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[Bis(trimethylsilyl)amido-κN]{*tert*-butyl[(*E*)-2-(*tert*-butylimino)ethyl]-amido-$\kappa^2 N,N'$}tin(II), a key intermediate in the synthesis of 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazastannole

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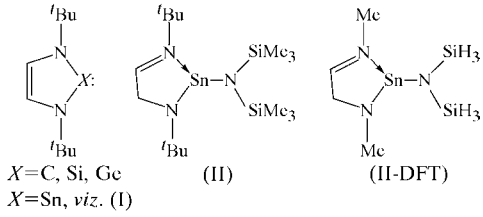
The title compound, $[Sn(C_{10}H_{21}N_2)(C_6H_{18}NSi_2)]$, contains the Sn^{II} centre in a trigonal–pyramidal geometry. The basal plane is formed by three N atoms and the fourth apical position is occupied by a stereoactive lone pair. The Sn atom is displaced from the plane of the three N atoms by 1.1968 (12) Å. The Sn—N bonds are highly polarized toward the N atoms, as confirmed by natural bonding orbital analysis.

Comment

The unsaturated N-heterocyclic divalent compounds of group 14 elements are key intermediates in many reactions (Arduengo, 1999; Gans-Eichler *et al.*, 2002, 2006; Haaf *et al.*, 2000; Hill & West, 2004; Hill *et al.*, 2005; Naka *et al.*, 2004; Tumanskii *et al.*, 2004, 2005). The chemistry of the C, Si and Ge analogues has been explored (*e.g.* Haaf *et al.*, 1998, 2000; Hill *et al.*, 2005; Naka *et al.*, 2004). However, the chemistry of the Sn congener has largely remained unknown. The first synthetic procedure for the preparation of 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazastannole, (I), was reported recently by Gans-Eichler *et al.* (2002) as a six-step synthesis. The experimental support for the proposed mechanism was based on detection of the title key intermediate, (II), by ^{1}H NMR spectroscopy. In the course of our studies of the chemistry of (I), we reproduced its synthesis (Gans-Eichler *et al.*, 2002) and successfully isolated and characterized the key intermediate, (II), thus obtaining direct evidence for the proposed mechanism. Here, we report the synthesis and structural and spectroscopic characterization of (II), and the results of our theoretical studies of a model analogue, (II-DFT).

Numerous attempts to prepare compound (I) in a toluene–hexane mixture and to isolate its crystals, as described by Gans-Eichler *et al.* (2002), were unsuccessful. We were only able to obtain a sample of diazastannole (I) as a mixture with stannylene (II) in a 1:4 ratio in the presence of $HN(SiMe_3)_2$, as suggested by the ^{1}H NMR spectrum. Compound (I) is characterized by a remarkable thermal instability and decomposes at 333 K (Gans-Eichler *et al.*, 2002). Our data suggest that the presence of some additives is necessary in order to promote the conversion of (II) into (I) and to improve the thermal stability of diazastannole (I). Additionally, preliminary density functional theory (DFT) studies of similar systems indicate that the conversion of (II) to (I) and appropriate by-products is favoured by about 5 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}).



To ascertain fully the formation of (II) during the synthesis, its solid-state structure was established by single-crystal X-ray analysis. The molecular structure of (II) is shown in Fig. 1, and important bond distances and angles are presented in Table 1. Compound (II) crystallizes in a triclinic space group as discrete monomeric molecules with no intermolecular Sn···Sn or Sn···N interactions. The Sn centre is trigonal–pyramidal, with three N atoms in the basal plane and a stereochemically active lone pair in the fourth vertex. Atom Sn1 is displaced from the plane defined by atoms N1, N2, and N3 by 1.1968 (12) Å. Similar geometries have been reported for a number of Sn^{II} compounds [Cambridge Structural Database (CSD), Version of November 2005; Allen, 2002].

We have also performed a density functional theory (DFT) study of a model analogue of (II), (MeN═CH—CH_2—NMe)Sn[$N(SiH_3)_2$], (II-DFT), using *GAUSSIAN03* (Frisch *et al.*, 2004) at different levels of theory and selected the PBE1PBE/SDD combination as the best. In 2000, Ayers *et al.*

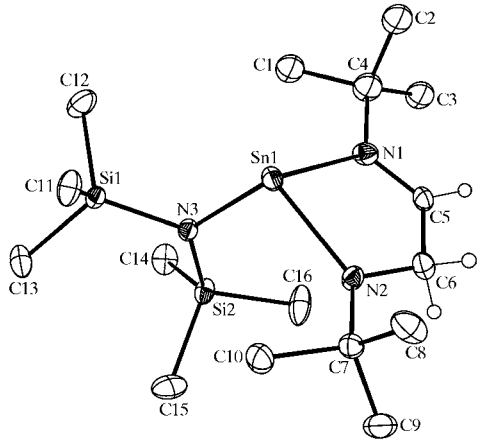


Figure 1
The molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level. The minor components of the disordered C atoms, and all H atoms except those on atoms C5 and C6, have been omitted for clarity.

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demonstrated that DFT methods produce reliable results for trigonal–pyramidal Ge and Sn systems similar to (II). The results of the geometry optimization and natural bonding orbital analysis (NBO; Weinhold, 2001) of (II-DFT) are discussed below.

