The first organoelement oxides containing three different metals; synthesis and structure of (Ph_2SiOR_2SnOMO) [R = $(CH_2)_3NMe_2$; M = $Bu^t{}_2Sn$, $Bu^t{}_2Ge$, PhB]† ‡

Jens Beckmann, Klaus Jurkschat,* Nicole Pieper and Markus Schürmann

Lehrstuhl für Anorganische Chemie II, Fachbereich Chemie der Universität Dortmund, D-44221 Dortmund, Germany. E-mail: kjur@platon.chemie.uni-dortmund.de

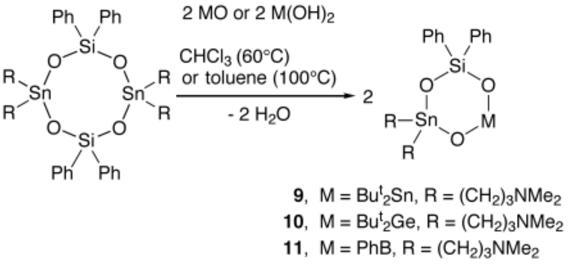
Received (in Cambridge, UK) 26th March 1999, Accepted 12th May 1999

***Umpolung* of ring strain by intramolecular Sn–N Lewis acid–Lewis base interaction is the key for the synthesis of the first organoelement oxides of the type (Ph_2SiOR_2SnOMO) [R = $(CH_2)_3NMe_2$; M = $Bu^t{}_2Sn$, $Bu^t{}_2Ge$, PhB] which hold potential as precursors to tertiary metal oxides.**

Recently, we reported the syntheses and structures of stannasiloxanes such as *cyclo*-$R_2Si(OSnBu^t{}_2)_2O$ (**1**, R = Bu^t; **2**, R = Ph),[1a,b] *cyclo*-$(Ph_2SiOR_2SnO)_2$ [**3**, R = Bu^t; **4**, R = $(CH_2)_3NMe_2$],[1b,c] *cyclo*-$R_2Sn(OSiPh_2)_2O$ [**5**, R = Bu^t; **6**, R = $(CH_2)_3NMe_2$],[1c,d] and of the germastannoxanes *cyclo*-$Bu^t{}_2Sn(OGePh_2)_2O$ **7**.[1c] Such compounds are of potential interest as molecular precursors for the synthesis by ring-opening polymerisation of inorganic polymers.[1d,2] The stannasiloxane $Bu^t{}_2Sn(OSiPh_2)_2O$ **5** contains a six-membered ring in solution but is the first well-defined polystannasiloxane in the solid state. The ring strain in **5** is the thermodynamic driving force for the polymerisation which however, is compensated in solution by entropy of a large number of monomers, *i.e.*, six-membered rings.[1d] In contrast, the related borasiloxane *cyclo*-$PhB(OSiPh_2)_2O$ **8** is a six-membered ring both in solution and in the solid state.[2b] The reaction of the eight-membered stannasiloxane ring *cyclo*-$(Ph_2SiOBu^t{}_2SnO)_2$ (**3**) with 2/3 mol equivalents *cyclo*-$(Bu^t{}_2SnO)_3$ quantitatively provided *in situ* the six-membered stannasiloxane ring $Ph_2Si(OSnBu^t{}_2)_2O$ **2**. However, this reaction is also an equilibrium and removal of the solvent quantitatively yielded the starting compounds *cyclo*-$(Bu^t{}_2SnO)_3$ and **3**.[1b]

In contrast, the reaction of the eight-membered intramolecularly coordinated stannasiloxane ring *cyclo*-$(Ph_2SiOR_2SnO)_2$ [**4**, R = $(CH_2)_3NMe_2$] with *cyclo*-$(Bu^t{}_2SnO)_3$ afforded the first *cyclo*-stannasiloxane **9** containing two different substituted tin atoms (Scheme 1).§

Furthermore, the reaction of compound **4** with di-*tert*-butylgermanium dihydroxide $Bu^t{}_2Ge(OH)_2$ and phenylboronic acid $PhB(OH)_2$ gave the first organoelement oxides **10** and **11**, respectively, being composed of three different metals or metalloids in the same ring (Scheme 1).§



Scheme 1

It seems that the intramolecular Sn–N coordination increases the ring strain in the eight-membered *cyclo*-stannasiloxane **6** but decreases the ring strain in the six-membered rings **9**–**11**. This means, the formation of **9**–**11** is favoured by both enthalpy and entropy.

