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# PAPER

# Crystalline metal (Li, Mg, Ca, Sr, Ba, Sn, Pb) complexes of the new chelating N,N'-dianionic [1,2-N(R)C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NR)]<sup>2-</sup> ligand (R = SiMe<sub>3</sub>, CH<sub>2</sub>Bu<sup>t</sup>)†‡

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2-Aminomethylaniline was converted into the N, N'-bis(pivaloyl) (1) or -bis(trimethylsilyl) (2) derivative, using 2 Bu'C(O)Cl or 2 Me<sub>3</sub>SiCl ( $\equiv$  RCl), respectively, with 2 NEt<sub>3</sub>, or for **2** from successively using 2 LiBu" and 2 RCl. N, N'-Bis(neopentyl)-2-(aminomethyl)aniline (3) was prepared by LiAlH<sub>4</sub> reduction of 1. From 2 or 3 and 2 LiBu<sup>n</sup>, the appropriate dilitiodiamide  $\{2-[\{N(Li)R\}C_6H_4\{CH_2N(Li)R\}(L)]_2$  (L absent, 4a; or L = THF, 4b) or the N,N'-bis(neopentyl) analogue (5) of 4a was prepared. Treatment of 4a with 2 Bu'NC, 2 (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC) or 2 Bu'CN ( $\equiv$  L') furnished the corresponding adduct  $[2-N{Li(L')R}C_6H_4{CH_2N(Li)R}]$  (4c, 4d or 4e, respectively), whereas 4b with 2 PhCN afforded  $[2-{N(Li)R}C_{6}H_{4}CH_{2}C(Ph) = NLi(NCPh)]$  (6). The dimeric bis(amido)stannylene  $[Sn{N(R)C_6H_4(CH_2NR)-1,2}]_2$  (7) was obtained from 4a and  $[Sn(\mu-Cl)NR_2]_2$ , while the N,N'-bis(neopentyl) analogue 8 of 7 was similarly derived from  $[Sn(\mu-Cl)NR_2]_2$  and 5. Reaction of two equivalents of the diamine 2 with  $Pb(NR_2)_2$  yielded 9, the lead homologue of 7. Oxidative addition of sulfur to 7 led to the dimeric bis(diamido)tin sulfide 10. Treatment of 2 successively with 'MgBu<sub>2</sub>' in  $C_5H_{12}$  and THF gave [Mg{N(R)C\_6H\_4(CH\_2NR)}(THF)]\_2 (11a), which by displacement of its THF by an equivalent portion of Bu'CN or PhCN produced  $[Mg{N(R)C_6H_4(CH_2NR)}(CNR^2)_n][R' = Bu', n = 1$ (11b);  $\mathbf{R}' = \mathbf{Ph}$ , n = 2 (11c)]. The Ca (12), Sr (13) or Ba (14) analogues of the Mg compound 11a were isolated from 2 and either the appropriate compound  $M(NR_2)_2$  (M = Ca, Sr, Ba), or successively 2 LiBu" and 2 M(OTos)<sub>2</sub>. The new compounds 1-14 were characterized by microanalysis (C, H, N; not for 1, 2, 3, 5), solution NMR spectra,  $v_{max}$  (C $\equiv$ N) (IR for 4c, 4d, 4e, 6, 11b, 11c), selected EI-MS peaks (for 1, 2, 3, 7, 8, 9, 10), and single crystal X-ray diffraction (for 4a, 4b, 11a).

# Introduction

Amides  $[N(R')(R'')]^-$  (R' and R" are the same or different and each is an alkyl, aryl or silyl group) represent possibly the most ubiquitous of all ligands and are found in compounds of all the elements except the lighter rare gases.<sup>1</sup> They may be bound to a metal of metalloid in a terminal or bridging (double or single) fashion. This paper continues our long held involvement in metal and metalloid amide chemistry. Simple *N*,*N*'-dianionic chelating ligands have been found *inter alia* in carbenes<sup>2</sup> and silylenes.<sup>3</sup> More directly relevant to the present paper are the 1,3-, 1,4- and particularly 1,2-benzene(diamido) ligands. The first example of the latter appears to have been in the pentacyclic dimeric magnesium complex Mg[N(R)C<sub>6</sub>H<sub>4</sub>N(R)-1,2] ( $\equiv$  A), obtained from the hydrocarbon-soluble dibutylmagnesium and

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 $C_6H_4\{N(H)R\}$ -1,2 (R = SiMe<sub>3</sub>).<sup>4</sup> The dianionic ligand of A, or the N,N'-bis(neopentyl) [C<sub>6</sub>H<sub>4</sub>(NR')<sub>2</sub>; R' = CH<sub>2</sub>Bu'] analogue, has featured in complexes of Li,<sup>5</sup> Si,<sup>6</sup> Ca,<sup>7</sup> Al,<sup>8</sup> Zn,<sup>7</sup> Ga,<sup>9</sup> Ge,<sup>10</sup> Y,<sup>5</sup> Zr,<sup>5</sup> Mo,<sup>11</sup> Sn,<sup>12</sup> Hf,<sup>13</sup> Ta,<sup>13</sup> W,<sup>10</sup> and Pb.<sup>12</sup> The references 2 to 13 are of relatively recent date and are intended to be illustrative rather than comprehensive.

# **Results and discussion**

The objective of this research was to begin to explore the synthesis and structures of metal complexes of the new N,N'-dianionic ligands [1,2-N(R or R')C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>N(R or R')}]<sup>2-</sup> (R = SiMe<sub>3</sub>, R' = CH<sub>2</sub>Bu'). A new feature of such a chelating bis(amido) ligand is its asymmetry, one *N*-centre being aromatic and the other aliphatic. This distinction is of particular significance in a bi- or oligonuclear [bis(amido)metal]<sub>n</sub> complex in determining the preferred bridge(s).

# Synthesis and structures of the dilithiodiamides 4a, 4b and 5

2-Aminobenzylamine with pivaloyl or trimethylsilyl chloride in the presence of triethylamine was N,N'-bis(acylated) or -bis(silylated)

<sup>‡</sup> This paper is dedicated to our friend and esteemed colleague Professor H. Schnöckel

yielding compounds 1 or 2, respectively. The latter was also prepared from the diamine by successive dilithiation and quenching with 2 Me<sub>3</sub>SiCl. The N,N'-bis(neopentyl)diamine 3 was obtained by reduction of 1. Compounds 2 and 3 were each N,N'-dilithiated, furnishing the crystalline dimer 4a (or its THF–adduct 4b) and 5. The routes to 4a, 4b and 5 are summarized in Scheme 1.



Scheme 1 Synthesis of the dilithiodiamides 4a, 4b and  $5 (R = SiMe_3, R' = CH_2Bu')$ .

Each of the crystalline compounds 1, 4a, 4b and 5, or the distillable liquids 2 and 3, were isolated in good yield and characterized by <sup>1</sup>H NMR spectroscopy, and for 4a and 4b by C, H and N microanalysis. The <sup>13</sup>C{<sup>1</sup>H} and <sup>7</sup>Li{<sup>1</sup>H} NMR spectra were recorded for 4a, 4b and 5 and the <sup>29</sup>Si{<sup>1</sup>H} spectra for 4a and 4b. Selected EI-mass spectral peaks are listed for 1, 2 and 3. The molecular structures of the dilithium diamides 4a and 4b were firmly established from single crystal X-ray diffraction.

The <sup>1</sup>H NMR spectrum of **4a** in  $C_7D_8$  at 298 K was completely assigned by NOE experiments. The  $CH_2$  protons were inequivalent, with doublets at  $\delta$  3.72 and 3.97 ppm; their relative proportions were invariant of concentration or temperature, ruling out an equilibrium. The major isomer was found to exchange with the minor, by saturation transfer experiments.

The <sup>1</sup>H NMR spectrum of **4b** in  $C_7D_8$  at 298 K showed a broad peak at  $\delta$  4.18 ppm, assigned to the  $CH_2$  protons, which did not split upon cooling to -78 °C. Likewise the <sup>7</sup>Li{<sup>1</sup>H} NMR spectral signal at  $\delta$  1.5 ppm at 298 K was unchanged at -78 °C.

The molecular structure of the crystalline compound **4a** is illustrated as an ORTEP diagram in Fig. 1a. Its core is a ladder like arrangement of three  $(LiN)_2$  rhombi; a central Li1N2Li3N4 is flanked by Li1N1Li2N4 and Li3N2Li4N3, as shown in Fig. 1b. Four of the endocyclic angles at the nitrogen atoms are narrower at



Fig. 1 (a) Molecular structure of crystalline 4a (30% thermal ellipsoids, hydrogens except [ $\{N(Li)SiMe_3\}C_6H_4\{CH_2N(Li)SiMe_3\}$ ] omitted). (b) Schematic representation of the core structure of 4a.

