

**A Model Intermediate for the Nucleophilic Substitution of  $(\text{Cp})_2\text{Sn}$ ;  
Synthesis and Structure of  $(\text{Cp})(\text{Me}_3\text{Si})_2\text{NSn}(\mu\text{-Cp})\text{Li}\cdot\text{pmdeta}$   
[ $\text{Cp} = \text{C}_5\text{H}_5$ ,  $\text{pmdeta} = (\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$ ]**

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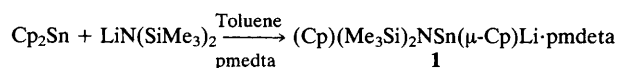
Reaction of  $\text{LiN}(\text{SiMe}_3)_2$  with  $\text{Cp}_2\text{Sn}$  and  $\text{pmdeta}$  produces  $(\text{Cp})(\text{Me}_3\text{Si})_2\text{NSn}(\mu\text{-Cp})\text{Li}\cdot\text{pmdeta}$  **1** which can be viewed as a model intermediate for nucleophilic substitution of  $\text{Cp}_2\text{Sn}$ .

We have used nucleophilic addition and substitution of heavy p block metal cyclopentadienyl derivatives of group 13 (E = Tl) and 14 (E = Sn, Pb) in the syntheses of a variety of organometallic complexes.<sup>1-6</sup> The metal centres within these species accept weak nucleophiles such as  $\text{Cp}^-$  and produce a range of complexes containing anionic organometallic frag-

ments.<sup>1-4</sup> However, more potent nucleophiles, such as imino anions and organometallics, substitute the Cp ligands of  $\text{Cp}_2\text{E}$  (E = Sn or Pb).<sup>5,6</sup> Thus reaction of  $\text{LiN}=\text{C}(\text{NMe}_2)_2$  with  $\text{Cp}_2\text{Sn}$  (1:1) produces the dimeric mixed ligand complex  $\{(\eta^3\text{-Cp})\text{Sn}\{\mu\text{-N}=\text{C}(\text{NMe}_2)_2\}\}_2$  in which only one of the Cp ligands is displaced.<sup>5</sup> 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 reagents employed. We report the synthesis and structure of  $(\text{Cp})(\text{Me}_3\text{Si})_2\text{NSn}(\mu\text{-Cp})\text{Li}\cdot\text{pmdeta}$  **1**. The complex is formally the first example of a mixed ligand triorganostannate complex and can be seen as a model intermediate for nucleophilic substitution of  $\text{Cp}_2\text{Sn}$ .

Reaction of  $(\text{Me}_3\text{Si})_2\text{NLi}$  with  $\text{Cp}_2\text{Sn}$  and *pmdeta* (1:1:1 equiv.) in toluene produces an orange solution from which colourless crystals of **1** are isolated.<sup>†</sup>



Scheme 1

An X-ray crystallographic study of **1**<sup>‡</sup> shows it to be a monomeric triorganostannate complex  $(\text{Cp})(\text{Me}_3\text{Si})_2\text{NSn}(\mu\text{-Cp})\text{Li}\cdot\text{pmdeta}$  **1** (Fig. 1). The Sn centre is attached to two distorted  $\eta^3\text{-Cp}$  ligands [Cp(X) and Cp(Y)] and to the planar N centre of a  $(\text{Me}_3\text{Si})_2\text{N}$  group [Sn(1)–N(1) 2.183(2) Å, *cf.* Sn–N in monomeric  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$  2.09 Å<sup>7</sup>]. This Sn centre has a distorted pyramidal geometry (sum of angles around Sn between the two Cp centroids $\S$  and N *ca.* 348°). The Cp(Y) ligand holds the Sn and Li<sup>+</sup> centres together in a bent  $\mu\text{-Cp}$  mode [Sn(1)–centroid Cp(Y)–Li(1) *ca.* 163°, centroid Cp(Y)–Li(1) 2.25 Å] and makes an  $\eta^3\text{-contact}$  with the Li centre. In contrast to the situation occurring in  $(\eta^5\text{-Cp})_2\text{Sn}-(\mu\text{-}\eta^5\text{-Cp})\text{Na}\cdot\text{pmdeta}$ ,<sup>1</sup> where long range C–H $\cdots$ Na contacts cause a bending of *ca.* 172°, the distortion of the Sn( $\mu\text{-Cp}$ )Li bridge of **1** does not result from intermolecular interactions. Evidently the Sn– $[\mu\text{-Cp(Y)}]$  interaction in **1** is comparatively weak judging by the distances involved [centroid Cp(Y)–Sn(1) 2.83 Å], which are considerably greater than the terminal Cp

