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Nucleophilic addition to a Sn(II) imido cubane, [SnNR]4; a new route to heteroleptic stannates

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Nucleophilic addition to Sn(II) imido cubanes provides a novel route to heteroleptic stannates, as exemplified by the formation of [{Sn(NHmmp)(O^{t}Bu)$_2$}K·thf]$_2$ (2) and [{Sn(MeNCH$_2$CH$_2$NMe)(NHmmp)}Li]$_\infty$ (3) from the *in situ* reactions of the imido Sn(II) cubane [Sn(Nmmp)]$_4$ (1) (mmp = 2-MeO-6-MeC$_6$H$_3$) with ^{t}BuOK and [MeN(Li)CH$_2$CH$_2$(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$_2$Si(NMe)$_2$Sn,[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$_4$N$_4$ cores occurring.[6] The only known reactions in which breakdown of the Sn$_4$N$_4$ 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^{t}Bu)$_2$ during the formation of the cubane [SnN^{t}Bu]$_4$ gives [{SnN^{t}Bu}$_2${(O^{t}Bu)$_2$Sn}], in which the dimeric constituents of the cubane, [SnN^{t}Bu]$_2$, 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$_6$H$_3$) results in the co-complex [{Sn(Nmmp)}$_2${(Me$_2$N)$_2$Sn}], 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).
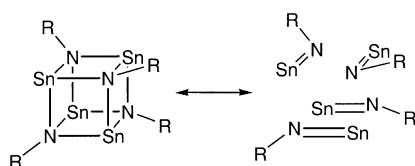
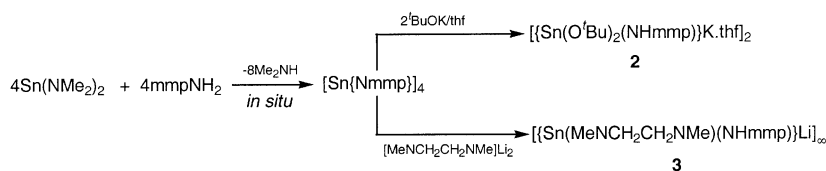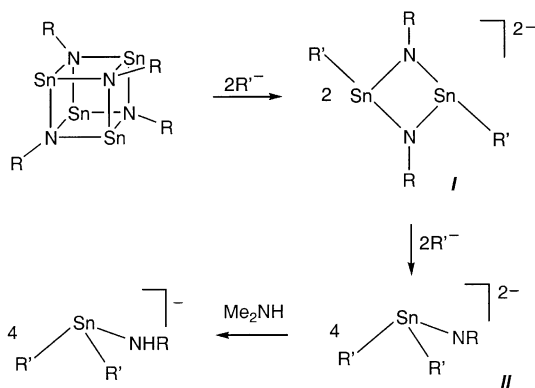**Scheme 1** The hypothetical dissociation of a [SnNR]$_4$ cubane into monomers.

We report here that the cubane 1 readily undergoes addition reactions with mono- and di-nucleophiles, leading to fragmentation of the Sn$_4$N$_4$ 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$_2$N)$_2$Sn}],[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$_2$CH$_2$N(Li)Me (1 equiv.)[10] both occur smoothly in thf, giving the products [{Sn(NHmmp)(O^{t}Bu)$_2$}K·thf]$_2$ (2) (79% based on Sn) and [{Sn(MeNCH$_2$CH$_2$NMe)(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 ^{1}H 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$_2$NH [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$_4$N$_4$ 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$_4$N$_4$ 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.)

$$4Sn(NMe_2)_2 + 4mmpNH_2 \xrightarrow[\textit{in situ}]{-8Me_2NH} [Sn\{Nmmp\}]_4$$

$$[Sn\{Nmmp\}]_4 \xrightarrow{2^tBuOK/thf} [\{Sn(O^tBu)_2(NHmmp)\}K.thf]_2 \quad \textbf{2}$$

$$[Sn\{Nmmp\}]_4 \xrightarrow[[MeNCH_2CH_2NMe]Li_2]{} [\{Sn(MeNCH_2CH_2NMe)(NHmmp)\}Li]_\infty \quad \textbf{3}$$