 $71.0 \pm 0.9^{\circ}$  than the two at the periphery N1 and N3 at  $74.8 \pm 0.2^{\circ}$ . The endocyclic angles at the lithium atoms range from the  $104.4 \pm$  $0.2^{\circ}$  at Li1 and Li3 in the outer rhombi to the  $110.45 \pm 0.05^{\circ}$ in their corresponding inner rhombi. The dihedral angle between the Li1N2Li3N4 rhombus and its Li1N1Li2N4 and Li3N2Li4N3 counterparts is 63.6(2)° and 63.7(2)°, respectively. Each of the fivecoordinate alkyl nitrogen atoms N2 and N4 has short contacts to three lithium atoms (at av. 2.05 Å), as well as bonds to its attached C<sub>sp</sub><sup>3</sup> and Si atoms. Each of the four-coordinate aryl nitrogen atoms N1 and N3 bridges two lithium atoms at distances of 1.945 and 2.035  $\pm$  0.006 Å, and binds to its adjacent C<sub>sp</sub><sup>2</sup> and Si atoms. Each of the four lithium atoms is in a three-coordinate environment; in the case of the peripheral Li atoms, Li2 and Li4, this is by virtue of having short contacts of  $2.33 \pm 0.03$  Å to the C19 and C6 atoms, respectively. These values may be compared with the Li  $\cdots$  C contacts of *ca*. 2.69, 2.34 or 2.27 Å found in Li{ $\mu$ - $N(CH_2Ph)_{3}^{14} [{Li(NBu')}_2SiMe_2]_2^{15} or [Li_2{NR}_2C_6H_4-1,2]_2^{16}$ respectively. Selected geometric parameters for 4a are listed in Table 1.

An ORTEP representation of the molecular structure of the crystalline **4b** is shown in Fig. 2. It is closely similar to that of **4a**, except that the peripheral lithium atoms Li3 and Li4 are attached to O1 and O2, respectively (rather than the C19 and C6 near to Li2 and Li4, respectively in **4a**). The central rhombus of **4b**, Li1N2Li2N4, is fused to the Li1N1Li3N4 and Li2N2Li4N3 rings. The endocyclic angles centred at the nitrogen atoms range

Li1_N1	2.030(6)	Li3_N2	2 083(6)
Li1_N2	2.030(0)	Li3_N3	2.005(0)
Li1_N4	2.015(6)	Li3_N4	2.020(0)
$L_{12} N_1$	1.045(6)	Lid N3	1.043(6)
LIZ-INI LIZ NA	2.040(6)	$L_1 + N_2$	2.041(6)
$L_{12}$ $C_{10}$	2.040(0) 2.214(7)	$L_{14} = N_{2}$	2.041(0) 2.252(7)
$112 \cdots 019$	2.314(7)	$L_1 4 \cdots C_0$	2.555(7)
NI-CI	1.405(4)	N1-511	1.702(3)
N2-C7	1.491(4)	N2-S12	1./11(3)
N3-C14	1.414(4)	N3-813	1.709(3)
N4-C20	1.501(4)	N4-S14	1.716(3)
C6–C7	1.504(5)	C19–C20	1.504(5)
C1–C6	1.423(4)	C14-C19	1.420(5)
N1-Li1-N2	109.0(3)	N2-Li3-N3	104.2(3)
N1-Li1-N4	104.6(3)	N2-Li3-N4	108.8(3)
N2-Li1-N4	110.5(3)	N3-Li3-N4	110.4(3)
N1-Li2-N4	109.2(3)	N3-Li4-N2	108 9(3)
N1-Li2-C19	137.0(3)	N3-Li4-C6	140.8(3)
N4-Li2-C19	68 6(2)	N2-Li4-C6	68 1(2)
Li1_N1_Li2	74.6(2)	Li3_N3_Li4	75.0(2)
Li1_N1_C1	109.2(2)	Li3_N3_C14	107.6(2)
Li2_N1_C1	109.2(2) 112.6(3)	Li3 N3 C14 Li4-N3-C14	107.0(2) 108.1(3)
Li2 N1 C1	112.0(3) 117.8(2)	Li3_N3_Si3	118 1(2)
Lii2_N1_Si1	117.0(2) 112.7(2)	Li3-N3-Si3	1210(2)
C1  N1 Sil	112.7(2) 121.0(2)	C14 N3 Si3	121.0(2) 118.8(2)
$L_{11} N_{2} L_{13}$	70.6(2)	L 11 N/ L 12	71.7(2)
$L_{11} = N_2 - L_{13}$	106.0(2)	$L_{11} = N_{4} = L_{12}$	106 4(2)
$L_{11} = 1N_2 = L_{14}$	71.8(2)	$L_{12}$ -IN4- $L_{13}$	100.4(2)
L13-IN2-L14 L11 N2 C7	/1.0(2)	$L_{11} = N_4 = L_{13}$	70.1(2)
LII-INZ-C/	00.3(2)	LI3-N4-C20	145.5(2)
LI3-IN2-C7	140.1(3)	L11-IN4-C20	143.3(3)
L14-N2-C7	92.7(2)	L12-IN4-C20	92.1(2)
$L_{11} = N_2 = S_{12}$	123.9(2)	L11-IN4-514	101.0(2)
L13-N2-S12	97.9(2)	L12-IN4-S14	123.0(2)
L14-IN2-512	122.1(2)	L13-IN4-514	124.6(2)
$C/-N_2-S_{12}$	113.8(2)	C20–N4–S14	112.7(2)
NI-CI-C6	121.4(3)	N3-C14-C15	121.4(3)
NI-CI-C2	122.4(3)	N3-C14-C19	121.5(3)
C1–C6–C7	120.4(3)	C14–C19–C20	121.0(3)
N2-C7-C6	111.5(3)	N4-C20-C19	110.2(3)
Dihedral Angles			
Li1-N2-Li3-N4 an	nd Li1–N1–Li2–N	<b>N</b> 4	63.6(2)
Li1-N2-Li3-N4 at	nd Li3–N2–Li4–N	N3	63.7(2)
N1-Li1-N2 and N	1-Li1-N4		61.8(2)
N3-Li3-N4 and N	3-Li3-N2		66.3(3)
N1-Li1-N2 and N	2-Li1-N4		65.6(3)
N3-Li3-N4 and N	2-Li3-N4		66.3(3)

Table 1 Selected bond lengths (Å) and angles (°) for 4a

from  $68.7 \pm 0.1^{\circ}$  at N2 and N4 of Li1N2Li2N4, through 72.2 ±  $0.3^{\circ}$  at these atoms in the adjacent rhombi, to  $76.0 \pm 0.2^{\circ}$  at N1 and N3. The endocyclic angles at the lithium atoms range from  $103.5 \pm 0.6^{\circ}$  at Li3 and Li4 (the peripheral atoms), through  $108.3 \pm 0.6^{\circ}$  at Li1 and Li2 (the outer rhombi), to  $111.4 \pm 0.6^{\circ}$ in Li1N2Li2N4. The dihedral angle between the Li1N2Li2N4 plane and the Li1N1Li3N4 or Li2N2Li4N3 is 50.8(2)° or 51.9(3)°, respectively. Each of the five-coordinate alkyl nitrogen atoms N2 and N4 has Li  $\cdots$  N contacts of an av. 2.06 ± 0.01 Å (ranging from 2.030 to 2.118 Å), as well as bonds to the attached  $C_{sp}^{3}$  and Si atoms. Each of the four-coordinate aryl nitrogen atoms N1 and N3 is a bridge between two Li atoms at distances of  $1.957 \pm 0.007$ and 2.017  $\pm$  0.015 Å. Each of the central lithium atoms, Li1 and Li2, has only three nitrogen atoms as near neighbours, whereas each of the peripheral equally three-coordinate lithium atoms Li3 and Li4 is also joined to an oxygen atom of tetrahydrofuran. Selected geometric parameters for 4b are listed in Table 2.



Fig. 2 Molecular structure of crystalline 4b (30% thermal ellipsoids, hydrogens except [ $\{N(Li)SiMe_3\}C_6H_4\{CH_2N(Li)SiMe_3\}$ ] omitted).

# Reactions of the dilithiodiamide 4a or 4b with a nitrile or an isonitrile

The outcome of the four reactions between the dilithiodiamide 4a or 4b and two equivalents of a nitrile or an isonitrile is summarized in Scheme 2. Thus, simple ligand addition from 4a (or ligand substitution from 4b) led to the isolation in high yield of the crystalline compounds 4c, 4d and 4e. However, from 4b and two equivalents of benzonitrile, the product 6 was the 1 : 1-benzonitrile adduct of the dilithium salt of a 2-ureidomethylanilide; evidently one of the PhCN reactants had inserted into the CH<sub>2</sub>N(R)-Li bond, while the other was found ligated to that lithium cation.



Scheme 2 Reactions of 4a/4b with Bu'NC, Bu'CN, PhCN or 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC (R = SiMe<sub>3</sub>).

