094, 1061, 1027, 998, 935, 869, 850, 802, 750, 688, 630, 592, 549, 501, 449.

**Synthesis of compound 4.** A degassed yellow suspension of digermene **3** (20 mg, 0.011 mmol) in 2 mL of 1,2-difluorobenzene under an ethene atmosphere (1 atm) was slowly warmed to 60 °C, giving a colourless solution after 16 hours. All volatile components were removed *in vacuo* and the residue was dissolved in benzene (0.3 mL) and stored at 6 °C to give colourless crystals of 1,2-digermycyclobutane **4**. Yield: 6 mg (0.003 mmol, 27%), m.p. 57–58 °C. Anal. Calcd for C<sub>112</sub>H<sub>144</sub>Cl<sub>2</sub>Ga<sub>2</sub>Ge<sub>2</sub>N<sub>4</sub>: C 70.73, N 2.95, H 7.63; found: C 70.20, N 3.13, H 7.54. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ [ppm] = 7.28 (m, 4H, ArH), 7.10 (m, 9H, ArH), overlapping with solvent resonances), 6.96 (m, 3H, ArH), 6.88 (m, 8H, ArH), 6.72 (m, 4H, ArH), 4.79 (s, 2H, γ-CH), 3.73 (sept, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.00 (sept, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.83 (sept, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.58 (s, 6H, CH<sub>3</sub>(Mes)), 2.51 (s, 6H, CH<sub>3</sub>(Mes)), 2.25 (s, 6H, CH<sub>3</sub>(Mes)), 2.10 (s, 6H, CH<sub>3</sub>(Mes)), 1.51 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.47 (s, 12H, NCCH<sub>3</sub>), 1.39 (s, 6H, CH<sub>3</sub>(Mes)), 1.31 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 14H, CH(CH<sub>3</sub>)<sub>2</sub> overlapping with CH<sub>2</sub>), 1.20 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.02 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.92 (d, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub> overlapping with CH<sub>3</sub>(Mes)), 0.88 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.72 (m, 2H, CH<sub>2</sub>), 0.49 (m, 1H, CH<sub>2</sub>), 0.19 (m, 2H, CH<sub>2</sub>), -0.80 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ [ppm] = 169.2 (NCCH<sub>3</sub>), 146.5 (Ar), 145.7 (Ar), 143.2 (Ar), 143.2 (Ar), 142.6 (Ar), 141.5 (Ar), 141.2 (Ar), 141.0 (Ar), 141.0 (Ar), 138.5 (Ar), 138.2 (Ar), 135.6 (Ar), 135.5 (Ar), 135.3 (Ar), 135.1 (Ar), 135.0 (Ar), 129.5 (Ar), 129.3 (Ar), 128.9 (Ar), 127.8 (Ar), 126.2 (Ar), 125.9 (Ar), 124.3 (Ar), 124.0 (Ar), 97.6 (γ-CH), 29.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.4 (CH<sub>3</sub>), 23.9, 23.8 (NCCH<sub>3</sub>), 22.5 (CH<sub>2</sub>), 22.5 (CH<sub>3</sub>), 22.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.7 (CH<sub>2</sub>), 21.5 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>), 21.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 16.8 (CH<sub>2</sub>), 5.1 (CH<sub>2</sub>), 1.7 (CH<sub>2</sub>). IR (ATR): ν [cm<sup>-1</sup>] = 2972, 2924, 2862, 1538, 1438, 1390, 1314, 1261, 1175, 1103, 1022, 935, 869, 845, 802, 760, 745, 639, 558, 453.

