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The molecular structure and one-pot synthesis of $[Li(thf)_3 \cdot Sn(SiMe_3)_3]$[1]

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Abstract

The molecular structure of $[Li(thf)_3 \cdot Sn(SiMe_3)_3]$, prepared by a new, one-pot synthesis in 44% yield, has been determined by a single crystal X-ray diffraction study using synchrotron radiation and a CCD detector. The $^+Li(thf)_3$ and $^-Sn(SiMe_3)_3$ moieties are joined by a Li–Sn bond, 2.865(5) Å in length. $[Li(thf)_3 \cdot Sn(SiMe_3)_3]$ is isomorphous with its germanium analogue. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium; Tin; Silicon; Synchrotron

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1. Introduction

Currently, one area of research in our laboratory (C.J.C., D.J.C., S.P.C.) centres around the application of the heavier divalent group 14 derivatives, ER_2 (E = Ge, Sn or Pb; R = alkyl, aryl, amide or silyl), in the preparation of mixed-metal (main group/transition metal) clusters [1–5]. Recently we reported on the syntheses and molecular structures of several novel 2-bis(trimethylsilyl)methylpyridine tin(II) derivatives, making use of the tris(trimethylsilyl)silyl and tris(trimethylsilyl)stannyl ligands [6,7] Much interest has recently been shown in the former ligand, due in part to its high steric bulk and its solubilising properties [8–13]. For example, the reaction of its lithium salt with the ytterbium(II) compound, bis(pentamethylcyclopentadienyl)ytterbium in ethereal solvents allows, via the elimination of LiC_5Me_5 [14], the isolation of the corresponding, heteroleptic ytterbium(II) silyl compound [11], the first structurally characterised compound containing an ytterbium–silicon bond. In contrast however, little or no interest has been directed towards the germanium- [15–19] and tin-based [20] ligands. A single crystal X-ray diffraction study of $[Li(thf)_3 \cdot Ge(SiMe_3)_3]$ has recently been reported. This and the related pmdeta-coordinated derivative, $[Li(pmdeta) \cdot Ge(SiMe_3)_3]$ (pmdeta = N,N,N',N'',N''-pentamethyldiethylenetriamine), are the only two structurally characterised lithium germyls [21]. Having utilised the tin analogue, $[Li(thf)_3 \cdot Sn(SiMe_3)_3]$, in the preparation of $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)\{Sn(SiMe_3)_3\}]$, the first structurally characterised compound containing a bivalent–tetravalent tin bond [7], we now report its molecular structure. Structural data for alkali metal derivatives of tin (containing tin–alkali contacts) are scarce: $[Li(pmdeta) \cdot SnPh_3]$ [22], $[K(\eta^6\text{-}C_6H_5Me)_3 \cdot Sn(CH_2Bu^t)_3]$ [23], the tripodal triamido $[Li(thf)_3 \cdot Sn\{(4\text{-}MeC_6H_4)NSiMe_2\}_3CH]$ [24] and the cyclosiloxytin(IV) $[\mu\text{-}\{Li(thf)_2\}_2 \cdot SnCl_2\{O(SiPh_2O)_2\}_2]$ [25].

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[1] Dedicated to Professor Brian Johnson, on the occasion of his 60th birthday, with the best wishes of the authors.

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2. Results and discussion

2.1. Synthesis of [Li(thf)$_3$·Sn(SiMe$_3$)$_3$]

In contrast to published methods for the preparation of [Li(thf)$_3$·E(SiMe$_3$)$_3$] (E = Si [26,27], Ge [21,28] or Sn [20]), whereby the corresponding tetrakis(trimethylsilyl)-substituted group 14 compounds are prepared and then treated with MeLi to generate the product with tetramethylsilane elimination (44, 88, and 54% yields, respectively), the title compound was prepared in a simple one-pot, two-step synthesis, from tin(IV) chloride. Chlorotrimethylsilane was added, on a ca. 0.5 mol scale, over a 20 min period to a cooled slurry (−10°C) of short pieces of lithium wire in thf, to generate Li(thf)$_n$·SiMe$_3$ in situ. After stirring for ca. 1 h, a 1/4 molar equivalent of tin(IV) chloride was slowly added, the mixture allowed to warm to ambient temperature and then stirred for a further 16 h. Subsequently, solids were allowed to settle and the yellow thf solution filtered. Diethyl ether was added to the solid residue remaining in the reaction Schlenk tube and the mixture stirred, solids allowed to settle, the solution filtered and the filtrate recombined with the thf filtrate. The ethereal solvents were then removed in vacuo to afford a white crystalline material and a small amount of a yellow oil. The extremely air- and moisture-sensitive white crystalline product, [Li(thf)$_3$·Sn(SiMe$_3$)$_3$], was purified by repeated washings with hexane (at just above its freezing point) and isolated in 44% yield. This yield is lower than that previously reported, although that for the preparation of the precursor, tetrakis(trimethylsilyl)tin(IV), is not given [20].

