

Synthesis and characterization of the unstable primary amido tin(II) dimer $\text{Sn}_2\{\text{N}(\text{H})\text{Dipp}\}_4$ (Dipp = $\text{C}_6\text{H}_3\text{-2,6-Pr}^i_2$) and the first sesqui-amido hemi-chloride derivative $\text{Sn}_2\{\text{N}(\text{H})\text{Dipp}\}_3\text{Cl}$: facile conversion of a primary amide to the imide $(\text{SnNDipp})_4$ †

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The primary tin(II) amido derivatives $\text{Sn}_2\{\text{N}(\text{H})\text{Dipp}\}_4$ (**1**) and $\text{Sn}_2\{\text{N}(\text{H})\text{Dipp}\}_3\text{Cl}$ (**2**) (Dipp = $\text{C}_6\text{H}_3\text{-2,6-Pr}^i_2$) have been prepared and characterized. Compound **1** was obtained by the transamination of $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ with H_2NDipp in a 1 : 2 ratio or by the reaction of two equivalents of $\text{LiN}(\text{H})\text{Dipp}$ with SnCl_2 . The attempted preparation of $\text{Sn}(\text{Cl})\{\text{N}(\text{H})\text{Dipp}\}$ by reaction of $\text{LiN}(\text{H})\text{Dipp}$ with SnCl_2 in a 1 : 1 ratio led to the isolation of the unique species $\text{Sn}_2\{\text{N}(\text{H})\text{Dipp}\}_3\text{Cl}$, which is the first example of a sesqui-amido derivative of a group 14 element. Both **1** and **2** were characterized by ^1H and ^{119}Sn NMR spectroscopy, X-ray crystallography and Mössbauer spectroscopy. The structures of **1** and **2** feature two tin centers bridged by $-\text{N}(\text{H})\text{Dipp}$ ligands with the terminal positions being occupied by two $\text{N}(\text{H})\text{Dipp}$ (**1**) or $-\text{N}(\text{H})\text{Dipp}$ and $-\text{Cl}$ (**2**) groups. The compound **1** was found to be unstable under ambient conditions and spontaneously converts to the imide tetramer $(\text{SnNDipp})_4$ in solution over several days at room temperature, representing a new synthetic route to group 14 element imides.

Introduction

Beginning with the synthesis and characterization of $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ in 1974,^{1,2} amido ($-\text{NR}_2$) ligands have played a leading role in the development of the chemistry of molecular tin(II) derivatives.^{3–9} Currently, about thirty homoleptic, $\text{Sn}(\text{NR}_2)_2$, (R = alkyl, aryl or silyl) and a similar number of heteroleptic, $\text{Sn}(\text{X})(\text{NR}_2)$, (X = halogen, pseudohalogen, amido, alkoxo, thiolato, *etc.*) tin(II) amides have been structurally characterized and their chemistry explored. The use of large substituents is crucial for the isolation of the homoleptic amides as monomers. These have v-shaped coordination and a lone pair of electrons at the tin center. Such derivatives are generally colored as a result of an n–p transition from the tin lone pair to the empty p-orbital. In contrast, primary amido ($-\text{N}(\text{H})\text{R}$) molecular tin(II) derivatives are rare owing to the diminished steric protection afforded by the ligand which carries only one organic substituent at nitrogen. At present, they are limited to just one structurally characterized example, the compound $\text{Sn}\{\text{N}(\text{H})\text{Mes}^*\}_2$ ($\text{Mes}^* = \text{C}_6\text{H}_2\text{-2,4,6-Bu}^t_3$).¹⁰ In addition, there are few structures known for tin(II) homoleptic amide dimers. The simplest is the dialkyl amide $\text{Sn}(\text{NMe}_2)_2$ ¹¹ which is associated through $-\text{NMe}_2$ bridging to afford $(\text{Me}_2\text{N})\text{Sn}(\mu\text{-NMe}_2)_2\text{Sn}(\text{NMe}_2)_2$ ¹² with pyramidally coordinated tins. Similarly, the chelated $\{\text{SnN}(\text{SiMe}_3)(\text{CH}_2)_4\text{N}(\text{SiMe}_3)\}_2$ is dimerized through bridging by one

of the amide nitrogens from each ring.¹³ In contrast, the derivative $\text{Sn}\{\text{N}(\text{Bu}^t)_2\text{SiMe}_2\}$ crystallizes both as a monomer and as a weakly associated dimer as a result of weak tin–tin bonding ($\text{Sn}–\text{Sn} = 3.68 \text{ \AA}$).¹⁴

