Syntheses and Structures of $[Sn\{NR\}_2\{Sn(\mu\text{-}NMe_2)\}_2]$: Model Intermediates in the Formation of Imido Group 14 Cages and Rings [R = 2,6-$Pr^i{}_2C_6H_3$ (Dipp), 2,4,6-$Me_3C_6H_2$ (Mes)]

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The 1:1 reactions of aliphatic primary amines $[RNH_2]$ with $[Sn(NMe_2)_2]$ yield the imido Sn(II) cubanes $[SnNR]_4$; however, for highly sterically crowded amines this reaction is retarded and the model intermediates $[Sn\{NR\}_2\{Sn(\mu\text{-}NMe_2)\}_2]$ [R = 2,6-$Pr^iC_6H_3$ (Dipp) (**1**), 2,4,6-$Me_3C_6H_2$ (Mes) (**2**)] can be isolated. The latter indicate that the formation of imido cubanes and trimers from the metalation reactions of primary amines with a range of group 14 precursors may occur via a common reaction sequence involving stepwise metalation. The low-temperature X-ray structures of **1** and **2** show them to have similar $[Sn_3N_4]$ cage arrangements consisting of a planar $\{Sn(NR)_2\}$ unit straddling a $\{Sn(\mu\text{-}NMe_2)\}_2$ ring. No intermolecular association occurs in the solid-state structure of **1**. However, the reduced steric demands of the Mes groups in **2** lead to a complicated three-dimensional network consisting of fused hexameric units linked by Sn···Sn interactions.

Introduction

During recent studies we have shown that the reagent $[Sn(NMe_2)_2]$[1] reacts with a range of aliphatic primary amines [RNH_2; R = Cy (cyclohexyl), Bu^t, CH_2(2-pyridyl)], yielding the imido tin(II) cubanes $[Sn(NR)]_4$.[2] Although several imido tin(II) cubanes have been prepared by a variety of routes,[3] the use of $[Sn(NMe_2)_2]$ allows the facile synthesis of such complexes at low temperature and with relatively nonacidic primary amines in which there is no conjugative stabilization of the resulting imido groups. Further work revealed that acid/base reactions of the cubane $[Sn(NBu^t)]_4$ with monolithiated primary amines and phosphines ([REHLi]; E = N, P) furnish a new route to cage complexes containing tin(II) imido and phosphinidine ligand systems.[4] Thus, cage expansion of $[Sn(NBu^t)]_4$ occurs on reaction with [CyPHLi], giving the metallacyclic tetraanion $[\{Sn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2{}^{4-}$.

We report here that the 1:1 reactions of $[Sn(NMe_2)_2]$ with sterically bulky aromatic amines in toluene can be controlled, giving the heteroleptic imido/amido Sn(II) complexes $[\{Sn(NR)_2\}\{Sn(\mu\text{-}NMe_2)\}_2]$ [R = 2,6-$Pr^i{}_2C_6H_3$ (Dipp) (**1**), 2,4,6-$Me_3C_6H_2$ (Mes) (**2**)]. These species are model intermediates in the formation of imido group 14 trimeric rings, $[ENR]_3$, and cubanes, $[ENR]_4$ (E = Ge−Pb), and their isolation indicates that the formation of such complexes from a variety of reactions occurs through a common sequence of reactions involving stepwise metalation.

Results and Discussion

Initially the 1:1 reactions of $[DippNH_2]$ and $[MesNH_2]$ with $[Sn(NMe_2)_2]$ in toluene were carried out with a view to investigating the influence of sterically demanding substituents (R) on the reactivity of the cubanes $[SnNR]_4$ with lithiated primary amines and phosphines ([R′EHLi]; E = N, P). Previously Power and co-workers have shown that imido Sn(II) cubanes are accessible by the reactions of $[Sn\{N(SiMe_3)_2\}_2]$ with primary amines at 50 °C in the melt, and the cubane $[SnNDipp]_4$ has been prepared by this method.[3d] However, in contrast to the solution reactions of aliphatic primary amines with $[Sn(NMe_2)_2]$ which generate the corresponding cubanes at low temperature, the reactions of $[DippNH_2]$ and $[MesNH_2]$ are incomplete and result in the mixed amido/imido complexes $[\{Sn(NR)_2\}\{Sn(\mu\text{-}NMe_2)\}_2]$ [R = Dipp (**1**), Mes (**2**)] even after brief refluxing (Scheme 1).

