

Reactions of Group 14 metallocenes with lithiated primary amines;
alternative pathways in the formation of the primary tris(amido)stannate
[(MANH)Sn(NHMA)₂Li·2THF] **1** and the cubanes [E(NCy)]₄ (E = Sn **2**,
Pb **3**; MA = (2-MeO)C₆H₄, Cy = C₆H₁₁)¹

Robert E. Allan, Michael A. Beswick^{*}, Maxwell K. Davies, Paul R. Raithby,
Alexander Steiner, Dominic S. Wright^{*}

Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, UK

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Abstract

Two alternative reaction pathways have been identified in the nucleophilic substitution reactions of Group 14 metallocenes with lithiated primary amines [RNHLi]. These are exemplified by the syntheses and structures of the tris(amido)stannate [(MANH)Sn(μ -NHMA)₂Li·2THF] **1**, obtained by the reaction of [(MA)NHLi] with [Cp₂Sn] (MA = 2-MeOC₆H₄), and the cubanes [E(NCy)]₄ (E = Sn **2**, Pb **3**; Cy = C₆H₁₁), prepared from [CyNHLi] and [Cp₂E]. The latter furnishes a new route to Group 14 imido cubanes. © 1998 Elsevier Science S.A.

1. Introduction

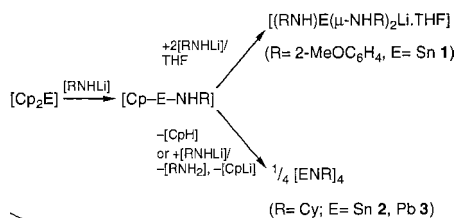
We have recently employed Group 14 metallocenes [Cp₂E] (E = Sn, Pb) as versatile precursors in the synthesis of a range of low valent organometallic and metallo-organic complexes [1–11]. The weak Cp[−] nucleophile undergoes addition to the metal centres in these species, giving a family of homologous anions of general formulae [Cp_(2n+1)E_n][−] [1–4]. Nucleophilic substitution of the Cp ligands occurs with stronger imino (R₂C=N[−]), amido (R₂N[−]) and organometallic anions, resulting in a variety of neutral and anionic complexes [2,5–11]. For example, monosubstitution of [Cp₂Sn] with [(Me₂N)₂C=NLi] gives the dimer [CpSn{ μ -N=C(NMe₂)₂}₂][−] [5] whereas the tris(imino)stannates [E{ μ -N=C(Bu^t)Ph}₃Li·THF] are formed with [LiN=C(Bu^t)Ph] and [Cp₂E] (E = Sn, Pb) [6,8]. A particular focus of our most recent studies has been the synthesis of imido p-block metal complexes

(containing RN^{2−} groups) [12]. The low-temperature reactions of [Sn(NMe₂)₂] with primary amines (RNH₂) furnish a simple and general route to imido Sn(II) cubanes [SnNR]₄ [13]. In view of use of the latter as precursors to Sn(II) imido and phosphinine anions [14] we have endeavoured to extend this route to imido Pb(II) cubanes. However, the intrinsic instability and poor solubility of the Pb(II) dimethylamido species make these unsuitable as precursors [15] and this has led us to investigate alternative strategies to Group 14 imido compounds.

We report here our first investigations of the interaction of lithiated primary amines [RNHLi] with [Cp₂E] and the observation of two possible reaction pathways. These are exemplified by the reaction of [(MA)NHLi] (MA = 2-MeOC₆H₄) with [Cp₂Sn] (3:1 equivalents) in THF, producing the primary tris(amido)stannate [(MANH)Sn(μ -HNMA)₂Li·2THF] **1**, and the reactions of [CyNHLi] with [Cp₂E] in THF or toluene, producing the imido cubanes [ENCy]₄ (E = Sn **2**, E = Pb **3**) (see Section 3). Clearly, complex **1** results from the substitution of the two Cp ligands of [Cp₂Sn] followed by addition of a third [MANH][−] anion. This reaction

^{*} Corresponding authors.