2.2. Multinuclear NMR spectroscopic data for [Li(thf)$_3$·Sn(SiMe$_3$)$_3$]

In addition to the previously reported ^{1}H- and ^{119}Sn{^{1}H}-NMR chemical shift data for the title compound, [Li(thf)$_3$·Sn(SiMe$_3$)$_3$], we present ^{13}C{^{1}H}- and ^{29}Si{^{1}H}-NMR spectroscopic data. The ^{1}H-NMR spectrum measured in C$_6$D$_6$ at 297 K exhibits three resonances: two multiplets at δ 3.68 and 1.61 and a singlet at δ 0.70. These were assigned, on the basis of their chemical shift, integral values (12:12:27) and for the resonance at δ 0.70, $^{119(117)}$Sn satellites [$^3J\{^{119(117)}\text{Sn}-^1\text{H}\}$ 8 Hz], to the α and β thf ^{1}H environments and the trimethylsilyl ^{1}H environments, respectively. Similarly, the ^{13}C{^{1}H}-NMR spectrum exhibits resonances corresponding to the three chemically distinct ^{13}C environments, at δ 68.61, 25.49, and 8.12 (α thf, β thf and trimethylsilyl, respectively). The resonance attributed to the ^{13}C environment of the trimethylsilyl groups exhibited $^1J(^{29}\text{Si}-^{13}\text{C})$ and $^2J\{^{119(117)}\text{Sn}-^{13}\text{C}\}$ couplings of 35 and 23 Hz, respectively. The ^{29}Si{^{1}H}-NMR spectrum measured in C$_6$D$_6$ at 300 K comprises a single resonance at δ −13 with well-resolved ^{119}Sn and ^{117}Sn satellites [$^1J(^{119}\text{Sn}-^{29}\text{Si})$ 134 Hz and $^1J(^{117}\text{Sn}-^{29}\text{Si})$ 128 Hz]: this chemical shift is ca. 8 and 10 ppm to lower frequency compared with those for the silicon [27] and germanium [21] analogues, respectively. The ^{119}Sn{^{1}H}-NMR spectrum comprises a single resonance at δ −878, with ^{29}Si satellites just resolvable [$^1J(^{29}\text{Si}-^{119}\text{Sn})$ 137 Hz]. Of note here is the fact that coupling between the ^{7}Li and ^{119,117}Sn nuclei is not observed and does not appear down to 203 K. In the ^{29}Si{^{1}H}-NMR spectrum of the analogous silicon compound at ambient temperature, the resonance for the central silicon atom appears as a 1:1:1:1 quartet with a $^1J(^7\text{Li}-^{29}\text{Si})$ coupling of 38.6 Hz. The ^{7}Li{^{1}H}-NMR spectrum at 223 K exhibits a sharp resonance with a corresponding $^1J(^{29}\text{Si}-^7\text{Li})$ coupling of 36.7 Hz. The ^{7}Li{^{1}H}-NMR spectrum of [Li(pmdeta)·SnPh$_3$] (in which the Li–Sn contact has been shown to persist in solution) has been recorded at 183 K and a $^1J(^7\text{Li}-^{119,117}\text{Sn})$ coupling of 412 Hz observed [22]. [Li(thf)$_3$·Sn(SiMe$_3$)$_3$] will be studied by us using CP MAS ^{7}Li- and ^{119}Sn-NMR spectroscopies to determine whether coupling between these two nuclei occurs in the solid state.

