

Synthesis and structural characterisation of low-valent Group 14 metal complexes containing tridentate 2,6-pyridyl-bridged bis(1-azaallyl) ligands

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Treatment of GeCl_2 (dioxane), SnCl_2 and PbCl_2 with appropriate alkali-metal compounds containing 2,6-pyridyl-bridged bis(1-azaallyl) dianionic ligands afforded bivalent Group 14 metal compounds $[\text{M}\{\{\text{N}(\text{SiMe}_3)\text{C}(\text{R})\text{CH}\}_2\text{-C}_5\text{H}_3\text{N-2,6}\}]$ [$\text{R} = \text{Ph}$, $\text{M} = \text{Ge}$ (**1**), Sn (**2**) and Pb (**3**); $\text{R} = \text{Bu}^t$, $\text{M} = \text{Sn}$ (**4**) and Pb (**5**)]. The structures of the monomeric complexes **1**, **2**, **3** and **5** have been confirmed by single-crystal X-ray structure determination; it has been shown that the 2,6-pyridyl-bridged bis(1-azaallyl) ligand is bonded to the metal centre in a $\text{N,N,N}'$ -chelate fashion.

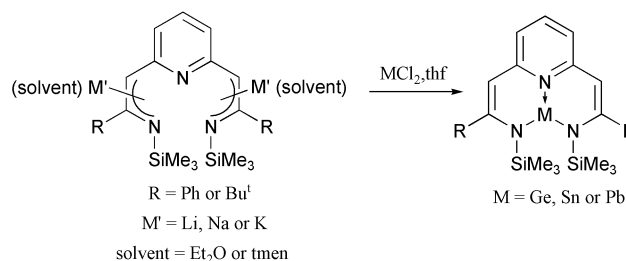
Introduction

The chemistry of low-valent Group 14 metal amides $\text{M}(\text{NR}_2)_2$ ($\text{R} = \text{alkyl}$ or phenyl) has attracted much attention in the past two decades. It has been realised that incorporating sterically hindered substituents at the metal center can stabilize these carbene analogues. Lappert and coworkers reported the first examples of stable metal diamides $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}]$ ($\text{M} = \text{Ge}^{1a,c}$, $\text{Sn}^{1b,e}$ or Pb^{1c}). These diamagnetic compounds exhibit V-shaped geometry as expected for a singlet electronic ground state, in which the metal atom possesses a stereochemically active lone pair of electrons. Among these Group 14 heavier metals, only a few thermally stable organolead(II) compounds are structurally characterised. For examples, monomeric Group 14 metal amides such as $\text{M}[\text{NC}(\text{Me})_2(\text{CH}_2)_3\text{CMe}_2]_2$ ($\text{M} = \text{Ge}^{1b,2a}$ or $\text{Sn}^{1a,2b}$), $\text{Ge}[1,2\text{-}\{\text{N}(\text{SiMe}_3)\}_2\text{-C}_6\text{H}_4]$,³ $\text{Sn}[1,2\text{-}\{\text{N}(\text{SiMe}_3)\}_2\text{-C}_6\text{H}_4(\mu\text{-tmen})]$,⁴ *meta*-bis(stannylamino)cyclophane,⁵ 1,4- $[\text{N}(\text{SiMe}_3)\text{Sn}(\text{NSiMe}_3)]_2\text{C}_6\text{H}_4$,⁶ $\text{Sn}[\text{N}(\text{Bu}^t)\text{SiMe}_2\text{NBu}^t]_n$,⁷ and $\text{M}[\text{RC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]$ ($\text{R} = \text{H}$, Me , Ph or CF_3 ; $\text{M} = \text{Sn}$ or Pb) have been reported.⁸ We reported the synthesis of a series of thermally stable alkali-metal compounds containing the bis(1-azaallyl) ligands.⁹ By using these alkali-metal compounds as transfer reagents, we here report the preparation and structural characterisation of a series of Group 14 metal compounds containing the tridentate bis(1-azaallyl) ligands $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{R})\text{CH}\}_2\text{C}_5\text{H}_3\text{N-2,6}\}]^{2-}$ [$\text{R} = \text{Ph}$ or Bu^t].

