

### Preliminary communication

## A BULKY SILYL DERIVATIVE OF TIN(II) \*

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### Summary

The reaction of  $\text{SnCl}_2$  with  $\text{Li}[\text{Si}(\text{SiMe}_3)_3] \cdot 3\text{THF}$  in  $\text{Et}_2\text{O}$  at  $-78^\circ\text{C}$  affords  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Sn}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ , the structure of which has been established by X-ray crystallography.

Tin(II) compounds have been isolated and characterized with e.g. alkyl [1], amido [2], phosphido [3], aryloxy [4], and arylthio [5] substituents. However, to the best of our knowledge, no silyl derivatives of tin(II) have been reported previously. Recognizing the need to suppress the oligomerization of  $\text{SnR}_2$  units, we opted to use the bulky  $(\text{Me}_3\text{Si})_3\text{Si}$  substituent.

Stannous chloride was treated with two equivalents of  $\text{Li}[\text{Si}(\text{SiMe}_3)_3] \cdot 3\text{THF}$  [6] in n-hexane at  $-78^\circ\text{C}$ . The initially yellow solution turned red upon warming to room temperature. Evaporation of the solvent, followed by re-dissolution of the residue in n-hexane, and storage at  $-20^\circ\text{C}$  afforded red crystals of  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Sn}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ . The presence of  $(\text{Me}_3\text{Si})_3\text{Si}$  groups in the product was evident from the  $^{29}\text{Si}$  NMR spectrum which exhibited peaks at  $\delta -22.14$  and  $-6.23$  in an approximately 3/1 intensity ratio. Unfortunately, only decomposition products were detected in the 70 eV electron-impact mass spectrum. It was therefore necessary to establish the identity of the product by X-ray crystallography.

*Crystal data:*  $\text{C}_{30}\text{H}_{78}\text{ClLiO}_3\text{Si}_8$ ,  $M = 872.73$ , monoclinic, space group  $P2_1/n$  (No. 14),  $a$  13.060(2),  $b$  23.484(3),  $c$  17.500(2) Å,  $\beta$  96.78(2)°,  $U$  5329.4 Å<sup>3</sup>,  $D_c$  1.088 g cm<sup>-3</sup>,  $Z = 4$ ,  $\lambda(\text{Mo-K}_\alpha)$  0.71073 Å,  $\mu(\text{Mo-K}_\alpha)$  7.3 cm<sup>-1</sup>. A red prismatic crystal (0.2 × 0.2 × 0.25 mm) was sealed under nitrogen in a Lindemann capillary, and data were collected at 24°C using an Enraf–Nonius CAD-4 diffractometer. A total of 4614 unique reflections were measured to  $2\theta$  max of 46.0°. The data were corrected for Lorentz, polarization and decay. An empirical absorption correction was also applied. The structure was solved (direct methods) and refined (difference Fourier, full-matrix, least-squares) using 1954 reflections with  $I > 3.0(I)$ . Unfortunately,

\* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

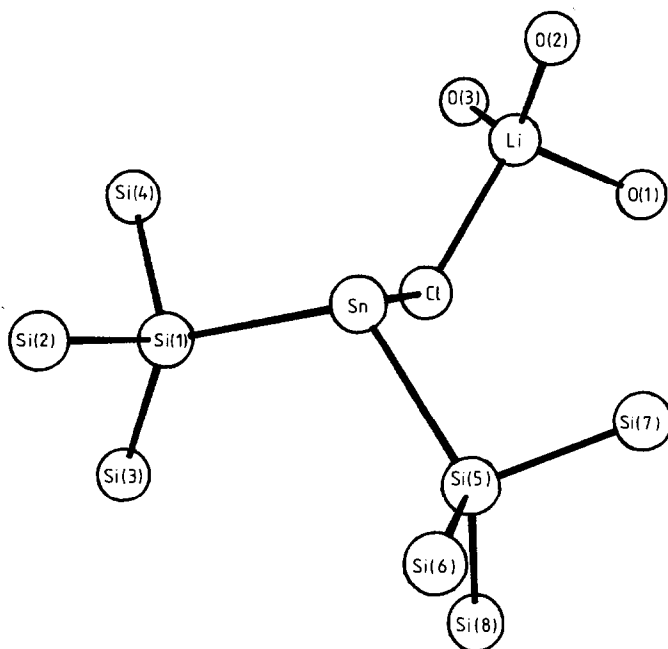


Fig. 1. View (ORTEP) of  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Sn}\cdot\text{LiCl}(\text{THF})_3$  (I) showing the atom numbering scheme. Only the oxygen atoms of the THF molecules are shown. Important parameters: Sn–Si(1) 2.666(11), Sn–Si(5) 2.681(12), Sn–Cl 2.754(5), Cl–Li, 2.53(10) Å, Si(1)–Sn–Si(5) 114.2(4), Si(1)–Sn–Cl 92.1(3), Si(5)–Sn–Cl 95.6(3), Sn–Cl–Li 113.0(2)°.

crystals of I do not diffract strongly, thus accounting for the somewhat high final residuals of  $R = 0.1032$  and  $R_w = 0.1177$ . Nevertheless the structure is of sufficient quality to permit discussion of the heavy atom skeleton. Mention should also be made of the presence of  $\sim 17\%$  of bromine in the chlorine atom positions. This results from the use of a MeLi/LiBr complex in the preparation of  $\text{Li}[\text{Si}(\text{SiMe}_3)_3] \cdot 3\text{THF}$  [6].

The structure of I (Fig. 1) involves a  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Sn}$  molecule coordinated to  $\text{LiCl}(\text{THF})_3$  moiety via a chloride bridge. The tricoordinate tin atom is highly pyramidal (sum of angles at Sn  $301.9(4)^\circ$ ). The Si(1)–Sn–Si(5) bond angle ( $114.2(4)^\circ$ ) is somewhat larger than those in dicoordinate tin molecules [1,7] or tricoordinate distannenes,  $\text{R}_2\text{SnSnR}_2$  [8]. At this point it is not clear whether this is due to the steric demands of the  $(\text{Me}_3\text{Si})_3\text{Si}$  groups or to the effect of solvated LiCl complexation. To the best of our knowledge, no structural information is available for  $\text{Sn}^{\text{II}}\text{--Si}$  bonds. The average tin–silicon bond length in I (2.673(12) Å) is slightly longer than the sum of the covalent radii for these elements (2.52 Å).

Efforts to remove the solvated LiCl from I were unsuccessful. Thus sublimation or prolonged refluxing in toluene resulted only in decomposition. Finally, we note that in preliminary experiments it has been established that  $\text{ZnBr}_2$  and  $\text{CdCl}_2$  undergo disubstitution reactions with  $\text{Li}[\text{Si}(\text{SiMe}_3)_3] \cdot 3\text{THF}$ .

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