Facile activation of alkynes with a boraguanidinato-stabilized germylene: a combined experimental and theoretical study†

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A boraguanidinato-stabilized germylene, [(i-Pr)2NB(N-2,6-Me2C6H3)2]Ge, reacts with alkynes RC≡CR selectively in a 2 : 1 molar ratio to afford 3,4-R,R′-1,2-digermacyclobut-3-enes 1a–e as the products of formal [2 + 2 + 2] cyclization [R/R′ = Me/Me (1a), Ph/Ph (1b), Ph/H (1c), t-Bu/H (1d) and Cy/H (1e)]. Ferroceny-substituted alkynes react similarly, yielding the corresponding ferrocenylated 3,4-R,R′-1,2-digermacyclobut-3-enes 2a–d (where R/R′ = Fc/H (2a), Fc/Me (2b), Fc/Ph (2c), and Fc/Fc (2d). Fc = ferrocenyl). By contrast, only one of the triple bonds available in conjugated diynes RC≡CC≡CR is activated with the germylene, while the second one remains intact even in the presence of an excess of the germylene. The exclusive formation of 3,4-R,(C≡CR)-1,2-digermacyclobut-3-enes 3a–c [R = Ph (3a), t-Bu (3b), and Fc (3c)] was ascribed to a steric repulsion around the second triple bond. On the other hand, the reaction of the germylene with more flexible dialkyne fC=CPh)2 (fC = ferrocene-1,1-diyl) proceeded in the expected manner, producing compound 4, where both triple bonds are transformed into 1,2-digermacyclobut-3-ene rings by reaction with four equivalents of the germylene. All compounds were characterized by multinuclear NMR spectroscopy, Raman and IR spectroscopy, and in the case of 1a–c, 2a, 2c, 3a, 3b and 4, also by single-crystal X-ray diffraction analysis. The ferrocenyl substituted compounds were studied by cyclic voltammetry (CV). Finally, the plausible reaction pathway was studied for a model reaction of [(i-Pr)2NB(N-2,6-Me2C6H3)2]Ge with MeC≡CMc using DFT computations.

Introduction

Germynes, as members of the tetrylene-family, have since Lappert’s landmark1 discoveries developed into an attractive area of main group chemistry.2 Thanks to the presence of both the lone pair and π-type empty orbital at the Ge atom, they often exhibit interesting and unexpected reactivity. Some of them were shown to efficiently activate various small molecules.3 The activation of dihydrogen and ammonia by a sterically shielded germylene reported by Power et al.16d represents one of the most important initial cornerstones in this area. Similarly, the formal dimers of germynes, digermenes, display remarkable reactivity that is connected with the presence of the Ge≡Ge bond.2h,d The reactivity of germynes and digermenes toward unsaturated substrates such as carbonyl compounds or alkynes and investigation of the corresponding reaction mechanisms is an interesting and rapidly developing area.5

The treatment of digermenes with alkynes produces 1,2-digermacyclobut-3-enes.5,6 Regarding the reactivity of germynes with alkynes, the initial studies were mainly focused on trapping elusive in situ generated germynes such as Me2Ge or on the reactivity of sterically shielded germynes.7 These reactions often led to diverse products whose formation was sensitive to both reaction conditions and substrates.7 Nevertheless, some of the reactions produced defined and isolable 1,2-digermacyclobut-3-enes.8 These cyclic compounds are rarely accessible via alternative routes such as the reduction of properly substituted bis(chlorodialkylgermyl)ethenes8 or the irradiation of hexa-tert-butyldicyclogermane in the presence of PhC≡CH.10 Krebs and Veith et al.11 showed that a 1,2-digermacyclobut-3-ene or a 1,2-distannacyclobut-3-ene may also be...
prepared by the reaction of a stable monomeric germylene (or stannylene) supported by a chelating bis-amido ligand \([\text{Me}_2\text{Si(\text{Nt-Bu})}_2]\text{E}^\text{12} \) (\(E = \text{Ge} \) or \(\text{Sn}\)) and a thiacycloheptyne (Scheme 1A). In this case, the authors suggested an initial formation of the corresponding three-membered rings (i.e. stannirene or germirene) and its subsequent reactions with the second molecule of the tetraylene leading to 1,2-digermacyclobut-3-ene or 1,2-distannacyclobut-3-ene. Interestingly, the same reaction using \textit{in situ} generated germylene \(\text{Me}_2\text{Ge} \) led to the formation of a stable germirene\textsuperscript{13}, whose structure was later established by X-ray diffraction analysis.\textsuperscript{14} Treatment of this germirene with \textit{in situ} generated \(\text{Me}_2\text{Ge} \) provided 1,2-digermacyclobut-3-ene in negligible yield (Scheme 1B).\textsuperscript{7,6} By contrast, thiacycloheptyne was smoothly converted to 1,2-digermacyclobut-3-ene upon reacting with \(\text{Me}_2\text{Ge} \) and the cyclic product could be isolated in 50% yield by sublimation (Scheme 1C).\textsuperscript{7} This finding proves the importance of the germanium precursor and also indicates that the germanium(ii) centre incorporated within a strained four-membered ring (Scheme 1A) may provide access to 1,2-digermacyclobut-3-ene rings.

However, to the best of our knowledge, no comprehensive study dealing with a tailored preparation of 1,2-digermacyclobut-3-enes starting from a similar \(N,N\)-chelated germylene, \(\text{[i-Pr]NB(N-2,6-Me}_2\text{C}_6\text{H}_3)_2\text{Ge}\),\textsuperscript{15} toward various alkynes and diynes affording a whole set of substituted 1,2-digermacyclobut-3-enes including those substituted with the redox active ferrocenyl moieties. The plausible mechanism of this particular cyclization reaction was studied from the theoretical viewpoint by DFT computations.

### Results and discussion

**Syntheses, characterization and structure of studied compounds**

Addition of the germylene, \(\text{[i-Pr]NB(N-2,6-Me}_2\text{C}_6\text{H}_3)_2\text{Ge}\), to simple alkynes \(\text{RC}==\text{CR}'\) (Scheme 2) resulted in a formal [2 + 2] cyclization involving the alkylene and 2 equiv. of the germylene to afford the respective 3,4-\(R'R'-1,2\)-digermacyclobut-3-enes 1a-e, where \(R/R'=\text{Me}/\text{Me} \) (1a), \(\text{Ph}/\text{Ph} \) (1b), \(\text{Ph}/\text{H} \) (1c), \(\text{t-Bu}/\text{H} \) (1d), and \(\text{Cy}/\text{H} \) (1e). Analogously, the ferrocene substituted 3,4-\(R'R'-1,2\)-digermacyclobut-3-enes 2a-d \([R'R'=\text{Fc}/\text{H} \) (2a), \(\text{Fc}/\text{Me} \) (2b), \(\text{Fc}/\text{Ph} \) (2c), and \(\text{Fc}/\text{Fc} \) (2d); \(\text{Fc} = \text{ferrocenyl}\) were smoothly obtained by the reaction of corresponding alkynes \(\text{FeC}==\text{CR}'\) with 2 equiv. of the parent germylene (Scheme 2).

