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

Michael A. Paver,* Christopher A. Russell,* Dietmar Stalke* and Dominic S. Wright* a

*a University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW

*b Institut für Anorganische Chemie, Tammannstrasse 4, D-37077 Göttingen, Germany

Reaction of \(\text{LiN(SiMe}_3)_2\) with \(\text{Cp}_2\text{Sn}\) and \(p\text{mdeta}\) produces \((\text{Cp})(\text{Me}_3\text{Si})_2\text{NSn}(\mu-\text{Cp})\text{Li}p\text{mdeta}\) 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 (\(E = \text{TI}\)) and 14 (\(E = \text{Sn, Pb}\)) in the syntheses of a variety of organometallic complexes.1–5 The metal centres within these species accept weak nucleophiles such as \(\text{Cp}^-\) and produce a range of complexes containing anionic organometallic fragments.1–4 However, more potent nucleophiles, such as imino anions and organometallics, substitute the \(\text{Cp}\) ligands of \(\text{Cp}_2\text{E}\) (\(E = \text{Sn or Pb}\)).5,6 Thus reaction of \(\text{LiN=C(NMe}_3)_2\) with \(\text{Cp}_2\text{Sn}\) (1:1) produces the dimeric mixed ligand complex \([\{(\eta^5\text{Cp})\text{Sn}(\mu-\text{N=C(NMe}_3)_2)\}_2\] in which only one of the \(\text{Cp}\) ligands is displaced.5 We have proposed that the major
An X-ray crystallographic study of I‡ shows it to be a monomeric triorganostannate complex (Cp(Me3Si)2NSn(Cp-Li)*pmdana (1). The Sn centre is attached to two distorted η3-Cp ligands [Cp(X) and Cp(Y)] and to the planar N centre of a (Me3Si)2N group \{Sn(1)-N(1)=2.183(2) Å, cf. Sn=N in monomeric [(Me3Si)2N]2Sn 2.09 Å\}. This Sn centre has a distorted pyramidal geometry (sum of angles around Sn 358°). The Cp(Y) ligand holds the Sn and Li+ centres together in a bent η3-Cp mode [Sn(1)-Cp(Y)-Li(1)] ca. 163°, centroid Cp(Y)-Li(1) 2.25 Å] and makes an η3-contact with the Li centre. In contrast to the situation occurring in (η5-Cp)Sn(μ-η5-Cp)Na*pmdana, where long range C-H-..Na contacts cause a bending of ca. 172°, the distortion of the Sn(μ-Cp)Li bridge of I does not result from intermolecular interactions. Evidently the Sn-[μ-Cp(Y)] interaction in I is comparatively weak judging by the distances involved [centroid Cp(Y)-Sn(1) 2.83 Å], which are considerably greater than the terminal Cp-

‡ A solution of hexamethyldisilazane [0.40 g, 2.5 mmol toluene (10 ml)] was reacted with BuLi (1.56 ml, 2.5 mmol, 1.6 mol dm-3 in hexanes) and the reaction mixture heated to reflux yielding a pale-brown solution. This solution was cooled to -30 °C and Cp2Sn 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 pmdana (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. The structure of Cp2Sn, which gives the dimeric substitution product \{Sn(η3-Cp)Li[Sn(η3-Cp)Li]2\}, shows it to be a monomeric triorganostannate complex (Cp(Me3Si)2NSn(Cp-Li)*pmdana. In the subsequent reaction of LiN(SiMe3)2 with Cp2Sn because the bulky (Me3Si)2N group precludes oligomerisation of (Cp(Me3Si)2NSn(Cp-Li)*pmdana (centroid Cp-Sn, 2.75 Å). Nucleophilic addition rather than substitution results when LiN(SiMe3)2 is reacted with Cp2Sn because the bulky (Me3Si)2N group precludes oligomerisation of (Cp)(Me3Si)2NSn(Cp-Li)*pmdana, which must therefore be electronically satisfied by loosely bonding to Cp-Li*pmdana. The complex can be characterised by a model intermediate for nucleophilic substitution of Cp2Sn. Two mechanisms are plausible, (i) a concerted (one-step) η5Sn2 type mechanism or (ii) an associative (two-step) mechanism. The structure of I can be interpreted in terms of the more probable associative pathway. In the initial step, addition of nucleophiles (RM) occurs at the Sn centre forming an intermediate [CpRSm(μ-Cp)M] similar to 1. In the subsequent step CpM is produced by breaking the weak Cp-.. Sn contact and producing Cp(RM).
the complex into two fragments [Fig. 2(a)]. The dissociative equilibrium constant for this process is ca. 0.04 mol dm$^{-3}$ ($\Delta G^\circ \text{ ca. } 7.4$ kJ mol$^{-1}$). The identities of these two fragments are largely confirmed by $^1$H NMR (250 MHz) studies of I in toluene [Fig. 2(b)]. At low concentration (ca. 0.03 mol dm$^{-3}$) and at 25 °C, two Cp resonances for (Me$_3$Si)$_2$N (A $\delta$ 0.18 and B $\delta$ 0.42; total 18 H) and two Cp (C $\delta$ 6.92 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 °C) at this concentration, the resonance at $\delta$ 0.18 can be assigned to 2 and that at $\delta$ 0.42 to undissociated I (observed ratio ca. 1.5 : 1). The (Me$_3$Si)$_2$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 $\delta$ 6.91 can be assigned to undissociated I 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 °C.

At higher concentrations the Cp resonances merge into a broad singlet (<0.07 mol dm$^{-3}$) and a sharp singlet is finally observed (ca. 0.2 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 (η$^5$-C$_5$)$_2$Sn(μ-η$^5$-C$_5$)Na-pmdeta, involving dissociation of I into Cp$_2$(Me$_3$Si)$_2$NSn$^-$ and Li-pmdeta$^+$ cannot be completely ruled out. However, the low energy for dissociation of 1 and the observation of two very distinct Cp and (Me$_3$Si)$_2$N resonances even at 25 °C supports the assertion that dissociation occurs at the apparently weaker Sn$^-$-(μ-Cp) contact in I rather than at the (μ-Cp)···Li contact, so giving two species in which very different ligand environments are present.

We gratefully acknowledge the SERC (D. S. W., M. A. P., C. A. R.), the Associated Octel Co. Ltd., Ellesmere Port, UK (D. S. W., M. A. P.), the Royal Society (D. S. W.) and the Nuffield Foundation (D. S. W.). We also thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (D. S.).

Received, 11th May 1993; Com. 302683C

References

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