The molecular structures¶ of compounds **10** and **11** are shown in Fig. 1 and 2, respectively. Compound **9** is isostructural with **10**. The Sn(1) atoms in **9**–**11** exhibit distorted octahedral configurations with the carbon atoms in mutual *trans* and the oxygen and nitrogen atoms in *cis* positions. The deviation from the ideal octahedral geometry is documented by the C(1)–Sn(1)–C(11) angles of 149.3(2)–152.30(2)° and the N(1)–Sn–N(2) angles of 105.4(1)–109.58(9)°. The O(1)–Sn(1)–O(3) angles fall in the range 90.30(8)–95.45(9)°. The intramolecular Sn–N distances in **9**–**11** [2.620(3)–2.764(3) Å] are shorter as compared to the Sn–N contacts in the eight-membered *cyclo*-stannasiloxane **4** [2.721(4)/2.811(4) Å].[1c] The Sn–N distances are quite different within each of the compounds **9**–**11**. This corresponds with previous observations on the intramolecularly coordinated organotin sulfide $\{[Me_2N(CH_2)_3]_2SnS\}_2$.[3]

Compared to the ^{119}Sn NMR chemical shifts in solution the ^{119}Sn MAS NMR spectra of **9**–**11** exhibit shifts of 52.9, 30.3 and 9.5/17.8 ppm‖ to low frequency which hints, especially for **10** and **11**, at a stronger Sn–N coordination in the solid state.

The synthetic concept introduced within this paper should also apply for the synthesis of organoelement oxides containing

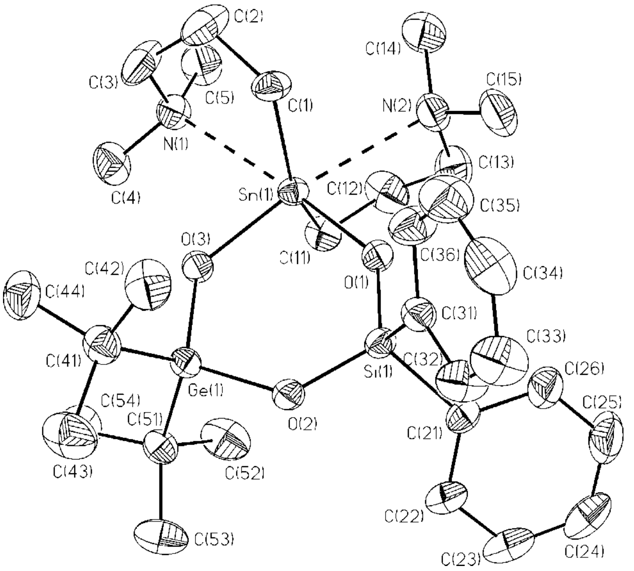


Fig. 1 General view of a molecule of **10** showing 30% probability displacement ellipsoids and the atom numbering. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–O(1/3) 2.010(2)/2.022(2), Sn(1)–N(1/2) 2.648(3)/ 2.752(3); O(1)–Sn(1)–O(3) 93.89(8), O(1)–Si(1)–O(2) 113.5(1); O(2)–Ge(1)–O(3) 109.1(1). Compound **9** is isostructural; Ge(1) is replaced by Sn(2). Sn(1)–O(1/3) 1.998(2)/2.026(2), Sn(1)–N(1/2) 2.683(3)/2.764(3); O(1)–Sn(1)–O(3) 95.45(9), O(1)–Si(1)–O(2) 114.2(1), O(2)–Sn(2)–O(3) 106.69(9).

---

† Dedicated to Professor Dietmar Seyferth on the occasion of his 70th birthday.

‡ This work contains part of the Ph.D. thesis of N. Pieper, Dortmund University 1998, and of the intended Ph.D. thesis of J. Beckmann.

