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# Nucleophilic addition to a Sn(II) imido cubane, $[SnNR]_4$; a new route to heteroleptic stannates

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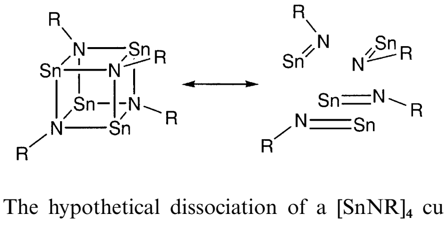
***Received 3rd May 2002, Accepted 8th July 2002***
***First published as an Advance Article on the web 12th August 2002***

Nucleophilic addition to Sn(II) imido cubanes provides a novel route to heteroleptic stannates, as exemplified by the formation of $[\{Sn(NHmmp)(O^tBu)_2\}K\cdot thf]_2$ (**2**) and $[\{Sn(MeNCH_2CH_2NMe)(NHmmp)\}Li]_\infty$ (**3**) from the *in situ* reactions of the imido Sn(II) cubane $[Sn(Nmmp)]_4$ (**1**) (mmp = 2-MeO-6-$MeC_6H_3$) with $^t$BuOK and $[MeN(Li)CH_2CH_2(Li)NMe]$. This pathway demonstrates that Sn(II) imido cubanes can act as synthons for their aza-stannylene constituents, RN=Sn:.

## Introduction

Sn(II) imido cubanes, $[SnNR]_4$, were first investigated by Veith in the early 1980s.[1] These species can be readily prepared by the reactions of bases [such as $Me_2Si(NMe)_2Sn$,[1] $Sn\{N(SiMe_3)_2\}_2$[2] and $Sn(NMe_2)_2$[3]] with primary amines ($RNH_2$) and the reactions of $RNH^-$[4] or $RN^{2-}$[5] anions with sources of Sn(II). Until recently, it appeared that such cubanes were chemically robust. For example, the reactions of $[SnNR]_4$ (R = $^t$Bu or $SiMe_3$) with metal salts or transition metal carbonyls result in coordination of the Sn(II) lone-pairs to the metal centres, with no breakdown of the $Sn_4N_4$ cores occurring.[6] The only known reactions in which breakdown of the $Sn_4N_4$ core occurs are those involving alkali metal primary amides and phosphides (R′EHM, E = N, P; M = alkali metal).[7] It was reported earlier, however, that the presence of $Sn(O^tBu)_2$ during the formation of the cubane $[SnN^tBu]_4$ gives $[\{SnN^tBu\}_2\{(O^tBu)_2Sn\}]$, in which the dimeric constituents of the cubane, $[SnN^tBu]_2$, have been intercepted.[8] More recently we have observed that the stability of the cubane core can depend on the organic substituent (R).[9] For example, addition of $[Sn(NMe_2)_2]$ to the *intact* cubane $[Sn(Nmmp)]_4$ (**1**) (mmp = 2-MeO-6-$MeC_6H_3$) results in the co-complex $[\{Sn(Nmmp)\}_2\{(Me_2N)_2Sn\}]$, again containing an apparently 'trapped' dimer unit. This intriguing observation has prompted us to wonder to what extent (as Veith had first suggested) the cubanes $[SnNR]_4$ can be regarded as oligomeric aza-stannylenes, [:Sn=NR] (Scheme 1).



**Scheme 1** The hypothetical dissociation of a $[SnNR]_4$ cubane into monomers.

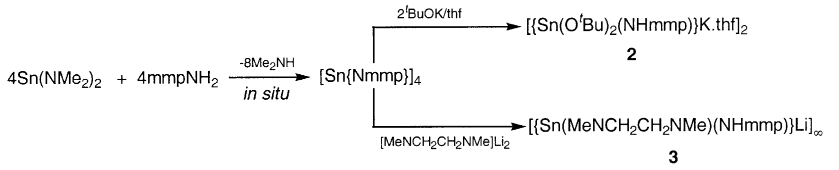
We report here that the cubane **1** readily undergoes addition reactions with mono- and di-nucleophiles, leading to fragmentation of the $Sn_4N_4$ core and the formation of heteroleptic stannates. This new reaction illustrates that imido Sn(II) cubanes of this type can behave as synthons for the stannylene monomer.

