

**A Model Intermediate for the Nucleophilic Substitution of $(\text{Cp})_2\text{Sn}$;
Synthesis and Structure of $(\text{Cp})(\text{Me}_3\text{Si})_2\text{NSn}(\mu\text{-Cp})\text{Li}\cdot\text{pmdeta}$
[Cp = C_5H_5 , 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 Cp_2Sn and 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 Cp_2Sn .

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.¹⁻⁶ The metal centres within these species accept weak nucleophiles such as Cp^- and produce a range of complexes containing anionic organometallic frag-

ments.¹⁻⁴ However, more potent nucleophiles, such as imino anions and organometallics, substitute the Cp ligands of Cp_2E (E = Sn or Pb).^{5,6} Thus reaction of $\text{LiN}=\text{C}(\text{NMe}_2)_2$ with Cp_2Sn (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.⁵ We have proposed that the major

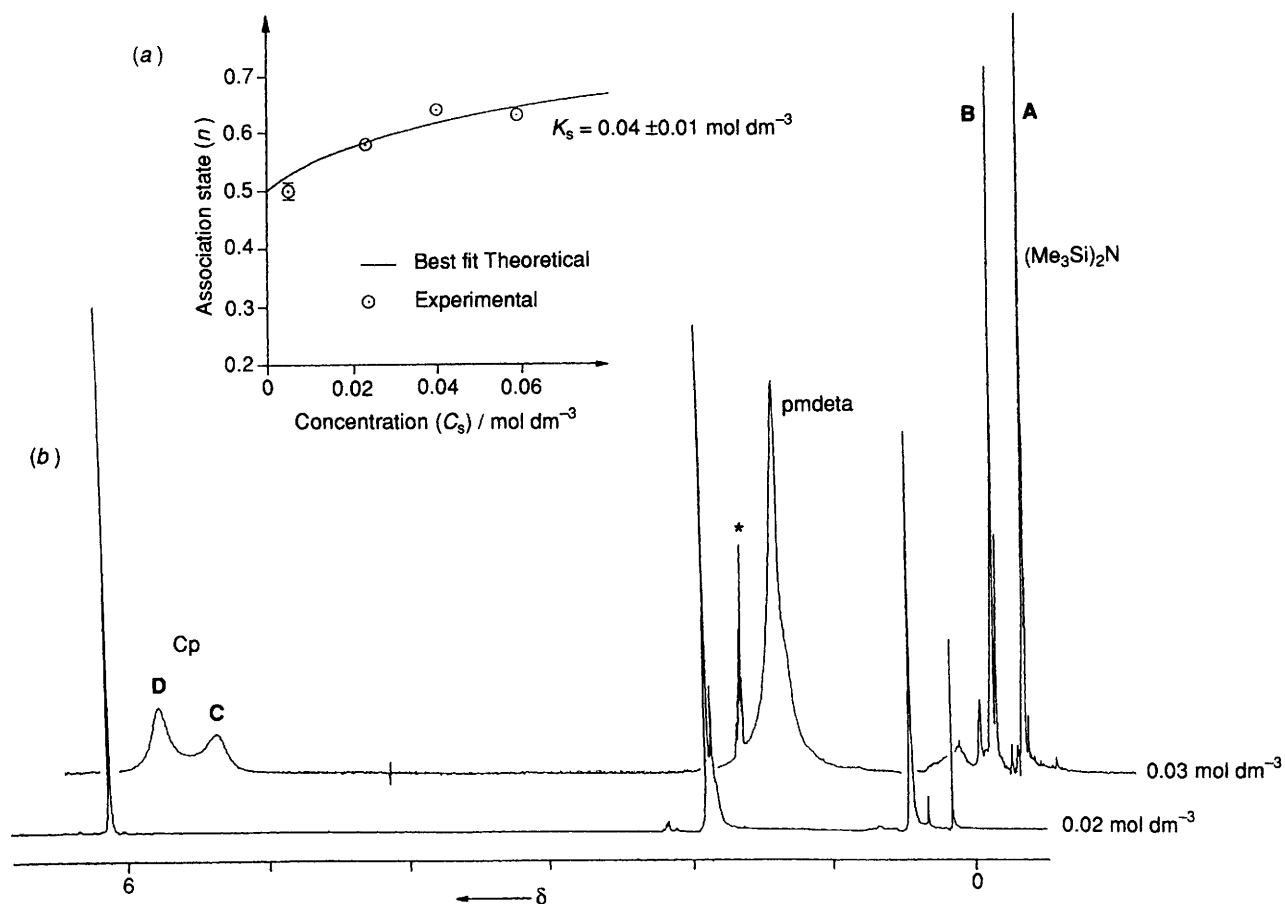


Fig. 2 (a) Variation of degree of association (n) with concentration of **1** in benzene (C_s): (—) best fit theoretical, \circ experimental, $K_s = 0.04 \pm 0.01 \text{ mol dm}^{-3}$; (b) variable-concentration ^1H NMR spectroscopy of **1** in toluene (25°C , 250 MHz)

the complex into two fragments [Fig. 2(a)].[¶] The dissociative equilibrium constant for this process is *ca.* 0.04 mol dm^{-3} (ΔG° *ca.* 7.4 kJ mol^{-1}). The identities of these two fragments are largely confirmed by ^1H NMR (250 MHz) studies of **1** in toluene [Fig. 2(b)]. At low concentration (*ca.* 0.03 mol dm^{-3}) and at 25°C , two Me resonances for $(\text{Me}_3\text{Si})_2\text{N}$ (A δ 0.18 and B 0.42; total 18 H) and two Cp (C δ 5.92 and D δ 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 δ 0.18 can be assigned to **2** and that at δ 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 δ 5.91 can be assigned to undissociated **1** and that at δ 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 ($<0.07 \text{ mol dm}^{-3}$) 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 (δ 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.¹ 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°C ¹ 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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[¶] 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 mol dm^{-3}), 0.63 ($0.059 \text{ mol dm}^{-3}$).