# Step-wise Nucleophilic Substitution of Bis(cyclopentadienyl)-tin(II); Synthesis and Structural Characterisation of $[\{Sn(\eta^3\text{-}C_5H_5)[\mu\text{-}N{=}C(NMe_2)_2]\}_2]$ and $[\{Sn[\overline{S(CH_2)_3SC}(R)][\mu\text{-}N{=}C(NMe_2)_2]\}_2]$ (R = H or $SiMe_3$)†

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Nucleophilic substitution of $Sn(C_5H_5)_2$ with $LiN{=}C(NMe_2)_2$ led to the monosubstitution of only one $C_5H_5$ ligand yielding dimeric $[\{Sn(\eta^3\text{-}C_5H_5)[\mu\text{-}N{=}C(NMe_2)_2]\}_2]$ in which the remaining $C_5H_5$ group can be further substituted by reactions with lithiated 1,3-dithianes to give the dimeric mixed-ligand imino–1,3-dithiane complexes $[\{Sn[\overline{S(CH_2)_3SC}(R)][\mu\text{-}N{=}C(NMe_2)_2]\}_2]$ (R = H or $SiMe_3$).

We have been interested recently in the occurrence of bonds between the p-block metals tin and lead and early main-group elements. The $[Ph_3E\text{-}Li\{Me_2N(CH_2)_2\}_2NMe]$ (E = Sn or Pb) complexes contain the first structurally authenticated early main-group metal to heavy p-block metal bonds.[1,2] Such triorganostannates and plumbates are valuable precursors in organic synthesis.[3] More recently we have been interested in the synthetic utility of heavy p-block metal cyclopentadienide complexes as precursors to organometallic and metal 'ate complexes.[4,5] The metal centres within these species accept weak nucleophiles such as $C_5H_5^-$ and produce a range of complexes containing anionic organometallic fragments, *e.g.*, nucleophilic *addition* of $Na(C_5H_5)$ or $Mg(C_5H_5)_2$ to $E(C_5H_5)_2$ produces ion-separated and ion-contacted complexes containing unusual $E(C_5H_5)_3^-$ 'paddle-wheel' ions.[4a–c] However, with more potent nucleophiles and $E(C_5H_5)_2$ we found that *substitution* occurs. Hence, the reaction of fluorenyllithium $Li(C_{13}H_9)$ with $Sn(C_5H_5)_2$ (2:1 or 3:1 mol equiv.) in tetrahydrofuran (thf) results in disubstitution followed by addition of a third fluorenyl ligand and in the formation of the triorganostannate, $[Li(thf)_4]^+[Sn(C_{13}H_9)_3]^-$.[4a] In a similar manner, we recently reported the syntheses and structures of the tris(imino) species $E[N{=}C(Bu^t)Ph]_3Li{\cdot}thf$ *via* the reaction between $LiN{=}C(Bu^t)Ph$ and $E(C_5H_5)_2$.[4b,d] Unexpectedly, however, the reaction between $LiN(SiMe_3)_2$ and $Sn(C_5H_5)_2$ (1:1) led to nucleophilic addition and to the formation of $[(C_5H_5)\{(Me_3Si)_2N\}Sn(\mu\text{-}C_5H_5)Li\{Me_2N(CH_2)_2\}_2NMe]$.[4c] This complex is formally the first example of a mixed-ligand triorganostannate complex and can be seen as a model intermediate for nucleophilic substitution of $Sn(C_5H_5)_2$.