## Results and discussion

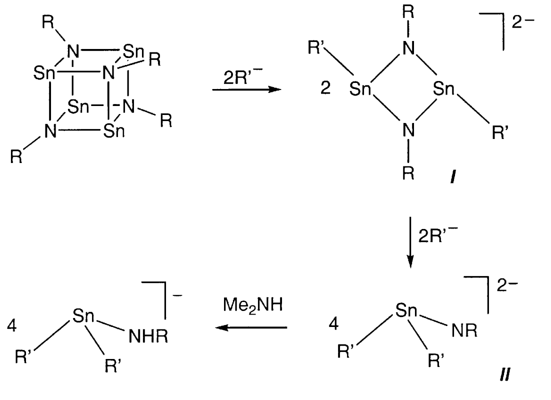
In light of the ability of $[Sn(Nmmp)]_4$ (**1**) to coordinate a $Sn(NMe_2)_2$ monomer unit within the structure of $[\{Sn(Nmmp)\}_2\{(Me_2N)_2Sn\}]$,[9] it was decided to investigate the reactions of **1** with a range of nucleophiles. The reactions of **1** with $^t$BuOK (1 equiv.) and $MeN(Li)CH_2CH_2N(Li)Me$ (1 equiv.)[10] both occur smoothly in thf, giving the products $[\{Sn(NHmmp)(O^tBu)_2\}K\cdot thf]_2$ (**2**) (79% based on Sn) and $[\{Sn(MeNCH_2CH_2NMe)(NHmmp)\}Li]_\infty$ (**3**) (14%), respectively (Scheme 2). For convenience, **1** was prepared by the *in situ* reaction of $Sn(NMe_2)_2$ with $mmpNH_2$ (1 : 1 equiv.),[4] prior to reaction with the mono- and di-nucleophiles. The initial choice of this procedure proved fortunate since later attempts to obtain the same products from the reactions of isolated samples of **1** with the same nucleophiles were unsuccessful. The reason for this failure became clear from $^1H$ and IR spectroscopic studies of **2** and **3**. These reveal the presence of NHmmp groups in both complexes, resulting presumably from the protonation of the imido group ($mmpN^{2-}$) by $Me_2NH$ [generated as a byproduct in the formation of **1** from $Sn(NMe_2)_2$ with $mmpNH_2$]. Preliminary analytical and spectroscopic investigations also showed that the $K^+$ ions of **2** are solvated by a thf ligand whereas the $Li^+$ cations of **3** are not solvated in this manner.

The formation of **2** and **3** corresponds formally to nucleophilic addition to the Sn centre of the stannylene mmpN=Sn: (see Scheme 1). However, it is unlikely that this stannylene has any *real* existence in solution. Studies of the reactions of $Sn(NMe_2)_2$ with sterically demanding primary amines suggest that the formation of $Sn_4N_4$ cubanes occurs through a series of oligomers rather than *via* oligomerisation of stannylenes.[11] We believe that a more plausible mechanism for the formation of **2** and **3** therefore involves step-wise breakdown of the $Sn_4N_4$ cubane core of **1** (as illustrated in Scheme 3). Attempts to explore the mechanism of the reaction using *in situ* $^{119}Sn$ NMR spectroscopic studies proved inconclusive. It should be noted that **2** can also be prepared in much reduced yield (15%) by the reaction of a mixture of $Sn(NMe_2)_2$ and $^t$BuOK (1 : 2 equiv.)

DOI: 10.1039/b204340h



**Scheme 2** The reactions producing **2** and **3**.



**Scheme 3** A plausible mechanism for nucleophilic addition to the cubane core.

with $NH_2mmp$ in thf. We believe that this reaction probably also occurs *via* **1**, which is formed rapidly in the reaction of $Sn(NMe_2)_2$ with $mmpNH_2$ even at low temperatures. In view of the fact that **2** was obtained using the 1 : 1 : 1 reaction of $Sn(NMe_2)_2$, $mmpNH_2$ and $^tBuOK$ (the reaction actually requiring a 1 : 1 : 2 stoichiometry), we reasoned that the use of a more sterically demanding alkoxide may allow us to trap an intermediate of type ***I*** in Scheme 3. However, no reactions occur between **1** and the sterically demanding aryloxides MesOLi and Mes*OLi (Mes = 2,4,6-$Me_3C_6H_2$, Mes* = 2,4,6-$^tBu_3C_6H_2$) and only the cubane **1** or the lithium alkoxide complexes could be isolated. This suggests that these nucleophiles are simply too sterically bulky to allow approach at the Sn(II) centres of **1**.

