



## New group 14 element(IV) $\beta$ -diiminates and a Sn(II) analogue

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### ABSTRACT

Seven group 14 element(IV) compounds **2–7** have been prepared, derived either (**2–5**) from the potassium  $\beta$ -diketiminatone K(L) [ $L = \{N(Ar)C(Me)\}_2CH$ , Ar = C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6] (**1**) or the known lithium  $\beta$ -dialdiminate Li(L') [ $L' = \{N(Ar)C(H)\}_2CPh$ , Ar = C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6]. Treatment of **1** with Bu<sup>t</sup>C(O)Cl, Me<sub>3</sub>SiCl, Ph<sub>3</sub>SnCl, or Me<sub>3</sub>SnCl afforded  $\{N(Ar)C(Me)\}_2C(H)C(O)Bu^t$  (**2**), [ArNC(Me)C(H)C(Me)N(Ar)SiMe<sub>3</sub>] (**3**), [HN(Ar)C(Me)C(H)C(CH<sub>2</sub>SnPh<sub>3</sub>)N(Ar)] (**4**), or [Me<sub>2</sub>SnN(Ar)C(Me)C(H)C{N(Ar)}CH<sub>2</sub>]<sub>2</sub> (**5**), respectively. Compounds **4** and **5** are remarkable as they have arisen from a tautomer of **1**; crystalline centrosymmetric **5** has a fused tricyclic structure, a central eight-membered ring flanked by two six-membered rings. The compounds [GeCl<sub>2</sub>(L')(OGeCl<sub>3</sub>)] (**6**) or [SnCl(L')Me<sub>2</sub>] (**7**), the first group 14 metal  $\beta$ -dialdiminates, were obtained from Li(L') and (GeCl<sub>3</sub>)<sub>2</sub>O or Me<sub>2</sub>SnCl<sub>2</sub>, respectively. The Sn(II) compound SnCl(L') (**8**) was prepared from SnCl<sub>2</sub> and K(L'). The molecular structures of the crystalline compounds **3–8** are reported.

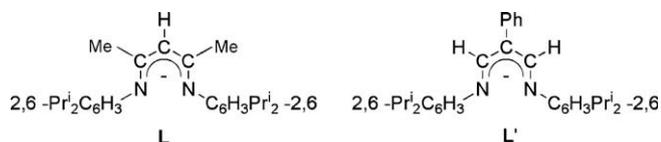
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### 1. Introduction

In the 2002 review of  $\beta$ -diketiminatometal complexes 10 different uninegative ligand–metal bonding modes were described [1]. Six had the  $N,N'$ -chelating ligands in different conformations in mono- or di-metal complexes, one in which the ligand was  $C$ -centred, two having the ligand  $N$ -centred or  $N,N'$ -bridging (in each of which there was substantial NCCN  $\pi$ -delocalisation), and finally one in which an  $\alpha$ -methyl substituent had been deprotonated (see Section 2.1). One of the most widely used  $\beta$ -diketiminatone ligands is **L**.

$\beta$ -Dialdiminatometal complexes, which have CH rather than CR groups adjacent to the nitrogen atoms, are much rarer. One such ligand, **L'**, was introduced in 2002 in the context of Cu<sup>I</sup> chemistry [2]. Other **L'** metal complexes to have been described are the crystalline Ti(L') [3], [Li(L')(thf)<sub>2</sub>] [4], [MCl<sub>2</sub>(L')] (M = Al, Ga) [4], and seven In<sup>III</sup> complexes of various types [4]. In each of these **L'**–metal complexes, the ligand was bound to the metal in the  $N,N'$ -chelating fashion.

The ligand **L'** differs from **L** in that the possibility of substitution reactions implicating the endocyclic carbon atoms of these metal complexes is inhibited. Illustrated below are the ligands **L** and **L'** in their monoanionic  $\pi$ -delocalised form.



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### 2. Results and discussion

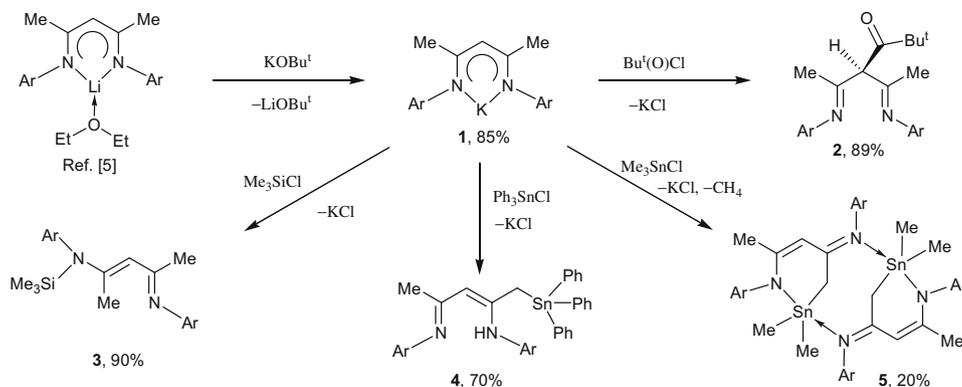
This part is divided into four sections. Sections 2.1. and 2.2 deal with the chemistry of compounds derived from ligand **L**, Section 2.3. describes the synthesis and structures of two group 14 metal(IV)  $\beta$ -dialdiminates, while the last relates to compound SnCl(L').

#### 2.1. Compounds derived from the potassium $\beta$ -diketiminatone K(L) (**1**)

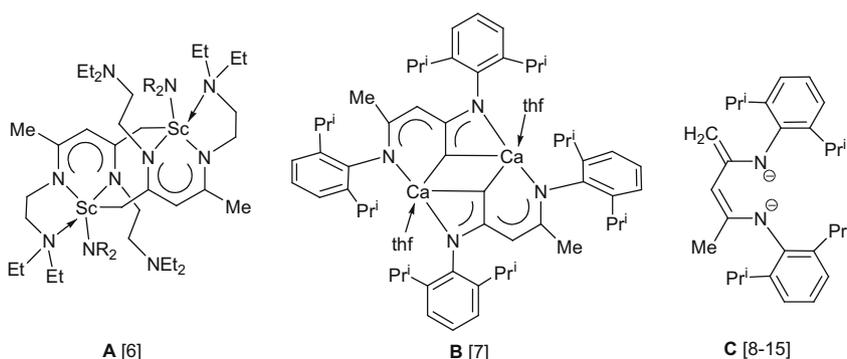
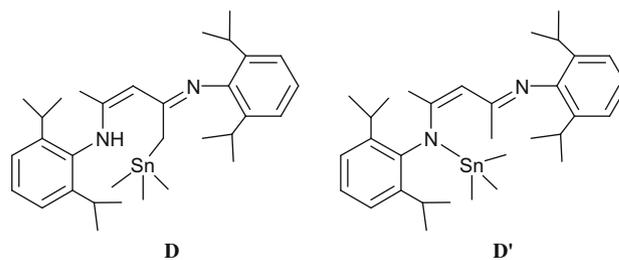
The synthesis of **1** and its conversion into the colourless **2–4** and the yellow **5** crystalline derivatives are summarised in Scheme 1.

