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Germane *vs.* digermane formation†‡

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Oxidative addition reactions of dialkylchalcogenanes R_2E_2 and $[Me_2Si(Nt\text{-}Bu)_2]Ge$ 1 yielded bis(alkylchalcogeno)germanes $Me_2Si(Nt\text{-}Bu)_2\text{-}Ge(ER)_2$ (R = Et, E = S 2, Se 3; R = Me, E = Se 4) and digermanes $[Me_2Si(Nt\text{-}Bu)_2Ge(EEt)]_2$ (E = S 5, Se 6). The reaction of 1 with Et_2Te_2 proceeds with formation of $Me_2Si(Nt\text{-}Bu)_2Ge(TeEt)_2$ 7, which slowly converts into the Te-bridged complex $[Me_2Si(Nt\text{-}Bu)_2GeTe]_2$ 8. 1–6 and 8 were characterized by single crystal X-ray diffraction.

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

Germylenes react with elemental chalcogenes with the formation of complexes containing chalcogen-bridges[15] or terminal Ge═E bonds[16] as well as polychalcogenides.[17] In addition, insertion reactions in E–C bonds[18] and E–E bonds (E = S, Se)[19] as well as reactions with $R_3P{=}E$[20] were reported. Our general interest in the reactivity of complexes with low-valent main group elements[21] prompted us to investigate reactions of $[Me_2Si(Nt\text{-}Bu)_2]Ge$ **1** with dialkyldichalcogenanes R_2E_2, which were recently shown to react with monovalent tin (RSnSnR), antimony (RSb), bismuth (RBi) and zinc complexes (R_2Zn_2) in oxidative addition reactions.[22,23] In addition, we report on the solid state structure of $[Me_2Si(Nt\text{-}Bu)_2]Ge$ **1** (Fig. 1).

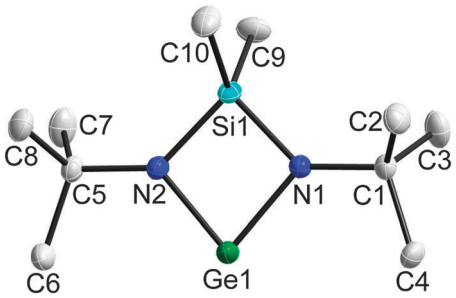
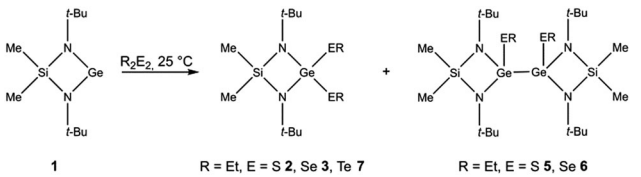


Fig. 1 Solid state structure of 1 as determined at 100(1) K. Non-H-atoms shown as thermal ellipsoids at 50% probability levels, H atoms omitted for clarity.

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.[30] **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 $[Me_2Si(Nt\text{-}Bu)_2]Ge$ **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 $Me_2Si(Nt\text{-}Bu)_2$ and the Et groups within each set of resonances in



Scheme 1 Synthesis of **2–7**.

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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

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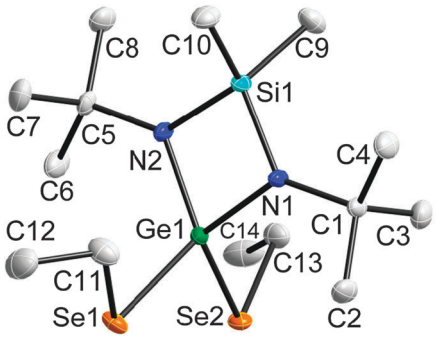

Fig. 2 Solid state structure of **3**. Non-H-atoms shown as thermal ellipsoids at 50% probability levels, H atoms omitted for clarity.

the ^{1}H NMR spectra were 1 : 2 and 1 : 1, respectively. In contrast, reactions of **1** with Me_2Se_2 and Et_2Te_2 at 25 °C only yielded [$Me_2Si(Nt\text{-}Bu)_2$]Ge(SeMe)$_2$ **4** and [$Me_2Si(Nt\text{-}Bu)_2$]Ge(TeEt)$_2$ **7**. Fractional crystallisation of the reaction mixtures gave [$Me_2Si(Nt\text{-}Bu)_2$]Ge(EEt)$_2$ (E = S **2**, Se **3**), which are the expected products from the insertion reaction of **1** into the E–E bond, and the digermanes [$Me_2Si(Nt\text{-}Bu)_2$]GeEEt$_2$ (E = S **5**, Se **6**). Attempts to grow single crystals of **7**, which slowly decomposes in solution into [$Me_2Si(Nt\text{-}Bu)_2$]Ge(μ-Te) **8** and TeEt$_2$ (ESI‡), failed.[24]