Low-temperature (180 K) X-ray crystallographic studies were undertaken on **2** and **3**. Details of the data collections and refinements are presented in Table 3, with key bond lengths and angles for **2** and **3** being listed in Tables 1 and 2, respectively.

Molecules of **2** consist of centrosymmetric dimers, of formula $[\{Sn(NHmmp)(O^tBu)_2\}K{\cdot}thf]_2$ (**2**), which result from the association of two $[Sn(NHmmp)(O^tBu)_2]^-$ stannate ions with two thf-solvated $K^+$ cations (Fig. 1). Metal coordination by the stannate ions using their N and two O centres (as well as by thf) results in a cage structure containing a central $K_2O_2$ ring, possessing a very distorted six-coordinate geometry for the $K^+$ cations [O–K–O and N–K–O range 62.46(5)–153.83(6)°]. The

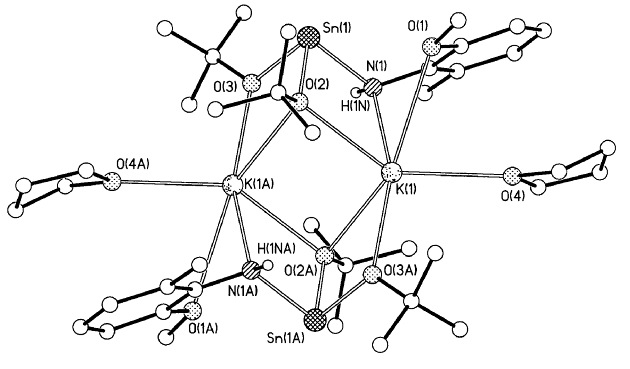


**Fig. 1** Structure of centrosymmetric dimer molecules of **2**.

**Table 1** Key bond lengths (Å) and angles (°) for $[\{Sn(NHmmp)(O^tBu)_2\}K{\cdot}thf]_2$ (**2**)[a]

| | | | |
|---|---|---|---|
| Sn(1)–O(3) | 2.082(2) | K(1)–O(2) | 2.734(2) |
| Sn(1)–O(2) | 2.086(2) | K(1)–O(2A) | 2.890(2) |
| Sn(1)–N(1) | 2.154(2) | K(1)–O(3A) | 2.688(2) |
| K(1)–O(1) | 3.075(2) | K(1)–O(4) | 2.799(2) |
| K(1)–N(1) | 2.905(2) | | |
| N(1)–Sn(1)–O(2) | 90.89(8) | O(2)–K(1)–O(2A) | 93.47(5) |
| N(1)–Sn(1)–O(3) | 83.82(8) | O(2)–K(1)–O(4) | 143.05(7) |
| O(2)–Sn(1)–O(3) | 88.08(7) | O(2A)–K(1)–O(4) | 121.65(7) |
| N(1)–K(1)–O(2) | 64.70(6) | O(2)–K(1)–O(3A) | 110.22(6) |
| N(1)–K(1)–O(4) | 100.68(7) | O(2A)–K(1)–O(3A) | 62.46(5) |
| N(1)–K(1)–O(1) | 52.10(6) | O(4)–K(1)–O(3A) | 97.17(7) |
| N(1)–K(1)–O(2A) | 91.03(6) | Sn(1)–N(1)–K(1) | 97.48(8) |
| N(1)–K(1)–O(3A) | 153.83(6) | Sn(1)–O(3)–K(1A) | 107.70(7) |
| O(1)–K(1)–O(2) | 70.20(6) | Sn(1)–O(2)–K(1) | 104.65(7) |
| O(1)–K(1)–O(2A) | 143.04(6) | Sn(1)–O(2)–K(1A) | 100.81(6) |
| O(1)–K(1)–O(4) | 74.29(7) | K(1)–O(2)–K(1A) | 86.53(5) |
| O(1)–K(1)–O(3A) | 153.83(6) | | |

[a] Symmetry transformations used to generate equivalent atoms labelled A: $-x, -y, -z + 2$.