The sparingly hexane-soluble crystalline potassium  $\beta$ -diketiminatone (**1**) was obtained as a precipitate by the metathetical exchange reaction between [Li(L)(OEt<sub>2</sub>)] [5] and KOBu<sup>t</sup> in hexane; its purity was established by <sup>1</sup>H NMR spectroscopy in a C<sub>6</sub>D<sub>6</sub> solution. Similar high yield reactions led to  $C$ -pivaloyl (**2**) and  $N$ -trimethylsilyl (**3**)  $\beta$ -diketiminates, from **1** and the appropriate chloride in toluene. Compound **2** was characterised by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of its solution, which showed only one signal for the  $\alpha$ -Me substituents (*cf.* two such signals for **3**), and its  $\nu(C=O)$  stretching frequency. For **3** the NMR data were supplemented by determination of its molecular structure (Section 2.2).

The crystalline (from toluene), low melting 1,5-bis(2',6'-diisopropylphenyl)-2-methyl-4-triphenylstannylmethyl-1,5-diazapentadiene (**4**) was prepared in good yield from equivalent portions of K(L) (**1**) and chlorotri(phenyl)stannane in diethyl ether. Its unexpected constitution was established not only by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of its solution, but also conclusively by its molecular structure derived from a single crystal X-ray study (Section 2.2). It

Scheme 1. (Ar = C<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6).

is unprecedented in being mononuclear and possessing an exocyclic metallomethyl substituent at an  $\alpha$ -carbon atom. There are earlier examples of products resulting from deprotonation of a methyl group attached to the  $\alpha$ -carbon atom of a  $\beta$ -diketiminate. However they relate either to a binuclear complex having a CH<sub>2</sub>-M or a ( $\mu$ -CH<sub>2</sub>)<sub>2</sub> moiety as in **A** [6], or **B** [7]; or are derived from a dianionic ligand **C**, as in [Ge(C)(H)B(H)( $\mu$ -H)<sub>2</sub>Li(OEt<sub>2</sub>)<sub>3</sub>] [8], [Ti(C)(NC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)(OEt<sub>2</sub>)<sub>2</sub>] [9], [Tm(L)(C)] [10], [Si(C)] [11], [Ge(C)] [12], [Si(C)( $\kappa^2$ -CH=CH)] [13], [Si(C)(H)(C=CH)] [13], [Y(C)<sub>2</sub>K(dme)<sub>2</sub>] [14] and [La(C)<sub>2</sub>K(thf)<sub>4</sub>]<sub>∞</sub> [15].



The formation of **4** rather than the expected *N*-substituted Sn(L)Ph<sub>3</sub> is explained by the significant steric demand of the SnPh<sub>3</sub> group, which impedes its approach to a nitrogen atom bearing a bulky aryl substituent. However, solution **1** may be in equilibrium with a minute concentration of its tautomer HN(Ar)-C(Me)C(H)C(=NAr)CH<sub>2</sub><sup>-</sup>K<sup>+</sup>, which with Ph<sub>3</sub>SnCl yields **4** with elimination of KCl.

The formation of **4** from **1** and Ph<sub>3</sub>SnCl may also be contrasted with the corresponding reaction of **1** with Me<sub>3</sub>SnCl in toluene, which led in low yield to the crystalline compound **5**, characterised solely by its X-ray molecular structure (Section 2.2).

Compound **5** has the Me<sub>2</sub>Sn moiety bound to the *N,C*-chelating dianionic ligand *N*(Ar)C(Me)C(H)C(N(Ar))CH<sub>2</sub>; **5** is dinuclear, the exocyclic nitrogen atom of each monomeric fragment being coordinated to the tin atom of its neighbouring "monomer". A possible intermediate is either **D** or **D'** which, upon elimination of methane, yields the monomeric fragment of dimer **5**. The reaction leading to **5** may also be contrasted with that in which K{[N(SiMe<sub>3</sub>)C(Ph)]<sub>2</sub>CH} (≡ **KL'**) with 2 equiv. of Me<sub>3</sub>SnCl gave SnCl(L')Me<sub>2</sub>, with SnMe<sub>4</sub> + KCl as supposed co-products [16].

## 2.2. The molecular structures of the crystalline complexes **3**, **4** and **5**

The molecular structure of crystalline Si(L)Me<sub>3</sub> (**3**) is illustrated in Fig. 1 and selected geometrical parameters are listed in Table 1. A zig-zag arrangement of the atoms N1, C1, C2, C3 and N2 is its core with mutually *trans*-methyl substituents at C1 and C3 and an SiMe<sub>3</sub> group cisoid to the latter. The CN and CC bond lengths are consistent with C1–N1 and C3–C2 being double and C1–C2 and N2–C3 being single bonds. The sum of the angles subtended at each of the three-coordinate atoms C1, C3 and N2 is 360 ± 1°. The dihedral angle between the N1C1C2 and C2C3N2 planes is 7.44°.

The molecular structure of crystalline [(Ar)N(H)C(Me)C(H)C(CH<sub>2</sub>SnPh<sub>3</sub>)N(Ar)] (**4**) is shown in Fig. 2; selected values for bond lengths and angles are given in Table 2. The framework atoms N1, C20, C21, C22 and N2 have a conformation similar to that in its precursor K(L), but **4** has alternating double (N1–C20 and C21–C22) and single (C20–C21 and C22–N2) bonds. Each of the C20 and C22 atoms is in an only slightly distorted trigonal planar environment. The three angles C20–N1–C24, C20–C21–C22

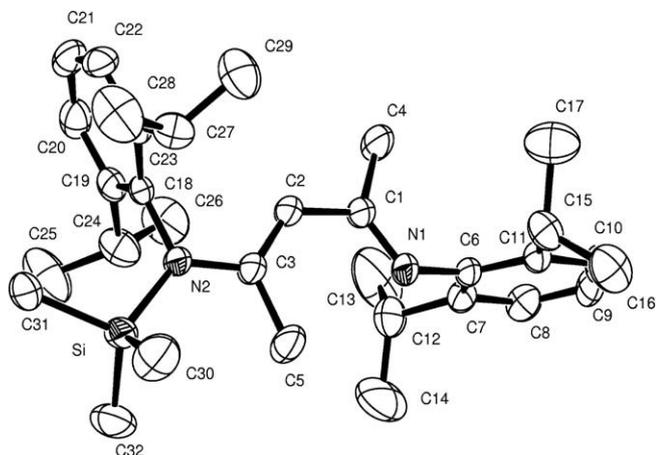


Fig. 1. The molecular structure of crystalline **3** with atom labelling scheme.

Table 1

Selected bond lengths (Å) and angles (°) for **3**.

