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Thomas Zöller, Michael Lutter, Thorsten Berends and Klaus Jurkschat*

The 2,8-dioxa-5-aza-1-sila-bicyclo[3.3.0$^{1.5}$]octane $PhN(CH_2CH_2O)_2SiH_2$ as reducing reagent: synthesis and molecular structure of $PhN(CH_2CH_2O)_2Sn$

Abstract: The synthesis of the 2,8-dioxa-5-aza-1-stanna-bicyclo[3.3.0$^{1.5}$]octane $[PhN(CH_2CH_2O)_2Sn]_n$ (**3**) by a combined ligand exchange/redox reaction and independently by the reaction of tin(II)butoxide with *N*-phenyldiethanolamine is reported. Compound **3** was characterized by elemental analysis and single crystal X-ray diffraction analysis. In the solid state, it is a coordination polymer via intermolecular O→Sn interactions at O-Sn distances of 2.325 (3) and 2.379 (3) Å. The intramolecular N→Sn interactions at distances of 2.818 (3) and 3.096 (3) Å are rather weak.

Keywords: alkoxysilane; ethanolamine; stannabicyclooctane; tin alkoxide; X-ray crystallography.

Introduction

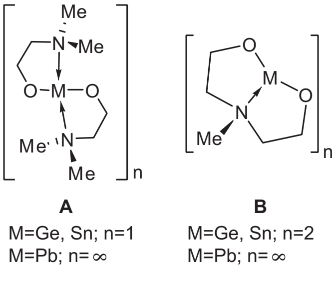
In recent years, the group 14 element derivatives of alkanol amines and the related substituted alcohols have attracted renewed interest (for reviews, see Verkade, 1994; Karlov and Zaitseva, 2001; Singh and Mehrotra, 2004; Cea-Olivares et al., 2005; Selina et al., 2006, 2007; Puri et al., 2011). The renaissance of this chemistry has emerged from academic curiosity into the enormous structural diversity that these compounds exhibit and, especially for the tin compounds, from their catalytic activity in, for instance, polyurethane formation (Krause et al., 2009; Zöller et al., 2011) and ring opening polymerization (Iovkova-Berends et al., 2011; Poirier et al., 2012).

The heavy carbene analogues of the types $(Me_2NCH_2CH_2O)_2M$ (**A**) (Zemlyansky et al., 2003) and $MeN(CH_2CH_2O)_2M$ (**B**) (Berends et al., 2009; Huang et al., 2012) (M = Ge, Sn) have been shown to be monomeric (**A**) and dimeric (**B**), respectively, by the stabilization through intramolecular N→Sn coordination (Scheme 1). In contrast to this, the corresponding plumbylenes form polymeric structures via intermolecular O→Pb coordination (Scheme 1) (Kemmitt et al., 2005; Aysin et al., 2011).

The structure of the *N*-phenyl-substituted tin(II) derivative $PhN(CH_2CH_2O)_2Sn$ has not been reported yet; however, based on DFT calculations, dimers were forecasted to be preferred over monomers (Mengmeng et al., 2009). A polymeric structure was, however, not considered in these calculations.

Recently, we reported the syntheses and structures of stannatranes of the type $N(CH_2CMe_2O)_3SnX$ (X = halogen, OR, SR) (Zöller et al., 2012) by the reaction of $N(CH_2CMe_2O)_3SnO$-*t*-Bu with the corresponding Brønsted acid HX. We also reported the synthesis and structure of the hydrido-substituted 2,8-dioxa-5-aza-1-sila-bicyclo[3.3.0$^{1.5}$]octane $PhN(CH_2CH_2O)_2SiH_2$ (Lutter et al., 2012).

Here, we present our attempt to employ the latter compound as a hydride transfer reagent for the synthesis of the hydrido-substituted stannatrane $N(CH_2CMe_2O)_3SnH$, which, however, unexpectedly afforded the *N*-phenyl-substituted tin(II) derivative $PhN(CH_2CH_2O)_2Sn$ and the novel silatrane $N(CH_2CMe_2O)_3SiO$*t*-Bu.



