

## The First Monomeric Crystalline Tin(II) Alkyls; X-Ray Structures of the $\beta$ -N-Functionalised Alkyls $\text{Sn}(\text{R})\text{X}$ [ $\bar{\text{R}} = \bar{\text{C}}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2$ and $\bar{\text{X}} = \bar{\text{R}}, \bar{\text{Cl}},$ or $\bar{\text{N}}(\text{SiMe}_3)_2$ ]†

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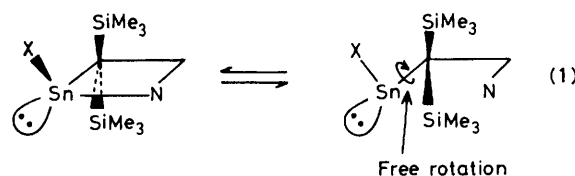
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Monomeric 2-pyridylbis(trimethylsilyl)methyltin(II) compounds  $\text{Sn}(\text{R})\text{X}$  [ $\bar{\text{R}} = \bar{\text{C}}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2$  and  $\bar{\text{X}} = \bar{\text{R}}$  (**1**),  $\bar{\text{Cl}}$  (**2**), or  $\bar{\text{N}}(\text{SiMe}_3)_2$  (**3**)] were prepared from  $(\text{LiR})_2$  and (a)  $\text{SnCl}_2$  or  $\text{Sn}(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})_2$  (**1**), (b)  $2\text{SnCl}_2$  (**2**), or (c)  $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$  (**3**); their X-ray structures show that the  $\bar{\text{R}}$  ligands are invariably bonded to tin in a chelating fashion in the crystal with Sn–C and Sn–NC<sub>5</sub>H<sub>4</sub> bond lengths of 2.35(2) and 2.42(2) (**1**), 2.32(2) and 2.27(3) (**2**), and 2.356(8) and 2.299(5) Å (**3**), respectively, but in C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> solution there appear to be (n.m.r.) C<sub>5</sub>H<sub>4</sub>N–Sn dissociative processes ( $\Delta G^\ddagger$  ca. 43 ± 2 kJ mol<sup>-1</sup>).

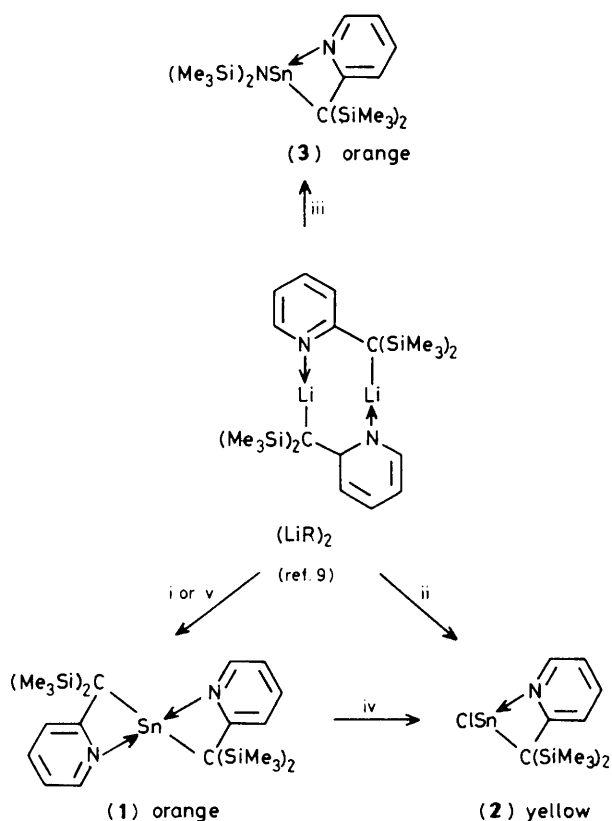
Homoleptic tin(II) hydrocarbyls have oligomeric structures with metal–metal bonding; the degree of molecular aggregation is sterically controlled. For example, the crystalline phenyl compound is a cyclohexamer,<sup>1</sup> crystalline  $[\text{Sn}(\text{CH}_2\text{SiMe}_3)_2]_4$ <sup>2</sup> and  $[\text{Sn}\{\text{CH}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{CH}(\text{SiMe}_3)\text{-meso-o}\}_4$ <sup>3</sup> are cyclotetramers, and crystalline  $[\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2]_2$  (**A**) is a dimer.<sup>4</sup> The influence of phase on molecular structure has only been explored for (**A**), which is a monomer in dilute cyclohexane solution or in the vapour (V-shaped, electron diffraction), but in more concentrated C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> solution there is a monomer ⇌ dimer equilibrium.<sup>5</sup>