Bond lengths			
N1–C1	1.284(3)	N1–C6	1.417(2)
N2–C3	1.397(3)	N2–C18	1.450(3)
C1–C2	1.462(3)	C3–C5	1.497(3)
C2–C3	1.351(3)	C1–C4	1.511(3)
N2–Si	1.7788(17)		
Bond angles			
C1–N1–C6	120.73(17)	N1–C1–C4	123.13(19)
C3–N2–C18	116.72(16)	N2–C3–C5	116.44(18)
N1–C1–C2	123.55(19)	C1–C2–C3	128.80(19)
N2–C3–C2	121.62(18)	C2–C3–C5	121.93(19)
C3–N2–Si	126.44(14)	C2–C1–C4	113.25(18)
C18–N2–Si	116.75(12)		

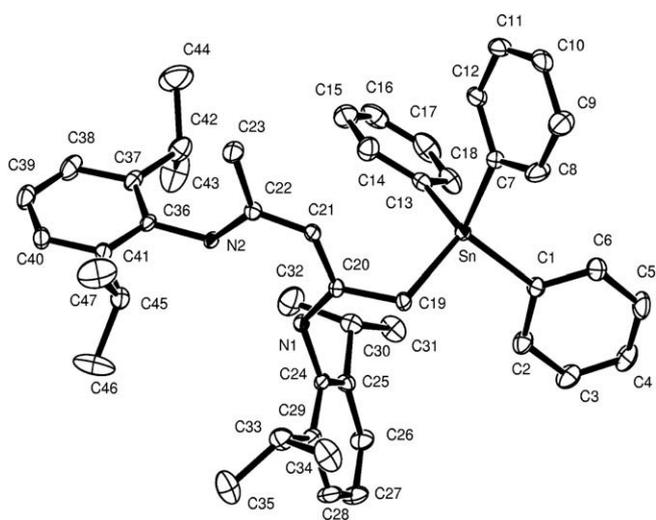


Fig. 2. The molecular structure of crystalline **4** with atom labelling scheme.

and C22–N2–C36 are within the range  $124.5 \pm 2.5^\circ$ . The dihedral angles between the planes (i) C24–N1–C20 and C19–C20–C21 and (ii) C36–N2–C22 and C22–C21–C20 are  $7.99^\circ$  (i) and  $2.95^\circ$  (ii).

An ORTEP representation of the molecular structure of the crystalline, centrosymmetric, dinuclear, fused tricyclic compound  $[\text{Me}_2\text{Sn}(\text{Ar})\text{C}(\text{Me})\text{C}(\text{H})\text{C}\{\text{N}(\text{Ar})\}\text{CH}_2]_2$  (**5**) is shown in Fig. 3, with selected geometrical parameters listed in Table 3. The central

Table 2  
Selected bond lengths (Å) and angles (°) for **4**.

Bond lengths			
N1–C20	1.308(6)	C19–Sn	2.174(5)
N2–C22	1.335(6)	N2–C36	1.441(6)
C20–C21	1.426(7)	N1–C24	1.428(6)
C21–C22	1.369(7)	C20–C19	1.505(7)
C22–C23	1.508(7)		
Bond angles			
C20–N1–C24	122.2(4)	C19–C20–C21	115.5(4)
C22–N2–C36	127.0(4)	C23–C22–C21	120.5(5)
N1–C20–C21	121.1(4)	C20–C19–Sn	113.0(3)
N2–C22–C21	121.3(5)	N1–C20–C19	123.5(4)
C20–C21–C22	126.2(5)	N2–C22–C23	118.2(5)

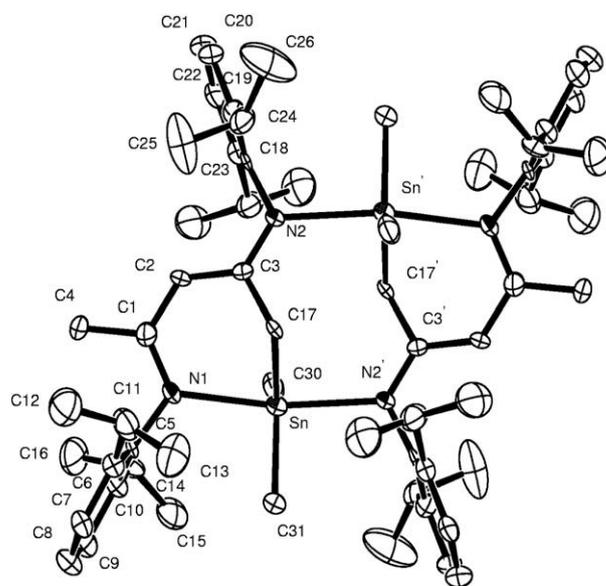


Fig. 3. An ORTEP representation of the molecular structure of the crystalline compound **5** with atom labelling scheme (the second independent molecule of **5** and the solvate molecules are omitted for clarity).

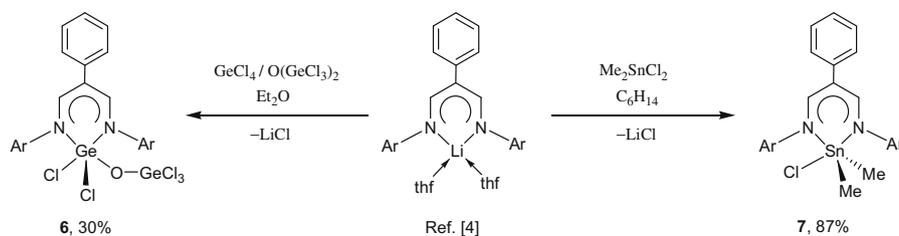
Table 3

Selected bond lengths (Å) and angles (°) for **5**.

Bond lengths			
N1–C1	1.345(9)	N1–C5	1.459(9)
N2–C3	1.330(9)	N2–C18	1.447(9)
C1–C2	1.395(10)	Sn–N1	2.335(6)
C2–C3	1.424(10)	Sn–N2'	2.387(6)
C1–C4	1.504(10)	Sn–C17	2.130(6)
C3–C17	1.503(9)	Sn–C30	2.133(7)
		Sn–C31	2.142(7)
Bond angles			
C1–N1–C5	119.3(6)	C2–C3–C17	117.8(6)
C3–N2–C18	119.3(6)	C4–C1–C2	117.6(6)
N1–C1–C2	123.1(7)	C3–C17–Sn	111.5(5)
N2–C3–C2	124.5(6)	N1–Sn–N2'	165.5(2)
C1–C2–C3	128.3(6)	N1–Sn–C17	78.5(2)

Symmetry transformations used to generate equivalent atoms: '  $-x + 1, -y + 1, -z + 1$ ; "  $-x, -y, -z + 1$ .

eight-membered puckered  $\text{SnC17C3N2Sn}'\text{C17}'\text{C3}'\text{N2}'$  ring is flanked by the two six-membered rings –  $\text{SnC17C3C2C1N1}$  and its symmetry-related counterpart; the substituents are two methyl groups at C1 and C1' and a 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$  group at each of the four nitrogen atoms. Each of the atoms N1, C1, C3 and N2 is in an only slightly distorted trigonal planar environment, the endocyclic angles at these atoms being  $120.4 \pm 3.2^\circ$ . The C1–C2, C2–C3 and

Scheme 2. (Ar = C<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6).

C3–N2 bond lengths are indicative of there being some  $\pi$ -delocalisation over these four atoms.