On the basis of these observations, we propose that the Li–Sn [formal Sn(II)] bond in [Li(thf)$_3$·Sn(SiMe$_3$)$_3$] is considerably more ionic in character than the corresponding bond in the analogous silicon compound.

2.3. Molecular Structure of [Li(thf)$_3$·Sn(SiMe$_3$)$_3$]

The molecular structure of [Li(thf)$_3$·Sn(SiMe$_3$)$_3$] is presented in Fig. 1. Table 1 contains a summary of cell constants and data collection parameters. Selected bond lengths (Å) and angles (°) are given in Table 2.

The distorted-tetrahedral Sn atom is bound to the three trimethylsilyl silicon atoms, Si(1), Si(2) and Si(3) [2.5815(8), 2.5708(9) and 2.5633(9) Å, respectively] and to the lithium atom [2.865(5) Å]. This Li–Sn distance is shorter than that in [Li(thf)$_3$·Sn{(4-MeC$_6$H$_4$)NSiMe$_2$}$_3$CH], 2.89(4) Å [24] and in [Li(pmdeta)·SnPh$_3$], av. 2.871(7) Å [22] but longer than the Li–E distances in the Ge and Si analogues, 2.666(6) [21] and av. 2.644(12) [27] Å, respectively. The Si–E–Si angles [E = Sn, av. 98.75(5)°] are, likewise, different from those found in the E = Ge and E = Si analogues [100.89(4) and av. 102.4(1)°, respectively] and distorted away from ideal, tetrahedral values; for [E(SiMe$_3$)$_4$], E = Ge 109.46(7) [21] or Si av. 109.5(1)° [27]. A similar observation was made for the [Li(pmdeta)·EPh$_3$] (E = Sn [22] or Pb [29]) derivatives whereby the corresponding C$_{ipso}$–E–C$_{ipso}$ angles are more compressed when E = Pb [av. 96.1(2) vs. 94.3(3)°]. This has been interpreted [29] as the central group 14 atom bonding to the three (silyl or aryl) ligands predominantly through the

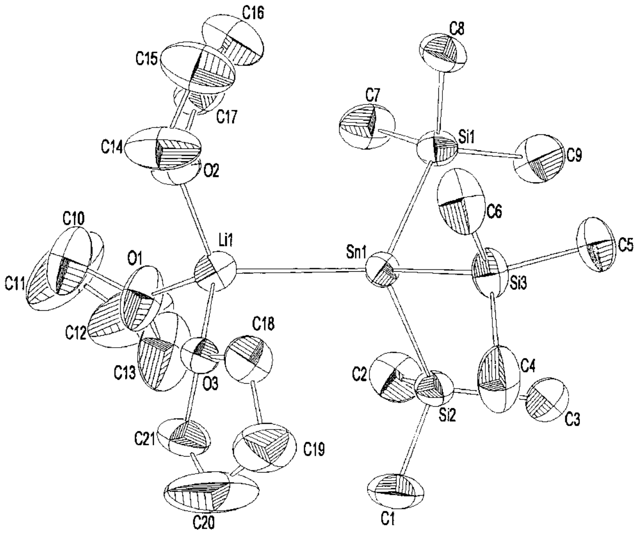

Fig. 1. The molecular structure of [Li(thf)$_3$·Sn(SiMe$_3$)$_3$] and atom numbering scheme; H atoms are omitted.

use of its *p* orbitals, with the lone-pair of electrons being largely *s* in character. However: (i) the steric demand of the ligand, which becomes less significant with increasing size of the central group 14 atom, will also influence the geometry; and (ii) from ab initio molecular orbital calculations performed on several Li(donor)$_n$·EPh$_3$ (E = Sn or Pb) compounds, it was shown that for lead, the 6p_z orbital has a significant interaction with both the lithium and the phenyl groups, influencing the orientation of the latter [29]. This was confirmed by model calculations on PbH$_4$ and Li·PbH$_3$ [29].

