

The First Monomeric Prochiral Tin(II) Complexes $\text{Sn}[\text{N}(\text{SiMe}_3)_2]\text{X}$

$[\text{X} = \text{OC}_6\text{H}_2\text{Bu}'_2\text{-2,6-Me-4}$, **1** or $\text{NCMe}_2(\text{CH}_2)_3\text{CMe}_2$, **2**]; the X-Ray Structure of **1** and Oxidative Addition Reactions of **2**†

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Monomeric, crystalline tin(II) amides $\text{Sn}(\text{NR}_2)\text{X}$ [$\text{X} = \text{OAr}$ **1** or NR'_2 **2**; $\text{R} = \text{SiMe}_3$, $\text{Ar} = \text{C}_6\text{H}_2\text{Bu}'_2\text{-2,6-Me-4}$, $\text{NR}'_2 = \text{NCMe}_2(\text{CH}_2)_3\text{CMe}_2$] have been prepared from (a) $\text{Sn}(\text{NR}_2)_2 + \text{SnX}_2$, (b) $[\text{Sn}(\mu\text{-Cl})(\text{NR}_2)]_2 + 2\text{LiX}$ or (c) $\text{Sn}(\text{NR}_2)_2 + \text{ArOH}$; **1** is V-shaped, O-Sn-N $96.4(1)^\circ$; **2** + A-B yields the adducts $\text{Sn}(\text{A})(\text{B})(\text{NR}_2)(\text{NR}'_2)$ [$\text{AB} = (\text{CF}_3\text{CO})_2\text{O}$ **3**, MeI **4** or (+)-EtCH(Me)CH₂Br **5**], in the case of **5** without significant diastereoselectivity.

The first thermally stable, heteroleptic, two-coordinate tin(II) compounds $\text{Sn}(\text{L})\text{L}'$, L and L' being monohapto ligands, free from significant intermolecular association, have been obtained by three methods, Scheme 1; a single group 14 element compound of this type has recently been reported, $\text{Ge}(\text{CR}_3)(\text{CHR}_2)$ ($\text{R} = \text{SiMe}_3$).¹ Crystalline $\text{Sn}(\text{NR}_2)(\text{OAr})$ **1** is V-shaped [Fig. 1; selected X-ray data,‡ compared with those

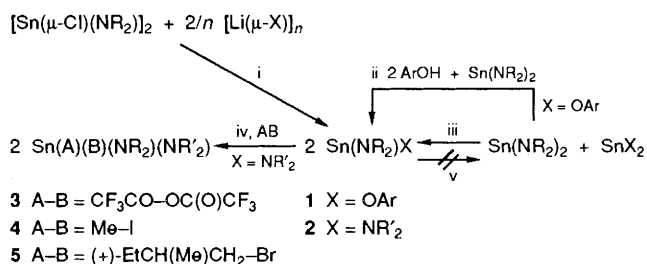
for $\text{Sn}(\text{NR}_2)_2$ ² and $\text{Sn}(\text{OAr})_2$,³ are in Table 1 ($\text{Ar} = \text{C}_6\text{H}_2\text{Bu}'_2\text{-2,6-Me-4}$]. The similarly diamagnetic and coloured low melting ($<30^\circ\text{C}$) $\text{Sn}(\text{NR}_2)(\text{NR}'_2)$ **2** presumably adopts a similar geometry; with reagents A-B it yielded the *Sn*-chiral adducts $\text{Sn}(\text{A})(\text{B})(\text{NR}_2)(\text{NR}'_2)$ **3-5** [Scheme 1: $\text{NR}'_2 = \text{NCMe}_2(\text{CH}_2)_3\text{CMe}_2$ and $\text{AB} = (\text{CF}_3\text{CO})_2\text{O}$ **3**, MeI **4** or (+)-EtCH(Me)CH₂Br **5**], for **5** without significant diastereoselectivity.