All products were isolated as crystalline solids by crystallization from hexane in moderate to good yields (31–77%), the lower yields in some cases being caused by their high solubility even at low temperatures (note: the compounds are also well soluble in aromatic solvents). Notably, all attempts to react the alkynes with only 1 equiv. of the germylene and trap a plausible germirene intermediate failed (see the discussion of the reaction mechanism below). The compounds were

<table>
<thead>
<tr>
<th>Compound</th>
<th>(i-\text{Pr-CH} )</th>
<th>(\text{Dmp-CH}_3 )</th>
<th>(\text{C=C} )</th>
<th>(\text{C==C} )</th>
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<tr>
<td></td>
<td>(\delta(1H) )</td>
<td>(\delta(13C) )</td>
<td>(\delta(1H) )</td>
<td>(\delta(13C) )</td>
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<td>46.2</td>
<td>2.28</td>
<td>19.9</td>
</tr>
<tr>
<td>1b</td>
<td>3.14</td>
<td>46.2</td>
<td>2.23</td>
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</tr>
<tr>
<td>1c</td>
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<td>46.2</td>
<td>2.16</td>
<td>19.9</td>
</tr>
<tr>
<td>1d</td>
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<td>46.1</td>
<td>2.30</td>
<td>20.2</td>
</tr>
<tr>
<td>1e</td>
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<td>46.1</td>
<td>2.30</td>
<td>19.9</td>
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<tr>
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<td>46.2</td>
<td>2.33</td>
<td>19.8</td>
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<tr>
<td>2b</td>
<td>3.20</td>
<td>46.3</td>
<td>2.33</td>
<td>20.3</td>
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<tr>
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<tr>
<td>2d</td>
<td>3.25</td>
<td>46.4</td>
<td>2.33</td>
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<td>3.25</td>
<td>46.4</td>
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\(\text{a Two overlapping signals.}\)
that cyclobutene and its derivatives show characteristic C−C stretching bands (weak in infrared but medium-to-strong in Raman spectra) in the region 1520−1600 cm−1.2a The presence of these bands is most probably retained in solution (i.e. the structure in the solid state is most probably retained in solution vide infra). Consequently, four singlets for the methyl groups of Dmp and twelve signals for aromatic carbons were observed for the non-symmetric compounds (1a-c; Table 1), because the symmetry of the central 1,2-digermacyclobut-3-ene ring is lost due to the presence of two different R and R′ substituents. Furthermore, the NMR spectra of 2a−2d displayed the characteristic signals of the ferrocenyl moieties (see the Experimental section). The presence of the C=C bond in the four-membered digermacycle was further evidenced by Raman spectroscopy. It is well known that cyclobutene and its derivatives show characteristic C=C stretching bands (weak in infrared but medium-to-strong intensity in Raman spectra) in the region 1520−1600 cm−1.2a However, relevant data for heterocyclic systems structurally related to our digermacyclobutenes are relatively sparse, the Raman spectra being reported only for several derivatives of 1,2-diosmacyclobut-3-ene (≈1500 cm−1), 1,2-palladastannacyclobut-3-ene (≈1466 cm−1), 1,2-disilacyclobut-3-ene (1558−1610 cm−1) and 3,4-bis(trifluoromethyl)-1,2-diselenete (1616 cm−1).17 In the Raman spectra of complexes 1–4 (Table 2), the band attributable to the C=C stretching vibration was clearly detected in the range 1511−1549 cm−1. The variation in the frequency of this band could be attributed to both the electronic influence of the double bond substituents and to the geometric strain of 1,2-digermacyclobut-3-ene in the particular compound. Besides, complexes 2a−2d showed an intense Raman line at 1110 ± 2 cm−1 attributable to the “ring-breathing” mode of the unsubstituted η5-coordinated cyclopentadienyl ring.18

![Molecular structures of 1a–c. Hydrogen atoms are omitted for clarity. Only one of the four independent molecules of 1c is presented and, in the case of 1a and 1c, only one position for the disordered i-Pr and Dmp groups is shown.](image)

Table 2 The solid-state Raman and IR data (in cm−1) for studied compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν_{C=C}</th>
<th>Raman (Ra)</th>
<th>IR (IR)</th>
<th>ν_{C=C}</th>
<th>Raman (Ra)</th>
<th>IR (IR)</th>
<th>ν_{C–C}</th>
<th>Raman (Ra)</th>
<th>IR (IR)</th>
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<tr>
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<tr>
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<td>n.o.</td>
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<tr>
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<td>1547w</td>
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<td></td>
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<tr>
<td>2c</td>
<td>1537w</td>
<td>1537w</td>
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<tr>
<td>3a</td>
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<td>1512m</td>
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<td>3c</td>
<td>1528w</td>
<td>1528w</td>
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The “ring-breathing” mode of the Fe(η5-C5H5) fragment. The band is split due to site-symmetry effects in the solid state.

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related analogues such as 1,1,2,2-(i-Pr)2-3-Ph-1,2-digermacyclobut-3-ene (2.439(7) Å),9 1,1,2,2-{t-Bu}3-Ph-1,2-digermacyclobut-3-ene (2.531(6) Å),10c, 1,2-dihydro-1,2-[(Me3Si)2C]2-3,4-Ph2-1,2-digermacyclobut-3-ene (2.514(2) Å)7 and, particularly, the closest analogue, which is Veith’s 1,2-digermacyclobut-3-ene (Scheme 1A; 2.549(1) Å).11 Bond angles within the C2Ge2 rings are significantly more acute at the germanium atoms (72.60 (10)–74.07(17)°) than at the carbon atoms (105.1(2)–109.3(2)°) reflecting the distortion of the four-membered ring by the longer Ge–Ge bonds. The coordination environment of the germanium atoms in 1a–c, 2a and 2c may be described as strongly distorted tetrahedral and the central Ge atoms are effectively chelated and shielded by the boraguanidinato ligand. The Ge–N bond lengths in the range 1.846(2)–1.866(3) Å are within the expected range (cf. Σr(Ge,N) = 1.92 Å).19

In contrast to simple internal alkynes, only one of the triple bonds available in conjugated diynes RC=CC=CR is attacked by the germylene as exemplified by the preparation of 3,4-R, (C=CR)-1,2-digermacyclobut-3-enes 3a–c, where R = Ph (3a), t-Bu (3b), and Fc (3c) (Scheme 3A). It is noteworthy, that even heating of isolated 3a–c with an excess of the germylene did not lead to the formation of the second four-membered digermacylobutadiene ring, which can be explained by a significant steric hindrance at the unreacted C=C bond (see the following discussion, Fig. 3).

The 1H and 13C{1H} NMR spectra of 3a–c (Table 1) were similar to those described above for 1a–e and 2a–d and in line with the proposed structures. The presence of an intact C=C bond was manifested through a pair of triple bond signals in the 13C{1H} NMR spectra (δ13C = 78.2–120.4 ppm), whereas the C=C moiety within the 1,2-digermacyclobut-3-ene rings gave rise to two signals at δ13C = 153.1–193.6 ppm. The presence of the C=C and C≡C bonds in 3a–3c was further evidenced by strong Raman lines at 1512–1539 cm⁻¹ and 2175–2191 cm⁻¹, respectively. The Raman and IR spectrum of 3c also showed a strong band at 1107 cm⁻¹ due to the ring-