Results and discussion

Group 14 metal compounds $[\text{M}\{\{\text{N}(\text{SiMe}_3)\text{C}(\text{R})\text{C}(\text{H})\}_2\text{-C}_5\text{H}_3\text{N-2,6}\}]$ [$\text{R} = \text{Ph}$, $\text{M} = \text{Ge}$ (**1**), Sn (**2**) and Pb (**3**); $\text{R} = \text{Bu}^t$, $\text{M} = \text{Sn}$ (**4**) and Pb (**5**)] were prepared by the reaction of 2 equivalents of the corresponding alkali-metal compounds $[\text{M}_2\text{L}(\text{tmen})_2]$ [$\text{M} = \text{Li}$, Na or K ; $\text{L} = \{\text{N}(\text{SiMe}_3)\text{C}(\text{R})\text{C}(\text{H})\}_2\text{-C}_5\text{H}_3\text{N-2,6}\}]^{2-}$; $\text{R} = \text{Ph}$ or Bu^t ; $\text{tmen} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$] with a slight excess (except for **2**) of GeCl_2 (1,4-dioxane), SnCl_2 or PbCl_2 in diethyl ether solution (Scheme 1).

The $\text{Ge}(\text{II})$ compound $[\text{Ge}\{\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{H})\}_2\text{-C}_5\text{H}_3\text{N-2,6}\}]$ (**1**) was isolated as a red crystalline solid with good solubility in solvents such as diethyl ether, toluene and THF. The $\text{Sn}(\text{II})$ compounds $[\text{Sn}\{\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{H})\}_2\text{-C}_5\text{H}_3\text{N-2,6}\}]$ (**2**) and $[\text{Sn}\{\{\text{N}(\text{SiMe}_3)\text{C}(\text{Bu}^t)\text{C}(\text{H})\}_2\text{-C}_5\text{H}_3\text{N-2,6}\}]$ (**4**) were isolated as orange crystalline solids in moderate yields. Compounds **2** and **4** are soluble in diethyl ether, THF or toluene. The $\text{Pb}(\text{II})$ compounds $[\text{Pb}\{\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{H})\}_2\text{-C}_5\text{H}_3\text{N-2,6}\}]$ (**3**) and $[\text{Pb}\{\{\text{N}(\text{SiMe}_3)\text{C}(\text{Bu}^t)\text{C}(\text{H})\}_2\text{-C}_5\text{H}_3\text{N-2,6}\}]$ (**5**) were prepared by



Scheme 1

the reaction of $\text{Li}_2\text{L}(\text{tmen})_2$ with PbCl_2 and isolated as red crystalline solids. These $\text{Pb}(\text{II})$ compounds are only soluble in THF or toluene. Among these Group 14 compounds the $\text{Pb}(\text{II})$ compounds **3** and **5** are less stable, as they decompose slowly in solution at room temperature to lead metal.

These compounds have been characterised by elemental analysis, spectroscopic methods and single-crystal X-ray structure analysis. As shown by the structural data, these compounds are more appropriately classified as dienamides rather than the π -bonded bis-azaallyl compounds. The enamido nitrogens are σ -bonded to the metal centre along with the coordination from the pyridyl nitrogen from the $\text{N,N,N}'$ -tridentate chelate complex. The π -bonded bis-azaallyl complex is not formed; probably due to the π electrons at the ligands remaining in nonbonding orbitals.

The ^1H NMR spectrum of **1** displayed sharp signals at δ 6.65 and δ 5.15 ppm which were assigned to the non-equivalent methine protons and signals at δ 0.27 and δ 0.09 ppm were assigned to the non-equivalent SiMe_3 groups. The ^{13}C spectrum of **1** was also consistent with non-equivalent CH and SiMe_3 groups. The non-equivalence could be due to the restricted rotation about the germanium–nitrogen bond. A similar phenomenon has been reported for some Group 13 compounds, but only a few examples have been observed for Group 14 compounds.^{10,11} In contrast, the ^1H and ^{13}C spectra of compounds **2–5** displayed only one set of signals for the ligands, suggesting that the compounds are centro-symmetric with the azaallyl arms positioned in the same chemical environment.

