



# A contribution to 1-azapentadienylmetal chemistry: Si, Sn(II), Fe(II) and Co(II) complexes

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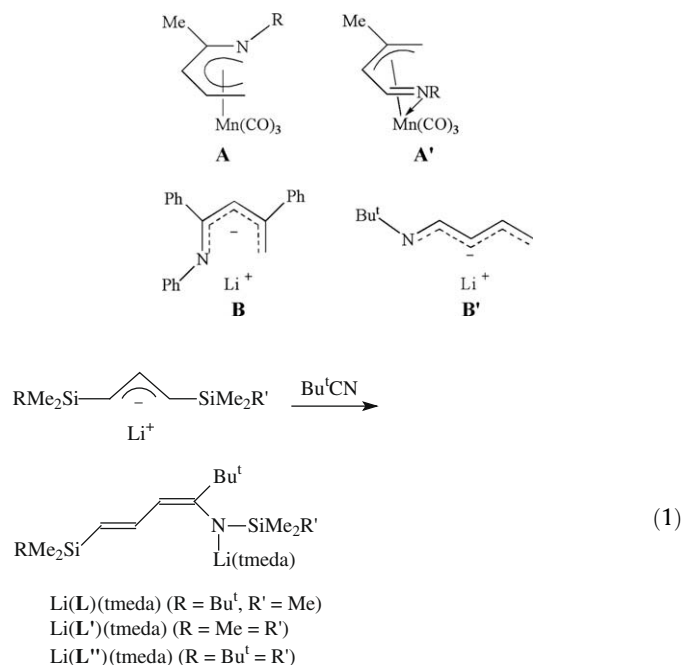
## ABSTRACT

Complexes of three related 1-azapentadienyl ligands  $[N(SiMe_2R^1)C(Bu^t)(CH)_3SiMe_2R^2]^-$ , abbreviated as **L** ( $R = Bu^t$ ,  $R^1 = Me$ ), **L'** ( $R = Me = R^1$ ), and **L''** ( $R = Bu^t = R^1$ ), are described. The crystalline compounds  $Sn(L)_2$  (**1**),  $Sn(L')$  (**2**),  $[Sn(L'')(\mu-Cl)]_2$  (**3**) and  $[Sn(L'')(\mu-Cl)]_2$  (**4**) were prepared from  $SnCl_2$  and 2 **K(L)**, 2 **K(L')**, **K(L')** and **K(L'')**, respectively, in thf. Treatment of the appropriate lithium 1-azapentadienyl with  $Si(Cl)Me_3$  yielded the yellow crystalline  $Me_3Si(L)$  (**5**) and the volatile liquid  $Me_3Si(L')$  (**6**) and  $Me_3Si(L'')$  (**7**), each being an *N,N,C*-trisilyldieneamine. The red, crystalline  $Fe(L)_2$  (**8**) and  $Co(L')$  (**9**) were obtained from thf solutions of  $FeCl_2$  with 2 **Li(L)(tmeda)** and  $CoCl_2$  with 2 **K(L')**, respectively. Each of **1–9** gave satisfactory C, H, N analyses; **6** and **7** (GC–MS) and **1**, **2**, **8** and **9** (MS) showed molecular cations and appropriate fragments (also **3** and **4**). The  $^1H$ ,  $^{13}C$  and  $^{119}Sn$  NMR (**1–4**) and IR spectra support the assignment of **1–4** as containing  $Sn-N(SiMe_2R^1)-C(Bu^t)(CH)_3SiMe_2R^2$  moieties and **5–7** as  $N(SiMe_3)(SiMe_2R^1)C(Bu^t)(CH)_3SiMe_2R^2$  molecules; for **1–4** this is confirmed by their X-ray structures. The magnetic moments for **8** ( $5.56 \mu_B$ ) and **9** ( $2.75 \mu_B$ ) are remarkably close to the appropriate Fe and Co complex  $[M\{\eta^3-N(SiMe_3)C(Bu^t)(H)SiMe_3\}_2]$ ; hence it is proposed that **8** and **9** have similar metal-centred, centrosymmetric, distorted octahedral structures.

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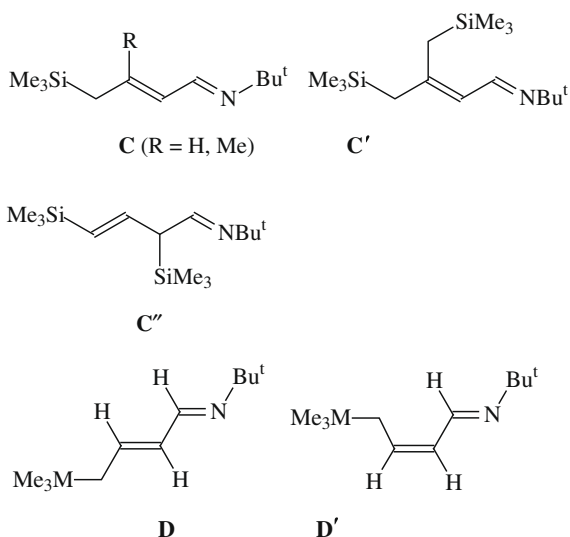
## 1. Introduction

Liu and coworkers isolated the first 1-azapentadienylmetal complexes **A** ( $R = Pr^i$ ,  $Bu^t$ ) in 1990 [1]. This was shortly (1991) followed by Würthwein and Wolf's characterisation of the lithium compounds  $Li[N(R)CHC(R')CHC(R'')CH_2]$ , having an NCCCC delocalised anion of varying conformation dependent on the nature of R, R' and R'': e.g., being, as in **B**, U-shaped; or, as in **B'**, W-shaped [2]. In 1999, we reported the preparation of the three compounds of formula  $Li\{N(SiMe_2R)C(Bu^t)(CH)_3SiMe_2R'\}$  (*tmeda*), Eq. (1), and the X-ray structure of one of them ( $R = Bu^t$ ,  $R' = Me$ ); each with  $KOBu^t$  was converted into the corresponding potassium compound  $K(L)$ ,  $K(L')$  and  $K(L'')$ ; X-ray data for crystalline  $[K(L)]_\infty$  were reported [3]. A similar *N*-lithio compound  $Li\{N(SiMe_2Bu^t)(CH)_3CH_2\}$  was obtained by the remarkable reaction of  $CH_2CHCH_2CH_2N(H)SiMe_2Bu^t$  with 2  $LiBu^t$  in thf [4].