### Table 3: Selected bond lengths [Å] and bonding angles [°] in studied compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond lengths [Å]</th>
<th>Bonding angles [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ge–Ge</td>
<td>Ge–N</td>
</tr>
<tr>
<td>1a</td>
<td>2.4426(7)</td>
<td>1.854(3), 1.856(3)</td>
</tr>
<tr>
<td>1b</td>
<td>2.4427(8)</td>
<td>1.860(3), 1.860(3)</td>
</tr>
<tr>
<td>1c</td>
<td>2.4572a</td>
<td>1.852u</td>
</tr>
<tr>
<td>2a</td>
<td>2.5029(5)</td>
<td>1.864(2), 1.857(2)</td>
</tr>
<tr>
<td>2b</td>
<td>2.4471(8)</td>
<td>1.860(4), 1.864(4)</td>
</tr>
<tr>
<td>3a</td>
<td>2.4682(7)</td>
<td>1.855(3), 1.856(3)</td>
</tr>
<tr>
<td>3b</td>
<td>2.4227(7)</td>
<td>1.861(2), 1.862(2)</td>
</tr>
<tr>
<td>4</td>
<td>2.4504(9)</td>
<td>1.869(5), 1.868(6)</td>
</tr>
</tbody>
</table>

*a Average value for four independent molecules in the unit cell is given.
breathing mode of the Fe(η⁵-C₅H₅) fragment. The molecular structures of 3a and 3b determined by single-crystal X-ray diffraction analysis (Fig. 3) confirm the presence of intact C=C bonds in the structures (C-C bond lengths: 1.187(5) and 1.182(7) Å in 3a and 3b, respectively; cf. Σ[<C=C>] = 1.2 Å (ref. 19)) and the formation of one 1,2-digermacyclobut-3-ene ring. The C=C bond lengths within the cycle of 1.349(4) and 1.347(7) Å for 3a and 3b, respectively, are comparable to those in 1a–c, 2a and 2c and their analogues.7,3–11 Similarly, the Ge–Ge bond lengths 2.4682(6) (3a) and 2.4207(8) (3b) approach the values found in 1a–c, 2a and 2c and even the coordination spheres around the germanium atoms are very similar (see Table 3).

In order to elicit the simultaneous addition of germylene, [(i-Pr)₂NB(N₂,6-Me₂C₆H₃)]₂Ge, across two C=C bonds in one molecule, we turned our attention to a diyne with a flexible backbone, 1,1′-bis(phenylethynyl)ferrocene, fc(C=CPh)₂ (fc = ferrocene-1,1′-diyl). Indeed, when treated with four molar equivalents of the germylene (Scheme 3B), this diyne smoothly reacted at both its C=C bonds and was converted to complex 4 comprising two chemically equivalent 1,2-digermacyclobut-3-ene rings. The ¹³C{¹H} NMR spectra of 4 displayed two signals at δ(C) = 169.9 and 170.6 ppm due to the C=C bond but no signals attributable to a C≡C bond. The presence of the bridging ferrocene unit was reflected through a pair of signals of the Cp protons (δ(C) = 3.37 and 4.30 ppm) in the ¹H NMR spectrum and three resonances in the ¹³C{¹H} NMR spectrum (δ(C) = 73.5, 74.7 (2 × CH), and 79.2 (Cipso) ppm). In addition, two sets of signals were observed for two magnetically non-equivalent boroguanidate ligands (Table 1 and Experimental section). A very strong Raman line at 1537 cm⁻¹ and a weak IR band at the same position attested to the presence of the C≡C bond in the 1,2-digermacyclobut-3-ene ring.

Compound 4 crystallizes in the centrosymmetric space group P1 and with the central iron atom residing on an inversion centre. Its molecular structure is presented in Fig. 4. The two structurally equivalent 1,2-digermacyclobut-3-ene rings in the structure of 4 are nearly ideal planar. The heterocycles facing in mutually opposite directions, minimizing their possible steric interactions. The C=C (1.350(14) Å) and Ge–Ge (2.4504(15) Å) distances in 4 compare well with the respective parameters discussed above (Table 3). Likewise, the Ge–N distances fall into an expected interval 1.861(8)–1.873(8) Å.

**Electrochemical measurements**

The electrochemical behaviour of ferrocenyl-containing derivatives 2a–d, 3c and 4 was studied by cyclic voltammetry (CV; in dichloromethane containing 0.1 M Bu₄N[Pf₆]). Redox potentials are given in Table 4 and the representative voltammograms are shown in Fig. 5 and 6. The cyclic voltammetric response of compounds 2a–d is generally similar (Fig. 5). The compounds undergo a reversible oxidation, which is followed by an irreversible multielectron redox event at more positive potentials. This first redox process, attributed to the oxidation of the ferrocene substituent, is controlled by diffusion (iₚα ∝ ν¹/₂; iₚα and ν stand for anodic peak potential and scan rate, respectively) and corresponds to a one-electron exchange. For
all compounds, the redox potentials of the first oxidation are more positive than that of ferrocene itself, suggesting an overall electron-withdrawing nature of the digermacyclobuta-
diene ring, and are only slightly affected by the other substituent R in the C(Fe)–C(R) moiety (R = H, Me, Ph). Compound 2d bearing two ferrocene substituents at the C=C double bond is oxidized in two separated reversible steps (Fig. 6) and a multielectron process at higher potentials (Table 4). The sequential oxidation of the chemically equivalent ferrocene moieties indicates their electronic communication between the ferrocene units. The calculated comproportionation constant $K_{\text{com}} \sim 18,000$ allows ranking the electrochemically generated monocation $2d^+$ as partly delocalized (class II) in the Robin–Day classification. Notably, the separation of the redox waves in 2d is substantially higher (0.25 V) than in FeC=CFc and cis-FeC=CFc (ca. 0.12 V),22 indicating a stronger electronic communication in the digermacyclobutadiene derivative. Two successive initial oxidations are observed also in the CV of 3c. In this case, however, the oxidations are due to the chemically different ferroenyl groups. Upon comparing the data for the monoferoenyl derivatives 2a–d, the first oxi-

**Table 4** Electrochemical data for 2a–d, 3c and 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>First oxidation $E^{\circ}$ [V]</th>
<th>Second oxidation $E_{\text{pa}}$ [V]</th>
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<tr>
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</tr>
<tr>
<td>2b</td>
<td>0.09</td>
<td>0.87</td>
</tr>
<tr>
<td>2c</td>
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<tr>
<td>2d</td>
<td>0.03, 0.28</td>
<td>0.98</td>
</tr>
<tr>
<td>3c</td>
<td>0.08, 0.24</td>
<td>0.88</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
<td>0.88</td>
</tr>
</tbody>
</table>

$E^{\circ}$ denotes formal potential determined as an average of anodic ($E_{\text{pa}}$) and cathodic ($E_{\text{pc}}$) peak potentials in cyclic voltammetry.

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**Fig. 4** Molecular structure of 4. Hydrogen atoms and the toluene solvate molecule are omitted for clarity.

**Fig. 5** Full (blue) and partial (red) cyclic voltammogram of 2a. The arrow indicates the scan direction (scan rate: 100 mV s$^{-1}$, glassy carbon electrode, CH$_2$Cl$_2$).

**Fig. 6** Full (blue) and partial (red) cyclic voltammograms of 2d. The arrow indicates the scan direction (scan rate: 100 mV s$^{-1}$, glassy carbon electrode, CH$_2$Cl$_2$).
dation of 3c occurring at $E^{0^*} = 0.11 \text{ V vs. ferrocene/ferrocenium}$ can be tentatively attributed to the ferrocenyl substituent at the four membered ring and the following one at $E^{0^*} = 0.24 \text{ V}$ to the FeC≡C moiety. Finally, the CV response of compound 4 in which the ferrocene-1,1'-dicyclodiene rings is similar to that of the simple representatives 2a-c except that the first reversible oxidation appears shifted to more positive potentials owing to the presence of two electron-withdrawing substituents at the ferrocene unit.