The formation and reactivity of **1** and **2** were conveniently monitored by ¹¹⁹Sn NMR spectroscopy, Table 2. It is noteworthy that **1** at 100°C was inert to redistributive symmetrisation (*v* in Scheme 1), whereas the reverse reaction of $\text{Sn}(\text{NR}_2)_2 + \text{Sn}(\text{OAr})_2$ was fast at 25°C . This is surprising because earlier attempts to make pure heteroleptic *Sn*^{II} compounds were unsuccessful; for example, experiments designed to yield $\text{Sn}(\eta\text{-C}_5\text{H}_5)(\text{NR}_2)$ gave 2 : 1 : 1 mixtures of the compound with $\text{Sn}(\text{NR}_2)_2$ and $\text{Sn}(\eta\text{-C}_5\text{H}_5)_2$.⁴ Earlier literature is cited in ref. 5, which also reported the structure of $\text{Sn}(\text{NCS})(\text{NR}_2)$, showing significant $\text{Sn}\cdots\text{S}$ interactions between neighbouring molecules.

The O-Sn-N angle in **1** of $96.4(1)^\circ$ is almost exactly the mean of the wider N-Sn-N' and the more acute O-Sn-O'

† No reprints available.

‡ Crystal data [T 22°C , Enraf-Nonius CAD-4 diffractometer, absorption correction, structural solution by heavy atom methods, full-matrix least-squares refinement with non-hydrogen atoms anisotropic; H atoms fixed other than C(15) methyl H atoms which were omitted, $w = 1/\sigma^2(F)$]: **1** $\text{C}_{21}\text{H}_{41}\text{NOSi}_2\text{Sn}$, $M = 498.4$, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.356(1)$, $b = 24.826(3)$, $c = 11.367(3)$ Å, $\beta = 99.58(2)^\circ$, $U = 2603.4$ Å³, $F(000) = 1040$; $Z = 4$, $D_c = 1.27$ g cm⁻³; $\mu(\text{Mo-K}\alpha) = 10.8$ cm⁻¹, specimen $0.5 \times 0.4 \times 0.3$ mm, 4692 unique reflections for $2 < \theta < 25^\circ$, 3467 reflections with $|F^2| > 2\sigma(F^2)$ used in the refinement; $R = 0.032$, $R_w = 0.044$, $S = 1.4$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1 R = SiMe₃, NR'₂ = NCMe₂(CH₂)₃CMe₂, Ar = C₆H₂Bu'₂-2,6-Me-4. *Reagents and conditions:* i, n-C₆H₁₄, 25 °C, 1 h; ii and iii, PhMe, 25 °C, ½ h; iv, excess AB, 25 °C (for **3**, n-C₆H₁₄, 2½ h; for **4**, n-C₆H₁₄, ½ h; for **5**, n-C₅H₁₂ + [2H₈]toluene, 14 h, reaction monitored by ¹¹⁹Sn NMR spectroscopy); v, PhMe, 100 °C, 1 h. *Characterisation:* the crystalline, bright yellow **1**, orange **2**, and yellow **3** gave satisfactory microanalyses and ¹H and ¹³C NMR spectra; § for ¹¹⁹Sn data, see Table 2; for the X-ray structure of **1**, see Fig. 1; **4** was identified by ¹H, ¹³C and ¹¹⁹Sn NMR spectral data; satisfactory FAB mass spectra (Nujol matrix) were recorded for **1**, **2** and **4**.

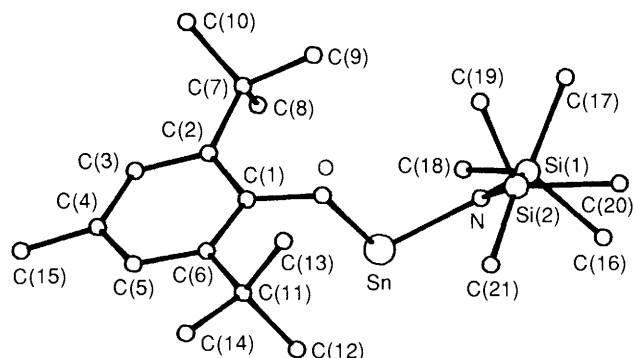


Fig. 1 The molecular structure of Sn[N(SiMe₃)₂][OC₆H₂Bu'₂-2,6-Me-4] **1** and atom numbering scheme