Table 1
Cell constants and data collection parameters for [Li(thf)$_3$·Sn(SiMe$_3$)$_3$]

Empirical formula	C$_{21}$H$_{51}$LiO$_3$Si$_3$Sn
M	561.52
Temperature (K)	160
Wavelength (Å)	0.6879
Habit	Colourless cubes
Crystal system	Orthorhombic
Space group	*P*2$_1$2$_1$2$_1$ (No. 19)
Unit cell dimensions	
a (Å)	10.7706(17)
b (Å)	15.842(2)
c (Å)	18.5521(17)
V (Å^3)	3165.5(8)
Z	4
$D_{\text{calc.}}$ (mg m^{-3})	1.178
μ (mm^{-1})	0.937
F(000)	1184
Data collection	
θ Range (°)	2.12–27.07
Index ranges	$-7\leq h\leq 13$, $-20\leq k\leq 20$, $-22\leq l\leq 22$
Reflections collected	18987
Independent reflections	6946 [R$_{\text{int}}$ = 0.0442]
Structure solution	Direct methods by SHELXS 97
Data/restraints/parameters	6946/0/261
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0379$, $wR_2 = 0.0978$
R indices (all data)	$R_1 = 0.0395$, $wR_2 = 0.0987$
Goodness-of-fit on F^2	1.076
Largest difference peak and hole (e Å^{-3})	1.115 and −0.482

Table 2
Selected bond lengths (Å) and angles (°) for [Li(thf)$_3$·Sn(SiMe$_3$)$_3$]

Bond lengths (Å)			
Sn(1)–Li(1)	2.865(5)	Li(1)–O(1)	1.937(6)
Sn(1)–Si(1)	2.5815(8)	Li(1)–O(2)	1.923(5)
Sn(1)–Si(2)	2.5708(9)	Li(1)–O(3)	1.925(5)
Sn(1)–Si(3)	2.5633(9)		
Bond angles (°)			
Si(1)–Sn(1)–Si(2)	98.43(3)	Li(1)–Sn(1)–Si(1)	119.87(9)
Si(1)–Sn(1)–Si(3)	98.88(3)	Li(1)–Sn(1)–Si(2)	118.38(11)
Si(2)–Sn(1)–Si(3)	98.93(3)	Li(1)–Sn(1)–Si(3)	118.11(10)

The remaining features of [Li(thf)$_3$·Sn(SiMe$_3$)$_3$] are unexceptional. The three thf ligands are bound to the lithium atom via their oxygen atoms [1.937(6), 1.923(5) and 1.925(5) Å], angled away from the Li–Sn bond, canted in a paddle-wheel arrangement and with respect to the trimethylsilyl ligands, adopt a staggered conformation (Fig. 2).

A further similarity between [Li(thf)$_3$·Sn(SiMe$_3$)$_3$] and its germanium isomorph is the racemically-twinned nature of its structure [orthorhombic space group *P*2$_1$2$_1$2$_1$ (No. 19)]: the silicon analogue crystallises in the trigonal spacegroup *R*3*c* (No. 161) which is inherently racemic.

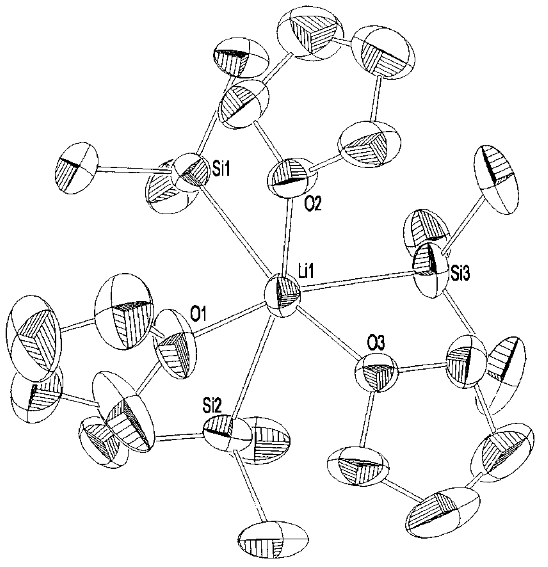

Fig. 2. The staggered conformation of the thf and trimethylsilyl ligands, as viewed down the Li–Sn bond.