¹ Dedicated to Professor Ken Wade on the occasion of his 65th birthday.



Scheme 1.

pathway is the same as that observed in the formation of $[\text{Li}(\text{THF})_4]^+[\text{Sn}(\mu^1\text{-Fl})_3]^-$ (Fl = fluoren-1-yl), $[\text{E}\{\text{N}=\text{C}(\text{Bu}^t)\text{Ph}\}_3\text{Li}\cdot\text{THF}]$ (E = Sn, Pb) [6,8], and $[\text{Pb}(2\text{-Py})_3\text{Li}\cdot\text{THF}]$ (2-Py = 2-pyridyl) [11] (Scheme 1). Although a range of possible intermediates may be present in the reactions producing **2** and **3**,² their formation is most readily conceived as occurring from initial nucleophilic substitution of one of the Cp ligands of $[\text{Cp}_2\text{E}]$ by $[\text{CyNH}]^-$, producing $[\text{CyNH-E-Cp}]$. The cubanes may then result from intramolecular elimination of CpH or by intermolecular deprotonation with another equivalent of $[\text{CyNHLi}]$ followed by elimination of $[\text{CpLi}]$ (Scheme 1).

Previously Veith and co-workers have shown that Sn(II) and Pb(II) imido cubanes can be prepared by the reactions of $[\text{E}(\text{Bu}^t\text{N})_2\text{SiMe}_2]$ with primary amines at room temperature or above [17–19]. This route allows the formation of complexes containing RN^{2-} dianions which are not stabilised by conjugation within the organic groups (R), e.g. $[\text{ENBu}^t]_4$. The method developed by Power and co-workers, involving the reactions of $[\text{E}\{\text{N}(\text{SiMe}_3)_2\}_2]$ with more acidic primary amines (at 50 °C in the melt) or borylamines (in hexane at reflux), [20] is more restricted in that only cubanes containing conjugatively stabilised RN^{2-} can be incorporated (i.e. R = 2,6-Pr₂C₆H₃ or {2,4,6-Me₃C₆H₂}₂B). As noted earlier, although the reactions of $[\text{Sn}(\text{NMe}_2)_2]$ with primary amines afford Sn(II) imido cubanes at low temperature ($\leq 20^\circ\text{C}$), this method is restricted to Sn owing to the unsuitability of the Pb(II) dimethylamido reagents [15]. The mode of reaction identified for **2** and **3**, which has not previously been observed, provides a new route to Group 14 imido cubanes. The nucleophilic substitution of $[\text{Cp}_2\text{E}]$ with $[\text{RNHLi}]$ is an extremely simple and cheap way by which complexes of this type can be prepared. As with Veith's method it allows 'unstabilised' RN^{2-} groups, in which there is no conjugative stabilisation within the organic group (R), to be incorporated.

² Some indication of other possible intermediates involved in the formation of these cubanes is given from recent studies of the reactions of $[\text{Sn}(\text{NMe}_2)_2]$ with $[\text{RNH}_2]$ in which stepwise metallation of a series of intermediates of various nuclearities is involved; see Ref. [16].

2. Results

Low-temperature (153 K) X-ray crystallographic studies of **1** and **3** were undertaken. The crystal structure of **2**, prepared by the reaction of $[\text{CyNH}_2]$ with $[\text{Sn}(\text{NMe}_2)_2]$, was reported by us previously [13]. Details of the structural refinements of both complexes are listed in Table 1, while their atomic coordinates and thermal isotropic displacement parameters are given in Tables 2 and 3. Selected bond lengths and angles for **1** and **3** are included in Tables 4 and 5 respectively.

