[Si(SiMe$_3$)$_2$(SiPh$_3$)]$^-$ can be used as a ligand in subvalent tin chemistry as shown by the

synthesis of [Sn(Si(SiMe$_3$)$_2$SiPh$_3$)$_2$Cl]$^-$ and Cl$_4$Sn$_4$[Si(SiMe$_3$)$_2$SiPh$_3$]$_4$.
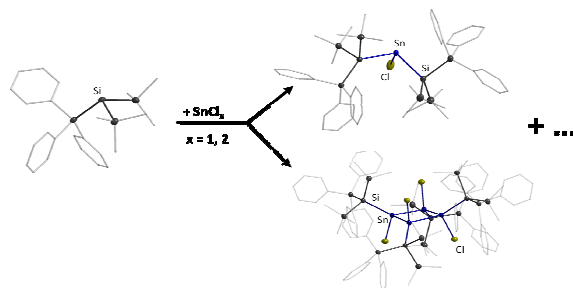
Si(SiMe$_3$)$_2$SiPh$_3$ – A Ligand for Novel Sub-valent Tin Cluster Compounds

R. Klink^a, C. Schrenk^a, A. Schnepf^{a*}

For the synthesis of metalloid tin cluster compounds applying the disproportionation reaction of a Sn(I) halide, silyl ligands, especially the symmetric Si(SiMe$_3$)$_3$ has proven to be extremely useful. Silyl ligands of lower symmetry where e.g. one SiMe$_3$ group is substituted with SiPh$_3$ are thereby unexplored, although the synthesis of the anionic silyl precursors is quite easy, referring to previously described methods. Here the synthesis of the silanide [Si(SiMe$_3$)$_2$(SiPh$_3$)]$^-$ **3** as its potassium (**3$_K$**) as well as its lithium salt (**3$_{Li}$**) in excellent yield is presented. **3** proved to be a suitable starting material for the synthesis of subvalent tin compounds as shown by the reaction with tin halides in oxidation state +2 (SnCl$_2$) and +1 (SnCl); i.e. on the one hand the anticipated stannide [Sn(Si(SiMe$_3$)$_2$SiPh$_3$)$_2$Cl]$^-$ could be isolated and on the other hand the unexpectedly partly substituted ring compound Cl$_4$Sn$_4$[Si(SiMe$_3$)$_2$SiPh$_3$]$_4$ is obtained. As no elemental tin is formed during the reaction with SnCl, metalloid tin clusters may be present in solution too, which is supported by the nearly black color of the reaction mixture, showing that **3** might be a suitable ligand for the synthesis of such cluster compounds.

Introduction

The chemistry of subvalent main group compounds has flourished in recent years, where molecules exhibiting multiple bonds in heavier main group elements have played a central role. This chemistry began with the first multiply bound phosphorous and silicon compounds RP=PR and Mes$_2$Si=SiMes$_2$ (R = 2,4,6-^{t}Bu$_3$-C$_6$H$_2$; Mes = 2,4,6-Me$_3$-C$_6$H$_2$) by Yoshifuji et al.[1] and West et al.,[2] respectively. Lately it has been shown that such unsaturated molecules of the heavier main group elements exhibit novel reactivity similar to transition metal chemistry, as discussed by Power et al.[3] In the field of main group cluster chemistry a similar procedure is leading to metalloid group 13 and group 14 cluster compounds.[4,5] This fruitful development in main group chemistry is based on the construction and application of bulky ligands that are able to protect the reactive sub-valent main group element core from subsequent reactions, such as compounds with magnesium in oxidation state +1.[6]

In the field of metalloid cluster compounds of tin we successfully used the hypersilyl ligand Si(SiMe$_3$)$_3$ for the synthesis of metalloid tin clusters, such as {Sn$_9$[Si(SiMe$_3$)$_3$]$_2$}$^{2-}$,[7] {Sn$_9$[Si(SiMe$_3$)$_3$]$_3$}$^-$,[8] {Sn$_{10}$[Si(SiMe$_3$)$_3$]$_5$}$^-$ [9] and Sn$_{10}$[Si(SiMe$_3$)$_3$]$_6$,[10] showing that anionic silyl ligands are very fruitful for the synthesis of metalloid tin clusters using Sn(I) halide solutions as the starting material.[11]

In this context we are interested in investigating modified silyl ligands with different substituents and their ability to stabilize tin clusters. Here our first steps in this direction are presented by the synthesis and application of the less symmetric silyl ligand Si(SiMe$_3$)$_2$SiPh$_3$ in subvalent tin chemistry, a ligand that has been first invented by Marschner et al..[14]

Results and Discussion

The Si(SiMe$_3$)$_3$ ligand is often used as a sterically demanding ligand in organometallic synthesis due to its high reactivity and good solubility in most aprotic organic solvents. For the synthesis of metalloid tin clusters, via the disproportionation reaction of a tin(I) halide the Si(SiMe$_3$)$_3$ ligand proved to be the most successful leading to a variety of metalloid clusters (*vide supra*).[13] To get an idea of how the ligand influences the formation, structure and properties of metalloid clusters a variation of the ligand is useful to obtain insight into this field. Hence, we decided to substitute one SiMe$_3$ group with another silyl (SiR$_3$; R = Et, Ph, etc.) group. Such ligand systems have been investigated by Marschner et al.[14] starting from KSi(SiMe$_3$)$_3$ **1**. Thus, the reaction of **1** with ClSiPh$_3$ gives Si(SiMe$_3$)$_3$(SiPh$_3$) **2** in high yield. Since structural characterization of **2** was missing we recrystallized **2** from ethanol and obtained colourless single crystals suitable for X-ray crystal structure analysis (figure 1).

Compound **2** crystallizes as colourless plates in the monoclinic c-centered crystal lattice in the space group C2/c with eight molecules in the unit cell. The central silicon atom in **2** is surrounded by three SiMe$_3$ substituents and one SiPh$_3$ group in a slightly distorted tetrahedral fashion. The distortion is due to the greater steric bulk of the SiPh$_3$ with respect to the SiMe$_3$ group. However, this leads only to small deviations of the Si-Si-Si bond angles, varying between 106.80(4) and 110.52(4)°. Additionally the Si-Si bond length to the bulkier SiPh$_3$ group is with 238.8(1) pm, slightly longer than the other Si-SiMe$_3$ bonds of 236.7(1) – 236.8(1) pm.
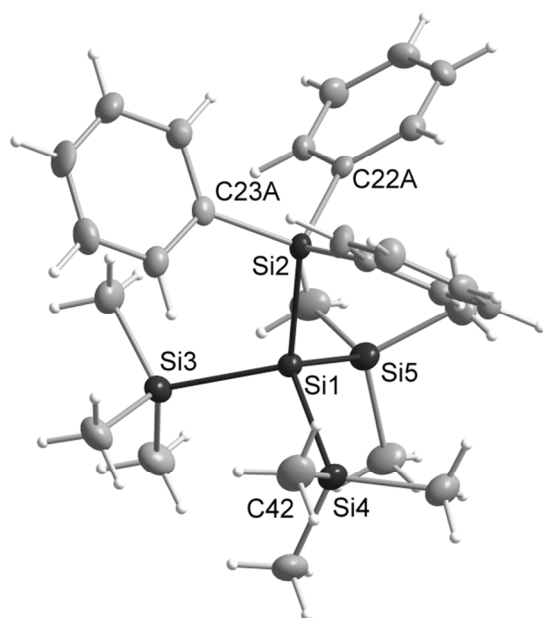
Figure 1: Molecular structure of $Si(SiMe_3)_3(SiPh_3)$ **2** (thermal ellipsoids with 50% probability). Selected bond lengths [pm] and angles [°]:Si1-Si2: 238.83(11); Si1-Si3: 236.78(11); Si1-Si4: 236.66(11); Si1-Si5: 236.76(12); Si4-C42: 186.2(3); Si2-C22a: 188.1(3); Si3-Si1-Si4: 106.80(4); Si2-Si1-Si5: 110.52(4).

