Germane vs. digermane formation†‡

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Oxidative addition reactions of dialkylchalcogenanes R_2E_2 and $[Me_2Si(Nt-Bu)_2]Ge$ 1 yielded bis(alkylchalcogeno)germanes $Me_2Si(Nt-Bu)_2-Ge(ER)_2$ ($R = Et$, $E = S$ 2, Se 3; $R = Me$, $E = Se$ 4) and digermanes $[Me_2Si(Nt-Bu)_2Ge(EEt)]_2$ ($E = S$ 5, 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,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–C⁵ and C–H bonds⁶ and to react in [2+1]- and [4+1]-cycloaddition reactions with alkenes and alkynes.^{2,7} Germynes 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. $[Me_2Si(Nt-Bu)_2]Ge$ 1 is monomeric in solution, while its solid state structure was not reported.¹⁴

Germynes react with elemental chalcogenes with the formation of complexes containing chalcogen-bridges¹⁵ or terminal Ge=E bonds¹⁶ as well as polychalcogenides.¹⁷ In addition, insertion reactions in E–C bonds¹⁸ 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 elements²¹ prompted us to investigate reactions of $[Me_2Si(Nt-Bu)_2]Ge$ 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.^{22,23} In addition, we report on the solid state structure of $[Me_2Si(Nt-Bu)_2]Ge$ 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.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 $[Me_2Si(Nt-Bu)_2]Ge$ 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 $Me_2Si(Nt-Bu)_2$ 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 ^1H 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 $[\text{Me}_2\text{Si}(\text{Nt-Bu})_2]\text{Ge}(\text{SeMe})_2$ **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**, Se **3**), which are the expected products from the insertion reaction of **1** into the E–E bond, and the digermanes $[\text{Me}_2\text{Si}(\text{Nt-Bu})_2]\text{GeEET}_2$ ($\text{E} = \text{S}$ **5**, 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 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

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**

	1 ^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 [$^\circ$] 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)

bonds²⁶ but are longer than those of $\text{Ge}=\text{E}$ double bonds (calc: S 2.05 Å; Se 2.18 Å²⁷).^{2d,15b} 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.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

The ratio of the $\text{Ge}(\text{III})$ and $\text{Ge}(\text{IV})$ species formed in the reactions with Et_2E_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°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. ^1H 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 digermanes $\text{R}_2\text{Ge}=\text{GeR}_2$ 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 ^1H NMR spectra were recorded at -60°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 digermanes,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 $\text{Ge}(\text{IV})$ 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.