**Table 2** Key bond lengths (Å) and angles (°) for $[\{Sn(MeNCH_2CH_2NMe)(NHmmp)\}Li]_\infty$ (**3**)[a]

| | | | |
|---|---|---|---|
| Sn(1)–N(1) | 2.213(2) | Li(1)–N(1) | 2.065(5) |
| Sn(1)–N(2) | 2.147(2) | Li(1)–N(3) | 2.043(5) |
| Sn(1)–N(3) | 2.156(2) | Li(1)–O(1) | 2.080(5) |
| Sn(1) ··· Li(1A) | 3.278(5) | Li(1)–N(2B) | 2.023(5) |
| N(1)–Sn(1)–N(2) | 91.19(9) | O(1)–Li(1)–N(3) | 103.4(2) |
| N(1)–Sn(1)–N(3) | 86.70(8) | Li(1)–N(1)–Sn(1) | 85.4(2) |
| N(2)–Sn(1)–N(3) | 81.11(8) | Li(1)–N(3)–Sn(1) | 87.4(2) |
| N(1)–Li(1)–O(1) | 77.6(2) | Sn(1)–N(2)–Li(1A) | 103.6(2) |
| N(1)–Li(1)–N(3) | 93.8(2) | | |

[a] Symmetry transformations used to generate equivalent atoms labelled A: $-x + 3/2, y + 1/2, -z + 3/2$; B: $-x + 3/2, y - 1/2, -z + 3/2$.

most closely related complexes to **2** are the dimeric, trisalkoxystannates $[\{Sn(O^tBu)_3\}_2M_2]$ (M = Li, Na).[12] In **2**, N(1) and O(3) bond to the two separate, symmetry related, $K^+$ ions, with bridge bonding of O(2) forming the central $K_2O_2$ ring. A similar metal-coordination mode by the three O centres of the stannate ions in $[\{Sn(O^tBu)_3\}_2M_2]$ (M = Li, Na) leads to the same type of core structure. However, unlike the heavier alkali metal complexes containing the $[Sn(O^tBu)_3]^-$ ligand, $[\{Sn(O^tBu)_3\}M]_\infty$ (M = K, Rb, Cs), where polymerisation of the dimer units occurs, the MeO/N chelation of the mmpNH group to the $K^+$ cations (as well as thf-solvation) ensures that a molecular structure is retained for **2**.

The pyramidal geometry of the $[Sn(NHmmp)(O^tBu)_2]^-$ stannate ions of **2** [with O–Sn–O and N–Sn–O angles of 83.82(8)–90.89(8)°] is symptomatic of the presence of a stereochemically active lone-pair on Sn(II). The noticeable compression of N(1)–Sn(1)–O(3) [83.82(8)°] well below 90° results primarily from the bonding of N(1) and O(3) to the separate $K^+$ cations of the central $K_2O_2$ ring unit. However, there are no obvious associated effects on the Sn–O [mean 2.084(2) Å] and Sn–N [Sn(1)–N(1) 2.154(2) Å] bond lengths within the stannate anion, which are typical of those previously observed for N and O bonds to three-coordinate Sn(II).[13] In particular, the