### 2.3. Synthesis and structures of the $\beta$ -dialdiminato-group 14 metal(IV) complexes **6** and **7**

The preparation of the crystalline group 14 metal(IV) derivatives **6** and **7** is summarised in Scheme 2. As far as we are aware, these are the first heavier group 14  $\beta$ -dialdiminates, and **6** is the first monosubstituted derivative of bis(trichlorogermyl) oxide. An analogue of **7**, the crystalline, X-ray-characterised compound [SnCl(L'')Me<sub>2</sub>], was previously obtained either from SnCl<sub>2</sub>Me<sub>2</sub> and Li(L'') or from SnClMe<sub>3</sub> and K(L'') [L'' = {N(SiMe<sub>3</sub>)C(Ph)<sub>2</sub>CH}] [16].

The reaction of equimolar portions of [Li(L')(thf)<sub>2</sub>] [4] and tetrachlorogermene in diethyl ether unexpectedly afforded the high melting complex [GeCl<sub>2</sub>(L')OGeCl<sub>3</sub>] (**6**) in moderate yield. The unusual outcome may be explained by the presence of bis(trichlorogermyl) oxide due to adventitious hydrolysis. Compound **6** was characterised by satisfactory microanalysis, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra in C<sub>6</sub>D<sub>6</sub>, and a single crystal X-ray diffraction study.

The molecular structure of the crystalline [GeCl<sub>2</sub>(L')OGeCl<sub>3</sub>] (**6**) is shown in Fig. 4; selected structural data are given in Table 4. Its core is a boat-shaped ring, having the Ge1 and C2 atoms 0.569 and 0.112 Å, respectively, out of the N1C1C3N2 plane. Although the endocyclic bond lengths indicate that there is substantial  $\pi$ -delocalisation over the N1C1C2C3N2 moiety, the pairs of bond lengths Ge1–N1/Ge1–N2, N1–C1/N2–C3 and C1–C2/C2–C3 differ by ca. 0.15, 0.05 and 0.03 Å, respectively. Likewise, the endocyclic bond angles subtended at the pairs N1/N2 and C1/C3 differ by ca. 1°

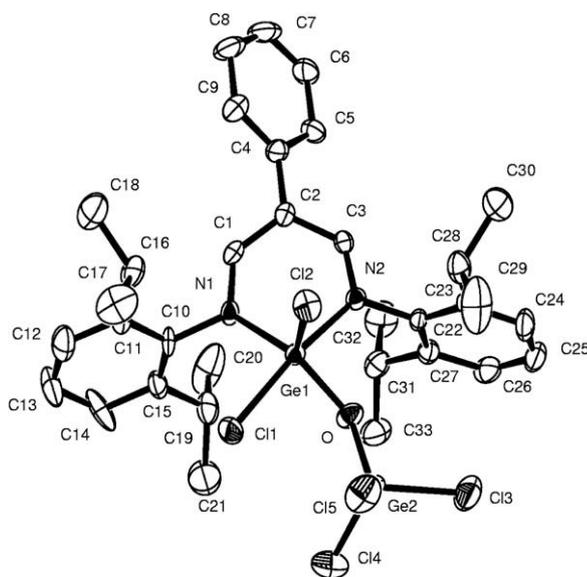


Fig. 4. The molecular structure of crystalline **6** with atom labelling scheme (solvate molecule is omitted for clarity).

Table 4  
Selected bond lengths (Å) and angles (°) for **6**.

Bond lengths			
N1–C1	1.341(12)	N1–C10	1.471(11)
N2–C3	1.298(12)	N2–C22	1.466(11)
C1–C2	1.393(13)	N2–Ge1	2.026(8)
C2–C3	1.419(13)	N1–Ge1	1.910(7)
C2–C4	1.465(14)	Ge1–Cl1	2.254(3)
Ge1–O	1.795(7)	Ge1–Cl2	2.150(3)
Ge2–O	1.704(7)	Ge2–Cl5	2.108(3)
Bond angles			
C1–N1–C10	114.4(8)	C1–C2–C4	119.2(9)
C3–N2–C22	113.2(7)	C3–C2–C4	120.7(8)
N1–C1–C2	129.3(9)	C22–N2–Ge1	122.7(6)
N2–C3–C2	125.9(8)	C10–N1–Ge1	121.8(1)
C1–C2–C3	118.9(9)	N1–Ge1–N2	89.4(3)
N1–Ge1–O	135.6(4)	Ge1–O–Ge2	135.3(4)
N2–Ge1–O	82.5(3)	O–Ge2–Cl5	116.1(3)

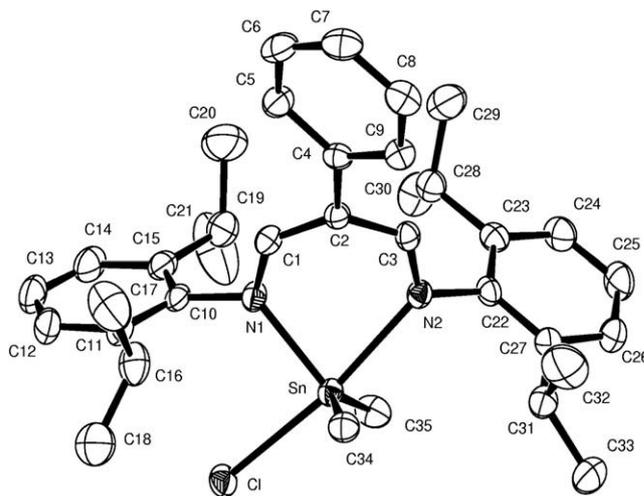


Fig. 5. The molecular structure of crystalline **7** with atom labelling scheme.

Table 5  
Selected bond lengths (Å) and angles (°) for **7**.

Bond lengths			
N1–C1	1.334(4)	N1–C10	1.456(4)
N2–C3	1.301(4)	N2–C22	1.451(4)
C1–C2	1.389(4)	N2–Sn	2.329(2)
C2–C3	1.421(4)	N1–Sn	2.148(2)
C2–C4	1.489(4)	Sn–Cl	2.5051(8)
Sn–C34	2.127(3)	Sn–C35	2.121(3)
Bond angles			
C1–N1–C10	114.3(2)	C1–C2–C4	119.3(3)
C3–N2–C22	116.0(2)	C3–C2–C4	117.8(2)
N1–C1–C2	130.1(3)	C22–N2–Sn	124.24(18)
N2–C3–C2	126.5(3)	C10–N1–Sn	123.76(18)
C1–C2–C3	122.4(3)	N1–Sn–N2	82.20(8)
N1–Sn–Cl	90.14(7)	N1–Sn–C35	117.31(12)
N2–Sn–Cl	170.67(6)	N2–Sn–C35	88.49(12)

and  $>3^\circ$ , respectively. The Ge1–Cl1 and Ge1–Cl2 bond lengths are significantly longer than each of the Ge2–Cl bond lengths, which range from 2.101(4) to 2.116(3) Å. The five-coordinate Ge1 atom is in a distorted trigonal bipyramidal environment, the Cl1 and N2 atoms occupying pseudo-axial positions. The Ge1–O–Ge2 angle is considerably wider than an  $sp^2$  value, consistent with the notion that the Ge2–O bond has some  $\pi$ -character, being much shorter than the Ge1–O bond. Each of the atoms N1, C2 and N2 is close to being in a distorted trigonal planar environment.