Complex **1** adopts the ion-contacted structure $[(\text{MANH})\text{Sn}(\mu\text{-NHMA})_2\text{Li}\cdot 2\text{THF}]$ in the solid state (Fig. 1). The complex is constructed from the association of the primary tris(amido)stannate $[\text{Sn}(\text{NHMA})_3]^-$ anion with a bis-THF solvated Li^+ cation, resulting in the formation of a planar SnN_2Li ring. As expected, the attachment of two of the amido N centres of the stannate to the Li atom (av. $\text{Li-N}(1,2)$ 2.05 Å and Sn-N-Li 90.0°) elongates the bridging Sn–N bonds compared to that made with the terminal amido group (av. $\text{Sn}(1)\text{-N}(1,2)$ 2.174 Å; cf. $\text{Sn}(1)\text{-N}(3)$ 2.118 Å). However, there are no resulting angular distortions within the tris(amido)stannate anion and the N–Sn–N angles (av. 86.4°) are identical within the crystallographic error. The compressed pyramidal geometry of this anion is typical of those observed in a range of triorganostannates (e.g. $[\text{Sn}\{\text{N}=\text{C}(\text{Bu}^t)\text{Ph}\}_3\text{Li}\cdot\text{THF}]$, av. N–Sn–N

Table 1
Crystal data and structure solutions of **1** and **3**^a

Empirical formula	$\text{C}_{31.5}\text{H}_{44}\text{LiN}_3\text{O}_5\text{Sn}$	$\text{C}_{24}\text{H}_{44}\text{N}_4\text{Pb}_4$
<i>M</i>	670.33	1217.39
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C_2/c
Crystal size (mm ³)	0.6 × 0.5 × 0.2	0.1 × 0.1 × 0.1
<i>a</i> (Å)	8.4493(3)	19.600(4)
<i>b</i> (Å)	26.60(1)	9.560(2)
<i>c</i> (Å)	14.322(5)	16.796(3)
β (deg)	95.13(4)	113.59(3)
<i>U</i> (Å ³)	3206(2)	2884(1)
<i>Z</i>	4	4
<i>D</i> _c (Mg m ⁻³)	1.389	2.804
θ range (deg)	4.08–22.50	4.02–22.52
Reflections collected	4245	1942
Independent reflections	4148	1876
Goodness of fit	1.046	1.096
Max., min. transmission	0.986, 0.600	0.941, 0.200
<i>R</i> indices ($F > 4\sigma(F)$) ^b	0.065, 0.148	0.055, 0.142
(reflections)	(4143)	(1874)
<i>R</i> indices (all data)	0.095, 0.188	0.065, 0.157
Final difference peak and hole (e ⁻ Å ⁻³)	1.374, –2.385	3.303, –2.644

^a Details in common: $\lambda(\text{Mo K}\alpha) = 0.71073$ Å; $T = 153(2)$ K.

^b $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{0.5}$, $w = 1 / [\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2) / 3$ [28].

