FULL PAPER

# Synthesis and structures of novel chiral lithium amidinates and mono- and di-lithium $(1R,2R)-(-)-1,2-(NHSiMe_3)_2C_6H_{10}$

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Four lithium salts derived from (1R,2R)-1,2-diaminocyclohexane are described. After the resolution of 1,2-diaminocyclohexane (DACH), (1R,2R)-(-)-1,2-(NHSiMe<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>10</sub> (1) was prepared from the (*R*,*R*) enatiomer by reaction with LiBu<sup>n</sup> and Me<sub>3</sub>SiCl. Treatment of 1 with one equiv. of LiBu<sup>n</sup> gave the single lithium salt (1R,2R)-(-)-1-Li(NSiMe<sub>3</sub>)-2-(NHSiMe<sub>3</sub>)C<sub>6</sub>H<sub>10</sub> (2). Double deprotonation of 1 with two equiv. of LiBu<sup>n</sup> yielded the dilithium salt Li<sub>2</sub>[(1*R*,2*R*)-(-)-1,2-(NSiMe<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>10</sub>] (3). The addition reaction of **2** or **3** with PhCN gave (1R,2R)-(-)-1-Li[NC(Ph)N(SiMe<sub>3</sub>)]-2-(NHSiMe<sub>3</sub>)C<sub>6</sub>H<sub>10</sub> (4) and Li<sub>2</sub>[(1*R*,2*R*)-(-)-1,2-{NC(Ph)N(SiMe<sub>3</sub>)}<sub>2</sub>C<sub>6</sub>H<sub>10</sub>] (5) respectively. Crystallographic studies and comparison of these lithium salts with β-diketiminates exhibit some noteworthy features.

# Introduction

trans-1,2-Diaminocyclohexane (DACH) as its (R,R) or (S,S)enatiomer has been utilised as a broad-range chiral reagent in the field of asymmetric synthesis and molecular recognition.<sup>1</sup> The (R,R) enatiomer when exposed to the known Jacobsen's catalysts<sup>2</sup> or other chiral metal catalysts<sup>3</sup> has been proved to be a very useful building block. The parent chiral DACH has been modified to give variants which bear appropriate structural and electronic features for intended specific reactions and its lithium salt derivatives are used as ligand transfer agents for metal complexes.<sup>4</sup> The mono- and di-lithium anions derived from  $(1R,2R)-(-)-1,2-(NHSiMe_3)_2C_6H_{10}$  are very useful parent systems for generating a variety of chiral derivatives. Surprisingly, such parent alkali metal anions seem not to have been characterized by X-ray diffraction so far, although the lithium salts have been prepared as mixtures of enatiomers in trans form.<sup>5</sup> For a detailed understanding and comparison, we therefore prepared mono- and di-lithium (1R,2R)-(-)-1,2-(NHSiMe<sub>3</sub>)<sub>2</sub>- $C_6H_{10}$  (2 and 3) and grew suitable single crystals for X-ray diffraction. Derived from compounds 2 and 3 two novel amidinate anions 4 and 5 were synthesized via an addition reaction with PhCN. The molecular structure of complex 4 shows that the central metal has a tridentate coordination environment similar to the alkylamidinate anions  $[CyNC(R)NCy]^-$  (Cy = cyclohexane, R = alkyl).<sup>6</sup> Especially as a ligand transfer agent for metal complexes it will be interesting to investigate the efficiency of the chiral reagent in asymmetric synthesis.