**Theoretical considerations**

To gain an insight into the plausible reaction mechanism and electronic structures of the species involved a theoretical study has been undertaken. The earlier mechanistic investigations of interactions between alkynes and derivatives of low-valent germanium are mainly represented by DFT calculations of reactions with (d)germenes, digermynes and ylide-like germynes which result in various types of cycloadditions and acetylene C–H bond activation. The formation of germacyclobutenes was observed with germynes. The diradical, zwitterionic, and concerted pathways were investigated. Notice, however, that the germanium bonding in gemynes and digermynes is quite different from the bonding situation in the complexes studied in the present work (vide infra). On the other hand, the interaction of zwitterionic N-heterocyclic germynes with HCCR resulted in (4 + 2) cycloadducts and the formation of alkynyl germylene, which was not observed in our study.

The elementary reactions accompanying the interaction of germylene, $[(i-Pr)_2NB(N-2,6-Me_2C_6H_3)_2]Ge$ (M1), and dimethylacetylene were simulated by DFT calculations at the M06-2X/DGDZVP level of theory in the gas phase as well as in C$_6$H$_6$ solution (Scheme 4 and Schemes S1, S2; see the ESI). Selected interatomic distances in the optimized gas-phase structures of the corresponding reactants, 3,4-Me$_2$-1,2-digermacyclobut-3-ene 1a and intermediates are given in Table S2. Generally, the optimized geometries agree very well with the experimental data determined from X-ray structures of 1a (Table 2) and dimer D1. The earlier NMR investigations detected only the monomer M1 species in solution. On the other hand, in crystal germylene forms dimeric molecules D1. An equilibrium involving the M1 and D1 species can, therefore, take place in C$_6$H$_6$ solution, the concentration of D1 being much lower than that of M1 (Scheme 4a). Hence, we analysed interactions of both M1 and D1 with C$_2$Me$_2$. Since our calculations indicate that the M1 triplet state is 56.6 kcal mol$^{-1}$ above the closed-shell singlet, the possible reaction mechanisms were simulated on the singlet potential energy surface. To study the electronic structures of selected species the molecular orbital (MO) and natural bond orbital (NBO) analyses as well calculations within Bader’s quantum theory of atoms in molecules (QTAIM) were carried out (for details, see the Experimental section).

The initial stage of the reaction between M1 and C$_2$Me$_2$ consists of a coordination of the alkyne to the germylene. In the resulting complex M2 (Scheme 4a), the linear alkyne donates electron density to the vacant orbital formed by the Ge 3p atomic wavefunction as indicated by NBO analysis. For the M2 species, at least two further reaction pathways are possible: one via germirene M3 (Scheme 4b) with a subsequent addition of a second M1 molecule (M2 $\rightarrow$ M3 $\rightarrow$ D2 $\rightarrow$ 1a) and the other via the dimer D3 bearing a weakly bound C$_2$Me$_2$ fragment (Scheme 4a). Notably, the former mechanism resembles that described in Scheme 1A. The M2 $\rightarrow$ M3 stage produces germirene M3 in which the three-membered GeC$_2$ ring is orthogonal to the GeN$_2$B cycle and the C=C–CH$_3$ angles are ca. 134°. However, this stage is endergonic ($\Delta G = 7.0$ kcal mol$^{-1}$). The formation of two Ge–C covalent

**Scheme 4** DFT-based mechanisms of the 3,4-Me$_2$-1,2-digermacyclobut-3-ene 1a formation via the weakly bound C$_2$Me$_2$ adducts M2 and D3 (a) and via germirenes M3 and D2 (b). The calculated changes of the electronic and Gibbs (in parentheses) free energies in C$_6$H$_6$ solution are given in kcal mol$^{-1}$. 

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bonds and transformation of alkyne to alkene on going from M2 to M3 appears to be accompanied by an increase in the electronic energy ($\Delta E_{el} = 6.0$ kcal mol$^{-1}$). Moreover, the corresponding gas-phase activation energy (Scheme 5) is rather high ($\Delta E_{a} = 24.7$ kcal mol$^{-1}$) which prevents the formation of germirene M3. Therefore, the formation of 1a via M3 seems to be hardly probable though the final stage ($D2 \rightarrow 1a$) is highly exergonic ($\Delta G = -35.8$ kcal mol$^{-1}$) and the corresponding activation energy is only 8.3 kcal mol$^{-1}$ (Scheme 5). This explains the failure of our attempts to trap germirene M3 experimentally (see above).

On the other hand, the interaction of M2 with the germilene species ($M2 \rightarrow D3$) is associated with a decrease in the electronic energy ($\Delta E_{el} = -12.9$ kcal mol$^{-1}$) and is characterized by a low positive $\Delta G$ value (2.7 kcal mol$^{-1}$). In contrast to the $M2 \rightarrow M3$ stage, the $D3$ dimer transformation into the 1a product is highly exergonic ($\Delta G = -26.9$ kcal mol$^{-1}$) and leads to a decrease in the electronic energy ($\Delta E_{el} = -30.0$ kcal mol$^{-1}$). The $D3 \rightarrow 1a$ gas-phase activation energy (15.7 kcal mol$^{-1}$, Scheme 5) is much lower than that of the $M2 \rightarrow M3$ stage. This pathway is, therefore, preferable both thermodynamically and kinetically as compared to that involving intermediate M3. Notably, the gas-phase reaction parameters (Scheme S2†) reveal similar trends, being indicative of the same mechanism.

In the course of a DFT search for additional possible reaction pathways other stable digermanium intermediates were found (Schemes S1, S2, Tables S2, S3, Fig. S4; see the ESI†). However, the mechanisms involving these species appeared to be less energetically favourable as compared to the pathway via M2 and D3 considered above (Scheme 4a). A detailed analysis of these possible mechanisms is given in the ESI†.

The $D3$ intermediate playing a key role in the formation of 1a (Scheme 4a) can be considered as an adduct of $C_{6}H_{6}$ and digermene $[(\text{P}r)m-N[H_{2}C_{6}H_{5}][\text{GeGe}(\text{P}r)m-N[H_{2}C_{6}H_{5}]]]D5$ (Scheme S1; see the ESI†) which represents an isomer of dimeric germilene. The intermetallic distances in $D3$ and $D5$ are, however, much longer than the single Ge–Ge bond length in 1a (Table S2†). The earlier DFT calculations$^{1,5}$ demonstrated that the Gibbs free energy of the $D5$ molecule in $C_{6}H_{6}$ solution exceeds that of $D1$ by 1.0 kcal mol$^{-1}$. The computations performed in this work provide a slightly larger $G$ difference of 3.5 kcal mol$^{-1}$ (Scheme S1†). Accordingly, no long-lived $D5$ species were detected experimentally. On the contrary, stable Ge(i)–Ge(i) bonded dimers were obtained with bulky amidinato and guanidinato ligands.$^{26}$ To reveal the reasons for such a different behaviour and to analyse the changes of the electronic structures on going from $D5$ to $D3$ and then to 1a we studied these systems with MO and NBO approaches. The coordination of a $C_{3}H_{5}$ molecule to $D5$ ($D5 \rightarrow D3$) causes no changes in the Ge–Ge bonding situation and the nature of frontier MOs (Fig. 7 and Fig. S3; see the ESI†). The HOMO isosurface of $D5$ (Fig. 7) appears to differ strongly from that of the amidinato complexes$^{26}$ where this orbital has a $\sigma$-bonding character relative to the Ge–Ge interaction. The HOMO of $D3$ and $D5$ represents mostly an antibonding combination of two Ge lone pairs. Moreover, the search of the lower-lying occupied MO in $D3$ and $D5$ revealed no Ge–Ge bonding orbitals except HOMO–1 with a weak positive overlap of the Ge wavefunctions. Correspondingly, the Ge–Ge distances (Table S2†) in the optimized gas-phase $D3$ and $D5$ structures (2.918 and 2.933 Å) appear to be much longer than those in the germanium(i) dimers stabilized by amidinato ligands$^{26}$ (2.679; 2.702 Å). In contrast to the latter compounds, NBO analysis reveals no Ge–Ge covalent bond in $D3$ or $D5$ and attributes the bonding between two monomers exclusively to the donation of the Ge lone pair (which has $s$ character) to the