We have proposed that the major influences on the products of these reactions are the nucleophilicity and steric bulk of the nucleophiles and the molar ratio of the reagents employed. The reaction of lithium tetramethylguanidinide $LiN{=}C(NMe_2)_2$ with $Sn(C_5H_5)_2$ is unusual in that the reaction can be controlled to give exclusively the dimeric complex $[\{Sn(\eta^3\text{-}C_5H_5)[\mu\text{-}N{=}C(NMe_2)_2]\}_2]$ **1** as the product of monosubstitution.[6] The substitution of just one cyclopentadienyl ligand in the synthesis of complex **1** from $Sn(C_5H_5)_2$ contrasts with the interaction of $LiC(SiMe_3)_3$ with $Sn(C_5Me_5)_2$ (1:1), where both cyclopentadienyl ligands are displaced.[7] The synthesis of complex **1** can be compared to the usual route to mixed-ligand complexes of tin(II) (SnRR′) which involves nucleophilic substitution of SnRX (R = organic anion, X = halide), generated from ligand-exchange reactions of $SnR_2$ with $SnX_2$, with alkali-metal organometallics (MR′, M = alkali metal) or ligand-exchange reactions of $SnR_2$ with $SnR'_2$. Jutzi *et al.*[8] have reported the synthesis of the monomeric mixed-ligand germanium complex $[Ge(R)\{C(SiMe_3)_3\}]$ in which the substitution of the $C_5Me_5$ ligand is the final step. However, to our knowledge, the facile stepwise substitution of Group 14 metallocenes $[E(C_5H_5)_2$, E = Ge, Sn or Pb], as precursors to mixed-ligand low-valent complexes $(ER^1R^2)$, has not been reported.

We report here the use of the stepwise substitution of $Sn(C_5H_5)_2$ in the generation of mixed-ligand complexes as exemplified by the syntheses of two mixed imino–1,3-dithiane complexes, $[\{Sn[\overline{S(CH_2)_3SC}(R)][\mu\text{-}N{=}C(NMe_2)_2]\}_2]$ (R = H **2** or $SiMe_3$ **3**), by the nucleophilic substitution reactions of the cyclopentadienyl ligands of $[\{Sn(\eta^3\text{-}C_5H_5)[\mu\text{-}N{=}C(NMe_2)_2]\}_2]$ **1** with lithiated 1,3-dithianes $Li[\overline{S(CH_2)_3SC}(R)]$ (1:1) in thf. This study illustrates the use of Group 14 metallocenes as simple precursors to mixed-ligand complexes in general. Complexes **2** and **3** are dimeric in the solid state and retain the $Sn_2N_2$ core structure present in complex **1**. In contrast to **2**, one of the sulfur centres of the trimethylsilyl-substituted 1,3-dithiane ligand of **3** is involved in an intramolecular bond to tin across its dimeric core.

## Results and Discussion

Bis(cyclopentadienyl)tin was prepared in the manner of Fischer and Grubert[9] by the reaction of $SnCl_2$ with a fresh solution of $Na(C_5H_5)$ in *ca.* 70% yield after sublimation. It is best handled as a standardised thf solution which can be stored for prolonged periods at −35 °C without significant polymerisation. Crystalline $[\{Sn(\eta^3\text{-}C_5H_5)[\mu\text{-}N{=}C(NMe_2)_2]\}_2]$ **1** can be easily prepared in *ca.* 80% yield from the 1:1 reaction of $LiN{=}C(NMe_2)_2$ with $Sn(C_5H_5)_2$ in thf–hexane solution by refrigeration at −35 °C.[6] The reactions of the 1,3-dithianes, $Li[\overline{S(CH_2)_3SC}(R)]$ (R = H for **2** or $SiMe_3$ for **3**), with complex **1** occur smoothly without any decomposition into elemental tin at −10 °C (Scheme 1). Both complexes **2** and **3** are stable at room temperature under argon. They are isolated in crystalline form in 36% yield for **2** and 29% yield for **3**. Both complexes are extremely thermally stable, with complex **2** decomposing at

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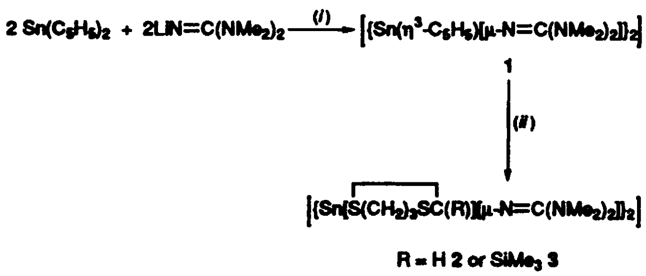
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