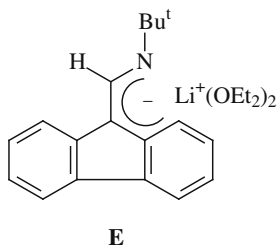
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The first silyl 1-azapentadienyls, **C**, **C'** and **C''** were synthesised from the appropriate compound  $RCH_2C(R')(CH)_2NBU^t$  and successively  $LiNPr^i_2$  or for **C''**  $LiTMP$  and  $Si(Cl)Me_3$  [5]. The group 14 metal (M) 1-azapentadienyls were prepared from the W-shaped  $Li[N(Bu^t)(CH)_3CH_2]$  and  $M(Cl)Me_3$ ; for  $M = Si$ , the *E,E*-compound **D** was the sole product, but both **D** and the *E,Z*-**D'** were isolated for  $M = Sn$  [6].



Noteworthy further contributions to 1-azapentadienylmetal chemistry include (i) for lithium compounds, the X-ray-characterised **E** [7a] and the use of in situ prepared compounds related to **B** for the synthesis of piperidine derivatives [7b]; and (ii) discussion of Ru [8a,8b] and Ir [8c] 1-azapentadienyls.

Bleeke's review of heteropentadienyl-transition metal complexes included a section on azapentadienyls [9]. Paz-Sandoval and Rangel-Salas surveyed group 1 metal, Mg, group 14- and d-metal azapentadienyls; such lithium, trimethylsilyl and stannyl compounds are of "increasing importance in organic synthesis, either as reagents for selective transformations or as intermediates for the creation of carbon-carbon bonds" [10]; they also suggested that the structure of **A** was better represented by **A'**.



## 2. Results and discussion

### 2.1. Objectives

As indicated in the preceding section, we had previously reported on six alkali metal 1-azapentadienyls:  $M(L)$ ,  $M(L')$  and  $M(L'')$  ( $M = Li, K$ ). The focus in this paper is on the synthesis and characterisation of successively four tin(II) disilylazapentadienyls, three trisilyl 1-azapentadienyls, and the homoleptic 3d metal complexes  $Fe(L)_2$  and  $Co(L'')_2$ .

### 2.2. Synthesis and characterisation of the tin(II) 1-azapentadienyls 1–4

The synthesis of the homoleptic tin(II) 1-azapentadienyls **1** and **2** and of the dimeric 1-azapentadienyl(chloro)tin(II) compounds **3** and **4** is outlined in Scheme 1. Each was obtained by treatment of tin(II) chloride with one or two equivalents of the appropriate potassium 1-azapentadienyl [3] in thf at ambient temperature and crystallisation from pentane (**1**, **2**) or hexane (**3**, **4**). No attempt was made to optimise yields of these yellow crystalline compounds, which for **1** and **4** were excellent and of **2** and **3** satisfactory.

Compounds **1–4** were characterised by satisfactory C, H and N microanalyses, NMR solution and mass spectra. X-ray diffraction studies showed that the crystalline homoleptic eneamidotin(II) compound **1** is a monomer [11], while the heteroleptic complex **4** is a bis( $\mu$ -Cl)-bridged dimer (*vide infra*). The  $^1H$  and  $^{13}C$  NMR spectral data for each of **1–4** were unexceptional. The  $^{119}Sn\{^1H\}$  NMR chemical shift for each of **1** or **2** was a singlet at  $\delta$  378  $\pm$  0.3 ppm. This is roughly intermediate between the values for homoleptic tin(II) amides, such as the  $\delta$  771 ppm for  $Sn[N(SiMe_3)_2]_2$  [12a] or  $\delta$  749 ppm for  $Sn[\overline{N}C(Me)_2(CH_2)_3CMe_2]_2$  [ $\equiv$   $Sn(TMP)_2$ ] [12b], and the enamide  $Sn[N(SiMe_3)C(Bu^t)=C(H)C_6H_3Me_2-2,5]_2$  at  $\delta$  61.5 ppm [12c]. The corresponding singlet for **3** or **4** was at  $\delta$  -27.3 (**3**) or -8.99 (**4**). As far as we are aware **3** and **4** have no precedent in eneamidotin(II) chlorides and hence a close comparison is not available; for two amidotin(II) chlorides  $[Sn(NR_2)(\mu-Cl)]_2$ , the  $^{119}Sn$  chemical shifts in benzene at ambient temperature are at  $\delta$  240 ( $NR_2 = TMP$ ) [12a] and  $\delta$  138 ppm ( $R = SiMe_3$ ) [12d]. For **1** and **2** the molecular cation ( $M^+$ ) was found in the EI-mass spectrum; for **3** and **4** significant fragments corresponded to  $[M - SnCl]^+$  (**3**) and  $[M/2]^+$  (**4**).

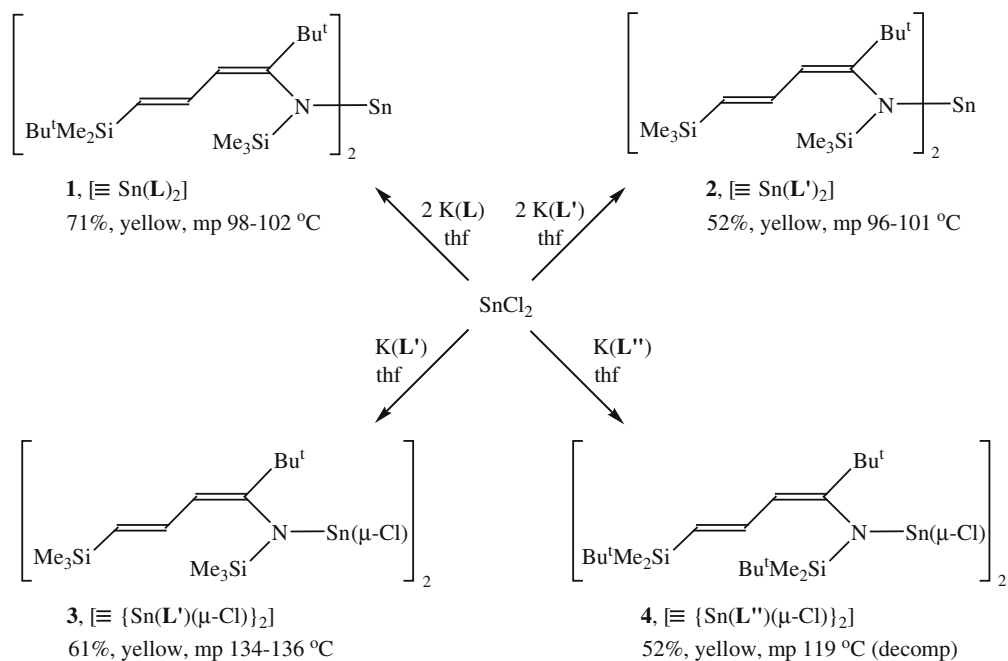
### 2.3. The X-ray structure of crystalline 4