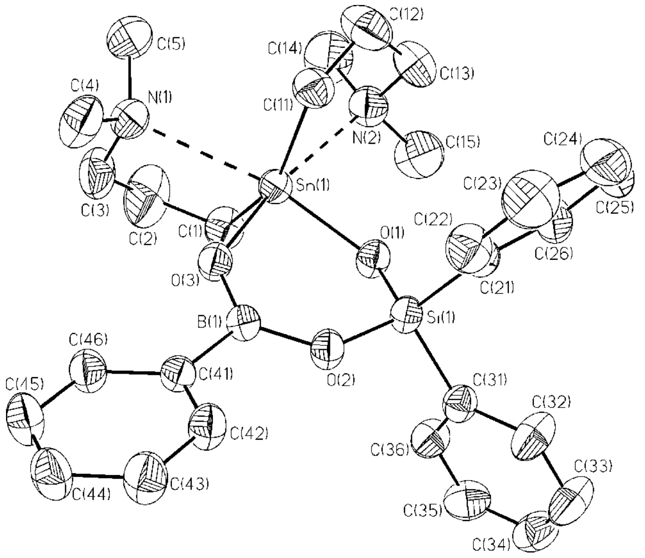


Fig. 2 General view of a molecule of **11** showing 30% probability displacement ellipsoids and the atom numbering. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–O(1/3) 2.038(2)/2.054(2) (2.017(2)/2.050(2)), Sn(1)–N(1/2) 2.620(3)/2.681(3) (2.649(3)/2.65(2)); O(1)–Sn(1)–O(3) 90.30(8)(91.75(8)); O(1)–Si(1)–O(2) 110.4(1) (112.9(1)), O(2)–B(1)–O(3) 124.2(3) (123.5(3)). The values given in parentheses refer to the second, symmetrically independent molecule of **11** in the unit cell which is not shown.

both main group elements and transition metals. Such compounds are of increasing interest as single source precursors for mixed metal oxides[4] which find applications in heterogeneous catalysis[5a] or for solar cells.[5b]

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Notes and references

§ Literature procedures were used to prepare *cyclo*-$(R_2SnOSiPh_2O)_2$ (**3**, R = Bu^t;[1b] **4**, R = $(CH_2)_3NMe_2$[1c]], *cyclo*-$(Bu^t{}_2SnO)_3$[6a] and $Bu^t{}_2Ge(OH)_2$.[6b]

Synthesis and selected spectroscopic data: 1,1-*di-tert-butyl*-3,3-*bis*(3-*dimethylaminopropyl*)-5,5-*diphenyl*-2,4,6-*trioxa*-5-*sila*-1,3-*distannacyclohexane* **9**: 1,1,5,5-tetrakis(3-dimethylaminopropyl)-3,3,7,7-tetraphenyl-2,4,6,8-tetraoxa-3,7-disila-1,5-distannacyclooctane **4** (500 mg, 0.495 mmol) and di-*tert*-butyltin oxide (246 mg, 0.330 mmol) were dissolved in chloroform (10 mL). The reaction mixture was kept at 60 °C for 12 h. The solvent was evaporated *in vacuo* and the residue recrystallised from *n*-hexane to give 271 mg (38 % yield) of **9** as colourless crystals, mp 135 °C. $^{29}Si\{^1H\}$ NMR δ −40.4 [$^2J(^{29}Si–O–^{119}Sn)$ 31 Hz]; $^{119}Sn\{^1H\}$ NMR δ −93.3 [$^2J(^{119}Sn–O–^{119/117}Sn)$ 371 Hz], −191.7 [$^2J(^{119}Sn–O–^{119/117}Sn)$ 377 Hz]; $^{119}Sn\{^1H\}$ MAS NMR: δ −92.7 [$^2J(^{119}Sn–O–^{119/117}Sn)$ 381 Hz], −244.6. MS: *m/z*: 697 ($C_{26}H_{41}N_2O_3SiSn_2^+$), 639 ($C_{22}H_{31}N_2O_3SiSn_2^+$), 583 ($C_{20}H_{28}O_3SiSn_2^+$), 206 ($C_5H_{12}Sn^+$). Elemental analysis (%): found: C, 47.81, H, 7.18, N, 3.65. Calc. for $C_{30}H_{52}N_2O_3Sn_2Si$: C 47.78, H 6.95, N 3.71%. Molecular weight ($CHCl_3$): found.: 543 g mol^{-1}; calc. for $C_{30}H_{52}N_2O_3Sn_2Si$: 754 g mol^{-1}.