# **Results and discussion**

## Synthesis of 2, 3, 4 and 5

The resolution of  $(\pm)$ -*trans*-DACH was carried out using L-(+)tartaric acid.<sup>7</sup> Treatment of (1R,2R)-DACH with 2 equiv. of LiBu<sup>n</sup> and 2 equiv. of Me<sub>3</sub>SiCl gave (1R,2R)-(NHSiMe<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>10</sub> (1), which was purified by distillation, yielding a colorless oil (1 mmHg, bp 62–64 °C).<sup>8</sup> The mono- and di-lithium anion complexes (1R,2R)-(-)-1-Li(NSiMe<sub>3</sub>)-2-(NHSiMe<sub>3</sub>)C<sub>6</sub>H<sub>10</sub> (2) and Li<sub>2</sub>[(1R,2R)-(-)-1,2-(NSiMe<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>10</sub>] (3) were obtained by carefully controlling the molecular ratio of LiBu<sup>n</sup> added

н N. `SiMe<sub>3</sub> SiMe<sub>3</sub> ii trans - (R,R)-SiMe<sub>3</sub> SiMe<sub>3</sub> 'N Li Ĥ 2 iii Li `NSiMe₃ N. SiMe<sub>3</sub> Li Li <sup>4</sup> SiMe \_\_\_\_NSiMe₃ ″N NNN Li 3 5 Scheme 1 Synthesis of 1, 2, 3, 4 and 5. Reagents and conditions: i. LiBu<sup>n</sup> in Et<sub>2</sub>O, 0 to 20 °C, then Me<sub>3</sub>SiCl in C<sub>6</sub>H<sub>14</sub>, 0 to 20 °C; ii,

i. LiBu<sup>n</sup> in Et<sub>2</sub>O, 0 to 20 °C, then Me<sub>3</sub>SiCl in C<sub>6</sub>H<sub>14</sub>, 0 to 20 °C; ii, 1 equiv. LiBu<sup>n</sup> in C<sub>6</sub>H<sub>14</sub>, 0 to 20 °C; iii, 2 equiv. LiBu<sup>n</sup> in C<sub>6</sub>H<sub>14</sub>, 0 to 20 °C; iv, 1 equiv. PhCN in C<sub>6</sub>H<sub>14</sub>, 0 to 20 °C; v, 2 equiv. of PhCN in Et<sub>2</sub>O, 0 to 20 °C.

(Scheme 1). Single crystals suitable for X-ray diffraction were obtained by crystallization from a concentrated solution of hexane at -30 °C for 7 days. Compounds **2** and **3** appeared as spiculate and hexagonal crystals, respectively.

The reaction of LiNR<sup>1</sup>R<sup>2</sup> with R<sup>3</sup>CN is a fascinating area in organometallic chemistry.<sup>9</sup> In our earlier publications we have

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shown that the interaction of a trimethylsilylmethyllithium reagent Li[CHR<sub>2</sub>] (R = SiMe<sub>3</sub>) with an  $\alpha$ -hydrogen-free nitrile R<sup>3</sup>CN can yield a 1-azaallyl- (A),<sup>10</sup>  $\beta$ -diketiminato- (B)<sup>11</sup> or 1,3-diazaallyl-lithium (C)<sup>12</sup> resulting from the 1,3-migration of an SiMe<sub>3</sub> group from carbon to nitrogen (Scheme 2).



Herein we have designed chiral tridentate and tetradentate ligands using mono- and di-lithium anions as nucleophiles *via* an addition reaction with benzonitrile (Scheme 1). However when using the nonaromatic nitrile Bu<sup>t</sup>CN there was no reaction, as proved by <sup>1</sup>H NMR spectroscopy. Treatment of compound **2** with one equiv. of PhCN in hexane at 0 °C gave  $(1R,2R)-(-)-1-\text{Li}[NC(Ph)N(SiMe_3)]-2-(NHSiMe_3)C_6H_{10}$  (**4**) in 90% yield. The molecular structure of complex **4** shows that the reaction involved a silicotropic rearrangement resulting in a  $\eta^3$ -NCN conjugate anion, and another terminal N atom also provides a coordination site, Fig 3. However the addition reaction of compound **3** with two equiv. of PhCN yielded Li<sub>2</sub>[(1R,2R)-(-)-1,2-{NC(Ph)N(SiMe\_3)}<sub>2</sub>C<sub>6</sub>H<sub>10</sub>] (**5**), confirmed by <sup>1</sup>H NMR and <sup>13</sup>C NMR. Ensuing work, especially using the anions as chiral ligands for transition metals, is under way.