Each of the yellow compounds **4c**, **4d**, **4e** and **6** was characterized by C, H and N microanalysis, NMR spectra in  $C_6D_6$  [<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} for each; <sup>7</sup>Li{<sup>1</sup>H} for **4d** and **6**; <sup>29</sup>Si{<sup>1</sup>H} for **4e** and **6**] and

Li1-N1	1 963(7)	Li2-N2	2 051(8)
Li1–N2	2.032(8)	Li2–N3	1.950(8)
Li1–N4	2.030(8)	Li2-N4	2.041(8)
Li3–N1	2.032(8)	Li4–N2	2.096(8)
Li3–N4	2.118(7)	Li4–N3	2.002(8)
N1-C1	1.409(5)	N3-C14	1.423(5)
N2-C7	1.492(5)	N4-C20	1.492(5)
Li3-01	1.979(8)	Li4–O2	1.973(8)
N1-Si1	1.698(3)	N3–Si3	1.707(3)
N2-Si2	1.711(3)	N4–Si4	1.704(3)
C6–C7	1.506(5)	C19–C20	1.510(5)
N1-Li1-N2	115.0(4)	N2-Li2-N3	107.7(4)
N1–Li1–N4	108.8(3)	N2-Li2-N4	110.8(3)
N2-Li1-N4	112.0(3)	N3-Li2-N4	114.4(4)
N1-Li3-N4	102.9(3)	N2-Li4-N3	104.1(3)
N1-Li3-O1	121.9(4)	N2-Li4-O2	129.5(4)
N4-Li3-O1	130.0(4)	N3–Li4–O2	122.3(4)
L11–N1–L13	75.8(3)	L12–N3–L14	76.1(3)
Lil–Nl–Cl	104.8(3)	L12–N3–C14	106.1(3)
L13–N1–C1	110.5(3)	L14-N3-C14	112.8(3)
L11-N1-S11	120.6(3)	L12-N3-S13	121.4(3)
L13-N1-511	110.9(3)	L14-IN3-513	115.1(3)
CI-INI-511	119.9(3)	C14 - IN3 - 513	118.2(3)
LII-INZ-LIZ	116 4(2)	L11-1N4-L12	117 2(2)
$L_{11} = 1N_2 = L_{14}$	71.0(3)	$L_{12}$ -1N4- $L_{13}$	72 A(3)
$L_{12} = N_2 = L_{14}$	1.9(3) 144.8(3)	$L_{11} = N_4 - L_{13}$	1/2.4(3) 1/5.2(3)
Li2-N2-C7	05 5(3)	$L_{11} = 104 - C_{20}$	96.2(3)
$L_{1}=N_{2}=C_{7}$	89.9(3)	Li2-N4-C20	89.3(3)
Lii=N2=C7 Lii=N2=Si2	117 3(3)	Li2-N4-Si4	110.9(3)
Lii-N2-Si2	100.5(3)	L12-104-514 L 11-N4-Si4	100.6(3)
Li2-N2-Si2 Li4-N2-Si2	100.5(3) 117 4(3)	Lii-N4-Si4	1143(3)
C7-N2-Si2	117.4(3) 114 2(3)	C20-N4-Si4	113.8(3)
C1-N1-Si1	120.9(4)	N3-C14-C15	121 4(4)
N1-C1-C6	122.8(3)	N3-C14-C19	121.7(4)
C1-C6-C7	121.9(4)	C14-C19-C20	122.5(4)
C5-C6-C7	118.5(4)	C18-C19-C20	118.6(4)
N2-C7-C6	113.7(6)	N4-C20-C19	113.3(3)
Dihedral Angles			
Li1-N2-Li2-N4	and		50.8(2)
L11-N1-Li3-N4	1		<b>51</b> 0/2
L11–N2–L12–N4 L12–N2–L14–N3	and		51.9(3)
N1-Li1-N2 and	N1–Li1–N4		53.5(4)
N3-Li2-N4 and	N3-Li2-N2		56.4(3)
N1-Li1-N2 and	N2-Li1-N4		55.2(4)
N3-Li2-N4 and	N2-Li2-N4		58.1(4)

IR v(N==C) stretching frequencies. These data firmly establish the structures of **4c**, **4d** and **4e**. The formulation is not so definitive for **6**. The spectral data for the latter showed that one of the two benzonitriles had behaved as a ligand (thus displacing THF from **4b**), whereas the other had been inserted into an RN–Li bond. More detailed NMR spectral studies of **6** (NOE, saturation transfer and 2D experiments) did not unambiguously establish the site of insertion; the assignment shown for **6** in Scheme 2 is based on the notion that PhCN would preferentially insert into the more basic amido groups: thus implicating the CH<sub>2</sub>N–Li rather than the ArN–Li bond.

The formation of a Bu'CN, ArNC or a Bu'NC adduct of the dilithium diamide **4c**, **4d** or **4e**, respectively, is attributed to steric constraints to the alternative of insertion of the nitrile or isonitrile into one of its Li–N bonds. In support, it is noted that treatment of LiNR<sub>2</sub> with Bu'CN yielded [Li( $\mu$ -NR<sub>2</sub>)(NCBu')]<sub>2</sub>,<sup>17</sup> while with PhCN the product was the benzamidinate [Li{N(R)C(Ph)NR}];<sup>18</sup> for other examples of dimeric crystalline *N*-trimethylsilylated lithium benzamidinates, see ref. 19 The compound [Li( $\mu$ -NR<sub>2</sub>)(CNPh)]<sub>2</sub> shows an isonitrile behaving as a ligand (*cf.* **4c**, **4d**), rather than inserting into an Li–NR<sub>2</sub> bond.<sup>20</sup>

#### Synthesis of the tin(II) (7, 8), tin(IV) (10) and lead(II) (9) compounds

The dimeric crystalline pentacyclic 1,2-bis(phenylenediamido)stannylenes 7 and 8 were obtained from the interaction of equivalent portions of the dinuclear amido( $\mu$ -chloro)stannane and the appropriate dilithiodiamide 4a and 5, respectively. The crystalline lead analogue 9 of 7 was prepared by the amine elimination reaction between the diamine 2 and bis[bis(trimethylsilyl)amido]lead. Treatment of 7 with two equivalents of sulfur in toluene afforded the crystalline dimeric *trans*-bis(phenylenediamido)tin(IV) sulfide 10. These syntheses are summarized in Scheme 3. The new colourless complexes 7–10 were isolated as crystals in excellent (10) or satisfactory yields. The pathway from  $7 \rightarrow 10$  is presumed to implicate successive dissociation of 7, oxidation of the monomer furnishing Sn(S)[N(R)C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NR)] (7') and dimerisation of the latter.



Scheme 3 Synthesis of the crystalline dimeric bis(amido)-group 14 metallenes 7, 8 and 9 and the cyclodi[tin(IV)sulfide] 10 (R = SiMe<sub>3</sub>, R' = CH<sub>2</sub>Bu').

Each of the compounds 7 to 10 was identified by C, H and N microanalysis, NMR spectra in  $C_6D_6$  [<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>29</sup>Si{<sup>1</sup>H} (not 8), <sup>119</sup>Sn{<sup>1</sup>H} (not 9) and <sup>207</sup>Pb{<sup>1</sup>H} for 9] and EI-mass spectra (selected highest m/z signals). The highest m/z peak in the mass

spectrum of both 8 and 9 showed in low intensity a signal attributed to the dimeric molecular ion. The same degree of molecular aggregation of 7 and 9 in solution in  $C_6D_6$  at 298 K is reflected in the values of the <sup>119</sup>Sn{<sup>1</sup>H} (7) and <sup>207</sup>Pb{<sup>1</sup>H} (9) chemical shifts; *cf*. Wrackmeyer's equation for isostructural Sn/Pb compounds:  $\delta_{Pb} = 3.30 (\delta_{sn}) + 2336.^{21}$  The <sup>1</sup>H NMR spectrum of 8 in  $C_6D_6$ at 298 K showed a distinctive pattern of doublets, assigned to magnetically inequivalent CH<sub>2</sub> protons from both the benzyl and neopentyl moieties. A pair of doublets and triplets from the  $C_6H_4$  protons was assigned by a two-dimensional (COSY) and a saturation transfer experiment.

A variable temperature <sup>119</sup>Sn{<sup>1</sup>H} NMR spectroscopic study for **8** in PhMe + C<sub>6</sub>D<sub>6</sub> indicated reversible equilibria. At 298 K, a single signal at  $\delta$  3.0 ppm was recorded, whereas at 168 K separate signals assigned to both **8** and **8'** were observed (Scheme 4).



Scheme 4 Solution-state equilibria of 8 and 10.

The crystalline dimeric diamidotin(IV) sulfide **10** has the *trans* configuration, but in hydrocarbon solution it exists as a mixture of the *trans*-(**10**) and the *cis*-(**10'**)-dimers; the more abundant is probably the former (Scheme 4). Thus, the <sup>1</sup>H NMR spectrum in PhMe + C<sub>6</sub>D<sub>6</sub> at 298 K showed two pairs of SiMe<sub>3</sub> resonances in a ratio of *ca*. 5 : 2. Correspondingly, there were four distinct signals in both the <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra attributed to four inequivalent SiMe<sub>3</sub> groups. The <sup>119</sup>Sn{<sup>1</sup>H} spectrum showed signals at  $\delta$  -75 (major) and -72 ppm, each with a set of satellites due to the <sup>2</sup>*J*(<sup>119</sup>Sn - <sup>117</sup>Sn) coupling of *ca*. 700 Hz. These data may be compared with the  $\delta$  <sup>119</sup>Sn{<sup>1</sup>H} of -106.6 ppm with <sup>2</sup>*J*(<sup>119</sup>Sn - <sup>117</sup>Sn) of 609 Hz for [Sn(NR<sub>2</sub>)(µ-S)]<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> at 298 K.<sup>22</sup> The route from crystalline **10** to a mixture of **10** and **10'** in solution is likely to implicate **7'** as an intermediate.