**Table 3** Crystal data and structural refinements for [{Sn(NHmmp)(O$^t$Bu)$_2$}K·thf]$_2$ (**2**) and [{Sn(MeNCH$_2$CH$_2$NMe)(NHmmp)}Li]$_\infty$ (**3**)

| Compound$^a$ | **2** | **3** |
|---|---|---|
| Empirical formula | $C_{40}H_{72}K_2O_8N_2Sn_2$ | $C_{12}H_{17}LiN_3OSn$ |
| Formula weight | 1024.58 | 344.92 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| $a$/Å | 11.9548(3) | 9.3386(2) |
| $b$/Å | 12.5067(4) | 9.7200(3) |
| $c$/Å | 16.5675(5) | 17.1794(6) |
| $\beta$/° | 92.344(2) | 97.946(2) |
| $V$/Å$^3$ | 2475.02(13) | 1544.42(8) |
| $Z$ | 2 | 4 |
| $\rho_{calc}$/Mg m$^{-3}$ | 1.375 | 1.483 |
| Independent reflections ($R_{int}$) | 4347 (0.035) | 3505 (0.046) |
| $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.028$, $WR2 = 0.068$ | $R1 = 0.028$, $WR2 = 0.070$ |
| $R$ indices (all data) | $R1 = 0.037$, $WR2 = 0.073$ | $R1 = 0.038$, $WR2 = 0.075$ |

$^a$ Data in common; $\lambda = 0.71073$ Å; $T = 180(2)$ K.

mean Sn–O bond lengths in **2** are similar to those found in the solid-state structure of [{Sn(O$^t$Bu)$_3$}K]$_\infty$ (mean 2.067 Å).[12] Although the range of K–O bond lengths found in **2** [2.688(2)–3.075(2) Å] is comparatively large, these distances are within the values found previously in K alkoxides and for donor-type K–O bonds.[14] The K(1)–N(1) bond length [2.905(2) Å] is also typical of K amides.[14]

The solid-state structure of **3** is that of a polymer composed of [{Sn(MeNCH$_2$CH$_2$NMe)(NHmmp)}Li] monomer units (Fig. 2a) which aggregate *via* N–Li bonding (Fig. 2b). Like **2**, the range of angles about the Sn(II) centre of the [Sn(MeNCH$_2$CH$_2$NMe)(NHmmp)]$^-$ anion is fairly typical of structurally characterised stannates [for **3**, N–Sn–N range 81.11(8)–91.19(9)°]. The most acute N–Sn–N angle is N(2)–Sn(1)–N(3), reflecting the small ligand bite of the Sn-chelating [MeNCH$_2$CH$_2$NMe] diamide. The Li$^+$ cations within each monomer unit of **3** are bonded to the [Sn(MeNCH$_2$CH$_2$NMe)(NHmmp)]$^-$ anion by *one* of the anionic N centres of the chelating [MeNCH$_2$CH$_2$NMe] group [N(3)–Li(1) 2.043(5) Å], and the anionic N [N(1)–Li(1) 2.065(5) Å] and neutral MeO [O(1)–Li(1) 2.080(5) Å] centres of the mmpNH group. The four-coordinate, pseudo-tetrahedral geometry of the Li$^+$ cations is completed by inter-monomer bonding with the *second* N centre of the chelating [MeNCH$_2$CH$_2$NMe] diamide ligand of an adjacent molecule [Li(1)–N(2B) 2.023(5) Å], an interaction which is responsible for the formation of a polymeric structure for **3**. The overall structure of polymeric strands of **3** is that of a helical chain formed by the association of molecules related by the crystallographic 2$_1$ axis (Fig. 2b). Adjacent chains, related by inversion symmetry, consist of the opposite enantiomers. This arrangement has a similar connectivity to that found for [{Sn(NMe$_2$)$_3$}Li]$_\infty$ in the solid state.[15]

Apart from providing unambiguous proof of the success of the addition reactions of $^t$BuOK and [MeNCH$_2$CH$_2$NMe]Li$_2$ to the cubane **1**, the structures of **2** and **3** also possess several novel features. Perhaps most importantly, to our knowledge, these are the first structurally characterised heteroleptic stannates. The closest representative of this type to be reported previously is [Cp$_2$SnN(SiMe$_3$)$_2$Li·PMDETA].[16] However, although formally containing the heteroleptic [Cp$_2${(Me$_3$Si)$_2$N}Sn]$^-$ anion, this is better regarded as a 'loose-contact' complex between Cp$_2$Sn and LiN(SiMe$_3$)$_2$ (into which it dissociates significantly in solution). A further noteworthy feature of **3** is the first observation of a chelating, dianionic substituent within a stannate anion.

