Subvalent Group 14 Metal Compounds. Part 16.[1] Synthesis, Crystal Structure and Characterisation of Some β-Functionalised-alkyltin(II) Complexes, SnR(X) {R = $C_5H_4N[C(SiMe_3)_2]$-2; X = R, Cl or $N(SiMe_3)_2$}*,†

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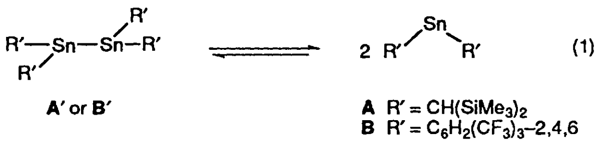
Crystalline monomeric alkyltin(II) compounds were prepared using the β-*N*-functionalised ligand 2-pyridylbis(trimethylsilyl)methyl, $C_5H_4N[C(SiMe_3)_2]$-2 (R): (*a*) SnR_2 **1** from $(LiR)_2$ and $SnCl_2$ or $Sn(OC_6H_3Bu^t_2\text{-}2,6)_2$ (*b*) SnR(Cl) **2** from $SnCl_2$ and SnR_2 or $\frac{1}{2}(LiR)_2$; and (*c*) $SnR[N(SiMe_3)_2]$ **3** from $Sn[N(SiMe_3)_2]_2$ and $\frac{1}{2}(LiR)_2$. Single-crystal X-ray diffraction data showed that in each of **1**–**3** R^- behaves as a chelating *C,N*-centred ligand, and that the lone pair on tin is stereochemically active. The mean Sn–C [and Sn–NC_5H_4] bond lengths (Å) are 2.35(2) [2.42(2)] in **1**, 2.32(2) [2.27(3)] in **2**, and 2.356(8) [2.299(5)] in **3**. Variable-temperature multinuclear (^1H, ^{13}C, ^{29}Si and ^{119}Sn) NMR spectral data were obtained for **1**–**3** in $[^2H_8]$toluene. These showed that dynamic processes were operative, believed to be Sn–$N(C_5H_4)$ dissociations, with $\Delta G^{\ddagger}_{T_c}$ = 43.5 ± 0.8 for **2** or 42.7 ± 0.8 kJ mol^{-1} for **3** (the coalescence temperature T_c being 220 ± 2 for **2** and 214 ± 2 K for **3**); for **3** a further fluxion with $\Delta G^{\ddagger}_{T_c}$ = 76.1 ± 0.8 kJ mol^{-1} (T_c = 368 ± 2 K) is attributed to the barrier to rotation about the tin–amide nitrogen bond. Attempts were made to reduce **2** [evidence for $(SnR)_n$], and to prepare analogues of Ge^{II} and Pb^{II} of **1** and **2**. A further β-functionalised complex, $SnCl(OCBu^t_2CH_2PMe_2)$ **4**, was obtained from $SnCl_2$ and $\frac{1}{2}[Li(OCBu^t_2CH_2PMe_2)]_2$; there was no evidence for ^{31}P–^{119}Sn coupling, and a plausible structure is $[Sn(\mu\text{-}Cl)(OCBu^t_2CH_2PMe_2)]_2$. A similar metathetical reaction between $SnCl_2$ and $Sn(OC_6H_3Bu^t_2\text{–}2,6)_2$ in tetrahydrofuran (thf) gave $\frac{1}{m}[SnCl(OC_6H_3Bu^t_2\text{–}2,6)(thf)_n]_m$, whereas $SnCl_2 + SnR'_2$ [R' = $CH(SiMe_3)_2$] yielded SnR'_2Cl_2 + Sn.

Earlier parts of this Series were concerned with thermally stable bivalent and trivalent compounds of germanium, tin and lead of formula MX_2 or MX(X') and (M ≠ Pb) MX_3; the ligands X^- and X'^- were chosen to be monohapto (excluding, for example, η-cyclopentadienyls) and monodentate. Only three such mononuclear tin(II) hydrocarbyls SnR'_2 have thus far been structurally characterised: $Sn[CH(SiMe_3)_2]_2$ **A**,[2] $Sn[C_6H_2(CF_3)_3\text{-}2,4,6]_2$ **B**[3] and $Sn[C(SiMe_3)_2(CH_2)_2C(SiMe_3)_2]$ **C**;[4] **A** by gas electron and **B** and **C** by X-ray diffraction. The monomeric structure for **A** was retained in very dilute hydrocarbon solution,[5] but in more concentrated solution it was shown to be in equilibrium with the dimer **A′**, equation (1);[6] the latter structure with a short Sn–Sn bond (2.768 Å) was found in the crystal.[7] Compound **B** has been reported in two crystal modifications: the monomer **B**[3] and the dimer **B′** having a long Sn ··· Sn contact of 3.639 Å;[8] **B** (Sn ··· Sn 6.31 Å)[3] and **B′** showed very similar SnR'_2 geometry with some close Sn ··· F contacts. A related compound $Sn[C_6H_3(CF_3)_2\text{-}2.6]_2$ was formulated as the monomer on the basis of its Mössbauer spectrum.[9]



The metallacycle **C** is a special case of a bis(hydrocarbyl)tin(II) complex SnR'_2 as defined above in that the two carbanions R'^- jointly comprise the bidentate ligand $^-C(SiMe_3)_2(CH_2)_2C(SiMe_3)_2$. Only one other bis(carbanionic) ligand, $C_6H_4[CH(SiMe_3)]_2$-1,2, has hitherto been used in the context of tin(II) chemistry; however, the derived crystalline complex $(SnR'_2)_4$ was found to be the cyclotetramer $[Sn\{C_6H_4[CH(SiMe_3)]_2\text{-}1,2\}\text{-}meso]_4$.[10] Monoanionic bidentate ligands have yielded homoleptic tin(II) aryls, in the case of crystalline $Sn[C_{10}H_6(NMe_2)\text{-}8]_2$ **D** with X-ray characterisation.[11] Preceding this disclosure was our preliminary communication dealing with SnR_2 **1** {R = $C_5H_4N[C(SiMe_3)_2]$-2} {as well as SnR(Cl) **2** and $SnR[N(SiMe_3)_2]$ **3**}.[12] The complex $Sn[C_6H_4(CH_2PPh_2)\text{-}2]_2$ is also probably a monomer: its derivative $[W(CO)_5\{Sn[C_6H_4(CH_2PPh_2)\text{-}2]_2\}]$ has been characterised by X-ray diffraction.[13] It is not inevitable that a bidentate monoanionic ligand should behave towards Sn^{II} in a chelating fashion, as shown in the binuclear tin(II) hydrocarbyl **E**, in which $^-C_6H_4PPh_2$-2 functions in a bridging mode.[14] The compounds $Sn[PPh_2CHPPh_2]_2$[15,16] and the structurally characterised $Sn[PMe_2C(PMe_2)PMe_2]_2$[15] are unlikely to have significant Sn–C bonding in the solid state.

Monomeric SnR'_2 molecules may only have a transient exist-

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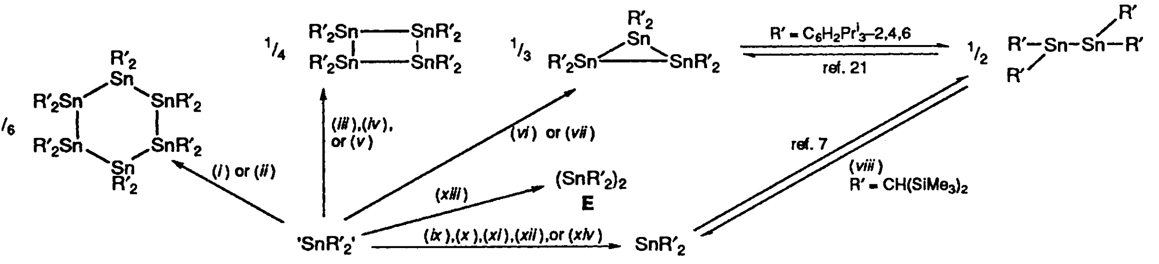
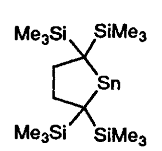
* No reprints available.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: Torr ≈ 133 Pa.



Scheme 1 Structures of bis(hydrocarbyl)tin(II) compounds $(SnR'_2)_n$ [generated from $SnCl_2$ or $SnBr_2$ + 2LiR′ or 2MgR′(Cl); or SnR'_2Cl_2 + 2Li; or SnR'_2H_2]: R′ = Ph (*i*),[17] CH_2Ph (*ii*),[18] CH_2SiMe_3 (*iii*),[19] $C_6H_4[CH(SiMe_3)_2]_2$-1,2 (*iv*),[10] Bu^t or *tert*-pentyl (*v*),[20] $C_6H_2Pr^i_3$-2,4,6 (*vi*),[21,22] $C_6H_3Et_2$-2,6 (*vii*),[23] $CH(SiMe_3)_2$ (*viii*) and (*ix*),[7] $C_6H_2(CF_3)_3$-2,4,6 (*x*)[3] (a 'dimer' $R'_2Sn\cdots SnR'_2$ is also known[8]), $C(SiMe_3)_2(CH_2)_2C(SiMe_3)_2$ (*xi*), $C_{10}H_6(NMe_2)$-8 (*xii*),[11] **1** $C_5H_4N[C(SiMe_3)_2]$-2 (*xiii*),[12] and $C_6H_4\overset{+}{P}Ph_2\overset{-}{O}H$-2 (*xiv*)[14]



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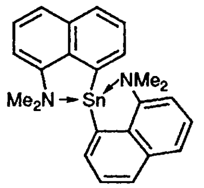

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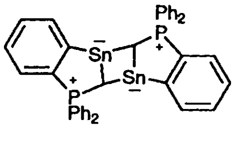

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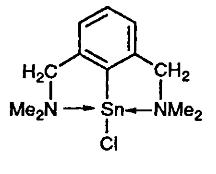

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Table 1 Principal mass spectrometry features with assignments for compounds SnR(X) {R = $C_5H_4N[C(SiMe_3)_2]$-2; X = R **1**, Cl **2** or $N(SiMe_3)_2$ **3**}

