Synthesis and structural characterization of a novel asymmetric distannene $[\{1\text{-}[N(Bu^t)C(SiMe_3)C(H)]\text{-}2\text{-}[N(Bu^t)(SiMe_3)CC(H)]C_6H_4\}Sn{\rightarrow}Sn\{1,2\text{-}[N(Bu^t)(SiMe_3)CC(H)]_2C_6H_4\}]$†

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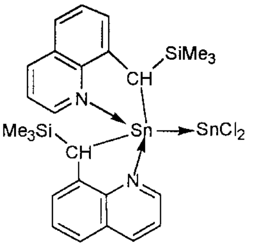
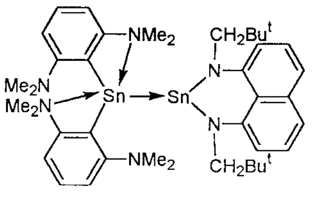
The reaction of dilithium complex $[\{1,2\text{-}[N(Bu^t)C(SiMe_3)C(H)]_2C_6H_4\}\{Li_2(TMEDA)_2\}]$ 1 with $SnCl_2$ yielded an unusual asymmetric distannene $[\{1\text{-}[N(Bu^t)C(SiMe_3)C(H)]\text{-}2\text{-}[N(Bu^t)(SiMe_3)CC(H)]C_6H_4\}Sn{\rightarrow}Sn\{1,2\text{-}[N(Bu^t)(SiMe_3)CC(H)]_2C_6H_4\}]$ 2 resulting from intramolecular self-rearrangements of the ligands; 2 has a tin–tin bond distance of 3.0087(3) Å.

Ethene analogues of tin containing homoleptic ligands such as $[SnR_2]_2$ have been an interesting topic of research. The first crystallographically characterized distannene $[Sn\{CH(SiMe_3)_2\}_2]_2$ [Sn–Sn 2.768(1) Å] was reported in 1976 by Lappert and coworkers.[1] Nearly two decades later, solid-state structures of three thermally stable compounds $[Sn\{Si(SiMe_3)_3\}_2]_2$,[2] $[Sn\{2,4,6\text{-}(CF_3)_3C_6H_2\}_2]_2$[3] and $[Sn(4,5,6\text{-}Me_3\text{-}2\text{-}Bu^tC_6H)_2]_2$[4] having tin–tin bonds [Sn–Sn 2.825(1), 3.64, 2.910(1) Å, respectively] were reported. These compounds were either partially or completely dissociated to the monomers SnR_2 in toluene or methylcyclohexane. There have been evidences for formation of an unstable dimer $[Sn(2,4,6\text{-}Pr^i{}_3C_6H_2)_2]_2$ from the photolysis of corresponding cyclotrimer $[Sn(2,4,6\text{-}Pr^i{}_3C_6H_2)_2]_3$ in methylcyclohexane at 205 K.[5] However, the dimer had not been structurally characterized owing to its complete reversion to the cyclotrimer at room temperature. To our knowledge, only two examples of structurally characterized bivalent tin complexes containing different ligands attached to each tin atom having a tin–tin bond have been reported. One of them reported by our group was a thermally labile compound $[\{8\text{-}(CHSiMe_3)C_9H_6N\}_2Sn{\rightarrow}SnCl_2]$ **I** with an Sn–Sn distance of 2.961(1) Å,[6] and the other compound $[\{2,6\text{-}(Me_2N)_2C_6H_3\}_2Sn{\rightarrow}Sn\{1,8\text{-}(NCHBu^t)_2C_{10}H_6\}]$ **II** [Sn–Sn 3.087(2) Å] reported recently by Lappert and coworkers.[7] These two complexes were obtained from the reactions of two tin(II) complexes, where each of the tin complexes either acts as a Lewis acid or a base. Here, we report a rare example of an asymmetric distannene having chelating ligands bonded in different modes to the tin metals resulted from intramolecular self-rearrangements within the binuclear tin(II) compound.