**Scheme 1** (*i*) thf; (*ii*) Li[$\overline{\mathrm{S(CH_2)_3SC}}\mathrm{(R)}$], thf

**Table 1** Crystal data and structure solution of complexes 2 and 3[a]

| | 2 | 3 |
|---|---|---|
| Empirical formula | $C_9H_{19}N_3S_2Sn$ | $C_{12}H_{27}N_3S_2SiSn$ |
| $M$ | 352.08 | 424.27 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ |
| Crystal size/mm | 0.49 × 0.45 × 0.44 | 0.35 × 0.33 × 0.32 |
| $a$/Å | 9.473(2) | 10.326(2) |
| $b$/Å | 15.552(3) | 12.020(2) |
| $c$/Å | 9.894(2) | 15.322(3) |
| $\beta$/° | 112.49(3) | 102.14(3) |
| $U$/Å$^3$ | 1346.8(5) | 1859.2(6) |
| $D_c$/Mg m$^{-3}$ | 1.736 | 1.516 |
| $\theta$ range/° | $3.5 < \theta < 22.5$ | $3.65 < \theta < 22.5$ |
| Reflections collected | 1867 | 2514 |
| Independent reflections | 1753 | 2408 |
| Goodness of fit | 1.491 | 1.333 |
| $R1$, $R2$ [$F > 4\sigma(F)$][b] | 0.0185, 0.0641 | 0.0195, 0.0644 |
| $R1$, $R2$ (all data)[b] | 0.0214, 0.0934 | 0.0227, 0.0866 |
| Final difference peak, hole/e Å$^{-3}$ | 0.509, −0.576 | 0.410, −0.526 |

[a] Details in common: $T = 153(2)$ K, $\lambda = 0.710\,73$ Å, $Z = 4$. [b] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $R2 = [\{\Sigma w(F_o^2 - F_c^2)^2\}/\Sigma wF_o^4]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.[11]

**Table 2** Atomic coordinates ( × 10$^4$) for complex 2

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Sn(1) | 777(1) | 585(1) | 4005(1) |
| S(1) | 1736(2) | −1434(1) | 3251(1) |
| S(2) | −1275(2) | −734(1) | 1215(2) |
| N(1) | 1427(4) | −267(3) | 5905(4) |
| N(2) | 3125(5) | −1273(3) | 7496(4) |
| N(3) | 4072(5) | −15(3) | 6929(5) |
| C(1) | 2094(6) | −2002(3) | 7065(6) |
| C(2) | 4252(7) | −1331(4) | 8981(6) |
| C(3) | 2804(6) | −505(3) | 6746(6) |
| C(4) | 5516(6) | −389(4) | 7054(7) |
| C(5) | 4015(6) | 916(4) | 6887(6) |
| C(6) | 652(6) | −497(3) | 2397(6) |
| C(7) | 1650(6) | −2000(4) | 1601(6) |
| C(8) | 37(6) | −2212(4) | 557(6) |
| C(9) | −928(7) | −1432(4) | −94(6) |

**Table 3** Atomic coordinates ( × 10$^4$) for complex 3

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Sn(1) | 1145(1) | 940(1) | 4815(1) |
| S(1) | 827(1) | 862(1) | 7002(1) |
| S(2) | 3481(1) | 654(1) | 6510(1) |
| Si(1) | 2079(1) | 2963(1) | 6373(1) |
| N(1) | −932(4) | 814(3) | 4889(2) |
| N(2) | −1890(4) | 2370(3) | 4071(3) |
| N(3) | −2958(3) | 1559(3) | 5085(3) |
| C(1) | −2435(5) | 3473(4) | 4170(4) |
| C(2) | −1252(5) | 2248(5) | 3321(3) |
| C(3) | −1880(4) | 1540(4) | 4686(3) |
| C(4) | −4295(5) | 1780(5) | 4563(4) |
| C(5) | −2894(5) | 1098(5) | 5967(3) |
| C(6) | 1927(4) | 1410(4) | 6341(3) |
| C(7) | 1845(6) | 849(5) | 8144(3) |
| C(8) | 3127(6) | 184(5) | 8235(3) |
| C(9) | 4088(5) | 673(5) | 7720(3) |
| C(10) | 3269(6) | 3430(4) | 5682(3) |
| C(11) | 2658(7) | 3637(5) | 7488(4) |
| C(12) | 414(6) | 3537(4) | 5872(5) |