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**

	x	y	z	U_{eq}^a
Sn(1)	1737(1)	1969(1)	3647(1)	26(1)
Li(1)	-1091(17)	1474(5)	2628(10)	20(3)
N(1)	1130(9)	1692(3)	2235(6)	25(2)
O(1)	1626(9)	1769(3)	403(5)	37(2)
C(11)	2016(12)	1321(4)	1807(7)	27(2)
C(12)	2660(13)	910(4)	2314(8)	36(3)
C(13)	3526(14)	548(4)	1883(8)	42(3)
C(14)	3784(14)	585(4)	970(9)	46(3)
C(15)	3165(13)	991(4)	430(8)	37(3)
C(16)	2272(12)	1361(4)	851(7)	31(2)
C(17)	2011(16)	1859(5)	-539(8)	51(3)
N(2)	-563(9)	1682(3)	3977(5)	23(2)
O(2)	-2702(8)	1885(2)	5209(5)	32(2)
C(21)	-701(11)	1358(3)	4737(7)	22(2)
C(22)	202(12)	925(4)	4877(7)	29(2)
C(23)	25(13)	600(4)	5615(7)	34(3)
C(24)	-1032(13)	715(4)	6253(7)	35(3)
C(25)	-1953(13)	1142(4)	6162(7)	34(3)
C(26)	-1805(12)	1461(4)	5415(7)	26(2)
C(27)	-3985(14)	1977(5)	5786(8)	44(3)
N(3)	504(10)	2634(3)	3213(6)	29(2)
O(3)	-1444(8)	3355(3)	2523(5)	33(2)
C(31)	1017(12)	3135(3)	3327(7)	26(2)
C(32)	2474(12)	3277(4)	3729(7)	28(2)
C(33)	2923(13)	3773(4)	3823(7)	34(3)
C(34)	1906(11)	4144(4)	3511(6)	25(2)
C(35)	428(13)	4019(4)	3062(7)	34(3)
C(36)	-23(13)	3521(4)	2968(7)	32(2)
C(37)	-2508(14)	3722(4)	2095(9)	45(3)
O(4)	-1725(9)	825(3)	2116(5)	36(2)
C(41)	-1862(14)	828(4)	1110(8)	39(3)
C(42)	-1183(19)	337(5)	817(10)	67(4)
C(43)	-1394(21)	11(6)	1594(11)	77(4)
C(44)	-1400(16)	325(4)	2450(9)	50(3)
O(5)	-2606(8)	1975(3)	2128(5)	34(2)
C(51)	-4189(12)	1970(4)	2446(8)	37(3)
C(52)	-5047(15)	2389(5)	1937(9)	49(3)
C(53)	-4313(15)	2392(5)	1014(9)	52(3)
C(54)	-2659(14)	2247(5)	1246(8)	47(3)
O(1T)	-4156(26)	-72(8)	3969(15)	36(5)
C(1T)	-4215(32)	406(9)	4267(19)	61(7)
C(2T)	-5578(40)	445(10)	4877(25)	87(10)
C(3T)	-5499(55)	-66(12)	5337(29)	131(15)
C(4T)	-4673(43)	-359(11)	4614(24)	83(10)

^a U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

88.0° [6,8]). Presumably, in order to minimise steric confrontation with the terminal MANH group, the two bridging amido groups of **1** adopt a cisoid orientation

Table 4

Selected bond lengths (Å) and angles (deg) for complex **1**

Sn(1)–N(3)	2.118(8)	Sn(1)–N(1)	2.169(8)	Sn(1)–N(2)	2.179(8)
Li(1)–N(2)	2.02(2)	Li(1)–N(1)	2.09(2)	Li(1)–O(4,5)	1.941 (av.)
N(3)–Sn(1)–N(1)		86.6(3)	N(3)–Sn(1)–N(2)		86.1(3)
N(1)–Sn(1)–N(2)		86.7(3)	Sn(1)–N(1,2)–Li(1)		90.0 (av.)
N(2)–Li(1)–N(1)		93.1(7)	O(4)–Li(1)–O(5)		108.7(8)

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**

	x	y	z	U_{eq}^a
Pb(1)	508(1)	962(1)	3642(1)	15(1)
Pb(2)	-837(1)	3486(1)	2650(1)	14(1)
N(1)	-713(9)	1106(18)	2610(10)	17(4)
N(2)	419(8)	3360(16)	3449(10)	11(3)
C(11)	-1274(10)	205(20)	2706(12)	15(4)
C(12)	-1276(12)	409(24)	3615(14)	25(5)
C(13)	-1896(12)	-464(23)	3698(14)	24(5)
C(14)	-1813(15)	-2005(28)	3535(17)	42(6)
C(15)	-1795(12)	-2187(26)	2653(14)	31(5)
C(16)	-1179(13)	-1309(24)	2553(15)	28(5)
C(21)	747(12)	4275(23)	4195(14)	24(5)
C(22)	1604(10)	4219(21)	4614(12)	16(5)
C(23)	1954(11)	5291(22)	5322(13)	21(5)
C(24)	1689(12)	6748(24)	5057(15)	25(5)
C(25)	833(12)	6787(25)	4724(15)	30(5)
C(26)	478(12)	5786(23)	3964(14)	26(5)

^a U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

with respect to the SnN_2Li ring. Although the structure of **1** is similar to that observed for $[\text{Bu}_2\text{Pb}(\mu\text{-PBu}_2)_2\text{Li} \cdot 2\text{TTHF}]$, where the tris(phosphido)stannate anion is attached to the Li^+ cation by two phosphido groups [21], amido stannates have rarely been structurally elucidated (for example see Ref. [22]) and **1** is the first structurally characterised primary tris(amido)stannate.