Scheme 1 Schematic drawings of Ge(II), Sn(II), and Pb(II) derivatives of alkanol amines (Zemlyansky et al., 2003; Kemmitt et al., 2005; Berends et al., 2009; Aysin et al., 2011; Huang et al., 2012).

***Corresponding author: Prof. Dr. Klaus Jurkschat**, Lehrstuhl für Anorganische Chemie II der Technischen Universität Dortmund, D-44221 Dortmund, Germany,
e-mail: klaus.jurkschat@tu-dortmund.de
Thomas Zöller M.Sc., Michael Lutter M.Sc. and Dr. Thorsten Berends: Lehrstuhl für Anorganische Chemie II der Technischen Universität Dortmund, D-44221 Dortmund, Germany

Experimental section

General

The experimental manipulations were carried out under argon atmosphere using Schlenk technique. All solvents were purified by distillation under argon from appropriate drying agents according to standard procedures (Amarego and Chai, 2003). Compounds **1** (Zöller et al., 2012) and **2** (Lutter et al., 2012) were prepared according to literature methods. The ^{29}Si nuclear magnetic resonance (NMR) spectrum was recorded at room temperature on a Bruker DPX 300 spectrometer (Karlsruhe, Germany). The chemical shift δ is given in ppm and is referenced to the solvent peaks with the usual values calibrated against tetramethylsilane. The elemental analyses were performed on a LECO CHNS-932 analyzer (LECO Corporation, St. Joseph, MI, USA). The electrospray mass spectra were recorded on a ThermoQuest Finnigan (San José, CA, USA) instrument using CH_2Cl_2 as a mobile phase. Melting points are uncorrected and were measured on a Büchi M-560 (Büchi Labortechnik AG, Flawil, Switzerland).

Crystallography

All intensity data were collected with an Xcalibur2 CCD diffractometer (Oxford Diffraction) using Mo-Kα radiation at 110 K. The structure was solved with direct methods using SHELXS-97 (Sheldrick, 2008) and refinements were carried out against F^2 by using SHELXL-97 (Sheldrick, 2008). All nonhydrogen atoms were refined using anisotropic displacement parameters. The C-H hydrogen atoms were positioned with idealized geometry and refined using a riding model. CCDC-923478 (**3**) contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The additional crystal data and structure refinement for compound **3** are shown in Table 1.

Synthesis of 5-Phenyl-(2,8-dioxa-5-aza-1-stanna)bicyclo[3.3.0$^{1.5}$] octane (**3**). (A) A solution of **1** (0.161 g, 0.382 mmol) in dry dichloromethane (10 ml) was cooled to -70°C. Under stirring, a solution of **2** (0.080 g, 0.382 mmol) in dry dichloromethane (10 ml) was added dropwise. The reaction mixture was stirred for 10 h during which it was allowed to warm to ambient temperature. Upon standing of the reaction mixture at room temperature, compound **3** was crystallized as a colorless prism that was suitable for single crystal X-ray diffraction analysis. The crystals were, however, almost insoluble in common organic solvents, thus precluding NMR measurements.

$^{29}Si[H\}$ NMR (59.63 MHz, C_6D_6) of the crude reaction mixture from which compound **3** had been isolated: δ-84.3. MS (ESI+): *m/z*=162.1 $[H_2N(CH_2CMe_2OH)_2]^+$, 234.2 $[HN(CH_2CMe_2OH)_3]^+$, 306.2 $[N(CH_2CMe_2OH)_4]^+$, 348.2, 378.3, 421.3 $[N(CH_2CMe_2O)_3SiO\text{-}t\text{-}Bu+H_3NCH_2CMe_2OH]^+$, 437.3 $[N(CH_2CMe_2O)_3SiOH+H_2N(CH_2CMe_2OH)_2]^+$, 439.3 $[N(CH_2CMe_2O)_3SiO(CH_2)_2N(Ph)(CH_2)_2OH+H]^+$, 485.3, 509.3 $[N(CH_2CMe_2O)_3SiOH+HN(CH_2CMe_2OH)_3]^+$.