The initial stage in the formation of **1** and **2** appears to be the single deprotonation of $[RNH_2]$ by $[Sn(NMe_2)_2]$. The intermediate produced, most likely the dimer $[(RNH)Sn(\mu\text{-}NMe_2)]_2$ in which the least sterically bulky NMe_2 groups are bridging, then undergoes further metalation with $[Sn(NMe_2)_2]$. Only with more extreme conditions do the 1:1 reactions of $[Sn(NMe_2)_2]$ with $[RNH_2]$ proceed to the cubanes $[Sn(NR)]_4$ (e.g., 2.5 days at reflux in toluene for **1**). The most plausible intermediate involved for the conversion of **1** into the latter is $[\{Sn(\mu\text{-}NR)\}_2\{Sn(NHR)_2\}]$ (structurally identical to the previously characterized complex $[\{Sn(\mu\text{-}NBu^t)\}_2\{Sn(NHBu^t)_2\}]$[5]). It is interesting to note that whereas the cubane $[Sn(NDipp)]_4$ is formed by the reaction of $[Sn\{N(SiMe_3)_2\}_2]$ with $[DippNH_2]$, the analogous reaction with $[Ge\{N(SiMe_3)_2\}_2]$ produces the trimer $[Ge(NDipp)]_3$.[3d,6] This can be explained by the reaction of an intermediate analogous to **1** [bearing $N(SiMe_3)_2$ groups instead of NMe_2] with $[DippNH_2]$, terminating the reaction sequence at the trimer. Thus, the isolation of **1** and **2** provides the first indication that the formation of group 14 imido cubanes from metalation reactions of primary amines with various group 14 reagents may proceed via a common sequence of reactions involving stepwise metalation of imido/amido intermediates (Scheme 2). This mechanistic scheme may also have implications in the formation of organooxocubanes and related sulfur compounds.[7] This is in contrast to the established mechanism

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(3) (a) Veith, M.; Schlemmer, G. *Chem. Ber*., **1982**, *115*, 2141. (b) Veith, M.; Recktenwald, O. *Z. Naturforsch., Teil B* **1983**, *38*, 1054. (c) Veith, M.; Grosser, M. *Z. Naturforsch., Teil B* **1982**, *37*, 1375. (d) Chen, H.; Bartlett, R. A.; Dias, H. V.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 3390.
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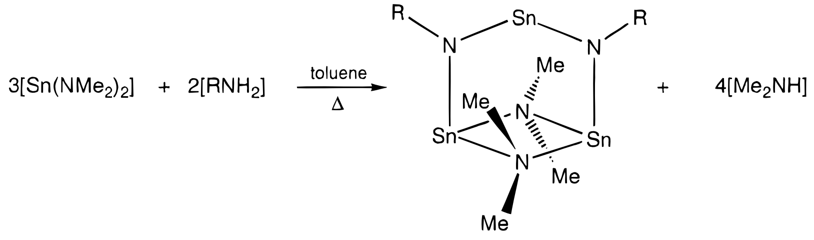
Scheme 1



R= 2,6-Pr^{i}C$_6$H$_4$ (Dipp) (**1**)
2,4,6-Me$_3$C$_6$H$_2$ (Mes) (**2**)