**Synthesis of compound 5.** A degassed purple solution of germylene L(Cl)GaGeN(SiMe<sub>3</sub>)Ar **2** (45 mg, 0.053 mmol) in 1 mL of toluene was stirred for 5 minutes under an ethene atmosphere (1 atm) to give a colourless solution. After the removal of all volatile components *in vacuo*, the residue was dissolved in *n*-pentane (1 mL) and stored at room temperature. Colourless crystals of 1,2-digermycyclobutane **5** were formed within 12 hours. Yield: 30 mg (0.017 mmol, 61%), m.p. 220–221 °C. Anal. Calcd for C<sub>94</sub>H<sub>146</sub>Cl<sub>2</sub>Ga<sub>2</sub>Ge<sub>2</sub>N<sub>4</sub>Si<sub>4</sub>: C 63.71, N 4.74, H 8.31; found: C 64.20, N 4.52, H 8.59. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ [ppm] = 7.16 (m, 8H, ArH), overlapping with solvent resonances), 7.12–7.05 (m, 12H, ArH), 6.99 (dd, <sup>3</sup>J<sub>HH</sub> = 7.0, 2.3 Hz, 2H, ArH), 4.85 (s, 2H, γ-CH), 3.76 (sept, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.56 (sept, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.41 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.11 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.04 (sept, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.68 (m, 2H, CH<sub>2</sub>), 1.50 (s, 6H, NCCH<sub>3</sub>), 1.46 (s, 6H,

NCCH<sub>3</sub>), 1.44–1.33 (m, 30H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.18 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.10 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.04 (d, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.02 (d, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.88 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 6H, CH<sub>2</sub>), 0.69 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.64–0.51 (m, 1H, CH<sub>2</sub>), 0.25 (m, 2H, CH<sub>2</sub>), -0.02 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ [ppm] = 169.27 (NCCH<sub>3</sub>), 147.3 (Ar), 146.6 (Ar), 146.2 (Ar), 146.0 (Ar), 143.5 (Ar), 142.8 (Ar), 142.2 (Ar), 141.6 (Ar), 140.6 (Ar), 127.6 (Ar), 125.8 (Ar), 125.5 (Ar), 124.9 (Ar), 124.2 (Ar), 124.1 (Ar), 123.8 (Ar), 123.4 (Ar), 97.9 (Ar), 34.4 (CH<sub>2</sub>), 29.41 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (CH<sub>2</sub>), 24.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.5 (NCCH<sub>3</sub>), 23.5 (NCCH<sub>3</sub>), 22.7 (CH<sub>2</sub>), 17.3 (CH<sub>2</sub>), 14.3 (CH<sub>2</sub>), 13.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 3.5 (CH<sub>2</sub>), 2.3 (Si(CH<sub>3</sub>)<sub>3</sub>). IR(ATR): ν [cm<sup>-1</sup>] = 3066, 2962, 2932, 2866, 1524, 1462, 1433, 1380, 1318, 1237, 1180, 1098, 1046, 1012, 922, 864, 830, 793, 749, 692, 638, 573, 540, 444.

## Conclusions

The distinct influence of aryl (DMP) and amino (N(SiMe<sub>3</sub>)Ar) substituents on the reaction pathway of L(Cl)Ga-substituted germynes LGa(μ-Cl)GeDMP **1** and L(Cl)GaGeN(SiMe<sub>3</sub>)Ar **2** with ethylene is demonstrated. Based on quantum chemical calculations (DFT), both germynes react with ethylene with [2 + 1] cycloaddition and formation of germiranes (Int-1), which undergo 1,2-migration of the C<sub>2</sub>H<sub>4</sub> unit into the Ge–Ga bonds to give the corresponding germynes (Int-2). Dimerisation of these germynes to the corresponding digermenes is proven by the isolation and structural characterisation of digermene **3**, which is stabilized by the sterically very demanding DMP substituent. In contrast, the amido-substituted digermene (Int-3b) directly reacts with one equivalent of C<sub>2</sub>H<sub>4</sub> *via* [2 + 2] cycloaddition to the corresponding 1,2-digermycyclobutane **5**. DFT calculations showed that this reaction is barrier free, whereas an activation energy of 35.1 kcal mol<sup>-1</sup> is found for the addition of C<sub>2</sub>H<sub>4</sub> to digermene **3** due to the bulky DMP ligands. As a consequence, digermene **3** only reacts with ethylene at elevated temperature to the corresponding 1,2-digermycyclobutane **4**.

## Conflicts of interest

There are no conflicts to declare.

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