The molecular structure of the crystalline centrosymmetric dinuclear compound **4** is shown in an ORTEP representation in Fig. 1. Selected bond lengths and angles are in Table 1. Unlike in crystalline *cis*- $[Sn(TMP)(\mu-Cl)]_2$  [12a], but as in *trans*- $[Sn\{N(SiMe_3)_2\}(\mu-Cl)]_2$  [12a], **4** has the *trans*-configuration. The  $SnClSnCl'$  ring of **4** is rhomboidal, the  $Sn-Cl$  and  $Sn-Cl'$  distances differ by more than 0.2 Å and the endocyclic angles subtended at the tin atom are more than 16° narrower than those at the tin atoms. The bond lengths and angles around the tin atom are close to those in *trans*- $[Sn\{N(SiMe_3)_2\}(\mu-Cl)]_2$  which has  $Sn-Cl$  2.598(1),  $Sn-Cl'$  2.741(1),  $Sn-N$  2.069(3) Å, and  $Cl-Sn-Cl'$  81.33(4),  $Sn-Cl-Sn'$  98.67(4),  $Cl-Sn-N$  94.20(9),  $Cl'-Sn-N$  101.08(8)° [12a]. The  $Sn-N-C=C-$  fragment of **4** resembles that of crystalline  $[Sn\{C(SiMe_3)_2C(Ph)\overline{N}(SiMe_3)\}\{N(SiMe_3)C(Ph)=C(SiMe_3)_2\}]$  in which the enamidotin moiety has  $Sn-N$ ,  $N-C$  and  $C-C$  bond lengths of 2.153(4), 1.432(5) and 1.365(6) Å, respectively, [12c].

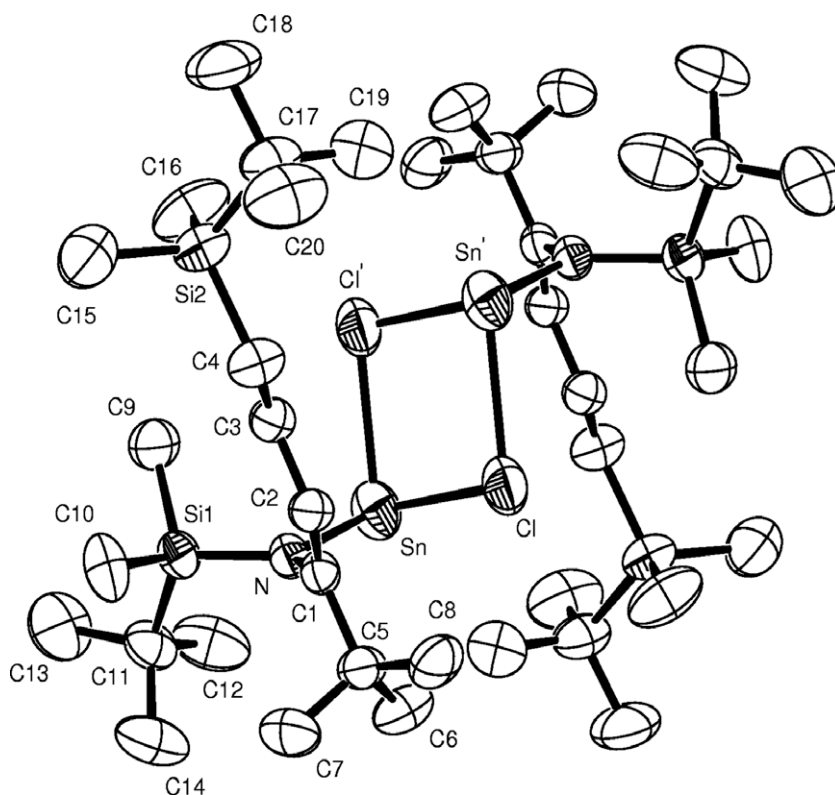
### 2.4. Synthesis and characterisation of the *N,N*-bis(silyl)-2-tert-butyl-1-azapentadienes 5–7

The title compounds were isolated in excellent (**5**), good (**6**) or modest (**7**) yield by the procedure of Scheme 2. The poorer outcome for **6** and **7** is attributed, in part, to their liquid state at ambient temperature, each compound having been purified by column chromatography.

As noted in the Introduction section, none of the previously characterised trimethylsilyl-1-azapentadienes (**C**, **C'**, **C''**, **D**, **D'**) had  $N-SiMe_3$  bonds. Likewise, earlier studies had shown that treatment of the enamine  $RCH_2CH=NR'$  [13] or an alkylazapentadiene [14] with successively  $LiMe$  or  $LiNPr^i_2/KOBu^t$  and  $Si(Cl)Me_3$  gave products in which the  $SiMe_3$  had been delivered to a terminal or central carbon atom.



Scheme 1.

Fig. 1. ORTEP representation of the molecular structure of crystalline **4**.

Compounds **5–7** gave satisfactory C, H, N microanalyses. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra exhibited similar carbon-centred skeletal shifts as their lithiated precursors. The  $^1\text{H}$  NMR spectra of each of **5** and **6** also showed that two  $\text{SiMe}_3$  groups were equivalent, consistent with their being attached to the nitrogen atom. The IR spec-

tra of each indicated the presence of a conjugated carbon–carbon double bond assembly by the strong absorption band at *ca.* 1610  $\text{cm}^{-1}$ ; an alkylaldimine feature, which would have been expected at *ca.* 1670  $\text{cm}^{-1}$ , was not observed. The GC–MS showed the parent molecular ion for each of **6** and **7**.