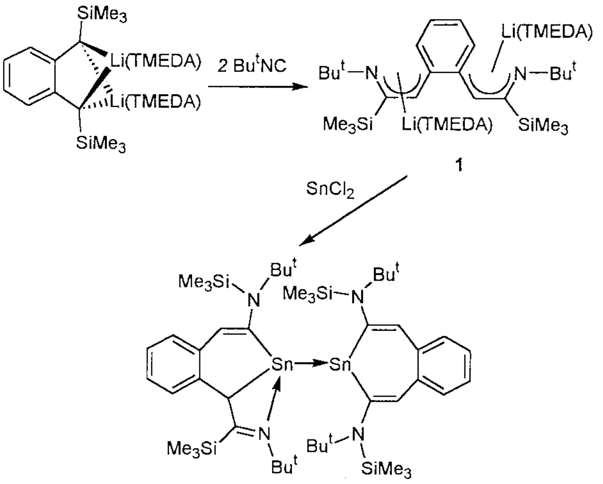


I



II

This novel distannene $[\{1\text{-}[N(Bu^t)C(SiMe_3)C(H)]\text{-}2\text{-}[N(Bu^t)(SiMe_3)CC(H)]C_6H_4\}Sn{\rightarrow}Sn\{1,2\text{-}[N(Bu^t)(SiMe_3)CC(H)]_2C_6H_4\}]$ **2** was prepared from the reaction of the bis(1-azaallyl) dilithium compound $[\{1,2\text{-}[N(Bu^t)C(SiMe_3)C(H)]_2C_6H_4\}\{Li_2(TMEDA)_2\}]$ **1** with $SnCl_2$ (Scheme 1). Dilithium compound **1** was prepared by the addition of isocyanide Bu^tNC to a diethyl ether solution of the dilithium dialkyl compound $[\{1,2\text{-}(CHSiMe_3)_2C_6H_4\}\{Li_2(TMEDA)_2\}]$. In this reaction, the isocyanide inserts into the Li–C bond followed by a 1,2-shift of the trimethylsilyl group along the carbon chains. Similar reaction with organonitrile Bu^tCN has been reported earlier.[8] Compound **1** has been characterized by ^1H and ^{13}C NMR spectroscopy, EI-MS spectrometry and elemental analysis.‡ The X-ray structure of **1** has been determined.



2

Scheme 1 Synthesis of complexes **1** and **2**.

Subsequent treatment of **1** with a slight excess of $SnCl_2$ led to the formation of **2** in 64.9% yield. By X-ray structure analysis of the product, it has found that the ligands bonded to the two tin(II) atoms undertake different rearrangements. One of the ligands undergoes two 1,2-shifts of the $SiMe_3$ group from C to N, and both of the 1-azaallyl arms are bonded to the tin(II) atom *via* the carbon atoms. The ligand attached to the other tin(II) core undergoes a 1,2-silyl migration. This rearrangement results in the two 1-azaallyl arms bonded to the tin atom in an η^1-C and η^2-C,N bonding mode, respectively. Compound **2** is soluble in toluene, Et_2O and THF, and slowly decomposes to tin metal in solution. It has been characterized by EI-MS spectrometry, ^1H, ^{13}C, ^{119}Sn NMR spectroscopy, elemental analysis‡ and X-ray structure analysis.§ The ^1H and ^{13}C NMR spectra of **2** in C_6D_6–C_5D_4N (4 : 1) showed only one set of signals corresponding to the ligand at ambient temperature. The ^{119}Sn NMR spectrum displayed a broad singlet at δ 333.04.