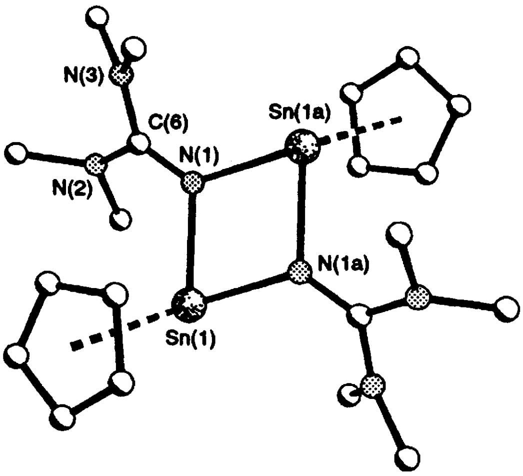


**Fig. 1** Structure of complex 1. Hydrogen atoms have been omitted for clarity

170 °C and complex 3 melting without decomposition at 182 °C.

Infrared studies on complexes 2 and 3 confirmed that substitution of the cyclopentadienyl ligand from complex 1 had occurred with the characteristic C–H stretching vibration at 3076 cm$^{-1}$ disappearing after the reactions. An additional characteristic feature of the C$\overset{\cdots}{-}$N stretching frequencies of the bridging imino groups of complexes 1–3 (1512 1,[6] 1525 cm$^{-1}$ 2 and 3) is that they all arise at lower energies than in the neutral imino ligand [HN=C(NMe$_2$)$_2$ 1600 cm$^{-1}$]. Such a reduction is unusual as compared to early main-group imino complexes where there is generally an increase in the C$\overset{\cdots}{-}$N stretching vibration from that of the neutral ligand, *e.g.*, LiN=C(NMe$_2$)$_2$ 1615 cm$^{-1}$.[10] Elemental analysis (C, H, N) of both complexes and $^1$H NMR studies confirm their identities. The synthesis of both complexes demonstrates the use of stepwise nucleophilic substitution of Sn(C$_5$H$_5$)$_2$ in the preparation of mixed-ligand tin(II) complexes.

X-Ray crystallographic studies were undertaken on complexes 2 and 3. Details of the structural refinements of the complexes are shown in Table 1. Atomic coordinates for complexes 2 and 3 are listed in Tables 2 and 3, respectively, and selected bond lengths and angles in Table 4. In addition, selected bond lengths and angles for complex 1 are included in Table 4 for comparison with the new complexes 2 and 3.

Since the synthesis and structure of complex 1 has been previously communicated,[6] a detailed structural discussion of this species is not given here. However, the X-ray crystallographic study of the complex shows it to be a centrosymmetric Sn$_2$N$_2$-ring dimer in the solid state, [{Sn(η$^3$-C$_5$H$_5$)[μ-N=C(NMe$_2$)$_2$]}$_2$] (Fig. 1), in which there is lattice solvation by one thf molecule per dimer unit.