We now report the preparation (in good yields; Scheme 1)

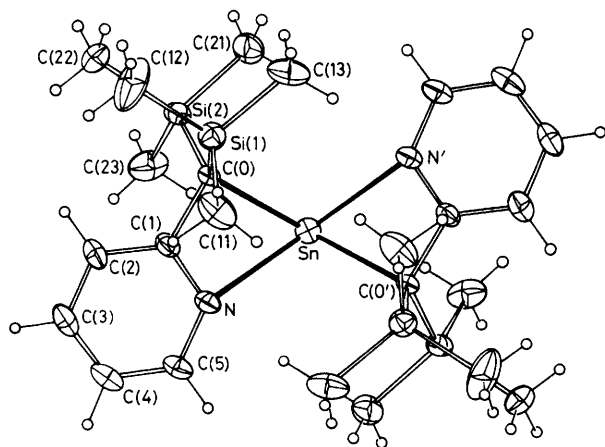
and structures (for X-ray data, see Figures 1–3) of three tin(II) alkyls (**1**)–(**3**), derived from the 2-pyridylbis(trimethylsilyl)methyl ligand  $\bar{\text{C}}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2$  ( $\bar{\text{R}}$ ). The following are novel features for crystalline Sn<sup>II</sup> alkyls  $\text{Sn}(\text{Alk})\text{X}$ : (i), in each of (**1**)–(**3**), the  $\bar{\text{R}}$  ligands are bonded in a chelating fashion; (ii),  $\text{SnR}_2$  (**1**) is the first mononuclear homoleptic Sn<sup>II</sup> alkyl, and the co-ordination number of four for a Sn<sup>II</sup> alkyl has



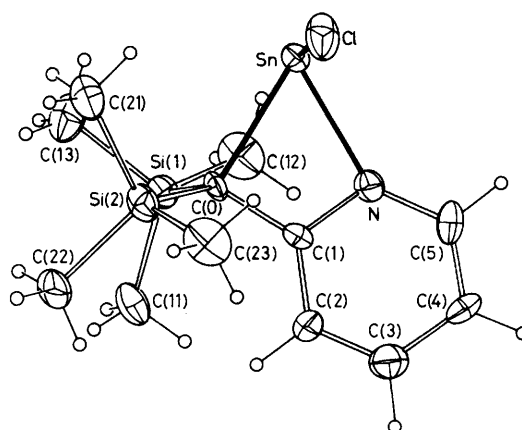
† No reprints available.



**Scheme 1.** Preparation of tin(II) alkyls containing the 2-pyridylbis-(trimethylsilyl)methyl ligand R [ $\text{R} = \text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2$ ]. *Conditions, reagents, and solvents:* mixing at  $-78^\circ\text{C}$ , then warming to ca.  $25^\circ\text{C}$  [for (2), work-up at  $-30^\circ\text{C}$ ]; i,  $\text{SnCl}_2$ , tetrahydrofuran or  $\text{OEt}_2$ ; ii,  $2\text{SnCl}_2$ ,  $\text{OEt}_2$ ; iii,  $2\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ ,  $\text{OEt}_2$ ; iv,  $\text{SnCl}_2$ ,  $\text{OEt}_2$ ; v,  $\text{Sn}(\text{OC}_6\text{H}_3\text{Bu}'_2-2,6)_2$ ,  $\text{OEt}_2$ .



