



## Germane vs. digermane formation†‡

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Cite this: *Chem. Commun.*, 2014, 50, 15461Received 7th October 2014,  
Accepted 10th October 2014

DOI: 10.1039/c4cc07921c

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**Oxidative addition reactions of dialkylchalcogenanes  $R_2E_2$  and  $[Me_2Si(Nt-Bu)_2]_2Ge$  1 yielded bis(alkylchalcogeno)germanes  $Me_2Si(Nt-Bu)_2-Ge(ER)_2$  ( $R = Et$ ,  $E = S$ ,  $Se$  3;  $R = Me$ ,  $E = Se$  4) and digermanes  $[Me_2Si(Nt-Bu)_2Ge(EER)]_2$  ( $E = S$ ,  $Se$  6). The reaction of 1 with  $Et_2Te_2$  proceeds with formation of  $Me_2Si(Nt-Bu)_2Ge(TeEt)_2$  7, which slowly converts into the Te-bridged complex  $[Me_2Si(Nt-Bu)_2GeTe]_2$  8. 1–6 and 8 were characterized by single crystal X-ray diffraction.**

Germynes  $R_2Ge$ , which have singlet ground states with a low-lying s lone-pair orbital and a higher-lying p orbital,<sup>1</sup> have evolved from exotic reaction intermediates to important reagents in organic chemistry.<sup>2</sup> They were shown to activate a large variety of bonds including P–Cl,<sup>3</sup> O–H,<sup>4</sup> Ge–C<sup>5</sup> and C–H bonds<sup>6</sup> and to react in [2+1]- and [4+1]-cycloaddition reactions with alkenes and alkynes.<sup>2,7</sup> Germynes tend to dimerize to digermenes  $Ge_2R_4$  or oligomerize into polygermanes, but monomeric  $R_2Ge$  were kinetically stabilized by bulky organic ligands.<sup>8</sup> Lappert's  $[(Me_3Si)_2CH]_2Ge$  is monomeric in the gas phase and in solution<sup>9,10</sup> and dimeric in the solid state,<sup>11</sup> while  $[(Me_3Si)_3C]_2Ge$ <sup>12</sup> and  $[(Me_3Si)_2N]_2Ge$ <sup>13</sup> are monomeric in solution and in the solid state.  $[Me_2Si(Nt-Bu)_2]_2Ge$  1 is monomeric in solution, while its solid state structure was not reported.<sup>14</sup>

Germynes react with elemental chalcogenes with the formation of complexes containing chalcogen-bridges<sup>15</sup> or terminal Ge=E bonds<sup>16</sup> as well as polychalcogenides.<sup>17</sup> In addition, insertion reactions in E–C bonds<sup>18</sup> and E–E bonds ( $E = S$ ,  $Se$ )<sup>19</sup> as well as reactions with  $R_3P=E$ <sup>20</sup> were reported. Our general interest in the reactivity of complexes with low-valent main group elements<sup>21</sup> prompted us to investigate reactions of  $[Me_2Si(Nt-Bu)_2]_2Ge$  1 with dialkylchalcogenanes  $R_2E_2$ , which were recently shown to

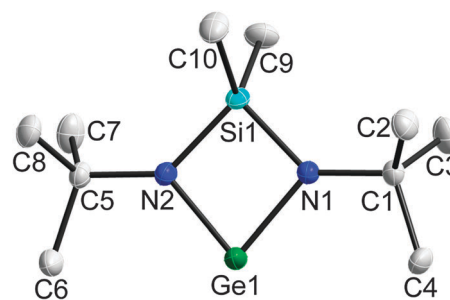


Fig. 1 Solid state structure of 1 as determined at 100(1) K. Non-H-atoms shown as thermal ellipsoids at 50% probability levels, H atoms omitted for clarity.

react with monovalent tin ( $RSnSnR$ ), antimony ( $RSb$ ), bismuth ( $RBi$ ) and zinc complexes ( $R_2Zn_2$ ) in oxidative addition reactions.<sup>22,23</sup> In addition, we report on the solid state structure of  $[Me_2Si(Nt-Bu)_2]_2Ge$  1 (Fig. 1).

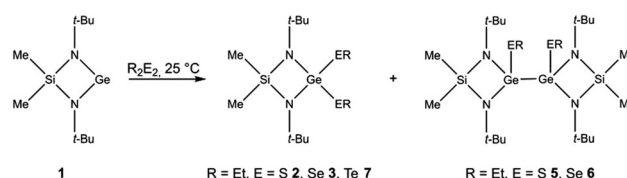
Crystals of 1 were grown in closed quartz glass capillaries under an Ar atmosphere at 100 K (**1lt**) and 230 K (**1ht**) using an IR-laser-assisted technique.<sup>30</sup> 1 crystallizes in the monoclinic space group  $P2_1/n$  with four molecules in the unit cell. The shortest Ge–Ge distance is 4.158 Å, so 1 is monomeric in the solid state.