The X-ray crystallographic study of **2** shows that the complex has the cubane structure $[\text{PbNCy}]_4$ in the solid state (Fig. 2). The structure confirms the very different outcome of the reaction of $[\text{Cp}_2\text{Pb}]$ compared to that seen in the formation of **1**. Although the Pb–N bond lengths are almost identical (range 2.29(2)–2.33(2) Å) and the average angles about the Pb (av. 81.2°) and N centres (av. 98.6°) are very similar to those found in the Sn(II) analogue $[\text{SnNCy}]_4$ **3** (av. N–Sn–N 80.8° and av. Sn–N–Sn 98.5°) [13], there are significant distortions within the core of **1**. Unlike the Sn(II) complex, the $[\text{Pb(1)N(1)Pb(1a)N(1a)}]$ and $[\text{Pb(2)N(2)Pb(2a)N(2a)}]$ dimer units of the cubane are butterfly-shaped (the Pb atoms being distorted out of the planes along their $\text{N} \cdots \text{N}$ vectors by ca. 6.6°). Similar distortion of the Pb_4N_4 core occurs in the only other structurally characterised imido Pb(II) cubane $[\text{PbN(2,6-Pr}_2\text{C}_6\text{H}_3)_4]$ [20].

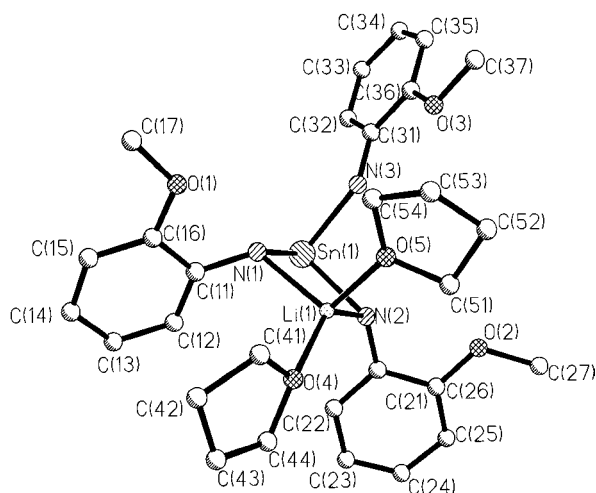


Fig. 1. Molecular structure of **1**. Hydrogen atoms, except those bonded to N, and the lattice-bound disordered half-molecule of THF have been omitted for clarity. Selected bond lengths and angles are given in Table 4.

The fact that **2** and **3** are formed irrespective of whether a coordinating or non-coordinating solvent is used in these reactions (toluene or THF) and regardless of the stoichiometry (1 or 3 equiv. of [CyNHLi] to each of [Cp₂E]), illustrates that the different reaction pathways observed between **1**, and **2** and **3** are not dependent on the potential solvation of the alkali metal cation (observed in the structure of **1**) or on the ratio of reactants employed. In view of the uncertainty concerning the exact nature of the intermediates involved in the formation of **2** and **3**, it is difficult to provide definitive reasons for the different outcomes of these reactions. However, the formation of these complexes can be interpreted in terms of the way in which further reaction of [Cp–E–NHR] (a likely common intermediate in the formation of the primary tris(amido) stannate and imido cubanes (Scheme 1)) may be governed by the steric bulk and/or basicity of [RNHLi]. Not only are sterically bulky substituents, such as Cy, accommodated most readily into a cubane structure which minimises steric congestion, but also in this case [RNH][–] will be a better base and a worse nucleophile. Thus, intramolecular elimination of CpH from [Cp–E–NHR] or its deprotonation by [RNH][–] followed by elimination of [CpLi] should be encouraged where sterically bulky