# Synthesis and structures of the group 2 metal complexes 11a, 11b, 11c, 12, 13 and 14

The crystalline pentacyclic bis(1,2-phenylenediamido)metal solvates  $[M{2-N(R)C_6H_4(CH_2NR)}(THF)]_2 [M = Mg (11a), Ca (12),$ 

Sr (13), Ba (14)] were prepared from the diamine 2 and the appropriate group 2 metal reagent by an elimination reaction [of  $C_4H_{10}$  (11a); or of HNR<sub>2</sub> (12, 13, 14)]. Alternatively, 12, 13 and 14 were obtained from 2 and successively 2 LiBu and M(OTos)<sub>2</sub>. Compound 11a with 2 Bu'CN or 2 PhCN gave Mg[{2-N(R)C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NR)}(NCR')<sub>n</sub>] [R' = Bu', n = 1 (11b); R' = Ph, n = 2 (11c)]; the 1 : 1 rather than the 1 : 2 (as for 11c) stoichiometry for 11b is noteworthy.

Each of the compounds of Scheme 5 was characterized by C, H and N microanalysis and <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra in C<sub>6</sub>D<sub>6</sub> at 298 K. The CN stretching frequencies for **11b** and **11c** were located at a higher wave number than in the free nitrile (Bu'CN at 2136 cm<sup>-1</sup> and PhCN at 2115 cm<sup>-1</sup>). The nitrile adducts **11b** and **11c** dissociated upon heating above 70 °C; no evidence of insertion of R'CN into a Mg–N bond was observed.



Scheme 5 Synthesis of the dimeric bis(amido)-group 2 metallenes 11a, 12, 13 and 14 and the conversion of 11a into the nitrile adducts 11b and 11c ( $R = SiMe_3$ ).

The molecular structure of the crystalline compound **11a**, comprising discrete dimers lying across a crystallographic inversion centre, is represented by the ORTEP of Fig. 3; selected bond lengths and angles are listed in Table 3. There is a central MgN1Mg'N1' rhombus with the endocyclic angle at the metal slightly wider than at the aliphatic nitrogen atom and the Mg–N1 bond *ca*. 0.02 Å shorter than the Mg'– N1' (which is *ca*. 0.08 Å longer than the bond between Mg and the aryl nitrogen atom N2). This rhombus is at the centre of an array of five fused rings: the adjacent puckered MgN1C7C1C2N2 to which is attached the aromatic ring *via* its C1 and C2 atoms. The endocyclic angles at

Table 3    Selected bond lengths (Å) and angles (°) for 11a				
Mg-N1	2.099(2)	N1–C7	1.150(3)	
Mg–N2	2.035(2)	N2-C2	1.396(3)	
Mg-N1'	2.116(2)	N1-Si1	1.731(2)	
Mg–O	2.078(2)	N2–Si2	1.717(2)	
C1–C2	1.419(2)	C1–C7	1.510(3)	
Mg–N1–Mg′	88.61(8)	N1-C7-C1	117.5(2)	
N1–Mg–N1′	91.39(8)	C7-C1-C2	121.1(2)	
N1–Mg–N2	102.31(9)	N2-C2-C1	121.2(2)	
N1'-Mg-N2	134.60(9)	Mg-O-C14	133.3(2)	
Mg–N1–C7	97.54(13)	Mg-O-C17	118.3(2)	
Mg-N2-C2	111.85(2)	Sil-N1-C7	114.5(2)	
Mg'-N1-C7	105.30(14)	O-Mg-N1	115.36(8)	
Mg–N1–Si1	121.19(11)	O-Mg-N1'	110.57(8)	
Mg'-N1-Si1	124.22(10)	O-Mg-N2	102.15(8)	
Distance from plane				
0	1.721(1) Å out of Mg-N1-Mg'-N1' plane			
Si	1.134(4) Å o	ut of Mg–N1–Mg	ý–N1′ plane	
Dihedral Angles				
N2-Mg-N1 and N1-Mg-N1	' 43.6(1)			
C7-N1-Mg and Mg-N1-Mg	y 74.8(1)			
C3-C2-C1 and C1-C2-N2	0.0(5)			

Symmetry transformations used to generate equivalent atoms for **11a**: '-x, -y, -z

26.0(4)

68.7(2)

C1-C2-N2 and C2-N2-Mg

C2-C1-C7 and C1-C7-N1



Fig. 3 Molecular structure of crystalline 11a (30% thermal ellipsoids, hydrogens except  $[Mg\{2-N(SiMe_3)C_6H_4(CH_2NSiMe_3)\}(THF)]_2$  omitted).

the Mg and N1 atoms are *ca*. 10° wider in the six-membered ring than in MgN1Mg'N1', and that at N2 is an additional *ca*. 10° wider. The Mg, N1 and N2 atoms are in a distorted tetrahedral, pyramidal and trigonal planar environment, respectively. The atoms O and Si1 are 1.721(3) Å and 1.134(4) Å on the same side of the MgN1Mg'N1' plane, respectively. The angles between the planes (i) N2MgN1 and N1MgN1', (ii) C7N1Mg and MgN1Mg', (iii) C3C2C1 and C1C2N2, (iv) C1C2N2 and C2N2Mg, and (v) C2C1C7 andC1C7N1 are 43.6(1)° (i), 74.8(1)° (ii), 0.0(5)° (iii), 26.0(4)° (iv) and 68.7(2)° (v), respectively. The structures of the crystalline dinuclear magnesium diamides  $[Mg\{(NR)_2C_6H_4-1,2\}(OEt_2)]_2(C),^4 [Mg(\mu-NR_2)(NR_2)]_2(D)^{23}$  and  $[Mg\{(NPh)_2CH_2CH_2\}(THF)_{1.5}]_2(E)^{24}$  are available for comparison with that of compound **11a**. Like the latter, **C** has distorted tetrahedrally centred Mg atoms, but in **D** and **E** the magnesium atoms are in a three- and five-coordinate environment, respectively. Their Mg–N bond lengths are 1.997(7) and 2.082(7) Å in C,<sup>4</sup> 1.975(7) and 2.145(5) Å in **D**<sup>23</sup> and 2.040(2) and 2.290(2) Å in E.<sup>24</sup> The N–Mg–N' angles are 87.8(3) and 93.9(3)° in C,<sup>4</sup> 95.5(2) and 96.1(2)° in **D**,<sup>23</sup> and 84.22(8) and 127.58(9)° in E.<sup>24</sup> The Mg–O bond lengths are 2.041(7) Å in C,<sup>4</sup> and 2.083(2) and 2.167(2) Å in E.<sup>24</sup>

# Conclusions

Metal complexes of the new asymmetric, N, N'chelating, dianionic ligands  $[N(R)C_6H_4(CH_2NR)-1,2]^2$  and  $[N(R')C_6H_4(CH_2NR')-1,2]^2$  (R = SiMe<sub>3</sub>, R' = CH<sub>2</sub>Bu') have been prepared and characterized. The particularity of these ligands lies in the chemically different nature of its amido groups: one being aliphatic and the other aromatic. In the dimeric crystalline compounds it is the former which feature as bridges in the central MNM'N' rhomboid [M = Li (4a, 4b), M = Mg (11a)].

### Experimental

#### General remarks

Syntheses were carried out under an atmosphere of argon or in a vacuum, using Schlenk apparatus and vacuum line techniques. The solvents used were reagent grade or better and were freshly distilled under dry nitrogen gas and then freeze-thaw degassed prior to use. Solvents were dried and distilled from sodium benzophenone (PhMe, Et<sub>2</sub>O, THF) or sodium-potassium alloy ( $C_5H_{12}$ ,  $C_6H_{14}$ ). The  $C_6D_6$ ,  $C_7D_8$ , CDCl<sub>3</sub> and  $C_5D_5N$  for NMR spectroscopy were stored over molecular sieves (4 Å) under an argon atmosphere. The NMR spectrometers were Bruker AC-P 250, WM 300 and DPX 300. IR Spectra were recorded as KBr discs on a Perkin Elmer 1720 instrument. The EI mass spectra were taken from solid samples using a Kratos MS 80 RF machine. Melting points were measured of samples in sealed capillaries. Elemental analyses were obtained from Brunel University. The following compounds were commercial samples (and were redistilled where appropriate): Bu'C(O)Cl, Me<sub>3</sub>SiCl, Bu'CN, PhCN, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, Et<sub>3</sub>N, 2- $(NH_2)C_6H_4CH_2NH_2$ , Li[AlH<sub>4</sub>], LiBu<sup>n</sup> in  $C_6H_{14}$  and "MgBu<sub>2</sub>" in  $C_6H_{14}$ . The compounds  $M(NR_2)_2$ ,<sup>25</sup>  $M(OTos)_2$  (M = Ca, Sr, Ba),<sup>26</sup>  $[Sn(\mu-Cl)NR_2)]_2^{27}$  and  $Pb(NR_2)_2^{28}$  (R = SiMe\_3) were prepared by published procedures.

# Preparation of 2- $[N(H)R'']C_6H_4[CH_2N(H)R'']$ (1) [R'' = C(O)Bu']

A solution of pivaloyl chloride (27.6 g, 0.23 mol) in THF (75 cm<sup>3</sup>) was added slowly to a stirring solution of 2-(NH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH<sub>2</sub> (14.0 g, 0.12 mol) and Et<sub>3</sub>N (23.2, 0.23 mol) in THF (100 cm<sup>3</sup>) at 0 °C. The mixture was heated under reflux for 2 h, then filtered. The filtrate was concentrated *in vacuo* and cooled to -5 °C yielding colourless needles of the diamide 1 (28.3 g, 85%), mp 160–162 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  1.19, 1.39 (s, 9H, CH<sub>3</sub>), 4.29 (d, 2H, CH<sub>2</sub>), 6.29 (s, 1H, NH), 7.11 (t, 1H, C<sub>6</sub>H<sub>4</sub>), 7.22 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 7.30 (t, 1H, C<sub>6</sub>H<sub>4</sub>), 7.83 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 9.23 ppm (s, 1H, NH).