Reactions of equimolar amounts of  $[Me_2Si(Nt-Bu)_2]_2Ge$  1 and  $Et_2E_2$  ( $E = S$ ,  $Se$ ) at 25 °C yielded two products in 2 : 1 ( $E = S$ ) and 4 : 1 ( $E = Se$ ) molar ratios as was shown using  $^1H$  and  $^{77}Se$  NMR spectroscopy (Scheme 1). The relative intensities of the signals due to the  $Me_2Si(Nt-Bu)_2$  and the Et groups within each set of resonances in

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† Dedicated to Prof. H. J. Frohn on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available: Experimental details, NMR spectra of 2–8; bond lengths and angles of 1–6. CCDC 1009920 (**1lt**), 1009921 (**1ht**), 1009925 (2), 1009924 (3), 1009923 (4), 1009922 (5), 1019789 (6) and 1010028 (8). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc07921c



Scheme 1 Synthesis of 2–7.



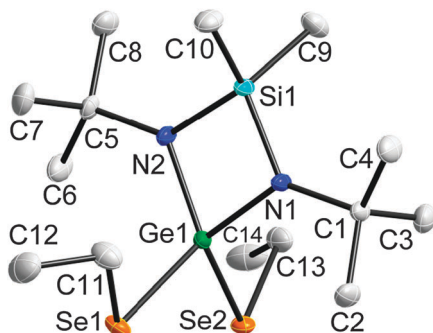


Fig. 2 Solid state structure of **3**. Non-H-atoms shown as thermal ellipsoids at 50% probability levels, H atoms omitted for clarity.

the  $^1\text{H}$  NMR spectra were 1:2 and 1:1, respectively. In contrast, reactions of **1** with  $\text{Me}_2\text{Se}_2$  and  $\text{Et}_2\text{Te}_2$  at  $25^\circ\text{C}$  only yielded  $[\text{Me}_2\text{Si}(\text{Nt-Bu})_2]\text{Ge}(\text{SeMe})_2$  **4** and  $[\text{Me}_2\text{Si}(\text{Nt-Bu})_2]\text{Ge}(\text{TeEt})_2$  **7**. Fractional crystallisation of the reaction mixtures gave  $[\text{Me}_2\text{Si}(\text{Nt-Bu})_2]\text{Ge}(\text{EET})_2$  ( $\text{E} = \text{S}$  **2**,  $\text{Se}$  **3**), which are the expected products from the insertion reaction of **1** into the E–E bond, and the digermenes  $[\text{Me}_2\text{Si}(\text{Nt-Bu})_2]\text{GeEET}_2$  ( $\text{E} = \text{S}$  **5**,  $\text{Se}$  **6**). Attempts to grow single crystals of **7**, which slowly decomposes in solution into  $[\text{Me}_2\text{Si}(\text{Nt-Bu})_2]\text{Ge}(\mu\text{-Te})$  **8** and  $\text{TeEt}_2$  (ESI $^\ddagger$ ), failed.<sup>24</sup>

Single-crystals of **2–6** were obtained from solutions in hexane upon storage at  $-30^\circ\text{C}$ , whereas **8** was obtained from a solution of **7** in  $\text{C}_6\text{D}_6$  after 72 h (Fig. 2 and 3). The bond lengths and angles within the  $\text{SiN}_2\text{Ge}$  ring in **2–6** are almost identical to those of **1** (Table 1). The Ge–E bond lengths agree with the calculated ( $\text{S}$  2.24 Å;  $\text{Se}$  2.37 Å)<sup>25</sup> and experimental values for Ge–E single

Table 2 Selected bond lengths [Å] and angles [ $^\circ$ ] of **5** and **6**

	<b>5</b>	<b>6</b>
Ge(1)–N(1)	1.855(3)	1.846(3)
Ge(1)–N(2)	1.845(4)	1.851(3)
Ge(1)–E(1)	2.2271(13)	2.3700(5)
Ge(1)–Ge(2)	2.4727(6)	2.4921(5)
N(1)–Ge(1)–N(2)	82.05(16)	81.75(13)
N(1)–Si(1)–N(2)	88.69(17)	88.40(14)

bonds<sup>26</sup> but are longer than those of  $\text{Ge}=\text{E}$  double bonds (calc:  $\text{S}$  2.05 Å;  $\text{Se}$  2.18 Å<sup>27</sup>).<sup>2d,15b</sup> The Ge–Se bond lengths in  $[\text{MeC}(\text{NCy})_2]\text{Ge}(\text{SePh})_2$  (2.3522(5), 2.4009(5) Å) are slightly elongated.<sup>19</sup> The Ge–Ge bond lengths (2.4727(6) **5**, 2.4921(5) Å **6**) are comparable to those observed in digermenes (Table 2).<sup>28</sup>