# NMR spectroscopy

The <sup>1</sup>H NMR spectra showed characteristic resonances for the protons of the cyclohexane groups in the region  $\delta 1.00-2.12$  (1),  $\delta 1.24-2.63$  (2),  $\delta 1.34-2.70$  (3),  $\delta 0.82-2.78$  (4),  $\delta 0.59-3.06$  (5). In the two asymmetric compounds 2 and 4, the protons of the SiMe<sub>3</sub> groups appear as two separate peaks ( $\delta 0.22$  and 0.37 for 2,  $\delta 0.26$  and 0.33 for 4). Additional support for the identification of the products was provided by the <sup>13</sup>C NMR spectra. It was observed that the <sup>13</sup>C NMR spectra of 2 and 4 showed all of the expected resonances for the carbon atoms and the symmetric complexes 1, 3 and 5 showed half of them.

### Crystal structures of complexes 2, 3 and 4

The crystal structures of the three lithium complexes 2, 3 and 4 were determined by X-ray diffraction. Selected bond distances and angles are listed in Tables 1-3.

The molecular structure of 2 is shown in Fig. 1. A centrosymmetric dimeric aggregation is observed which is built around a strict (LiN)<sub>2</sub> rhombus (with the Li–N bonds ranging



Fig. 1 Molecular structure of compound 2.

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Table 1 Selected bond distances (Å) and bond angles (°) for 2

Li1–N1	2.008(7)	N3-C13	1.470(5)
Li1–N3	1.980(8)	C13-C18	1.550(6)
N3–Li2	2.019(8)	C18–N4	1.474(5)
Li2–N1	1.985(7)	C1-N1	1.474(4)
Li2–Li1	2.363(10)	C6-C1	1.556(5)
Li1–N2	2.050(8)	N2-C6	1.477(5)
Li2–N4	2.112(8)		
N1–Li1–N3	107.7(3)	N1-Li1-N2	91.2(3)
Li1-N3-Li2	72.4(3)	C1-C6-Li1	79.0(2)
N3-Li2-N1	107.1(3)	N3-C13-C18	110.9(3)
Li2-N1-Li1	72.5(3)	C13-C18-Li2	82.3(3)
C6-Li1-N1	66.5(2)	C18-Li2-N3	68.0(2)
Li1-N1-C1	N1-C1 100.8(3) Li2-N3-C13		147.1(4)

Table 2Selected bond distances (Å) and bond angles (°) for 3

Li1–Li4	2.362(11)	N3–Li4	1.984(8)	
Li1–Li3	2.365(10)	Li4–N1	2.087(8)	
N2–Li3	2.094(8)	N1–Li2	2.048(8)	
Li1-N2	2.021(9)	N2-C6	1.477(5)	
Li1-N1	2.072(8)	N1-C1	1.487(5)	
Li4–N1–I	Li2 69.4(3)	N4–Li1–N2	109.3(4)	
N1-Li2-l	N3 108.9(4)	Li1-N2-Li3	70.1(3)	
N1-Li1-l	N2 88.1(3)	N2-Li3-N4	109.5(3)	
N3-Li4-1	N1 109.5(4)	Li3–N4–Li1	70.5(3)	