Scheme 2

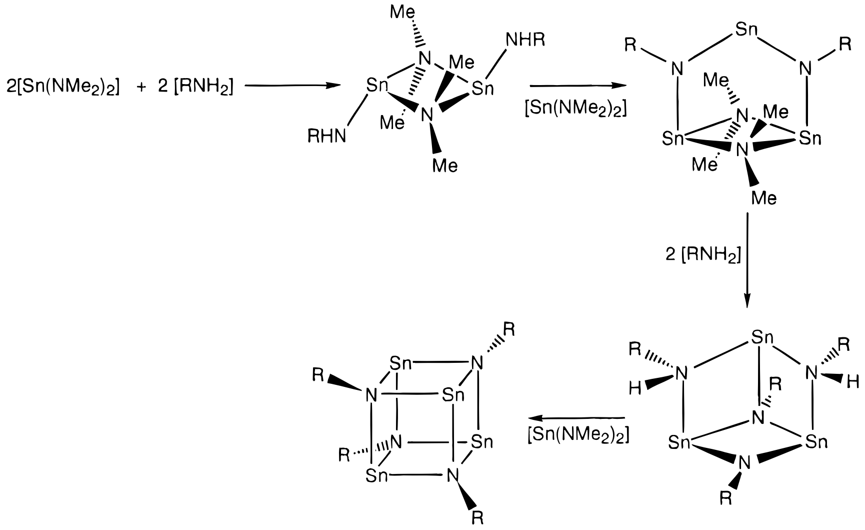


Table 1. Crystal Data for **1** and **2**

	C$_{28}$H$_{46}$N$_4$Sn$_3$	C$_{73}$H$_{110}$N$_{12}$Sn$_9$
formula weight	794.76	2223.94
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	10.582(5)	15.442(4)
b (Å)	13.997(4)	19.919(6)
c (Å)	21.647(7)	15.201(5)
α (deg)	90	103.72(3)
β (deg)	93.67(4)	100.36(2)
γ (deg)	90	69.51(2)
V (Å^3)	3200(2)	4231(2)
Z	4	2
ρ_{calc} (g cm^{-3})	1.650	1.746
μ (cm^{-1})	0.2345	0.2654
T (°C)	120(2)	120(2)
λ (Å)	0.71069	0.71069
R indices [$F > 4\sigma(F)$]^a	R1 = 0.042, $_w$R2 = 0.094	R1 = 0.058, $_w$R2 = 0.103
R indices (all data)	R1 = 0.098, $_w$R2 = 0.146	R1 = 0.126, $_w$R2 = 0.155

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $_wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.[14]

Table 2. Selected Bond Lengths and Angles for [{Sn(NDipp)$_2$}{Sn(μ-NMe$_2$)}$_2$] (**1**)

Bond Lengths (Å)			
Sn(1)−N(1)	2.104(6)	Sn(2)−N(2)	2.067(6)
Sn(1)−N(3)	2.254(7)	Sn(3)−N(2)	2.113(6)
Sn(1)−N(4)	2.272(7)	Sn(3)−N(3)	2.280(7)
Sn(2)−N(1)	2.056(6)	Sn(3)−N(4)	2.280(6)
Bond Angles (deg)			
N(1)−Sn(1)−N(3)	95.0(2)	N(3)−Sn(3)−N(4)	78.0(2)
N(1)−Sn(1)−N(4)	96.6(2)	Sn(2)−N(1)−Sn(1)	134.7(3)
N(3)−Sn(1)−N(4)	78.7(2)	Sn(2)−N(2)−Sn(3)	134.6(3)
N(1)−Sn(2)−N(2)	99.1(2)	Sn(1)−N(3)−Sn(3)	99.1(3)
N(2)−Sn(3)−N(3)	96.0(2)	Sn(1)−N(4)−Sn(3)	98.6(3)
N(2)−Sn(3)−N(4)	94.9(2)		

of formation of [SnNBu^t]$_4$ from the thermolysis of [(Me$_2$Si)(NBu^t)$_3$Sn$_2$], in which oligomerization of the "stannylene" [:Sn−NBu^t] is involved.[8]

Prior to their characterization by X-ray crystallography, complexes **1** and **2** were basically characterized by obtaining their melting points and elemental analyses (C, H, N) and by IR and NMR (^{1}H, ^{13}C, and ^{119}Sn) spectroscopy. In particular, the structural similarity of **1** and **2** and the rigidity of their structures in solution is shown by NMR studies. Two separate Sn environments are found at room temperature for the imido/amido linked centers and the two-coordinate imido Sn center (δ = 706.8 and 1000.8, respectively) for **1**. Owing to restricted rotation of the μ-NMe$_2$ groups, two separate Me resonances occur in the room temperature ^{1}H and ^{13}C NMR spectra of **1** due to the resulting exo and endo Me environments. Similar observations are made in the room temperature ^{1}H NMR spectrum of **2**. The inaccessibility of the NMe$_2$ groups of **1** and **2**, which are buried within the cage arrangement and not made available by fluxional interchange, may explain their resistance to proceed, by further reaction with the primary amines, to the cubanes.

The low-temperature (−120 °C) X-ray structures of **1** and **2** were obtained. Details of the structural refinements of both are given in Table 1. Tables 2 and 3 list selected bond lengths and angles for complexes **1** and **2**, respectively.