**Table 1**  
Selected bond distances (Å) and angles (°) for **4**.<sup>a</sup>

|           |          |           |          |
|-----------|----------|-----------|----------|
| Sn–Cl     | 2.546(2) | C2–C3     | 1.445(5) |
| Sn–Cl'    | 2.755(2) | C3–C4     | 1.332(5) |
| Sn–N      | 2.082(3) | N–Si1     | 1.754(3) |
| N–C1      | 1.435(5) | C4–Si2    | 1.853(4) |
| C1–C2     | 1.336(5) |           |          |
| Sn–Cl–Sn' | 98.15(5) | C1–N–Si1  | 123.2(2) |
| Cl–Sn–Cl' | 81.85(5) | N–C1–C2   | 122.0(3) |
| N–Sn–Cl   | 96.38(9) | C1–C2–C3  | 127.6(4) |
| N–Sn–Cl'  | 99.77(9) | C2–C3–C4  | 125.1(4) |
| Sn–N–C1   | 119.0(2) | C3–C4–Si2 | 127.7(3) |

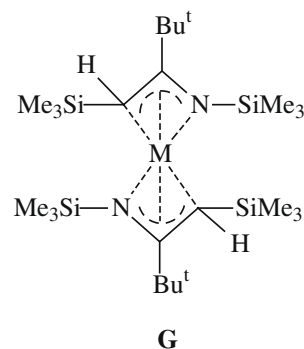
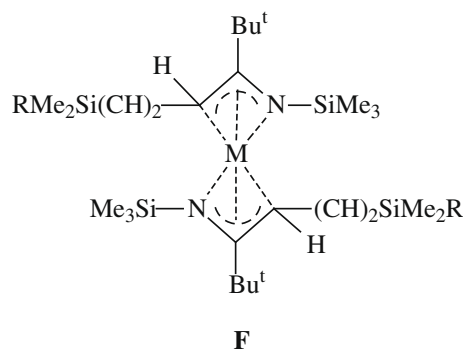
<sup>a</sup> Symmetry transformations to generate equivalent atoms:  $-x, -y, -z$ .**2.5. Synthesis and characterisation of the bis[bis(silyl)-2-tert-butyl-1-azapentadienyl]metal(II) complexes **8** (M = Fe) and **9** (M = Co)**

The red, lipophilic, homoleptic iron(II) and cobalt(II) title compounds were prepared as shown in Scheme 3. Each was purified by crystallisation. No attempt was made to optimise the yields of the crystalline compounds **8** and **9**.

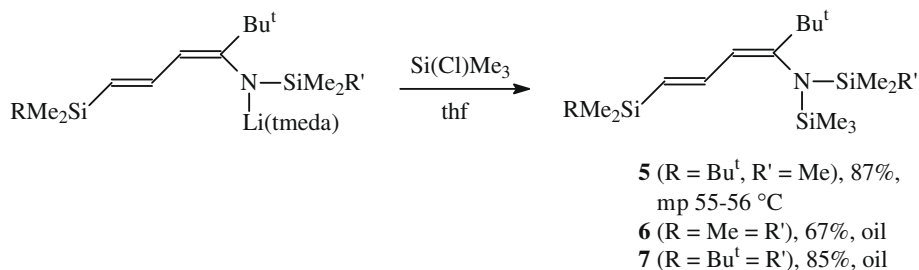
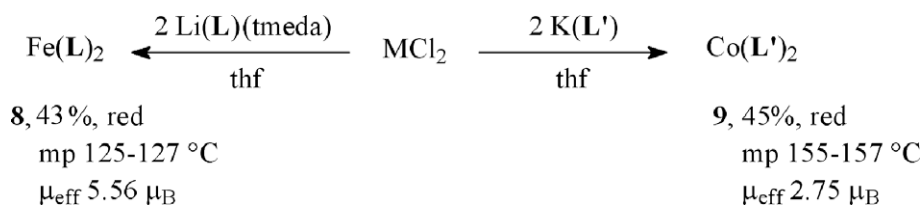
Complexes **8** and **9** gave satisfactory C, H, N microanalyses. Their EI-mass spectra showed the parent molecular cation and appropriate fragments. Being paramagnetic, no attempt was made to record their <sup>1</sup>H NMR solution spectra, which were uninformative. Their magnetic moments, measured in benzene at ambient temperature by the Evans method [15], showed that the iron complex **8** had the high-spin d<sup>6</sup> and the cobalt analogue **9** the low-spin d<sup>7</sup> configuration. The experimental value for μ<sub>eff</sub> for **8** was very close to the theoretical of μ<sub>S+L</sub> of 5.48 μ<sub>B</sub>, and consistent with numerous high-spin Fe(II) complexes for which μ<sub>eff</sub> falls in the range 5.1–5.7 μ<sub>B</sub> [16]. Whereas the theoretical spin-only magnetic moment for one unpaired spin is 1.73 μ<sub>B</sub>, the experimental data for low-spin Co(II) complexes are generally found at 2.2–2.9 μ<sub>B</sub>, this being attributed to an unquenched orbital contribution from the first excited state [16].

Although **8** and **9** were readily crystallised from hexane or pentane, X-ray quality crystals were not obtained. A plausible structural assignment **F** is based on analogy with the crystalline 1-azaallyl complexes [M{N(SiMe<sub>3</sub>)C(Bu<sup>t</sup>)CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (M = Fe, Co)

[17]. The latter were prepared from the appropriate MCl<sub>2</sub> and two equivalents of the lithium 1-azaallyl in Et<sub>2</sub>O; μ<sub>eff</sub> was 5.61 μ<sub>B</sub> (Fe) or 2.73 μ<sub>B</sub> (Co) at ambient temperature in benzene. Their centrosymmetric structures are sketched in **G**, showing the metal M to be at the centre of a distorted octahedron composed of two staggered azaallyls and the C<sub>α</sub>–M distances slightly shorter than the C<sub>β</sub>–M [17].

**3. Experimental****3.1. General details**

Syntheses were carried out in an atmosphere of argon or in a vacuum, using Schlenk apparatus and vacuum line techniques.