Table 3 Selected bond distances (Å) and bond angles (°) for 4

Li1-N23	2.115(5)	Li1-N11	2.018(5)
Li1–N22	2.056(5)	N23-C43	1.486(3)
Li1–N12	2.133(5)	C11-N11	1.319(3)
Li2-N22	2.151(5)	C11-N12	1.340(3)
Li2–Li1	2.572(6)	C18–C23	1.536(4)
N21–Li2	2.036(5)	N13-C23	1.485(4)
N13-Li2	2.180(5)	C31–Li2	2.424(5)
C11–Li1	2.400(5)		
N12-Li1-N22	103 3(2)	N11-Li1-N12	66 92(16)
Li1–N12–Li2	75.31(19)	C38-C43-Li1	79.51(16)
N12-Li2-N22	102.0(2)	N12-C18-C23	110.7(2)
Li2-N22-Li1	75.34(19)	C18-C23-Li2	78.79(16)
C43-Li1-N22	60.72(14)	C23-Li2-N12	59.46(14)
Li1-N22-C38	106.16(19)	Li2-N12-C18	107.7(2)

from 1.980(8) to 2.019(8) Å). Two of the five-membered Li–N–C–C–N rings adopt an envelope conformation.

The molecular structure of **3** is shown in Fig. 2; it has rigorous  $C_2$ -symmetry. Dimeric aggregation is revealed, which is built around two (LiN)<sub>2</sub> rhombi consisting of N3–Li4–N1– Li2 and N4–Li1–N2–Li3. Between these two (LiN)<sub>2</sub> rhombi there are distorted Li<sub>4</sub>-tetrahedra with N atoms capping the triangular faces.



Fig. 2 Molecular structure of compound 3.

Table 4 Some important geometric data (bond lengths in Å, angles in °) on compounds 2, 3, 4, 6 and 7





Fig. 3 Molecular structure of compound 4.

The dinuclear lithium complex 4 (Fig. 3) presents a nearly planar  $(\text{LiN})_2$  ring. The N–C–N fragment is in the form of a  $\eta^3$ -anion and has some degree of  $\pi$ -electron delocalisation providing a lithium coordinate site [Li–C distance, 2.424(5) Å; Li–N distances, 2.151(5) and 2.036(5)Å]. Interestingly, the other nitrogen atom on the cyclohexane provides another coordination site having an intermolecular Li–N<sub>sp2</sub> bond [Li–N distance, 2.115(5) Å].

A study of the key bond angles and distances in these complexes reveals some noteworthy trends. A comparison of the structural data for complexes 2, 3, and 4 with the dinuclear  $\beta$ -diketiminates [Li{N(R)C(Ph)C(H)C(Bu<sup>t</sup>)NR}]<sub>2</sub> (6)<sup>9a</sup> and [Li{N(R)C(Ph)C(H)C(Ph)NR}]<sub>2</sub> (7)<sup>9b</sup> (prepared in our earlier work and shown schematically in Scheme 3) is given in Table 4. It should be noted that the N(1)-Li-N(2) angles broaden with increasing length of the carbon chain of the distorted or planar fragments NCN [66.92(16)° (4)], NCCN [91.2(3)° (2) and 88.1(3)° (3)] and NCCCN [100.0(7)° (6) and 103.0(4)° (7)]. All the N-Li-N angles at the lithium atom of the (LiN)<sub>2</sub> cores in 2, **3**, **4**, **6** and **7** [107.7(3)° (**2**), 109.5(4)° (**3**), 103.3(2)° (**4**), 103.8(7)° (6) and  $105.0(4)^{\circ}$  (7)] are wider than the Li–N–Li angle at nitrogen  $[72.5(3)^{\circ}$  (2), 69.4(3)° (3), 75.34(19)° (4), 76.2(6)° (6) and  $75.0(4)^{\circ}$  (7)]. The addition products 4 and 5 are interesting for us due to their  $\eta^3$ -electron delocalisation and possible utilization as chiral ligands. The intramolecular distance from the lithium to the chiral center Li-C(chiral) in 4 [4.122(5) and 3.474(9) Å] is longer than the intermolecular distance [2.674(5) Å]. As a ligand it might be more useful to prepare the catalyst of the dinuclear metal complex in an asymmetrical syntheses. As a comparison of the mono-lithium salts, the  $\beta$ -diketiminato ligands 6 and 7 with different substituents (Ph, Bu<sup>t</sup> in 6, Ph, Ph in 7) have shorter intramolecular Li– $N_{sp3}$  bonds [2.04(2) (6) and