The molecular structure of the crystalline  $[\text{SnCl}(\text{L})\text{Me}_2]$  (**7**) is illustrated in Fig. 5; selected geometrical parameters are listed in Table 5. The core boat-shaped ring is very similar to that in **6**, having the atoms Sn and C2 0.933 and 0.166 Å out of the N1C1C3N2 plane. The difference in lengths between the pairs of endocyclic bonds at the metal, nitrogen and  $\alpha$ -carbon atoms is *ca.* 0.18, 0.03 and 0.03 Å, respectively. The corresponding angles at N1 and N2 are almost identical at  $119.65 \pm 0.15^\circ$ , but that at C1 is significantly wider than that at C3. Each of the atoms C2 and N2 is close to being in a distorted trigonal planar environment, but N1 deviates from this to some extent. The dihedral angle between (i) the C3–N2–C22 and the C3–N2–Sn, (ii) the C1–N1–C10 and the C1–N1–Sn and (iii) the C4–C2–C1 and the C4–C2–C3 planes is  $0.73^\circ$  (i),  $17.21^\circ$  (ii) and  $7.48^\circ$  (iii) respectively. The corresponding values in **6** with Ge1 in place of Sn are  $0.02^\circ$  (i),  $9.42^\circ$  (ii) and  $12.17^\circ$  (iii) respectively.

#### 2.4. Synthesis and structure of the $\beta$ -dialdiminatotin(II) chloride **8**

The crystalline, high melting compound **8** was prepared as shown in Eq. (1). It was characterised by C, H and N microanalytical data, appropriate  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in  $\text{C}_6\text{D}_6$  and showed the parent molecular ion as the highest  $m/e$  signal in its EI-mass spectrum.

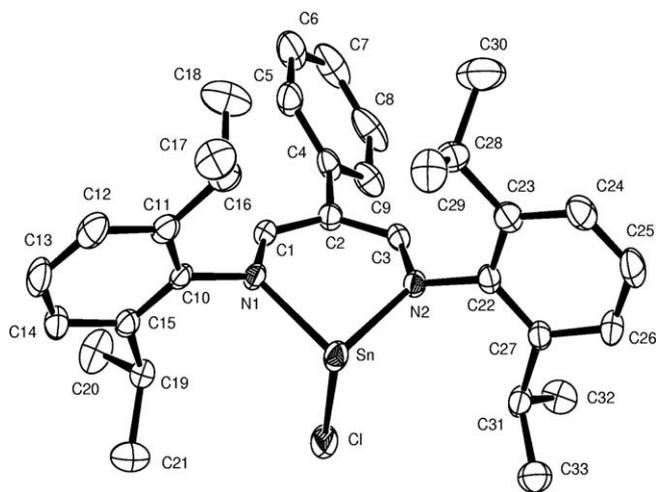
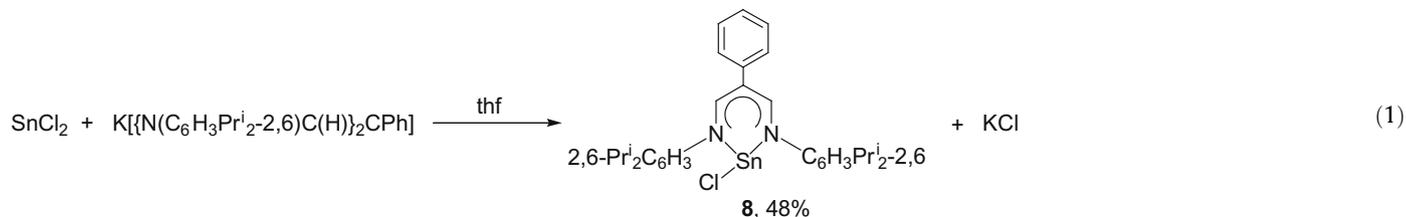
**Table 6**  
Selected bond lengths (Å) and angles ( $^\circ$ ) for **8**.

Bond lengths			
Sn–N1	2.190(2)	N1–C1	1.316(4)
Sn–N2	2.182(2)	N2–C3	1.324(4)
Sn–Cl	2.457(1)	C1–C2	1.401(4)
C2–C4	1.487(4)	C2–C3	1.401(4)
N1–C10	1.455(3)	N2–C22	1.447(3)
Bond angles			
N1–Sn–N2	84.50(8)	Sn–N1–C1	125.15(18)
N1–Sn–Cl	92.75(7)	Sn–N2–C3	125.18(18)
N2–Sn–Cl	92.82(7)	C1–C2–C3	123.6(3)
N1–C1–C2	128.0(3)	Sn–N1–C10	118.12(16)
N2–C3–C2	128.2(3)	Sn–N2–C22	118.68(17)
C1–C2–C4	118.8(3)	C1–N1–C10	116.5(2)
C3–C2–C4	116.7(2)	C3–N2–C22	115.7(2)

One reason for choosing to prepare **8** was as a potential precursor to a dimeric tin(I) compound  $\text{L}'\text{Sn}–\text{SnL}'$ , having noted that two  $N,N'$ -chelated Ge(I) compounds  $[\text{Ge}\{\{\text{N}(\text{C}_6\text{H}_3\text{Pr}^i_2-2,6)\}_2\text{CR}\}]_2$  ( $\text{R} = \text{Bu}^t$  or  $\text{NPr}^i_2$ ) had been obtained from the appropriate germanium(II) chloride and potassium [19]. In the event, treatment of **8** with Na/K alloy or  $\text{KC}_8$  invariably afforded metallic tin.

Analogues of **8** are the crystalline compounds (i)  $[\text{Sn}(\text{Cl})(\text{L})]$  (**E**) [17,18], (ii)  $[\text{Sn}(\text{Cl})(\text{L}'')]$  [20] and (iii)  $[\text{Sn}(\text{Cl})(\text{L}''')]$  [21] obtained from  $\text{SnCl}_2$  and the appropriate Li  $\beta$ -diketiminato in diethyl ether  $[\text{L}'' = \{\text{N}(\text{C}_6\text{H}_2\text{Me}_3-2,4,6)\text{C}(\text{Me})_2\text{CH}\}]$ .

The molecular structure of crystalline  $[\text{Sn}(\text{Cl})(\text{L})]$  (**8**) is shown in Fig. 6 and selected geometrical parameters are listed in Table 6. The core is a boat-shaped ring having the Sn and C2 atoms out of the N1C1C3N2 plane by 0.48 and 0.085 Å, respectively. The dihedral angle between that plane and the C1C2C3 or N1SnN2 plane is



**Fig. 6.** The molecular structure of crystalline **8** with atom labelling scheme.

$7.4(3)^\circ$  or  $17.3(1)^\circ$ , respectively. The endocyclic bond lengths demonstrate that there is significant  $\pi$ -delocalisation in the N1C1C2C3N2 moiety. The fragment  $\text{ClSn}(\text{N1})\text{N2}$  in **8** is very similar to that in **E**: the latter having Sn–N1, Sn–N2 and Sn–Cl bond lengths of 2.185(2), 2.180(2) and 2.473(9) Å, respectively; and N1–Sn–N2, N1–Sn–Cl and N2–Sn–Cl bond angles of  $85.21(8)^\circ$ ,  $90.97(6)^\circ$  and  $93.47^\circ$ , respectively [18].