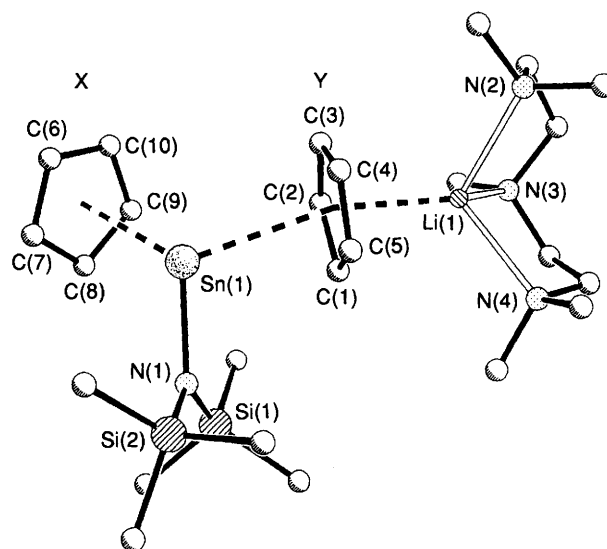
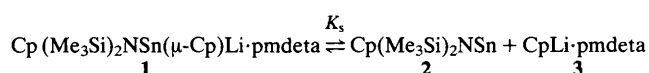


Fig. 1 Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): ring X, C(6)–Sn(1) 3.095(2), C(7)–Sn(1) 2.836(2), C(8)–Sn(1) 2.557(2), C(9)–Sn(1) 2.633(2), C(10)–Sn(1) 2.991(2), centroid Cp(X)–Sn(1) 2.57; ring Y, C(1)–Sn(1) 2.796(2), C(2)–Sn(1) 2.882(2), C(3)–Sn(1) 3.225(2), C(4)–Sn(1) 3.338(2), C(5)–Sn(1) 3.095(2), centroid Cp(Y)–Sn(1) 2.83, C(1)–Li(1) 2.502(4), C(2)–Li(1) 2.647(4), C(3)–Li(1) 2.645(4), C(4)–Li(1) 2.515(4), C(5)–Li(1) 2.418(4), centroid Cp(Y)–Li(1) 2.25, centroid Sn(1)–centroid Cp(Y)–Li 163;  $(\text{Me}_3\text{Si})_2\text{N}$ , Sn(1)–N(1) 2.183(2), Si(1,2)–N(1) 1.710(2), Si(1)–N(1)–Si(2) 122.9(1), Si(1)–N(1)–Sn(1) 124.1(1), Si(2)–N(1)–Sn(1) 112.2(1).

contacts in **1** [centroid Cp(X)–Sn(1) 2.57 Å], and are also slightly greater than the bridging Sn–( $\mu\text{-}\eta^5\text{-Cp}$ ) distances in  $(\eta^5\text{-Cp})_2\text{Sn}-(\mu\text{-}\eta^5\text{-Cp})\text{Na}\cdot\text{pmdeta}$  (centroid Cp–Sn, 2.75 Å).<sup>1</sup>

Nucleophilic addition rather than substitution results when  $\text{LiN}(\text{SiMe}_3)_2$  is reacted with  $\text{Cp}_2\text{Sn}$  because the bulky  $(\text{Me}_3\text{Si})_2\text{N}$  group precludes oligomerisation of  $(\text{Cp})(\text{Me}_3\text{Si})_2\text{NSn}$ , which must therefore be electronically satisfied by loosely binding to  $\text{CpLi}\cdot\text{pmdeta}$ . The latter can be compared with the outcome of the reaction of  $\text{LiN}=\text{C}(\text{NMe}_2)_2$  with  $\text{Cp}_2\text{Sn}$ , which gives the dimeric substitution product  $[(\eta^3\text{-Cp})\text{Sn}\{\mu\text{-N}=\text{C}(\text{NMe}_2)_2\}]_2$ .<sup>5</sup> Complex **1** can be regarded as a model intermediate for nucleophilic substitution of  $\text{Cp}_2\text{Sn}$ . Two mechanisms are plausible, (i) a concerted (one-step)  $\text{S}_{\text{N}}2$  type mechanism or (ii) an associative (two-step) mechanism. The structure of **1** can be interpreted in terms of the more probable associative pathway.<sup>8</sup> In the initial step, addition of nucleophiles (RM) occurs at the Sn centre forming an intermediate  $[\text{CpRSn}(\mu\text{-Cp})\text{M}]$  similar to **1**. In the subsequent step CpM is produced by breaking the weak Cp $\cdots$ Sn contact and producing  $\text{CpRSn}$ .