![Scheme 5](image_url) Transition states corresponding to the key stages of the 1a formation mechanisms predicted by DFT. Calculated gas-phase activation energies $\Delta E_{a}$ and Gibbs free energies of activation $\Delta G^{\ddagger}$ (in parentheses) are given in kcal mol$^{-1}$.

![Fig. 7](image_url) Isosurfaces (isovalue 0.05) and energies of frontier MOs of $D5$ (top) and 1a (bottom). Hydrogen atoms are omitted for clarity.
empty p orbital of the second Ge atom. This can be explained\textsuperscript{27} by the large singlet-triplet energy gap in the M1 germylene (56.6 kcal mol\textsuperscript{-1}). The replacement of a carbon atom in the four-membered heterocycle of the germanium amidinato complexes with boron results, therefore, in substantial weakening of the Ge–Ge bond. On the other hand, the long Ge–Ge distance in D3 provides additional possibilities for the alkyne → alkene transformation necessary to form the 1a product.

On going from D5 or D3 to 1a, the frontier MOs change dramatically (Fig. 7). The 1a HOMO is responsible for the Ge–Ge σ-bonding. The NBO approach describes this interaction as a covalent bond formed by an electron pair shared by both Ge atoms. The HOMO energy decreases on going from D5 to 1a while the LUMO energy increases. These changes lead to an increased stability of 1a.

The MO and NBO approaches show that the D3 and D5 molecules represent the case examples of digermenes where the Ge–Ge bonding is provided exclusively by donor-acceptor interactions while the 1a species bear a Ge–Ge shared electron pair. The electron pairs can be visualized by calculation of the corresponding electron localization functions (ELF). The shared nature of the Ge electron pairs in 1a is clearly demonstrated by the isosurface of the germanium contribution to ELF (Fig. 8). This isosurface is shifted off the Ge–Ge connecting line which illustrates the bent character of the Ge–Ge bond in 1a. On the contrary, in D5 the electron pairs are localized on each Ge atom (Fig. 8). The Ge–Ge electron density distribution remains practically unchanged on going from D5 to D3. The MO, NBO and ELF approaches thus provide complementary data indicating that the transformation of digermene D3 to 1,2-digermacyclobut-3-ene 1a is accompanied by dramatic changes in the nature of the Ge–Ge interactions. This is confirmed by the QTAIM calculations (see the ESI†).

Conclusions

We have clearly demonstrated that germylene, [(i-Pr)\textsubscript{2}NB(N-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{2}]Ge, reacts with a variety of alkynes under selective formation of the corresponding substituted 1,2-digermacyclo-

but-3-enes by a formal [2 + 2 + 2] cycloaddition. Furthermore, it has been shown that only one triple bond in conjugated diynes RC≡CC≡CR enters into such cyclization reactions, whereas less sterically crowded compounds such as fc (C≡CPh)\textsubscript{2} (fc = 1,1′-ferrocendiyld) can react at both C≡C bonds. In particular, the interaction of fc(C≡CPh)\textsubscript{2} with the title germylene gives rise to an unprecedented bis(1,2-digermacyclobut-3-ene) bridged by an organometallic ferrocene fragment.

DFT calculations suggest that a plausible reaction mechanism involves weak complexes of germylene and the corresponding digermene with alkynes. The formation of a germirene appears to be unfavourable both thermodynamically and kinetically. The transformation of the digermene-alkyne complex into 1,2-digermacyclobut-3-ene as the final product is accompanied by a substantial decrease in the electronic and Gibbs free energy of the system and also by substantial changes in the Ge–Ge bonding. Further investigation will be targeted mainly at an elucidation of the reactivity of the germylene with variously substituted alkynes and diynes and other substrates containing C-heteroatom multiple bonds.

Experimental section

General considerations

Manipulations with air and moisture sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques. Germylene [(i-Pr)\textsubscript{2}NB(N-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{2}]Ge,\textsuperscript{15} FeC≡CR (R = H,\textsuperscript{28} Me,\textsuperscript{29} Ph,\textsuperscript{30} and Fe\textsuperscript{31} ), FeC≡CC≡CPh\textsubscript{2} and fc(C≡CPh)\textsubscript{2} \textsuperscript{32} were prepared according to the literature procedures. All other materials were obtained from commercial suppliers and were used without any additional purification. All solvents were dried using an MD7 Pure Solv instrument (Innovative Technology, MA, USA).

\textsuperscript{1}H and \textsuperscript{13}C(\textsuperscript{1}H) NMR spectra were recorded on a Bruker 400 or Bruker 500 spectrometer, using a 5 mm tunable broadband probe. Chemical shifts in the \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were referenced to the residual solvent (\textsuperscript{1}H) = 7.16 ppm, (\textsuperscript{13}C) = 128.39 ppm). Elemental analyses were determined with a LECO-CHNS-932 analyser. Infrared spectra were recorded in the 4000–600 cm\textsuperscript{-1} range on a Nicolet 6700 FTIR spectrometer using a silicon ATR crystal (resolution 2 cm\textsuperscript{-1}). The Raman spectra of solid samples sealed in a quartz capillary were obtained on a Nicolet iS50 equipped with an iS50 Raman module (excitation laser 1064 nm, resolution 2 cm\textsuperscript{-1}).

Cyclic voltammetric (CV) measurements were performed with a computer-controlled potentiostat μAUTOLAB III (Eco Chemie, the Netherlands) at room temperature (23 °C) using a standard Metrohm three-electrode cell equipped with a glassy carbon disc working electrode (2 mm diameter), platinum sheet auxiliary electrode, and a double-junction Ag/AgCl (3 M KCl) reference electrode. The compounds were dissolved in dry dichloromethane to give a solution containing ca. 1 mM of the analysed sample (or a saturated solution for poorly soluble compounds) and 0.1 M Bu\textsubscript{4}NPF\textsubscript{6} (Fluka, puriss for...
electrochemistry). The solutions were purged with argon before the measurement and then kept under an argon blanket. The redox potentials (accuracy ca. 5 mV) were recorded relative to internal decamethylferrocene/decamethylferroenium [added during the final scans] and then converted to the ferrocene/ferroenium scale by subtracting 0.548 V.  