### 3. Experimental

#### 3.1. General details

Syntheses were carried out under an atmosphere of argon or in vacuum, using Schlenk apparatus and vacuum line techniques. The solvents employed were reagent grade or better and were freshly distilled under dry nitrogen gas and freeze/thaw degassed prior to use. The drying agents were sodium benzophenone (PhMe,  $\text{Et}_2\text{O}$ ) or sodium potassium alloy ( $\text{C}_5\text{H}_{12}$ ,  $\text{C}_6\text{H}_{14}$ ). The  $\text{C}_6\text{D}_6$  for NMR spectroscopy was stored over molecular sieves (A4). Elemental analyses were provided by the University of North London. Melting points were taken in sealed capillaries. The  $^1\text{H}$ ,  $^{13}\text{C}$  and

$^{119}\text{Sn}$  NMR spectra were recorded in  $\text{C}_6\text{D}_6$  at ambient temperature using a Bruker DPX 300 instrument and were referenced internally ( $^1\text{H}$ ,  $^{13}\text{C}$ ) to residual solvent resonances or externally ( $^{119}\text{Sn}$ , with  $\text{SnMe}_4$  as standard). Electron impact mass spectra were taken from solid samples, using a Kratos MS 80RF instrument. IR spectra were measured on a Perkin Elmer 1720 FT spectrometer, as “Nujol” mulls. The compounds  $\text{Li}\{[\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{C}(\text{Me})_2\text{CH}](\text{OEt}_2)\}$  (**5**) and  $\text{Li}\{[\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{C}(\text{H})_2\text{CPh}](\text{thf})_2\}$  (**4**) were prepared by published procedures. Other starting materials were purchased (Aldrich) and were rigorously dried before use.

### 3.2. Preparation of $\text{K}\{[\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{C}(\text{Me})_2\text{CH}]\}$ (**1**)

Potassium *tert*-butoxide (2.76 g, 0.023 mol) was added slowly with stirring to a solution of  $\text{Li}\{[\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{C}(\text{Me})_2\text{CH}](\text{OEt}_2)\}$  (12.58 g, 0.023 mol) in hexane (30 mL) at  $0^\circ\text{C}$ . The mixture was stirred for 12 h at  $25^\circ\text{C}$ , then filtered. The colourless precipitate of **K(L)** (**1**) (8.93 g, 85%) was washed with hexane (4 × 50 mL) and dried *in vacuo*.  $^1\text{H}$  NMR:  $\delta$  1.23 (d, 12H,  $\text{CHMe}_2$ ), 1.27 (d, 12H,  $\text{CHMe}_2$ ), 1.89 (s, 6H,  $\text{NCMe}$ ), 3.34 (septet, 4H,  $\text{CHMe}_2$ ), 4.71 (s, 1H,  $\text{CH}_{\text{middle}}$ ), 7.07–7.16 ppm (m, 6H,  $\text{C}_6\text{H}_3\text{Pr}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  23.4 ( $\text{Pr}^i$ ), 23.7 ( $\text{Pr}^i$ ), 24.45 ( $\text{Pr}^i$ ), 27.7 ( $\text{NCMe}$ ), 91.3 ( $\text{C}_{\text{middle}}$ ); 121.3, 123.55, 123.6, 139.6, 142.75, 150.8 ( $\text{C}_6\text{H}_3\text{Pr}_2$ ), 161.7 ppm ( $\text{NCMe}$ ).

### 3.3. Preparation of $\{[\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{C}(\text{Me})_2\text{C}(\text{H})\text{C}(\text{O})\text{Bu}^t]\}$ (**2**)

Pivaloyl chloride (0.34 mL, 2.75 mmol) was added slowly to a solution of **K(L)** (**1**) (1.26 g, 2.75 mmol) in toluene (30 mL) at  $0^\circ\text{C}$ . The mixture was stirred for 24 h at  $25^\circ\text{C}$ , then filtered. The volatiles were removed from the filtrate *in vacuo*. The residue was extracted into hexane (50 mL). Concentration of this extract to ca. 20 mL yielded, after cooling at  $-25^\circ\text{C}$  for 2 d, colourless crystalline **2** (1.23 g, 89%).  $^1\text{H}$  NMR:  $\delta$  1.15 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95,  $\text{CHMe}_2$ ], 1.17 (s, 9H,  $\text{Bu}^t$ ), 1.18 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95,  $\text{CHMe}_2$ ], 1.21 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95,  $\text{CHMe}_2$ ], 1.22 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95 Hz,  $\text{CHMe}_2$ ], 1.73 (s, 6H,  $\text{NCMe}$ ), 2.97 [septet, 2H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95,  $\text{CHMe}_2$ ], 3.14 [septet, 2H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95 Hz,  $\text{CHMe}_2$ ], 5.24 (s, 1H,  $\text{CH}_{\text{middle}}$ ), 7.07–7.18 ppm (m, 6H,  $\text{C}_6\text{H}_3\text{Pr}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  20.1 ( $\text{NCMe}$ ), 23.4, 23.5, 23.9 and 24.3 ( $\text{CHMe}_2$ ); 26.5 ( $\text{CMe}_3$ ), 28.0 and 28.1 ( $\text{CHMe}_2$ ); 45.8 ( $\text{CMe}_3$ ), 68.6 ( $\text{C}_{\text{middle}}$ ); 123.3 and 123.4 (m-C); 124.4 (p-C), 136.3 and 136.5 (o-C); 146.0 (*ipso*-C), 167.8 ( $\text{NCMe}$ ), 209.6 ppm (C=O). IR:  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 1646 (C=N), 1703 (C=O).

### 3.4. Preparation of $\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{SiMe}_3$ (**3**)

Chloro(trimethyl)silane (0.36 mL, 2.8 mmol) was added slowly to a solution of **K(L)** (**1**) (1.29 g, 2.8 mmol) in toluene (40 mL) at  $0^\circ\text{C}$ . The mixture was stirred for 24 h at  $25^\circ\text{C}$ , then filtered. The volatiles were removed from the filtrate *in vacuo*; the residue was extracted into hexane (20 mL). Concentration of this extract to ca. 15 mL yielded, after cooling at  $-25^\circ\text{C}$  for 2 d, colourless crystals of **3** (1.31 g, 90%).  $^1\text{H}$  NMR:  $\delta$  0.06 (s, 9H,  $\text{SiMe}_3$ ), 1.14 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 1.17 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 1.22 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 1.25 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 1.33 (s, 3H,  $\text{NCMe}$ ), 2.90 (s, 3H,  $\text{NCMe}$ ), 3.03 [septet, 2H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95 Hz,  $\text{CHMe}_2$ ], 3.19 [septet, 2H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95 Hz,  $\text{CHMe}_2$ ], 4.62 (s, 1H,  $\text{CH}_{\text{middle}}$ ), 7.03–7.19 ppm (m, 6H,  $\text{C}_6\text{H}_3\text{Pr}_2$ ).

