ChemComm

COMMUNICATION



View Article Online View Journal | View Issue

Germane vs. digermane formation †‡

P. Steiniger, G. Bendt, D. Bläser, C. Wölper and S. Schulz*

Cite this: Chem. Commun., 2014, 50, 15461

Received 7th October 2014, Accepted 10th October 2014

DOI: 10.1039/c4cc07921c

CrossMark

www.rsc.org/chemcomm

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.

Germylenes R₂Ge, 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} Germylenes tend to dimerize to digermenes Ge₂R₄ or oligomerize into polygermanes, but monomeric R₂Ge were kinetically stabilized by bulky organic ligands.⁸ Lappert's [(Me₃Si)₂CH]₂Ge is monomeric in the gas phase and in solution^{9,10} and dimeric in the solid state,¹¹ while [(Me₃Si)₃C]₂Ge¹² and [(Me₃Si)₂N]₂Ge¹³ are monomeric in solution and in the solid state. [Me₂Si(N*t*-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-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 dialkyldichalcogenanes 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 ⁷⁷Se 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



Scheme 1 Synthesis of 2-7

University of Duisburg-Essen, Universitätsstr. 5-7, S07 S03 C30, 45117 Essen, Germany. E-mail: stephan.schulz@uni-due.de; Fax: +49 201 1833830; Tel: +49 201 1834635

^{101: +49 201 1834035}

 $[\]dagger\,$ 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



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 Me₂Se₂ and Et₂Te₂ at 25 °C only yielded [Me₂Si(N*t*-Bu)₂]Ge(SeMe)₂ 4 and [Me₂Si(N*t*-Bu)₂]Ge(TeEt)₂ 7. Fractional crystallisation of the reaction mixtures gave [Me₂Si(N*t*-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 [Me₂Si(N*t*-Bu)₂]GeEEt₂ (E = S 5, Se 6). Attempts to grow single crystals of 7, which slowly decomposes in solution into [Me₂Si(N*t*-Bu)₂]Ge(μ -Te) 8 and TeEt₂ (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 C₆D₆ after 72 h (Fig. 2 and 3). The bond lengths and angles within the SiN₂Ge 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 [°] 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).

View Article Online

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)

bonds²⁶ but are longer than those of Ge—E double bonds (cale: S 2.05 Å; Se 2.18 Å²⁷).^{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

The ratio of the Ge(m) and Ge(m) 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 tailed 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 [Me2Si(Nt-Bu2]Ge 1 into the Ge-E bond of initially formed 2 and 3. Since digermenes R₂Ge=GeR₂ are known to react with water, alcohols, carboxylic acids, CCl₄, CHCl₃ or HN₃ in a 1,2 fashion with the formation of the corresponding digermanes,29 ¹H NMR spectra were recorded at -60 °C and +60 °C to investigate whether 1 formed a temperaturedependent 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.

Notes and references

- (*a*) C. Boehme and G. Frenking, *J. Am. Chem. Soc.*, 1996, **118**, 2039;
 (*b*) M. Z. Kassaee, 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. Kühl, 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.
- 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. Stammler, Organometallics, 1996, 15, 741; (c) B. Gehrhus, 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. Stammler 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. Stauf, 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. Růžička and L. Dostál, Organometallics, 2013, 32, 239; (c) P. Simon, R. Jambor, A. Růžička 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. Pyykkö 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. Pyykkö 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.
- (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.