General synthetic procedure

The respective alkyne was added to a light yellow solution of \([(i-Pr)_2NB(N-2,6-Me_2C_6H_3)_2]Ge\) in toluene (10 mL; hexane was used in the case of 1b) at room temperature (r.t.) and the reaction mixture was stirred for a given time. Then, the reaction mixture was evaporated in *vacuo* and the solid residue was extracted with hexane (15 mL). The coloured extract was concentrated to one third of the original volume and then stored at a temperature [specified below] to induce crystallization of the product, which was subsequently filtered off and dried in *vacuo*.

**Synthesis of** \([(i-Pr)_2NB(N-2,6-Me_2C_6H_3)_2]Ge_2\) (1a).

0.02 mL (0.3 mmol) of neat MeC≡CMe and 0.25 g (0.6 mmol) of \([(i-Pr)_2NB(N-2,6-Me_2C_6H_3)_2]Ge\) were reacted for 24 h. After workup, the light yellow concentrated extract was stored at r.t. and compound 1a was isolated as white crystals. Yield: 0.10 g (38%), m.p.: 210 °C with decomposition. Anal. calc. for C_{18}H_{26}B_2GeN_6: C 65.9, H 7.2%. 1H NMR (500 MHz, CDCl_3): δ 0.87 (d, 24H, i-Pr-CH_3, J\_HH = 6.8 Hz), 2.16 (s, 6H, Dmp-CH_3), 2.37 (s, 6H, Dmp-CH_3), 2.42 (s, 6H, Dmp-CH_3), 2.44 (s, 6H, Dmp-CH_3), 3.16 (h, 4H, i-Pr-CH, J\_HH = 6.9 Hz), 6.83 (m, 6H, Dmp-H + Ph-H), 6.95 (m, 6H, Dmp-H + Ph-H), 7.03 (m, 3H, Dmp-H + Ph-H), 7.43 (m, 2H, Ph-H_2), 8.28 (s, 1H, C = CH) ppm. 13C NMR (125.7 MHz, CDCl_3): δ 19.9 (s, Dmp-CH_3), 20.2 (s, Dmp-CH_3), 20.7 (s, Dmp-CH_3), 20.8 (s, Dmp-CH_3), 23.8 (s, i-Pr-CH), 23.9 (s, i-Pr-CH), 46.2 (s, i-Pr-CH), 124.2 (s, Dmp-C), 124.3 (s, Dmp-C), 128.7 (s, Ph-C), 128.8 (s, Ph-C), 128.9 (s, Dmp-C), 135.3 (s, Dmp-C), 149.4 (s, Dmp-C), 160.2 (s, C = CH), 182.8 (s, C = CH) ppm.

**Synthesis of** \([(i-Pr)_2NB(N-2,6-Me_2C_6H_3)_2]Ge_2\) (1b).

0.07 g (0.4 mmol) of solid PhC≡CPh and 0.35 g (0.8 mmol) of \([(i-Pr)_2NB(N-2,6-Me_2C_6H_3)_2]Ge\) were reacted in hexane for 2 h. After workup, the light yellow concentrated extract was stored at r.t. and compound 1b was isolated as colorless crystals. Yield: 0.30 g (62%), m.p.: 183 °C dec. Anal. calc. for C_{34}H_{52}B_2GeN_6: C 62.8, H 7.3%. 1H NMR (500 MHz, CDCl_3): δ 0.88 (s[br], 24H, i-Pr-CH_3), 2.23 (s, 12H, Dmp-CH_3), 2.42 (s, 12H, Dmp-CH_3), 3.14 (h, 4H, Dmp-H), 2.65 (d, 4H, Dmp-H), 6.71 (d, 4H, Ph-H_2), 6.92 (J\_HH = 7.8 Hz), 6.81 (m, 2H, Ph-H_2), 6.88 (m, 8H, Ph-H_4 + Ph-H_3), 9.65 (d[br], 4H, Dmp-H_3), 7.00 (d[br], 4H, Dmp-H_3) ppm. 13C NMR (125.7 MHz, CDCl_3): δ 20.5 (s, Dmp-CH_3), 20.7 (s, Dmp-CH_3), 23.8 (s, i-Pr-CH), 46.2 (s, i-Pr-CH), 124.2 (s, Dmp-C), 124.7 (s, Ph-C), 127.3 (s, Ph-C), 128.5 (s, Ph-C), 128.8 (s, Dmp-C), 129.0 (s, Dmp-C), 135.5 (s, Dmp-C), 136.2 (s, Dmp-C), 139.4 (s, Ph-C), 145.1 (s, Dmp-C), 176.3 (s, C = CH) ppm.