The solid-state structures of **1** (Figure 1) and **2** (Figure 2) are similar heteroleptic imido/amido cage complexes, [{Sn-

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Table 3. Selected Bond Lengths and Angles for [{Sn(NMes)$_2$}{Sn(μ-NMe$_2$)}$_2$] (**2**) (Ranges over Three Independent Molecules)

	Bond Lengths (Å)		
Sn(3,6,9)−(imido)N	2.06(1)−2.072(9)	Sn(1,2,4,5,7,8)−NMe$_2$	2.20(1)−2.29(1)
Sn(1,2,4,5,7,8)−(imido)N	2.084(9)−2.12(1)		
	Bond Angles (deg)		
N−Sn(3,6,9)−N	97.9(4)−99.0(4)	Sn−{μ-N(imido)}−Sn	132.8(5)−134.6(5)
(imido)N−Sn−NMe$_2$	93.2(4)−97.9(4)	Sn−(μ-NMe$_2$)−N	97.1(4)−99.1(4)
NMe$_2$−Sn−NMe$_2$	77.3(3)−79.7(3)		

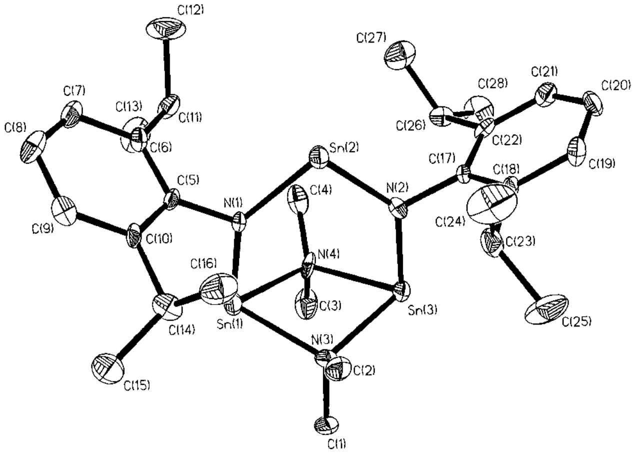

Figure 1. Structure of [{Sn(NDipp)$_2$}{Sn(μ-NMe$_2$)}$_2$] (**1**). Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.

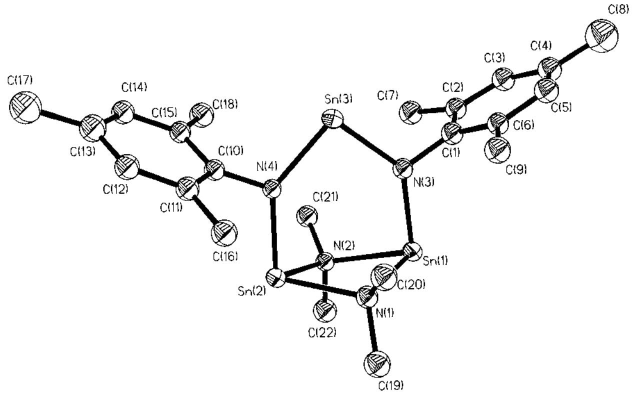

Figure 2. Structure of [{Sn(NMes)$_2$}{Sn(μ-NMe$_2$)}$_2$] (**2**). Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.