angles in Sn(NR₂)₂² and Sn(OAr)₂,³ Table 1. The greater steric demand of the -NR₂ in relation to the -OAr ligand is also reflected in the longer Sn-O but shorter Sn-N distances in **1** in comparison with Sn(OAr)₂ and Sn(NR₂)₂, respectively, and in the smaller difference between the two Sn-N-Si angles in **1** compared with that in Sn(NR₂)₂ (in each case, the wider angle is on the side of the molecule *trans* to the lone pair).

The ¹¹⁹Sn NMR chemical shift for **1** is intermediate between those for Sn(NR₂)₂ and Sn(OAr)₂, Table 2. The highly deshielded value observed for **2** is characteristic of homoleptic monomeric Sn^{II} amides (a much higher frequency δ[¹¹⁹Sn] would have been expected had **2** been a dimer in solution), as is its considerable temperature dependence (footnote *b* in Table 2). Characterisation of **2** was also achieved by identification of its oxidative adducts **3** and **4** [Scheme 1; *cf.*⁶ related reactions of Sn(NR₂)₂ and Sn(NR'₂)₂ with MeI or (CF₃CO)₂O]. ¹H and ¹³C NMR spectroscopy § revealed that

§ *Selected ¹H, ¹³C and ¹⁹F NMR spectroscopic data:* (at ca. 300 K in [2H₆]benzene or PhMe with [2H₆]benzene or [2H₈]toluene as lock solvents) **1**: ¹H δ 0.32 (s, 18 H, SiMe₃), 1.49 (s, 18 H, Bu'), 1.56 (s, 3 H, Me) and 7.19 (s, 2 H, C₆H₂); ¹³C δ 5.68 (q, SiMe₃), 21.47 (q, Me), 32.93 (q, CMe₂), 35.14 (s, CMe₃), 126.09, 140.59 (s, *o*- and *p*-C), 127.08 (d, *m*-C) and 157.41 (s, *ipso*-C). **2**: ¹H δ 0.29 (s, 18 H, SiMe₃) and 1.53 (s, 12 H, Me); ¹³C {¹H} δ 5.22 (s, SiMe₃), 18.19 (s, δ-CH₂), 36.50 (s, Me), 42.64 (s, γ-CH₂) and 59.30 (s, β-C). **3**: ¹H δ 0.28 (s, SiMe₃), 1.19 and 1.30 (s, Me); ¹³C {¹H} δ 5.16 (s, SiMe₃), 17.95 (s, δ-CH₂), 33.79, 33.93 (s, Me), 40.66 (s, γ-CH₂), 58.36 (s, β-C), 116.2 (q, COCF₃) (¹J_{C-F} 288 Hz), 116.8 (q, OCOCF₃) (¹J_{C-F} 298 Hz), 160.0 (q, COCF₃, ³J_{C-F} 41 Hz) and 217.5 (q, OCOCF₃) (³J_{C-F} 39 Hz); ¹⁹F δ -75.48 (s) and -74.55 (s) [³J(¹⁹F-¹¹⁹Sn) 44 Hz]. **4**: ¹H δ 0.33 (s, SnMe), 0.40 (s, SiMe₃), 1.40 and 1.42 (s, Me); ¹³C {¹H} δ 6.25 (s, SiMe₃), 17.98 (s, δ-CH₂), 22.79 (s, SnMe), 33.81, 34.03 (s, Me), 42.20 (s, γ-CH₂) and 58.66 (s, β-C).