### 3.5. Preparation of $(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{N}(\text{H})\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{CH}_2\text{SnPh}_3)\text{NC}_6\text{H}_3\text{Pr}_2\text{-}2,6$ (**4**)

Triphenyltin chloride (1.62 g, 4.2 mmol) was added slowly to a solution of **K(L)** (**1**) (1.92 g, 4.2 mmol) in diethyl ether (30 mL) at

$0^\circ\text{C}$ . The mixture was stirred for 24 h at  $25^\circ\text{C}$ , then filtered. The volatiles were removed from the filtrate *in vacuo*. The residue was extracted into hexane (20 mL). Concentration of this extract to ca. 10 mL yielded, after cooling at  $-15^\circ\text{C}$  for 24 h, colourless crystals of **4** (2.26 g, 70%), mp  $54^\circ\text{C}$ ,  $^1\text{H}$  NMR:  $\delta$  1.08 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 1.09 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 1.15 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 1.26 [d, 6H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 1.46 (s, 3H,  $\text{NCMe}$ ), 2.71 [s, with  $^{119}\text{Sn}$  satellites,  $^2\text{J}(\text{H}-^1\text{H}) = 34$ , 2H,  $\text{CH}_2\text{Sn}$ ], 3.23 [septet, 2H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 3.38 [septet, 2H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83 Hz,  $\text{CHMe}_2$ ], 5.14 (s, 1H,  $\text{CH}_{\text{middle}}$ ), 7.16 (m, 15H,  $\text{C}_6\text{H}_3\text{Pr}_2 + m$ - and  $p$ -CH of Ph), 7.55 (m, 6H,  $o$ -CH of Ph), 12.4 ppm (s, 1H, NH);  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  20.2 ( $\text{CH}_2\text{Sn}$ ), 23.65 ( $\text{Pr}^i$ ), 24.6 ( $\text{Pr}^i$ ), 24.8 ( $\text{Pr}^i$ ), 28.5 ( $\text{NCMe}$ ); 100.8 ( $\text{C}_{\text{middle}}$ ); 123.65, 124.8, 126.8, 127.8, 137.4, 139.0, 141.1, 144.75 ( $\text{C}_6\text{H}_3\text{Pr}_2 + \text{Ph}$ ), 158.8 ( $\text{CCH}_2\text{Sn}$ ), 165.9 ppm ( $\text{NCMe}$ ).

### 3.6. Preparation of $[\text{Me}_2\text{SnN}(\text{Ar})\text{C}(\text{Me})\text{C}(\text{H})\text{C}\{\text{N}(\text{Ar})\}\text{CH}_2]_2$ (**5**)

Trimethyltin chloride (0.44 g, 2.2 mmol) was added to a solution of **K(L)** (**1**) (1.13 g, 2.5 mmol) in diethyl ether (20 mL) at  $0^\circ\text{C}$ . The mixture was stirred for 24 h at  $25^\circ\text{C}$ , then filtered. The volatiles were removed from the filtrate *in vacuo*. The residue was extracted into hexane (ca. 20 mL). Concentration of this extract to ca. 10 mL yielded, after cooling at  $-25^\circ\text{C}$  for 3 weeks, yellow crystals of **5** (0.30 g, 20%). Recrystallisation from toluene afforded X-ray quality crystals.

### 3.7. Preparation of $\text{Ge}(\text{Cl})_3\text{OGe}(\text{Cl})_2\{[\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{C}(\text{H})_2\text{CPh}]\}$ (**6**)

$[\text{Li}(\text{L}')(\text{thf})_2]$  (0.50 g, 0.81 mmol) was added to tetrachlorogermane (0.17 g, 0.81 mmol) in diethyl ether (30 mL) at  $0^\circ\text{C}$ . The mixture was stirred for 12 h at  $25^\circ\text{C}$ , then filtered. The volatiles were removed from the filtrate *in vacuo*. The residue was extracted into hexane (30 mL). Concentration of the extract to ca. 15 mL yielded, after cooling at  $25^\circ\text{C}$  for 2 h, colourless crystals of **6** (0.19 g, 30%), mp  $198^\circ\text{C}$ . Anal. Calc. for  $\text{C}_{33}\text{H}_{41}\text{Cl}_5\text{Ge}_2\text{N}_2\text{O}$ : C, 49.3; H, 5.14; N, 3.48. Found: C, 49.5; H, 5.21; N 3.46%.  $^1\text{H}$  NMR:  $\delta$  1.19 [d, 12H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 1.21 [d, 12H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83,  $\text{CHMe}_2$ ], 3.45 [septet, 4H,  $^3\text{J}(\text{H}-^1\text{H})$  6.83 Hz,  $\text{CH}(\text{CH}_3)_2$ ], 7.10–7.25 [m, 11H,  $\text{C}_6\text{H}_3\text{Pr}_2 + \text{Ph}$ ], 7.77 ppm (s, 2H, NCH);  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  23.9 ( $\text{Pr}^i$ ), 28.7 ( $\text{Pr}^i$ ), 106.5, C(Ph); 123.7, 125.15, 125.4, 126.05, 129.05, 140.4, 141.9, 143.9 ( $\text{C}_6\text{H}_3\text{Pr}_2 + \text{Ph}$ ), 155.8 ppm (NCH).

### 3.8. Preparation of $\text{SnCl}(\text{Me})_2\{[\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{C}(\text{H})_2\text{CPh}]\}$ (**7**)

$[\text{Li}(\text{L}')(\text{thf})_2]$  (0.64 g, 1.00 mmol) was added to dimethyltin dichloride (0.26 g, 1.18 mmol) in hexane (30 mL) at  $0^\circ\text{C}$ . The mixture was stirred for 12 h at  $25^\circ\text{C}$ , then filtered. The filtrate was concentrated to ca. 10 mL which, after 12 h at  $-25^\circ\text{C}$ , yielded yellow X-ray quality crystals of **7** (0.59 g, 87%), mp  $103^\circ\text{C}$ . EI-MS (70 eV)  $m/z$  (% assignment): 650 (5,  $[\text{M}]^+$ ), 635 (35,  $[\text{M}-\text{Me}]^+$ ), 615 (10,  $[\text{M}-\text{Cl}]^+$ ), 585 (20,  $[\text{M}-2\text{Me}-\text{Cl}]^+$ ), 466 ( $[\text{L}'\text{H}]^+$ , 100).  $^1\text{H}$  NMR:  $\delta$  1.11 (s, 6H,  $\text{SnMe}_2$ ), 1.16 [d, 12H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95,  $\text{CHMe}_2$ ], 1.38 [d, 12H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95,  $\text{CHMe}_2$ ], 3.39 [septet, 4H,  $^3\text{J}(\text{H}-^1\text{H})$  6.95 Hz,  $\text{CHMe}_2$ ], 7.00–7.40 (m, 11H,  $\text{C}_6\text{H}_3\text{Pr}_2 + \text{Ph}$ ), 7.70 ppm (s, 2H, NCH);  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  7.38 ( $\text{SnMe}_2$ ), 23.4 ( $\text{Pr}^i$ ), 23.8 ( $\text{Pr}^i$ ), 25.5 ( $\text{Pr}^i$ ), 29.0 ( $\text{Pr}^i$ ), 101.2 (CPh); 124.2, 125.8, 126.1, 127.35, 129.2, 140.2, 143.6, 146.5 ( $\text{C}_6\text{H}_3\text{Pr}_2 + \text{Ph}$ ), 164.4 ppm [NCH(Ph)];  $^{119}\text{Sn}\{^1\text{H}\}$  NMR:  $\delta$  183.8 ppm;  $^{119}\text{Sn}$  NMR: 183.8 ppm [spt,  $^2\text{J}(\text{H}-^1\text{H})$  37 Hz].