Compound **2** crystallized from a solvent mixture of THF and toluene (1 : 10) as a THF solvate (Fig. 1). It is comprised of two

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† Electronic supplementary information (ESI) available: characterization data for compounds **1** and **2**. See http://www.rsc.org/suppdata/b0/b000268m/

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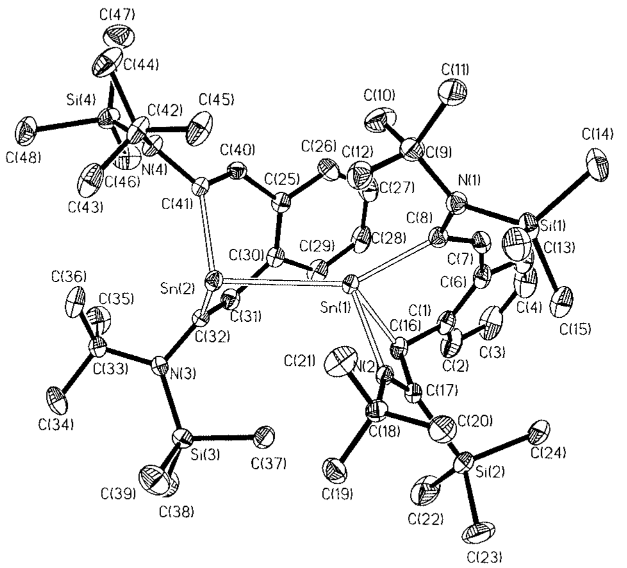

Fig. 1 Molecular structure of [{1-[N(Bu^t)C(SiMe$_3$)C(H)]-2-[N(Bu^t)(SiMe$_3$)CC(H)]C$_6$H$_4$}Sn$\rightarrow$Sn{1,2-[N(Bu^t)(SiMe$_3$)CC(H)]$_2$C$_6$H$_4$}] **2**. Hydrogen atoms and solvent molecule have been omitted for clarity. Selected bond distances (Å) and angles (°): Sn(1)–Sn(2) 3.0087(3), Sn(1)–C(8) 2.208(2), Sn(1)–C(16) 2.219(2), Sn(1)–N(2) 2.266(1), Sn(2)–C(32) 2.209(2), Sn(2)–C(41) 2.255(2); C(8)–Sn(1)–C(16) 89.53(7), C(8)–Sn(1)–N(2) 91.32(6), C(16)–Sn(1)–N(2) 61.70(6), C(8)–Sn(1)–Sn(2) 144.21(4), C(16)–Sn(1)–Sn(2) 126.22(5), N(2)–Sn(1)–Sn(2) 106.25(4), C(32)–Sn(2)–C(41) 90.05(6), C(32)–Sn(2)–Sn(1) 93.42(4), C(41)–Sn(2)–Sn(1) 97.18(4).

independent stannylene moieties linked by a tin–tin bond at a distance of 3.0087(3) Å. The coordination geometries at the tin atoms are different. The Sn(1) centre adopts a distorted tetrahedron with the Sn(1)–Sn(2) vector residing on one of the vertices. The 1-azaallyl ligand attached to the Sn(1) atom undergoes a further 1,2-shift of the SiMe$_3$ group, resulting in a C(7)–C(8) double bond [1.352(2) Å] and C(8)–N(1) single bond [1.431(2) Å]. The other 1-azaallyl skeleton of the same ligand links to the Sn(1) atom in an η^2-C,N coordination mode, with an Sn(1)–C(16) bond distance of 2.219(2) Å and an Sn(1)–N(2) bond distance of 2.266(1) Å. The Sn(1)–N(2) bond distance is somewhat longer than the average Sn–N(amido) distances of 2.092 Å in [Sn{N(SiMe$_3$)$_2$}$_2$],[9] and 2.085 Å in **II**,[7] and comparable to the Sn–N distances of 2.153(4) and 2.288(4) Å in [Sn{C(SiMe$_3$)$_2$C(Ph)N(SiMe$_3$)}$_2$].[10] Unlike most 1-azaallyl complexes, no distinctive electron delocalization was found within the C(16)C(17)N(2) part. The C(16)–C(17) bond [1.539(3) Å] is a normal C–C single bond and the C(17)–N(2) bond distance [1.279(2) Å] coincides with the C–N double bond. The angle sum around N(2) is 359.97°, indicative of an sp^2 hybridization. Sn(2) adopts a trigonal pyramidal environment with an angle sum of 280.65° at Sn(2). This value is comparable to similar angles in **I** and **II**. In **I**, SnCl$_2$ acts as a Lewis acid, and the angle sum around Sn is 282.6°.[6] In **II**, the three-coordinate Sn core behaves as an acceptor with an angle sum of 279.4°.[7] The Sn(2) moiety in **2** can be viewed as an acceptor, and the Sn(1) fragment as a donor. Both of the 1-azaallyl ligands of Sn(2), undergo a 1,2-SiMe$_3$ migration, and are bonded to the Sn(2) atom in an η^1-C bonding mode. The Sn–C bond distances of 2.255(2) and 2.209(2) Å in **2** are shorter than those in [Sn{2-C(SiMe$_3$)$_2$C$_5$H$_3$N}$_2$] [2.334(6), 2.346(6), 2.377(7) Å],[11] and [Sn{2-C(SiMe$_3$)(Ph)C$_5$H$_3$N}$_2$] [2.329(4), 2.333(4) Å],[12] and comparable to the corresponding Sn–C distances in **I** [2.200(8), 2.203(8) Å],[6] and **II** [2.186(6), 2.196(7) Å].[7]