The ^{119}Sn NMR chemical shift of δ 5.37 ppm for **3** is significantly different from the chemical shifts of the three-coordinate tin(II) compounds $[\text{Sn}\{\text{CH}(\text{SiMe}_3)\text{C}_9\text{H}_6\text{N-8}\}\text{X}]$ ($\text{X} = \text{Cl}$, δ 327 ppm; Br , δ 353 ppm; I , δ 386 ppm).¹² It is also lower than those for the tin(II) amide $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ (δ 776 ppm) and the amide $[\text{Sn}(\mu\text{-Cl})\{\text{N}(\text{SiMe}_3)_2\}_2]$ (δ 138 ppm).⁵ The ^{207}Pb NMR spectra of the three-coordinate $\text{Pb}(\text{II})$ compounds **3** and **5** showed peaks at δ 1577.36 and δ 994.11 ppm, respectively, which are

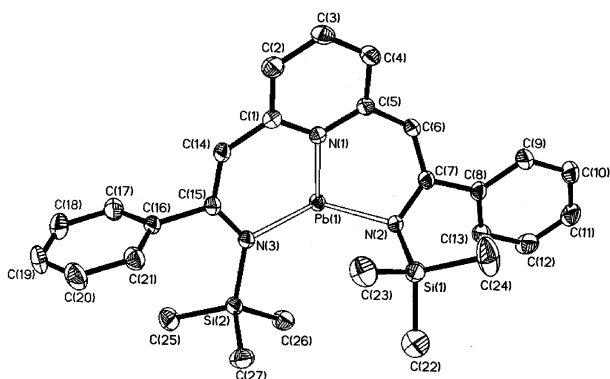
Table 1 Selected bond distances (Å) and angles (°) for compounds **1–3** and **5**

	1	2	3	5
M–N(1)	2.0196(14)	2.224(3)	2.323(3)	2.330(3)
M–N(2)	1.9922(16)	2.171(3)	2.264(3)	2.316(4)
M–N(3)	1.9798(15)	2.204(3)	2.300(3)	2.298(4)
N(2)–Si(1)	1.7719(14)	1.727(4)	1.726(3)	1.734(4)
N(3)–Si(2)	1.7327(17)	1.753(4)	1.751(3)	1.720(4)
N(2)–C(7)	1.379(2)	1.398(5)	1.382(4)	1.383(5)
N(3)–C(15)	1.384(2)	1.382(5)	1.350(4)	1.421(7)
C(1)–C(14)	1.441(3)	1.426(6)	1.435(5)	1.419(6)
C(5)–C(6)	1.425(3)	1.453(6)	1.465(5)	1.401(7)
C(6)–C(7)	1.364(2)	1.372(6)	1.357(5)	1.393(6)
C(14)–C(15)	1.368(3)	1.359(6)	1.377(5)	1.339(6)
N(1)–M–N(2)	92.97(6)	81.8(1)	79.81(10)	85.81(12)
N(1)–M–N(3)	86.62(6)	87.7(1)	85.62(10)	78.63(12)
N(2)–M–N(3)	108.31(7)	107.1(1)	108.04(10)	110.38(14)
M–N(2)–C(7)	121.67(12)	102.8(3)	102.4(2)	114.5(3)
M–N(3)–C(15)	103.20(12)	116.9(3)	117.5(2)	95.3(3)

significantly lower than those of δ 1981 ppm in the four-coordinate $[\text{Pb}\{\text{CH}(\text{SiMe}_3)(\text{C}_5\text{H}_5\text{N}-8)\}_2]^{13}$ and δ 3919 ppm in the two-coordinate $[\text{Pb}\{\text{C}_6\text{H}_5(\text{NMe}_2)_2-2,6\}]^{14}$.

Molecular structures

The single-crystal X-ray structures of **1**, **2**, **3** and **5** have been determined. They are isostructural and only the molecular structure of **3** is shown in Fig. 1. Selected bond distances and angles for **1**, **2**, **3** and **5** are shown in Table 1. All the compounds are monomeric with the dianionic ligand $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{R})\text{CH}\}_2\text{C}_5\text{H}_3\text{N}-2,6\}^{2-}$ bonded in a $[\text{N},\text{N},\text{N}]$ -chelate fashion to the metal centre. The geometry at the metal centre is trigonal pyramidal with a stereo-active lone pair at the metal. The distance between the metal and the centre of the trigonal plane described by the three nitrogens is 1.030 Å (for **1**), 1.223 Å (for **2**), 1.302 Å (for **3** and **5**). In each case, for the two azaallyl moieties the bonding is delocalised along the C(6)C(7)N(2) and C(14)C(15)N(3) backbones. The sum of the bond angles around atoms N(2) and N(3) suggests that they are sp^2 hybridized. Within a homologous series, the metal–nitrogen distance of the divalent Group 14 metal compounds varies according to the size of the metal atoms. The sum of bite angles subtended at the metal centres in **1**, **2**, **3** and **5** are 287.9, 276.7, 273.5 and 274.8°, respectively. Suitable crystals of the tin(II) analogue **4** could not be obtained, but the spectral data are similar to those of **2** and **5**. It is proposed that **4** has a structure similar to its analogues. The structures of the analogous dilithium, dipotassium, and lithium–potassium 2,6-pyridyl-bridged bis-azaallyl complexes showed that one of the metals is bonded to the ligand in a tridentate-chelate fashion, while the other metal interacts with the π -orbitals of the azaallyl arm.⁹