Compound	Mass spectrometry assignments (*m*/*z* in parentheses)
1	M^+ (591), $[M - R]^+$ (355), $[M - C(SiMe_3)_2]^+$ (431), $[M - RSiMe_3]^+$ (282)
2	M^+ (390), $[M - Me]^+$ (375), $[M - SnCl]^+$ (236), $[M - C(SiMe_3)_2]^+$ (230)
3	M^+ (515), $[M - Me]^+$ (500), $[M - C(SiMe_2)_2]^+$ (356), $[M - R]^+$ (279)

ence when freshly prepared prior to undergoing oligomerisation, as summarised in Scheme 1.[5–8,10–12,17–23] Compounds **1**–**3** are derived from the 2-[bis(trimethylsilyl)methyl]pyridyl ligand, R^-. It has previously been shown that R^- is capable of ligating in one of three modes: terminal, as in $LiR(NMe_2CH_2CH_2NMe_2]$;[24] bridging, as in MRMR (M = Li,[25] Cu or Ag[26]); or chelating, as in $\overline{MR}_2$ (M = Mg,[27] Co,[28] Zn,[27] Cd or Hg), $\overline{MR}Cl_2$ (M = As, Sb or Bi),[29] $\overline{SiR}Cl_2X$ (X = H or Me),[30] $[\overline{AlR}_2][AlCl_4]$,[31] or $\overline{GaR}_2Cl$.[32]

Compounds SnRX [X = Cl **2** or $N(SiMe_3)_2$ **3**] were the first heteroleptic mononuclear tin(II) compounds to be reported; X-ray data showed them to have three-co-ordinate tin.[12] By contrast, in crystalline 2,6-bis(dimethylaminomethyl)phenyltin(II) chloride **F** tin is four-co-ordinate.[33] There appear to be as yet only two crystalline two-co-ordinate heteroleptic tin(II) compounds: $Sn[N(SiMe_3)_2]X$ {X = $OC_6H_2Bu^t_2$-2,6-Me-4[34] or $N(C_6H_2Me_3$-2,4,6)$BBu^t[N(SiMe_3)_2]$[35]}. The analogue in which X = Cl has the dimeric structure $\{Sn(\mu\text{-}Cl)[N(SiMe_3)_2]\}_2$;[36] the homoleptic crystalline $Sn[N(SiMe_3)_2]_2$ is a monomer,[37] unlike the polymeric $SnCl_2$, which reverts to the monomer only at high temperature.[38]

An aim of the present work was to explore the potential of the ligand $C_5H_4N[\bar{C}(SiMe_3)_2]$-2 ($R^-$) in the context of the chemistry of the heavier Group IV (Group 14. Ölander numbering) metals in the +2 oxidation state. Preliminary results on the mononuclear tin(II) compounds **1**–**3** have been published:[12] these are now elaborated and extensions to analogues of Ge^{II} and Pb^{II} are reported. A further objective was to examine the role of another bidentate monoanionic ligand $^-OCBu^t_2CH_2PMe_2$ in tin(II) chemistry; previously the crystalline compounds $[\overline{M(\mu\text{-}OCBu^t_2CH_2P}Me_2)]_2$ (M = Li[39a] or Na[39b]) and $[\overline{Ln(OCBu^t_2CH_2P}Me_2)_3]$ (Ln = Y or Nd)[40] were reported, as well as $HOCBu^t_2CH_2PMe_2$.[39] Finally, we sought to examine the reactions of $SnCl_2$ with some monomeric homoleptic SnX_2 compounds [X = R, R′, or $OC_6H_3Bu^t_2$-2,6; R′ = $CH(SiMe_3)_2$]. Previously it had been found that the heteroleptic compounds $[SnCl(X)]_n$ were formed for X = OMe,[41] η^5-C_5H_5 or η-C_5Me_5,[42] or $N(SiMe_3)_2$,[36] but only the last of these compounds was crystallographically characterised.

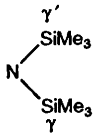
Results and Discussion

Routes to the compounds SnR_2 **1**, SnR(Cl) **2**, and $SnR[N(SiMe_3)_2]$ **3** are summarised in Scheme 2 {R = $C_5H_4N[C(SiMe_3)_2$-2}. The lithium alkyl $(LiR)_2$[25] was the common starting material, yielding (*a*) **1** with $SnCl_2$ [(*i*) in Scheme 2] or $Sn(OC_6H_3Bu^t_2\text{-}2,6)_2$[43] [(*v*) in Scheme 2], (*b*) **2** with $2SnCl_2$ [(*ii*) in Scheme 2] and (*c*) **3** with $2Sn[N(SiMe_3)_2]_2$[5] [(*iii*) in Scheme 2]; additionally, **2** was accessible from **1** + $SnCl_2$ [(*iv*) in Scheme 2]. The use of an aryl oxide/alkyl-exchange reaction [(*v*) in Scheme 2] for the preparation of SnR_2 **1** has precedents, *e.g.*[10] as a route to $(SnR'_2)_4$ {R'_2 = $C_6H_4[CH(SiMe_3)_2]$-1,2}. However, when $Sn(OC_6H_3Bu^t_2\text{-}2,6)_2$ was treated with $\frac{1}{2}(LiR)_2$ the expected $SnR(OC_6H_3Bu^t_2$-2,6) was not obtained. This could be due either to the instability of the latter with respect to redistribution, or to the greater rate of reaction of the lithium alkyl with the latter than with $Sn(OC_6H_3Bu^t_2\text{-}2,6)_2$, coupled with the low reactivity between SnR_2 and $Sn(OC_6H_3Bu^t_2\text{-}2,6)_2$.

Mass spectrometric data for compounds **1**–**3** are in Table 1, while in Table 2 are listed the ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectral chemical shifts with assignments: included also are similar data on $SnCl(OCBu^t_2CH_2PMe_2)$ **4**.

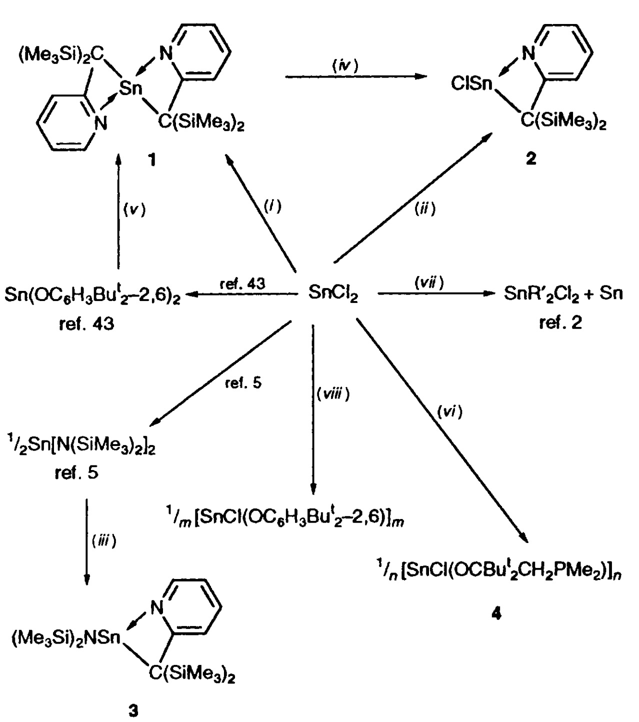
Dynamic Processes in Solutions of Complexes SnR(X) [X = R **1**, Cl **2** *or* $N(SiMe_3)_2$ **3**].—Variable-temperature ^{119}Sn NMR spectral chemical shift data in $[^2H_8]$toluene were collected for compounds **1** and **3**, Table 3. The significant variation of $\delta[^{119}Sn\text{-}\{^1H\}]$ with temperature particularly for **1** is consistent with the view that the dative pyridyl N→Sn bond is weak, and that at the higher temperatures the equilibrium shifts from the co-ordination number of tin of four in crystalline **1** (or three in **3**): thus the higher positive chemical shift corresponds to a higher equilibrium concentration of the three- (**1**) [or two-(**3**)]

Table 2 The NMR spectral chemical shifts (δ)[a] for compounds SnR(X) {R = $C_5H_4N[C(SiMe_3)_2]$-2; X = R **1**, Cl **2**, or $N(SiMe_3)_2$ **3**} and $SnCl(OCBu^t{}_2CH_2PMe_2)$ **4**



	R					$N(SiMe_3)_2$		R	$N(SiMe_3)_2$		
	$^1H^b$			$^{13}C^c$				$^{29}Si^b$			
Compound	β	γ	γ′	β	α	γ	γ′	β	γ	γ′	$^{119}Sn^d$
1	0.26			3.88	40.60			−2.69			141.0
2	0.18			2.05	43.62			−1.58			350.6
3	0.21	0.09	0.24	5.88	46.60	2.36	3.89	−4.09	−2.10	−2.41	325.8
4[e]	[^1H: 1.06 (Bu^t), 0.86(d) (PMe_2), 1.56(d) (CH_2)]										1034

[a] Spectra were recorded in C_6D_6 at 305 K for compounds **1**–**3** or $C_6D_5CD_3$ for **4**; each assignment refers to a singlet [or doublet (d)] signal. [b] ^1H and ^{29}Si chemical shifts relative to $SiMe_4$. [c] ^{13}C chemical shifts (proton decoupled) relative to C_6D_6 (at δ 128.0). [d] ^{119}Sn chemical shifts relative to $SnMe_4$. [e] $\delta(^{31}P)$ −144.7 (relative to 85% aqueous H_3PO_4).



Scheme 2 Preparation of tin(II) alkyls **1**–**3** containing the 2-pyridylbis(trimethylsilyl)methyl ligand R^- {$C_5H_4N[C(SiMe_3)_2]$-2}, and $SnCl_2$–SnX_2 metathetical reactions [X = R, $CH(SiMe_3)_2$, or OC_6H_3-$Bu^t{}_2$-2,6]. Reagents and conditions: (*i*) $(LiR)_2$, thf or OEt_2, −78 °C; (*ii*) $\frac{1}{2}(LiR)_2$, OEt_2, −78 °C; (*iii*) $\frac{1}{2}(LiR)_2$, OEt_2, −78 °C; (*iv*) $SnCl_2$, OEt_2, −78 °C; (*v*) $(LiR)_2$, OEt_2, −78 °C; (*vi*) $\frac{1}{2}[Li(OCBu^t{}_2CH_2PMe_2)]_2$, thf, −30 °C; (*vii*) SnR'_2 [R′ = $CH(SiMe_3)_2$], OEt_2, 25 °C; (*viii*) Sn-$(OC_6H_3Bu^t{}_2$-2,6$)_2$, thf, 25 °C

co-ordinate tin complex. In support of the notion that the large temperature dependence of $\delta[^{119}Sn\text{-}\{^1H\}]$ is attributable in part to a structural change at any rate for the case of the homoleptic alkyl **1**, we find that for $Sn[N(SiMe_3)_2]_2$, known to be a monomer in the crystal, in solution in benzene, and in the gas phase shows a temperature shift of 10 ppm for a 120 °C temperature change, having δ +769 at 343 K and +759 at 263 K. For a similar 80 K temperature difference the shift is *ca.* 20 for **1** and *ca.* 14 ppm for **3**.