We now report that the reaction of $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ with two equivalents of the primary amine H_2NDipp (Dipp = $\text{C}_6\text{H}_3\text{Pr}^i_2\text{-2,6}$) under mild conditions afforded the first homoleptic, primary amido, tin dimer $\{\text{Dipp}(\text{H})\text{N}\}\text{Sn}\{\mu\text{-N}(\text{H})\text{Dipp}\}_2\text{Sn}\{\text{N}(\text{H})\text{Dipp}\}$ (**1**) as yellow crystals in moderate yield. The derivative **1** was also prepared by the reaction of $\text{LiN}(\text{H})\text{Dipp}$ with SnCl_2 in a 2 : 1 ratio. The attempted synthesis of the heteroleptic derivative $[\text{Sn}(\mu\text{-Cl})\{\text{N}(\text{H})\text{Dipp}\}]_2$ via the 1 : 1 reaction of $\text{LiN}(\text{H})\text{Dipp}$ and SnCl_2 led only to the unique sesqui-dimer $\{\text{Dipp}(\text{H})\text{N}\}\text{Sn}\{\mu\text{-N}(\text{H})\text{Dipp}\}_2\text{SnCl}$ (**2**). Solutions of **1** in toluene were found to be unstable as they eliminated H_2NDipp over several hours to afford the previously reported Sn_4N_4 cubane species $(\text{SnNDipp})_4$.¹⁵

Experimental

General procedures

All manipulations were performed with the use of modified Schlenk techniques under argon or in a Vacuum Atmospheres drybox under N_2 . Solvents were dried and collected using a Grubbs-type solvent purification system¹⁶ (Glass Contour) and degassed by sparging with dry Ar for 10 min, while ether solvents were degassed via two freeze–pump–thaw cycles. DippNH_2 was purchased from Aldrich and distilled from a small amount of CaH_2 onto activated 4 Å molecular sieves. SnCl_2 was obtained from Aldrich and used without further purification. LiNHDipp was prepared by treatment of the corresponding aniline with $n\text{BuLi}$ (1.6 M in hexanes, Acros) in hexanes at 0 °C followed by decanting of the supernatant, washing the precipitated product

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once with cold hexane and removal of the solvent under reduced pressure. $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ was prepared according to the literature procedure¹ from the corresponding lithium amide and SnCl_2 . All physical measurements were obtained under strictly anaerobic and anhydrous conditions. ^1H and ^{13}C NMR spectra were acquired on either a Varian Mercury 300 MHz or Varian Inova 400 MHz instrument and referenced internally either to residual protio benzene or trace silicone vacuum grease, δ 0.29 ppm in C_6D_6 . ^{119}Sn NMR spectra were acquired on either a Varian Inova 600 MHz instrument (223.7 MHz) or a Varian Inova 400 MHz (149.1 MHz) and were externally referenced to Bu_4Sn in C_6D_6 (−11.7 ppm). IR spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 1430 spectrophotometer. UV-vis spectra were recorded as dilute hexane solutions in 3.5 mL quartz cuvettes using a HP8452 diode array spectrophotometer. Melting points were determined on a Meltemp II apparatus using glass capillaries sealed with vacuum grease, and are uncorrected.

Preparation of $\text{Sn}_2\{\text{N}(\text{H})\text{Dipp}\}_4$ (1)

Method A. To DippNH_2 (0.370 g, 2.1 mmol) in 25 mL hexanes at 0 °C was added $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ (0.439 g, 1 mmol) in 25 mL of hexanes, also at 0 °C. The resulting clear pale yellow reaction mixture was stirred for 30 min and kept cold, then stored overnight at −13 °C, after which the solvent was removed under reduced pressure giving a bright yellow oil. Vacuum was applied at room temperature for an additional 20 min to remove the $\text{HN}(\text{SiMe}_3)_2$ byproduct. The residue was extracted with cold n-hexane (*ca.* 10 mL), and stored at −13 °C for 2 d, affording pale yellow plates of **2** suitable for X-ray diffraction. Yield *ca.* 0.30 g (63%), mp 106 °C (darkens). IR (cm^{-1}): 3360, 3280 $\nu(\text{N-H})$; 350br $\nu(\text{Sn-N})$. ^1H NMR (C_6D_6 , 25 °C) δ 1.14 (d, 12H, $J = 6.9$ Hz, DippNH_2 co-product from spontaneous transformation, CH_3), 1.17 (d, 12H, $J = 6.9$ Hz, CH_3), 1.31 (d, 12H, $J = 6.9$ Hz, compound **3** co-product, CH_3), 2.63 (sept, 2H, $J = 6.9$ Hz, DippNH_2 co-product, CH), 2.99 (sept, 2H, $J = 6.9$ Hz, DippNH- , CH), 3.19 (s br, DippNH_2 co-product, NH_2), 3.48 (sept, 2H, $J = 6.9$ Hz, compound **3** co-product, CH), 3.83 (s br, DippNH-), 4.17 (s br, DippNH-), 4.65 (s), 4.75 (s), 5.01 (s), 6.90 (m, ArH), 7.08 (m, ArH) $^{13}\text{C}\{^1\text{H}\}$ NMR (75.44 MHz, C_6D_6 , 25 °C). δ 146.99, 140.43, 138.41, 124.22, 123.69, 122.75. ^{119}Sn NMR (223.7 MHz, C_6D_6 , 25 °C) δ −79.3 (s, br).