**Fig. 1** Molecular structure of **3**; hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at 30%.

In **1**, the Ge–N(2) and Ge–N(3) distances of 1.992(2) Å and 1.979(8) Å are comparatively longer than those found for related Ge–N(amido) distances, such as 1.87(1) Å and 1.90(1) Å in $[\text{Ge}[\text{NCMe}_2(\text{CH}_2)_3\text{CMe}_2]_2]^{2a}$ and 1.878(5) Å and 1.873(5) Å in $[\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2]^{1a}$. The Ge–N(1) distance of 2.019(6) Å is shorter than the distance of 2.0814(16) Å in $[\text{Ge}\{\text{Si}(\text{Me}_2)\text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2\}]^{15}$.

In **2**, the Sn–N(2) and Sn–N(3) distances of 2.204(3) Å and 2.171(3) Å fall in the range of normal Sn–N(amido) bond distances, and are comparable with the Sn–N distances of 2.153(4) and 2.288(4) Å in $[\text{Sn}\{\text{C}(\text{SiMe}_3)_2\text{C}(\text{Ph})\text{N}(\text{SiMe}_3)\}_2]^{16}$. The Sn–N(1) distance is marginally shorter than that found for related Sn–N(pyridyl) distances, e.g. 2.26(2) Å and 2.27(2) Å in $[\text{Sn}\{2\text{-C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}\}\text{Cl}]^{17}$, 2.288(2) Å in $[\text{Sn}\{2\text{-C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}\}\{\text{Sn}(\text{SiMe}_3)_3\}]^{18}$, 2.449(7) Å in $[\text{Sn}\{2\text{-C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}\}_2]^{19}$, and 2.300(6) Å in $[\text{Sn}\{2\text{-C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}\}\{\text{CH}(\text{PPh}_2)_2\}]^{19}$.

Compound **3** crystallized in a triclinic space group $P\bar{1}$ and exhibits a molecular geometry similar to compound **5**. Plumblylenes are regarded as carbene-analogues, the energetically most favourable electronic state is the singlet $^1\sigma^2$ found by experiment and calculation.²⁰ The structure of the singlet plumblylenes as well as other carbene analogues can be described by the following two geometries. (A) The non-bonding electron pair occupies an s-orbital, the bonding electrons occupy p-orbitals, while the third p-orbital remains empty with a bond angle of exactly 90°. (B) Both non-bonding and bonding electron pairs occupy sp^2 -hybrid orbitals while a p-orbital is unoccupied with a bond angle of 120°. As the bond angle of N(2)–Pb–N(3) is 110.4°, compound **5** is expected to be of geometry B. However, as mentioned before, the lone pair on the Pb(II) atom involved may lead to sp^3 hybridization. The Pb–N distances of 2.330(3) Å, 2.316(4) Å and 2.298(4) Å in compound **5** are almost the same as those in compound **3**, indicating both Ph and Bu^t substituents make no significant difference to the stability of the compound.

In conclusion, the dianionic bis(1-azaallyl) ligands $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{R})\text{CH}\}_2\text{C}_5\text{H}_3\text{N}-2,6\}^{2-}$ [R = Ph or Bu^t] are capable of forming thermally stable bivalent Group 14 metal dienamides through the coordination of the pyridyl nitrogen.