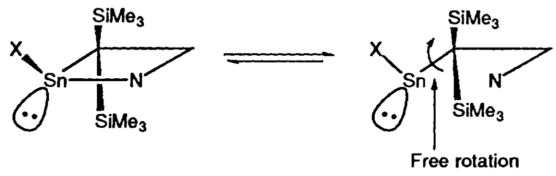
The ^1H NMR spectrum of compound **3** in $[^2H_8]$toluene at 193 K showed four distinct $SiMe_3$ signals. Two of these merged

Table 3 Tin-119 NMR spectral chemical shifts (δ)[a] for SnR_2 **1** or $SnR[N(SiMe_3)_2]$ **3** {R = $C_5H_4N[C(SiMe_3)_2]$-2} as a function of temperature[a]

1 δ (*T*/K)[b]	**3** δ (*T*/K)[b]
118.5 (213)	315.7 (268)
124.2 (233)	319.4 (288)
130.8 (263)	323.0 (308)
138.9 (293)	326.1 (328)
148.4 (323)	329.4 (348)

[a] In $[^2H_8]$toluene. [b] Chemical shifts relative to $SnMe_4$.

at 214 ± 2 K, the coalescence temperature T_c, corresponding to $\Delta G^\ddagger{}_{T_c}$ = 42.7 ± 0.8 kJ mol^{-1}, while the two others coalesced at 368 ± 2 K, corresponding to $\Delta G^\ddagger{}_{T_c}$ = 76.1 ± 0.8 kJ mol^{-1}. The former fluxional process is attributed to the equivalencing of the two $SiMe_3$ groups of the R^- ligand, as summarised in equation (2) [X = $N(SiMe_3)_2$], while the latter is believed to



(2)

arise from restriction to rotation about the $(Me_3Si)_2N$ nitrogen–tin bonds; the closed structure corresponds to that found in the crystal.

The ^1H NMR spectrum of SnR(Cl) **2** at 193 K showed two sharp $SiMe_3$ signals separated by 93.9 Hz. Variable-temperature studies showed that these coalesced at 220 ± 2 K, corresponding to $\Delta G^\ddagger{}_{T_c}$ 43.5 ± 0.8 kJ mol^{-1}. As for **3**, the low-temperature regime is believed to correspond to that of the closed three-co-ordinate tin structure, whereas the equivalencing of the $SiMe_3$ signals is attributed to the fast-exchange process between the former and the open two-co-ordinate structure, equation (2) (X = Cl).

Variable-temperature ^1H NMR spectra were not recorded for SnR_2 **1**. However, in the light of the $\delta(^{119}Sn)$ data of Table 3 and analogy with the ^1H NMR data cited above for **2** and **3**, it is likely that for **1** there is a dynamic process of type (2) in solution, involving not only a four- but also a three-co-ordinate tin structure.

The Molecular Structures of the Crystalline Complexes **1**–**3**.—The results of the single-crystal structure determinations are consistent with the presence of discrete molecules of the above tin(II) complexes **1**–**3**, as regards stoichiometries and connectivities; in each case the *C*,*N*-ligand(s) chelate the tin atom. Figs. 1 and 2 show the molecular projections of one of the independent molecules of complexes **1** and **2**, respectively; Fig. 3 shows a molecular projection of **3**. Intramolecular bond lengths and angles are in Tables 4–6, respectively, and non-hydrogen atom coordinates in Tables 7–9, respectively. We comment on individual features as follows.

The molecules of SnR_2 **1** are all disposed on the two-fold axes of the *C*2/*c* cell, Fig. 1; there are three such independent species, so that only one half of each molecule is crystallographically independent and the asymmetric unit comprises three half-molecules. In each molecule all of the four *C*,*N*-chelating atoms lie to one side of a plane normal to the two-fold axis, suggestive of the presence of a sterically active lone pair which must lie to the other side; surprisingly the gallium compound GaR_2Cl was found to be 'isostructural' [space group *C*2/*c*, $a = 15.957(6)$, $b = 27.979(5)$, $c = 21.592(4)$ Å, $\beta = 103.76(3)°$, $U = 9364$ Å^3] with the chlorine atom replacing the lone pair without any substantial effect on crystal packing.[32] Of the three molecules contained within the cell on the line $(0, y, \frac{1}{4})$, two (molecules 1,3) have the tin–lone pair vector oriented similarly; molecule 2, disposed between them, is oppositely directed so that the two tin atoms of molecules 1 and 2 lie in confrontation but separated by 6.5 Å. Although broadly similar in conformation, the three molecules show significant differences, molecules 2 and 3 more closely resembling each other than 1. Among the bond lengths and angles (Table 4), we note very substantial differences (up to 14°) between the interligand angles in particular, C(O)–Sn–C(O′) being the most sensitive discriminant. Wide variations are observed also further from the metal in respect of the angles at C(O) and the silicon atoms. The tin atom deviations from the C_5N pyridine skeletal planes for molecules 1, 2 and 3 are respectively 0.555, 0.272 and 0.243 Å, toward the lone pair. The Si(2) atoms deviate by 1.562, 1.938 and 1.994 Å from the same ligand planes, also toward the lone pair, while the Si(1) atoms are directed away from the lone pair by −1.621, −1.080 and −0.989 Å, from the ligand planes.

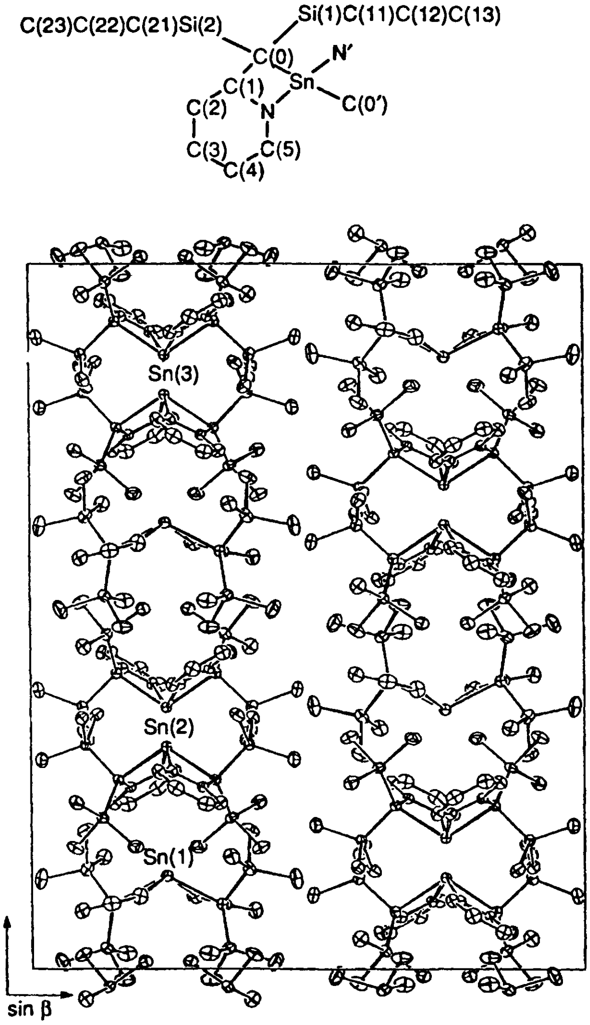


Fig. 1 Unit-cell contents of $Sn\{C_5H_4N[C(SiMe_3)_2]\text{-}2\}_2$ **1**, showing the three independent molecules with 20% thermal ellipsoids: full atom numbering is given in ref. 12 and is as for compound **3**

The two independent molecules of SnR(Cl) **2** comprising the asymmetric unit are devoid of any intrinsic or crystallographically imposed symmetry although they are pseudo-symmetrically disposed within the cell, and pack pairwise in a pseudo-two-fold array, Fig. 2. The geometries of the two independent molecules differ only trivially. Again, crowding of

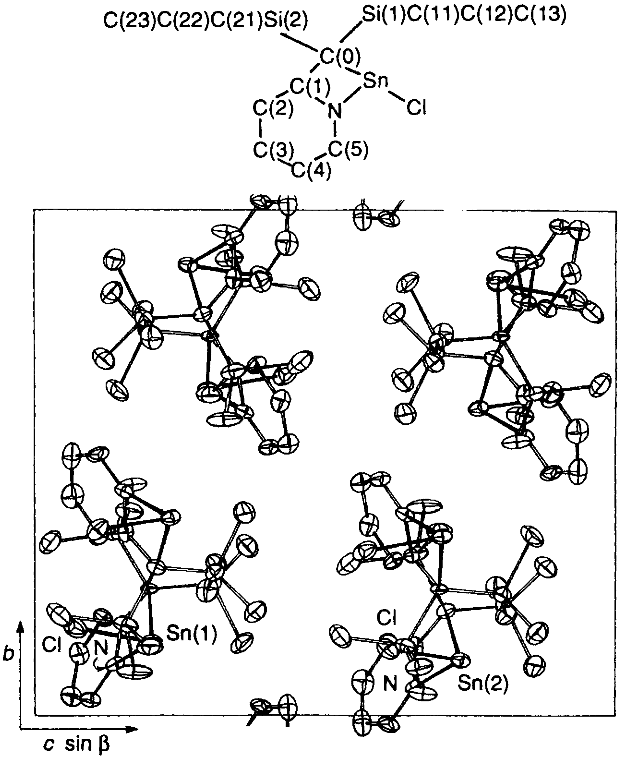


Fig. 2 Unit-cell contents of $Sn\{C_5H_4N[C(SiMe_3)_2]\text{-}2\}Cl$, **2**, showing the two independent molecules with ellipsoids; full atom numbering is given in ref. 12 and is as for compound **3**

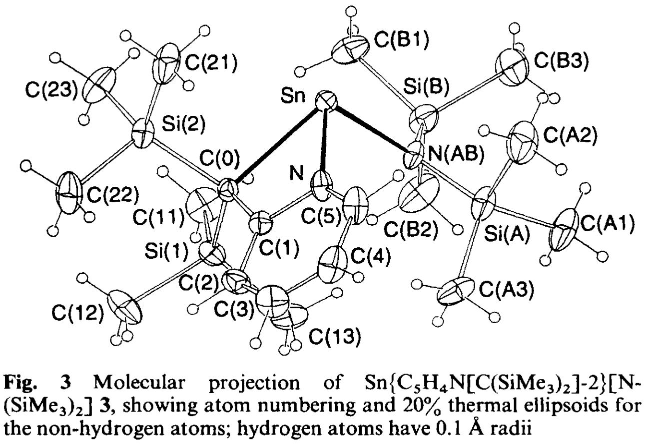


Fig. 3 Molecular projection of $Sn\{C_5H_4N[C(SiMe_3)_2]\text{-}2\}[N(SiMe_3)_2]$ **3**, showing atom numbering and 20% thermal ellipsoids for the non-hydrogen atoms; hydrogen atoms have 0.1 Å radii