The new synthetic approach reported here should provide access to a broad range of new heteroleptic stannates. A future aim of these studies will be to explore the potential for attack of metal-based nucleophiles in the synthesis of transition metal/Sn(II) clusters, *e.g.*, mono-nucleophiles such as [(CO)$_5$Mn]$^-$ and di-nucleophiles such as [(CO)$_4$Fe]$^{2-}$. A particular future prospect is the observation of alkene-like, [Sn=NR], isonitrile-like, [Sn$^-$≡N$^+$R], and butadiene-like, [SnNR]$_2$, fragments within these systems.

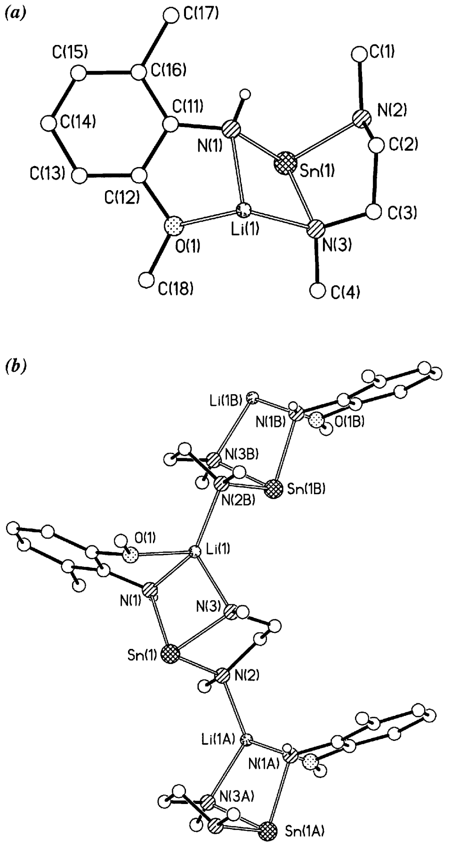


**Fig. 2** (a) Structure of monomer units of **3**, and (b) propagation of the polymer chain along the crystallographic 2$_1$ axis parallel to the *b*-axis of the unit cell.

## Experimental

### General

Compounds **1**–**3** are air- and moisture-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques and under dry/oxygen-free argon.[17] Toluene and thf were dried by distillation over sodium/benzophenone prior to the reactions. The products were isolated and characterized with the aid of a nitrogen-filled glove box fitted with a Belle Technology O$_2$ and H$_2$O internal recirculation system. Sn(NMe$_2$)$_2$ was prepared using the literature procedure, from the reaction of anhydrous SnCl$_2$ with a suspension of LiNMe$_2$

in $Et_2O$.[18] The amine 2-methoxy-6-methylaniline ($mmpNH_2$) and $MeN(H)CH_2CH_2N(H)Me$ were acquired from Aldrich and were used as supplied. Melting points were not corrected. Elemental analyses were performed by first sealing the samples under argon in air-tight aluminium boats (1–2 mg) and C, H and N content was analysed using an Exeter Analytical CE-440 Elemental Analyser. Proton NMR spectra were recorded on a Bruker AM 400 MHz spectrometer in dry deuterated DMSO (using the solvent resonances as the internal reference standard).

### Synthesis of 2

**Method A.** A solution of **1** (1.0 mmol) was prepared by the reaction of 2-methoxy-6-methylaniline (0.88 ml, 8.0 mmol) with $Sn(NMe_2)_2$ (1.66 g, 8.0 mmol) in thf (40 ml) at −78 °C. The suspension of **1** produced after warming to room temperature was dissolved by gentle heating. The solution was added to a solution of $^t$BuOK (0.90 g, 8.0 mmol) in thf (20 ml) at −78 °C. The reaction was brought to room temperature and a small quantity of insoluble white precipitate was removed by filtration (Celite, P3). The solvent volume was reduced to less than 10 ml and the golden brown solution was stored at −5 °C. Colourless crystalline blocks of **2** grew after 7–14 days. Yield 1.62 g (79% based on Sn). Mp 112–114 °C to a brown oil. IR (Nujol, NaCl), $\nu$/cm$^{-1}$ = 3355(w) (N–H str.), other bands at 1205(s), 1073(s), 940(s), 838(m), 733(s). $^1$H NMR ($D_6$-DMSO, +25 °C, 400.129 MHz), $\delta$ = 6.65 [d, $J$ = 4 Hz, 1H, C(3)–H of mmp group], 6.57 [d, $J$ = 4 Hz, 1H, C(5)–H of mmp group], 6.45 [dd, $J$ = 4 Hz, 1H, C(4)–H], 5.34 (s., 1H, N–H), 3.74 (s, 3H, 2-MeO), 3.60 (m, *ca.* 3H, thf), 2.06 (s, 3H, 6-Me), 1.76 (m, *ca.* 3H, thf), 1.17 (s, 18H, $^t$BuO). Elemental analysis, found C 44.9, H 6.3, N 2.8; calc., for **2**·thf, C 45.4, H 6.8, N 2.9%.