1.965(9) Å (7)] than the intermolecular Li–N<sub>sp3</sub> bond [2.17(2) (6) and 2.095(9) Å (7)]; however, amide and amidinate complexes **2** and **4** have longer intramolecular Li–N<sub>sp3</sub> bonds [2.008(7) (**2**) and 2.133(5) Å (**4**) than intermolacular Li–N<sub>sp3</sub> bonds 1.980(8) (**2**) and 2.056(5) Å (**4**)]. In addition, the N–C bond distances in **2** and **3** are around 1.477 ± 0.001 Å, but the pairs of N–C bonds in **4** [1.319(3) and 1.340(3) Å], **6** [1.27(1) and 1.33(1) Å] and **7** [1.337(6) and 1.299(6) Å] having some degree of  $\pi$ -electron delocalisation are far from being identical.

It is observed that for the mono-lithium salts 2, 4, 6 and 7, anionic nitrogen N(1) is four-co-ordinate and bridging, and the other N(2) three-co-ordinate; for di-lithium salt 3, all nitrogen atoms are four-co-ordinate and bridging. All the cyclohexanyl groups of the three complexes 2, 3 and 4 adopt chair conformations.

Compounds	2	3	4
Formula	C <sub>24</sub> H <sub>54</sub> Li <sub>2</sub> N <sub>4</sub> Si <sub>4</sub>	C <sub>24</sub> H <sub>56</sub> Li <sub>4</sub> N <sub>4</sub> Si <sub>4</sub>	C <sub>19</sub> H <sub>34</sub> LiN <sub>3</sub> Si <sub>2</sub>
M	524.95	540.85	367.61
Temperature/K	298 (2)	293 (2)	173 (2)
Crystal system	Monoclinic	Trigonal	Monoclinic
Space group	$P2_1$	$P3_1$	$P2_1$
aĺÅ	9.778(3)	10.5111(14)	9.9459(4)
b/Å	18.113(5)	10.5111(14)	20.6507(9)
c/Å	10.387(3)	27.891(5)	11.0775(4)
a/°	90	90	90
β/°	103.643(5)	90	96.703(1)
y/°	90	120	90
$U/Å^3$	1787.7(8)	2668.7(7)	2259.7(2)
Z	2	3	4
$\mu/\mathrm{mm}^{-1}$	0.183	0.184	0.163
Reflections collected	8423	11141	16443
Independent reflections	6875	6280	5212
$R1 \ (\hat{I} > 2\sigma(I))$	0.0570	0.0591	0.0373
$wR_2$ (all data)	0.1525	0.1536	0.0814

# Experimental

## **General procedures**

All manipulations were carried out under argon, using standard high-vacuum, Schlenk techniques. Hexane, Et<sub>2</sub>O, benzene- $d_6$  were distilled from Na/K alloy. Optical rotation was recorded using a standard cell with a 10 cm pass on a Perkin-Elmer 241 polarimeter. <sup>1</sup>H (300 MHz) and <sup>13</sup>C (75.47 MHz) NMR spectra were recorded on a Bruker DRX-300 spectrometer at ambient temperature.