Method B. To SnCl_2 (0.379 g, 2.0 mmol) suspended in 20 mL of Et_2O at 0 °C was added dropwise a solution of LiNHDipp (0.732 g, 4.0 mmol) in 30 mL of Et_2O . The reaction was stirred for 10 h at room temperature, followed by removal of the solvent under reduced pressure. The resulting dark yellow solid was extracted with hexanes (*ca.* 30 mL), filtered, and concentrated under reduced pressure. Crystals of **1** suitable for X-ray diffraction appeared after storage for several days at −13 °C. Yield 0.425 g (45%).

Preparation of $\text{Sn}_2\{\text{N}(\text{H})\text{Dipp}\}_3\text{Cl}$ (2)

$\text{LiN}(\text{H})\text{Dipp}$ (0.732 g, 4 mmol) was dissolved in 50 mL of cold diethyl ether (0 °C) and added to an Et_2O suspension of SnCl_2 (0.758 g, 4 mmol), also at 0 °C. After stirring at *ca.* 25 °C for 20 h, the solvent was removed under reduced pressure and the residue was extracted with hexanes (30 mL). The solution was filtered from its light yellow precipitate using a filter cannula.

Storage at *ca.* −13 °C for 3 d afforded **2** as pale yellow block-shaped crystals suitable for X-ray diffraction. Yield 0.06 g (4%), mp 124–128 °C. IR (cm^{-1}): 3360, 3280 $\nu(\text{N-H})$; 375br $\nu(\text{Sn-N})$. ^1H NMR (300 MHz, C_6D_6 , 25 °C) δ 1.14 (d, 12H, $J = 6.9$ Hz, DippNH_2 decomp. product, CH_3), 1.19 (d, 12H, $J = 6.9$ Hz, CH_3), 1.24 (d, 12H, $J = 6.9$ Hz, CH_3), 1.30 (d, 12H, $J = 6.9$ Hz, CH_3), 1.38 (d, 12H, $J = 6.9$ Hz, CH_3), 2.65 (sept, 2H, $J = 6.9$ Hz, DippNH_2 decomp. product, CH), 3.19 (s br, DippNH_2 decomp. product, NH_2), 3.32 (sept, 2H, $J = 6.9$ Hz, CH), 3.55 (sept br, 2H, $J = 6.9$ Hz, CH), 5.28 (d br), 6.91 (t, 3H, $J = 6.9$ Hz, ArH), 7.04 (d, 2H, $J = 6.9$ Hz, ArH), 7.10 (m, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.44 MHz, C_6D_6 , 25 °C) δ 147.09, 140.68, 139.44, 134.55, 132.33, 124.66, 123.61, 123.29, 123.13, 118.97, 117.97, 29.74, 28.16, 22.63. ^{119}Sn NMR (149.1 MHz, C_6D_6 , 25 °C) δ −29.5 (s, br), −49.7 (s, br).

Preparation of $(\text{SnNDipp})_4$ (3)

Method A. In a manner similar to that reported in ref. 15, DippNH_2 (0.355 g, 2 mmol) and $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ (0.878 g, 2 mmol) were combined in a Schlenk flask and subsequently heated to *ca.* 60 °C for 10 min, over which time vapors of $\text{HN}(\text{SiMe}_3)_2$ byproduct were observed, and intermittent vacuum was applied. Toluene (*ca.* 20 mL) was added to the resulting yellow solid and the mixture briefly refluxed. After removal of the solvent *ca.* 25 mL of hexanes were added and the mixture filtered *via* cannula. The resulting yellow solution was concentrated and stored for 2 d at −13 °C, affording yellow blocks of **3**. Yield 0.92 g (78%) IR (cm^{-1}): no $\nu(\text{N-H})$ observed; 385 br $\nu(\text{Sn-N})$. ^1H NMR (C_6D_6 , 25 °C) δ 1.29 (d, 48H, $J = 6.9$ Hz, DippN- , CH_3), 3.46 (sept, 8H, $J = 6.9$ Hz, DippN- , CH), 6.90 (t, 4H, $J = 6.9$ Hz, C_6H_5 , *p-H*), 7.13 (d, 8H, $J = 6.9$ Hz, C_6H_5 , *m-H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.44 MHz, C_6D_6 , 25 °C) δ 148.08, 141.95, 125.44, 121.31, 30.59, 29.97. ^{119}Sn NMR (C_6D_6 , 25 °C, 223.7 MHz) δ 315.0 (s, br).

Method B. $[(\text{DippNH})_2\text{Sn}]_2$ (**2**) (0.473 g, 0.5 mmol) was dissolved in 30 mL toluene and stirred at *ca.* 25 °C for 4 d. After the solvent was removed under reduced pressure, the oily residue was heated in a 50 °C oil bath for 2 h and then extracted with 10 mL of hexanes. Storage at −13 °C for 5 d afforded yellow crystals of **3**. Yield 0.15 g (51%).