The crystal structures of 2 (Fig. 2) and 3 (Fig. 3), obtained at low temperature, show that both complexes have similar dimeric structures in the solid state. The centrosymmetric Sn$_2$N$_2$ core of the precursor complex 1 is retained upon reaction with the 1,3-dithiane anions. The cyclopentadienyl ligands of 1

**Table 4** Selected bond lengths (Å) and angles (°) for complexes 1–3

| 1 | | 2* | | 3* | |
|---|---|---|---|---|---|
| Sn(1)–N(1) | 2.196(3) | Sn(1)–N(1) | 2.187(4) | Sn(1)–N(1) | 2.177(4) |
| Sn(1)–N(1a) | 2.185(3) | Sn(1)–N(1a) | 2.180(4) | Sn(1)–N(1a) | 2.178(3) |
| Sn(1)–C(4) | 2.432(4) | Sn(1)–C(6) | 2.288(5) | Sn(1)–C(6) | 2.375(4) |
| Sn(1)–Cp(centroid) | 2.432(4) | N(1)–C(3) | 1.304(7) | N(1)–C(3) | 1.298(6) |
| N(1)–C(6) | 1.294(5) | N(3)–C(3) | 1.378(6) | N(3)–C(3) | 1.379(6) |
| C(6)–N(2) | 1.371(5) | N–Me (average) | 1.449 | N–Me (average) | 1.456 |
| C(6)–N(3) | 1.370(5) | Sn · · · S | 4.44 | Sn · · · S | 3.77 |
| N–Me (average) | 1.445(7) | | | C(6)–Si(1) | 1.874(5) |
| N(1)–Sn(1)–N(1a) | 75.4(1) | N(1)–Sn(1)–N(1a) | 77.7(2) | N(1)–Sn(1)–N(1a) | 77.2(1) |
| Sn(1)–N(1)–Sn(1a) | 104.6(1) | Sn(1)–N(1)–Sn(1a) | 102.3(2) | Sn(1)–N(1)–Sn(1a) | 102.8(1) |
| N(1)–Sn(1)–C(4) | 91.6(2) | N(1)–Sn(1)–C(6) | 94.3(2) | N(1)–Sn(1)–C(6) | 95.8(1) |
| N(1a)–Sn(1)–C(4) | 93.8(2) | N(1a)–Sn(1)–C(6) | 93.8(2) | N(1a)–Sn(1)–C(6) | 93.1(1) |

* Symmetry operation for complexes 2 and 3: $-x$, $-y$, $-z + 1$.