Table 4 Intramolecular distances (Å) and angles (°) for SnR_2 **1** {R = $C_5H_4N[C(SiMe_3)_2]$-2}, with standard deviations in parentheses; primed atoms are generated by the intramolecular 2 axis

	Molecule		
	1	2	3
Sn(*n*)–N(*n*)	2.449(7)	2.384(6)	2.420(6)
Sn(*n*)–C(*n*0)	2.377(7)	2.346(6)	2.334(6)
N(*n*)–C(*n*1)	1.331(9)	1.356(9)	1.360(9)
N(*n*)–C(*n*5)	1.36(1)	1.36(1)	1.36(1)
C(*n*1)–C(*n*2)	1.38(1)	1.39(1)	1.38(1)
C(*n*2)–C(*n*3)	1.37(2)	1.37(1)	1.37(1)
C(*n*3)–C(*n*4)	1.36(1)	1.37(1)	1.36(2)
C(*n*4)–C(*n*5)	1.36(2)	1.34(1)	1.34(1)
C(*n*1)–C(*n*0)	1.50(1)	1.51(1)	1.49(1)
C(*n*0)–Si(*n*1)	1.868(7)	1.883(7)	1.891(7)
C(*n*0)–Si(*n*2)	1.887(7)	1.892(7)	1.898(8)
Si(*n*1)–C(*n*11)	1.85(1)	1.865(9)	1.868(11)
Si(*n*1)–C(*n*12)	1.86(1)	1.877(10)	1.881(9)
Si(*n*1)–C(*n*13)	1.87(1)	1.876(11)	1.879(10)
Si(*n*2)–C(*n*21)	1.87(1)	1.868(9)	1.864(9)
Si(*n*2)–C(*n*22)	1.86(1)	1.870(8)	1.867(10)
Si(*n*2)–C(*n*23)	1.86(1)	1.876(10)	1.869(10)
N(*n*)–Sn(*n*)–C(*n*0)	59.0(2)	60.7(2)	60.0(2)
N(*n*)–Sn(*n*)–N(*n*′)	141.3(2)	134.6(2)	133.7(2)
N(*n*)–Sn(*n*)–C(*n*0′)	102.1(2)	93.0(2)	94.2(2)
C(*n*0)–Sn(*n*)–C(*n*0′)	125.0(2)	111.1(2)	114.1(2)
Sn(*n*)–N(*n*)–C(*n*1)	93.4(5)	94.4(4)	93.4(5)
Sn(*n*)–N(*n*)–C(*n*5)	143.9(6)	144.5(5)	145.7(5)
C(*n*1)–N(*n*)–C(*n*5)	120.7(8)	120.2(6)	120.2(6)
N(*n*)–C(*n*1)–C(*n*2)	119.0(7)	118.7(7)	117.7(8)
N(*n*)–C(*n*1)–C(*n*0)	113.9(7)	112.9(5)	113.0(6)
C(*n*4)–C(*n*1)–C(*n*0)	127.1(7)	128.3(7)	128.8(7)
C(*n*1)–C(*n*2)–C(*n*3)	120.7(8)	120.5(8)	121.2(8)
C(*n*4)–C(*n*3)–C(*n*4)	119.3(11)	119.1(8)	120.3(8)
C(*n*3)–C(*n*4)–C(*n*5)	119.3(10)	119.7(9)	118.5(10)
N(*n*)–C(*n*5)–C(*n*4)	120.9(8)	121.7(8)	122.1(8)
Sn(*n*)–C(*n*0)–C(*n*1)	91.9(4)	91.9(4)	93.6(4)
Sn(*n*)–C(*n*0)–Si(*n*1)	124.1(4)	124.2(3)	123.7(3)
Sn(*n*)–C(*n*0)–Si(*n*2)	99.7(3)	101.2(3)	100.5(3)
C(*n*1)–C(*n*0)–Si(*n*1)	110.4(5)	118.7(5)	117.9(5)
C(*n*1)–C(*n*0)–Si(*n*2)	112.2(5)	104.9(4)	106.2(4)
Si(*n*1)–C(*n*0)–Si(*n*2)	116.0(3)	112.5(4)	111.9(4)
C(*n*0)–Si(*n*1)–C(*n*11)	108.5(4)	118.8(4)	110.9(4)
C(*n*0)–Si(*n*1)–C(*n*12)	112.3(4)	112.0(4)	113.1(4)
C(*n*0)–Si(*n*1)–C(*n*13)	115.8(5)	111.0(4)	117.4(4)
C(*n*11)–Si(*n*1)–C(*n*12)	112.0(5)	104.2(4)	105.6(5)
C(*n*11)–Si(*n*1)–C(*n*13)	103.6(6)	102.2(4)	104.8(5)
C(*n*12)–Si(*n*1)–C(*n*13)	104.3(7)	107.6(5)	104.0(4)
C(*n*0)–Si(*n*2)–C(*n*21)	116.1(4)	109.9(4)	115.3(4)
C(*n*0)–Si(*n*2)–C(*n*22)	110.9(4)	114.4(4)	112.3(3)
C(*n*0)–Si(*n*2)–C(*n*23)	110.4(4)	112.0(3)	109.7(4)
C(*n*21)–Si(*n*2)–C(*n*22)	105.4(5)	104.6(4)	107.3(4)
C(*n*21)–Si(*n*2)–C(*n*23)	102.9(5)	107.4(4)	103.9(4)
C(*n*22)–Si(*n*2)–C(*n*23)	110.8(5)	108.1(4)	107.9(4)

the ligating atoms to one side of the tin suggests a sterically active lone pair. With fewer co-ordinating atoms, the metal–ligand distances (Table 5) are appreciably shorter than their counterparts in compound **1**. In molecules 1 and 2, the tin atoms lie 0.085 and 0.123 Å out of their C_5N planes, respectively, to the same side of the plane as Si(2) (deviations 1.479 and 1.425 Å) and opposite to Si(1) (−1.688 and −1.726 Å).

A single molecule of $SnR[N(SiMe_3)_2]$ **3** comprises the asymmetric unit of the structure, also devoid of intrinsic or crystallographic symmetry. Once more, the crowding of the ligating atoms to one side of tin suggests a sterically active lone pair, although the angular geometry (Table 6) is expanded somewhat relative to that of complex **2**, with tin–ligand distances perhaps slightly longer. The tin deviation from the C_5N plane is 0.095 Å, with silicon deviations of 1.202 and −1.866 Å, respectively. The nitrogen atom of the $^-N(SiMe_3)_2$ ligand is, like the pyridine nitrogen, planar, but much more strongly bound.

Selected geometric parameters for the alkyltin(II) complexes **1**–**3** are available for comparison with: (*a*) mononuclear tin(II) complexes containing Cl^- or $^-N(SiMe_3)_2$ ligands and the three-co-ordinate tin(II) complex $\{Sn(\mu\text{-}Cl)[N(SiMe_3)_2]\}_2$, Table 10;[36] (*b*) mononuclear tin(II) hydrocarbyls, Table 11; and (*c*) isoleptic complexes of formulae MR_2 or $[MR_2]^+$, Table 12 (for **1**).

Figs. 1–3, and angles around the metal centres, Table 10, support the presence of a stereochemically active lone pair of electrons in compounds **1**–**3**. For the three-co-ordinate species, **2** and **3**, the sum of the angles subtended at the metal is 252.9 and 263.7°, respectively. Further support for a lone pair in **1** comes from a comparison of structural data with other MR_2 species and also with AlR_2^+,[31] which are all devoid of a lone pair of electrons, Table 12. While the N–M–C chelate ring angle in **1** (and also in **2** and **3**) is within the range found in MR_2 and AlR_2^+ species, the interligand angles are well removed, in a way consistent with the presence of a 'fifth group' on the metal centre in **1**.

The Sn–C distances in compounds **1**–**3**, 2.35, 2.32 and 2.356(8) Å, respectively, are significantly longer than those in related tin(II) hydrocarbyl species, Tables 10 and 11, although the latter are either aryl rather than alkyl species (compounds **B**, **D** and **F**) and/or have no chelation from neutral donor groups (compounds **A** and **C**). The Sn–N distances in **2** and **3** are similar and, as expected, are shorter than those in **1**, by *ca.* 0.12 Å; and these are shorter than those in **D** and **F** by *ca.* 0.15 Å, where the donor N atom is sp^3 rather than sp^2 hybridised. The $Sn\text{–}N_{amido}$ distance in **2** is unexceptional.

Some Exploratory Reactions with SnR(Cl) **2**.—Two reaction types were explored: reduction to a tin(I) compound, and a H^-/Cl^- displacement process: no meaningful results emerged from the reaction between **2** and $Li[BHEt_3]$. As for the former, the first suggestion of the existence of such species came from photolysis experiments of hydrocarbon solutions of SnX_2 [X = $CH(SiMe_3)_2$ or $N(SiMe_3)_2$], leading to the stable tin(III) compounds SnX_3;[44] the diamagnetic coproduct(s) was assumed to be a $(SnX)_n$ oligomer. Some well characterised crystalline compounds, including decakis(2,6-diethylphenyl)-decastanna[5]prismane $(SnR')_{10}$ (R′ = $C_6H_3Et_2$-2,6)[45] and the cubane $(SnR')_8$[46] have now been firmly established.

Three reducing agents were employed: (*i*) sodium–potassium alloy proved to be too powerful, yielding tin metal; (*ii*) sodium–naphthalene in tetrahydrofuran gave a deep red oil; and (*iii*) dilithium cyclooctatetraenediide afforded a brown microcrystalline product **5**. We propose that the latter was formed by the process (3). The NMR spectral data in C_6D_6 showed that **5** was

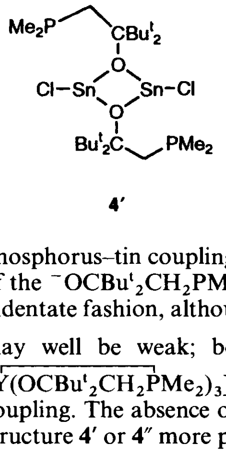
$$2SnR(Cl) + Li_2[C_8H_8] \longrightarrow \underset{\mathbf{5}}{\tfrac{2}{n}(SnR)_n} + 2LiCl + C_8H_8 \qquad (3)$$

diamagnetic and contained R^- as the sole organic ligand: $\delta(^1H)$ 2.06 ($SiMe_3$), $\delta[^{13}C\text{-}\{^1H\}]$ 3.87 ($SiMe_3$) and 47.5 (α-C), δ-$[^{119}Sn\text{-}\{^1H\}]$ 143.8. The highest peak in its mass spectrum corresponded to $[(SnR)_2]^+$. Tentatively, we suggest that its molecular structure may be $\overline{\text{R–Sn}}\text{–}\overline{\text{Sn–R}}$ or a tetrastannatetrahedrane with terminal R^- ligands. Further efforts will be made to obtain X-ray-quality crystals.