EI-MS [*m*/*z* (assignment and rel. intensity, %): [*M*]<sup>+</sup>, 25, 290; [*M* - Me]<sup>+</sup>, 100, 276; [*M* - 2Me]<sup>+</sup>, 15, 261.

# Preparation of 2-[N(H)R]C<sub>6</sub>H<sub>4</sub>[CH<sub>2</sub>N(H)R] (2)

*Method a.* Me<sub>3</sub>SiCl (49.30 g, 0.46 mol) in PhMe (100 cm<sup>3</sup>) was added to a stirring solution of 2-(NH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH<sub>2</sub> (27.73 g, 0.23 mol) and Et<sub>3</sub>N (45.94 g, 0.46 mol) in toluene (100 cm<sup>3</sup>) at 0 °C. The mixture was heated at 100 °C for 2 h, then filtered. Volatiles were removed from the filtrate *in vacuo*; distillation yielded the colourless diamine **2** (45.4 g, 75%), bp 96–98 °C/0.1 mmHg. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  0.12, 0.28 (s, 9H, CH<sub>3</sub>), 3.85 (d, 2H, CH<sub>2</sub>), 3.86, 5.33 (s, 1H, NH), 6.66–6.76 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.05–7.12 ppm (m, 2H, C<sub>6</sub>H<sub>4</sub>). EI-MS [*m*/*z* (assignment and rel. intensity, %): [*M*]<sup>+</sup>, 25, 266, [*M* – Me]<sup>+</sup>, 2, 251; [*M* – SiMe<sub>3</sub>]<sup>+</sup>, 100, 193.

*Method b.* LiBu<sup>*n*</sup> (82.9 cm<sup>3</sup> of a 1.6 mol dm<sup>-3</sup> hexane solution, 0.13 mol) was added to 2-(NH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH<sub>2</sub> (8.09 g, 0.07 mol) in THF (250 cm<sup>3</sup>) at 0 °C. The mixture was stirred for 2 h at *ca.* 20 °C, then cooled to 0 °C. Me<sub>3</sub>SiCl (16.9 cm<sup>3</sup>, 0.13 mol) was slowly added. The mixture was heated under reflux for 3 h and set aside with stirring for *ca.* 12 h. Volatiles were removed *in vacuo*; distillation afforded the diamine **2** (14.2 g, 81%), bp 96–98 °C/0.1 mmHg. The <sup>1</sup>H NMR spectrum was identical to that recorded for (a).

# Preparation of 2- $[N(H)R']C_6H_4[CH_2N(H)R']$ (3) (R' = CH<sub>2</sub>Bu')

The *N*,*N*-pivaloyldiamide **1** (28.3 g, 0.10 mol) in THF (75 cm<sup>3</sup>) was added dropwise to a stirring suspension of Li[AlH<sub>4</sub>] (7.41 g, 0.19 mol) in THF (100 cm<sup>3</sup>) at 0 °C. The mixture was heated under reflux for 10 h, cooled (0 °C) and water (20 cm<sup>3</sup>) was carefully added, then filtered. Removal of volatiles from the filtrate *in vacuo* and distillation furnished the colourless diamine **3** (19.2 g, 75%), bp 116–118 °C/0.2 mmHg. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  1.52, 1.64 (s, 9H, CH<sub>3</sub>), 3.00, 3.51 (s, 2H, CH<sub>2</sub>Bu'), 4.40 (d, 2H, CH<sub>2</sub>), 5.20, 6.70 (s, 1H, NH), 7.20–7.90 ppm (m, 4H, C<sub>6</sub>H<sub>4</sub>). EI-MS [*m*/*z* (assignment and rel. intensity, %): [*M*]<sup>+</sup>, 29, 262; [*M* – Me]<sup>+</sup>, 2, 247; [*M* – Bu']<sup>+</sup>, 100, 205.

# Preparation of $[2-{N(Li)R}C_6H_4{CH_2N(Li)R}]_2$ (4a)

LiBu" (4.8 cm<sup>3</sup> of a 1.6 mol dm<sup>-3</sup> solution in hexane, 7.8 mmol) was added to the diamide **2** (1.04 g, 3.2 mmol) in hexane (50 cm<sup>3</sup>) at 25 °C. After *ca.* 2 h volatiles were removed *in vacuo*, leaving a pale yellow solid. Crystallisation from pentane (20 cm<sup>3</sup>) gave colourless crystals of **4a** (0.65 g, 87%) (C<sub>26</sub>H<sub>48</sub>Li<sub>4</sub>N<sub>4</sub>Si<sub>4</sub> requires C, 56.1; H, 8.63; N, 10.1. Found: C, 55.7; H, 8.58; N, 9.97%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.50 (s, 9H, CH<sub>3</sub>), 0.22 (s, 9H, CH<sub>3</sub>), 3.69 (d, 1H, CH<sub>2</sub>), 4.21 (d, 1H, CH<sub>2</sub>), 6.27 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 6.58 (t, 1H, <sup>3</sup>*J* = 7.2 Hz, C<sub>6</sub>H<sub>4</sub>), 6.81 (d, 1H, <sup>3</sup>*J* = 6.81 Hz, C<sub>6</sub>H<sub>4</sub>), 6.94 ppm (t, 1H, <sup>3</sup>*J* = 6.0 Hz, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.9 (CH<sub>3</sub>), 2.9 (CH<sub>3</sub>), 48.7 (CH<sub>2</sub>); 119.1, 125.7, 129.6, 131.6, 136.5, 157.2 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  -8.5, -4.4 ppm; <sup>7</sup>Li{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  1.7 ppm.

# Preparation of $[2-{N(Li)R}C_6H_4{CH_2N(Li)R}(THF)]_2$ (4b)

LiBu<sup>*n*</sup> (5.38 cm<sup>3</sup> of a 1.6 mol dm<sup>-3</sup> solution in hexane, 8.6 mmol) was added to the diamide **2** (1.15 g, 4.3 mmol) in THF (50 cm<sup>3</sup>) at 25 °C. After *ca*. 4 h, volatiles were removed *in vacuo* affording

a yellow solid. Crystallisation from pentane (10 cm<sup>3</sup>) yielded pale yellow crystals of **4b** (1.36 g, 90%) ( $C_{34}H_{64}Li_4N_4O_2Si_4$  requires C, 58.3; H, 9.14; N, 8.00. Found: C, 58.4; H, 9.03; N, 7.89%). <sup>1</sup>H NMR ( $C_6D_6$ , 298 K):  $\delta$  0.18 (s, 9H, CH<sub>3</sub>), 0.30 (s, 9H, CH<sub>3</sub>), 1.26 (m, 4H, THF), 3.40 (m, 4H, THF), 4.15 (br s, 2H, CH<sub>2</sub>), 6.50 (t, 1H, <sup>3</sup>J = 7.0 Hz), 6.92 (d, 1H, <sup>3</sup>J = 6.8 Hz), 7.02 (t, 1H, <sup>3</sup>J = 6.8 Hz), 7.09 ppm (d, 1H, <sup>3</sup>J = 6.5 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 298 K):  $\delta$ 2.5 (CH<sub>3</sub>), 2.7 (CH<sub>3</sub>), 25.5 (THF), 68.4 (THF); 105.4, 113.8, 122.1, 129.6, 135.4, 157.9 ppm ( $C_6H_4$ ); <sup>29</sup>Si{<sup>1</sup>H} NMR ( $C_6D_6$ , 298 K):  $\delta$ -11.5, -8.5 ppm; <sup>7</sup>Li{<sup>1</sup>H} NMR ( $C_6D_6$ , 298 K):  $\delta$  1.5 ppm.

#### Preparation of $[2-\{N(Li)R'\}C_6H_4\{CH_2N(Li)R'\}]$ (5)

LiBu" (30 cm<sup>3</sup> of a 1.6 mol dm<sup>-3</sup> solution in hexane, 48.0 mmol) was added to the diamide **3** (6.27 g, 24.0 mmol) in Et<sub>2</sub>O (50 cm<sup>3</sup>) at 25 °C. After *ca*. 2 h volatiles were removed *in vacuo*, leaving the pale yellow solid **5** (6.22 g, 95%), mp 185 °C (decomp.). <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$  0.70, 0.96 (s, 9H, CH<sub>3</sub>), 2.44, 3.30 (s, 2H, CH<sub>2</sub>), 4.06 (s, 2H, CH<sub>2</sub>), 6.21 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 6.92 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 7.20–7.40 ppm (m, 2H, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$  28.03, 29.26, 31.36, 35.13 (Me<sub>3</sub>), 61.01, 62.62 (*C*H<sub>2</sub>Me<sub>3</sub>), 65.79 (CH<sub>2</sub>); 103.29, 108.88, 129.91, 131.56, 139.49, 162.48 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>7</sup>Li{<sup>1</sup>H} NMR (PhMe + C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  –1.7 ppm.