**Figure 1.** Molecular projection of one of the three independent molecules of  $\text{Sn}[\text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2]_2$ , (1), showing 20% thermal ellipsoids for the non-hydrogen atoms; hydrogen atoms have 0.1 Å radii. Selected bond distances (Å) and angles ( $^\circ$ ) (values for molecules 1, 2, and 3, respectively): Sn–C(0) 2.377(7), 2.346(6), 2.334(6); Sn–N 2.449(7), 2.384(6), 2.420(6); C(0)–Sn–N 59.0(2), 60.7(2), 60.0(2); Sn–N–C(1) 93.4(5), 94.4(4), 93.4(5), Sn–N–C(5) 143.9(6), 144.5(5), 145.7(5); Sn–C(0)–C(1) 91.9(4), 91.9(4), 93.6(4); Sn–C(0)–Si(1) 124.1(4), 124.2(3), 123.7(3); Sn–C(0)–Si(2) 99.7(3), 101.2(3), 100.5(3).



**Figure 2.** Molecular projection of one of the two independent molecules of  $\text{Sn}[\text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2]\text{Cl}$ , (2), showing 20% thermal ellipsoids for the non-hydrogen atoms; hydrogen atoms have radii of 0.1 Å. Selected bond distances (Å) and angles ( $^\circ$ ) (values for molecules 1 and 2, respectively): Sn–C(0) 2.32(2), 2.32(2); Sn–N 2.27(2), 2.26(2); Sn–Cl 2.440(5), 2.446(5); Cl–Sn–C(0) 101.6(4); Cl–Sn–N 91.8(4), 89.1(4); C(0)–Sn–N 61.4(6), 61.7(6); Sn–N–C(1) 95(1), 95(1); Sn–N–C(5) 144(1), 145(2); Sn–C(0)–C(1) 89.8(10), 89.7(11); Sn–C(0)–Si(1) 105.6(8), 104.9(9); Sn–C(0)–Si(2) 115.0(7), 113.5(8).

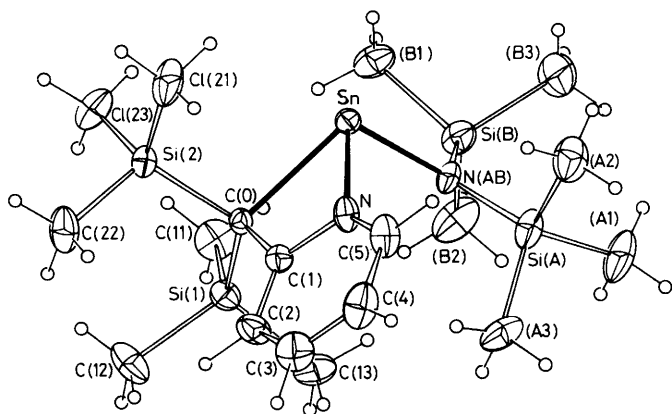
hitherto been structurally authenticated solely in tetravalent compounds such as  $(\text{SnPh}_2)_6$ ; (iii),  $\text{Sn}(\text{R})\text{Cl}$  (2) and  $\text{Sn}(\text{R})[\text{N}(\text{SiMe}_3)_2]$  (3) have no forerunners as well characterised heteroleptic (chiral)  $\text{Sn}^{\text{II}}$  alkyls or as monomeric compounds of the wider class  $\text{Sn}(\text{Y})\text{Y}'$  ( $\text{Y}$  and  $\text{Y}'$  are monodentate ligands, or one of them is bidentate); the co-ordination number of three for an X-ray-characterised  $\text{Sn}^{\text{II}}$  alkyl has previously been exclusively found in (A). Additionally, (iv), variable temperature multinuclear n.m.r. experiments show that compounds (1)–(3) undergo dynamic processes in  $\text{C}_6\text{D}_5\text{CD}_3$  solution. Finally, (v), we believe that compounds (2) and (3) have much potential as precursors to a wider range of heteroleptic  $\text{Sn}^{\text{II}}$  complexes  $\text{Sn}(\text{R})\text{Y}$ ; and (1)–(3) are plausible models for isoleptic alkyls of  $\text{Ge}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$ . {The compound  $\text{Sn}(\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2-o)_2$  was suggested to have a square based pyramidal structure, similar to that of (1), on the basis of the X-ray structure for  $[(\text{OC})_5\text{W}:\text{Sn}(\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2-o)_2]$ .<sup>6</sup>