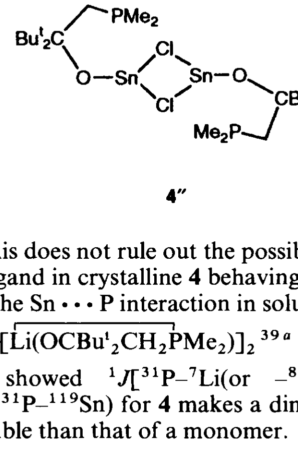
The Chlorotin(II) *Alkoxide* $SnCl(OCBu^t_2CH_2PMe_2)$ **4**.—The preparation of compound **4** from $2SnCl_2$ and $[\overline{Li(OCBu^t_2CH_2P}Me_2)]_2$[39a] is shown in Scheme 2, reaction (*vi*). It is a white crystalline solid, which was characterised by microanalysis (Table 1) and multinuclear NMR spectroscopic data (Table 2). Neither the ambient temperature $^{119}Sn\text{-}\{^1H\}$ nor the $^{31}P\text{-}\{^1H\}$ NMR spectrum in $[^2H_8]$toluene revealed

Table 5 Intramolecular distances (Å) and angles (°) for SnR(Cl) {R = $C_5H_4N[C(SiMe_3)_2]$-2}, with standard deviations in parentheses; the two values in each entry are for molecules *n* = 1 and 2

Sn(*n*)–Cl(*n*)	2.440(5), 2.446(5)	C(*n*4)–C(*n*5)	1.33(4), 1.35(4)
Sn(*n*)–N(*n*)	2.27(2), 2.26(2)	C(*n*0)–Si(*n*1)	1.85(1), 1.85(2)
Sn(*n*)–C(*n*0)	2.32(2), 2.32(2)	C(*n*0)–Si(*n*2)	1.90(2), 1.90(2)
N(*n*)–C(*n*1)	1.34(2), 1.35(3)	Si(*n*1)–C(*n*11)	1.84(2), 1.86(3)
N(*n*)–C(*n*5)	1.37(3), 1.36(3)	Si(*n*1)–C(*n*12)	1.88(2), 1.82(3)
C(*n*1)–C(*n*2)	1.39(3), 1.39(4)	Si(*n*1)–C(*n*13)	1.85(3), 1.89(2)
C(*n*1)–C(*n*0)	1.46(3), 1.46(3)	Si(*n*2)–C(*n*21)	1.89(3), 1.88(3)
C(*n*2)–C(*n*3)	1.35(3), 1.39(5)	Si(*n*2)–C(*n*22)	1.92(2), 1.92(3)
C(*n*3)–C(*n*4)	1.41(4), 1.35(4)	Si(*n*2)–C(*n*23)	1.84(2), 1.87(3)
Cl(*n*)–Sn(*n*)–C(*n*0)	101.6(4), 101.1(4)	C(*n*1)–C(*n*0)–Si(*n*1)	112(1), 112(1)
Cl(*n*)–Sn(*n*)–N(*n*)	91.8(4), 89.1(4)	C(*n*1)–C(*n*0)–Si(*n*2)	114(1), 117(1)
C(*n*0)–Sn(*n*)–N(*n*)	61.4(6), 61.7(6)	Si(*n*1)–C(*n*0)–Si(*n*2)	117.1(8), 116.8(9)
Sn(*n*)–N(*n*)–C(*n*1)	95(1), 95(1)	C(*n*0)–Si(*n*1)–C(*n*11)	112.7(8), 111.8(10)
Sn(*n*)–N(*n*)–C(*n*5)	144(1), 145(2)	C(*n*0)–Si(*n*1)–C(*n*12)	110.2(8), 111.1(9)
C(*n*1)–N(*n*)–C(*n*5)	121(2), 120(2)	C(*n*0)–Si(*n*1)–C(*n*13)	110.2(9), 108.9(8)
N(*n*)–C(*n*1)–C(*n*0)	114(2), 113(2)	C(*n*11)–Si(*n*1)–C(*n*12)	104(1), 110(1)
N(*n*)–C(*n*1)–C(*n*2)	118(2), 118(2)	C(*n*11)–Si(*n*1)–C(*n*13)	111(1), 106(1)
C(*n*0)–C(*n*1)–C(*n*2)	128(2), 128(2)	C(*n*12)–Si(*n*1)–C(*n*13)	108(1), 108(1)
C(*n*1)–C(*n*2)–C(*n*3)	120(2), 119(2)	C(*n*0)–Si(*n*2)–C(*n*2)	110.7(10), 111.3(10)
C(*n*2)–C(*n*3)–C(*n*4)	121(2), 121(3)	C(*n*0)–Si(*n*2)–C(*n*22)	111.3(8), 111.6(9)
C(*n*3)–C(*n*4)–C(*n*5)	116(2), 118(3)	C(*n*0)–Si(*n*2)–C(*n*23)	110.4(10), 109.7(10)
N(*n*)–C(*n*5)–C(*n*4)	124(2), 123(2)	C(*n*21)–Si(*n*2)–C(*n*22)	108(1), 108(1)
Sn(*n*)–C(*n*0)–C(*n*1)	89.8(10), 89.7(11)	C(*n*21)–Si(*n*2)–C(*n*23)	108(1), 109(1)
Sn(*n*)–C(*n*0)–Si(*n*1)	105.6(8), 104.9(9)	C(*n*22)–Si(*n*2)–C(*n*23)	107(1), 107(1)
Sn(*n*)–C(*n*0)–Si(*n*2)	115.0(7), 113.5(8)		



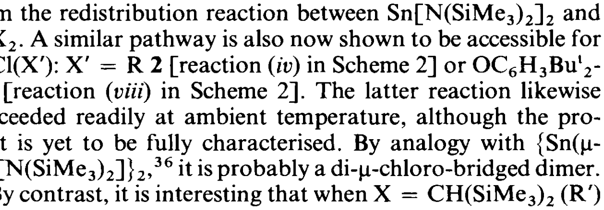
4′



4″

phosphorus–tin coupling. This does not rule out the possibility of the $^-OCBu^t_2CH_2PMe_2$ ligand in crystalline **4** behaving in a bidentate fashion, although the Sn ··· P interaction in solution may well be weak; both $[Li(OCBu^t_2CH_2PMe_2)]_2$[39a] and $[Y(OCBu^t_2CH_2PMe_2)_3]$[40] showed $^1J[^{31}P–^7Li(\text{or } –^{89}Y)]$ coupling. The absence of $^1J(^{31}P–^{119}Sn)$ for **4** makes a dimeric structure **4′** or **4″** more plausible than that of a monomer.

Some Reactions of $SnCl_2$ *with Homoleptic Tin*(II) *Compounds* SnX_2.—These reactions are summarised in equation (4). As

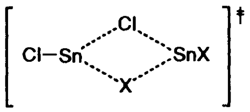


$$SnCl_2 \xrightarrow{SnX_2} \begin{cases} \xrightarrow{X\,=\,CH(SiMe_3)_2} SnCl_2X_2 + Sn \\ \xrightarrow{X\,=\,R \text{ or } OC_6H_3Bu^t_2\text{-}2,6} \tfrac{2}{n}[SnCl(X)]_n \end{cases} \qquad (4)$$

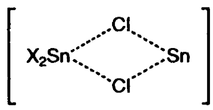
noted in the introduction, examples exist of two crystallographically authenticated compounds $\{Sn[N(SiMe_3)_2]X\}_n$:X = Cl, *n* = 2;[36] X = $OC_6H_2Bu^t_2$-2,6-Me-4, *n* = 1,[34] both accessible from the redistribution reaction between $Sn[N(SiMe_3)_2]_2$ and SnX_2. A similar pathway is also now shown to be accessible for SnCl(X′): X′ = R **2** [reaction (*iv*) in Scheme 2] or $OC_6H_3Bu^t_2$-2,6 [reaction (*viii*) in Scheme 2]. The latter reaction likewise proceeded readily at ambient temperature, although the product is yet to be fully characterised. By analogy with $\{Sn(\mu\text{-}Cl)[N(SiMe_3)_2]\}_2$,[36] it is probably a di-μ-chloro-bridged dimer.

By contrast, it is interesting that when X = $CH(SiMe_3)_2$ (R′) the reaction took a different course, a redox process yielding SnR'_2Cl_2 + Sn. This is probably the most convenient way of making that dialkyltin(IV) chloride, which previously had been made from $SnCl_4$ + 2LiR′.[2]

The redistribution reactions between $SnCl_2$ and the various SnX_2 molecules probably involve the transition state **G** which will only be readily accessible if the ligand X^- is capable of functioning in a bridging mode. Otherwise, **H** shows that there is a facile pathway to the disproportionation products by an inner-sphere electron-transfer mechanism. For the case of SnX_2 being SnR_2 **1**, the transition state **G** could be available *via* the intramolecular N→Sn bond reverting to its intermolecular counterpart.



G



H

Experimental

General procedures have been described in Part 15.[1]

Synthesis of Di[2-*pyridylbis*(*trimethylsilyl*)*methyl*]*tin*(II) **1**.—(*a*) Solid tin(II) chloride (0.6 g, 3.2 mmol) was added to a stirred solution of 2-pyridylbis(trimethylsilyl)methyllithium[25] [1.17 g, 3.5 mmol (based on dimer)] in thf (25 cm^3) at −78 °C. Stirring was continued for 3 h while the reaction mixture was allowed to warm to *ca.* −40 °C. The solution became red-orange. The volatiles were removed *in vacuo* and the crude product was extracted into C_5H_{12} at *ca.* −30 °C. Concentration of the filtrate and cooling to −30 °C yielded orange crystals of the compound **1** (0.66 g, 34%) (Found: C, 48.2; H, 8.3; N, 5.2. $C_{24}H_{44}N_2Si_4Sn$ requires C, 48.7; H, 7.5; N, 4.7%).

