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Supplemental Information for

$Sn[Si(SiMe_3)_3]_3^-$ and $Sn_3[Si(SiMe_3)_3]_4$: First insight onto the mechanism of the disproportionation of a tin monohalide gives access to the shortest double bond of tin.

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Experimental

General considerations

All manipulations were carried out under nitrogen or *in vacuo* in Schlenk-type glassware on a dual manifold Schlenk line. Solvents were pre-dried over molecular sieves. Thf was distilled from sodium benzophenone. SnBr was synthesized in a home-made co condensation apparatus.[1]

Synthesis of (THF)-Li-$Sn[Si(SiMe_3)_3]_3$ 2 and $Sn_3(Si(SiMe_3)_3)_4 \cdot Sn_{10}(Si(SiMe_3)_3)_6$ 3

A metastable Sn(I)Br solution was prepared using a co condensation technique, where 1.88 g (15.8 mmol) tin reacted with 20 mmol of HBr at 1240°C and the resulting Sn(I)Br was condensed at -196°C with a mixture of toluene and NBu_3 in a volume ratio of 4:1. After warming up to -78°C a metastable solution of Sn(I)Br is obtained. To this metastable solution, a solution of 10.6 g (22 mmol) $LiSi(SiMe_3)_3 \cdot 3$ thf in 50 mL toluene was added at -78°C.

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[1] R. Köppe, A. Schnepf, *Z. Anorg. All. Chem.* **2002**, *628*, 2914 – 2918.

Afterwards, the reaction mixture was slowly warmed up to room temperature and a black reaction solution is obtained. Removing the solvent in *vacuo* leads to a black residue, which was extracted with 150 mL of pentane leading to a black pentane extract. Cooling to -30° C leads to dark red rhombic crystals of $(thf)LiSn(Si(SiMe_3)_3)_3$ (50 mg).

Removing half of the solvent and cooling to -30°C gives black rod-like crystals of the metalloid cluster compound $Sn_{10}(Si(SiMe_3)_3)_6$ (400 mg).

Further concentration of the black pentane solution and further cooling to -30°C leads to dark rhombic crystals of $Sn_3(Si(SiMe_3)_3)_4 \cdot Sn_{10}(Si(SiMe_3)_3)_6$ (300 mg).

NMR $(thf)LiSn(Si(SiMe_3)_3)_3$

^{1}H-NMR (400 MHz, C_6D_6): $\delta = 0.48$ ppm (s, 81H, CH_3). **^{13}C-NMR**: (100 MHz, C_6D_6): $\delta = 2.71$ ppm (CH_3). **^{29}Si-NMR** (100 MHz, C_6D_6): $\delta = -7.90$ ppm($SiMe_3$).

The NMR signal of thf is not detectible due to the evaporation of the crystals during the preparation of the nmr tube where the thf is almost completely removed from the crystals.

NMR $Sn_3(Si(SiMe_3)_3)_4 \cdot Sn_{10}(Si(SiMe_3)_3)_6$

^{1}H-NMR (400 MHz, C_6D_6): $\delta = 0.48$ ppm (s, 108H, CH_3), 0.58 ppm (s, 162H, CH_3) **^{13}C-NMR**: (100 MHz, C_6D_6): $\delta = 4.06$ ppm (s, 6C, CH_3), 5.89 ppm (s, 6C, CH_3), 6.30 ppm (s, 18C, CH_3). **^{29}Si-NMR** (100 MHz, C_6D_6): $\delta = -4.59$ ($SiMe_3$), -6.90 ppm ($SiMe_3$), -54.84 ppm (Si) **^{119}Sn-NMR** (150 MHz, C_6D_6): $\delta = -552$ ppm (SnR_2), 539 ppm (SnR)

X-ray crystallography

Table S1 contains the crystal data and details of the X-ray structural determination for $\{Sn[Si(SiMe_3)_3]_3\}^-$ **2** and $Sn_3[Si(SiMe_3)_3]_4$ **3**. The data were collected at 150 K on a Bruker IPDS II diffractometer employing monochromated Mo(Kα, 0.71073 Å) radiation from a sealed tube and equipped with an Oxford Cryosystems cryostat. A numeric absorption correction was applied using the optically determined shape of the crystals. The structure was solved by direct methods and refined by full-matrix least-square techniques (Programms used:

SHELXS and SHELXL[2]). The non hydrogen atoms, without the carbon atoms of split positions were refined anisotropically and the hydrogen atoms were calculated using a riding model.

As the cell edges a and c are nearly identical for **3** also a larger unit cell (orthorhombic c) might be possible for structure solution. However structure solution in the orthorhombic crystal system (space group: $C222_1$) leads to a comparable structure where large unassigned electron density remains near all the anisotropically refined tin atoms leading to a R_1 value of only 9%. In the monoclinic crystal system structure solution also leads to a structure with large unassigned electron density at places that make physically no sense. However as the cell edges are nearly identical twinning might be possible and structure solution applying the twin matrix 0 0 1 0 -1 0 1 0 0 leads to a solution without large remaining unassigned electron density with an acceptable R_1 value of 6.3% for the twinned structure. However, structure solution is additionally complicated as some $Si(SiMe_3)$ are disordered over two positions leading to a so called "umbrella" disorder as it is well known from XY_3 ligands like *t*Bu, Si*t*Bu_3, $C(SiMe_3)_3$ etc..

The presence of a twinned crystal is additionally in line with the observation of a large mosaic spread due to the different domains of the twin. We also measured the crystals at higher temperatures up to 230K hoping that a phase transition might take place leading to a non twinned structure. However also at higher temperatures the same problems; twin, disorder and large mosaic spread are present, thus we used the low temperature data for structure solution.

CCDC-781711 **2** and CCDC-781710 **3** contains the supplementary crystallographical data for this paper. These data can be obtained online free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ; Fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

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[2] G. M. Sheldrick, *SHELXTL*, Version 5.1, Bruker AXS, **1998**.

Table S1: Crystal data and details of structural determinations

	$\{Sn[Si(SiMe_3)_3]_3\}^-$ **2** $Li^+(THF)$	$Sn_3[Si(SiMe_3)_3]_4$ **3•1** · Pentane
Formula	$SnSi_{12}C_{31}H_{89}LiO$	$Sn_{13}Si_{40}C_{90}H_{270}\cdot C_5H_{12}$
Formula wt.	940.73	4091.78
T [K]	150	150
Crystal system	monoclinic	monoclinic
Space group	Cc	P2(1)
a [Å]	12.937(3)	15.3571(9)
b [Å]	23.193(5)	43.515(3)
c [Å]	18.878(4)	15.3357(8)
α [°]	90	90
β [°]	104.04(3)	103.427(4)
γ [°]	90	90
V [$Å^3$]	5494.9(19)	9968.2(11)
Z	4	2
μ [mm^{-1}]	0.748	1.876
δ [gcm^{-3}]	1.137	1.369
Reflns. meas.	10481	19643
Reflns. obsd. ($I > 2\sigma I$)	10086	17032
R(int.)	0.0426	0.0501
Goof	1.023	1.124
Parameters	469	861
R_1 ($I < 2\sigma$)	0.0299	0.0634
wR_2 (all data)	0.0760	0.1817
Flack	0.069(10)	0 (racemic twin)