(NR)$_2$}{Sn(μ-NMe$_2$)}$_2$], containing seven-membered Sn$_3$N$_4$ cores. There are three independent chemically identical molecules in the asymmetric unit of **2** together with a disordered lattice-bound toluene molecule. Complexes **1** and **2** are constructed from the fusion of {Sn(μ-NMe$_2$)}$_2$ rings with planar {Sn(NR)$_2$} units. The Sn−N bonds within the {Sn(μ-NMe$_2$)}$_2$ rings of both complexes are all of similar lengths [2.254(7)−2.280(7) Å in **1**, 2.10(1)−2.29(1) Å in **2**] that are close to the Sn−N bond lengths in the planar dimeric core of the starting material [Sn(NMe$_2$)$_2$]$_2$ (average 2.27 Å).[1] However, puckering of the {Sn(μ-NMe$_2$)}$_2$ units of **1** and **2** occurs as a result of the attachment of the imido N centers of the {Sn(NR)$_2$} moieties to the Sn atoms of these rings. The Sn−N bonds linking the {Sn(NR)$_2$} groups to the {Sn(μ-NMe$_2$)}$_2$ rings in each complex [Sn(1,3)−N(1,2) average 2.109 Å in **1**, 2.084(9)−2.12(1) Å in **2**] are slightly longer than those found for the Sn centers within the {Sn(NR)$_2$} units [Sn(2)−N(1,2) average 2.061 Å in **1**, Sn(3,6,9)−N 2.06(1)−2.072(9) Å in **2**], reflecting the coordination numbers and connectivities of the Sn(II) centers involved. An unprecedented feature of **1** and **2** is the coordination of the Sn centers within their {Sn(NR)$_2$} units exclusively by only two imido N centers. These are the first examples of such a coordination environment for Sn(II), and as a result of the low coordination number of these Sn centers, the imido-N−Sn interactions involved are the shortest yet observed.[2−6,8,9] In the heptaatomic cage [{SnNBu^t}$_2${Sn(OBu^t)$_2$}], which has a composition similar to that of **1** and **2**, a different structural arrangement is observed in which the Sn(II) centers have three- and four-coordinate geometries.[8]

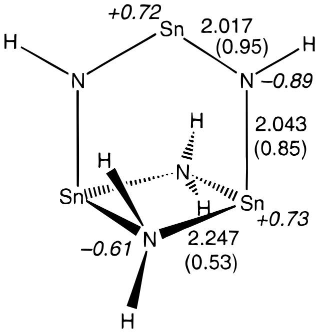

Figure 3. MNDO optimized geometry of [{Sn(NH)$_2$}{Sn(μ-NH$_2$)}$_2$] showing key bond lengths (Å), charges (in italics), and bond orders (in parentheses).

An MNDO optimization of [{Sn(NH)$_2$}{Sn(μ-NH$_2$)}$_2$][10] as a model for **1** and **2** shows a similar pattern of (short, medium, and long) Sn−N bond lengths and similar geometries for the Sn centers compared to those found in both complexes (Figure 3). Significantly, although π-bonding between the vacant p orbital on Sn and the lone pairs of the imido groups might be envisaged within the {Sn(NR)$_2$} units in **1** and **2**, this calculation indicates that no such bonding is involved and the imido-N−Sn bonds to the two-coordinate Sn atom in the calculated structure have identical bond orders close to unity.

The molecular arrangement found in **1** and **2** and the previous model MO calculation suggest that the two Sn(II) environments present will have markedly different donor/acceptor character. The 8e Sn centers within the {Sn(μ-NMe$_2$)}$_2$ units have the greatest donor character while the 6e centers present in the {Sn(NR)$_2$} units, possessing vacant p orbitals, have the greatest acceptor character. This feature is reflected in the pattern of Sn···Sn interactions which link molecules of **2** into a complicated three-dimensional network in the lattice. Intermolecular Sn···Sn interactions occur between one of the Sn atoms of the {Sn(μ-NMe$_2$)$_2$} (formally donor) unit of one molecule and the {Sn(NMes)$_2$} (formally acceptor) unit of a neighboring molecule. The result is the formation of loosely-linked hexameric rings (range 3.54−3.91 Å, average 3.68 Å) (Figure 4) which are connected via Sn···Sn (donor/acceptor and donor/donor type) contacts (range 3.74−3.87 Å) into a system of fused four-, six-, and eight-membered rings. The occurrence of (relativistic) Sn···Sn interactions within the structures of various Sn(II)

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(9) For further examples of imido Sn(II) complexes, see: Veith, V. *Chem. Rev.* **1990**, *90*, 3. Veith, M. *Angew. Chem.* **1987**, *99*, 1; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1 and references therein.

(10) (a) H, N: Dewar, M. J. S. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) Sn: taken from AMPAC2.1. (c) Rauhut, G.; Alex, A; Chaudrasekkar, J.; Steinke, T.; Sauer, W.; Beck, B.; Hutter, M.; Clark, T. *VAMP*; Erlangen, 1995.