(B) Freshly prepared tin(II) butoxide (3.280 g, 12.390 mmol) was reacted with 1 molar equivalent (2.243 g) of *N*-phenyldiethanolamine in toluene (250 ml). The toluene/butanol azeotropic mixture was distilled off and the stannylene $Sn(OCH_2CH_2)_2NPh$ was isolated as a very poorly soluble white solid (3.690 g, 99% yield) with a m.p. of 212°C (decomposition). Anal. calcd. for $C_{10}H_{13}NO_2Sn$ (%): C 40.3, H 4.4, N 4.7. Found: C 40.4, H 4.9, N 4.7.

Table 1 Crystal data and structure refinement for compound **3**.

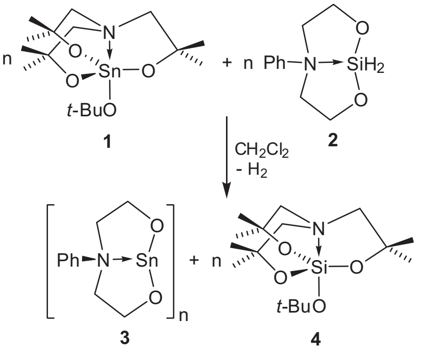
	3
Empirical formula	$C_{20}H_{26}N_2O_4Sn_2$
Formula weight	595.81
Temperature (K)	173 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	10.5832 (9)
b (Å)	11.0641 (7)
c (Å)	11.5701 (7)
α (°)	98.939 (5)
β (°)	110.745 (7)
γ (°)	116.790 (7)
Volume (Å^3)	1047.3 (2)
Z	2
D_c (g cm^{-3})	1.889
Absorption coefficient (mm^{-1})	2.413
F (000)	584
Crystal size (mm)	0.16×0.07×0.04
θ range for data collection	2.03–24.90
Reflections collected	11154
Independent reflections	3495 [R (int)=0.0471]
Data/restraints/parameters	3495/0/227
Completeness to θ_{max} (%)	95.8
Goodness-of-fit on F^2	0.807
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0263, wR_2=0.0386
R indicies (all data)	R_1=0.0525, wR_2=0.0399
Largest diff. peak and hole, eÅ^{-3}/eÅ^{-3}	0.591 and -0.617

Results and discussion

The reaction of the *t*-butoxy-substituted stannatrane $N(CH_2CMe_2O)_3SnO$-*t*-Bu (**1**) with the hydrido-substituted 2,8-dioxa-5-aza-1-sila-bicyclo[3.3.0$^{1.5}$]octane $PhN(CH_2CH_2O)_2SiH_2$, (**2**), afforded, in a combined redox and ligand exchange reaction, the 2,8-dioxa-5-aza-1-sila-bicyclo[3.3.0$^{1.5}$] octane $[PhN(CH_2CH_2O)_2Sn]_n$ (**3**) and the hexamethyl-substituted *t*-butoxysilatrane **4** (Scheme 2).

Compound **3** was crystallized from the crude reaction mixture as colorless prisms that were almost insoluble in common organic solvents such as hexane, diethyl ether, tetrahydrofurane, dichloromethane, and toluene.

The silatrane **4** was not isolated from the reaction mixture, but its formation is strongly supported by NMR spectroscopy as well as electrospray ionization-mass spectrometry (hereafter referred to as ESI-MS). In the crude reaction mixture, the ^{29}Si NMR spectrum (in CH_2Cl_2/C_6D_6) showed a single resonance at δ-84.3 that is comparable with the chemical shift reported for the 1-*t*-butoxysilatrane



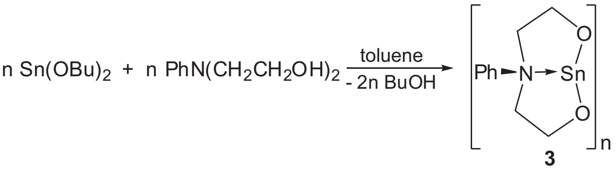
Scheme 2 Synthesis of compound **3** by a redox reaction accompanied with ligand exchange.