To obtain the modified ligand system $[Si(SiMe_3)_2SiPh_3]^-$, we used Marschner's method[15] by treating **2** with one equivalent of KOtBu in thf. This reaction pathway is selective for the cleavage of a $SiMe_3$ group by generating the volatile ether $Me_3SiOtBu$, however, in the case of **2** the cleavage is discussed to be less selective.[14] In our synthetic procedure (see experimental section) we now observed selective Si-SiMe$_3$ cleavage, which was monitored via ^1H and ^{29}Si NMR spectroscopics, indicating a quantitative conversion to the silanide $[Si(SiMe_3)_2(SiPh_3)]^-$. We were unable to obtain single crystals from the reaction performed in thf; thf seems inappropriate as a solvent to obtain single crystals as previously described by Marschner et al. for comparable systems.[12] We suspended a mixture of **2** and KOtBu in toluene with one equivalent of [18]-crown-6. The reaction mixture changed from colourless to yellow and a large amount of a yellow precipitate appeared. Layering the toluene solution with pentane leads to single crystals of ([18]-crown-6)$KSi(SiMe_3)_2(SiPh_3)$ **3$_{KC}$**, suitable for x-ray diffraction measurements (figure 2). The potassium salt **3$_{KC}$** crystallizes as yellow blocks in the triclinic space group P-1 with two molecules in the asymmetric unit. The potassium cation in **3$_{KC}$** is coordinated to [18]crown-6 with nearly planar six-fold coordination, with the potassium cation located near the center of the crown ether vacancy. The formal negatively charged central silicon atom (Si1) is, on first glance, tetrahedrally bound to three silicon atoms with an average Si-Si bond length of 234 pm, which is within the normal range for Si-Si single bonds. The fourth coordination site is occupied by the potassium cation at a distance of 356.30(1) pm, which is in the range of other structurally characterized potassium silanides.[12,14] Due to the fact that both $[K([18]crown-6)]^+$ and the SiPh$_3$ group are bulkier than the SiMe$_3$ groups, the tetrahedral arrangement is slightly distorted leading to Si-Si-Si bond angles in the range of 103 – 106°. To obtain a lithium salt of the new silanide we treated a thf solution of **2** with MeLi in

analogy to the classic synthesis of $LiSi(SiMe_3)_3$.[16] After complete conversion and recrystalization from diethyl ether, single crystals of the corresponding lithium salt **3$_{Li}$** (figure 3) of the modified silanide were obtained. Complex **3$_{Li}$** crystallizes in the monoclinic space group P2(1)/n as colourless plates. The molecular structure of the silanide (Figure 3) shows only minor differences from **3$_K$**. However, in the case of **3$_{Li}$** the addition of a crown-ether is not necessary to obtain single crystals. The lithium cation in **3$_{Li}$** is tetrahedrally coordinated by the central silicon atom of the ligand and three thf molecules, which come from the solvent. This arrangement is normal for lithium silanide compounds, including the silanide $Li(thf)_3Si(SiMe_3)_3$, which is described in the literature.[17]
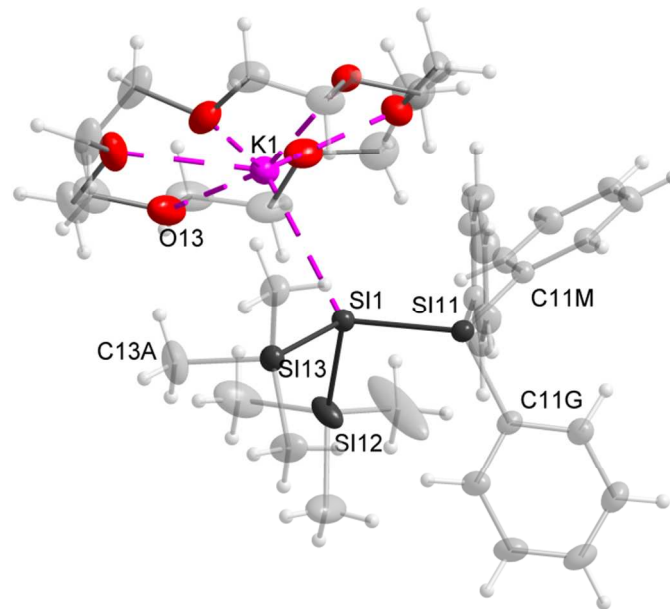

Figure 2: Molecular structure of $([18]$-crown-6)$KSi(SiMe_3)_2(SiPh_3)$ **3$_{KC}$**. Non-hydrogen atoms are shown by thermal ellipsoids with 50% probability. Carbon and Hydrogen atoms are shown with 50% transparency for clarity. Selected bond distances [pm] and angles [°]:K1-O13 287.81(16), K1-Si1 356.30(6), Si1-Si13 233.81(7), Si1-Si11 234.36(6), Si1-Si12 234.52(7), Si11-C11G 190.09(17), Si11-C11M 190.96(18), Si13-C13A 188.9(2); O13-K1-Si1 113.67(3), Si13-Si1-Si11 105.18(2), Si13-Si1-Si12 103.15(3), Si11-Si1-Si12 105.60(3), Si11-Si1-K1 127.08(2), C11G-Si11-C11M 104.51(7), C11M-Si11-Si1 108.73(5), C13A-Si13-Si1 108.25(7).