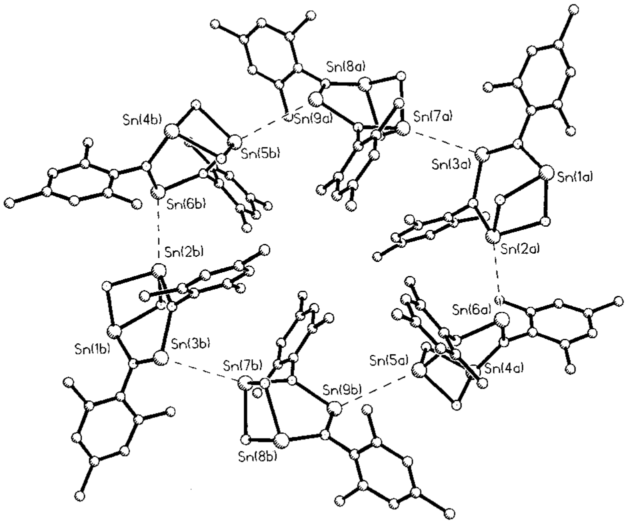

Figure 4. Cyclic association of **2** in the lattice.

compounds is now well established, and intermolecular distances similar to those found in **2** have been observed in imido Sn(II) cubanes (ca. 3.41−4.00 Å) in which sterically undemanding groups (R) are present.[2,3a−c] Despite the potential donor and acceptor nature of the Sn centers of **2**, bearing in mind the distances involved it is unlikely that the Sn···Sn interactions in **2** involve any significant degree of electron transfer, and their nature is probably similar to the nature of interactions occurring in the latter. The greater steric bulk of the Dipp group presumably shields the Sn centers in **1**, which as a result are far more loosely associated than in **2** (the Sn···Sn contacts of ca. 4.40−4.42 Å are close to the value expected for van der Waals interactions).

Complexes **1** and **2** are interesting new precursors for the preparation of novel tin(II) imido complexes. We are investigating the preparation of previously unknown trimeric imido Sn(II) rings $[\{Sn(NR)\}_2Sn(NR')]$ and the formation of heteroleptic cubanes $[\{Sn(NR)\}_2\{Sn(ER')\}_2]$ (E = N, P, As) utilizing these as precursors (R′ being a less sterically bulky group). The reactions of **1** and **2** with lithiated primary amines and phosphines also provides a potential method of synthesis of a new range of polyimido and polyphosphinidine anions.

Experimental Section

General Preparative Techniques. All of the reactions were undertaken under dry, O_2-free argon using a vacuum line and standard inert-atmosphere techniques.[11] THF and toluene were dried by distillation over Na/benzophenone. The 2,6-diisopropylaniline ($DippNH_2$) and 2,4,6-trimethylaniline ($MesNH_2$) were used as supplied after drying with molecular sieves (13X). $[Sn(NMe_2)_2]$ was prepared in the manner described in the literature by the 2:1 reaction of $[Me_2NLi]:SnCl_2$ in Et_2O.[1] Complexes **1** and **2** were isolated and characterized with the aid of a N_2-filled glovebox (Miller-Howe, fitted with a Belle internal circulation system). Melting points were determined using a conventional apparatus and samples sealed in capillaries under N_2. Elemental analyses (C, H, and N) were performed by first sealing samples in air-tight aluminum boats (1−2 mg) prior to analysis using a Perkin-Elmer 240 elemental analyzer. ^1H NMR spectra were recorded on a Bruker WH 250 MHz spectrometer, using the NMR solvents as internal reference standards, and ^{119}Sn and ^{13}C NMR spectra were recorded using a Bruker WH 400MHz spectrometer (relative to the solvent resonances for ^{13}C and to $SnCl_2$ in D_2O for ^{119}Sn).