^{119}Sn Mössbauer effect spectroscopy

Mössbauer experiments were carried out in transmission mode using an ~5 mCi source of ^{119}Sn in a BaSnO_3 matrix.¹⁷ Spectroscopic calibration was accomplished by using a 20 mg cm^{-2} α -Fe absorber at room temperature (^{57}Co in Rh source). Isomer shifts are reported with respect to the centroid of the room-temperature BaSnO_3 spectrum. The samples were transferred in an inert atmosphere glovebox to O-ring sealed plastic sample holders and immediately cooled to liquid nitrogen temperature. They were then transferred to a precooled cryostat and examined in transmission geometry. All temperature-dependent Mössbauer data were obtained in both warming and cooling modes, and no evidence of hysteresis was observed. The experimental details of the Mössbauer data acquisition and reduction have been described previously.¹⁷ Temperature monitoring was effected using the DASWIN software also described previously.^{17a}

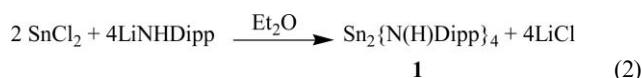
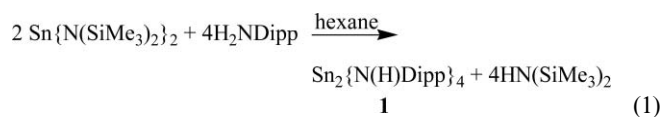
X-Ray crystallography

Crystals of appropriate quality for X-ray diffraction studies were removed from a Schlenk tube under a stream of nitrogen and immediately covered with a thin layer of hydrocarbon oil (Paratone). A suitable crystal was then selected and attached to a glass fiber and quickly placed in a low-temperature stream of nitrogen (90(2) K).¹⁸ Data for all compounds were obtained on a Bruker SMART 1000 instrument using Mo K α radiation ($\lambda = 0.71073$ Å) in conjunction with a CCD detector. The collected reflections were corrected for Lorentz and polarization effects by using Blessing's method as incorporated into the program SADABS.^{19,20} The structures were solved by direct methods and refined with the SHELXTL v.6.1 software package.²¹ Refinement was by full-matrix least-squares procedures with all carbon-bound hydrogen atoms included in calculated positions and treated as riding atoms. N-bound hydrogens were located directly from the Fourier difference map. A summary of crystallographic and data collection parameters is given in Table 1.

Results and discussion

Synthesis

The bis(amido) tin(II) dimer **1** was synthesized by two different methods in accordance with eqn (1) and (2).



The transamination reaction (eqn (1)) proceeds smoothly in hexanes below room temperature to afford **1** as pale yellow crystals in good (63%) yield. The salt elimination approach (eqn (2)) proceeds in diethyl ether between 0 °C and room temperature to produce **1** in 45% yield (not optimized). Crystals of **1** are very air and moisture sensitive pale yellow plates which melt with decomposition at 106 °C. Freshly prepared crystalline samples afford relatively "clean" ¹H NMR and ¹¹⁹Sn NMR spectra initially, although some transformation into **3** is immediately apparent even at ambient temperature in C₆D₆ as evidenced by the development of a septet signal at 3.46 ppm (**3**) and at 2.63 ppm (DippNH₂ co-product). The ¹H NMR spectrum of **1** displays two sets of signals in a 1 : 1 ratio for the bridging and terminal –N(H)Dipp groups, whereas the ¹¹⁹Sn NMR spectrum displays just one signal at $\delta = -79.3$, which is well upfield of the values reported for {SnN(SiMe₃)(CH₂)_nN(SiMe₃)₂}₂ [$n = 3$ ($\delta = 148$) or 4 ($\delta = 165$)],¹³ or for the three coordinate tin in [SnN(SiMe₃)(CH₂)₂NMe(CH₂)₂N(SiMe₃)] ($\delta = 158$),²² and is far upfield of the two three-coordinate tins in [Sn(NDipp)₂{Sn(μ-NMe₂)₂}₂] ($\delta = 1000.8, 706.8$).²³

Crystals of **3** could be readily isolated from toluene solutions of **1** upon standing for 4 days at ambient temperature. Moreover the conversion of **1** into **3** was immediately apparent from ¹H NMR spectroscopy. A sample of **1** in C₆D₆ in a sealed NMR tube afforded several ¹H signals at 25 °C that corresponded not only to the bridging and terminal DippN(H)– moieties in **1** but also to small amounts of **3** as well as free DippNH₂ evolved during conversion. There were also additional DippN(H)– methyl, methine, and amino-H signals likely resulting from a monomer–dimer equilibrium involving **1**. The ¹¹⁹Sn NMR spectrum of **1** showed the characteristic singlet at –79.3 ppm along with a signal at 315.0 ppm due to **3**. Additional minor signals were also observed at $\delta = -74.2, 155.1, \text{ and } 301.2$ ppm. After the NMR tube was