**Synthesis of** \([(i-Pr)_2NB(N-2,6-Me_2C_6H_3)_2]Ge_2\) (1c).

0.06 mL (0.5 mmol) of neat PhC≡CPh and 0.45 g (1.1 mmol) of \([(i-Pr)_2NB(N-2,6-Me_2C_6H_3)_2]Ge\) were stirred in toluene for 24 h. After workup, the light yellow concentrated extract was stored at −8 °C and compound 1c was isolated as colorless crystals. Yield: 0.28 g (55%), m.p.: 111 °C dec. Anal. calc. for C_{34}H_{52}B_2GeN_6: C 66.0, H 7.5%. 1H NMR (500 MHz, CDCl_3): δ 0.87 (d, 24H, i-Pr-CH_3, J\_HH = 6.8 Hz), 2.16 (s, 6H, Dmp-CH_3), 2.37 (s, 6H, Dmp-CH_3), 2.42 (s, 6H, Dmp-CH_3), 2.44 (s, 6H, Dmp-CH_3), 3.16 (h, 4H, i-Pr-CH, J\_HH = 6.9 Hz), 6.83 (m, 6H, Dmp-H + Ph-H), 6.95 (m, 6H, Dmp-H + Ph-H), 7.03 (m, 3H, Dmp-H + Ph-H), 7.43 (m, 2H, Ph-H_2), 8.28 (s, 1H, C = CH) ppm. 13C NMR (125.7 MHz, CDCl_3): δ 19.9 (s, Dmp-CH_3), 20.2 (s, Dmp-CH_3), 20.7 (s, Dmp-CH_3), 20.8 (s, Dmp-CH_3), 23.8 (s, i-Pr-CH), 23.9 (s, i-Pr-CH), 46.2 (s, i-Pr-CH), 124.2 (s, Dmp-C), 124.3 (s, Dmp-C), 128.7 (s, Ph-C), 128.8 (s, Ph-C), 128.9 (s, Dmp-C), 135.3 (s, Dmp-C), 149.4 (s, Dmp-C), 160.2 (s, C = CH), 182.8 (s, C = CH) ppm.
Synthesis of \(\text{[(i-Pr)NB(N\text{-2,6-Me}_2\text{C}_6\text{H}_3)]]}\text{[Ge(FC\text{C} \equiv \text{CH})]}}\) (2a). 0.06 g (0.3 mmol) of solid \(\text{FeC\equiv \text{C} \equiv \text{CH}}\) and 0.22 g (0.5 mmol) of \(\text{[(i-Pr)NB(N\text{-2,6-Me}_2\text{C}_6\text{H}_3)]]}\text{Ge}\) were stirred in toluene for 24 h. After workup, the red dark concentrated extract was stored at 4 °C and compound 2a was isolated as dark red crystals. Yield: 0.15 g (55%), m.p.: 196 °C. Anal. calc. for \(\text{C}_\text{a}\text{H}_{\text{b}}\text{B}_{\text{c}}\text{FeGe}_{\text{d}}\text{N}_{\text{e}}\) (1035.97): C, 63.8%; H, 7.1%; found: C, 63.6%; H, 7.3%. \(^1\text{H}\) NMR (500 MHz, \(\text{C}_6\text{D}_6\)): 6.88 ppm (m, 24H, \(\text{i-Pr}-\text{CH}\)); 2.33 ppm (s, 6H, \(\text{Dmp}-\text{CH}_3\)), 2.35 ppm (s, 6H, \(\text{Dmp}-\text{CH}_3\)), 2.49 ppm (s, 6H, \(\text{Dmp}-\text{CH}_3\)), 2.53 ppm (s, 6H, \(\text{Dmp}-\text{CH}_3\)), 3.17 ppm (s, 4H, \(\text{Dmp}-\text{CH}_3\)), 3.60 ppm (m, 2H, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 4.06 ppm (d, 2H, \(\text{CC} \equiv \text{C} \equiv \text{CH}\)); 1.93 ppm (t, 2H, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 3.02 ppm (s, 6H, \(\text{Dmp}-\text{CH}_3\)). \(^13\text{C}\) NMR (125.7 MHz, \(\text{C}_6\text{D}_6\)): 81.3 ppm (s, \(\text{C}_\text{a} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 21.6 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 46.3 ppm (s, \(\text{i-Pr}-\text{CH}\)), 46.5 ppm (s, \(\text{i-Pr}-\text{CH}\)), 70.3 ppm (s, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)). 0.86 g (0.3 mmol) of solid \(\text{FeC\equiv \text{C} \equiv \text{CH}}\) and 0.27 g (0.5 mmol) of \(\text{[(i-Pr)NB(N\text{-2,6-Me}_2\text{C}_6\text{H}_3)]]}\text{Ge}\) were reacted in toluene for 24 h. After workup, the red dark concentrated extract was stored at r.t. and compound 2b was isolated as red crystals. Yield: 0.11 g (34%), m.p.: 211 °C. Anal. calc. for \(\text{C}_\text{a}\text{H}_{\text{b}}\text{B}_{\text{c}}\text{FeGe}_{\text{d}}\text{N}_{\text{e}}\) (1237.99): C, 64.0%; H, 6.7%; found: C, 64.2%; H, 6.6%. \(^1\text{H}\) NMR (500 MHz, \(\text{C}_6\text{D}_6\)): 0.89 ppm (s, 2H, \(\text{i-Pr}-\text{CH}\)), 2.40 ppm (s, 2H, \(\text{Dmp}-\text{CH}_3\)), 3.18 ppm (d, 4H, \(\text{Dmp}-\text{CH}_3\)), 4.13 ppm (s, 2H, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 5.68 ppm (s, 2H, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 6.86 ppm (s, 2H, \(\text{Dmp}-\text{CH}_3\)). \(^13\text{C}\) NMR (125.7 MHz, \(\text{C}_6\text{D}_6\)): 81.3 ppm (s, \(\text{C}_\text{a} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 21.3 ppm (s, 2H, \(\text{Dmp}-\text{CH}_3\)), 21.8 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 24.1 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 24.1 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 46.3 ppm (s, \(\text{i-Pr}-\text{CH}\)), 46.5 ppm (s, \(\text{i-Pr}-\text{CH}\)), 70.3 ppm (s, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)). 0.86 g (0.3 mmol) of solid \(\text{PhC\equiv \text{CC} \equiv \text{C} \equiv \text{Ph}}\) and 0.27 g (0.5 mmol) of \(\text{[(i-Pr)NB(N\text{-2,6-Me}_2\text{C}_6\text{H}_3)]]}\text{Ge}\) were stirred in toluene for 5 h. After workup, the yellow concentrated extract was stored at r.t. and compound 3a was isolated as yellow crystals. Yield: 0.17 g (51%), m.p.: 176 °C. Anal. calc. for \(\text{C}_{\text{a}}\text{H}_{\text{b}}\text{C}_{\text{c}}\text{Ge}_{\text{d}}\text{N}_{\text{e}}\) (1046.17): C, 68.9%; H, 7.1%; found: C, 69.0%; H, 7.1%. \(^1\text{H}\) NMR (500 MHz, \(\text{C}_6\text{D}_6\)): 0.89 ppm (m, 2H, \(\text{i-Pr}-\text{CH}\)), 2.15 ppm (s, 6H, \(\text{Dmp}-\text{CH}_3\)), 2.39 ppm (s, 6H, \(\text{Dmp}-\text{CH}_3\)), 2.46 ppm (s, 6H, \(\text{Dmp}-\text{CH}_3\)), 2.72 ppm (s, 2H, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 6.83 ppm (m, 2H, \(\text{Dmp}-\text{CH}_3\)), 7.00 ppm (m, 10H, \(\text{Dmp}-\text{CH}_3\)). \(^13\text{C}\) NMR (125.7 MHz, \(\text{C}_6\text{D}_6\)): 81.3 ppm (s, \(\text{C}_\text{a} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 20.2 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 20.6 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 20.8 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 21.6 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 24.0 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 24.1 ppm (s, \(\text{i-Pr}-\text{CH}\)), 46.3 ppm (s, \(\text{i-Pr}-\text{CH}\)), 69.9 ppm (s, \(\text{PhC\equiv \text{CC} \equiv \text{C} \equiv \text{Ph}}\)); 70.4 ppm (s, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 71.8 ppm (s, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 81.3 ppm (s, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)); 124.1 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 124.1 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 128.7 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 128.9 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 135.1 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 136.2 ppm (s, \(\text{Dmp}-\text{CH}_3\)), 168.3 ppm (s, \(\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}\)).
135.9 (s, Dmp-C2), 136.0 (s, Dmp-C2), 136.0 (s, Dmp-C2), 138.7 (s, Ph-C1), 144.6 (s, Dmp-C1), 144.7 (s, Dmp-C1), 153.1 (s, C≡C-Ph), 180.4 (s, C=C=C-Fc) ppm.

**Synthesis of \{[(i-Pr)NB(N-2,6-Me2C6H4)2]Ge\}2(t-BuCC≡CC≡CrBu) (3b)\**: 0.05 g (0.3 mmol) of t-BuCC≡CC≡CrBu and 0.23 g (0.6 mmol) of \{[(i-Pr)NB(N-2,6-Me2C6H4)2]Ge\}2 were stirred in toluene for 5 d. After workup, the yellow concentrated extract was stored at r.t. and compound 3b was isolated as yellow crystals. Yield: 0.11 g (38%), m.p.: 202 °C. Anal. calcd for C14H16Ge2: δ 60.6 (s, 1H, i-Pr-C3), 3.22 (m, 4H, i-Pr-C3), 4.17 (s, 5H, Cp-C3), 2.59 (s, 6H, Dmp-C3), 2.55 (s, 6H, Dmp-C3), 2.74 (s, 6H, Dmp-C3), 3.21 (h, 4H, i-Pr-CH, 3J_{HH} = 6.8 Hz), 6.83 (t, 2H, Dmp-H3), 6.98 (m, 4H, Dmp-H3, 7.06 (dbr, 2H, Dmp-H3), 7.05 (ppm). 13C NMR (125.7 MHz, CD6): δ 20.7 (s, Dmp-C3), 21.0 (s, Dmp-C3), 21.4 (s, Dmp-C3), 21.7 (s, Dmp-C3), 23.9 (s, i-Pr-C3), 30.3 (s, t-Bu-C3), 30.8 (s, t-Bu-C3), 40.0 (s, t-Bu-C), 46.2 (s, i-Pr-C), 46.6 (s, i-Pr-C), 78.2 (s, C=C-t-Bu), 120.4 (s, C=C=C=C), 123.9 (s, C=C=C), 124.1 (s, Dmp-C4), 124.1 (s, Dmp-C4), 128.3 (s, Dmp-C35), 128.8 (s, Dmp-C35), 129.1 (s, Dmp-C35), 129.2 (s, Dmp-C35), 134.8 (s, Dmp-C2), 135.1 (s, Dmp-C2), 135.7 (s, Dmp-C2), 135.9 (s, Dmp-C2), 144.8 (s, Dmp-C1), 154.3 (s, C=C=t-Bu), 193.6 (s, C=C=C-Fc) ppm.