$N(CH_2CH_2O)_3SiOt$-Bu (δ -95, $CDCl_3$) (Voronkov et al., 1988). The ESI-MS showed major mass clusters centered at *m/z* 234.2 and 306.2 that are assigned to $[HN(CH_2CMe_2OH)_3]^+$ and $[N(CH_2CMe_2OH)_4]^+$, respectively. Also present are the less intense mass clusters at *m/z* 162.1, 421.3, 437.3, 439.3, and 509.3 that are assigned to $[H_2N(CH_2CMe_2OH)_2]^+$, $[N(CH_2CMe_2O)_3SiO$-*t*-$Bu+H_3NCH_2CMe_2OH]^+$, $[N(CH_2CMe_2O)_3SiOH+H_2N(CH_2CMe_2OH)_2]^+$, $[N(CH_2CMe_2O)_3SiO(CH_2)_2N(Ph)(CH_2)_2OH+H]^+$, and $[N(CH_2CMe_2O)_3SiOH+HN(CH_2CMe_2OH)_3]^+$, respectively.

A common approach to the synthesis of 2,8-dioxa-5-aza-1-stanna-bicyclooctanes is the reaction of tin(II) alkoxides, $Sn(OR)_2$, with the corresponding amino alcohols (Zeldin and Gsell, 1976). In a control experiment, the reaction of *N*-phenyldiethanolamine, $PhN(CH_2CH_2OH)_2$, with tin(II) butoxide, $Sn(On$-$Bu)_2$, gave compound **3** in high yield (Scheme 3).

The molecular structure of **3**, as determined by single crystal X-ray diffraction analysis, is shown in Figure 1. Selected bond distances and bond angles are summarized in Table 2.

In contrast to its dimeric analogues $[MeN(CH_2CR_2O)_2Sn]_2$ (R=H (**5**) (Berends et al., 2009), Me (Iovkova-Berends et al., 2012b), $[DCH_2CH_2N(CH_2CMe_2O)_2Sn]_2$ (D=MeO, Me_2N) (Iovkova-Berends et al., 2012a), and $[MeN(CH_2CMe_2O)[(S)$-$CH\ (Me)$-(R)-$CH(Ph)O\}Sn]_2$ (Iovkova-Berends et al., 2011), compound **3** forms a coordination polymer via intermolecular O→Sn interactions. So far, the only other polymeric structure of a 2,8-dioxa-5-aza-1-stanna(II)-bicyclooctane was found for $[\{HOCMe_2CH_2N(CH_2CMe_2O)_2Sn\}_2]_n$ (Zöller et al., 2011) in which the polymer is formed by intermolecular head to tail O-H…O hydrogen bonds.



Scheme 3 Alternative synthesis of **3**.