(*b*) Solid 2-pyridylbis(trimethylsilyl)methyllithium (0.27 g, 0.6 mmol) was added to a stirred solution of bis(2,6-di-*tert*-butylphenoxo)tin(II)[42] (0.7 g, 1.3 mmol) in thf (10 cm^3) at −78 °C. The solution became red almost immediately. Stirring was continued for 2 h, whereafter the reaction mixture was allowed to warm to *ca.* −15 °C. The volatiles were removed *in vacuo* and the crude product was extracted into C_5H_{12}.

Concentration of the filtrate and cooling to −30 °C yielded orange crystals of compound **1** (0.4 g, 52%) (Found: C, 47.2; H, 7.8; N, 4.1%), m.p. *ca.* 188 °C (decomp.); δ(^{119}Sn) 141.0.

Synthesis of Chloro[*2-pyridylbis*(*trimethylsilyl*)*methyl*]*tin*(II) **2**.—(*a*) Solid tin(II) chloride (0.7 g, 3.7 mmol) was added to a stirred solution of 2-pyridylbis(trimethylsilyl)methyllithium (0.9 g, 1.9 mmol) in OEt_2 (20 cm^3) at −78 °C. Stirring was continued for 3 h while the reaction mixture was allowed to warm to *ca.* −40 °C. The solution became red-orange. The volatiles were removed *in vacuo* and the crude product was extracted into C_5H_{12} at *ca.* −30 °C. Concentration of the filtrate and cooling at −30 °C yielded yellow-orange crystals of the compound **2** (0.7 g, 48%) (Found: C, 36.3; H, 5.7; N, 3.4. $C_{12}H_{22}ClNSi_2Sn$ requires C, 36.9; H, 5.7; N, 3.6%), m.p. 206 °C (decomp.).

Table 6 Intramolecular distances (Å) and angles (°) for SnR[N-$(SiMe_3)_2$] **3** {R = $C_5H_4N[C(SiMe_3)_2]$-2}, with standard deviations in parentheses *

Sn–N	2.299(5)	Si(1)–C(12)	1.872(12)
Sn–C(0)	2.356(8)	Si(1)–C(13)	1.849(7)
Sn–N(AB)	2.144(5)	Si(2)–C(21)	1.852(10)
N–C(1)	1.356(11)	Si(2)–C(22)	1.862(11)
N–C(5)	1.341(9)	Si(2)–C(23)	1.847(8)
C(1)–C(2)	1.388(10)	N(AB)–Si(A)	1.724(5)
C(1)–C(0)	1.482(8)	N(AB)–Si(B)	1.713(6)
C(2)–C(3)	1.360(10)	Si(A)–C(A1)	1.870(9)
C(3)–C(4)	1.362(15)	Si(A)–C(A2)	1.881(11)
C(4)–C(5)	1.374(12)	Si(A)–C(A3)	1.866(9)
C(0)–Si(1)	1.872(6)	Si(B)–C(B1)	1.869(7)
C(0)–Si(2)	1.890(6)	Si(B)–C(B2)	1.851(9)
Si(1)–C(11)	1.863(7)	Si(B)–C(B3)	1.876(13)
N–Sn–C(0)	61.1(2)	C(12)–Si(1)–C(13)	105.6(4)
N–Sn–N(AB)	97.2(2)	C(0)–Si(2)–C(21)	111.3(4)
C(0)–Sn–N(AB)	105.4(2)	C(0)–Si(2)–C(22)	113.0(3)
Sn–N–C(1)	95.8(4)	C(0)–Si(2)–C(23)	111.9(3)
Sn–N–C(5)	143.7(6)	C(21)–Si(2)–C(22)	104.6(4)
C(1)–N–C(5)	120.5(6)	C(21)–Si(2)–C(23)	107.7(4)
N–C(1)–C(0)	112.9(6)	C(22)–Si(2)–C(23)	108.0(4)
N–C(1)–C(2)	118.9(6)	Sn–N(AB)–Si(A)	120.5(3)
C(0)–C(1)–C(2)	128.2(7)	Sn–N(AB)–Si(B)	112.9(2)
C(1)–C(2)–C(3)	119.9(9)	Si(A)–N(AB)–Si(B)	122.9(3)
C(2)–C(3)–C(4)	120.9(8)	N(AB)–Si(A)–C(A1)	114.1(3)
C(3)–C(4)–C(5)	118.1(7)	N(AB)–Si(A)–C(A2)	109.3(3)
C(4)–C(5)–N	121.6(9)	N(AB)–Si(A)–C(A3)	115.4(4)
Sn–C(0)–C(1)	90.0(5)	C(A1)–Si(A)–C(A2)	107.0(5)
Sn–C(0)–Si(1)	120.0(3)	C(A1)–Si(A)–C(A3)	102.1(4)
Sn–C(0)–Si(2)	105.2(3)	C(A2)–Si(A)–C(A3)	108.5(4)
C(1)–C(0)–Si(1)	115.9(4)	N(AB)–Si(B)–C(B1)	111.2(3)
C(1)–C(0)–Si(2)	108.3(4)	N(AB)–Si(B)–C(B2)	112.4(3)
Si(1)–C(0)–Si(2)	114.5(4)	N(AB)–Si(A)–C(B3)	114.4(4)
C(0)–Si(1)–C(11)	112.8(3)	C(B1)–Si(B)–C(B2)	108.4(4)
C(0)–Si(1)–C(12)	114.6(3)	C(B1)–Si(B)–C(B3)	102.1(4)
C(0)–Si(1)–C(13)	110.9(3)	C(B2)–Si(B)–C(B3)	107.6(5)
C(11)–Si(1)–C(12)	104.8(4)		
C(11)–Si(1)–C(13)	107.5(4)		

* For atom numbering scheme, see Fig. 3.

(*b*) Solid tin(II) chloride (0.15 g, 0.8 mmol) was added to a stirred solution of SnR_2 **1** (0.4 g, 0.7 mmol) in OEt_2 (15 cm^3) at −78 °C. After stirring for *ca.* 1 h the $SnCl_2$ had not dissolved. The reaction mixture was slowly (*ca.* 18 h) allowed to warm to *ca.* 20 °C while stirring. The mixture gradually became largely homogeneous. It was filtered; the filtrate was concentrated and cooled to −30 °C to yield yellow crystals of compound **2** (0.3 g, 55%) (Found: C, 35.9; H, 5.2; N, 4.0%), m.p. *ca.* 207 °C (decomp.).

Synthesis of [*Bis*(*trimethylsilyl*)*amido*][*2-pyridylbis*(*trimethylsilyl*)*methyl*]*tin*(II) **3**.—Solid 2-pyridylbis(trimethylsilyl)methyllithium (0.9 g, 1.8 mmol) was added to a stirred solution of $Sn[N(SiMe_3)_2]_2$ [5] (1.6 g, 3.6 mmol) in OEt_2 (20 cm^3) at −78 °C. Stirring was continued for 4 h, while the reaction mixture was allowed to warm to ambient temperature. The volatiles were then removed *in vacuo* and the crude product was extracted into C_5H_{12}. Concentration of the extract and cooling to −30 °C yielded orange crystals of the compound **3** (0.95 g, 50%) (Found: C, 41.8; H, 8.1; N, 5.4. $C_{18}H_{40}N_2Si_4Sn$ requires C, 41.9; H, 7.8; N, 5.4%), m.p. *ca.* 50 °C (decomp.).

Preparation of Chloro[*1,1-di-*tert*-butyl-2-*(*dimethylphosphino*)*ethoxo*]*tin*(II) **4**.—Solid 1,1-di-*tert*-butyl-2-(dimethylphosphino)ethoxolithium [39a] (0.86 g, 1.9 mmol) was added to a stirred solution of $SnCl_2$ (1.0 g, 5.3 mmol) in thf (20 cm^3) at −30 °C. The reaction mixture was refluxed for 24 h, whereafter the volatiles were removed *in vacuo*. The crude residual product was extracted into toluene. Concentration of the filtrate and cooling to −30 °C afforded white crystals of the compound **4** (0.4 g, 30%) (Found: C, 38.3; H, 7.2. $C_{12}H_{26}ClOPSn$ requires C, 38.8; H, 70%), m.p. *ca.* 150 °C (decomp.).

Some Exploratory Reactions of Compound **2**.—(*a*) *With* Na–K *alloy*. A solution of SnR(Cl) **2** (1.3 g, 3.3 mmol) in C_6H_{14} (10 cm^3) was rapidly added with stirring to Na–K alloy (0.12 g, 1.1 mmol) under C_6H_{14} (10 cm^3) at 0 °C. A metallic precipitate and a brown solution were instantly formed.

(*b*) *With* $Na[C_{10}H_8]$. A solution of sodium dihydronaphthylide in thf (7.6 cm^3 of a 0.1 mol dm^{-3} solution, 0.76 mmol) was added to a stirred solution of SnR(Cl) (0.33 g, 0.77 mmol) in thf