1,1-*di-tert-butyl*-3,3-*bis*(3-*dimethylaminopropyl*)-5,5-*diphenyl*-3-*germa*-2,4,6-*trioxa*-5-*sila*-1-*stannacyclohexane* **10**: 1,1,5,5-tetrakis(3-dimethylaminopropyl)-3,3,7,7-tetraphenyl-2,4,6,8-tetraoxa-3, 7-disila-1, 5-distannacyclooctane **4** (500 mg, 0.495 mmol) and di-*tert.*-butylgermanium dihydroxide (240 mg, 1.087 mmol) were dissolved in toluene (15 mL). The reaction mixture was kept at 100 °C for 2 d. The solvent was distilled off and the residue was recrystallised from *n*-hexane to give 268 mg (36 % yield) of colourless crystals of **10**, mp. 148 °C. $^{29}Si\{^1H\}$ NMR δ −42.2 [$^2J(^{29}Si–O–^{119/117}Sn)$ 32 Hz]; $^{119}Sn\{^1H\}$ NMR δ −231.6; $^{119}Sn\{^1H\}$ MAS NMR: δ −261.9. MS: *m/z*: 707 ($C_{30}H_{51}N_2O_3GeSiSn^+$), 650 ($C_{26}H_{42}N_2O_3GeSiSn^+$), 621 ($C_{25}H_{39}NO_3GeSiSn^+$), 536 ($C_{20}H_{28}O_3GeSiSn^+$), 478 ($C_{16}H_{18}O_3GeSiSn^+$), 206 ($C_5H_{12}Sn^+$). Elemental analysis (%): found: C, 51.09; H, 7.57; N, 3.92; calc. for $C_{30}H_{52}N_2O_3GeSiSn$: C, 50.89; H, 7.40; N, 3.96. Molecular weight ($CHCl_3$): found: 657 g mol^{-1}; calc. for $C_{30}H_{52}N_2O_3GeSiSn$: 708 g mol^{-1}.

3,3-*bis*(3-*dimethylaminopropyl*)-3,5,5-*triphenyl*-3-*bora*-2,4,6-*trioxa*-5-*sila*-1-*stannacyclohexane* **11**: 1,1,5,5-tetrakis(3-dimethylaminopropyl)-3,3,7,7-tetraphenyl-2,4,6,8-tetraoxa-3,7-disila-1, 5-distannacyclooctane **4** (455 mg, 0.450 mmol) and phenylboronic acid (110 mg, 0.902 mmol) were dissolved in chloroform (10 mL). The reaction mixture was kept at 60 °C for 12 h. The solvent was removed *in vacuo* and the residue was recrystallised from *n*-hexane to give 335 mg (61% yield) of colourless crystals of **11**, mp 132 °C. $^{29}Si\{^1H\}$ NMR δ −38.7 [$^2J(^{19}Si–O–^{119/117}Sn)$ 19 Hz]; $^{119}Sn\{^1H\}$ NMR δ −259.1; $^{119}Sn\{^1H\}$ MAS NMR: δ −268.6, −276.9. MS: *m/z* 609 ($C_{28}H_{38}N_2O_3BSiSn^+$), 523 ($C_{23}H_{26}NO_3BSiSn^+$), 430 ($C_{17}H_{21}NO_2BSiSn^+$), 206 ($C_5H_{12}NSn^+$). Elemental analysis (%): found: C 55.25, H 6.85, N 4.50; calc. for $C_{28}H_{39}N_2O_3BSiSn$: C 55.20, H 6.45, N 4.60. Molecular weight ($CHCl_3$): found: 517 g mol^{-1}; calc. for $C_{28}H_{39}N_2O_3BSiSn$: 609 g mol^{-1}.

^1H and ^{13}C NMR data for compounds **9**–**11** can be viewed electronically, see: http://www.rsc.org/suppdata/1999/1095/.

¶ The structures of **9**–**11** were refined in the triclinic space group $P\bar{1}$.

9: $C_{30}H_{52}N_2O_3SiSn_2$, M_r = 754.21, crystal dimensions: 0.70 × 0.18 × 0.15 mm, a = 9.302(1), b = 10.824(1), c = 17.897(1) Å, α = 81.611(1), β = 88.994(1), γ = 85.935(1)°, V = 1778.1(3) Å^3, Z = 2, μ = 1.467 mm^{-1}, D_c = 1.409 Mg m^{-3}, D_m = 1.420(2) Mg m^{-3}, $2\theta_{max}$ = 29.61°, 21528 measured, 8738 (R_{int} = 0.032) independent and 5324 observed reflections with $I > 2\sigma(I)$, $R1$ = 0.036, $wR2$ = 0.0748 for 355 parameters, S = 0.907, Δ/ρ_{max} = 0.672 e Å^{-3}.