# Reactions of $[2-\{N(Li)R\}C_6H_4\{CH_2N(Li)R\}]_2$ (4a) with a nitrile or isonitriles

*tert*-Butyl isocyanide (0.67 cm<sup>3</sup>, 6.47 mmol) was added to a solution of **4a** (0.89 g, 3.23 mmol) in pentane (50 cm<sup>3</sup>) at –78 °C. A white precipitate developed immediately which dissolved when set aside for 12 h at 25 °C. Volatiles were removed *in vacuo* to give a yellow solid; pentane (5 cm<sup>3</sup>) was introduced and the resulting solution was stored at 4 °C for 4 h, whereafter yellow crystals of [2-{N(Li)R}C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>N(Li)R.(CNBu')}] (**4c**) (0.99 g, 85%) (C<sub>18</sub>H<sub>33</sub>Li<sub>2</sub>N<sub>3</sub>Si<sub>2</sub> requires C, 59.8; H, 9.14; N 11.6. Found: C, 59.2; H, 9.11; N, 11.2%) were collected. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.18 (s, 9H, SiCH<sub>3</sub>), 0.33 (s, 9H, SiCH<sub>3</sub>), 0.90 (s, 9H, CCH<sub>3</sub>), 3.77 (d, 1H, CH<sub>2</sub>), 4.54 (d, 1H, CH<sub>2</sub>), 6.32–7.21 ppm (m, 4H, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  3.1 and 3.4 (SiCH<sub>3</sub>), 29.6 and 36.0 (CCH<sub>3</sub> and CCH<sub>3</sub>), 49.7 (CH<sub>2</sub>); 117.2, 118.2, 127.6, 129.7 (C<sub>6</sub>H<sub>4</sub>), 134.5 (NCBu'), 147.6 and 158.2 ppm (C<sub>6</sub>H<sub>4</sub>). IR: *v*(NC) 2161 cm<sup>-1</sup>.

2,6-Dimethyl(isocyano)benzene (0.12 g, 2.0 mmol) and **4a** (0.28 g, 1.0 mmol) in pentane (50 cm<sup>3</sup>) similarly afforded yellow crystals of [2-{N(LiR)C<sub>6</sub>H<sub>4</sub>NR.(CNC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)}] (**4d**) (0.40 g, 74%) (C<sub>22</sub>H<sub>33</sub>Li<sub>2</sub>N<sub>3</sub>Si<sub>3</sub> requires C, 68.9; H, 7.78; N, 10.4. Found: C, 68.8; H, 7.69; N, 10.5%). <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, 298 K):  $\delta$  –0.13 (s, 9H, SiCH<sub>3</sub>), 0.13 (s, 9H, SiCH<sub>3</sub>), 2.01 (s, 6H, CH<sub>3</sub>), 3.26 (d, 1H, CH<sub>2</sub>), 3.92 (d, 1H, CH<sub>2</sub>), 6.10 (d, 2H, <sup>3</sup>*J* = 3.8 Hz, C<sub>6</sub>H<sub>4</sub>), 6.60 – 6.69 (m, 3H, C<sub>6</sub>H<sub>4</sub>), 6.91–7.01 (m, 3H, C<sub>6</sub>H<sub>4</sub>), 7.12 ppm (t, 2H, <sup>3</sup>*J* = 7.4 Hz, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>, 298 K):  $\delta$  2.9 and 3.6 (SiCH<sub>3</sub>), 18.6 (CH<sub>3</sub>), 49.8 (CH<sub>2</sub>); 117.3, 118.3, 127.3, 129.2, 129.8, 130.2, 131.9, 135.1, 158.2 (C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>3</sub>), 166.8 ppm (CNC<sub>6</sub>H<sub>3</sub>); <sup>r</sup>Li{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>, 298 K):  $\delta$  2.91, 2.93 ppm. IR: *v*(NC) 2144 cm<sup>-1</sup>.

*tert*-Butyl cyanide (1 cm<sup>3</sup>) was added to **4a** (0.14 g). The solution was set aside for 2 h at 25 °C, whereafter volatiles were removed *in vacuo*. The residue was washed with pentane (10 cm<sup>3</sup>) furnishing the dark yellow adduct **4e** (0.14 g, 79%) ( $C_{18}H_{33}Li_2N_3Si_2$  requires C,

59.8; H, 9.14; N, 11.6. Found: C, 60.4; H, 9.19; N, 11.4%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.29 (s, 9H, SiMe<sub>3</sub>), 0.53 (s, 9H, SiMe<sub>3</sub>), 4.24 (br s, 2H, CH<sub>2</sub>), 6.54 (t, 1H, <sup>3</sup>*J* = 7.0 Hz), 7.06 – 7.20 ppm (m, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  3.0 and 3.2 (SiCH<sub>3</sub>), 27.9 and 28.4 (*C*CH<sub>3</sub> and *C*CH<sub>3</sub>), 52.7 (CH<sub>2</sub>); 111.8, 122.0 (C<sub>6</sub>H<sub>4</sub>), 125.49 (CN); 129.5, 133.1, 160.0 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$ –17.1, –11.1 ppm. IR: *v*(CN) 2255 cm<sup>-1</sup>.

Benzonitrile (0.82 cm<sup>3</sup>, 8.0 mmol) and 4a (1.12 g, 4.0 mmol) in THF (50 cm<sup>3</sup>) were mixed at -40 °C. The resultant orange solution was set aside at 25 °C for 2 h. Removal of volatiles in vacuo furnished an orange-red solid, which was washed with pentane (20 cm<sup>3</sup>). The residue was washed with hot toluene (40 cm<sup>3</sup>); concentration of the extract in vacuo and storage at -20 °C yielded pale yellow crystals of [2- ${N(Li)R}C_{6}H_{4}{CH_{2}N(R)C(Ph)NLi.(NCPh)}]$  (6) (1.85 g, 95%) (C<sub>27</sub>H<sub>34</sub>Li<sub>2</sub>N<sub>4</sub>Si<sub>2</sub> requires C, 66.9; H, 7.02; N, 11.5. Found: C, 66.7, H, 7.05; N, 11.2%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.15 (s, 9H, SiMe<sub>3</sub>), 0.34 (s, 9H, SiMe<sub>3</sub>), 4.30 (d, 1H, CH<sub>2</sub>), 4.51 (d, 1H, CH<sub>2</sub>), 6.64 6.81 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 7.14–7.35 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 7.35 (d, 2H,  ${}^{3}J = 6.5$ Hz,  $C_6H_4$ ), 7.59 ppm (d, 2H,  ${}^{3}J = 7.3$  Hz,  $C_6H_4$ );  ${}^{13}C{}^{1}H$  NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 3.2 and 3.3 (SiCH<sub>3</sub>), 53.0 (CH<sub>2</sub>); 111.1, 116.9; 124.6 (CN); 127.2, 129.1, 130.8, 132.1, 133.2, 136.5, 140.6, 157.8, 178.8 ppm (C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, C=N); <sup>7</sup>Li{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$ 1.4 and 1.8 ppm; <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  –8.7, –6.8 ppm.

## Preparation of $[Sn{(NR)C_6H_4(CH_2NR)-1,2}]_2$ (7)

The salt (4a) (1.14 g, 4.10 mmol) in hexane (35 cm<sup>3</sup>) was added to  $[Sn(\mu-Cl)NR_2]_2$  (2.58 g, 4.10 mmol) in hexane (35 cm<sup>3</sup>) at 25 °C. The mixture was stirred for 12 h then filtered. The filtrate was concentrated *in vacuo* to *ca*. 5 cm<sup>3</sup> and set aside at –5 °C affording colourless crystals of the diamide 7 (0.63 g, 40%) (C<sub>26</sub>H<sub>48</sub>N<sub>4</sub>Si<sub>4</sub>Sn<sub>2</sub> requires C, 40.8; H, 6.31; N, 7.31. Found: C, 40.4; H, 6.35; N, 7.16%), mp 150–152 °C (decomp.). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.10, 0.39 (s, 9H, CH<sub>3</sub>), 4.17 (s, 2H, CH<sub>2</sub>); 6.73 (t, 1H, <sup>3</sup>*J* = 7.0 Hz, C<sub>6</sub>H<sub>7</sub>), 7.05 – 7.15 ppm (m, 3H, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub> + PhMe, 298 K):  $\delta$  0.6 and 2.7 (CH<sub>3</sub>), 48.9 (CH<sub>2</sub>); 118.3, 122.5, 127.8, 130.0, 132.7, 151.0 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub> + PhMe, 298 K):  $\delta$  118.0 ppm. EI-MS [*m*/*z* (assignment and rel. intensity, %): [*M*/2]<sup>+</sup>, 52, 383; [*M*/2 – (CH<sub>3</sub> + 1)]<sup>+</sup>, 15, 367; [*M*/2 – SiMe<sub>3</sub> + 1]<sup>+</sup>, 69, 311; [*M*/2 – SiMe<sub>3</sub> – Me]<sup>+</sup>, 17, 296.