Variable-temperature and -concentration <sup>1</sup>H NMR spectroscopy and cryoscopic molecular mass measurements in arene solutions suggest that **1** is in equilibrium with  $(\text{Cp})(\text{Me}_3\text{Si})_2\text{NSn}$  **2** and  $\text{CpLi}\cdot\text{pmdeta}$  **3**.



Scheme 2

Measurements of the degree of association (*n*) of  $[(\text{Cp})(\text{Me}_3\text{Si})_2\text{NSn}(\mu\text{-Cp})\text{Li}\cdot\text{pmdeta}]_n$  **1** in benzene at various concentrations (0–0.07 mol dm<sup>−3</sup>) conform to the dissociation of

<sup>†</sup> A solution of hexamethyldisilazane [0.40 g, 2.5 mmol toluene (10 ml)] was reacted with  $\text{Bu}^n\text{Li}$  (1.56 ml, 2.5 mmol, 1.6 mol dm<sup>−3</sup> in hexanes) and the reaction mixture heated to reflux yielding a pale-brown solution. This solution was cooled to −30 °C and  $\text{Cp}_2\text{Sn}$  was added [0.63 g, 2.5 mmol, in tetrahydrofuran (1.4 ml)]. Warming to 50 °C and stirring (5 min) gave a yellow precipitate. Addition of *pmdeta* (0.53 ml, 2.5 mmol) produced an orange solution, which was reduced *in vacuo* to 4 ml. Subsequent storage at −35 °C for one week yielded colourless, air-sensitive crystalline rods of **1** in low (though reproducible) yield (*ca.* 20%, first batch): melting point 58 °C, decomp. 150 °C; IR  $\nu/\text{cm}^{-1}$  (Nujol), 3039 (Cp–H); <sup>1</sup>H NMR (+25 °C, 250 MHz, 0.2 mol dm<sup>−3</sup> in [<sup>2</sup>H<sub>8</sub>]toluene)  $\delta$  6.13 (s, 10 H, Cp), 1.92 (s) and 1.87 (s) (23 H, *pmdeta*), 0.47 (s) and 0.17 (s) [18 H,  $(\text{Me}_3\text{Si})_2\text{N}$ ]; Satisfactory elemental analyses (C, H, N) were obtained.

<sup>‡</sup> *Crystal data*:  $\text{C}_{25}\text{H}_{51}\text{LiN}_4\text{Si}_2\text{Sn}$ , *M* = 589.5, monoclinic, space group  $P2_1/c$ , *a* = 9.854(1), *b* = 22.939(2), *c* = 13.975(1) Å,  $\beta$  = 90.360(10)°, *V* = 3144.1(5) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.245 Mg m<sup>−3</sup>,  $\lambda$  = 0.71073 Å, *T* = 153 K,  $\mu(\text{Mo-K}\alpha)$  = 0.907 mm<sup>−1</sup>. Data were collected on a Siemens-Stoe AED using an oil-coated rapidly cooled crystal (T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, in the press) of dimensions 0.3 × 0.3 × 0.3 mm by the  $2\theta/\omega$  method ( $8^\circ \leq 2\theta \leq 50^\circ$ ). Of a total of 6328 reflections collected, 5515 were independent. A semi-empirical method from psi-scans was used in the absorption correction. The structure was solved by Patterson methods (SHELXS-90; G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467) and refined by full-matrix least squares on *F*<sup>2</sup> with to *R*1 (*F* > 4 $\sigma$ *F*) and *wR*2 (all data) of 0.022 and 0.058, respectively {*R*1 =  $\sum |F_o - F_c| / \sum F_o$  and *wR*2 =  $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$ } (G. M. Sheldrick, SHELXL-92, Göttingen, 1992). Largest peak and hole in the final difference map 0.906 and −0.404 e Å<sup>−3</sup>. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$\S$  Bond lengths and bond angles involving the Cp rings in **1** are defined arbitrarily in terms of the centroids of all five C atoms of the Cp rings throughout the text for simplicity.