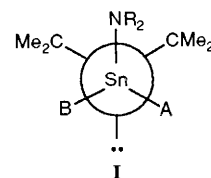
Table 1 Comparative selected structural data for some crystalline tin(II) amides and aryloxides

	Sn(OAr) ₂	Sn(NR ₂) ₂	Sn(NR ₂)(OAr) 1
Sn-O/Å	2.022(4) 1.995(4)	—	2.055(2)
Sn-N/Å	—	2.096(1) 2.088(6)	2.079(3)
O-C/Å	1.375(6) 1.367(6)	—	1.365(4)
<N-Si>/Å	—	1.742(6)	1.733(3)
E-Sn-E'/°	88.8(2)	104.7(2)	96.4(1)
Sn-O-C/P	128.6(4) 121.8(3)	—	115.1(2)
Sn-N-Si/P	—	124.9(2) 113.1(2)	122.0(1) 114.7(1)
Ref.	3	2	This work

Table 2 ¹¹⁹Sn NMR chemical shifts for some tin compounds^a

Compound	δ
Sn(OAr) ₂	-193
Sn(NR ₂) ₂	766 (283 K)
Sn(NR' ₂) ₂	738 (283 K)
Sn(NR ₂)(OAr) 1	277
Sn(NR ₂)(NR' ₂) 2	705 (283 K) ^b
Sn(COCF ₃)(NR ₂)(NR' ₂)(OCOCF ₃) 3	-299 ^c
Sn(I)(Me)(NR ₂)(NR' ₂) 4	-207
Sn(Br)[(+)-CH ₂ CH(Me)Et](NR ₂)(NR' ₂) 5	-89.3, -89.6

^a Unless otherwise stated, data obtained at ca. 300 K in [2H₆]benzene or PhMe with [2H₆]benzene or [2H₈]toluene as lock solvents. ^b δ 677 (213 K), 732 (363 K). ^c Quartet, ³J(¹¹⁹Sn-¹⁹F) 46 Hz.



the magnetic equivalence of the Me groups of the -NR'₂ ligand in **2** is not preserved in **3** or **4**. This may arise from *Sn*-chirality in the latter (*q.v.* the Newman projection **I**, through the Sn-N bond, assuming non-planarity at the NR'₂ nitrogen atom); alternatively, since the β-carbon atoms remain identical, restricted rotation about the Sn-NR'₂ bond in the Sn^{IV} adducts may be implicated.

A prochiral tin(II) complex, such as **2**, is of interest because reaction with an optically active addendum A-B offers the possibility of achieving for the first time an asymmetric synthesis at a tin(IV) centre, with groups bulky enough to make it likely that the product Sn(A)(B)(NR₂)(NR'₂) would be stereochemically rigid and hence inert. It had previously been shown that the addition of a bromohydrocarbon R^bBr to Sn(NR₂)₂ is first order in each reagent [*k*₁ = 6.87 × 10⁻⁵ s⁻¹ for Sn(NR₂)₂ + PhBr in C₆H₆ at 300 K], the rate-determining step being the formation of the radical pair ·Br and the pyramidal ·SnBr(NR₂)₂.⁶ We therefore selected as AB (+)-EtCH(Me)CH₂Br, the simplest optically active bromoalkane without chirality at C_α, but its reaction with **2** gave a mixture of the two diastereoisomers of **5**, without significant selectivity, Table 2. The reaction, which was monitored by ¹¹⁹Sn NMR spectroscopy, was first order in Sn(NR₂)(NR'₂) with *k*₁ = 5.30 × 10⁻⁵ s⁻¹ at ca. 300 K.

In principle, diastereoselectivity is only achievable if (*i*) the rate of interconversion of the (*R*) and (*S*) σ-radicals ·Sn(Br)(NR₂)(NR'₂) (*via* the energetically readily accessible planar π-radical transition state) is rapid with respect to its

combination with optically active EtCH(Me) \dot{C} H₂, and (ii) there is a clear preference for the reaction of the latter with either the (*R*) or (*S*) *Sn*-centred radical. Regarding (ii), further efforts will be made using a stereochemically more demanding bromoalkane. As for (i), we have previously studied inversion at a three-coordinate tin(II) centre of [Sn(μ -Cl)(NR'₂)₂],⁷ and we shall seek to determine inversion barriers for tin-centred radicals.

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