The identity of the alkyls (1)–(3) was established by satisfactory microanalyses, mass spectra (including parent molecular ions, by electron impact), and n.m.r.‡ and X-ray§

‡ *Selected n.m.r. data:*  $\delta$ ,  $\text{C}_6\text{D}_6$ , 305 K [ $^1\text{H}$  360.14;  $^{13}\text{C}$  ( $^1\text{H}$ ) 90.56;  $^{29}\text{Si}$  71.55 MHz;  $^{119}\text{Sn}$  134.30 MHz ( $\delta$  in p.p.m. rel. to  $\text{SnMe}_4$ ): (1)  $^1\text{H}$  0.26 ( $\text{SiMe}_3$ ),  $^{13}\text{C}$  3.88 ( $\text{CH}_3$ ), 40.60 [ $\text{C}(\text{SiMe}_3)_2$ ],  $^{29}\text{Si}$  –2.69,  $^{119}\text{Sn}$  141.0; (2)  $^1\text{H}$  0.18 ( $\text{SiMe}_3$ ),  $^{13}\text{C}$  2.05 ( $\text{CH}_3$ ), 43.62 [ $\text{C}(\text{SiMe}_3)_2$ ],  $^{29}\text{Si}$  –1.58,  $^{119}\text{Sn}$  350.6; (3)  $^1\text{H}$  0.21 [ $\text{C}(\text{SiMe}_3)_2$ ], 0.09 and 0.24 [ $\text{N}(\text{SiMe}_3)_2$ ],  $^{13}\text{C}$  5.88 [ $\text{C}(\text{SiMe}_3)_2$ ], 46.60 [ $\text{C}(\text{SiMe}_3)_2$ ], 2.36 and 3.89 [ $\text{N}(\text{SiMe}_3)_2$ ],  $^{29}\text{Si}$  –4.09 [ $\text{C}(\text{SiMe}_3)_2$ ], –2.10 and –2.41 [ $\text{N}(\text{SiMe}_3)_2$ ],  $^{119}\text{Sn}$  325.8.

§ *Crystal data:* (Mo- $K_\alpha$  radiation, 295 K): for (1),  $\text{C}_{24}\text{H}_{44}\text{N}_2\text{Si}_4\text{Sn}$ , monoclinic,  $C2/c$ ,  $a = 15.963(1)$ ,  $b = 27.333(4)$ ,  $c = 21.856(2)$  Å,  $\beta = 103.66(1)^\circ$ ,  $Z = 12$ ,  $D_c = 1.27$  g  $\text{cm}^{-3}$ , 4959 'observed' reflections [ $I > 3\sigma(I)$ ],  $2\theta_{\text{max}} = 50^\circ$ ,  $R = 0.051$ ,  $R_w = 0.072$ . For (2),  $\text{C}_{12}\text{H}_{22}\text{ClNSi}_2\text{Sn}$ , monoclinic,  $P2_1/n$ ,  $a = 15.604(5)$ ,  $b = 14.411(5)$ ,  $c = 17.413(8)$  Å,  $\beta = 112.56(3)^\circ$ ,  $Z = 8$ ,  $D_c = 1.44$  g  $\text{cm}^{-3}$ , 2539 'observed' reflections [ $I > 2\sigma(I)$ ],  $2\theta_{\text{max}} = 40^\circ$ ,  $R = 0.064$ ,  $R_w = 0.074$ . For (3),  $\text{C}_{18}\text{H}_{40}\text{N}_2\text{Si}_4\text{Sn}$ , monoclinic,  $P2_1/c$ ,  $a = 12.076(5)$ ,  $b = 17.290(5)$ ,  $c = 14.646(8)$  Å,  $\beta = 117.20(3)^\circ$ ,  $Z = 4$ ,  $D_c = 1.26$  g  $\text{cm}^{-3}$ , 2564 'observed' reflections [ $I > 3\sigma(I)$ ],  $2\theta_{\text{max}} = 50^\circ$ ,  $R = 0.040$ ,  $R_w = 0.035$ .