10: $C_{30}H_{52}GeN_2O_3SiSn$, M_r = 708.11, crystal dimensions: 0.40 × 0.20 × 0.20 mm, a = 9.190(1), b = 10.833(1), c = 17.730(1) Å, α = 80.144(1), β = 89.614(1), γ = 86.402(1)°, V = 1735.6(3) Å^3, Z = 2, μ = 1.649 mm^{-1}, D_c = 1.355 Mg m^{-3}, $2\theta_{max}$ = 25.66°, 23559 measured, 6102 (R_{int} = 0.035) independent and 4234 observed reflections with $I > 2\sigma(I)$, $R1$ = 0.031, $wR2$ = 0.0604 for 355 parameters, S = 0.950, Δ/ρ_{max} = 0.277 e Å^{-3}.

11: $C_{28}H_{39}BN_2O_3SiSn$, M_r = 609.20, crystal dimensions: 0.20 × 0.10 × 0.10 mm, a = 10.630(1), b = 17.201(1), c = 17.300(1) Å, α = 100.001(1), β = 90.737(1), γ = 104.343(1)°, V = 3012.9(4) Å^3, Z = 4, μ = 0.917 mm^{-1}, D_c = 1.343 Mg m^{-3}, D_m = 1.387(2) Mg m^{-3}, $2\theta_{max}$ = 25.68°, 41 109 measured, 10 578 ($R_{int.}$ = 0.024) independent and 7733 observed reflections with $I > 2\sigma(I)$, $R1$ = 0.031, $wR2$ = 0.0735 for 696 parameters, S = 0.999, Δ/ρ_{max} = 0.442 e Å^{-3}.

CCDC 182/1261. See: http://www.rsc.org/suppdata/cc/1999/1095/ for crystallographic files in .cif format.

‖ The unit cell of **11** consists of two independent conformers and consequently two signals are observed in the $^{119}Sn\{^1H\}$ MAS NMR spectrum.

1 (*a*) J. Beckmann, K. Jurkschat, B. Mahieu and M. Schürmann, *Main Group Met. Chem.*, 1998, **21**, 113; (*b*) J. Beckmann, B. Mahieu, W. Nigge, D. Schollmeyer, K. Jurkschat and M. Schürmann, *Organometallics*, 1998, **17**, 5697; (*c*) J. Beckmann, K. Jurkschat, U. Kaltenbrunner, N. Pieper and M. Schürmann, *Organometallics*, 1999, **18**, 1586; (*d*) J. Beckmann, K. Jurkschat, D. Schollmeyer and M. Schürmann, *J. Organomet. Chem.*, 1997, **543**, 229.
2 (*a*) I. Manners, *Angew. Chem.*, 1996, **108**, 1712; (*b*) D. A. Foucher, A. J. Lough and I. Manners, *Inorg. Chem.* 1992, **31**, 2034.
3 K. Jurkschat, S. Van Dreumel, G. Dyson, D. Dakternieks, T. J. Bastow, M. E. Smith and M. Dräger, *Polyhedron*, 1992, **11**, 2747.
4 (*a*) M. Veith, S. Mathur and V. Huch, *J. Am. Chem. Soc.*, 1996, **118**, 903; (*b*) M. Veith, S. Mathur and V. Huch, *Inorg. Chem.*, 1996, **35**, 7295.
5 (*a*) A. de Mallmann, O. Lot, N. Perrier, F. Lefebvre, C. Santini and J. M. Basset, *Organometallics*, 1998, **17**, 1031; (*b*) V. M. Jimenez, J. A. Mejias, J. P. Espinos and A. R. Gonzales-Elipe, *Surf. Sci.*, 1996, **366**, 545.
6 (*a*) H. Puff, W. Schuh, R. Sievers, W. Wald and R. Zimmer, *J. Organomet. Chem.*, 1984, **260**, 271; (*b*) H. Puff, S. Franken, W. Schuh and W. Schwab, *J. Organomet. Chem.* 1983, **254**, 33.

Communication 9/02428J