Table 7 Non-hydrogen atom coordinates for SnR_2 **1**

	Molecule 1			2			3		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Sn(*n*)	0	0.132 11(3)	$\frac{1}{4}$	0	0.370 22(2)	$\frac{1}{4}$	0	0.814 42(2)	$\frac{1}{4}$
N(*n*)	0.110 3(4)	0.102 5(2)	0.198 0(3)	0.141 8(4)	0.403 9(2)	0.275 2(3)	0.141 9(4)	0.779 6(2)	0.259 5(3)
C(*n*1)	0.053 2(5)	0.091 4(3)	0.144 9(3)	0.132 4(4)	0.425 8(3)	0.328 9(3)	0.142 9(5)	0.758 0(2)	0.315 7(3)
C(*n*2)	0.081 9(6)	0.083 (0)	0.091 0(4)	0.203 3(5)	0.448 8(3)	0.367 2(4)	0.217 8(6)	0.735 2(3)	0.346 8(4)
C(*n*3)	0.168 0(7)	0.082 9(4)	0.092 8(5)	0.282 0(5)	0.447 6(3)	0.352 3(5)	0.288 6(6)	0.734 0(4)	0.321 8(5)
C(*n*4)	0.225 6(6)	0.092 7(3)	0.148 2(6)	0.289 3(5)	0.424 4(4)	0.298 0(6)	0.286 8(6)	0.756 4(4)	0.266 2(5)
C(*n*5)	0.196 1(6)	0.103 4(4)	0.200 0(5)	0.220 1(5)	0.402 8(3)	0.261 1(4)	0.213 9(6)	0.779 1(3)	0.236 2(4)
C(*n*0)	−0.038 8(5)	0.091 9(2)	0.150 9(3)	0.043 5(4)	0.418 8(2)	0.340 4(3)	0.063 6(5)	0.768 0(2)	0.3384(3)
Si(*n*1)	−0.086 1(2)	0.029 14(8)	0.139 0(1)	−0.017 1(2)	0.474 15(8)	0.358 0(1)	0.008 7(2)	0.714 34(8)	0.367 9(1)
C(*n*11)	0.000 0(8)	−0.015 8(4)	0.171 0(7)	−0.082 2(6)	0.510 2(3)	0.291 0(4)	−0.065 2(6)	0.736 0(3)	0.417 0(4)
C(*n*12)	−0.180 5(7)	0.022 0(4)	0.174 4(7)	0.056 5(7)	0.520 5(3)	0.406 5(5)	0.086 6(7)	0.671 5(3)	0.419 7(5)
C(*n*13)	−0.126 9(12)	0.009 6(5)	0.055 4(6)	−0.099 7(6)	0.456 7(4)	0.402 4(4)	−0.059 6(8)	0.673 1(3)	0.307 3(5)
Si(*n*2)	−0.103 8(2)	0.142 03(9)	0.102 3(1)	0.057 8(1)	0.370 93(8)	0.404 6(1)	0.093 1(1)	0.817 80(8)	0.399 7(1)
C(*n*21)	−0.148 5(7)	0.127 9(5)	0.017 1(4)	0.142 0(6)	0.325 9(3)	0.395 6(4)	0.146 2(7)	0.796 3(4)	0.480 6(4)
C(*n*22)	− 0.198 6(6)	0.158 6(4)	0.133 6(5)	0.096 9(6)	0.395 6(4)	0.486 2(4)	−0.002 1(6)	0.855 4(3)	0.406 2(4)
C(*n*23)	−0.035 1(7)	0.196 5(3)	0.099 6(5)	−0.044 2(6)	0.335 9(3)	0.401 4(4)	0.174 6(6)	0.859 7(3)	0.378 6(4)

Table 8 Non-hydrogen atom coordinates for SnR(Cl) **2**

	Molecule 1			2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sn(*n*)	0.474 71(9)	0.145 15(9)	0.202 00(9)	0.491 24(10)	0.108 73(9)	0.734 70(8)
Cl(*n*)	0.347 7(4)	0.174 3(4)	0.068 9(4)	0.352 2(4)	0.131 7(4)	0.608 6(3)
C(*n*0)	0.586(1)	0.250(1)	0.197(1)	0.596(1)	0.207(1)	0.710(1)
N(*n*)	0.571(1)	0.102(1)	0.138(1)	0.566(1)	0.056(1)	0.655(1)
C(*n*1)	0.616(1)	0.183(1)	0.150(1)	0.612(1)	0.136(1)	0.657(1)
C(*n*2)	0.684(1)	0.193(1)	0.118(1)	0.667(2)	0.142(2)	0.610(1)
C(*n*3)	0.704(1)	0.123(2)	0.076(1)	0.675(2)	0.065(2)	0.565(2)
C(*n*4)	0.656(2)	0.038(2)	0.063(1)	0.628(2)	−0.015(2)	0.564(1)
C(*n*5)	0.592(2)	0.031(1)	0.096(1)	0.576(2)	−0.018(1)	0.610(1)
Si(*n*1)	0.670 6(4)	0.260 4(4)	0.306 1(3)	0.695 0(4)	0.216 3(4)	0.810 6(3)
C(*n*11)	0.785(1)	0.301(1)	0.313(1)	0.803(1)	0.253(2)	0.797(1)
C(*n*12)	0.695(2)	0.143(2)	0.358(1)	0.669(2)	0.295(2)	0.881(1)
C(*n*13)	0.624(2)	0.336(2)	0.366(1)	0.719(2)	0.098(2)	0.862(1)
Si(*n*2)	0.537 9(4)	0.361 7(4)	0.139 4(4)	0.541 4(5)	0.320 1(4)	0.657 0(4)
C(*n*21)	0.436(1)	0.405(1)	0.163(2)	0.455(2)	0.365(1)	0.698(2)
C(*n*22)	0.631(2)	0.457(1)	0.169(2)	0.633(2)	0.414(1)	0.672(2)
C(*n*23)	0.498(2)	0.343(2)	0.027(1)	0.482(2)	0.301(2)	0.543(2)

Table 9 Non-hydrogen atom coordinates for SnR[N(SiMe$_3$)$_2$] **3**

Atom	*x*	*y*	*z*
Sn	0.147 77(4)	0.150 89(3)	0.155 82(3)
Pyridine ligand			
N(1)	0.193 5(5)	0.265 3(3)	0.245 6(4)
C(1)	0.136 7(6)	0.246 9(4)	0.304 0(5)
C(2)	0.142 8(7)	0.298 8(4)	0.378 4(5)
C(3)	0.203 8(7)	0.367 1(3)	0.390 9(6)
C(4)	0.258 3(7)	0.386 0(4)	0.330 4(7)
C(5)	0.250 2(7)	0.333 9(4)	0.256 8(6)
C(O)	0.070 6(5)	0.171 7(3)	0.275 3(4)
Si(1)	0.108 4(2)	0.101 6(1)	0.382 9(2)
C(11)	0.069 9(8)	−0.000 2(4)	0.337 8(6)
C(12)	0.024 2(9)	0.119 4(5)	0.461 2(6)
C(13)	0.275 9(7)	0.105 0(5)	0.474 9(5)
Si(2)	−0.101 2(2)	0.191 3(1)	0.195 4(2)
C(21)	−0.130 7(7)	0.251 0(5)	0.081 5(7)
C(22)	−0.169 6(8)	0.248 0(5)	0.265 4(7)
C(23)	−0.191 7(7)	0.101 1(5)	0.149 2(7)
Amide ligand			
N(AB)	0.325 8(4)	0.097 0(3)	0.241 0(4)
Si(A)	0.459 8(2)	0.151 9(1)	0.293 1(2)
C(A1)	0.606 6(7)	0.094 0(5)	0.342 0(7)
C(A2)	0.459 8(8)	0.219 2(5)	0.192 2(7)
C(A3)	0.484 7(7)	0.210 2(5)	0.408 1(6)
Si(B)	0.324 9(2)	0.000 7(1)	0.213 5(2)
C(B1)	0.164 6(7)	−0.032 8(4)	0.122 9(5)
C(B2)	0.384 1(8)	−0.060 6(5)	0.330 0(7)
C(B3)	0.415 3(9)	−0.024 5(6)	0.142 1(8)

(20 cm^3) at 0 °C, which instantly became red-brown. Stirring was continued for 18 h, whereafter volatiles were removed *in vacuo*. The residue was extracted into C_6H_{14}. Repeated concentration and cooling (−30 °C) of the red extract failed to induce crystallisation. Removal of all volatiles *in vacuo* gave a deep red oil.

(*c*) *With* Li$_2$[C$_8$H$_8$]. A solution of dilithium cyclooctatetraenediide (7.9 cm^3 of a 0.215 mol dm^{-3} solution, 1.7 mmol) was added to a stirred solution of SnR(Cl) (1.3 g, 3.4 mmol) in OEt$_2$ (15 cm^3) at −78 °C. The solution gradually became red and a white precipitate was produced. Stirring was continued for 2 h, whereafter the mixture was allowed to warm to −30 °C and was filtered. Concentration of the filtrate and cooling at −30 °C yielded brown crystals of a compound **5** (0.35 g), m.p. 164–165 °C.

Lack of Reaction between Bis[bis(trimethylsilyl)amido]tin(II) *and* 2-[*Bis(trimethylsilyl)methyl*]*pyridine*.—A solution of RH (0.6 g, 2.5 mmol) in thf (5 cm^3) was rapidly added to a stirred solution of the tin(II) amide (1.10 g, 2.5 mmol) in thf (10 cm^3) at 20 °C. After stirring for 18 h, an aliquot (5 cm^3) was removed; this was separated by distillation at 10^{-2} Torr into the more volatile RH and a residue of Sn[N(SiMe$_3$)$_2$]$_2$. The remaining reaction mixture was then refluxed for 24 h; a similar work-up to that of the aliquot showed that even under reflux no reaction had taken place.

Attempted Preparation of Bis[2-*pyridylbis(trimethylsilyl)methyl*]*germanium*(II).—(*a*) *From dichloro(dioxane)germanium*. Solid [LiR(OEt$_2$)]$_2$ (0.5 g, 1.6 mmol) was added to a stirred slurry of dichloro(dioxane)germanium(II) (0.38 g, 1.6 mmol) in OEt$_2$ (20 cm^3) at −78 °C. Stirring was continued for 3 h while the mixture was allowed to warm to *ca.* −30 °C to yield an orange solution. On further warming to 0 °C the solution became colourless.

(*b*) From *bis[bis(trimethylsilyl)amido]germanium*(II).[5] Solid [LiR(OEt$_2$)]$_2$ (0.75 g, 2.4 mmol) was added to a stirred solution of the germanium(II) amide (0.75 g, 1.9 mmol) in OEt$_2$ (10 cm^3) at −78 °C. Stirring was continued for 4 h while the mixture was allowed to warm to *ca.* −30 °C. The volatiles were removed *in vacuo* at −30 °C and the residue was extracted into C_5H_{12} at −78 °C. Concentration of the extract yielded unidentified yellow crystals [Found: C, 56.3; H, 3.9; N, 5.3. Calc. for $C_{24}H_{44}GeN_2Si_4$ (GeR$_2$): C, 52.8; H, 8.1; N, 5.1%], m.p. *ca.* 135 °C (decomp.).

A solution of (LiR)$_2$ (0.74 g, 1.5 mmol) in OEt$_2$ (10 cm^3) was added to a stirred solution of Ge[N(SiMe$_3$)$_2$]$_2$ (1.2 g, 3 mmol) in OEt$_2$ (10 cm^3) at −78 °C. Stirring was continued for 3 h while the solution (which became red) was allowed to warm to ambient temperature. The volatiles were removed *in vacuo* and the residue was extracted into C_6H_{14}. Concentration of the extract and cooling to −30 °C yielded an orange crystalline solid (0.4 g), m.p. 105–106 °C, identified as {Li[μ-N-SiMe$_3$)$_2$](OEt$_2$)}$_2$.[47] Repeated concentration and cooling to −30 °C of the remaining solution yielded no further crystals. The remaining volatiles were removed *in vacuo* to give a red oil.