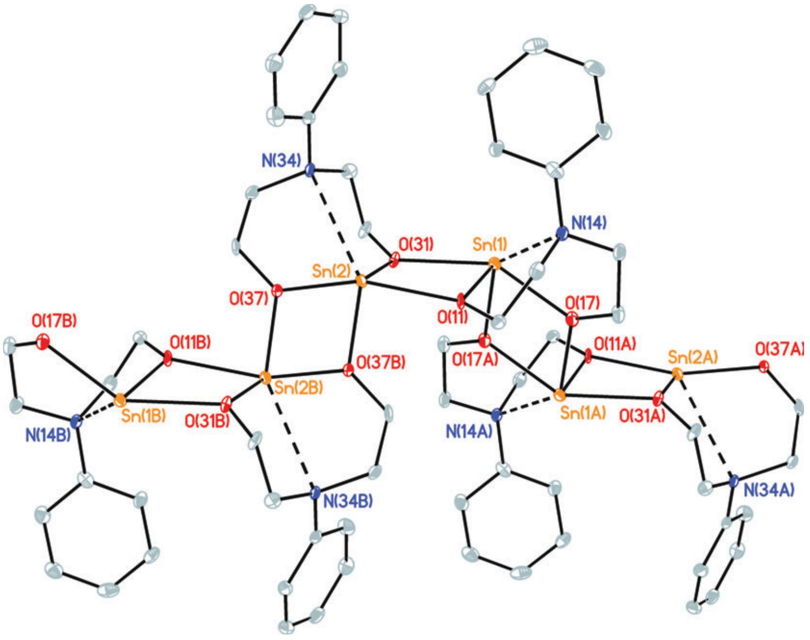


Figure 1 Polymeric structure of compound **3** (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). Hydrogen atoms are omitted for clarity.
Symmetry codes: (A) -x+1, -y+1, -z+1; (B) -x, -y+1, -z+1.

Table 2 Selected bond distances (Å) and angles (°) for compounds **3** and $[MeN(CH_2CH_2O)_2Sn]_2$ (**5**) (Berends et al., 2009).

	3 (X=3)	5 (X=2)		3 (X=3)	5 (X=2)
Sn (1)-O (11)	2.104 (3)	2.176 (9)	Sn (2)-O (11)	2.325 (3)	2.239 (9)
Sn (1)-O (17)	2.261 (3)	2.061 (7)	Sn (2)-O (X1)	2.097 (3)	2.192 (8)
Sn (1)-O (17A)	2.153 (3)		Sn (2)-O (X7)	2.238 (3)	2.069 (7)
Sn (1)-O (X1)	2.379 (3)	2.200 (9)	Sn (2)-O (37B)	2.134 (3)	
Sn (1)-N (14)	2.818 (3)	2.447 (10)	Sn (2)-N (X4)	3.096 (3)	2.413 (10)
O (11)-Sn (1)-O (17)	87.3 (1)	103.6 (3)	O (11)-Sn (2)-O (37B)	86.1 (1)	
O (11)-Sn (1)-O (17A)	90.9 (1)		O (11)-Sn (2)-N (X4)	121.3 (1)	133.5 (3)
O (11)-Sn (1)-O (X1)	66.9 (1)	70.7 (3)	O (X1)-Sn (2)-O (X7)	85.8 (1)	103.7 (3)
O (11)-Sn (1)-N (14)	67.6 (1)	72.1 (3)	O (31)-Sn (2)-O (37B)	93.9 (1)	
O (17)-Sn (1)-O (17A)	69.8 (1)		O (X1)-Sn (2)-N (X4)	66.0 (1)	73.4 (3)
O (17)-Sn (1)-O (X1)	145.2 (1)	85.4 (3)	O (37)-Sn (2)-O (37B)	70.4 (1)	
O (17)-Sn (1)-N (14)	66.6 (1)	76.2 (4)	O (X7)-Sn (2)-N (X4)	64.0 (1)	76.7 (4)
O (17A)-Sn (1)-O (21)	86.9 (1)		O (37B)-Sn (2)-N (34)	130.8 (1)	
O (17A)-Sn (1)-N (14)	131.7 (1)		Sn (1)-O (11)-Sn (2)	112.3 (1)	108.5 (4)
O (X1)-Sn (1)-N (14)	119.1 (1)	132.8 (4)	Sn (1)-O (X1)-Sn (2)	110.4 (1)	109.4 (4)
O (11)-Sn (2)-O (X1)	68.1 (1)	69.7 (3)	Sn (1A)-O (17A)-Sn (1)	110.3 (1)	
O (11)-Sn (2)-O (X7)	143.6 (1)	85.5 (3)	Sn (2B)-O (37)-Sn (2)	109.6 (1)	