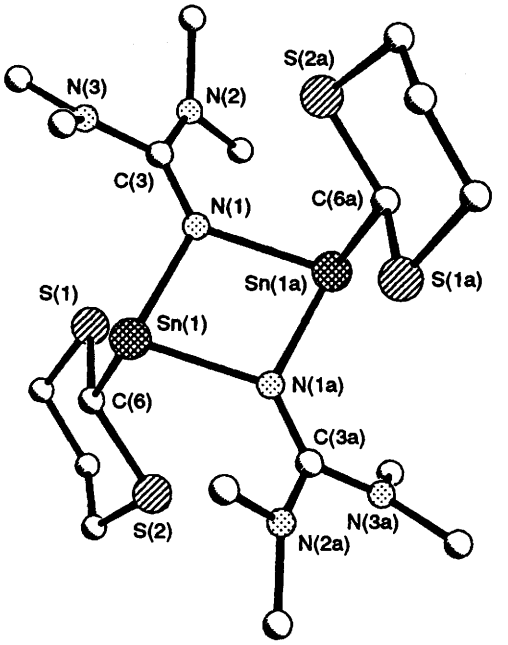


**Fig. 2** Structure of complex 2. Hydrogen atoms have been omitted for clarity

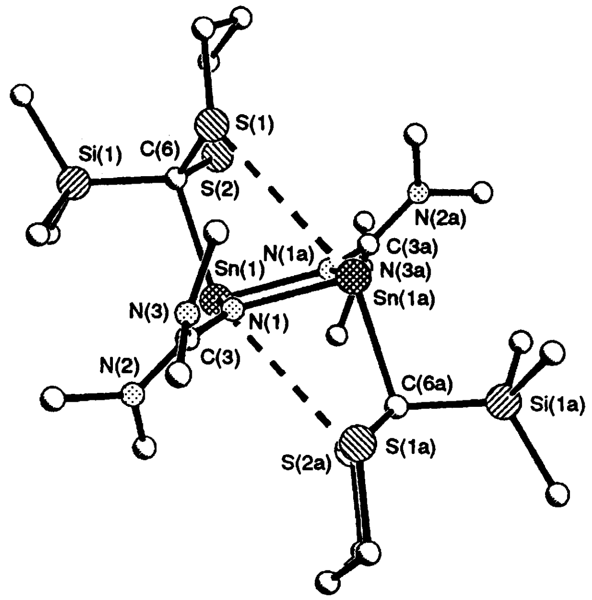


**Fig. 3** Structure of complex 3. Hydrogen atoms have been omitted for clarity

have been substituted for the 1,3-dithianes giving, in both cases, *trans* isomers in the solid state.

The rhombic $Sn_2N_2$ cores of complexes 2 and 3 are very similar in terms of the angles at tin and nitrogen [N–Sn–N and Sn–N–Sn 77.7(2) and 102.3(2)° in 2, 77.2(1) and 102.8(1)° in 3]. Within these rings the Sn–N bonds are of typical lengths compared to other amido-tin compounds, *e.g.*, 2.202(1) Å (average) in $[\{Sn(NBu^t)\}_4]$,[12] and are almost completely symmetrical [2.187(4) and 2.180(4) Å in 2, 2.177(4) and 2.178(3) Å in 3]. The cores of 2 and 3 can be compared to imino-aluminium complexes where similar μ-metal bridging of imino groups has been seen, with the $Al_2N_2$ cores showing a similar rhombic distortion to that seen in 2 and 3 although with less acute angles at their metal centres (N–Al–N average *ca.* 83°).[13]

The μ-N=C(NMe$_2$)$_2$ ligands of complexes 2 and 3 are, like those of complex 1, tilted out of the plane of the $Sn_2N_2$ ring (by *ca.* 27 2, *ca.* 38 3; *cf. ca.* 37° 1). Presumably the eclipsed, tilted conformation of these ligands arises, for similar reasons to those in 1, in order to avoid steric crowding in the $Sn_2N_2$ plane with the terminal *trans*-substituted 1,3-dithiane ligands. This interpretation is consistent with the fact that the imino ligands of 2, in which the less sterically demanding unsubstituted 1,3-dithiane is present, are tilted out of the $Sn_2N_2$ ring plane by a smaller degree than occurs in 3. The Sn–C bond lengths observed in 2 and 3 to the 1,3-dithiane ligands are in the expected range for σ-co-ordinated tin(II) organometallics {2.288(5) 2, 2.375(4) Å 3; *cf.* 2.281 Å in $Sn[CH(SiMe_3)_2]_2$[14]} and are (not surprisingly) shorter than the Sn–C contacts to the π-$C_5H_5$ ligands in 1 [shortest 2.432(4) Å[6]]. However, although the elongation in the Sn–C bond of complex 3 compared to that in 2 (*ca.* 0.10 Å) may partly be due to steric reasons, this feature may also reflect an element of intramolecular S · · · Sn bonding in 3. Whereas the unsubstituted 1,3-dithiane ligands of 2 are orientated ('side-on') in such a way as to give two equivalent long Sn · · · S contacts to the opposite tin atom of the dimer (4.44 Å), the trimethylsilyl-substituted 1,3-dithiane ligand of 3 has rotated about the Sn–C bond so as to bring one of the sulfur centres into closer contact with the opposite tin atom of the dimer (3.77 Å; *cf.* sum of van der Waals radii of Sn and S, 4.0 Å[15]).