Attempted Preparation of Chloro[2-*pyridylbis(trimethylsilyl)methyl*]*germanium*(II).—Solid dichloro(dioxane)germanium (0.8 g, 3.5 mmol) was added to a stirred solution of (LiR)$_2$ (0.6 g, 0.18 mmol) in OEt$_2$ (25 cm^3) at −78 °C. Stirring was continued for 1 h; the solution gradually became deep yellow. After *ca.* 18 h

Table 10 Comparative selected structural data for crystalline tin(II) compounds having $C_5H_4N[\bar{C}(SiMe_3)_2\text{-}2]$ ($\equiv \bar{R}$), $^-N(SiMe_3)_2$ or Cl^- ligands

	Bond angle (°)		Bond length (Å)				
Compound SnL(L′)	L–Sn–L′[a]	C_5H_4N–Sn–C	Sn–C	Sn–NC_5H_4	Sn–NSi_2	Sn–Cl	Ref.
1 SnR_2[b]	116.7	59.9	2.35	2.42			This work, 12
2 SnR(Cl)[b]	101.3	61.5	2.32	2.27		2.44	This work, 12
3 $SnR[N(SiMe_3)_2]$	105.4(2)	61.1(2)	2.356(8)	2.299(5)	2.14(5)		This work, 12
$Sn[N(SiMe_3)_2]_2$	104.7(2)				2.09(1)[b]		37
$\{Sn(\mu\text{-}Cl)[N(SiMe_3)_2]\}_2$	101.08(8) 94.20(8)				2.069(3)	2.741(1)	36
$SnCl_2$	88.5[c]					2.74[c]	38
$Sn[N(SiMe_3)_2](OR^1)$[d]	96.4(1)				2.079(3)		34
$Sn[N(SiMe_3)_2](NR^2R^3)$[e]	106.0(2)				2.120(6)		35

[a] L–N–L′ refers to C–Sn–C (**1**), C–Sn–Cl (**2**), C–Sn–N (**3**) or N–Sn–Cl in $\{Sn(\mu\text{-}Cl)[N(SiMe_3)_2]\}_2$. [b] Average values cited. [c] Values are averages of 105.6, 79.9, and 79.9° and 2.66, 2.78, and 2.78 Å respectively. [d] $OR^1 = OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4$. [e] $NR^2R^3 = N(C_6H_2Me_3\text{-}2,4,6)BBu^t[N(SiMe_3)_2]$.

Table 11 Comparative selected structural data for crystalline monomeric tin(II) hydrocarbyls other than **1**–**3** and gaseous $Sn[CH(SiMe_3)_2]_2$

	Bond angle (°)	Bond length (Å)		
Compound SnL_2 or SnL(Cl)	C–Sn–L′ (L′ = C or Cl)	Sn–C	Sn–NMe_2	Ref.
B $Sn[C_6H_2(CF_3)_3\text{-}2,4,6]_2$[a]	98.3(1)	2.278(4) 2.284(5)		3
C $Sn[C(SiMe_3)_2(CH_2)_2C(SiMe_3)_2]$	86.7(2)	2.218(7) 2.223(7)		4
D $Sn[C_{10}H_6(NMe_2)\text{-}8]_2$	93.8(5)	2.229(9) 2.233(10)	2.555(8) 2.578(8)	11
F $Sn[C_6H_3(CH_2NMe_2)_2\text{-}2,6]Cl$[b]	95.0(3)	2.158(8)	2.525(8) 2.602(8)	33
A $Sn[CH(SiMe_3)_2]_2$ (g)	97(2)	2.22(2)		2

[a] There are close Sn ··· F contacts: 2.663(4), 2.681(4), 2.807(4) and 2.833(4) Å. [b] Sn–Cl 2.488(3) Å.

Table 12 Comparative selected structural data (average values) for the crystalline isoleptic complexes MR_2 $\{R = C_5H_4N[\bar{C}(SiMe_3)_2]_2\text{-}2\}$

	Bond angle (°)				Bond length (Å)		
M	C–M–N[a]	C–M–N[b]	C–M–C	N–M–N	M–C	M–N	Ref.
Mg	67.3	126.3	157.1	117.4	2.22	2.13	27
Al[c]	72.9	123.5	152.2	114.6	1.99	1.92	31
Co	69.6(2)				2.094(6)	1.919(4)	28
Zn	67.1	123.3	164.4	107.5	2.07	2.29	27
Cd	59.8	124.4	174.3	108.9	2.27	2.49	27
Hg	56.6	123.3	179.5	115.6	2.16	2.78	27
Sn	59.9	96.4	116.7	136.5	2.35	2.42	This work, 12

[a] Intraligand. [b] Interligand. [c] This refers to $[AlR_2][AlCl_4]$.

at −30 °C it had become colourless. In another experiment, normal work-up at ⩽ −30 °C yielded yellow-orange crystals which were dried *in vacuo*; they decomposed rapidly (as evident by their decolourisation) on warming to 0 °C.

Reaction of Iodomethane with the in situ *Product of the 2-Pyridylbis(trimethylsilyl)methyllithium–Germanium Dichloride Reaction.*—Solid $GeCl_2$ (0.7 g, 4.9 mmol) was added to a stirred solution of $(LiR)_2$ (1.2 g, 2.5 mmol) in thf (15 cm^3) at −78 °C. After stirring for 2 h the solution had become deep yellow. Iodomethane (0.3 cm^3) was added and the mixture became colourless almost immediately. Stirring was continued for 2 h while the mixture was allowed to warm to ambient temperature. The volatiles were removed *in vacuo* and the residue was extracted into C_6H_{14}. Concentration of the extract and cooling to −30 °C yielded a white crystalline solid (0.8 g), m.p. 84–88 °C.

Attempted Preparation of [2-Pyridylbis(trimethylsilyl)methyl]lead(II) Compounds.—(*a*) PbR_2. A solution of $(LiR)_2$ (0.85 g, 1.7 mmol) in thf (20 cm^3) was added to a stirred slurry of $PbCl_2$ (0.5 g, 1.8 mmol) in thf (10 cm^3) at −78 °C. [The experiment was carried out in the dark, the all-glass apparatus was covered in aluminium foil and the temperature was kept at ⩽ −30 °C during work-up.] Stirring was continued for 3 h and the volatiles were removed *in vacuo*. The residue was extracted into C_6H_{14} to yield an orange solution. Cooling to −50 °C yielded red-orange crystals (0.6 g), m.p. 142 °C (decomp.).

(*b*) PbR(Cl). Solid $PbCl_2$ (1.0 g, 5 mmol) was added to a stirred solution of $(LiR)_2$ (0.85 g, 1.75 mmol) in thf (20 cm^3) at −78 °C in the dark. Stirring was continued for 2 h; a black metallic precipitate formed. The solution was filtered and the volatiles were removed from the filtrate *in vacuo* to yield a yellow oil. Distillation afforded a colourless liquid (0.6 g), b.p. 45–55 °C (10^{-2} Torr) identified as RH.

Reaction of Bis[bis(trimethylsilyl)methyl]tin(II)[2] *with Tin(II) Chloride.*—The solid chloride (0.26 g, 1.37 mmol) was added to a stirred deep purple solution of the tin(II) alkyl (0.60 g, 1.4 mmol) in diethyl ether (25 cm^3) at 25 °C. The solution initially changed to cherry-red, but after a few minutes a black precipitate (Sn) was deposited. The mixture was filtered; the

Table 13 X-Ray crystallographic data for SnR_2 **1**, SnR(Cl) **2**, and $Sn[N(SiMe_3)_2]$ **3**

	1	**2**	**3**
Formula	$C_{24}H_{44}N_2Si_4Sn$	$C_{12}H_{22}ClNSi_2Sn$	$C_{18}H_{40}N_2Si_4Sn$
M	591.7	390.6	516.6
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	15.963(1)	15.604(5)	12.076(5)
b/Å	27.333(4)	14.411(5)	17.290(5)
c/Å	21.856(2)	17.413(8)	14.646(8)
β/°	103.66(1)	112.56(3)	117.20(3)
Z	12	8	4
U/Å	9266	3616	2720
D_c/g cm^{-3}	1.27	1.44	1.26
F(000)	3696	1568	1072
N	7987	3163	4586
N_o	4959	2539	2564
μ_{Mo}/cm^{-1}	10.0	16.8	11.2
Specimen/mm	0.40 × 0.25 × 0.40	≈0.4	0.14 × 0.24 × 0.24
$A^*_{\mathrm{min,max}}$	1.1, 1.25	*	1.3, 1.5
n in $[I > n\sigma(I)]$	3	2	3
$2\theta_{\mathrm{max}}$/°	50	40	50
R	0.051	0.064	0.040
R'	0.072	0.074	0.035

* Spheroid; no correction.

filtrate was concentrated to dryness *in vacuo*. Sublimation of the residue at 10^{-2} Torr gave a white sublimate of bis[bis(trimethylsilyl)methyl]dichlorotin(IV)[2] (0.45 g, 65%) (Found: C, 34.1; H, 8.0. Calc. for $C_{14}H_{38}Cl_2Si_4Sn$: C, 33.1; H, 7.5%), m.p. 89–91 °C.

Reaction of Bis(2,6-*di*-tert-*butylphenoxo*)*tin*(II)[43] *with Tin*(II) *Chloride*.—The solid chloride (0.10 g, 0.5 mmol) was added to a stirred yellow solution of the tin(II) phenoxide (0.30 g, 0.5 mmol) in thf (15 cm^3). The colour was almost completely discharged. Stirring was continued for 2 h. The mixture was filtered. The filtrate was evaporated to dryness and the residue was washed with pentane. The pale yellow insoluble material was identified as chloro(2,6,-di-*tert*-butylphenoxo)tin(II) (0.30 g, 75%) (Found: C, 45.1; H, 5.6. Calc. for $C_{14}H_{21}ClOSn$: C, 46.7; H, 5.8%), m.p. *ca.* 170 °C (decomp.).

X-Ray Data Collection, Structure Solution and Refinement for the Tin(II) *Alkyls* **1**–**3**.—The appropriate details are in Table 13. Unique sets of data were measured within the specified $2\theta_{\mathrm{max}}$ limits (Table 13) using a Syntex $P2_1$ four-circle diffractometer in a conventional 2θ–θ scan mode; T was 295 K and a monochromatic Mo-Kα radiation source was used (λ = 0.710 69 Å). N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the 9 × 9 block-diagonal least-squares refinement after analytical absorption correction and solution of each structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{\mathrm{iso}})$H constrained to reasonable values and U_{iso} values taken as equal to those of the atoms to which each H is attached. Reflection weights were $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[48] Computation used the X-RAY 76 program system[49] implemented on a Perkin Elmer 3240 computer by S. R. Hall.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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