Notes and references

- 1 (a) C. Boehme and G. Frenking, *J. Am. Chem. Soc.*, 1996, **118**, 2039; (b) M. Z. Kassaei, S. Soleimani-Amiri, M. Ghambarian, F. Boazar and E. Motamedi, *THEOCHEM*, 2008, **849**, 37; (c) A. Bundhun, P. Ramasami and H. F. Schaefer III, *J. Phys. Chem. A*, 2009, **113**, 8080.
- 2 (a) W. P. Neumann, *Chem. Rev.*, 1991, **91**, 311; (b) N. Tokitoh and R. Okazaki, *Coord. Chem. Rev.*, 2000, **210**, 251; (c) O. Köhl, *Coord. Chem. Rev.*, 2004, **248**, 411; (d) S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457; (e) Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479.
- 3 (a) M. Veith, M. Grosser and V. Huch, *Z. Anorg. Allg. Chem.*, 1984, **513**, 89; (b) J. K. West and L. Stahl, *Organometallics*, 2012, **31**, 2042.
- 4 R. D. Sweeder, K. A. Miller, F. A. Edwards, J. Wang, M. M. Banaszak Holl and J. W. Kampf, *Organometallics*, 2003, **22**, 5054.
- 5 P. Bleckmann, R. Minkwitz, W. P. Neumann, M. Schriewer, M. Thibud and B. Watta, *Tetrahedron Lett.*, 1984, **25**, 2467.
- 6 (a) L. Lange, B. Meyer and W.-W. du Mont, *J. Organomet. Chem.*, 1987, **329**, C17; (b) P. Jutzi, H. Schmidt, B. Neumann and H.-G. Stammer, *Organometallics*, 1996, **15**, 741; (c) B. Gehrhuis, P. Hitchcock and M. F. Lappert, *Angew. Chem., Int. Ed.*, 1997, **36**, 2514; (d) R. H. Walker, K. A. Miller, S. L. Scott, Z. T. Cygan, J. M. Bartolin, J. W. Kampf and M. M. Banaszak Holl, *Organometallics*, 2009, **28**, 2744.
- 7 M. Schriewer and W. P. Neumann, *J. Am. Chem. Soc.*, 1983, **105**, 897.
- 8 M. Weidenbruch, *Eur. J. Inorg. Chem.*, 1999, 373.
- 9 T. Fjeldberg, A. Haaland, B. E. R. Schilling, M. F. Lappert and A. J. Thorne, *J. Chem. Soc., Dalton Trans.*, 1986, 1551.
- 10 P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.
- 11 P. B. Hitchcock, M. F. Lappert, S. J. Miles and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 480.
- 12 P. Jutzi, A. Becker, H. G. Stammer and B. Neumann, *Organometallics*, 1991, **10**, 1647.
- 13 (a) D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895; (b) R. W. Chorley, P. B. Hitchcock, M. F. Lappert and W.-P. Leung, *Inorg. Chim. Acta*, 1992, **198**, 203.
- 14 M. Veith and M. Grosser, *Z. Naturforsch., B: J. Chem. Sci.*, 1982, **37**, 1375.
- 15 (a) G. Pfister-Guillouzo and C. Guimon, *Phosphorus and Sulphur*, 1985, **23**, 197; (b) P. B. Hitchcock, H. A. Jasim, M. F. Lappert, W.-P. Leung, A. K. Rai and R. E. Taylor, *Polyhedron*, 1991, **10**, 1203; (c) D. Ellis, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1992, 3397.
- 16 (a) N. Tokitoh, T. Matsumoto, K. Manmaru and R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 8855; (b) T. Matsumoto, N. Tokitoh and R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2316; (c) N. Tokitoh, T. Matsumoto and R. Okazaki, *J. Am. Chem. Soc.*, 1997, **119**, 2337; (d) R. K. Siwatch, D. Yadav, G. Mukherjee, G. Rajaraman and S. Nagendran, *Inorg. Chem.*, 2014, **53**, 5073.
- 17 (a) N. Tokitoh, T. Matsumoto and R. Okazaki, *Tetrahedron Lett.*, 1992, **33**, 2531; (b) T. Matsumoto, N. Tokitoh and R. Okazaki, *Organometallics*, 1995, **14**, 1008.
- 18 T. Chen, W. Hunks, P. S. Chen, G. T. Stauff, T. M. Cameron, C. Xu, A. G. DiPasquale and A. L. Rheingold, *Eur. J. Inorg. Chem.*, 2009, 2047.
- 19 S. R. Foley, G. P. A. Yap and D. S. Richeson, *J. Chem. Soc., Dalton Trans.*, 2000, 1663.
- 20 S. R. Foley and D. S. Richeson, *J. Chem. Soc., Chem. Commun.*, 2000, 1391.
- 21 S. Schulz, *Chem. – Eur. J.*, 2010, **16**, 6416.
- 22 (a) M. Wagner, C. Dietz, M. Bouška, L. Dostál, Z. Padělková, R. Jambor and K. Jurkschat, *Organometallics*, 2013, **32**, 4973; (b) P. Simon, R. Jambor, A. Růžicka and L. Dostál, *Organometallics*, 2013, **32**, 239; (c) P. Simon, R. Jambor, A. Růžicka and L. Dostál, *J. Organomet. Chem.*, 2013, **740**, 98.
- 23 S. Gondzik, S. Schulz, D. Bläser and C. Wölper, *J. Chem. Soc., Chem. Commun.*, 2014, **50**, 1189.
- 24 M. Veith, M. Notzel, L. Stahl and V. Huch, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1264.
- 25 P. Pykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 186.
- 26 CCDC search: Ge=S cn(S) = 1, hits (bond(s) 95(198), range 2.05–2.387, mean 2.146(52)); Ge–S–Ge hits (bond(s) 113(586), range 2.11–2.472, mean 2.238(38)); Ge–S–C cn(S) = 2, hits (bond(s) 107(246), range 2.115–2.412, mean 2.241(43)); Ge=Se cn(S(e)) = 1, hits (bond(s) 63(117), range 2.172–2.426, mean 2.271(54)); Ge–Se–Ge, hits (bond(s) 49(302), 2.304–2.459, mean 2.374(24)); Ge–Se–C cn(S(e)) = 2, hits (bond(s) 20(40), 2.314–2.511, mean 2.379(51)).
- 27 P. Pykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 12770.
- 28 (a) M. Hölbling, S. L. Masters, M. Flock, J. Baumgartner, K. Hassler, H. E. Robertson and D. A. Wann, *Inorg. Chem.*, 2008, **47**, 3023; (b) K. V. Zaitsev, A. A. Kapranov, A. V. Churakov, O. Kh. Poleshchuk, Y. F. Oprunenko, B. N. Tarasevich, G. S. Zaitseva and S. S. Karlov, *Organometallics*, 2013, **32**, 6500.
- 29 (a) B. Pampuch, W. Saak and M. Weidenbruch, *J. Organomet. Chem.*, 2006, **691**, 3540; (b) W. J. Leigh, F. Lollmahomed, C. R. Harrington and J. M. McDonald, *Organometallics*, 2006, **25**, 5424; (c) L. A. Huck and W. J. Leigh, *Organometallics*, 2007, **26**, 1339; (d) K. L. Hurni, P. A. Rupar, N. C. Payne and K. M. Baines, *Organometallics*, 2007, **26**, 5569; (e) K. Mochida, T. Kayamori, M. Wakasa, H. Hayashi and M. P. Egorov, *Organometallics*, 2000, **19**, 3379; (f) M. S. Samuel, M. C. Jennings and K. M. Baines, *Organometallics*, 2001, **20**, 590; (g) H. Schäfer, W. Saak and M. Weidenbruch, *J. Organomet. Chem.*, 2000, **604**, 211.
- 30 R. Boese and M. Nussbaumer, *in situ* Crystallisation Techniques, in *Organic Crystal Chemistry*, ed. D. W. Jones, Oxford University Press, Oxford, England, 1994, p. 20.
- 31 (a) N. Tokitoh and W. Ando, in *Reactive Intermediate Chemistry*, ed. R. A. Moss, M. S. Platz and M. Jones, Jr., Wiley-Interscience, New York, 2004, pp. 651–715; (b) W. P. Neumann, *Chem. Rev.*, 1991, **91**, 311; (c) M. Nag and P. P. Gaspar, *Organometallics*, 2009, **28**, 5612; (d) K. Mochida, T. Kayamori, M. Wakasa, H. Hayashi and M. P. Egorov, *Organometallics*, 2000, **19**, 3379.
- 32 M. Veith, A. Rammo, S. Faber and B. Schillo, *Pure Appl. Chem.*, 1999, **71**, 401.