To summarize the ligand synthesis, the silanide ligand $[Si(SiMe_3)_2SiPh_3]^-$ can be easily synthesized as its potassium or lithium salts, starting from $Si(SiMe_3)_3SiPh_3$ **2** via Marschner's route or via the reaction with MeLi as the metallating reagent, respectively. Consequently, the modified silanide ligand is available with different countercations, which modifies the reactivity and solubility of the anionic silyl reagent for further reactions.
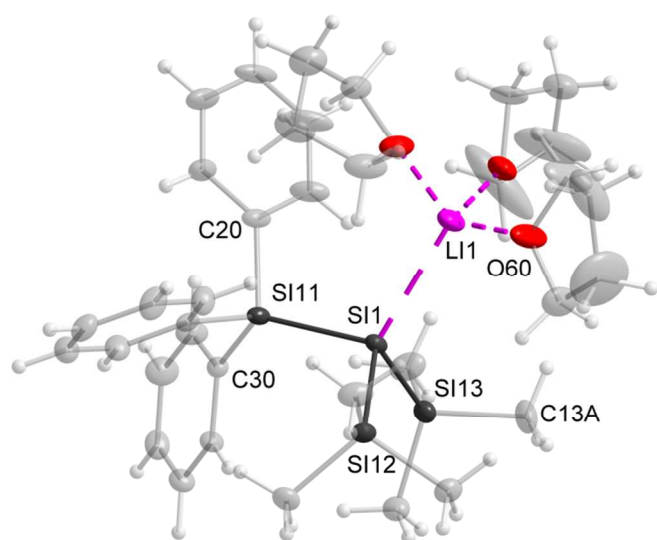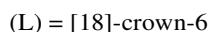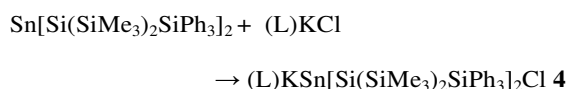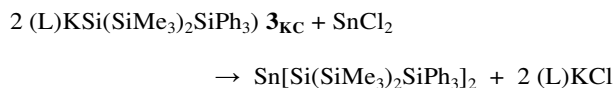
Figure 3: Molecular structure of $(thf)_3LiSi(SiMe_3)_2(SiPh_3)$ **3_{Li}**. Non-hydrogen atoms are shown by their thermal ellipsoids with 25% probability. Carbon and hydrogen atoms are shown with 50% transparency for clarity. Selected bond distances [pm] and angles [°]:Li(1)-O60 196.4(7), Si11-C30 189.6(3), Si11-C20 190.5(3), Si11-Si1 235.04(12), Si1-Si13 235.04(14), Si1-Si12 235.07(12), Si1-Li1 275.0(6), Si13-C13A 188.4(4); C30-Si11-C20 103.45(14), C30-Si11-Si1 120.09(10), C20-Si11-Si1 108.69(12), Si13-Si1-Si11 103.63(5), Si13-Si1-Si12 100.88(4), Si11-Si1-Si12 106.34(5), Si13-Si1-Li1 115.47(17), Si11-Si1-Li1 111.03(14), Si12-Si1-Li1 118.01(16), C13A-Si13-Si1 109.42(16), O60-Li1-Si1 113.7(3).

In the following we present the first results applying the potassium as well as the lithium salt of the modified silanide ligand $[Si(SiMe_3)_2SiPh_3]^-$ in the field of subvalent tin chemistry. Hence, we first reacted **3_K** with commercially available $SnCl_2$ to obtain the corresponding stannylene. The coordination sphere of the potassium cation affects the reactivity of **3_K** with $SnCl_2$. In case of the crown ether-coordinated potassium cation **3_{KC}**, shown in figure 2, the reaction with $SnCl_2$ in thf leads, after work-up of the reaction mixture, to the single crystalline product K([18]crown-6)Sn$[Si(SiMe_3)_2SiPh_3]_2$Cl **4**, which can be described as a K([18-crown-6)Cl complex of the anticipated stannylene Sn$[Si(SiMe_3)_2SiPh_3]_2$:

2 (L)KSi(SiMe_3)_2SiPh_3) **3_{KC}** + SnCl_2

$\rightarrow$ Sn$[Si(SiMe_3)_2SiPh_3]_2$ + 2 (L)KCl

Sn$[Si(SiMe_3)_2SiPh_3]_2$ + (L)KCl

$\rightarrow$ (L)KSn$[Si(SiMe_3)_2SiPh_3]_2$Cl **4**

(L) = [18]-crown-6

Compound **4** crystallizes as red blocks in a monoclinic crystal lattice in the space group P2(1)/n. The tin and chlorine atoms are disordered over two positions with a ratio of 92:8; only the major component of 92% is discussed below. The tin atom (Sn1), which formally bears the negative charge, is bound to two ligands and a chlorine atom with Sn-Si and Sn-Cl distances of 269.3(1) and 256.6(1) pm respectively, which are in the

normal range for Sn-Si and Sn-Cl single bonds.[18] However, since the modified silanide ligand is bulkier than the chlorine atom, the bond angles between the halide and each ligand are 99.67(2)° and 93.88(2)°, which are significantly smaller than the Si-Sn-Si bond angle between both ligands of 114.25(2)°. The potassium countercation is six coordinate to [18]crown-6 and shows no direct contact to the anionic stannide which differs to the precursor where a direct contact between cation and anion is present.

To elucidate the impact of the crown ether on the reactivity of the silanide we reacted **3_K**, where the potassium cation is only coordinated by one thf molecule[19] with $SnCl_2$. We were unable to isolate the stannide, probably due to a more complex reaction based on multiple signals within the ^{1}H NMR spectrum (supporting information). However, we were able to isolate red needle-like single crystals. X-ray crystal structure analysis of these crystals revealed the formation of the partly substituted tin(II) halide compound $Cl_4Sn_4[Si(SiMe_3)_2SiPh_3]_4$ **5**. Compound **5** crystallizes in the triclinic space group P-1 together with 4.5 molecules of toluene in the asymmetric unit. The four tin atoms in **5** are arranged in a nearly square planar geometry (Sn-Sn-Sn angles 90±1°) with an average Sn-Sn-distance of 293 pm. The average Sn-Si (265 pm), Sn-Cl (242 pm) and Sn-Sn distances are similar to the isostructural compound $(RSnCl)_4$ **5a** $[R = Si(SiMe_3)_3]$.[20]
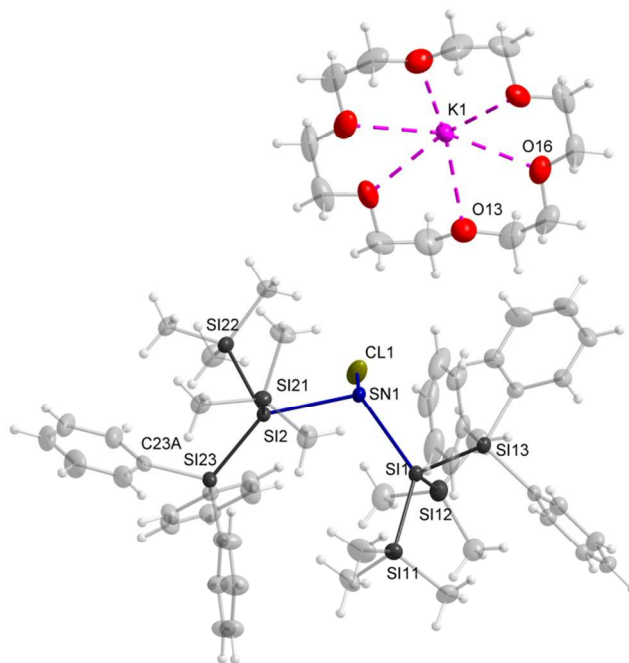
Figure 4: Molecular structure of K([18]crown-6)Sn$[Si(SiMe_3)_2SiPh_3]_2$Cl **4**. Non-hydrogen atoms are shown as their thermal ellipsoids with 50% probability. Carbon and hydrogen atoms are shown with 50% transparency for clarity. Selected bond lengths [pm] and angles [°]:Sn1-Cl1 256.64(8), Sn1-Si2 269.32(6), Sn1-Si1 269.39(7), K1-O16 280.2(2), K1-O13 286.6(2), Si1-Si11 235.90(9), Si1-Si13 236.25(9), Si1-Si12 236.84(10), Si2-Si21 235.92(9), Si2-Si22 237.11(9), Si2-Si23 237.13(8), Si23-C23A 189.7(2); Cl1-Sn1-Si2 99.67(2), Cl1-Sn1-Si1 93.88(2), Si2-Sn1-Si1 114.250(19), O16-K1-O13 58.62(7), Si11-Si1-Si13 108.60(4), Si11-Si1-Si12 102.44(4), Si13-Si1-Si12 110.25(3), Si11-Si1-Sn1 122.23(3), Si13-Si1-Sn1 96.78(3), Si12-Si1-Sn1 116.18(3), Si21-Si2-Si22 103.71(3), Si21-Si2-Si23 111.14(3), Si22-Si2-Si23 103.74(3), Si21-Si2-Sn1 96.57(3), Si22-Si2-Sn1 101.43(3), Si23-Si2-Sn1 136.34(3), C23A-Si23-Si2 111.52(7).