Experimental

General procedures

All manipulations were carried out either in a nitrogen-filled dry-box or under nitrogen using standard Schlenk techniques. Solvents were dried over and distilled from sodium/benzophenone (diethyl ether and tetrahydrofuran) or sodium/potassium alloy (pentane). *n*-Butyllithium, potassium *tert*-butoxide, tin(II) chloride and lead(II) chloride were purchased from Aldrich and used without further purification. Benzonitrile and *N,N,N',N'*-tetramethylethylenediamine (tmen) were purchased from Aldrich and distilled from KOH prior to use. GeCl_2 (dioxane) was prepared according to the literature.¹ 2,6-Bis(trimethylsilylmethyl)-pyridine was prepared as described in the literature.²¹ ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively, using a Bruker DPX-300 spectrometer in sealed tubes at ambient probe temperature. The ^1H chemical shifts were referenced to internal $\text{C}_6\text{D}_5\text{H}$ (δ 7.15 ppm), ^{13}C chemical shifts were referenced to C_6D_6 (δ 128.0 ppm), ^{119}Sn chemical shifts to SnMe_4 and ^{207}Pb chemical shifts to PbCl_2 in D_2O . Mass spectral data were recorded on a 5989-In mass spectrometer. Elemental analyses were performed at MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, UK.

Preparation of compounds

[Ge{N(SiMe₃)C(Ph)CH}₂C₅H₃N-2,6} (1). To a stirred suspension of GeCl_2 (dioxane) (0.311 g, 1.34 mmol) in diethyl ether (20 ml) was added a solution of $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{CH}\}_2$ -

Table 2 Selected structural data for compounds **1**, **2**, **3** and **5**

	1	2	3	5
Empirical formula	C ₂₇ GeH ₃₃ N ₃ Si ₂	C ₂₇ H ₃₃ N ₃ Si ₂ Sn	C ₂₇ H ₃₃ N ₃ PbSi ₂	C ₂₃ H ₄₁ N ₃ PbSi ₂
<i>M</i>	528.33	574.43	662.93	622.96
Colour, shape	Red, block	Orange, prism	Red, block	Red, block
<i>T</i> /K	293(2)	293(2)	293(2)	294(2)
Crystal size/mm	0.67 × 0.65 × 0.66	0.50 × 0.50 × 0.26	0.53 × 0.48 × 0.45	0.26 × 0.25 × 0.22
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	13.876 (2)	8.6497 (17)	8.569 (1)	9.7518 (2)
<i>b</i> /Å	13.739 (2)	11.619 (2)	11.720 (2)	12.115 (3)
<i>c</i> /Å	14.587 (2)	13.869 (3)	13.850 (2)	12.609 (3)
<i>α</i> /°	90	84.69 (3)	84.487 (2)	103.360 (8)
<i>β</i> /°	95.110 (3)	83.38 (3)	83.495 (3)	100.73 (1)
<i>γ</i> /°	90	88.21 (3)	87.398 (3)	100.66 (1)
<i>V</i> /Å ³	2770.0 (6)	1378.3 (5)	1375.0 (3)	1382.8 (5)
<i>Z</i>	4	2	2	2
<i>ρ</i> /Mg m ⁻³	1.267	1.384	1.601	1.496
<i>μ</i> /mm ⁻¹	1.212	1.033	6.242	6.200
No. of reflns collected	18346	4629	9250	4104
No. of indept reflns (<i>R</i> _{int})	6692 (0.0234)	4629 (0.0000)	6468 (0.0161)	4104 (0.0000)
No. of obsd reflns [<i>I</i> > 2σ(<i>I</i>)]	6672	4507	6280	3456
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0305, 0.0708	0.0501, 0.1484	0.0251, 0.0595	0.0616, 0.1651
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0483, 0.0827	0.0509, 0.1497	0.0297, 0.0605	0.0677, 0.1746