In (II), the *tert*-butyl{2-[(*E*)-*tert*-butylimino]ethyl}amine ligand coordinates to the Sn centre in an asymmetric four-electron σ-bonding κ^2-fashion, forming a five-membered heterocycle. The Sn1—N1 and Sn1—N2 distances to the bidentate ligand [2.278 (2) and 2.139 (2) Å, respectively] clearly demonstrate the distinction between formally dative and formally covalent bonds. However, such a dramatic difference is hardly expected based on the sum of the angles about atoms N1 and N2, *viz*. atom N1 is sp^2-hybridized [the sum of the angles about N1 is 358.6 (2)°] and atom N2 exhibits a slight sp^3 character [the sum of the angles about N2 is 356.0 (2)°]. Both Sn—N distances fall in the expected range for single Sn—N bonds. These observations are in accord with the theoretical findings for (II-DFT), in which Sn1—N1 = 2.36 Å and Sn1—N2 = 2.12 Å. The distance to the third N atom [Sn1—N3 = 2.150 (2) Å] is similar to Sn1—N2 and somewhat longer than the relevant Sn—N(SiMe$_3$)$_2$ distance of 2.08 (4) Å obtained by averaging the distances in eight compounds selected from the CSD based on rigorous search criteria. The corresponding value in (II-DFT) of 2.13 Å is in excellent agreement with the observed distance.

The NBO analysis suggests that compound (II-DFT) is highly ionic, with the Sn—N bonds strongly polarized toward the N atoms. The Sn lone pair is $sp^{0.21}$-hybridized, indicating predominant *s* character, an observation in harmony with Bent's rule (Weinhold & Landis, 2005). The ionic nature of this metal complex is also evident from the high natural charges: Sn1 1.32, N1 −0.60, N2 −0.98 and N3 −1.72. The Sn1—N3 bond distance is not the shortest among the three Sn1—N bonds because atom N3 bears two SiH$_3$ groups with an average positive charge of 0.48.

The five-membered heterocycle is in an envelope conformation, with Sn1 being the flip atom. Atom Sn1 is displaced from the plane defined by atoms N1/C5/C6/N2 by 0.383 (5) Å. The flip angle of the envelope, defined as the dihedral angle between the planes defined by atoms N1/C5/C6/N2 and N1/Sn1/N2, is 12.70 (19)°. In the theoretical model, (II-DFT), the five-membered ring is substantially more planar, with a small 0.07 Å displacement of Sn1 from the plane defined by N1/C5/C6/N2 and a 2.3° envelope-folding angle. Interestingly, the orientation of the Sn1—N3 vector relative to the plane of the heterocycle is different in (II) and (II-DFT). This is illustrated by the C5—(midpoint of bond C5—C6)—Sn1—N3 pseudo-torsion angle. In (II) this angle is 89.1°, but in (II-DFT) the N(SiH$_3$)$_2$ substituent is considerably more tilted to the side of C5, at an angle of 79.7°.

The *tert*-butyl{2-[(*E*)-*tert*-butylimino]ethyl}amide bite angle N1—Sn1—N2 in (II) spans 75.37 (8)°, a value typical of ligands forming five-membered rings with an Sn centre. This magnitude is in good agreement with both the average of 18 angles in ten relevant Sn compounds found in the CSD [77 (3)°] and the angle of 73.4° computed for (II-DFT). It is noteworthy that the other two N—Sn1—N angles in (II) average 100 (1)°, while in (II-DFT) they were much closer to a right angle [average 92.3 (5)°], corresponding to a small extent of orbital hybridization at the metal centre.

Finally, the solid-state structure of (II) exhibits some positional disorder: each methyl group at C4 is disordered over two positions in a 53:47 ratio.

Experimental

The title stannylene, (II), was prepared according to the literature procedure of Gans-Eichler *et al.* (2002). Orange crystals suitable for X-ray analysis were obtained by recrystallization of the crude product from a small volume of hexane. ^{1}H NMR (C$_6$D$_6$): δ 0.45 (*s*, 18H, SiMe$_3$), 1.04 (*s*, 9H, *tert*-Bu), 1.36 (*s*, 9H, *tert*-Bu), 3.82 [*dd*, ^2J(H,H) = 25 Hz], 4.49 [*dd*, ^2J(H,H) = 25 Hz], 7.31 (*s*, 1H, N═CH); ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ: 6.85, 30.55, 31.64, 54.32, 59.08, 60.34, 172.45.

Crystal data

[Sn(C$_{10}$H$_{21}$N$_2$)(C$_6$H$_{18}$NSi$_2$)]	Z = 2
M_r = 448.37	D_x = 1.304 Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
a = 9.2875 (3) Å	Cell parameters from 7833 reflections
b = 10.3056 (3) Å	θ = 2.2–28.3°
c = 13.3897 (4) Å	μ = 1.23 mm^{-1}
α = 81.4680 (10)°	T = 100 (2) K
β = 85.4160 (10)°	Block, orange
γ = 64.2700 (10)°	0.39 × 0.34 × 0.23 mm
V = 1141.55 (6) Å^3	

Data collection

Bruker SMART1000 CCD area-detector diffractometer	5449 independent reflections
0.30° ω scans	5137 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	R_{int} = 0.015
T_{min} = 0.646, T_{max} = 0.766	θ_{max} = 28.3°
10674 measured reflections	h = −12 → 12
	k = −13 → 13
	l = −17 → 17

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 1.7884P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.031	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.080	$\Delta\rho_{max}$ = 2.38 e Å^{-3}
S = 1.09	$\Delta\rho_{min}$ = −1.36 e Å^{-3}
5449 reflections	
207 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °) for (II).

Sn1—N2	2.139 (2)	Si1—N3	1.734 (2)
Sn1—N3	2.150 (2)	Si2—N3	1.718 (2)
Sn1—N1	2.278 (2)		
N2—Sn1—N3	99.15 (8)	N3—Sn1—N1	101.21 (8)
N2—Sn1—N1	75.37 (8)		

All H atoms were placed in idealized positions and refined as riding, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for atom C5, C—H = 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C) for atom C6, and C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl groups.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1279). Services for accessing these data are described at the back of the journal.

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