Figure 5: Molecular structure of $Cl_4Sn_4[Si(SiMe_3)_2SiPh_3]_4$ **5**. Non-hydrogen atoms are shown as their thermal ellipsoids with 50% probability. Carbon and hydrogen atoms are shown with 50% transparency for clarity. Selected bond lengths [pm] and angles [°]:Sn1-Cl1 241.32(15), Sn1-Si1 265.06(15), Sn1-Sn2 292.91(6), Sn1-Sn4 294.09(6), Sn2-Cl2 242.05(15), Sn2-Si2 266.07(15), Sn2-Sn3 291.40(6), Sn3-Cl3 241.16(15), Sn3-Si3 264.29(16), Sn3-Sn4 292.20(6), Sn4-Cl4 241.75(15), Sn4-Si4 266.63(17), Si2-Si21 236.3(2), Si2-Si20 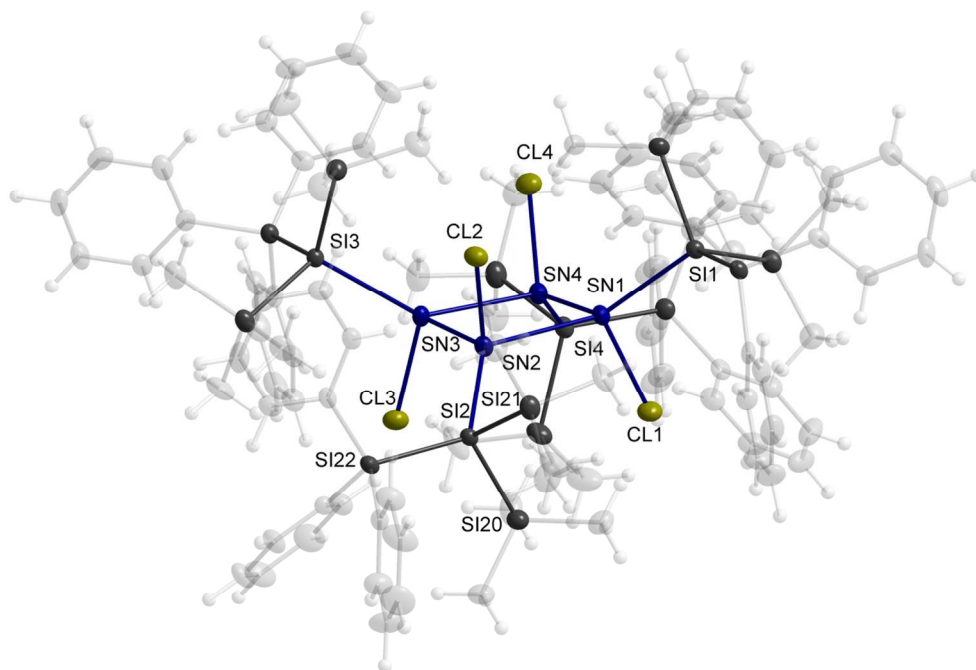238.3(2), Si2-Si22 238.5(2); Cl1-Sn1-Si1 101.76(5), Cl1-Sn1-Sn2 106.40(4), Si1-Sn1-Sn2 132.14(4), Cl1-Sn1-Sn4 98.89(4), Si1-Sn1-Sn4 123.12(3), Sn2-Sn1-Sn4 89.825(15), Cl2-Sn2-Si2 102.48(5), Cl2-Sn2-Sn3 106.56(4), Si2-Sn2-Sn3 131.87(4), Cl2-Sn2-Sn1 97.16(4), Si2-Sn2-Sn1 123.57(4), Sn3-Sn2-Sn1 89.928(15), Cl3-Sn3-Si3 104.86(5), Cl3-Sn3-Sn2 96.60(4), Si3-Sn3-Sn2 121.25(4), Cl3-Sn3-Sn4 104.38(4), Si3-Sn3-Sn4 133.14(4), Sn2-Sn3-Sn4 90.492(15), Cl4-Sn4-Si4 103.43(5), Cl4-Sn4-Sn3 97.18(4), Si4-Sn4-Sn3 124.03(4), Cl4-Sn4-Sn1 105.10(4), Si4-Sn4-Sn1 131.97(4), Sn3-Sn4-Sn1 89.542(15), Si21-Si2-Si20 108.91(8).

In the four-membered ring in **5**, every tin atom is bound to one silanide and a chlorine atom, where the average Sn-Cl distance of 242 pm is significantly shorter than in **4** (256.64(8) pm), where two silanide ligands are bound to the tin atom.

In both compounds **4** and **5** the tin atoms exhibit the oxidation state +2, however in case of **5** the tetrameric four membered ring seems to be more stable than the monomeric stannylene SnRCl. To check if this is only a packing effect in the solid state we calculated the energy difference between four monomers, two dimers and one tetramers in the gas phase by quantum chemical calculations.[21] We calculated the energy by applying the BP86-functional with and without DFT-D3 dispersion correction to gain insight into the dispersion energy holding the dimer and tetramer together (table 1). The calculations directly show that the oligomerization is strongly exothermic and exergonic, where the dispersion energy is most important, which is expected since the $Si(SiMe_3)_2SiPh_3$ ligand is a strong dispersion energy donor.[22] Thus it appears that the tetramer is mostly held together by dispersion forces which may be expected as the tin-tin bonds within the four-membered ring are elongated (293 pm) with respect to normal tin-tin single bonds as found in α-tin (281 pm). The synthesis of **4** and **5** shows that the reaction of the potassium compound $LK[Si(SiMe_3)_2SiPh_3]$ (L = thf, [18]crown-6) with $SnCl_2$ is strongly influenced by the Lewis base bound to the potassium cation. In the case of using thf as the Lewis base a complex reaction occurs and **5** could be isolated only in small quantities.[23]

Reaction	ΔG [kJ mol⁻¹] BP86	ΔG [kJ mol⁻¹] DFT-D3
2 RSnCl → (RSnCl)₂	-6.8	-58.8
2 (RSnCl)₂ → (RSnCl)₄	+29.4	-246.5
4 RSnCl → (RSnCl)₄	+15.8	-873.4

Table 1: Comparison of the calculated free reaction enthalpy of the possible formation steps of a distannene and a tetrameric (RSnCl)-Ring with (right column) and without (middle column) consideration of dispersion energy (R = $Si(SiMe_3)_2(SiPh_3)$).