(C₅H₃N-2,6){Li(Et₂O)}₂ (0.810 g, 1.31 mmol) in diethyl ether (30 ml) at -78 °C. The mixture was warmed to ambient temperature and then stirred for 17 h to give a red slurry. The white precipitate formed was filtered off and the filtrate was concentrated to ca. 10 ml. Red crystals of **1** were obtained, yield 0.410 g (59.2%, 0.78 mmol). Anal. Calcd for C₂₇GeH₃₃N₃Si₂: C, 61.38; H, 6.30; N, 7.95. Found: C, 60.57; H, 6.59; N, 8.11%. ¹H NMR (300 MHz, C₆D₆: C₅D₅N (2 : 1)): δ 0.09 (s, 9H, SiMe₃), 0.27 (s, 9H, SiMe₃), 5.15 (s, 1H, CH), 6.41 (t, *J* = 8.4 Hz, 2H, *m*-C₅H₃N), 6.56 (s, 1H, CH), 7.00 (t, *J* = 7.8 Hz, 1H, *p*-C₅H₃N), 7.18 (m, 6H, *p*-C₆H₅ and *m*-C₆H₅), 7.41 (dd, 2H, *o*-C₆H₅), 7.67 (dd, 2H, *o*-C₆H₅). ¹³C NMR (75.5 MHz, C₆D₆: C₅D₅N (2 : 1)): δ 3.41, 4.44, 103.07, 107.92, 115.26, 119.62, 128.90, 129.22, 136.16, 138.10, 142.07, 144.24, 144.77, 148.83, 150.84, 153.14, 157.45, 158.97, 161.64. MS (EI, 70 eV): *m/z* 528 (29, [M]⁺), 455 (83, [M - SiMe₃]⁺), 382 (45, [M - 2 SiMe₃]⁺).

[Sn{N(SiMe₃)C(Ph)C(H)}₂C₅H₃N-2,6}] (**2**). To a suspension of SnCl₂ (0.240 g, 1.27 mmol) in THF was added a solution of [N(SiMe₃)C(Ph)C(H)}₂C₅H₃N-2,6){Li(Et₂O)}₂ (0.891 g, 1.27 mmol) in THF (20 ml) at -78 °C. After the mixture was warmed to 21 °C and stirred for 16 h, the solvent was removed under vacuum and the residue was extracted with *n*-hexane (20 ml). Concentration to ca. 5 ml and cooling to -30 °C gave orange crystals of **2**, yield 0.362 g (53.1%, 0.221 mmol). Anal. Calcd for C₂₇H₃₃N₃Si₂Sn: C, 56.45; H, 5.79; N, 7.31. Found: C, 56.73; H, 5.72; N, 7.27%. ¹H NMR (300 MHz, C₆D₆: C₅D₄N (4 : 1)): δ 0.11 (s, 18H, SiMe₃), 5.65 (s, 2H, CH), 6.63 (d, *J* = 7.8 Hz, 2H, *p*-C₅H₃N), 7.12 (m, 7H, *m*-C₅H₃N and C₆H₅), 7.62 (dd, 4H, C₆H₅). ¹³C NMR (75.5 MHz, C₆D₆: C₅D₄N (4 : 1)): δ 1.64, 102.28, 118.29, 128.53, 128.94, 136.11, 142.13, 153.13, 157.46.

[Pb{N(SiMe₃)C(Ph)C(H)}₂C₅H₃N-2,6}] (**3**). To a suspension of PbCl₂ (0.801 g, 2.88 mmol) in THF (40 ml) was added a red solution of [N(SiMe₃)C(Ph)C(H)}₂C₅H₃N-2,6}{K(tmen)}₂ (1.88 g, 2.45 mmol) in THF (40 ml) at -78 °C. The mixture was warmed to room temperature and then stirred for 24 h. The solvent was removed under reduced pressure and Et₂O (30 ml) was added for extraction. Filtration and concentration (ca. 10 ml) of the resulting red solution afforded **3** as yellow crystals, yield 0.450 g (27.7%, 0.680 mmol). Some black solid precipitate was formed due to the decomposition of the product at room temperature. Anal. Calcd for C₂₇H₃₃N₃PbSi₂: C, 48.92; H, 5.02; N, 6.34. Found: C, 48.97; H, 5.10; N, 6.62%. ¹H NMR (300 MHz, C₇D₈): δ 0.24 (s, 18H, SiMe₃), 5.38 (d, 2H, *J* = 2.1 Hz, CH), 6.29 (d, *J* = 7.5 Hz, 2H, *m*-C₅H₃N), 6.92 (m,

1H, *p*-C₅H₃N), 7.07 (m, 6H, *p*-C₆H₅ and *m*-C₆H₅), 7.51 (br, 2H, *o*-C₆H₅). ¹³C NMR (75.5 MHz, C₇D₈): δ 4.81, 45.83, 58.16, 98.13, 112.63, 125.55, 126.54, 127.44, 129.03, 135.53, 152.82, 159.28, 158.97, 166.95. MS (EI, 70 eV): *m/z* 663 (30, [M]⁺), 591 (44, [M - SiMe₃ + 1]⁺).