3. Experimental details

All experiments were carried out under an inert atmosphere of argon or dinitrogen. All chemical manipulations were performed using, either standard Schlenk line techniques employing a dual manifold vacuum/argon line fitted exclusively with Young's type greaseless taps, or in a Miller–Howe glove box under an inert atmosphere of dinitrogen operating at <1 ppm O_2 and <5 ppm H_2O. Solvents were predried by distillation over the appropriate drying agent for 72 h prior to use, freeze–thaw degassed and stored in ampoules under dinitrogen or argon, in the presence of a potassium mirror (diethyl ether or hexane) or a sodium mirror (thf). Lithium wire, chlorotrimethylsilane and tin(IV) chloride were purchased from Aldrich Chemicals and used as received.

3.1. Preparation of $[Li(thf)_3 \cdot Sn(SiMe_3)_3]$

To a 500 cm^3 Schlenk tube charged with a large stirrer bar, Li wire (11.75 g, 1693.08 mmol; cut into 3–4 mm long pieces), thf (200 cm^3), cooled to −10°C using a dry ice/acetone bath, was added $SiMe_3Cl$ (107.40 cm^3, 91.97 g, 846.54 mmol) over a 20 min period. After stirring for 1 h, $SnCl_4$ (24.77 cm^3, 55.13 g, 211.64 mmol) was added dropwise over a 30 min period. The mixture was stirred for 16 h, solids allowed to settle and the yellow thf solution filtered. Diethyl ether (100 cm^3) was added to the solid residue remaining and the mixture stirred, allowed to settle, the solution filtered and recombined with the thf solution. The ethereal solvents were removed in vacuo to afford a white crystalline material and a small amount of a yellow oil. The extremely O_2- and H_2O-sensitive white crystalline $[Li(thf)_3 \cdot Sn(SiMe_3)_3]$ was purified by repeated washings with freezing-cold hexane (yield, 52.24 g, 93.03 mmol, 44%).

3.2. NMR spectroscopy

^1H- and $^{13}C\{^1H\}$-NMR spectra were recorded using a Bruker WM 250 instrument (operating at a field strength of 5.8719 T with observational frequencies of 250.133, and 62.896 MHz, respectively). The ambient temperature $^{29}Si\{^1H\}$- and $^{119}Sn\{^1H\}$ spectra were recorded on a Bruker DPX 250 instrument (operating at a field strength of 5.8719 T with observational frequencies of 49.643 and 93.113 MHz, respectively). The low temperature $^{119}Sn\{^1H\}$-NMR spectrum was recorded on a Bruker DMX 400 instrument (operating at a field strength of 9.395 T with an observational frequency of 149.089 MHz). ^1H-, $^{13}C\{^1H\}$- and $^{29}Si\{^1H\}$-NMR spectra were referenced externally to $SiMe_4$ and the $^{119}Sn\{^1H\}$-NMR spectrum referenced externally to $SnMe_4$.

3.3. X-Ray crystallography

A colourless orthorhombic crystal of $[Li(thf)_3 \cdot Sn(SiMe_3)_3]$, $0.1 \times 0.1 \times 0.1$ mm in size, was used for the X-ray diffraction measurements. The crystal was mounted at the end of a glass fibre under perfluoropolyether RS 3000 and quickly placed in a nitrogen stream at 160 K. The intensities were collected using synchrotron radiation ($\lambda = 0.6879$) and a Siemens SMART CCD area detector system at the SRS, station 9.8, Daresbury [30].

The structure was solved by direct methods using SHELXS 97. Data were corrected for adsorption using SADABS. Hydrogen atoms were included in the calculated positions for final refinement cycles. All non-hydrogen atoms were refined anisotropically. This structure exhibits racemic twinning in the space group $P2_12_12_1$ (No. 19) which could be refined very well due to the excellent quality of the synchrotron data: on refinement of the two hands, conventional R values of 0.0373 and 0.0365 for the two hands separately after convergence, with corresponding Flack parameters of 0.4372 (estimated S.D. 0.0215) and 0.5706 (estimated S.D. 0.0220), were obtained. Disordered thf was then modelled. Twin refinement gave a final value of 0.43(2) for the twin fraction, with a conventional R value of 0.0379. The twin refinement is therefore highly satisfactory, but the modelling of the disordered thf only moderately so. Table 1 contains a summary of cell constants and data collection parameters. Selected bond lengths (Å) and angles (°) are given in Table 2. The program ZORTEP was used to produce the molecular structures presented in Fig. 1 and Fig. 2. Tables of fractional atomic coordinates and thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge crystallographic data centre.

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