#### Preparation of $[Sn{NR'}C_6H_4(CH_2NR')-1,2]_2$ (8) (R' = CH<sub>2</sub>Bu')

As for 7, the salt 5 (1.20 g, 4.38 mmol) and  $[Sn(\mu-Cl)NR'_2]_2$  (27.5 g, 4.38 mmol) furnished the colourless crystalline diamide **8** (0.94 g, 56%) (C<sub>34</sub>H<sub>56</sub>N<sub>4</sub>Sn<sub>2</sub> requires C, 53.9; H, 7.49; N, 7.39. Found: C, 54.0; H, 7.51; N, 7.31%), mp 195–197 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.87, 0.90 (s, 9H, CH<sub>3</sub>), 2.23, 2.66 (d, 1H, <sup>2</sup>J = 14.0 Hz, CH<sub>2</sub>Bu'), 3.87, 4.30 (d, 1H, <sup>2</sup>J = 11.0 Hz, CH<sub>2</sub>Bu'); 6.65 (t, 1H, C<sub>6</sub>H<sub>4</sub>), 7.07 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 7.26 ppm (d, 1H, <sup>3</sup>J = 7 Hz, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub> + PhMe, 298 K):  $\delta$  27.7, 29.9, 33.2 (CH<sub>3</sub>), 57.0, 57.7 (CH<sub>2</sub>Bu'), 62.3 (CH<sub>2</sub>N); 114.3, 115.4, 133.7, 136.7, 136.9, 155.7 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub> + PhMe 298 K):  $\delta$  3.0 ppm. EI-MS [*m*/*z* (assignment and rel. intensity,%): [*M*]<sup>+</sup>, 1, 758; [*M*/2]<sup>+</sup>, 14, 380; [*M*/2 – Bu']<sup>+</sup>, 86, 323; [*M*/2 – Sn]<sup>+</sup>, 61, 260.

#### Preparation of $[Pb\{(NR)C_6H_4\{CH_2NR\}, 1,2\}]_2$ (9)

The salt **4a** (0.71 g, 2.70 mmol) was added to a stirring solution of Pb(NR<sub>2</sub>)<sub>2</sub> (1.41 g, 2.70 mmol) in hexane (80 cm<sup>3</sup>) at 25 °C. After 12 h the solution was concentrated *in vacuo* to *ca*. 5 cm<sup>3</sup>, from which colourless crystals of the lead(II) diamide **9** (0.83 g, 65%) (C<sub>26</sub>H<sub>48</sub>N<sub>4</sub>Pb<sub>2</sub>Si<sub>4</sub> requires C, 33.1; H, 5.13; N, 5.94. Found: C, 33.0; H, 5.10; N, 5.90%), mp 138–142 °C (decomp.), were isolated. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.00, 0.36 (s, 9H, CH<sub>3</sub>), 5.61 (s, 2H, CH<sub>2</sub>), 6.61 (t, 1H, C<sub>6</sub>H<sub>4</sub>), 7.00 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 7.10 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 7.30 ppm (d, 1H, <sup>3</sup>*J* = 7 Hz, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub> + PhMe, 298 K):  $\delta$  1.5, 3.3 (CH<sub>3</sub>), 49.3 (CH<sub>2</sub>); 118.5, 125.4, 129.2, 131.0, 135.2, 153.3 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub> + PhMe, 298 K):  $\delta$  –0.4, 10.4 ppm; <sup>207</sup>Pb{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub> + PhMe, 298 K):  $\delta$  2722 ppm. EI-MS [*m*/*z* (assignment and rel. intensity,%): [*M*]<sup>+</sup>, 5, 943; [*M* – CH<sub>3</sub>]<sup>+</sup>, 10, 928.

#### Preparation of $[Sn{(NR)C_6H_4(CH_2NR)-1,2}(\mu-S)]_2$ (10)

A solution of the diamidotin(II) compound 7 (1.03 g, 1.34 mmol) in toluene (50 cm<sup>3</sup>) was added to a stirring suspension of sulfur (0.09 g, 2.70 mmol) in toluene (50 cm<sup>3</sup>) at -78 °C. After 12 h at 25 °C the mixture was filtered. Removal of volatiles in vacuo from the filtrate gave a colourless solid, which was extracted into hexane (20 cm<sup>3</sup>). The extract was concentrated to ca. 5 cm<sup>3</sup>, from which colourless crystals of the dimeric bis(amido)tin(IV) sulfide 10 (0.90 g, 80%) (C<sub>34</sub>H<sub>56</sub>N<sub>4</sub>S<sub>2</sub>Sn<sub>2</sub> requires C, 37.6; H, 5.83; N, 6.75. Found: C, 37.0; H, 5.72; N, 6.55%), mp 178-182 °C, were isolated. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.30, 0.31 (2 s, 18H, CH<sub>3</sub>), 0.45, 0.46 (2 s, 18H, CH<sub>3</sub>), 4.04 (s, 4H, CH<sub>2</sub>), 6.79–7.19 ppm (m, 8H, C<sub>6</sub>H<sub>4</sub>).  $^{13}C{^{1}H}$  NMR (C<sub>6</sub>D<sub>6</sub> + PhMe, 298 K):  $\delta$  2.1, 2.2, 3.0, 3.7 (CH<sub>3</sub>); 50.0, 50.2 (CH<sub>2</sub>); 123.2, 123.6, 138.2, 140.4, 147.6 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (PhMe + C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  9.6, 11.1, 12.1 ppm; <sup>119</sup>Sn{<sup>1</sup>H} NMR (PhMe + C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  -72 ppm (<sup>2</sup>J = 6.85 and 7.10 Hz). EI-MS  $[m/z \text{ (assignment and rel. intensity, %): } [M]^+$ , 1, 830;  $[M - CH_3]^+$ , 1, 815;  $[M/2 - S]^+$ , 15, 383.

#### Preparation of $[Mg{2-N(R)C_6H_4(CH_2NR)}(THF)]_2$ (11a)

A solution of "MgBu<sub>2</sub>" (4 cm<sup>3</sup> of a 1 mol dm<sup>-3</sup> solution in hexane, 4.0 mmol) was added dropwise to a stirred solution of the diamine 2 (1.06 g, 4.0 mmol) at 0 °C, then set aside for 4 h at 25 °C. Volatiles were removed in vacuo and the residue was dissolved in THF (5 cm<sup>3</sup>). After 1 h, volatiles were again eliminated in vacuo. The residue was crystallised from hot toluene yielding pale yellow crystals of the dimeric bis(amido)magnesium-THF-solvate 11a (1.20 g, 83%) (C<sub>34</sub>H<sub>64</sub>Mg<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Si<sub>4</sub> requires C,56.7; H, 8.89; N, 7.78. Found: C, 55.4; H, 8.79; N, 7.82%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.20 (s, 9H, CH<sub>3</sub>), 0.33 (s, 9H, CH<sub>3</sub>), 1.41 (m, 4H, THF), 3.52 (m, 4H, THF), 4.44 (d, 1H, CH<sub>2</sub>), 4.84 (d, 1H, CH<sub>2</sub>), 6.69 (t, 1H,  ${}^{3}J = 7.1$  Hz, C<sub>6</sub>H<sub>4</sub>), 7.15 (d, 1H,  ${}^{3}J = 6.9$  Hz, C<sub>6</sub>H<sub>4</sub>), 7.29 (t, 1H,  ${}^{3}J = 7.3 \text{ Hz}, C_{6}H_{4}), 7.39 \text{ ppm } (d, 1H, {}^{3}J = 7.9 \text{ Hz}, C_{6}H_{4}); {}^{13}C{}^{1}H$ NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 3.2, 3.3 (CH<sub>3</sub>), 25.4 (THF), 52.3 (CH<sub>2</sub>), 67.3 (THF); 113.5, 120.5, 128.5, 130.7, 132.7, 158.0 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  1.1, 4.8 ppm.

# Reactions of $[Mg\{2\text{-}N(R)C_6H_4(CH_2NR)\}(THF)]_2$ (11a) with nitriles

*tert*-Butyl cyanide (0.1 cm<sup>3</sup>, 1 mmol) was added to a solution of **11a** (0.18 g, 0.5 mmol) in tetrahydrofuran (30 cm<sup>3</sup>) at

Table 4	Crystal data and structure refinement for 4a, 4b and 11a
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Compound	4a	4b	11a
Formula	$C_{26}H_{48}Li_4N_4Si_4$	$C_{34}H_{64}Li_4N_4O_2Si_4$	$C_{34}H_{64}Mg_2N_4O_2Si_4(C_7H_8)$
М	556.8	701.0	814.0
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (non-standard No.14)	$P2_1/c$ (No.14)	<i>P</i> 1(No.2)
a (Å)	9.729(2)	19.787(7)	10.380(5)
$b(\mathbf{A})$	21.316(5)	9.808(3)	10.726(3)
$c(\mathbf{A})$	16.744(4)	21.951(9)	11.752(4)
$\alpha$ (°)	90	90	77.64(2)
$\beta$ (°)	97.90(2)	99.70(3)	66.68(3)
$\gamma$ (°)	90	90	82.20(3)
$V(\mathbf{A}^3)$	3439.5(14)	4199(3)	1171.8(8)
Z	4	4	1
Absorption coefficient (mm <sup>-1</sup> )	0.19	0.17	0.19
Unique reflections, $R_{\rm int}$	6025, 0.060	5146, 0.069	4120, 0.000
Reflections with $I > 2\sigma(I)$	4032	3736	3392
Final <i>R</i> indices $I > 2\sigma(I) R_1$ , $wR_2$	0.056, 0.131	0.056, 0.132	0.047, 0.0123
$R$ indices (all data) $R_1, wR_2$	0.098, 0.154	0.086, 0.150	0.059, 0.131