**Method B.** 2-Methoxy-6-methylaniline (0.4 ml, 4.0 mmol) was added to a solution of $Sn(NMe_2)_2$ (0.83 g, 4.0 mmol) and $^t$BuOK (0.45 g, 4.0 mmol) in thf (40 ml) at −78 °C, producing a pale yellow solution. The reaction was brought to room temperature and a small quantity of insoluble white precipitate was removed by filtration (Celite, P3). The solvent volume was reduced to less than 10 ml and the golden brown solution was stored at −5 °C. Colourless crystalline blocks of **2** grew after 7 days. Yield 0.18 g (15% based on Sn).

### Synthesis of 3

A solution of **1** (1.0 mmol) was prepared by the reaction of 2-methoxy-6-methylaniline (0.4 ml, 4.0 mmol) with $Sn(NMe_2)_2$ (0.83 g, 4.0 mmol) in thf (20 ml) at −78 °C. The suspension of **1** produced after warming to room temperature was heated gently into solution. This solution was added to a solution of $MeN(Li)CH_2CH_2N(Li)Me$ (4.0 mmol) at −78 °C [prepared previously by the reaction of $MeNHCH_2CH_2NMe$ (0.4 ml, 4.0 mmol) with $^n$BuLi (5.2 ml, 1.5 mol dm$^{-3}$, 8.0 mmol) in thf (20 ml)]. The reaction mixture was brought to room temperature and stirred for 2 h. A small quantity of insoluble precipitate was then removed by filtration (Celite, P3), and the solvent volume reduced to *ca.* 20 ml. Colourless crystalline blocks of **3** were formed after storage at −5 °C (24 h). Yield 0.20 g (14%). Decomp. to a black solid 193 °C. IR (Nujol, NaCl), $\nu$/cm$^{-1}$ = 3584(w), 3482(w), 3391(w) (N–H str.), other bands at 1238(m), 1170(m), 1093(s), 1068(s), 1018(s), 780(s), 758(m), 726(s). $^1$H NMR ($D_6$-DMSO, +25 °C, 400.129 MHz), $\delta$ = 6.55–6.40 [m (overlapping doublets), 3H, aromatic C–H], 3.51 (s, 3H, MeO), 2.24 (s, 4H, $CH_2CH_2$), 2.06 (s, 3H, Me–N), Elemental analysis, found C 41.2, H 5.8, N 12.0; calc., for **3**, C 41.4, H 5.8, N 12.1%.

### X-Ray crystallographic studies of 2 and 3

Crystals of **2** and **3** were mounted directly from solution under argon using an inert oil which protects them from atmospheric oxygen and moisture.[19] X-Ray intensity data for both complexes were collected using a Nonius Kappa CCD diffractometer. Details of the data collections and structural refinements are given in Table 3. The structures were solved by direct methods and refined by full-matrix least squares on $F^2$.[20]

CCDC reference numbers 185248 and 185249.

See http://www.rsc.org/suppdata/dt/b2/b204340h/ for crystallographic data in CIF or other electronic format.

## Acknowledgements

We garefully acknowledge the EPSRC (A. D. B., E. A. H., G. T. L.) and Ministrerio de Ciencia y tecnologia (Acciones Integradas HB1999-009) (M. E. G. M.) for financial support. We also thank Dr J. E. Davies for collecting X-ray data.

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