Synthesis of 1. $[DippNH_2]$ (0.38 mL, 2.0 mmol) was added to a solution of $[Sn(NMe_2)_2]$ (0.620 g, 3.0 mmol) in toluene (15 mL) under argon. On being brought to reflux (5 min) the solution became dark orange. The solution was filtered (Celite) and reduced *in vacuo* until an orange solid precipitated. This was gently warmed back into the solution. Storage (12 h at 25 °C) gave crystalline orange rods of **1** (0.62 g, 78%). For **1**: dec >140 °C to black solid; IR (Nujol), ν_{max}/cm^{-1} *ca.* 3070 (aryl C−H stretch), 1585 (aryl C$\overset{\cdots}{-}$C stretch), other major bands at 1420, 1307, 1226, 1167, 1097, 826, 766, 682; ^1H NMR (250 MHz, d_7-DMF, +25 °C), δ = 6.92 (d, 2H, aryl H(3, 5)), 6.60 (t, 1H, aryl H(4)), 3.02 (sept, 2H, C−H of Pr^i), 2.95 (s, 3H, Me of NMe_2), 2.77 (s, 3H, Me of NMe_2), 1.17 (d, 12H, Me of Pr^i); ^{13}C NMR (100.16 MHz, C_6D_6, +25 °C), δ = 144.7 (aryl C(1)), 128.3 (aryl C(2,6)), 123.5 (aryl C(3,4,5)), 123.1 (aryl C(3,4,5)), 122.8 (aryl C(3,4,5)), 118.9 (aryl C(3,4,5)), 45.1 (NMe_2), 43.3 (NMe_2), 28.3 (C of Pr^i Me), 28.2 (C of Pr^i CH), 25.3 (C of Pr^i Me), 24.6 (C of Pr^i Me), 22.5 (C of Pr^i Me); ^{119}Sn NMR (149.12 MHz, C_6D_6, +25 °C), δ = 1000.8 (1Sn, DippN−Sn−NDipp), 706.8 (2Sn, NDipp−Sn−NMe_2). Anal. Found: C, 40.4; H, 5.8; N, 7.1. Calcd for **1**: C, 42.1; H, 5.8; N, 7.0.

Synthesis of 2. The reaction was carried out in precisely the manner and using the same molar quantities as described for **1** (above). However, the reaction occurs immediately and is completed by bringing to reflux briefly. Reduction of the orange filtrate produced followed by crystallization of the complex (12 h, 25 °C) gave orange cubic crystals of **2**. Although there is one-third of a toluene molecule per formula unit of **2** within the crystal structure, placing the complex under vacuum (0.1 atm, 10 min) removes this solvation. The following data refers to the dry material produced (0.39 g, 55%): dec > 180 °C; IR (Nujol), ν_{max}/cm^{-1} *ca.* 3030 (aryl C−H stretch), 1603 (aryl C$\overset{\cdots}{-}$C stretch), other major bands at 1193, 1139, 1119, 1034, 851, 771, 162; ^1H NMR (250 MHz, C_6D_6, +25 °C), δ = 7.16 (s, 2H, aryl C(3,5)−H), 2.63 (s, 3H, Me of NMe_2), 2.47 (s, 3H, *p*-Me of Mes), 2.38 (s, 6H, *o*-Me of Mes), 2.34 (s, 3H, Me of Me_2N). Anal. Found: C, 38.1; H, 4.8; N, 6.9. Calcd for **2**: C, 37.2; H, 4.8; N, 7.9. Some problems were experienced in obtaining data for the analysis of **2**, probably owing to the retention of trace amounts of lattice solvent in samples.

X-ray Structure Determinations. Crystals were mounted directly from solution under argon using a perfluorocarbon oil which protects them from atmospheric O_2 and moisture.[12] The oil freezes at reduced temperatures and holds the crystal static in the X-ray beam. Data were collected on a Stoe-Siemens AED four-circle diffractometer, and semiempirical absorption corrections based on ψ-scans were employed for all complexes.[13] In **1**, all of the non-hydrogen atoms were refined anistropically. In **2**, only the Sn atoms were refined anisotropically. The toluene molecule in **2** (a third per formula unit) is disordered over two (50:50) sites about a 2-fold axis. The structures of both complexes were solved by direct methods (SHELXTL PLUS) and refined by full-matrix least squares on F^2 (SHELXL-93[14]). Largest difference between peak and hole in the final electron density map: for **1**, 0.959, −1.204 e $Å^{-3}$, and for **2**, 1.663, −1.328 e $Å^{-3}$. Details of the structure refinements for both complexes are shown in Table 1. Atom coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallography Data Centre.

MNDO Calculations. These were performed using the calculational program VAMP on a Silicon Graphics work station.[10] The geometry of $[\{Sn(NH)_2\}\{Sn(\mu\text{-}NH_2)\}_2]$ was fixed in C_{2v} symmetry in which the $\{Sn(NH)_2\}$ unit was restricted to a planar arrangement during refinement.

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Supporting Information Available: For the crystal structures of **1** and **2**, tables of crystal data and structural refinements, anisotropic and isotropic thermal parameters, bond distances and angles, and atomic coordinates (14 pages). Two crystallographic files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

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