Table 1 Selected crystallographic data for compounds **1–3**

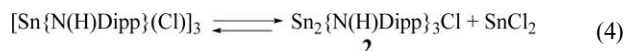
Compound	1 ·hexane	2	3
Formula	C ₅₄ H ₈₆ N ₄ Sn ₂	C ₃₆ H ₅₄ ClN ₃ Sn ₂	C ₄₈ H ₆₈ N ₄ Sn ₄
FW	1028.65	801.65	1175.82
Color, habit	Yellow plate	Yellow block	Yellow block
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄
<i>a</i> /Å	11.5303(8)	12.9777(5)	12.1960(7)
<i>b</i> /Å	26.4308(17)	14.6393(5)	19.1210(11)
<i>c</i> /Å	17.8070(11)	19.3383(7)	21.4771(13)
α /°	90	90	84.2250(10)
β /°	98.771(2)	98.017(2)	76.2090(10)
γ /°	90	90	86.7710(10)
<i>V</i> /Å ³	5363.3(6)	3638.1(2)	4836.7(5)
<i>Z</i>	4	4	4
Crystal dimension/mm	0.40 × 0.40 × 0.20	0.50 × 0.30 × 0.30	0.40 × 0.25 × 0.25
<i>T</i> /K	90(2)	90(2)	90(2)
<i>d</i> _{calc} /g cm ^{–3}	1.274	1.464	1.615
Abs. coefficient μ /mm ^{–1}	0.968	1.474	2.077
θ Range/°	1.39 to 27.50	1.75 to 27.50	0.98 to 27.53
Reflections collected	61636	48673	64111
Unique reflections	12312	8365	22200
<i>R</i> (int)	0.0716	0.0200	0.0927
Obs. reflections [<i>I</i> > 2 σ (<i>I</i>)]	8693	7728	17000
Data/restraints/parameters	12312/0/576	8365/0/403	22000/0/1009
<i>R</i> ₁ , observed reflections	0.0425	0.0177	0.0344
<i>wR</i> ₂ , all	0.1118	0.0464	0.0893

gently heated for *ca.* 30 s, the ^1H spectrum displayed only signals corresponding to DippNH_2 and **3** in a roughly 1:1 ratio. The same sample, recorded at 70 °C, also gave a much cleaner ^{119}Sn spectrum which consisted of a major singlet at 321.8 ppm and another minor signal at 315.1 ppm, the former corresponding to **3**, which was shifted downfield due to the well-known temperature dependence of ^{119}Sn chemical shift.²⁴

The sesqui complex **2** was synthesized by the reaction of a 1:1 ratio of SnCl_2 and *in situ* generated LiNHDipp in diethyl ether solution. The intention was to synthesize the complex $\text{Sn}\{\text{N}(\text{H})\text{Dipp}\}(\text{Cl})$ (as in eqn (3)) which was expected to be dimeric with either chloride or amido bridging.

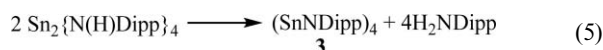


Instead the unique species $\text{Sn}\{\text{N}(\text{H})\text{Dipp}\}_3\text{Cl}$ (**2**) was obtained in low yield as yellow crystals. The mechanism whereby **2** is formed is currently unknown. One possibility is that a trimeric species $[\text{Sn}(\text{Cl})\{\text{NHDipp}\}]_3$ is formed in solution. Trimers of this type are preceded by the structurally characterized $[\text{Sn}(\mu\text{-Cl})\{\text{N}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})\text{SiMe}_3\}]_3$ and they may exist in equilibrium with complexes of type **2** as described in eqn (4).



The integrity of **2** is maintained in solution as evidenced by its ^1H , ^{13}C and ^{119}Sn NMR spectra. The ^{119}Sn NMR spectrum of **2** displays two signals of equal intensity at $\delta = -29.5$ and -49.7 , upfield of that of the trimeric $\{\text{Sn}(\mu\text{-Cl})[\text{N}(\text{Mes})\text{SiMe}_3]\}_3$ ($\delta = 67$),²⁵ and of $\{\text{Sn}(\mu\text{-Cl})\text{NR}_2\}_2$ ($\text{NR}_2 = \text{NCMe}_2(\text{CH}_2)_3\text{CMe}_2$) ($\delta = 240$),²⁶ but well downfield of that reported for $\{\text{Sn}(\mu\text{-Cl})\text{NMe}_2\}_2$ ($\delta = -333$).²⁷

The previously reported cubane species **3**, synthesized by the 1:1 reaction of $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}$ and H_2NDipp_2 ,¹⁵ was obtained by a spontaneous elimination of H_2NDipp from **2** under ambient conditions to afford **3**, the overall reaction being described by eqn (5).