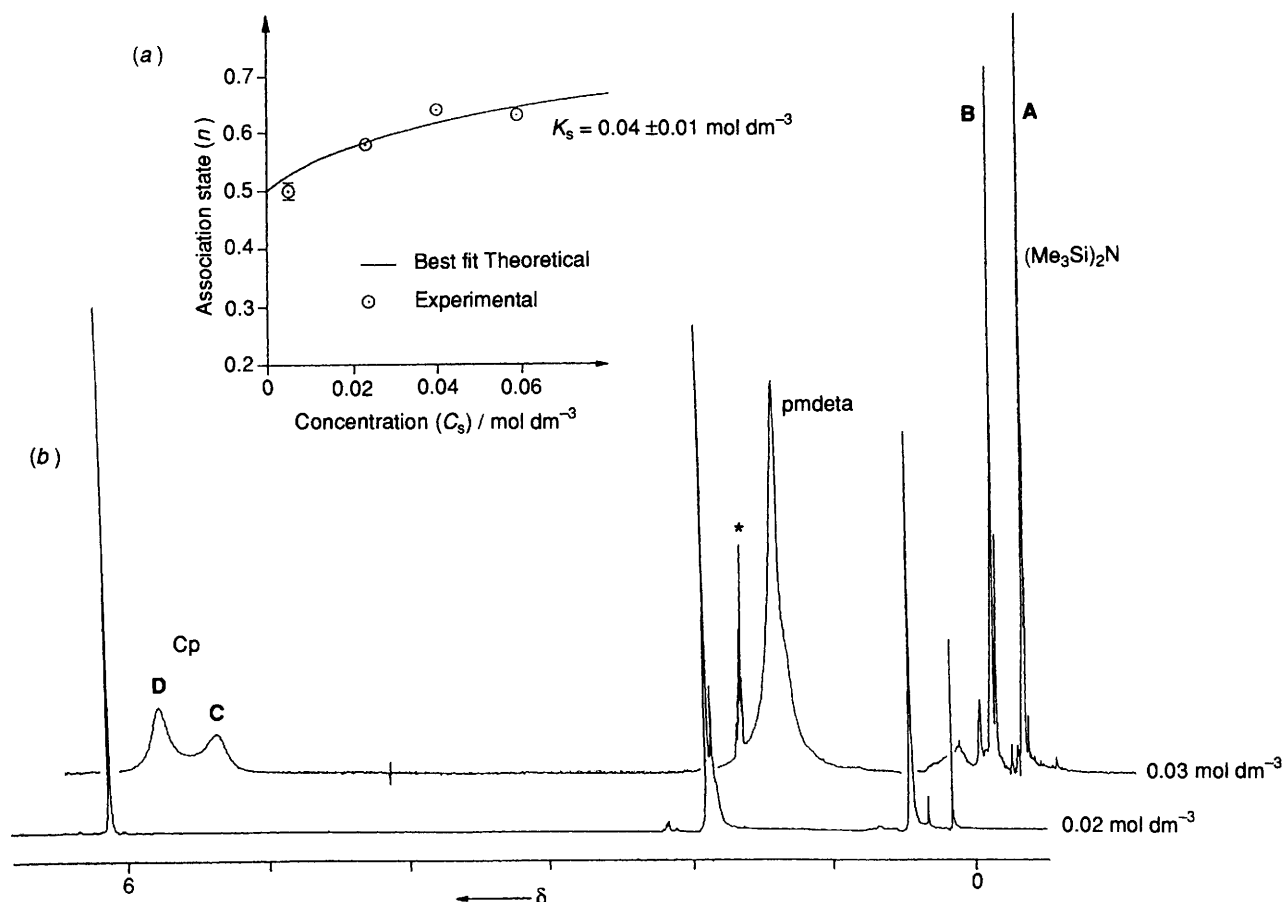


Fig. 2 (a) Variation of degree of association ( $n$ ) with concentration of **1** in benzene ( $C_s$ ): (—) best fit theoretical,  $\circ$  experimental,  $K_s = 0.04 \pm 0.01 \text{ mol dm}^{-3}$ ; (b) variable-concentration  $^1\text{H}$  NMR spectroscopy of **1** in toluene ( $25^\circ\text{C}$ , 250 MHz)