The solution dynamics of complex 1 have been investigated by variable-concentration and variable-temperature $^1H$ NMR studies (in toluene and thf) and by cryoscopic molecular-mass measurements. These studies show that the complex is involved in an intramolecular *cis–trans* equilibrium in thf solutions even at room temperature.[6] In complexes 2 and 3 *cis–trans* isomerism of the dithiane ligands of both complexes is also evident at room temperature in thf solutions. Thus, there are two $SiMe_3$ resonances at δ 0.15 and 0.20 in the $^1H$ NMR spectrum of 3 and, for both 2 and 3, the $NMe_2$ resonances of the

$\mu$-N=C(NMe$_2$)$_2$ ligands appear as a singlet due to the *cis* form (δ 2.9 **2**, *ca.* δ 3.0 **3**) and as an apparent doublet due to the *trans* form (δ 2.7 **2**, δ 2.65 **3**). The *cis* and *trans* isomers of complex **1** are also observed in the $^1$H NMR spectrum at 25 °C in exactly the same pattern and at similar chemical shifts to those observed in the spectra of **2** and **3**. The splitting of the imino signals in the *trans* isomers of **1**–**3** is due to the restricted rotation of the imino groups which are trapped between the terminal ligands thus rendering the imino methyl groups inequivalent. For complex **2** the coincidence of one of the 1,3-dithiane resonances with the *trans*-NMe$_2$ resonance (at δ 2.7) makes integration of the *trans* resonance difficult. However, our best estimate of the ratio of the *cis* to the *trans* isomer is *ca.* 1 : 1 at room temperature. This is approximately the same ratio as that observed for complex **1** in thf at 25 °C and implies that the energy requirements for interconversion of the *cis* and *trans* isomers of **1** and **2** are very similar. The low solubility of crystalline **3** in thf and particularly the broadness of the *cis* imino methyl resonance (δ 2.5–3.5) makes the relative integration of the *cis* and *trans* imino resonances impossible. Thus, it was not possible to assign the two much sharper SiMe$_3$ resonances to either the *cis* or *trans* isomers on the basis of the ratio of the *cis* and *trans* imino peaks. However, it is clear from the integration of the SiMe$_3$ resonances that the *cis* and *trans* isomers coexist in a *ca.* 2 : 1 (or 1 : 2) ratio. As with complex **1** an intramolecular *cis*–*trans* isomerism for complexes **2** and **3**, as opposed to an intermolecular equilibrium (*e.g.*, monomer–dimer), is confirmed by the fact that changing the concentrations of both complexes does not alter the ratios of the *cis* and *trans* NMe$_2$ resonances in complex **2** or the ratio of the two SiMe$_3$ resonances in complex **3**. The occurrence of *cis*–*trans* equilibria in thf solutions of complexes **1**–**3** is similar to that occurring in [{Sn($\mu$-Cl)[NCMe$_2$(CH$_2$)$_3$CMe$_2$]}$_2$] where a *cis*–*trans* equilibrium occurs in toluene solutions.[16]

## Conclusion

The study presented illustrates for the first time that stepwise nucleophilic substitution of the cyclopentadienyl ligands of Sn(C$_5$H$_5$)$_2$ can be used as an effective method in the synthesis of mixed-ligand complexes of tin(II). Selective monosubstitution gives rise to mixed-cyclopentadienyl-ligand complexes (*e.g.*, complex **1**), the functionality of which can be further modified by reactions of other nucleophiles (*e.g.*, as shown in the synthesis of complexes **2** and **3** from **1**). The ready syntheses of prochiral complexes[16] of general formula [{Sn(RR′)}$_2$] should, in principle, provide a simple route to potentially chiral triorganostannates [Sn(RR′R″)]$^-$ *via* nucleophilic addition of a third nucleophile (R″$^-$).