These results imply that a complicated reaction sequence takes place but also shows that $[Si(SiMe_3)_2SiPh_3]^-$ is a suitable ligand for the synthesis of subvalent tin compounds.

Hence, the question arises if $[Si(SiMe_3)_2SiPh_3]^-$ can also be used as a ligand for the synthesis of metalloid tin clusters via the disproportionation reaction of a tin(I)halide solution. To clarify this question we reacted the lithium salt **3_Li** with a metastable Sn(I)Cl solution (solvent: toluene; donor: PnBu₃) leading to a nearly black reaction mixture and a white precipitate of LiCl, indicating that the metathesis reaction proceeds.

After work-up and the addition of tmeda (tmeda = N,N,N'N'-Tetramethylethylendiamine), we were able to isolate an oxidation product of disproportionation $[Li(tmeda)_2][Sn(Si(SiMe_3)_2SiPh_3)_2Cl]$ **6** in form of orange crystals.[24]
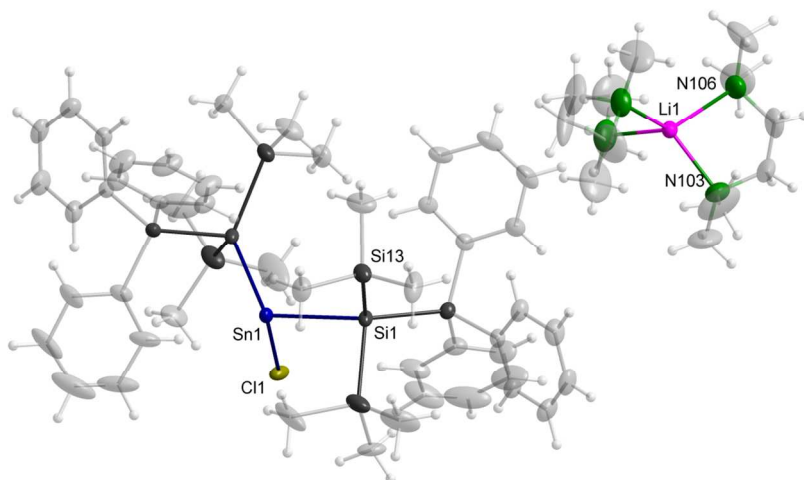
Figure 6: Molecular structure of [Li(tmeda)$_2$][Sn(Si(SiMe$_3$)$_2$SiPh$_3$)$_2$Cl] **6**. Non-hydrogen atoms are shown as their thermal ellipsoids with 25% probability. Carbon atoms are shown with 50% transparency for clarity. Selected bond lengths [pm] and angles [°]:Sn1-Cl1 251.6(3); Sn1-Si1 268.98(13); Si1 Si13 236.28(13); Li1-N103 207.5(7); Li1-N106 214.7(7); Cl1-Sn1-Si1 95.70(19); Sn1-Si1-Si13 97.75(5); N103-Li1-N106 86.8(6).

Compound **6** crystallizes in the monoclinic c-centered space group C2/c with 4 molecules in the asymmetric unit and is isostructural to **4**, which is expected since both compounds are separated cation-anion-pairs between the anion [Sn(Si(SiMe$_3$)$_2$SiPh$_3$)$_2$Cl]$^-$ and the different cations ([K([18]crown-6)]$^+$ (**4**); Li(tmeda)$_2$ (**6**)) present in the solid state.

However, the synthesis of **6** starts from a Sn(I)Cl solution, indicating that **6** is the oxidation product of disproportionation: 2 SnCl → SnCl$_2$ + Sn.[24] No elemental tin is formed during the reaction, so metalloid tin clusters may be present in solution which is supported by the nearly black color of the reaction mixture.

Conclusion and Outlook

For the synthesis of metalloid tin cluster compounds via the disproportionation reaction of a Sn(I) halide silyl ligands, especially the symmetric Si(SiMe$_3$)$_3$ has proven to be extremely useful. Silyl ligands of lower symmetry where e.g. one SiMe$_3$ group is substituted by SiPh$_3$ are thereby unexplored, although the synthesis of the anionic silyl precursors is quite easy referring to previously described methods. In the case of the silanide [Si(SiMe$_3$)$_2$(SiPh$_3$)]$^-$ **3** it is possible to synthesize the potassium (**3$_K$**) as well as the lithium salt (**3$_{Li}$**) in excellent yield. The potassium as well as the lithium salt proved to be suitable starting materials for the synthesis of subvalent tin compounds as shown by the reaction with tin halides in oxidation state +2 (SnCl$_2$) and +1 (SnCl). The results from the reaction with SnCl$_2$ indicate that the cation has a strong influence on the complexity of the reaction, leading on the one hand to the expected stannide K([18]crown-6)Sn[Si(SiMe$_3$)$_2$SiPh$_3$]$_2$Cl **4** and on the other hand to the

unexpectedly partly substituted ring compound Cl$_4$Sn$_4$[Si(SiMe$_3$)$_2$SiPh$_3$]$_4$ **5**. The reaction with a SnCl solution further shows that the ligand seems suitable for the synthesis of cluster compounds, however, at the moment only the product of the oxidation side of the disproportionation reaction, the stannide [Li(tmeda)$_2$][Sn(Si(SiMe$_3$)$_2$SiPh$_3$)$_2$Cl] **6** could be isolated. Since no elemental tin is observed during the reaction metalloid clusters may also be formed which is currently under investigation in our lab. The synthesis and structural characterization of such metalloid cluster compounds with the silyl ligand Si(SiMe$_3$)$_2$SiPh$_3$ will give the first experimental information about how the structure and properties of metalloid cluster compounds are influenced by the protecting ligand.

Acknowledgement

Experimental

All solvents were dried and purified by standard procedures. All reactions were carried out under nitrogen atmosphere using Schlenk techniques. A solution of Sn(I)Cl in a mixture of toluene and tributylphosphene is synthesized via a preparative co condensation technique as described elsewhere.[25] Bruker DRX-250 spectrometers were used to obtain ^{1}H, ^{13}C, ^{29}Si spectra. ^{1}H, ^{13}C and ^{29}Si chemical shifts δ are given in ppm and were referenced to Me$_4$Si. NMR spectra were recorded at room temperature. Elemental analyses were performed on a varioMICROcube in the CHNS mode.