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 3.** Molecular projection of  $\text{Sn}[\text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2][\text{N}(\text{SiMe}_3)_2]$ , (**3**) showing 20% thermal ellipsoids for the non-hydrogen atoms: hydrogen atoms have arbitrary radii. Selected bond distances (Å) and angles ( $^\circ$ ) are as follows: Sn–C(0) 2.356(8); Sn–N 2.299(5); Sn–N(AB) 2.144(5); N–Sn–C(0) 61.1(2); C(0)–Sn–N(AB) 105.4(2); N–Sn–N(AB) 97.2(2); Sn–N–C(1) 95.8(4); Sn–N–C(5) 143.7(6); Sn–C(0)–C(1) 90.0(5); Sn–C(0)–Si(1) 120.0(3); Sn–C(0)–Si(2) 105.2(3).

data. The sum of the three angles around Sn is  $252.9^\circ$  in the chloride (**2**) and  $263.7^\circ$  in the amide (**3**); hence the lone pair on tin is stereochemically active, as is also probably the case for  $\text{SnR}_2$  (**1**), by comparison with *X*-ray data on the isoleptic lone pair-free complexes  $\text{MR}_2$  ( $\text{M} = \text{Mg}, \text{Zn}, \text{or Cd}$ )<sup>7</sup> and  $[\text{AlR}_2]^+$ .<sup>8</sup>

<sup>1</sup>H n.m.r. spectra for the heteroleptic compounds (**2**) and (**3**) in  $\text{C}_6\text{D}_5\text{CD}_3$  showed that the  $\text{C}(\text{SiMe}_3)_2$  protons gave rise to a doublet signal only upon cooling. The coalescence temperatures  $T_c$  were  $-53 \pm 2^\circ\text{C}$  (**2**) and  $-59 \pm 2^\circ\text{C}$  (**3**), corresponding to  $\Delta G^\ddagger T_c$   $43.5 \pm 0.8$  (**2**) and  $42.7 \pm 0.8$  kJ mol<sup>-1</sup> (**3**), respectively, for the process assumed to be Sn–N(py) bond dissociation [equation (1)]. The same phenomenon is believed to be the cause of the strong temperature-dependence of the <sup>119</sup>Sn chemical shift in each of (**1**)–(**3**); e.g. for  $\text{SnR}_2$  (**1**), the  $\delta(^{119}\text{Sn})$  value ranged from 118.5 p.p.m.

at  $-60^\circ\text{C}$  to 148.4 p.p.m. at  $+50^\circ\text{C}$ . The  $\text{N}(\text{SiMe}_3)_2$  <sup>29</sup>Si signal in (**3**) at ambient temperature was a 1:1 doublet;† this is attributed to restricted rotation about the Sn–N( $\text{SiMe}_3$ )<sub>2</sub> bond.

The present *X*-ray structural data on  $\text{Sn}^{\text{II}}$  complexes derived from the  $\beta$ -*N*-functionalised alkyl ligand  $\bar{\text{R}}$  are available for comparison with such information on related complexes of some other metals. Previously  $\bar{\text{R}}$  was found to behave as (i), a monodentate *C*-centred ligand in  $\text{HgR}_2$ ,<sup>7</sup> (ii), an  $\eta^3$ -aza-allyl ligand in  $\text{LiR}(\text{tmeda})$  ( $\text{tmeda} = \text{Me}_2\text{N}[\text{CH}_2]_2\text{NMe}_2$ ) or  $\text{LiR}(\text{RH})$ ,<sup>9</sup> (iii), a chelating (*C,N*) ligand in  $[\text{M}'\text{R}_2]$  ( $\text{M}' = \text{Mg}, \text{Zn}, \text{or Cd}$ )<sup>7</sup> or  $[\text{AlR}_2]^+$ ,<sup>8</sup> or (iv), a bridging (*C,N*) ligand in  $[(\text{MR})_2]$  ( $\text{M} = \text{Li}, \text{Cu}, \text{or Ag}$ ).<sup>10</sup>

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