**Scheme 2.****Scheme 3.**

The solvents were reagent grade or better and were freshly distilled under dry nitrogen gas and freeze/thaw degassed prior to use. The drying agents employed were sodium benzophenone (C<sub>6</sub>H<sub>6</sub>, thf) or sodium–potassium alloy (C<sub>5</sub>H<sub>12</sub>, C<sub>6</sub>H<sub>14</sub>). The C<sub>6</sub>D<sub>6</sub> for NMR spectroscopy was stored over molecular sieves (A4). Elemental analyses were obtained by Medac Ltd., Brunel University. Melting points were measured in sealed capillaries. The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>119</sup>Sn{<sup>1</sup>H} NMR solution spectra were recorded using a Bruker DPX-300 or WM-360 instrument at 298 K and were referenced internally (<sup>1</sup>H, <sup>13</sup>C) to residual solvent resonances or externally (<sup>119</sup>Sn, with SnMe<sub>4</sub> as standard). Electron impact mass spectra (70 eV) were taken from solid samples, with a VG Autospec instrument; GC–MS data were recorded using an MD800 apparatus. The magnetic moments were determined by Evans' method [15] on dilute standard solutions in C<sub>6</sub>H<sub>6</sub>/C<sub>6</sub>D<sub>6</sub> at ambient temperature, with C<sub>6</sub>H<sub>6</sub> in a sealed capillary as external standard. The compounds Li{N(SiMe<sub>2</sub>R)C(Bu<sup>t</sup>)(CH)<sub>3</sub>SiMe<sub>2</sub>R}(tmeda) (i.e., LiL: R = Me, R' = Bu<sup>t</sup>; LiL': R = Me = R'; LiL'': R = Bu<sup>t</sup> = R') and the potassium analogues KL' and KL'' were obtained as described in the literature [3]; the chlorides Si(Cl)Me<sub>3</sub>, FeCl<sub>2</sub> and CoCl<sub>2</sub> were commercial samples, which were distilled [Si(Cl)Me<sub>3</sub>] or rigorously dried before use.

### 3.2. Preparation of [Sn{N(SiMe<sub>3</sub>)C(Bu<sup>t</sup>)(CH)<sub>3</sub>SiMe<sub>2</sub>Bu<sup>t</sup>}]<sub>2</sub> (1)

Tin(II) chloride (0.30 g, 1.58 mmol) was added to a stirred solution of [K(L)] (1.28 g, 3.67 mmol) in thf (20 cm<sup>3</sup>) at –78 °C. The mixture was allowed to warm to room temperature and was stirred for 20 h. Volatiles were removed *in vacuo* and the residue was extracted with pentane. The filtered extract was concentrated *in vacuo* to ca. 2 cm<sup>3</sup> which, after 15 h at room temperature, had yielded yellow crystals of Sn(L)<sub>2</sub> (1) (0.83 g, 71%), m.p. 98–102 °C. Anal. Calc. for C<sub>34</sub>H<sub>72</sub>N<sub>2</sub>Si<sub>4</sub>Sn: C, 55.2; H, 9.81; N, 3.79. Found: C, 55.2; H, 9.72; N, 3.72%. <sup>1</sup>H NMR: δ 0.12 [s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>], 0.48 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 0.93 [s, 9 H, SiC<sub>4</sub>H<sub>9</sub>], 1.21 [s, 9 H, CC<sub>4</sub>H<sub>9</sub>], 5.89 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 18.3, CH], 6.32 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, CH], 6.92 ppm [dd, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, 18.3 Hz, CH]; <sup>13</sup>C NMR: δ –5.56 [Si(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 4.38 [Si(CH<sub>3</sub>)<sub>3</sub>]; 17.2, 26.7 [Me<sub>2</sub>SiC(CH<sub>3</sub>)<sub>3</sub>]; 29.5, 36.7 [CC(CH<sub>3</sub>)<sub>3</sub>]; 110.1, 121.5, 143.3 (CH); 157.5 ppm (CN); <sup>119</sup>Sn{<sup>1</sup>H} NMR: δ 377.9 ppm.

### 3.3. Preparation of [Sn{N(SiMe<sub>3</sub>)C(Bu<sup>t</sup>)(CH)<sub>3</sub>SiMe<sub>3</sub>}]<sub>2</sub> (2)

The complex Sn(L')<sub>2</sub> (2) (0.93 g, 52%) was prepared, using a similar procedure to that for 1, from K(L') (1.74 g, 5.67 mmol) and SnCl<sub>2</sub> (0.49 g, 2.73 mmol). The crystalline yellow complex 2 had m.p. 96–101 °C. Anal. Calc. for C<sub>28</sub>H<sub>60</sub>N<sub>2</sub>Si<sub>4</sub>Sn: C, 51.3; H, 9.22; N, 4.27. Found: C, 50.9; H, 9.17; N, 4.14%. <sup>1</sup>H NMR: δ 0.14 [s, 9 H, CSi(CH<sub>3</sub>)<sub>3</sub>], 0.45 [s, 9 H, NSi(CH<sub>3</sub>)<sub>3</sub>], 1.10 [s, 9 H, Bu<sup>t</sup>], 5.85 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 18.4, CH], 6.26 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, CH], 6.90 ppm [dd, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, 18.4 Hz, CH]; <sup>13</sup>C NMR: δ –0.80 [CSi(CH<sub>3</sub>)<sub>3</sub>], 4.39 [NSi(CH<sub>3</sub>)<sub>3</sub>]; 29.5, 36.7 [C(CH<sub>3</sub>)<sub>3</sub>]; 110.1, 121.2, 142.0 (CH); 157.7 ppm (CN); <sup>119</sup>Sn{<sup>1</sup>H} NMR: δ 378.3 ppm.

### 3.4. Preparation of [Sn{N(SiMe<sub>3</sub>)C(Bu<sup>t</sup>)(CH)<sub>3</sub>SiMe<sub>3</sub>}(μ-Cl)]<sub>2</sub> (3)

Tin(II) chloride (2.5 g, 13.1 mmol) was added to a stirred solution of [K(L'')] (1.26 g, 4.1 mmol) in thf (20 cm<sup>3</sup>) at –78 °C. The mixture was allowed to warm to room temperature and was stirred for ca. 12 h. The solvent was evaporated *in vacuo* and the solid residue was extracted with hexane. The filtered extract was concentrated *in vacuo* to ca. 2 cm<sup>3</sup>. After 15 h at ambient temperature, yellow crystals of [Sn(L'')(μ-Cl)]<sub>2</sub> (3) (1.06 g, 61%), m.p. 134–136 °C. Anal. Calc. for C<sub>14</sub>H<sub>30</sub>ClNSi<sub>2</sub>Sn: C, 39.8; H, 7.15; N, 3.31. Found: C, 40.3; H, 7.22; N, 3.04%, were obtained. <sup>1</sup>H NMR: δ 0.20 (s, 9 H, CSiMe<sub>3</sub>), 0.48 (s, 9 H, NSiMe<sub>3</sub>), 1.14 (s, 9 H, Bu<sup>t</sup>), 5.83 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 18.2,

CH], 6.32 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, CH], 7.23 ppm [dd, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, 18.2 Hz, CH]; <sup>13</sup>C NMR: δ –0.56 [CSi(CH<sub>3</sub>)<sub>3</sub>], 4.42 [NSi(CH<sub>3</sub>)<sub>3</sub>]; 30.4, 37.1 [C(CH<sub>3</sub>)<sub>3</sub>]; 110.1, 124.3, 142.4 (CH); 157.8 ppm (CN); <sup>119</sup>Sn{<sup>1</sup>H} NMR: δ –27.3 ppm.