X-ray crystallography

Table 2 contains the crystal data and details of the X-ray structural determination for all compounds. The data were collected at 150 K or 200 K on a Bruker APEX 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 (Programs used: SHELXS and SHELXL[26]). The non hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated using a riding model.

CCDC-1014875 **2**, CCDC-1014872 **3$_{KC}$**, CCDC-1014873 **3$_{Li}$**, CCDC-1014874 **4**, CCDC-1014871 **5** and CCDC-1014870 **6** contain 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.

Identifier	**2**	**3$_{KC}$**	**3$_{Li}$**	**4**	**5**	**6**
Formula wt.	507.06	736.77	657.12	1325.28	2758.05	1261.22
T [K]	150	150	150	150	150	200
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	P-1	P2(1)/n	P2(1)/n	P-1	C2/c
a [Å]	16.8986(6)	11.7102(2)	12.5556(6)	13.1663(7)	17.0858(12)	17.1264(8)
b [Å]	9.8453(3)	17.9702(4)	21.5357(12)	19.2365(10)	18.5269(12)	18.2815(8)
c [Å]	36.7537(15)	20.3053(4)	14.6869(9)	27.4977(15)	24.0591(15)	27.4389(11)
α [°]	90	96.452(1)	90	90	75.208(2)	90
β [°]	91.496(1)	98.177(1)	95.444(3)	91.834(2)	89.665(2)	105.365(2)
γ [°]	90	96.297(1)	90	90	70.392(2)	90
V [Å^3]	6112.7	4168.26(14)	39533(4)	6960.9(6)	6909.7(8)	8284.0(6)
Z	8	4	4	4	2	4
μ [mm^{-1}]	0.247	0.282	0.181	0.647	0.975	0.488
δ [gcm^{-3}]	1.102	1.174	1.104	1.265	1.326	1.011
Reflns. meas.	17794	94482	23918	59766	49702	30965
Reflns. uniqe	5251	25318	9798	15550	25261	5941
R(int.)	0.0589	0.0571	0.0862	0.0417	0.0465	0.0774
Goof	0.932	1.021	1.019	1.025	1.014	1.033
R$_1$ (I < 2σ)	0.0419	0.0476	0.0702	0.0383	0.0520	0.0543
wR$_2$ (all data)	0.0885	0.1167	0.1943	0.0947	0.1275	0.1379

Table 2: Crystal data and details of the X-ray structural determination for Si(SiMe$_3$)$_3$(SiPh$_3$) **2**, ([18]-crown-6)KSi(SiMe$_3$)$_2$(SiPh$_3$) **3$_{KC}$**, (thf)$_3$LiSi(SiMe$_3$)$_2$(SiPh$_3$) **3$_{Li}$**, ([18]crown-6)KSn[Si(SiMe$_3$)$_2$SiPh$_3$]$_2$Cl **4**, Cl$_4$Sn$_4$[Si(SiMe$_3$)$_2$SiPh$_3$]$_4$ **5** and [Li(tmeda)$_2$][Sn(Si(SiMe$_3$)$_2$SiPh$_3$)$_2$Cl] **6**.

Synthesis of Si(SiMe$_3$)$_3$(SiPh$_3$) 2

Si(SiMe$_3$)$_3$(SiPh$_3$) was prepared by using Marschner's route according to the literature.[14] In a Schlenk type vessel 39.4 g (0.12 mol) of Si(SiMe$_3$)$_4$ was mixed with 14.5 g of KO^{t}Bu (0.13 mol) and the solid mixture was dissolved in 250 mL thf. This mixture was stirred for 12 hours at room temperature. The formation of the intermediate product KSi(SiMe$_3$)$_3$ was monitored via NMR spectroscopy. After the reaction has finished, 41.1 g (0.14 mol) of ClSiPh$_3$ was dissolved in 300 mL toluene and added dropwise to the potassium silanide mixture, which was cooled before to -78°C. After the complete addition, the mixture was slowly heated to room temperature and stirred for another 12 hours. The reaction mixture was quenched with an ice cold aqueous HCl solution. The organic phase was separated and the aqueous phase was extracted with diethyl ether. All organic phases were combined, dried over Na$_2$SO$_4$ and the solvent was removed *in vacuo* leading to a pale yellow solid. Si(SiMe$_3$)$_3$(SiPh$_3$) was recrystallized by dissolving the solid in 500 mL hot ethanol to give colorless plates (43g, 60% yield).

^{1}H-NMR (250 MHz, C$_6$D$_6$) δ: 0.22 (s, 27H, Si*Me$_3$*), 7.13 – 7.21 (m, 9H, Si*Ph$_3$*), 7.68 – 7.72 (m, 6H, Si*Ph$_3$*); **^{13}C{^{1}H}-NMR** (63 MHz, C$_6$D$_6$) δ: 3.2 (s, Si*Me$_3$*), 128.1 (s, Si*Ph$_3$*), 129.5 (s, Si*Ph$_3$*), 136.8 (s, Si*Ph$_3$*), 136.9 (s, Si*Ph$_3$*); **^{29}Si-NMR** (50 MHz, C$_6$D$_6$) δ: -9.7 (decet, Si*Me$_3$*), -10.5 (m, Si*Ph$_3$*), -131.5 (s, *Si*(SiMe$_3$)$_3$).
Elemental analysis: % measured (% calculated): C 63.86 (63.95), H: 8.35 (8.44)

Synthesis of KSi(SiMe$_3$)$_2$(SiPh$_3$) 3$_K$

5 g (9.9 mmol) of Si(SiMe$_3$)$_3$(SiPh$_3$) and 1.16 (10.3 mmol) of KO^{t}Bu were mixed in a flask and dissolved in 100 mL of thf. The mixture was stirred for 12 hours, while the colour changed from colorless to intensive orange. The solvent was removed *in vacuo* which leads to a yellow residue. The solid was redissolved in diethyl ether and filtered from insoluble byproducts. The solvent was then removed *in vacuo*, which leads to a yellow powder of KSi(SiMe$_3$)$_2$(SiPh$_3$) • thf (7.3 g, 79% yield)

^{1}H-NMR (250 MHz, C$_6$D$_6$) δ: 0.29 (s, 18H, Si*Me$_3$*), 1.39 (m, 4H, THF), 3.52 (m, 4H, THF), 7.05 – 7.31 (m, 9H, Si*Ph$_3$*), 8.01 – 8.03 (m, 6H, Si*Ph$_3$*); **^{13}C{^{1}H}-NMR** (63 MHz, THF-d$_8$) δ: 7.0 (s, Si*Me$_3$*), 125.8 (s, Si*Ph$_3$*), 126.1 (s, Si*Ph$_3$*), 137.1 (s, Si*Ph$_3$*), 147.0 (s, Si*Ph$_3$*); **^{29}Si{^{1}H}-NMR** (50 MHz, THF-d$_8$) δ: 2.50 (s, Si*Ph$_3$*), -5.8 (s, Si*Me$_3$*), -189.0 (s, *Si*(SiMe$_3$)$_3$).