## Experimental

Bis(cyclopentadienyl)tin[9] and complexes **1**–**3** are air- and/or moisture-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques[17] and under dry or oxygen-free argon. Tetrahydrofuran was dried using sodium–benzophenone and degassed prior to the reactions. Bis(cyclopentadienyl)tin was prepared in the manner described in the literature from SnCl$_2$ and Na(C$_5$H$_5$) in thf, the product being purified by sublimation.[9] Degassed HN=C(NMe$_2$)$_2$ was stored in a Schlenk tube over a molecular sieve (13X). All complexes were isolated and characterised with the aid of an argon-filled glove box (Faircrest Mark 4A) fitted with an O$_2$ and H$_2$O recirculation system (Type B). Melting points were determined by using a conventional apparatus and sealing samples in capillaries under argon. IR spectra were recorded as Nujol mulls using NaCl windows and were run on a Perkin-Elmer 2400 spectrophotometer. Elemental analyses were performed by first sealing samples under argon in air-tight aluminium boats (1–2 mg) and the C, H and N contents determined using a Perkin-Elmer 240 elemental analyser. Proton NMR spectra were recorded on a Bruker WH 250 MHz spectrometer in dry C$_4$D$_8$O (using the solvent resonances as the internal reference standard), at 25 °C, 400.13 MHz.

*Synthesis of* [{Sn[S(CH$_2$)$_3$SCH][$\mu$-N=C(NMe$_2$)$_2$]}$_2$] **2**.—To a stirred solution of 1,3-dithiane (0.3 g, 2.5 mmol) in thf (10 cm$^3$) was added LiBu$^n$ (1.56 cm$^3$, 1.6 mol dm$^{-3}$ in hexanes). After cooling of the resulting solution (after 10 min) to $-10$ °C, a thoroughly dried sample of complex **1** (0.745 g, 1.25 mmol of unsolvated material) in thf (20 cm$^3$) was added. Gentle warming to reflux yielded a bright yellow solution, which was reduced to *ca.* 8 cm$^3$, whereupon a pale yellow precipitate developed. This redissolved upon warming and storage at room temperature for 24 h produced yellow crystalline blocks of complex **2**. First batch yield 0.32g (36%); m.p. 170 °C (decomp.) (Found: C, 30.9; H, 5.5; N, 12.0. Calc. for C$_{18}$H$_{38}$N$_6$S$_4$Sn$_2$: C, 30.7; H, 5.4; N, 11.9%). IR (Nujol mull): ν(C=N str.) 1525 cm$^{-1}$. $^1$H NMR: δ 2.9 (s, NMe$_2$ of *cis* form), 2.7 (d, NMe$_2$ *trans* form), 2.5–2.3 [br, S(C*H*$_2$)$_3$SC*H*].

*Synthesis of* [{Sn[S(CH$_2$)$_3$SC(SiMe$_3$)][$\mu$-N=C(NMe$_2$)$_2$]}$_2$] **3**.—2-Trimethylsilyl-1,3-dithiane (0.48 g, 2.5 mmol) was treated in an identical way as that described for complex **2**. The resulting yellow solution was reduced to *ca.* 6 cm$^3$ and the yellow precipitate produced was redissolved by gentle warming. Subsequent storage at room temperature for 24 h yielded yellow crystalline blocks of complex **3**. First batch yield 0.31 g (29%); m.p. 182 °C (Found: C, 33.6; H, 6.2; N, 10.1. Calc. for C$_{24}$H$_{54}$N$_6$S$_4$Si$_2$Sn$_2$: C, 33.8; H, 6.3; N, 9.9%). IR (Nujol mull): ν (C=N str.) 1525 cm$^{-1}$. $^1$H NMR: δ 2.5–3.5 (NMe$_2$ of *cis* and *trans* forms respectively), 1.7–2.5 [br, S(C*H*$_2$)$_3$SC(SiMe$_3$)], 0.15 and 0.20 (d, SiMe$_3$).

*X-Ray Crystallography.*—Crystals of complexes **2** and **3** were mounted directly from solution at room temperature under argon using a perfluorocarbon oil to protect them from atmospheric moisture and oxygen (Riedel–deHaën). The oil 'freezes' at reduced temperatures and holds the crystal static in the X-ray beam.[18] Data were collected on a Stoe AED diffractometer and a semiempirical absorption correction based on ψ-scans was employed. Details of the structural solution and refinement of **2** and **3** are shown in Table 1. The structures were solved by direct methods (SHELXTL PLUS)[19] and refined by full-matrix least squares on $F^2$ (SHELXL 93).[11]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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