### 3.5. Preparation of [Sn{N(SiMe<sub>2</sub>Bu<sup>t</sup>)C(Bu<sup>t</sup>)(CH)<sub>3</sub>SiMe<sub>2</sub>Bu<sup>t</sup>}(μ-Cl)]<sub>2</sub> (4)

The complex [Sn(L'')(μ-Cl)]<sub>2</sub> (4) was obtained, using a similar procedure to that for 3, from [K(L'')] (1.17 g, 2.99 mmol) and SnCl<sub>2</sub> (1.20 g, 6.31 mmol). The crystalline yellow complex 4 (83%). Anal. Calc. for C<sub>20</sub>H<sub>42</sub>ClNSi<sub>2</sub>Sn requires C, 47.4; H, 8.35; N, 2.76. Found: C, 47.7; H, 8.25; N, 2.77% had m.p. 119 °C (decomp); <sup>1</sup>H NMR: δ 0.23 [s, 6 H, CSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 0.26 [s, 3 H, NSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 0.51 [s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 0.99 [s, 9 H, CSiMe<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>], 1.03 [s, 9 H, NSiMe<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>], 1.17 [s, 9 H, CC(CH<sub>3</sub>)<sub>3</sub>], 5.79 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 18.3, CH], 6.21 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, CH], 7.32 ppm [dd, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, 18.3 Hz, CH]; <sup>13</sup>C NMR: δ –5.10 [CSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], –2.02, 1.57 [NSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 17.2, 20.5 [Me<sub>2</sub>SiC(CH<sub>3</sub>)<sub>3</sub>]; 26.9, 28.7 [CC(CH<sub>3</sub>)<sub>3</sub>]; 110.1, 121.1, 144.8 (CH); 160.8 ppm (CN); <sup>119</sup>Sn{<sup>1</sup>H} NMR: δ –8.99 ppm.

### 3.6. Preparation of [(Me<sub>3</sub>Si)<sub>2</sub>NC(Bu<sup>t</sup>)(CH)<sub>3</sub>SiMe<sub>2</sub>Bu<sup>t</sup>]] (5)

Chloro(trimethyl)silane (0.2 cm<sup>3</sup>, 1.58 mmol) was added to a stirred solution of Li(L)(tmeda) (0.65 g, 1.5 mmol) in thf (30 cm<sup>3</sup>) at room temperature; stirring was continued for 3 h, whereafter the mixture was heated under reflux for 2 h. Volatiles were removed *in vacuo* and the residue was extracted with hexane. The filtered extract was concentrated *in vacuo* to ca. 2 cm<sup>3</sup> and then passed through an Al<sub>2</sub>O<sub>3</sub> column. Volatiles were removed from the eluent *in vacuo*, affording the colourless solid Me<sub>3</sub>Si(L) (5) (0.50 g, 87%), m.p. 55–56 °C. Anal. Calc. for C<sub>20</sub>H<sub>45</sub>NSi<sub>3</sub>: C, 62.6; H, 11.8; N, 3.65. Found: C, 62.6; H, 11.6; N, 3.63%. <sup>1</sup>H NMR: δ 0.16 [s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 0.25 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>], 0.96 [s, 9 H, SiC<sub>4</sub>H<sub>9</sub>], 1.11 [s, 9 H, CC<sub>4</sub>H<sub>9</sub>], 5.82 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 18.3, CH], 6.22 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, CH], 7.02 ppm [dd, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, 18.3 Hz, CH]; <sup>13</sup>C NMR: δ –5.55 [CSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 3.35 [NSi(CH<sub>3</sub>)<sub>3</sub>]; 17.0, 26.8 [Me<sub>2</sub>SiC(CH<sub>3</sub>)<sub>3</sub>]; 31.2, 37.6 [CC(CH<sub>3</sub>)<sub>3</sub>]; 126.5, 126.6, 144.7 (CH); 156.7 ppm (CN). IR (Nujol) very strong ν<sub>max</sub> absorption at 2926, 2855, 1607, 1313, 1253, 1057, 927 and 839 cm<sup>–1</sup>.

### 3.7. Preparation of [(Me<sub>3</sub>Si)<sub>2</sub>NC(Bu<sup>t</sup>)(CH)<sub>3</sub>SiMe<sub>3</sub>]] (6)

The complex Me<sub>3</sub>Si(L) (6) (0.54 g, 67%) was obtained, using a similar procedure to that for 5, from Li(L')(tmeda) (0.92 g, 2.35 mmol) and Si(Cl)Me<sub>3</sub> (0.30 cm<sup>3</sup>, 2.37 mmol). The colourless oil 6 [Anal. Calc. for C<sub>17</sub>H<sub>39</sub>NSi<sub>3</sub>: C, 59.8; H, 11.5; N, 4.10. Found: C, 60.0; H, 11.6; N, 4.05%. GC–MS: *m/e* 341 (M<sup>+</sup>)] had the following IR (liquid film) very strong ν<sub>max</sub> features: 2955, 2903, 1610, 1313, 1253, 1056, 927, 876 and 838 cm<sup>–1</sup>. <sup>1</sup>H NMR: δ 0.17 [s, 9 H, CSi(CH<sub>3</sub>)<sub>3</sub>], 0.23 [s, 18 H, N{Si(CH<sub>3</sub>)<sub>3</sub>}<sub>2</sub>], 1.12 [s, 9 H, CC<sub>4</sub>H<sub>9</sub>], 5.77 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 18.6, CH], 6.13 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, CH], 6.99 ppm [dd, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, 18.6 Hz, CH]; <sup>13</sup>C NMR: δ –0.74 [CSi(CH<sub>3</sub>)<sub>3</sub>], 3.37 [NSi(CH<sub>3</sub>)<sub>3</sub>]; 31.3, 37.6 [CC(CH<sub>3</sub>)<sub>3</sub>]; 126.5, 129.3, 143.4 (CH); 156.7 ppm (CN).