A detailed mechanism for this reaction is not known although the structures of intermediate stages of the process probably resemble those described for the transamination reactions of $\{\text{Sn}(\text{NMe}_2)_2\}_2$ with H_2NDipp . A ^{119}Sn NMR spectrum of **3** displayed a signal $\delta = 315$ which is upfield of those previously observed for $(\text{SnNSiBu}^t\text{Me}_2)_4$ ($\delta = 742$),²⁸ or for $(\text{SnNEMe}_3)_4$ [$\text{E} = \text{Si}$ ($\delta = 782$),²⁹ Ge ($\delta = 954$),³⁰ or Sn ($\delta = 797$)³⁰].

Structures

The structures of **1** and **2** are illustrated in Fig. 1 and 2. Selected bond distances and angles are given in Table 2. In the structure of **1**, two $\text{N}(\text{H})\text{Dipp}$ groups bridge the tin centers in a symmetric fashion. The Dipp groups are *syn* with respect to Sn_2N_2 core which is folded (fold angle = 142.1°) along the Sn–Sn vector. The coordination at each tin is completed by a terminally bound $\text{N}(\text{H})\text{Dipp}$ group. These terminal amide groups are also disposed in a *syn* fashion with respect to each other, but are *anti* with respect to the bridging amides. The overall configuration of the core is presumably a result of steric effects

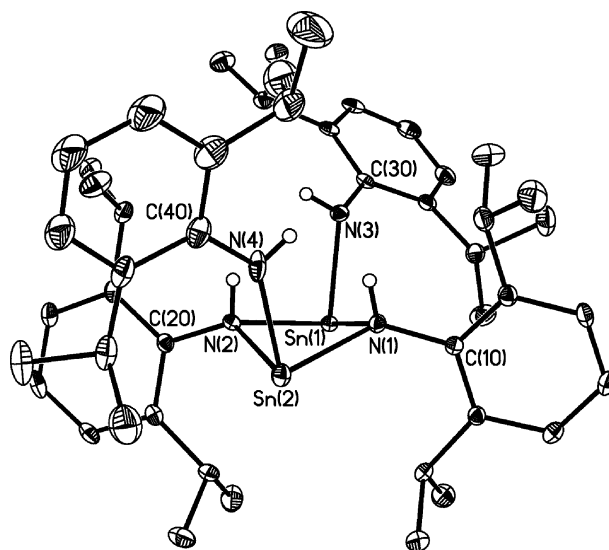


Fig. 1 Molecular structure of **1**, C-bound hydrogen atoms omitted for clarity.

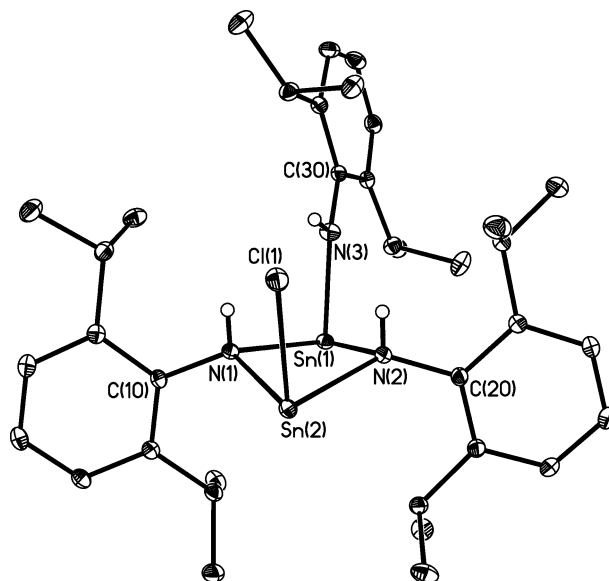


Fig. 2 Molecular structure of **2**, C-bound hydrogen atoms omitted for clarity.

of the bulky Dipp substituents. The bridging Sn–N distances average 2.28(2) Å and span the range 2.248(3)–2.329(3) Å; the terminal Sn–N bond lengths average 2.119(2) Å. These may be compared to the 2.266(5) Å average bridging Sn–N distance in $\{\text{Sn}(\text{NMe}_2)_2\}_2$ ¹² and the 2.256(6) and 2.397(6) Å bridging distances in $\{\text{SnN}(\text{SiMe}_3)(\text{CH}_2)_4\text{N}(\text{SiMe}_3)\}_2$,¹³ as well as the terminal Sn–N distances of 2.067(4) Å in $\{\text{Sn}(\text{NMe}_2)_2\}_2$ and 2.083(6) Å in $\{\text{SnN}(\text{SiMe}_3)(\text{CH}_2)_4\text{N}(\text{SiMe}_3)\}_2$, in which the terminal Sn–N bond lengths are statistically longer than those previously observed.