Synthesis of (18-crown-6)KSi(SiMe$_3$)$_2$(SiPh$_3$) 3$_{KC}$

To get single crystals of KSi(SiMe$_3$)$_2$(SiPh$_3$), the reaction procedure has to be modified by using toluene as a solvent and 18-crown-6, dissolved in toluene, for complexing the potassium cation. 4 mL of a 0.95 M solution of 18-crown-6 in toluene was added to 2 g (3.9 mmol) of Si(SiMe$_3$)$_3$(SiPh$_3$) and 0.44 g (3.9 mmol) of KO^{t}Bu. The solution colour changed immediately to orange. After 5 minutes, a yellow solid appears. The solution was filtered and layered with pentane, where after 2 hours yellow crystals of (18-crown-6)KSi(SiMe$_3$)$_2$(SiPh$_3$) appeared. Yield: 82% (2.3 g)
^{1}H-NMR (250 MHz, THF-d$_8$) δ: -0.10 (s, 18H, Si*Me$_3$*), 3.62 (m, 24H, 18-crown-6), 7.03 – 7.18 (m, 9H, Si*Ph$_3$*), 7.67 – 7.71 (m, 6H, Si*Ph$_3$*); **^{13}C{^{1}H}-NMR** (63 MHz, THF-d$_8$) δ: 6.9 (s, Si*Me$_3$*), 70.6 (s, 18-crown-6) 125.8 (s, Si*Ph$_3$*), 126.1 (s, Si*Ph$_3$*), 137.1 (s, Si*Ph$_3$*), 147.0 (s, Si*Ph$_3$*); **^{29}Si{^{1}H}-NMR** (50 MHz, THF-d$_8$) δ: 2.50 (s, Si*Ph$_3$*), -5.8 (s, Si*Me$_3$*), -189.0 (s, *Si*(SiMe$_3$)$_3$).
Elemental analysis: % measured (% calculated): C 59.2 (58.6), H: 7.9 (7.8)

Synthesis of LiSi(SiMe$_3$)$_2$(SiPh$_3$) • 3 thf 3$_{Li}$

LiSi(SiMe$_3$)$_2$(SiPh$_3$) was prepared in a similar way described for LiSi(SiMe$_3$)$_3$ in the literature.[16] 5 g (9.9 mmol) of Si(SiMe$_3$)$_3$(SiPh$_3$) was dissolved in 50 mL thf. An equimolar amount of MeLi (1.7 M in ether, 6.2 mL) was added dropwise over 30 minutes. The mixture was stirred for 20 hours leading to an orange solution. The solvent was removed *in vacuo* leading to a yellowish residue, which could be recrystallized in diethyl ether at -30°C, leading to 5 g (77%) of LiSi(SiMe$_3$)$_2$(SiPh$_3$) • 3 thf as pale green needles.

^{1}H-NMR (250 MHz, C$_6$D$_6$) δ: 0.44 (s, 18H, Si*Me$_3$*), 1.29 (m, 12H, 3 THF), 3.35 (m, 12H, 3 THF), 7.15 – 7.23 (m, 9H, Si*Ph$_3$*), 7.89 – 7.93 (m, 6H, Si*Ph$_3$*); **^{13}C{^{1}H}-NMR** (63 MHz, C$_6$D$_6$) δ: 6.8 (s, Si*Me$_3$*), 25.3 (s, THF), 68.3 (s, THF), 127.2 (s, Si*Ph$_3$*), 137.1 (s, Si*Ph$_3$*), 144.5 (s, Si*Ph$_3$*); **^{29}Si-NMR** (50 MHz, C$_6$D$_6$) δ: -0.12 (m, *Si*Ph$_3$), -6.7 (dez., *Si*Me$_3$), -179.9 (s, *Si*(SiMe$_3$)$_3$).

Elemental analysis: % measured (% calculated): C 65.2 (65.7), H: 8.7 (8.6)

Synthesis of (18-crown-6)KSn(Si(SiMe$_3$)$_2$(SiPh$_3$))$_2$Cl 4

0.19 g (1 mmol) of SnCl$_2$ and 1.5 g (2 mmol) of (18-crown-6)KSi(SiMe$_3$)$_2$(SiPh$_3$) were mixed in a Schlenk flask and dissolved at -78°C in 40 mL thf. The orange mixture was stirred for 20 hours and was allowed to reach room temperature leading to a deep red reaction solution. The solvent was removed *in vacuo* and the remaining residue was washed with 30 mL pentane. The solid was dissolved in 20 mL toluene and layered with pentane leading to red crystals of (18-crown-6)KSn(Si(SiMe$_3$)$_2$(SiPh$_3$))$_2$Cl over 2 weeks. Yield: 30% (400 mg)

^{1}H-NMR (250 MHz, C$_6$D$_6$) δ: 0.47 (s18H, Si*Me$_3$*) 0.52 (s, 18H, Si*Me$_3$*), 3.04 (m, 24H, 18-crown-6), 7.14 – 7.27 (m, 18H, Si*Ph$_3$*), 8.02 – 8.05 (m, 12H, Si*Ph$_3$*); **^{13}C{^{1}H}-NMR** (63 MHz, C$_6$D$_6$) δ: 5.7 (s, Si*Me$_3$*), 69.9 (s, 18-crown-6), 127.6 (s, Si*Ph$_3$*), 128.2(s, Si*Ph$_3$*), 137.7 (s, Si*Ph$_3$*), 141.1 (s, Si*Ph$_3$*); **^{29}Si-NMR** (50 MHz, C$_6$D$_6$) δ: -3.7 (m, *Si*Me$_3$), -5.3 - -6.0 (m., *Si*Me$_3$), -116.2 (s, *Si*(SiMe$_3$)$_2$); **^{119}Sn-NMR** (93 MHz, C$_6$D$_6$) δ: 545.8 (s, Sn(Si(SiMe$_3$)$_2$(SiPh$_3$))$_2$Cl)

Synthesis of Sn$_4$[Si(SiMe$_3$)$_2$(SiPh$_3$)]$_4$Cl$_4$ 5

1.1 g (2 mmol) of KSi(SiMe$_3$)$_2$(SiPh$_3$) • 1 thf and 0.19 g (1 mmol) of SnCl$_2$ were cooled to -78°C and dissolved under stirring in 30 mL thf. The mixture was allowed to reach room temperature over 20 hours. The solvent of the nearly black solution was removed *in vacuo*. The resulting black residue was washed with pentane and extracted with toluene. After one day at -28°C a voluminous precipitate appeared. The solution was decanted and the remaining solid was recrystallized from toluene at 7°C. After one week few red needles of Sn$_4$[Si(SiMe$_3$)$_2$(SiPh$_3$)]$_4$Cl$_4$. could be crystallized. As only a few crystals are obtained, further characterization (NMR, elemental analysis) was not possible.