[Sn{N(SiMe₃)C(Bu)^tC(H)}₂C₅H₃N-2,6}] (**4**). To a suspension of SnCl₂ (0.250 g, 1.32 mmol) in THF (10 ml) was added a solution of [Na{N(SiMe₃)C(Bu)^tC(H)}₂C₅H₃N-2,6}{Na(tmen)}₂ (1.10 g, 0.950 mmol) in THF (40 ml) at -78 °C. The mixture was warmed to ambient temperature and then stirred for an additional 20 h. The solvent was removed under reduced pressure and Et₂O (40 ml) was added for extraction. Filtration and concentration (ca. 10 ml) of the resulting reddish orange solution afforded **4** as orange microcrystals, yield 0.121 g (23.6%, 0.221 mmol). mp 117–120 °C. Anal. Calcd for C₂₃H₄₁N₃Si₂Sn: C, 54.82; H, 9.60; N, 12.79. Found: C, 54.52; H, 9.53; N, 11.26%. ¹H NMR (300 MHz, C₇D₈): δ 0.15 (s, 18H, SiMe₃), 1.17 (s, 18H, CMe₃), 5.66 (s, 2H, CH), 6.95 (d, *J* = 7.8 Hz, 2H, *m*-C₅H₃N), 7.17 (t, *J* = 7.8 Hz, 1H, *p*-C₅H₃N). ¹³C NMR (75.5 MHz, C₇D₈): δ 2.24, 29.68, 45.89, 101.97, 118.93, 135.41, 157.99, 158.53. MS (EI, 70 eV): *m/z* 535 (21, [M + 1]⁺), 416 (50, [M - Sn]⁺).

[Pb{N(SiMe₃)C(Bu)^tC(H)}₂C₅H₃N-2,6}] (**5**). To a suspension of PbCl₂ (0.701 g, 2.53 mmol) in THF (40 ml) was added an orange solution of [Li{N(SiMe₃)C(Bu)^tC(H)}₂C₅H₃N-2,6}{Li(tmen)}₂ (1.63 g, 2.46 mmol) in THF (40 ml) at -78 °C. The mixture was warmed to ambient temperature and then stirred for a further 16 h. The solvent was removed under reduced pressure and Et₂O (30 ml) was added for extraction. Filtration and concentration (ca. 10 ml) of the resulting red solution and storage at -30 °C afforded **5** as red crystals, yield 1.17 g (76.4%, 1.88 mmol). mp 117–120 °C. Anal. Calcd for C₂₃H₄₁N₃PbSi₂: C, 44.34; H, 6.63; N, 6.74. Found: C, 44.34; H, 6.51; N, 6.96%. ¹H NMR (300 MHz, C₆D₆: C₅D₅N (4 : 1)): δ 0.35 (s, 18H, SiMe₃), 1.21 (s, 18H, CMe₃), 5.90 (s, 2H, CH), 6.35 (d, *J* = 7.8 Hz, 2H, *m*-C₅H₃N), 6.94 (t, *J* = 7.8 Hz, 1H, *p*-C₅H₃N). ¹³C NMR (75.5 MHz, C₆D₆: C₅D₅N (4 : 1)): δ 5.53, 30.57, 40.50, 107.83, 118.30, 138.22, 154.33, 167.34. MS (EI, 70 eV): *m/z* 623 (65, [M]⁺), 550 (40, [M - SiMe₃]⁺), 495 (37, [M - SiMe₃ - CMe₃ + 2]⁺).

X-Ray crystallography

Crystals of compounds **3** and **5** were grown from diethyl ether while those of compounds **1** and **2** were grown from diethyl

ether-hexane and hexane respectively. X-Ray data were collected using single crystals sealed in capillaries under dinitrogen, and raw intensities were collected on a Bruker SMART CCD diffractometer at 294 K for **1** and **3**, while the raw intensities of **2** and **5** were collected on Rigaku RAXIS IIC and IIIIP Rigaku diffractometers at 294 K, respectively. The structures were solved by direct phase determination, and all non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically (C-H bonds fixed at 0.96 Å) and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. Computations were performed using the Siemens SHELXTL PC program package²² on a PC 486 computer, and anomalous dispersion corrections were incorporated. The crystallographic data for **1**, **2**, **3** and **5** are shown in Table 2.

CCDC reference numbers 198206–198209.

See <http://www.rsc.org/suppdata/dt/b2/b211305h/> for crystallographic data in CIF or other electronic format.

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