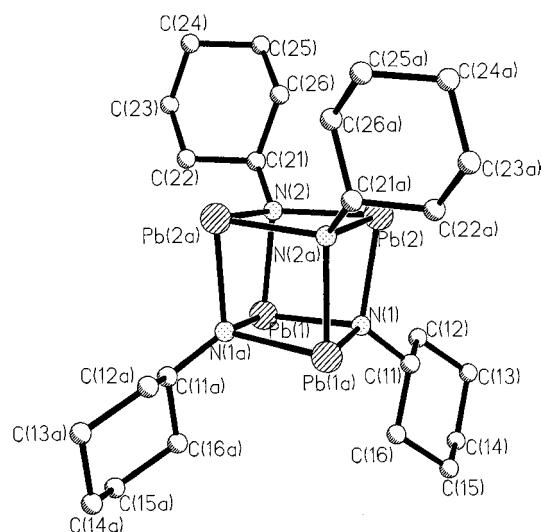


Fig. 2. Molecular structure of **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are given in Table 5.

organic groups (R) are present, leading to the formation of cubanes. For less sterically demanding groups, such as 2-MeOC₆H₄[–], substitution of the second Cp should become the favoured pathway.

3. Experimental section

3.1. General experimental

The products **1**, **2** and **3** and the starting materials [Cp₂Sn] and [Cp₂Pb] are all air sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques and under dry O₂-free Ar [23]. [Cp₂Sn] and [Cp₂Pb] were prepared in the manner described in the literature and purified by sublimation (0.1 atm, 125 °C for [Cp₂Sn] and 140 °C for [Cp₂Pb]) [24,25]. (**Important safety notice**—extreme care should be taken in disposing of the black residue formed after sublimation. Sudden air-exposure can lead to spontaneous ignition followed by explosion (as does addition of strong acids). Do not attempt to fight the fire.) The toluene and thf solvents were dried using sodium-benzophenone and degassed prior to the reactions, and the amines (CyNH₂ and (MA)NH₂) were dried using

Table 5
Selected bond lengths (Å) and angles (deg) for complex **3**^a

Pb(1)–N(1a)	2.30(2)	Pb(1)–N(2)	2.31(2)	Pb(1)–N(1)	2.33(2)
Pb(2)–N(2)	2.29(2)	Pb(2)–N(1)	2.29(2)	N(2)–Pb(2a)	2.30(2)
Pb(1) ⋯ Pb(2)	3.469(1)	Pb(1) ⋯ Pb(2a)	3.474(1)	Pb(1) ⋯ Pb(1a)	3.545(2)
Pb(2) ⋯ Pb(2a)	3.512(2)				
Pb(2)–N(2a)–Pb(2a)		99.9(6)	N(2)–Pb(2)–N(2a)		79.8(6)
N(2)–Pb(2)–N(1)		82.1(6)	Pb(2)–N(1)–Pb(1)		97.3(6)

^a Symmetry transformations used to generate equivalent atoms 1a; $-x, y, -z + \frac{1}{2}$.

molecular sieves (13 ×). All compounds were isolated and characterised with the aid of an argon-filled glove box (Miller–Howe) fitted with oxygen- and water-recirculation systems. Melting points were determined by using a conventional apparatus and sealing samples in capillaries under Ar. Infrared spectra were recorded as Nujol mulls (NaCl windows) on a Perkin–Elmer Paragon 1000 spectrometer and ¹H NMR spectra were obtained using a Bruker WH 250 MHz spectrometer in dry C₆D₆ and (CD₃)₂S=O (using the solvent resonances as the internal reference).