### 3.8. Preparation of [(Bu<sup>t</sup>Me<sub>2</sub>Si)N(SiMe<sub>3</sub>)C(Bu<sup>t</sup>)(CH)<sub>3</sub>SiMe<sub>2</sub>Bu<sup>t</sup>]] (7)

The complex Me<sub>3</sub>Si(L'') (7) (0.74 g, 35%) was prepared, using a similar procedure to that for 5, from Li(L'')(tmeda) (2.40 g, 5.05 mmol) and Si(Cl)Me<sub>3</sub> (0.80 cm<sup>3</sup>, 6.31 mmol). The colourless oil 7 [Anal. Calc. for C<sub>23</sub>H<sub>51</sub>NSi<sub>3</sub>: C, 64.9; H, 12.1; N, 3.29. Found: C, 65.3; H, 11.9; N, 3.03%. GC–MS: *m/e* 425 (M<sup>+</sup>)] had the following IR (liquid film) very strong ν<sub>max</sub> features: 2955, 2932, 2898, 2858, 1607, 1256, 1039, 906 and 855 cm<sup>–1</sup>. <sup>1</sup>H NMR: δ 0.17 [s, 3 H,

CSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 0.21 [s, 3 H, CSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 0.29 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 0.37 [s, 3 H, NSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 0.97 (s, 9 H, CSiC<sub>4</sub>H<sub>9</sub>), 1.05 (s, 9 H, NSiC<sub>4</sub>H<sub>9</sub>), 1.12 (s, 9 H, CC<sub>4</sub>H<sub>9</sub>), 5.82 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 18.5, CH], 6.23 [d, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.2, CH], 7.02 ppm [dd, 1 H, <sup>2</sup>J(<sup>1</sup>H–<sup>1</sup>H) 10.1, 18.5 Hz, CH]; <sup>13</sup>C NMR: δ –5.54 [CSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], –5.45 [CSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], –1.01 [NSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 1.50 [NSi(CH<sub>3</sub>)<sub>2</sub>Bu<sup>t</sup>], 4.52 [NSi(CH<sub>3</sub>)<sub>3</sub>]; 17.0, 21.6 [NSi(Me)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]; 26.8, 29.3 [CSi(Me)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]; 31.8, 37.9 [CC(CH<sub>3</sub>)<sub>3</sub>]; 127.1, 127.9, 144.9 (CH), 157.2 ppm (CN).

### 3.9. Preparation of [Fe{N(SiMe<sub>3</sub>)C(Bu<sup>t</sup>)(CH)<sub>3</sub>SiMe<sub>2</sub>Bu<sup>t</sup>}]<sub>2</sub> (**8**)

Iron(II) chloride (0.35 g, 2.76 mmol) was added to a stirred solution of Li(L)(tmeda) (2.40 g, 5.54 mmol) in thf (30 cm<sup>3</sup>) at –78 °C. The mixture was brought to room temperature, then stirred for ca. 12 h. Volatiles were removed *in vacuo* and the residue was extracted with pentane. The filtered extract was concentrated *in vacuo* to ca. 2 cm<sup>3</sup>, which after ca. 15 h yielded the red crystalline complex [Fe(L)<sub>2</sub>] (**8**) (0.80 g, 43%). Anal. Calc. for C<sub>34</sub>H<sub>72</sub>FeN<sub>2</sub>Si<sub>4</sub>: C, 60.3; H, 10.7; N, 4.14. Found: C, 59.9; H, 10.7; N, 4.12%, m.p. 125–127 °C, μ<sub>eff</sub> 5.56 μ<sub>B</sub>.

### 3.10. Preparation of [Co{N(SiMe<sub>3</sub>)C(Bu<sup>t</sup>)(CH)<sub>3</sub>SiMe<sub>3</sub>}]<sub>2</sub> (**9**)

The complex [Co(L)<sub>2</sub>] (**9**) (0.87 g, 45%) was prepared, using a similar procedure to that for **8**, from K(L) (2.00 g, 6.51 mmol) and cobalt(II) chloride (0.40 g, 3.07 mmol). The crystalline red complex **9**. Anal. Calc. for C<sub>28</sub>H<sub>60</sub>CoN<sub>2</sub>Si<sub>4</sub>: C, 56.4; H, 10.1; N, 4.70. (Found: C, 56.5; H, 10.1; N, 4.56% had m.p. 155–157 °C, μ<sub>eff</sub> 2.75 μ<sub>B</sub>).

### 3.11. Mass spectra of **1–4** and **8** and **9**

The four highest *m/e* peaks in the EI-mass spectrum of these compounds, with assignments, are listed in Table 2.

### 3.12. X-ray crystallographic study on **1** and **4**

Diffraction data were collected at 293(2) K on an Enraf-Nonius CAD4 diffractometer using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). Crystals were mounted in an inert atmosphere into a capillary which was then sealed. All non-hydrogen atoms were anisotropic; H's were included in riding mode with  $U_{iso}(H) = 1.2 U_{eq}(C)$  or  $1.5 U_{eq}(C)$  for methyl groups. The structure was refined on all  $F^2$  using SHELXL-97 [18]. Further details are in Table 3.

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### Appendix A. Supplementary data

CCDC 732070 contains 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.jorganchem.2009.07.033](https://doi.org/10.1016/j.jorganchem.2009.07.033).

### References

- [1] M.-H. Cheng, C.-Y. Cheng, S.-L. Wang, S.-M. Peng, R.-S. Liu, *Organometallics* 9 (1990) 1853.