The two crystallographic independent tin atoms in compound **3** are each coordinated by four oxygen atoms [O (11), O (17), O (17A), and O (31) at Sn (1) and O (11), O (31), O (37), and O (37B) at Sn (2)] and exhibit strongly distorted pseudo-trigonal-bipyramidal environments with the lone electron pair occupying the equatorial position. The Sn-O distances vary between 2.097 (3) [Sn (2)-O (31)] and 2.379 (3) [Sn (1)-O (31)] Å. In addition, there are intramolecular N→Sn interactions at Sn (1)-N (14)/Sn (2)-N (34) distances of 2.818 (3)/3.096 (3) Å that are shorter than the sum of the van der Waals radii (Mantina et al., 2009) of tin (2.17 Å) and nitrogen (1.55 Å). They are significantly longer than the N-Sn distances in previously reported 2,8-dioxa-5-aza-1-stanna(II)-bicyclooctanes (2.356–2.561 Å) (Berends et al., 2009; Iovkova-Berends et al., 2011, 2012a,b; Zöller et al. 2011). It appears that the phenyl substituent reduces the donor strength of the nitrogen atom, weakens the N→Sn coordination compared with the *N*-methyl-substituted analogue, and thus allows polymerization by intermolecular O→Sn interactions. This interpretation is confirmed by the difference in N-Sn distances in the corresponding tungstenpentacarbonyl complexes $[RN(CH_2CH_2O)_2SnW(CO)_5]\cdot nW(CO)_6$ [(R=Me, n=0, N-Sn=2.356 (5)/2.360 (6) Å (Berends et al., 2009); R=Ph, n=0.5, N-Sn=2.507 (3)/2.391 (3) Å (Berends et al., 2010)], indicating an increased donor capacity of the N atoms for the methyl-substituted derivative.

The asymmetric unit of **3** consists of a *cis*-configurated dimer (Figure 2), whereas the polymeric chain is formed by 2,8-dioxa-5-aza-1-stanna(II)-bicyclooctane molecules alternating in *cis*- and *trans*-positions.

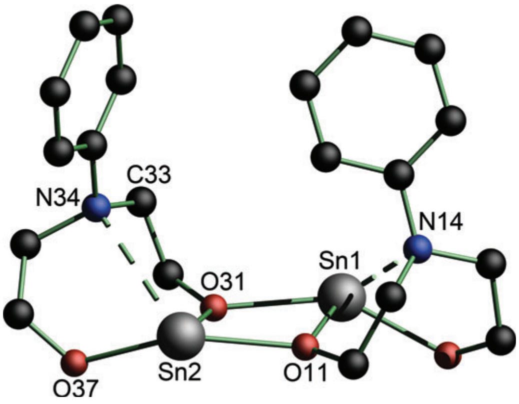


Figure 2 Asymmetric unit of compound **3** (Ball and stick presentation and atom numbering scheme. H atoms are omitted for clarity).

Conclusion

We have demonstrated the ability of the 1,1-dihydrido-2,8-dioxa-5-aza-1-sila-bicyclooctane **2** to reduce the *t*-butoxy-substituted stannatrane **1** under mutual transfer of the aminoalkoholate ligands to give the corresponding tin(II) compound $PhN(CH_2CH_2O)_2Sn$, **3**, the *t*-butoxy-substituted silatrane $N(CH_2CMe_2O)_3SiO$-*t*-Bu, **4**, and molecular hydrogen, H_2. Compound **2** might hold potential to be applied for the reduction of other alkoxido-substituted metallatranes as well. Compound **3** is the first example among the 2,8-dioxa-5-aza-1-stanna(II)-bicyclooctanes, which is a polymer in the solid state via intermolecular O→Sn interactions. Apparently, there is a fine balance between the donor strength of the nitrogen atom as controlled by the organic substituent, the donor strength of the alkoxido-oxygen atoms, and the Lewis acidity of the tin atom that governs the structure actually observed.

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