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Notes and references

‡ *Selected spectroscopic data* for **1**: ^{1}H NMR [300 MHz, C$_6$D$_6$–C$_5$D$_4$N(2 : 1), 25 °C]: δ 0.52 (s, 18 H, SiMe$_3$), 1.57 (s, 18 H, CMe$_3$), 2.03 (s, 24 H, NMe$_2$), 2.12 (s, 8 H, CH$_2$N), 5.11 (s, 2 H, CH), 6.49 (br, 2 H, C$_6$H$_4$), 9.67 (br, 2 H, C$_6$H$_4$); ^{13}C{^{1}H} NMR [75.5 MHz, C$_6$D$_6$–C$_5$D$_4$N (2 : 1), 25 °C]: δ 4.95, 34.80, 46.03, 53.34, 57.73, 94.73, 119.22, 133.41, 137.45, 162.73; EI-MS (70 eV): *m/z* (%) 416 (21.9, M$^+$ − 2 Li − 2 TMEDA + 2). For **2**: ^{1}H NMR [300 MHz, C$_6$D$_6$–C$_5$D$_4$N(4 : 1), 25 °C]: δ 0.42 (s, 18 H, SiMe$_3$), 1.57 (s, 18 H, CMe$_3$), 6.69 (dd, 2 H, C$_6$H$_4$), 6.98 (dd, 2 H, C$_6$H$_4$), 7.51 (s, 2 H, CH); ^{13}C{^{1}H} NMR [75.5 MHz, C$_6$D$_6$–C$_5$D$_4$N (4:1), 25 °C]: δ 6.55, 32.93, 55.33, 123.51, 128.71, 132.71, 135.82, 182.27; ^{119}Sn NMR [149.2 MHz, C$_6$D$_6$–C$_5$D$_4$N (4 : 1), 25 °C]: δ 333.04 (br); EI-MS (70 eV): *m/z* 878 (2.6, M$^+$ − SiMe$_3$ − 2 Bu^t − 1).

§ *Crystal data* for **2**: C$_{52}$H$_{92}$N$_4$OSi$_4$Sn$_2$, M = 1139.04, crystal dimensions 0.36 × 0.20 × 0.14 mm, monoclinic, space group $P2_1/c$ (no. 14), a = 12.108(1), b = 36.869(3), c = 14.320(1) Å, β = 105.004(2)°, U = 6174.7(9) Å^3, Z = 4, μ = 0.922 mm^{-1}, T = 294(2) K, 42889 reflections collected for 1.57 < θ < 28.30°, 15255 independent reflections, $R1$ = 0.0540 for reflections with $I > 2\sigma(I)$, $wR2$ = 0.1435 (for all data). Data collection Bruker SMART CCD detector (0.3° ω scans), full-matrix least-squares refinement on F^2, SHELXTL-97. CCDC 182/1542. See http://www.rsc.org/suppdata/cc/b0/b000268m/ for crystallographic files in .cif format.

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