Synthesis of (tmeda)$_2$LiSn[Si(SiMe$_3$)$_2$(SiPh$_3$)]$_2$Cl 6

SnCl: 2.7 g (4.1 mmol) of (thf)$_3$LiSi(SiMe$_3$)$_2$(SiPh$_3$) was reacted with 20 mL of a 0.2 M solution of Sn(I)Cl(4 mmol) at -78°C and was warmed under stirring at room temperature over 10 hours. All volatiles are removed *in vacuo* leading to a black oily precipitate. This was washed with pentane and extracted with 20 mL of toluene. The black toluene solution was treated with 1 mL of tmeda, concentrated and stored at -30°C for 2 weeks. A little amount of crystals of (tmeda)$_2$LiSn[Si(SiMe$_3$)$_2$(SiPh$_3$)]$_2$Cl could be obtained (20 mg, 1% yield).

SnCl$_2$: Treating 1 mmol (190 mg) of SnCl$_2$ with 1.35 g (2 mmol) of (thf)$_3$LiSi(SiMe$_3$)$_2$(SiPh$_3$) in thf, removing the solvent *in vacuo* and extracting with toluene leads thereby to the same compound if 1 mL of tmeda is added. Yield: 30% (300 mg)

^{1}H-NMR (250 MHz, C$_6$D$_6$) δ: 0.13 (s, 9H, Si*Me$_3$*) 0.31 (s, 27H, Si*Me$_3$*), 2.10 (s, 24H, tmeda), 2.30 (s, 8H, tmeda), 7.10 – 7.20 (m, 18H, Si*Ph$_3$*), 7.69 – 7.73 (m, 12H, Si*Ph$_3$*); **^{13}C{^{1}H}-NMR** (63 MHz, C$_6$D$_6$) δ: 2.3 (s, Si*Me$_3$*), 4.8 (s, Si*Me$_3$*), 45.9 (s, tmeda), 58.4 (s, tmeda), 128.6 (s, Si*Ph$_3$*), 129.6 (s, Si*Ph$_3$*), 135.8 (s, Si*Ph$_3$*), 136.5 (s, Si*Ph$_3$*), 138.5 (s, Si*Ph$_3$*); **^{29}Si-NMR** (50 MHz, C$_6$D$_6$) δ: -2.9 (m, *Si*Me$_3$), -11.4 (m, *Si*Me$_3$), -8.0 (m, *Si*Ph$_3$), -8.7 (m, *Si*Ph$_3$), -54.5 (s, *Si*(SiMe$_3$)$_2$).

Notes and references

^{a} Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany; Tel.: Int. Code +49 (7071) 29 – 76635; Email: andreas.schnepf@uni-tuebingen.de.

1   M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc*. **1981**, *103*, 4587-4589.

2   R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343-1344.

3   P. P. Power, *Nature* **2010**, *463*, 171-177.

4   For an overview of metalloid group 13 clusters, see: A. Schnepf, H. Schnöckel, *Angew. Chem.* **2002**, *114*, 3682-3704; *Angew. Chem. Int. Ed.* **2002**, *41*, 3532-3554; H. Schnöckel, *Chem. Rev.* **2010**, *110*, 4125-4163 and references therein.

5   For recent developments in group 14 cluster chemistry, see: A. Schnepf, *Chem. Soc. Rev.* **2007**, *36*, 745-758 and references therein.

6   S. P. Green, C. Jones, A. Stasch, *Angew. Chem.* **2008**, *120*, 9219-9223; *Angew. Chem. Int. Ed.* **2008**, *47*, 9079-9083.

7   C. Schrenk, F. Winter, R. Pöttgen, A. Schnepf, *Inorg. Chem.* **2012**, *51*, 8583-8588.

8   C. Schrenk, M. Neumaier, A. Schnepf, *Inorg. Chem.* **2012**, *51*, 3989-3995.

9   C. Schrenk, J. Helmlinger, A. Schnepf, *Z. Anorg. Allg. Chem.* **2012**, *638*, 589-593.

10 C. Schrenk, I. Schellenberg, R. Pöttgen, A. Schnepf, *Dalton Trans.* **2010**, *39*, 1872-1876.

11 Beside metalloid cluster compounds also unsaturated tin compounds like the cyclo-tristannene Sn$_3$R$_4$ as well as small polyhedral cluster compounds like Sn$_4$R$_4$Si(SiMe$_3$)$_2$ are obtained via the reaction of a Sn(I) halide solution with LiR (R = Si(SiMe$_3$)$_3$); C. Schrenk, A. Schnepf, *Chem. Commun.*, **2010**, 46, 6756 – 6758; C. Schrenk, A. Kubas, K. Fink, A. Schnepf, *Angew. Chem.* **2011**, *123*, 7411 – 7415; *Angew. Chem. Int. Ed.* **2011** *50*, 7273 – 7277.

12 C. Kayser, R. Fischer, J. Baumgartner, C. Marschner, *Organometallics* **2002**, 21, 1023-1030.

13 C. Schrenk, A. Schnepf, *Rev. Inorg. Chem.* **2014**, *34*, 93-118.

14 C. Marschner, *Eur. J. Inorg. Chem.* **1998**, 221-226.

15 C. Marschner, *Organometallics* **2006**, *245*, 2110-2125.

16 G. Gutekunst, A. G. Brook, *J. Organomet. Chem.* **1982**, *225*, 1-3.

17 a) A. Heine, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *Inorg. Chem.* **1993**, *32*, 2694-2698;
    b) H. V. R. Dias, M. M. Olmstead, K. Ruhlandt-Senge, P. P. Power, *J. Organomet. Chem.* **1993**, *462*, 1-6.

18 P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186 – 197.

19 The amount of thf molecules present in the precursor is checked by proton NMR, where the integral for the thf signals show that only one thf molecule per anion is present.

20 S. P. Mallela, Y. Saar, S. Hill, R. A. Geanangel, *Inorg. Chem.* **1999**, *38*, 2957-2960.

21 Quantum-chemical calculations were carried out with the RI-DFT version of the Turbomole program package by employing the BP86-functional with and without DFT-D3 dispersion correction. The basis sets were of SVP quality. Turbomole: O. Treutler, R. Ahlrichs*, J. Chem. Phys.* **1995**, *102*, 346–354; BP86 functional: J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822; A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; DFT-D3: S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**; *132*, 154104; RI-DFT: K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283–290; SVP: A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2751.

22 S. Grimme, P. R. Schreiner, *Angew. Chem.* **2011**, *123*, 12849-12853; *Angew. Chem. Int. Ed.* **2011**, *50*, 12639-12642.

23 However, **4** is also formed during the reaction in small amount as indicated by the signals in the proton NMR spectra of the crude reaction mixture (supporting information).

24 Compound **6** is also formed in higher yield by the reaction of $Sn(II)Cl_2$ with **3**$_{Li}$;see experimental section for details.

25 C. Schrenk, R. Köppe, I. Schellenberg, R. Pöttgen, A. Schnepf, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1541 – 1548; A. Pacher, C. Schrenk, A. Schnepf, *J. Organomet. Chem.* **2010**, *695*, 941 – 944.

26 Sheldrick, G.M. *Acta Cryst*. **2008**, *A64*, 112-122.