The ratio of the  $\text{Ge}(\text{III})$  and  $\text{Ge}(\text{IV})$  species formed in the reactions with  $\text{Et}_2\text{E}_2$  ( $\text{E} = \text{S}, \text{Se}$ ) depends on the reaction temperature and the molar ratio of the starting reagents. **2** and **3** were formed in equimolar ratios at  $70^\circ\text{C}$ . **5** was formed in 36% yield together with **2** in the reaction of **1** and  $\text{Et}_2\text{S}_2$  in a 2 : 1 molar ratio at  $-30^\circ\text{C}$ , while **6** was obtained in less than 25% yield together with **3**. Equimolar amounts of **1** and  $\text{Et}_2\text{S}_2$  reacted at  $-30^\circ\text{C}$  to **2** and **5**, while the reaction of **1** with 0.5 equivalents of  $\text{Et}_2\text{S}_2$  at  $70^\circ\text{C}$  gave **2** and unreacted **1**. The reaction of **5** with  $\text{Et}_2\text{S}_2$  failed to give **2** even after heating to  $70^\circ\text{C}$  for 1 h, hence proving that **5** is no reaction intermediate in the formation of **2** (Fig. S22, ESI $^\ddagger$ ). In contrast, **5** was quantitatively converted at  $100^\circ\text{C}$  in solution into **1** and **2** by disproportionation reaction (Fig. S11, ESI $^\ddagger$ ).

The formation of digermenes **5** and **6** is without precedence in germylene chemistry.  $^1\text{H}$  NMR spectroscopy studies on the reactions of **1** with isolated **2** and **3** did not show the formation of **5** and **6**, hence excluding the formation of **5** and **6** by insertion of the germylene  $[\text{Me}_2\text{Si}(\text{Nt-Bu})_2]\text{Ge}$  **1** into the Ge–E bond of initially formed **2** and **3**. Since digermenes  $\text{R}_2\text{Ge}=\text{GeR}_2$  are known to react with water, alcohols, carboxylic acids,  $\text{CCl}_4$ ,  $\text{CHCl}_3$  or  $\text{HN}_3$  in a 1,2 fashion with the formation of the corresponding digermenes,<sup>29</sup>  $^1\text{H}$  NMR spectra were recorded at  $-60^\circ\text{C}$  and  $+60^\circ\text{C}$  to investigate whether **1** formed a temperature-dependent germylene–digermene equilibrium in solution. However, only a single set of resonances was observed. In addition, reactions of **1** with 2-methylbutadiene, a trapping agent for transient and stable germynes and digermenes,<sup>31</sup> at  $25^\circ\text{C}$  and  $-60^\circ\text{C}$  only yielded the germylene products (germacyclopentene) as was reported previously,<sup>32</sup> whereas no sign of the digermene reaction products was observed. A possible explanation for the formation of **5** and **6** is the presence of a loosely bound dimer in solution, held together by weak dispersion forces. Computational studies are currently being performed in order to address this hypothesis.

Oxidative addition reactions of dichalcogenanes to germylene **1** at elevated temperature yielded the expected  $\text{Ge}(\text{IV})$  species, whereas the reactions at low temperatures proceeded with the predominant formation of digermenes **5** and **6**, in which the Ge atoms adopted the formal oxidation state of +III. These findings indicate that **1** forms a loosely bound dimer in solution.

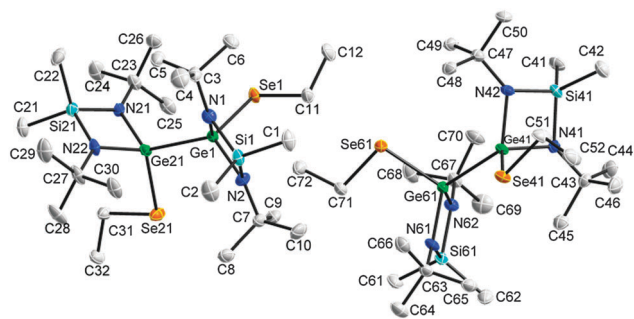


Fig. 3 Solid state structure of **6** (2 independent molecules). Non-H-atoms shown as thermal ellipsoids at 50% probability levels, H atoms omitted for clarity.

Table 1 Selected bond lengths [Å] and angles [ $^\circ$ ] of **1–4**

	<b>1</b> <sup>b</sup>	<b>2</b>	<b>3</b>	<b>4</b> <sup>a</sup>
Ge(1)–N(1)	1.8574(13)	1.8400(7)	1.8444(19)	1.8451(9)
Ge(1)–N(2)	1.8584(13)	1.8410(7)	1.8411(18)	1.8451(9)
Ge(1)–E(1)	—	2.2072(2)	2.3355(4)	2.3439(2)
Ge(1)–E(2)	—	2.2070(2)	2.3371(4)	2.3439(2)
N(1)–Ge(1)–N(2)	81.33(6)	82.93(3)	82.74(8)	82.89(6)
E(1)–Ge(1)–E(2)	—	101.15(1)	102.05(2)	102.53(1)
N(1)–Si(1)–N(2)	88.82(6)	88.70(3)	88.80(9)	89.00(6)

<sup>a</sup> Special position. Equal values are symmetry equivalent and labeling may differ. <sup>b</sup> Structural parameters of the “ht” version of **1** are almost identical (ESI).



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