The structure of **2** resembles that of **1** in its dimeric nature and in the orientation of the bridging and terminal amido ligands. The major difference is that one of the terminal amides is replaced by a chloride. Oddly, this does not introduce any major changes to the Sn–N distances within the Sn_4N_4 core and an almost identical average Sn–N bond length of 2.284(4) Å is observed. The fold angle

Table 2 Important bond distances (Å) and angles (°) for compounds **1** and **2**

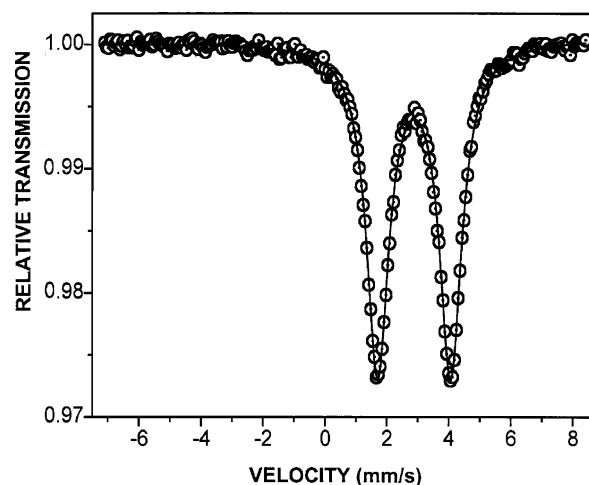
{(DippNH) ₂ Sn} ₂ (1)			
Sn(1)–N(1)	2.304(3)	N(1)–Sn(1)–N(3)	87.58(12)
Sn(1)–N(2)	2.248(3)	N(2)–Sn(1)–N(3)	93.37(12)
Sn(1)–N(3)	2.117(3)	N(1)–Sn(1)–N(2)	75.24(11)
Sn(2)–N(1)	2.233(3)	N(1)–Sn(2)–N(4)	89.86(13)
Sn(2)–N(2)	2.329(3)	N(2)–Sn(2)–N(4)	85.89(13)
Sn(2)–N(4)	2.120(4)	N(1)–Sn(2)–N(2)	75.02(11)
Sn(1)–Sn(2)	3.484	Sn(1)–N(3)–C(30)	121.4(2)
N(1)–C(10)	1.441(5)	Sn(1)–N(2)–C(20)	118.7(2)
N(2)–C(20)	1.433(5)	Sn(1)–N(1)–C(10)	119.6(2)
N(3)–C(30)	1.408(4)	Sn(2)–N(1)–C(10)	122.9(2)
N(4)–C(40)	1.397(5)	Sn(2)–N(2)–C(20)	124.5(2)
		Sn(2)–N(4)–C(40)	137.1(3)
Sn ₂ (DippNH) ₃ Cl (2)			
Sn(1)–N(1)	2.2937(13)	N(1)–Sn(1)–N(2)	76.42(4)
Sn(1)–N(2)	2.2850(13)	N(1)–Sn(2)–N(2)	76.82(5)
Sn(1)–N(3)	2.1019(14)	N(1)–Sn(1)–N(3)	90.14(5)
Sn(2)–N(1)	2.2770(13)	N(2)–Sn(1)–N(3)	86.37(5)
Sn(2)–N(2)	2.2815(12)	N(1)–Sn(2)–Cl(1)	86.23(3)
Sn(2)–Cl(1)	2.4901(4)	N(2)–Sn(2)–Cl(1)	86.13(3)
Sn(1)–Sn(2)	3.495	Sn(1)–N(1)–C(10)	129.06(10)
N(1)–C(10)	1.4414(18)	Sn(1)–N(2)–C(20)	114.26(9)
N(2)–C(20)	1.4367(19)	Sn(1)–N(3)–C(30)	138.61(11)
N(3)–C(30)	1.395(2)	Sn(2)–N(1)–C(10)	113.59(9)
		Sn(2)–N(2)–C(20)	129.55(10)

along the Sn–Sn vector is 148.5°, a little wider than that seen in **1**, and the terminal Sn(1)–N(3) distance is 2.102(1) Å which is very close to that seen in **1**.

Crystals of **3** proved to have identical crystallographic parameters to those reported earlier¹⁵ for (SnNDipp)₄ which has a distorted cubane structure with an average Sn–N distance near 2.2 Å and N–Sn–N and Sn–N–Sn angles near 81 and 98°.

Mössbauer spectroscopy

Compound **1**. The Mössbauer spectra of **1** consist of a single doublet and a typical spectrum is shown in Fig 3. The hyperfine parameters at 90 K, as well as the temperature dependence of the recoil-free fraction, f are summarized in Table 3. The isomer shift (IS) of 2.884 ± 0.013 mm s^{−1} at 90 K clearly indicates the tin site is Sn(II). The temperature dependence of the IS parameter is too small to be statistically significant, and a meaningful value of the effective vibrating mass (M_{eff}) could not be obtained. Similarly, the quadrupole splitting (QS) parameter temperature dependence is very small, and an average value of 2.355 ± 0.009 mm s^{−1} is included in Table 3. A 5 minute exposure of **1** to ambient laboratory conditions is sufficient to turn the virgin pale yellow compound to a white decomposition product. Mössbauer analysis of this product at room temperature showed the presence of Sn(IV) to Sn(II) in the ratio of ~3:1. The IS and QS of the Sn(IV) site,

**Fig. 3** ¹¹⁹Sn Mössbauer spectrum of **1** at 88.7 K. The isomer shift scale is with respect to a BaSnO₃ absorber spectrum at room temperature.