the complex into two fragments [Fig. 2(a)].<sup>¶</sup> The dissociative equilibrium constant for this process is *ca.*  $0.04 \text{ mol dm}^{-3}$  ( $\Delta G^\circ$  *ca.*  $7.4 \text{ kJ mol}^{-1}$ ). The identities of these two fragments are largely confirmed by  $^1\text{H}$  NMR (250 MHz) studies of **1** in toluene [Fig. 2(b)]. At low concentration (*ca.*  $0.03 \text{ mol dm}^{-3}$ ) and at  $25^\circ\text{C}$ , two Me resonances for  $(\text{Me}_3\text{Si})_2\text{N}$  (A  $\delta$  0.18 and B 0.42; total 18 H) and two Cp (C  $\delta$  5.92 and D  $\delta$  6.32; total 10 H) are observed. On the basis of a molar ratio of *ca.* 1.9 : 1 calculated from the cryoscopically determined equilibrium constant (in benzene at  $6^\circ\text{C}$ ) at this concentration, the resonance at  $\delta$  0.18 can be assigned to **2** and that at  $\delta$  0.42 to undissociated **1** (observed ratio *ca.* 1.5 : 1). The  $(\text{Me}_3\text{Si})_2\text{N}$  and Cp resonances occur in pairs each with the same relative ratio of *ca.* 18 H : 10 H, respectively (A + D, B + C). Hence, the Cp resonance at  $\delta$  5.91 can be assigned to undissociated **1** and that at  $\delta$  6.32 to **2** + **3**. The separate Cp ligands of **2** and **3** could not be resolved by reducing the temperature to  $-90^\circ\text{C}$ .

At higher concentrations the Cp resonances merge into a broad singlet ( $<0.07 \text{ mol dm}^{-3}$ ) and a sharp singlet is finally observed (*ca.*  $0.2 \text{ mol dm}^{-3}$ ) at the average position of the Cp resonances (C and D) seen at low concentration ( $\delta$  6.13). It should be noted that an alternative equilibrium, akin to that proposed for  $(\eta^5\text{-Cp})_2\text{Sn}(\mu\text{-}\eta^5\text{-Cp})\text{Na}\cdot\text{pmdeta}$ , involving dissociation of **1** into  $\text{Cp}_2(\text{Me}_3\text{Si})_2\text{NSn}^-$  and  $\text{Li}\cdot\text{pmdeta}^+$  cannot be completely ruled out.<sup>1</sup> However, the low energy for

dissociation of **1** and the observation of two very distinct Cp and  $(\text{Me}_3\text{Si})_2\text{N}$  resonances even at  $25^\circ\text{C}$ <sup>1</sup> supports the assertion that dissociation occurs at the apparently weaker  $\text{Sn}\cdots(\mu\text{-Cp})$  contact in **1** rather than at the  $(\mu\text{-Cp})\cdots\text{Li}$  contact, so giving two species in which very different ligand environments are present.

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<sup>¶</sup> Cryoscopic data: The analysis of the cryoscopic data was carried out by a curve fitting analytical method (M. G. Davidson, D. Stalke, R. Snaith and D. S. Wright, *J. Org. Chem.*, 1993, **58**, 2810). The data conform to the general dissociation equation [ $\text{A} \rightleftharpoons \text{B} + \text{C}$ ;  $K_s = C_s(1 - n)^2/n(2n - 1)$ ] with a best-fit curve calculated from the experimental points  $>0.01 \text{ mol dm}^{-3}$ :  $n = 0.50 \pm 0.01$  ( $0.005 \text{ mol dm}^{-3}$ ), 0.58 ( $0.023 \text{ mol dm}^{-3}$ ), 0.64 ( $0.04 \text{ mol dm}^{-3}$ ), 0.63 ( $0.059 \text{ mol dm}^{-3}$ ).