3.1.1. Synthesis of **1**

H₂N(MA) (0.74 g, 6 mmol) in THF (20 ml) was reacted with BuⁿLi (4.0 ml, 1.5 mol dm⁻³, 6 mmol) at 0 °C. To the yellow solution of the lithiate was added [Cp₂Sn] (2.5 ml, 0.8 mol dm⁻³ in THF, 2 mmol) at room temperature. The reaction mixture was briefly heated to reflux (changing to a more intense yellow colour) and the solvent was reduced in vacuo to ca. 8 ml, whereupon a yellow solid precipitated. The solid was redissolved by heating gently and storage at room temperature (24 h) gave a crop of yellow crystalline blocks of **1**. The low-temperature X-ray structure of **1** shows that the complex has the formula [(HMA)Sn(μ-HMA)₂Li · 2THF] · 0.5THF. The half-molecule of THF in the lattice is removed when the complex is placed under vacuum (ca. 15 min, 10⁻¹ atm) during isolation. The following analytical and spectroscopic data refer to the dry amorphous powder produced; yield 0.98 g (77%); m.p. 226 °C; IR (Nujol), ν_{max}/cm⁻¹ = 3327 (w., N–H str), 1588 (m., C=C str), 1223 (s., C–O str), 734 (s., o-substituted Ph ring); ¹H NMR (+25 °C, 250 MHz, (CD₃)₂SO), δ = 6.67 (3H, d.d., C(3)–H), 6.55 (3H, d.d., C(6)–H), 6.46 (3H, t.d., C(4)–H), 6.09 (3H, t.d., C(5)–H), 3.72 (3H, s., N–H), 3.64 (9H, s., MeO), 3.57 (24H, m., THF), 1.73 (24H, m., THF). Analyses, calc. C 54.7, H 6.3, N 6.6, found C 53.4, H 6.3, N 6.4.

3.1.2. Synthesis of **2**

To a suspension of [CyNHLi], produced in situ by the reaction of [CyNH₂] (1.15 ml, 5 mmol) with BuⁿLi (3.35 ml, 5 mmol, 1.5 mol dm⁻³ in hexanes) in toluene (30 ml), was added [Cp₂Sn] (5 mmol, 2.7 ml, 1.85 mol dm⁻³ in THF). An immediate reaction occurs, with the precipitation of a white solid and the formation of a golden yellow solution. After being brought to reflux (2 min), the solid was filtered off (Celite, porosity 3) to give a clear solution. The solvent was reduced under vacuum to ca. 15 ml, with the formation of a precipitate. This was heated gently into solution. Storage at 20 °C (12 h) gave large cubic crystals of **2** (0.42 g (39%)). Elemental analysis (C, H, N), m.p. and ¹H NMR data are in accord with [SnNCy]₄ [5].

3.1.3. Synthesis of **3**

To a solution of [Cp₂Pb] (1.5 g, 4.5 mmol) in toluene (20 ml) was added a suspension of [CyNHLi] prepared by the reaction of [CyNH₂] in toluene (10 ml) with BuⁿLi in hexanes. The mixture was brought to reflux (5 min) after which all the white [CyNHLi] had dissolved and a yellow/orange solution had formed. The solution was filtered (Celite) and reduced in volume until a yellow precipitate was observed the precipitate was gently warmed back into solution. Storage at room temperature for several hours yielded yellow blocks of **3**; yield 0.68 g (50%); decomp. slowly > 230 °C; IR (Nujol), ν_{max}/cm⁻¹ = 1300(m), 1064(s), 971(m), 887(m), 801(w); ¹H NMR (+25 °C, 250 MHz, C₆D₆), δ = 1.1–2.5 (br. overlapping multiplets, Cy). Analyses, calc. C 23.6, H 3.6, N 4.6, found C 23.5, H 3.6, N 4.6.

3.2. X-ray crystallography

Crystal of complexes **1** and **3** were mounted directly from solution at room temperature under Ar using a perfluorocarbon oil which protects them from atmospheric moisture and oxygen (Reidel–deHaën). The oil ‘freezes’ at reduced temperatures and holds the crystal static in the X-ray beam [26]. Data were collected on a Stoe AED diffractometer, and a semi-empirical absorption correction based on ψ-scans was employed. The structures were solved by the direct method (SHELXTL PLUS) [27] and refined by full-matrix least squares of *F*² (SHELXL 93) [28]. The lattice-bound THF solvent molecule of **1** was modelled using distance restraints. The H atoms were fixed geometrically in both structures. Details of the structure solutions and refinements for **1** and **3** are listed in Table 1.

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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