**Table 2**

Mass spectral data (EI, 70eV) on **1–4** and **8** and **9**.<sup>a</sup>

| Compound                                 | <i>m/e</i> (Relative intensity, %) and assignment   |
|--|---|
| [Sn(L) <sub>2</sub> ] ( <b>1</b> )       | 738 (3), [M] <sup>+</sup> ; 681 (2), [M–Bu <sup>t</sup> ] <sup>+</sup> ; 563 (88), [M–SiMe <sub>3</sub> –Bu <sup>t</sup> –3Me] <sup>+</sup> |
| [Sn(L') <sub>2</sub> ] ( <b>2</b> )      | 655 (16), [M] <sup>+</sup> ; 583 (19), [M+1–SiMe <sub>3</sub> ] <sup>+</sup> ; 521 (39), [L' <sub>2</sub> –Me] <sup>+</sup>                 |
| [Sn(L)(μ-Cl)] <sub>2</sub> ( <b>3</b> )  | 691 (8), [M–SnCl] <sup>+</sup> ; 633 (14), [M–SnCl–Bu <sup>t</sup> –1] <sup>+</sup> ; 521 (17), [L <sub>2</sub> –Me] <sup>+</sup>           |
| [Sn(L')(μ-Cl)] <sub>2</sub> ( <b>4</b> ) | 647 (4), [L' <sub>2</sub> –Bu <sup>t</sup> ] <sup>+</sup> ; 507 (2), [M/2] <sup>+</sup> ; 450 (28), [M/2–Bu <sup>t</sup> ] <sup>+</sup>     |
| [Fe(L) <sub>2</sub> ] ( <b>8</b> )       | 677 (15), [M] <sup>+</sup> ; 520 (5), [M–Bu <sup>t</sup> CH=NSiMe <sub>3</sub> ] <sup>+</sup> ; 365 (25), [M–L–1] <sup>+</sup>              |
| [Co(L') <sub>2</sub> ] ( <b>9</b> )      | 595 (38), [M] <sup>+</sup> ; 326 (65), [M–L'–1] <sup>+</sup> ; 156 (100), [Bu <sup>t</sup> C=NSiMe <sub>3</sub> ] <sup>+</sup>              |

<sup>a</sup> [M]<sup>+</sup> represents parent molecular ion, only the three highest *m/e* peaks are listed.

**Table 3**

Selected crystallographic data for **1** [11] and **4**.

|  | <b>4</b>   | <b>1</b>  |
|--|--|---|
| Formula  | C <sub>40</sub> H <sub>84</sub> Cl <sub>2</sub> N <sub>2</sub> Si <sub>4</sub> Sn <sub>2</sub> | C <sub>34</sub> H <sub>72</sub> N <sub>2</sub> Si <sub>4</sub> Sn |
| <i>M</i>   | 1013.7   | 740.0   |
| Crystal system   | Triclinic  | Monoclinic  |
| Space group  | <i>P</i> $\bar{1}$ (No. 2)   | <i>C</i> 2/ <i>c</i> (No. 15)                                     |
| <i>a</i> (Å)   | 10.112(3)  | 24.227(8)   |
| <i>b</i> (Å)   | 10.488(3)  | 8.135(2)  |
| <i>c</i> (Å)   | 13.653(3)  | 22.524(6)   |
| $\alpha$ (°)   | 79.38(2)   | 90  |
| $\beta$ (°)  | 77.33(2)   | 94.58(3)  |
| $\gamma$ (°)   | 74.25(2)   | 90  |
| <i>U</i> (Å <sup>3</sup> )   | 1347.6(6)  | 4425(2)   |
| <i>Z</i>   | 1  | 4   |
| Absorption coefft. (mm <sup>–1</sup> )   | 1.14   | 0.71  |
| Unique reflections   | 6484   | 3975  |
| Reflections with $I > 2\sigma(I)$  | 3984   | 2663  |
| Final <i>R</i> indices [ $I > 2\sigma(I)$ ] <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> | 0.052, 0.097   | 0.047, 0.120  |
| <i>R</i> indices (all data)  | 0.103, 0.115   | 0.155   |

- [2] G. Wolf, E.-U. Würthwein, *Chem. Ber.* 124 (1991) 889.  
 [3] P.B. Hitchcock, M.F. Lappert, W.-P. Leung, D.-S. Liu, T.C.W. Mak, Z.-X. Wang, *J. Chem. Soc., Dalton Trans.* (1999) 1263.  
 [4] M.A. Jacobson, P.G. Williard, *J. Org. Chem.* 67 (2002) 3915.  
 [5] M. Bellassoued, A. Majidi, *J. Organomet. Chem.* 444 (1993) C7.  
 [6] J.A. Gutiérrez, M.A. Paz-Sandoval, J. Robles, *J. Organomet. Chem.* 599 (2000) 147.  
 [7] (a) M. Könemann, G. Erker, R. Fröhlich, E.-U. Würthwein, *J. Am. Chem. Soc.* 119 (1997) 11155;  
 (b) W. Aelterman, N. De Kimpe, *Tetrahedron* 54 (1998) 2563.  
 [8] (a) J.A. Gutiérrez, M.E.N. Clemente, M.A. Paz-Sandoval, A.M. Arif, R.D. Ernst, *Organometallics* 18 (1999) 1068;  
 (b) A. Rajapakshe, M.A. Paz-Sandoval, J.A. Gutiérrez, M.E. Navarro-Clemente, P.J. Saavedra, N.E. Gruhn, D.L. Lichtenberger, *Organometallics* 25 (2006) 1914;  
 (c) J.R. Bleeke, S.T. Luaders, K.R. Robinson, *Organometallics* 13 (1994) 1592.  
 [9] J.R. Bleeke, *Organometallics* 24 (2005) 5190.  
 [10] M.A. Paz-Sandoval, I.I. Rangel-Salas, *Coord. Chem. Rev.* 250 (2006) 1071.  
 [11] Z.-X. Wang, D. Phil. Thesis, University of Sussex, 1996.  
 [12] (a) R.W. Chorley, P.B. Hitchcock, B.S. Jolly, M.F. Lappert, G.A. Lawless, *J. Chem. Soc., Chem. Commun.* (1991) 1302;  
 (b) R.W. Chorley, P.B. Hitchcock, M.F. Lappert, W.-P. Leung, P.P. Power, M.M. Olmstead, *Inorg. Chim. Acta* 198–200 (1992) 203;  
 (c) P.B. Hitchcock, M.F. Lappert, M. Layh, J.R. Severn, *J. Chem. Soc., Chem. Commun.* (1997) 1189;  
 (d) R.W. Chorley, D. Phil. Thesis, University of Sussex, 1991.  
 [13] J.K. Whitesell, M.A. Whitesell, *Synthesis* (1983) 517 (and refs. therein).  
 [14] A. Ricci, A. Guerrini, G. Seconi, A. Mordini, T. Constantieux, J.-P. Picard, J.-M. Aizpurua, C. Palomo, *Synlett* (1994) 955.  
 [15] D.F. Evans, *J. Chem. Soc.* (1951) 2003.  
 [16] M.C. Day, Jr., J. Selbin, *Theoretical Inorganic Chemistry*, 2nd ed., Reinhold, New York, 1969, pp. 492–495.  
 [17] A.G. Avent, P.B. Hitchcock, M.F. Lappert, R. Sablong, J.R. Severn, *Organometallics* 23 (2004) 2591.  
 [18] G.M. Sheldrick, SHELXL-97, Programs for the Refinement of Crystal Structures, Universität Göttingen, 1997.