Single-crystals of **2–6** were obtained from solutions in hexane upon storage at −30 °C, whereas **8** was obtained from a solution of **7** in C_6D_6 after 72 h (Fig. 2 and 3). The bond lengths and angles within the SiN_2Ge ring in **2–6** are almost identical to those of **1** (Table 1). The Ge–E bond lengths agree with the calculated (S 2.24 Å; Se 2.37 Å)[25] and experimental values for Ge–E single bonds[26] but are longer than those of Ge═E double bonds (calc: S 2.05 Å; Se 2.18 Å[27]).[2d,15b] The Ge–Se bond lengths in [MeC(NCy)$_2$]Ge(SePh)$_2$ (2.3522(5), 2.4009(5) Å) are slightly elongated.[19] The Ge–Ge bond lengths (2.4727(6) **5**, 2.4921(5) Å **6**) are comparable to those observed in digermanes (Table 2).[28]

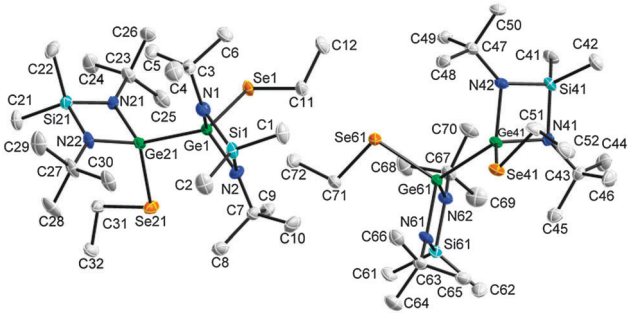

Fig. 3 Solid state structure of **6** (2 independent molecules). Non-H-atoms shown as thermal ellipsoids at 50% probability levels, H atoms omitted for clarity.

Table 1 Selected bond lengths [Å] and angles [°] of **1–4**

	1lt[b]	**2**	**3**	**4**[a]
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)

[a] Special position. Equal values are symmetry equivalent and labeling may differ. [b] Structural parameters of the "ht" version of **1** are almost identical (ESI).

Table 2 Selected bond lengths [Å] and angles [°] of **5** and **6**

	5	**6**
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)

The ratio of the Ge(III) and Ge(IV) species formed in the reactions with Et_2E_2 (E = S, Se) depends on the reaction temperature and the molar ratio of the starting reagents. **2** and **3** were formed in equimolar ratios at 70 °C. **5** was formed in 36% yield together with **2** in the reaction of **1** and Et_2S_2 in a 2 : 1 molar ratio at −30 °C, while **6** was obtained in less than 25% yield together with **3**. Equimolar amounts of **1** and Et_2S_2 reacted at −30 °C to **2** and **5**, while the reaction of **1** with 0.5 equivalents of Et_2S_2 at 70 °C gave **2** and unreacted **1**. The reaction of **5** with Et_2S_2 failed to give **2** even after heating to 70 °C for 1 h, hence proving that **5** is no reaction intermediate in the formation of **2** (Fig. S22, ESI‡) In contrast, **5** was quantitatively converted at 100 °C in solution into **1** and **2** by disproportionation reaction (Fig. S11, ESI‡).

The formation of digermanes **5** and **6** is without precedence in germylene chemistry. ^{1}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 [$Me_2Si(Nt\text{-}Bu)_2$]Ge **1** into the Ge–E bond of initially formed **2** and **3**. Since digermenes $R_2Ge{=}GeR_2$ are known to react with water, alcohols, carboxylic acids, CCl_4, $CHCl_3$ or HN_3 in a 1,2 fashion with the formation of the corresponding digermanes,[29] ^{1}H NMR spectra were recorded at −60 °C and +60 °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 germylenes and digermenes,[31] at 25 °C and −60 °C only yielded the germylene products (germacyclopentene) as was reported previously,[32] whereas no sign of the digermane 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 Ge(IV) species, whereas the reactions at low temperatures proceeded with the predominant formation of digermanes **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.

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