-40 °C. The pale yellow solution was stored at 25 °C for 12 h. Volatiles were removed *in vacuo* to leave the pale yellow solid [Mg{2-N(R)C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NR}(NCBu')] (**11b**) (0.25 g, 96%) (C<sub>18</sub>H<sub>33</sub>MgN<sub>3</sub>Si<sub>2</sub> requires C, 58.2; H, 8.89; N, 11.3. Found: C, 57.5; H, 8.75; N, 11.6%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.27 (s, 9H, SiCH<sub>3</sub>), 0.39 (s, 9H, SiCH<sub>3</sub>), 0.77 (s, 9H, CCH<sub>3</sub>), 4.46 (d, 1H, CH<sub>2</sub>), 4.85 (d, 1H, CH<sub>2</sub>), 6.42 (d, 1H, <sup>3</sup>*J* = 4.9 Hz, C<sub>6</sub>H<sub>4</sub>), 6.76 (t, 1H, <sup>3</sup>*J* = 6.2 Hz, C<sub>6</sub>H<sub>4</sub>), 7.35 (t, 1H, <sup>3</sup>*J* = 7.9 Hz, C<sub>6</sub>H<sub>4</sub>), 7.43 ppm (d, 1H, <sup>3</sup>*J* = 7.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 3.7, 3.8 (SiCH<sub>3</sub>), 27.8, 28.2 (*CC*H<sub>3</sub>), 5.27 (CH<sub>2</sub>); 113.9, 116.3, 117.5 (C<sub>6</sub>H<sub>4</sub>); 120.9 (CN); 128.9, 131.1, 158.3 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 1.0, 4.9 ppm. IR: *v*(CN) 2276 cm<sup>-1</sup>.

Pale yellow crystals of  $[Mg\{2-N(R)C_6H_4(CH_2NR)\}(NCPh)_2]$ (11c) (0.39 g, 90%) (C<sub>27</sub>H<sub>34</sub>MgN<sub>4</sub>Si<sub>2</sub> requires C, 58.2; H, 8.89; N, 11.3. Found: C, 57.5; H 8.75; N, 11.6%) were obtained from benzonitrile (0.11 cm<sup>3</sup>, 1.1 mmol) and **11a** (0.41 g, 1.1 mmol) in toluene (40 cm<sup>3</sup>), using procedures similar to those for **11b**. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.04 (s, 9H, SiCH<sub>3</sub>), 0.35 (s, 9H, SiCH<sub>3</sub>), 4.84 (d, 1H, CH<sub>2</sub>); 6.65–6.78 (m, 5H, C<sub>6</sub>H<sub>4</sub>, 6.89–6.95 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.05 (d 1H, <sup>3</sup>J = 1.4 Hz, C<sub>6</sub>H<sub>4</sub>), 7.25–7.45 ppm (m, 2H, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  3.7, 4.0 (SiCH<sub>3</sub>), 52.7 (CH<sub>2</sub>); 113.9 (C<sub>6</sub>H<sub>4</sub>), 120.9 (CN); 128.9, 131.1, 132.0, 132.3, 158.3 ppm + 2 others (C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  –8.4, 2.4 ppm. IR: *v*(CN) 2277 cm<sup>-1</sup>.

# Preparation of $[Ca{2-N(R)C_6H_4(CH_2NR)}(THF)]_2$ (12)

A solution of the diamine **2** (0.60 g, 2.2 mol) in pentane (30 cm<sup>3</sup>) was added dropwise to a solution of Ca(NR<sub>2</sub>)<sub>2</sub> (0.45 g, 2.2 mmol) in pentane (50 cm<sup>3</sup>) at 0 °C, then set aside for 4 h at 25 °C. Volatiles were removed *in vacuo*. The residue was dissolved in tetrahydrofuran (10 cm<sup>3</sup>), then eliminated *in vacuo*. The residual solid, upon crystallisation from hot toluene, yielded yellow crystals of **12** (0.61 g, 74%) (C<sub>34</sub>H<sub>64</sub>Ca<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Si<sub>4</sub> requires C, 54.3; H, 8.51; N, 7.45. Found: C, 53.5; H, 8.47; N, 7.41%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.25 (s, 9H, CH<sub>3</sub>), 0.55 (s, 9H, CH<sub>3</sub>), 1.11 (m, 4H, THF), 3.17 (m, 4H, THF), 4.13 (d, 1H, CH<sub>2</sub>), 4.32 (d, 1H, CH<sub>2</sub>), 6.60 (t, 1H, <sup>3</sup>J = 7.1 Hz, C<sub>6</sub>H<sub>4</sub>), 6.91 (1H, <sup>3</sup>J = 7.9 Hz, C<sub>6</sub>H<sub>4</sub>), 7.06 (t, 1H, <sup>3</sup>J = 8.0 Hz, C<sub>6</sub>H<sub>4</sub>), 7.20 ppm (d, 1H, <sup>3</sup>J = 7.3 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  2.5, 2.6 (SiCH<sub>3</sub>), 25.3 (THF), 53.4 (CH<sub>2</sub>),

67.4 (THF); 112.6, 126.6, 128.5, 129.1, 132.2, 159.3 ppm ( $C_6H_4$ ); <sup>29</sup>Si{<sup>1</sup>H} NMR ( $C_6D_6$ , 298 K):  $\delta$  –8.3, 2.3 ppm.

Compound **12** (1.00 g, 61%) was also obtained by successive addition of Ca(OSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub> (1.64 g, 4.3 mmol) to the dilithium salt **4b** (1.2 g, 4.3 mmol) in tetrahydrofuran at 25 °C, filtration, removal of volatiles from the filtrate, washing the residue with pentane, and drying *in vacuo*.

### Preparation of $[Sr{2-N(R)C_6H_4(CH_2NR)}(THF)]_2$ (13)

Using similar procedures as for **12**, the yellow solid strontium salt **13** (0.25 g, 76%; or 1.66 g, 89%) was prepared either from Sr(NR<sub>2</sub>)<sub>2</sub> (0.45 g, 0.8 mmol) and the diamine **2** (0.20 g, 0.8 mmol), or Sr(OSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub> (1.89 g, 4.4 mmol) and the dilithium salt **4b** (1.22 g, 4.4 mmol), respectively. (C<sub>34</sub>H<sub>64</sub>Sr<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Si<sub>4</sub> requires C, 48.2; H, 7.57; N, 6.62. Found: C, 47.9; H, 7.56; N, 6.64%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.16 (s, 9H, CH<sub>3</sub>), 0.22 (s, 9H, CH<sub>3</sub>), 1.41 (m, 4H, THF), 3.52 (m, 4H, THF), 4.41 (d, 1H, CH<sub>2</sub>), 4.61 (d, 1H, CH<sub>2</sub>), 6.57 (t, 1H, <sup>3</sup>*J* = 7.3 Hz, C<sub>6</sub>H<sub>4</sub>), 7.24 ppm (d, 1H, <sup>3</sup>*J* = 6.8 Hz, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  2.8, 3.0 (SiCH<sub>3</sub>), 25.7 (THF), 54.0 (CH<sub>2</sub>), 67.7 (THF); 112.2, 121.5, 127.0, 129.2, 132.5, 160.3 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  –8.3, -4.4 ppm.

### Preparation of $[Ba{2-N(R)C_6H_4(CH_2NR)}(THF)]_2$ (14)

As for **12** or **13**, the yellow solid barium salt **14** (0.34 g, 33%; or 1.39 g, 70%) was obtained either from Ba(NR<sub>2</sub>)<sub>2</sub> (0.47 g, 1.6 mmol) and the diamine **2** (0.42 g, 1.6 mmol), or Ba(OSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub> (2.00 g, 4.2 mmol) and the dilithium salt **4b** (1.17 g, 4.2 mmol), respectively. (C<sub>34</sub>H<sub>64</sub>Ba<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Si<sub>4</sub> requires C, 43.1; H, 6.77; N, 5.92. Found: C, 42.9; H, 6.72, N, 5.87%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  0.01 (s, 9H, CH<sub>3</sub>), 0.19 (s, 9H, CH<sub>3</sub>), 1.22 (m, 4H, THF), 3.11 (m, 4H, THF), 3.71 (d, 1H, CH<sub>2</sub>), 4.22 (d, 1H, CH<sub>2</sub>), 6.72 (t, 1H, <sup>3</sup>*J* = 6.4 Hz, C<sub>6</sub>H<sub>4</sub>), 6.86 (d, 1H, <sup>3</sup>*J* = 8.0 Hz, C<sub>6</sub>H<sub>4</sub>), 6.97 (d, 1H, <sup>3</sup>*J* = 7.4 Hz, C<sub>6</sub>H<sub>4</sub>), 7.12 ppm (t, 1H, <sup>3</sup>*J* = 6.1 Hz, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  2.1, 2.7 (SiCH<sub>3</sub>), 25.4 (THF), 55.9 (CH<sub>2</sub>), 67.7 (THF); 116.3, 117.5, 128.5, 129.9, 133.2, 157.7 ppm; <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  -11.9, -8.5 ppm.

#### X-Ray crystallographic studies for 4a, 4b and 11a

Diffraction data were collected at 173(2) K on an Enraf–Nonius CAD4 diffractometer using monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystals were coated in oil and then directly mounted on the diffractomer under a stream of cold nitrogen gas. The structures were refined on all  $F^2$  with H atoms in riding mode using SHELXL97.<sup>29</sup> Further details are in Table 4.

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