**Synthesis of \{[(i-Pr)NB(N-2,6-Me2C6H4)2]Ge\}2(FeC≡CC≡Fe) (3c)\**: 0.15 g (0.4 mmol of FeC≡CC≡Fe and 0.30 g (0.7 mmol) of \{[(i-Pr)NB(N-2,6-Me2C6H4)2]Ge\}2 were reacted in toluene for 7 d. After workup, the dark red concentrated extract was stored at r.t. and compound 3c was isolated as dark red crystals. Yield: 0.35 g (78%), m.p.: 212 °C. Anal. calcd for C30H28Ge2: δ 66.3 (s, subst-Cp-C1), 67.2 (s, subst-Cp-C1), 71.1 (s, subst-Cp-C1), 71.2 (s, subst-Cp-C1), 71.3 (s, subst-Cp-C1), 71.9 (s, subst-Cp-C1), 81.8 (s, Cp-C1), 87.2 (s, C≡C-Fc), 110.4 (s, C≡C=C-C≡C), 124.4 (overlap of two signals, Dmp-C4), 128.8 (s, Dmp-C35), 128.9 (s, Dmp-C35), 129.0 (s, Dmp-C35), 129.0 (s, Dmp-C35), 135.7 (s, Dmp-C35), 136.1 (s, Dmp-C2), 136.1 (s, Dmp-C2), 136.2 (s, Dmp-C2), 144.8 (s, Dmp-C1), 145.1 (s, Dmp-C1), 148.1 (s, C≡C-Fc), 177.2 (s, C≡C=C≡C) ppm.

**DFT calculations**

The mechanism of the reaction between germylene, [(i-Pr)NB(N-2,6-Me2C6H4)2]Ge, and dimethylacylene was modeled by the DFT method employing the Gaussian09 package. All the calculations were performed at the M062X/DGDZVP level. M062X is a hybrid meta-GGA exchange–correlation functional recommended for the studies of main-group thermochemistry, kinetics and non-covalent interactions. The double-$\zeta$ plus polarization DGDZVP basis set was shown to be a good choice when describing the electronic structures of organosilanes. The molecular geometries were fully optimized in closed-shell singlet states, the experimental X-ray structures being used as the starting points for the germylene dimer and the final complex. Harmonic vibrational frequencies were computed to confirm the convergence to a minimum or a first-order saddle point on the potential energy surface and to estimate Gibbs energies. The electronic energies of the optimized geometries were taken for the reaction $\Delta E$ calculations. For transition states, the quadratic synchronous transit (QST3) method was applied. Solvent effects in benzene were evaluated by means of the polarizable continuum model (PCM) at the same level of DFT. The PCM and gas-phase optimized geometries were very similar. Gibbs energies in solution $(G_{sol})$ were calculated on the basis of the gas-phase values $(G_{gas})$ and electronic energy changes on solvation as follows:

$$G_{sol} = G_{gas} + (E_{sol} - E_{gas}).$$

For transition states in solution the gas-phase optimized geometries were used. The basis set superposition errors (BSSE) were taken into account by the counterpoise corrections.
The DFT calculations of selected species were accompanied by NBO analysis using NBO Version 3.1 incorporated into the Gaussian package. The QTAIM computations were carried out with the AIMALL program suite. To study the ELF topology, the Multiwfn code was used.

X-ray crystallography

The X-ray data for colorless crystals of 1a, 1b, 1c, 2a, 2c, 3a and 3b were obtained at 150(2) K using an Oxford Cryostream low-temperature device and a Nonius Kappa CCD diffractometer equipped with Mo/Kα radiation (λ = 0.71073 Å) using a graphite monochromator and the φ and χ scan modes. Data reductions were performed with DENZO-SMN. The absorption was corrected by integration methods or performed analytically using SADABS software for 3b and 4. Structures were solved by direct methods (SIR92) and refined by the full matrix least-squares method based on \(F^2\) (SHELXL97). Full-sets of the diffraction data for 4 were collected at 150(2) K with a Bruker D8-Venture diffractometer equipped with Mo (Mo/Kα radiation; λ = 0.71073 Å) microfocus X-ray (µS) sources, a Photon CMOS detector and an Oxford Cryosystems cooling device. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The data were corrected for absorption effects using the multi-scan method (SADABS). The structures were solved and refined using XT-version 2014/5 and SHELXL-2014/7 software implemented in an APEX3 v2016.5-0 (Bruker AXS) system.

Hydrogen atoms were mostly localized on a difference Fourier map. However to ensure uniformity of treatment of the crystal structures, all hydrogen were recalculated into their idealized positions (riding model) and assigned temperature factors \(U_{	ext{eq}}(H) = 1.2U_{	ext{eq}}(\text{pivotal atom})\) or of \(1.5U_{	ext{eq}}\) (methyl). Hydrogen atoms in methyl, methylene, methine, and vinylidene moieties and hydrogen atoms in aromatic rings were placed in their theoretical positions with C–H distances of 0.96, 0.97, 0.98, 0.93 and 0.93 Å (0.86 or 0.82 Å for N–H or O–H bonds).

The structure of 1a contains four positionally disordered isopropyl groups and one 2,6-dimethyl phenyl group which were split into two positions with approximate occupancy 1 : 1. These disorders have been modeled according to the positions of the residual electron density maxima on the Fourier electron density maps and treated by the standard SHELXL instructions. The structure of 1c contains four positionally disordered isopropyl groups, which were treated by the SAME, RIGU and EADP instructions. A disorder was observed also in the structure of 3a, which was dealt with similarly. In this case, a disordered isopropyl groups was split into two groups with occupancy of 1 : 1. In the structure of 3b, the same procedure was used for modelling disorder at one of the tert-butyl groups (occupancies 55 : 45).

Residual electron maximum and small cavities were observed within the unit cell of 1b probably originating from an unsolved disorder. PLATON/SQUEEZZE was used to mask the cavity. A potential solvent volume of 224 Å³ was found with 16 electrons per unit cell that were located in the void which does not respond to any of the solvents used. On the other hand, the structure of 3c contained residual electron maxima attributable to disordered hexane. PLATON/SQUEEZZE was used to correct the data for the presence of this disordered solvent. A potential solvent volume of 559 Å³ was found with 109 electrons per unit cell worth scattering located in the void. The amount of solvent was calculated to be two molecules of hexane per unit cell which results in 100 electrons per unit cell. A similar problem was encountered in the case of compound 4. Even in this case PLATON/SQUEEZZE procedure was used to correct the data. A potential solvent volume of 566 Å³ was found with 200 electrons per unit cell, which corresponds to six molecules of toluene.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre under CCDC no. 1533462–1533469.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


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