### 3.9. Preparation of $\text{SnCl}\{[\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6)\text{C}(\text{H})_2\text{CPh}]\}$ (**8**)

**K(L)** (49 mL of a solution in THF, 6.70 mmol) was added to a solution of tin(II) chloride (1.26 g, 6.70 mmol) in THF (30 mL) at

**Table 7**  
Crystal data and structure refinement for **3**, **4**, **5**, **6**, **7** and **8**.

Compound	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
Formula	C <sub>32</sub> H <sub>50</sub> N <sub>2</sub> Si	C <sub>47</sub> H <sub>56</sub> N <sub>2</sub> Sn	C <sub>62</sub> H <sub>92</sub> N <sub>4</sub> Sn <sub>2</sub> · 4(C <sub>7</sub> H <sub>8</sub> )	C <sub>33</sub> H <sub>41</sub> Cl <sub>5</sub> Ge <sub>2</sub> N <sub>2</sub> O · (C <sub>6</sub> H <sub>14</sub> )	C <sub>35</sub> H <sub>47</sub> ClN <sub>2</sub> Sn	C <sub>33</sub> H <sub>41</sub> ClN <sub>2</sub> Sn
<i>M</i>	490.83	767.63	1499.31	890.28	649.89	619.82
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> <sub>2</sub> <sub>1</sub> (No. 4)	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> <sub>1</sub> (No. 2)
<i>a</i> (Å)	12.8574(2)	11.6059(2)	15.3418(2)	16.9671(2)	11.7221(2)	11.5242(3)
<i>b</i> (Å)	13.6643(3)	20.5020(3)	21.5983(3)	12.4687(2)	24.6221(3)	11.5988(4)
<i>c</i> (Å)	18.8496(4)	8.9658(2)	24.1733(3)	20.3478(3)	11.7804(2)	13.4950(4)
$\alpha$ (°)	90	90	90	90	90	90.979(2)
$\beta$ (°)	105.670(1)	97.294(1)	98.082(1)	96.589(1)	93.888(1)	96.756(2)
$\gamma$ (°)	90	90	90	90	90	118.604(2)
<i>U</i> (Å <sup>3</sup> )	3188.55(11)	2116.10(7)	7930.4(2)	4276.30(11)	3392.27(9)	1567.10(9)
<i>Z</i>	4	2	4	4	4	2
Absorption coefficient (mm <sup>-1</sup> )	0.09	0.64	0.68	1.75	0.86	0.92
Unique reflections, <i>R</i> <sub>int</sub>	5612, 0.062	7195, 0.040	13756, 0.056	7224, 0.064	5876, 0.062	6177, 0.056
Reflections with <i>I</i> > 2σ( <i>I</i> )	4159	6863	9922	6516	4979	5147
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.053, 0.133	0.037, 0.102	0.078, 0.159	0.092, 0.236	0.035, 0.069	0.034, 0.082
<i>R</i> indices (all data) <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.081, 0.154	0.040, 0.103	0.107, 0.170	0.099, 0.239	0.047, 0.074	0.048, 0.093

0 °C. The resulting mixture was stirred for 48 h at 25 °C, whereafter volatiles were removed *in vacuo*. The residue was washed with hexane (30 mL). The yellow-orange extract was concentrated *in vacuo* to ca. 15 mL which, after 24 h at –25 °C, furnished yellow-orange crystals of **8** (1.97 g, 48%), mp 179–181 °C. Anal. Calc. for C<sub>33</sub>H<sub>41</sub>ClN<sub>2</sub>Sn: C, 63.9; H, 6.61; N, 4.52. Found: C, 63.8; H, 6.62; N 4.44%. <sup>1</sup>H NMR: δ 1.03 [d, 6H, <sup>3</sup>J(<sup>1</sup>H–<sup>1</sup>H) 6.6, CHMe<sub>2</sub>], 1.14 [d, 6H, <sup>3</sup>J(<sup>1</sup>H–<sup>1</sup>H) 6.6, CHMe<sub>2</sub>], 1.23 [d, 6H, <sup>3</sup>J(<sup>1</sup>H–<sup>1</sup>H), CHMe<sub>2</sub>], 1.41 [d, 6H, <sup>3</sup>J(<sup>1</sup>H–<sup>1</sup>H) 6.6, CHMe<sub>2</sub>], 3.24 [septet, 2H, <sup>3</sup>J(<sup>1</sup>H–<sup>1</sup>H) 6.6, CHMe<sub>2</sub>], 4.21 [septet, 2H, <sup>3</sup>J(<sup>1</sup>H–<sup>1</sup>H) 6.6 Hz, CHMe<sub>2</sub>], 7.00–7.21 (m, br, 11H, C<sub>6</sub>H<sub>3</sub>Pr<sup>+</sup><sub>2</sub> + Ph), 7.74 ppm [s, with <sup>119</sup>Sn satellites, <sup>3</sup>J(<sup>119</sup>Sn–<sup>1</sup>H) = 19 Hz, 2H, NCH]; <sup>13</sup>C{<sup>1</sup>H} NMR: δ 23.4, 25.2, 25.3, 25.6 (CHMe<sub>2</sub>) 28.2, 29.8 (CHMe<sub>2</sub>); 110.5 (CPh); 123.6, 125.7, 125.8, 126.7, 127.8, 129.2, 140.6, 142.8, 144.6, 145.3 (C<sub>6</sub>H<sub>3</sub>Pr<sup>+</sup><sub>2</sub> + Ph); 158.9 ppm [NCH(Ph)]. EI-MS: *m/z* (% assignment): 619 (36, [M–1]<sup>+</sup>), 584 (55, [M–Cl–1]<sup>+</sup>), 466 (100, [LH]<sup>+</sup>).

### 3.10. X-ray crystallographic studies for **3**, **4**, **5**, **6**, **7** and **8**

Diffraction data were collected on a Nonius Kappa CCD diffractometer using monochromated Mo Kα radiation, λ 0.71073 Å at 173(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. The structures were refined on all *F*<sup>2</sup> using SHELXL-97 [22]; absorption corrections for **4**, **5**, **6**, **7** and **8** were applied using MULTISCAN. Drawings used ORTEP-3 for Windows. For **5**, there were two independent dimers, both lying on an inversion centre. There were also four independent toluene solvate molecules all included with C6 rings as rigid bodies and with isotropic C atoms. Further details are given in Table 7.

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### Appendix A. Supplementary material

CCDC 721035, 721036, 721037, 721038, 721039 and 721040 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2009.03.044.

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