0.067 ± 0.006 and 0.66 ± 0.01 mm s^{−1} respectively, strongly suggest that the decomposition product is a form of stannic oxide. The minority site is undecomposed **1** remaining in the sample.

The Mössbauer spectrum of **3** resembles that of **1**. The associated parameters are included in Table 3. Again, the temperature-dependence of IS is not sufficiently sensitive over the accessible temperature range to permit an evaluation of M_{eff} . The QS parameter is slightly more temperature dependent and shows the normal decrease in QS with increasing temperature, associated with normal thermal expansion of covalent solids.

The Mössbauer spectra of **2** are both qualitatively and quantitatively different from those of **1** and **3** and clearly show the presence of two distinct tin sites in the structure. A representative spectrum is shown in Fig. 4 and the hyperfine and derived parameters are included in Table 3. Assuming equal recoil-free fractions at 89 K, the ratio of the two sites is ~1:1.13. The isomer shift of both sites 3.042 ± 0.011 and 3.222 ± 0.012 mm s^{−1} at 89 K clearly identify the metal atom as Sn(II). As in the case of **1** and **3** there is no evidence for resonant absorbance at ~0 mm s^{−1} and thus decomposition of the sample (to a Sn(IV) oxide) prior to spectroscopic analysis can be ruled out. The assignment of which pair of hyperfine parameters belong to the tin atom ligated to three nitrogens, and which to the tin atom ligated to two nitrogens and a chlorine clearly cannot be made on the basis of the presently available data since contributions to the QS parameter come not only from the nearest neighbor ligand atoms, but also from the lone pair of electrons associated with each Sn(II) site. A selective isotopic labeling procedure, using either enriched or depleted ¹¹⁹Sn in one of the two molecular sites would be required to settle this point definitively.

Mössbauer data for tin amides are relatively scarce. Lappert's monomeric amide Sn{N(SiMe₃)₂}₂ affords an isomer shift of

Table 3 Mössbauer parameters for **1**, **2** and **3**

Parameter	1	2 Sn(Cl)	2 Sn{N(H)Dipp}	3
IS(90)/mm s ^{−1}	2.884(13)	3.222(10)	3.042(10)	2.905(13)
QS(90)/mm s ^{−1}	2.356(13)	1.654(10)	2.414(10)	2.167(13)
−[dlnA/dT]/K ^{−1} × 10 ³	15.29(2)	19.1(10)	17.39(3)	15.49(19)

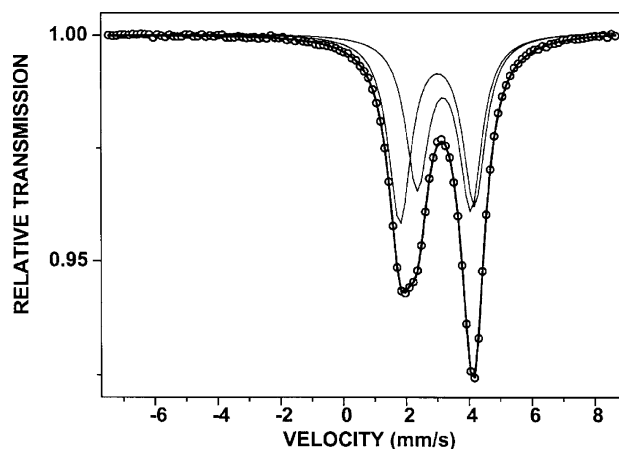


Fig. 4 ^{119}Sn Mössbauer spectrum of compound **2** at 150 K. The two tin site absorbances (assuming equal recoil-free fractions) are nearly equal, consistent with the known molecular structure, but the present data do not permit assignment of which doublet arises from which of the two distinct metal atoms in the molecule.

2.88 mm s^{-1} and a quadrupole splitting of 3.52 mm s^{-1} , while the corresponding amide-chloride shows an IS of 3.18 mm s^{-1} and a QS of 2.64 mm s^{-1} .² The amide derivatives most relevant to **1–3** concern $\{\text{Sn}(\text{NMe}_2)_2\}_2$ and $\{\text{Sn}(\overline{\text{NCH}_2\text{CH}_2})_2\}_2$, both of which have isomer shift values of 2.72 mm s^{-1} , and quadrupole splittings of 2.03 and 2.07 mm s^{-1} , respectively.^{31,32} The values obtained for the tin sites bound to three nitrogens in **1–3** (Table 3) resemble these shifts with only the chloride-bound tin in **2** displaying a substantially different value.

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