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

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

with NH$_2$mmp 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 ^{t}BuOK (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$_3$C$_6$H$_2$, Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) 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^{t}Bu)$_2$}K·thf]$_2$ (**2**), which result from the association of two [Sn(NHmmp)(O^{t}Bu)$_2$]$^-$ stannate ions with two thf-solvated K$^+$ cations (Fig. 1). Metal coordination by the
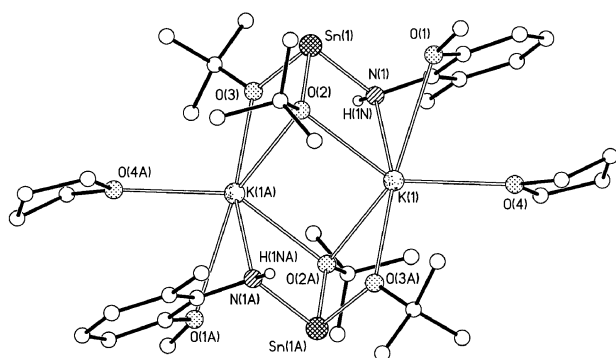
Fig. 1 Structure of centrosymmetric dimer molecules of **2**.

stannate ions using their N and two O centres (as well as by thf) results in a cage structure containing a central K$_2$O$_2$ 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

Table 1 Key bond lengths (Å) and angles (°) for [{Sn(NHmmp)-(O^{t}Bu)$_2$}K·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$_2$CH$_2$-NMe)(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) $\cdots$ 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^{t}Bu)$_3$}$_2$M$_2$] (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$_2$O$_2$ ring. A similar metal-coordination mode by the three O centres of the stannate ions in [{Sn(O^{t}Bu)$_3$}$_2$M$_2$] (M = Li, Na) leads to the same type of core structure. However, unlike the heavier alkali metal complexes containing the [Sn(O^{t}Bu)$_3$]$^-$ ligand, [{Sn(O^{t}Bu)$_3$}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^{t}Bu)$_2$]$^-$ 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$_2$O$_2$ 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$_2$O$_8$N$_2$Sn$_2$	C$_{12}$H$_{17}$LiN$_3$OSn
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)
β/°	92.344(2)	97.946(2)
V/Å^3	2475.02(13)	1544.42(8)
Z	2	4
ρ_{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(Me-NCH$_2$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 pro-
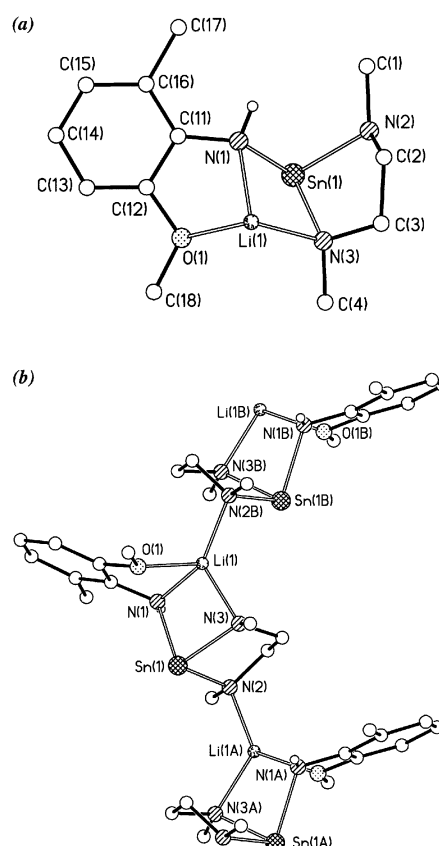
Fig. 2 (a) Structure of monomer units of **3**, and (b) propagation of the polymer chain along the crystallographic 2$_1$ axis parallel to the *b*-axis of the unit cell.

spect is the observation of alkene-like, [Sn=NR], isonitrile-like, [Sn$^-$≡N$^+$R], and butadiene-like, [SnNR]$_2$, fragments within these systems.

Experimental

General

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$_2$CH$_2$N(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), v/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), δ = 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$_2$CH$_2$N(Li)Me (4.0 mmol) at −78 °C [prepared previously by the reaction of MeNHCH$_2$CH$_2$NMe (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), v/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), δ = 6.55–6.40 [m (overlapping doublets), 3H, aromatic C–H], 3.51 (s, 3H, MeO),

2.24 (s, 4H, CH$_2$CH$_2$), 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.

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