## Preparations

 $(1R,2R)-(-)-1,2-(NHSiMe_3)_2C_6H_{10}$  1. A commercially available mixture of cis- and trans-1,2-diaminocyclohexane was dealt with by the reported procedure to give (1R,2R)-DACH;  $[\alpha]_{D}^{20} = -25^{\circ}$  (c = 5, 1 N HCl). LiBu<sup>n</sup> (14.2 cm<sup>3</sup>, 1.23 M in hexane) was added by syringe to a stirred solution of (1R,2R)-DACH (1.00g, 8.76 mmol) in Et<sub>2</sub>O (ca. 20 cm<sup>3</sup>) at 0 °C. The mixture was warmed to room temperature slowly, stirred for 12 h, and filtered. The white precipitate isolated was dried in vacuum to give  $(1R,2R)-(-)-1,2-(LiNH)_2C_6H_{10}$ , (0.98 g, 89%). To this compound was added Me<sub>3</sub>SiCl (15.5 mmol, 1.96 cm<sup>3</sup>) in hexane (ca. 20 cm<sup>3</sup>) at 0 °C. The mixture was warmed to ambient temperature, stirred for 12 h, and then filtered. The filtrate was distilled at reduced pressure, and a fraction was collected at 1 mmHg, bp 62-64 °C to give a colorless compound (1.97 g, 87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta - 0.04$  (s, NSiMe<sub>3</sub>), 0.65 (br, NH, 2H), 1.00 (m, CH, 2H), 1.15 (m, CH, 2H), 1.55 (m, CH, 2H), 1.81 (m, CH, 2H), 2.12 (m, CH, 2H), <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.7 (s, SiMe<sub>3</sub>), 26.5 (s, NCCC), 37.6 (s, NCC), 59.7 (s, CN).

(1*R*,2*R*)-(-)-1-Li(NSiMe<sub>3</sub>)-2-(NHSiMe<sub>3</sub>)C<sub>6</sub>H<sub>10</sub> 2. LiBu<sup>n</sup> (2.0 cm<sup>3</sup>,1.61 M in hexane) was added to a solution of 1 (0.851 g, 3.30 mmol) in hexane (15 cm<sup>3</sup>) carefully by syringe at 0 °C, The mixture was warmed to ambient temperature slowly and stirred overnight. The clear solution was concentrated to *ca*. 8 cm<sup>3</sup>, to give colorless spiculate crystals (0.31 g, 36%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.22 (s, NSiMe<sub>3</sub>), 0.37 (s, NSiMe<sub>3</sub>), 1.24 (m, CH, 4H), 1.72 (m, CH, 2H), 2.08 (m, CH, 2H), 2.63 (m, CH, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.8 (s, SiMe<sub>3</sub>), 2.9 (s, SiMe<sub>3</sub>), 26.9 (s, NCCC), 27.2 (s, NCCC), 38.6 (s, NCC), 45.0 (s, NCC), 61.6 (s, CN), 65.8 (s, CN).

Li<sub>2</sub>[(1*R*,2*R*)-(-)-1,2-(NSiMe<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>10</sub>] 3. LiBu<sup>n</sup> (3.8 cm<sup>3</sup>, 1.61 M in hexane) was added to a solution of 1 (0.796 g, 3.08 mmol) in hexane (*ca.* 25 cm<sup>3</sup>) at 0 °C. The mixture was warmed to ambient temperature slowly and stirred for 12 h. The resulting

solution was concentrated and left to stand for one week, allowing the isolation of colorless crystals of compound **3** (0.34 g, 41%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  0.31 (s, NSiMe<sub>3</sub>), 1.34 (m, CH, 4H), 1.69 (m, CH, 2H), 2.43 (m, CH, 2H), 2.70 (m, CH, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ ):  $\delta$  3.7 (s, SiMe<sub>3</sub>), 26.8 (s, NCCC), 40.0 (s, NCC), 67.4 (s, CN).

(1*R*,2*R*)-(-)-1-Li[NC(Ph)N(SiMe<sub>3</sub>)]-2-(NHSiMe<sub>3</sub>)C<sub>6</sub>H<sub>10</sub> 4. PhCN (0.16 cm<sup>3</sup>, 1.58 mmol) was added by syringe to a solution of 2 (0.417 g, 1.58 mmol) in hexane (*ca.* 25 cm<sup>3</sup>) at 0 °C. The mixture was slowly warmed to ambient temperature and stirred for 12 h. The clear solution was concentrated and allowed to stand for one week; crystalline products were obtained (0.52 g, 90%) (Found: C, 63.05; H, 9.22; N, 11.10. C<sub>19</sub>H<sub>34</sub>N<sub>3</sub>LiSi<sub>2</sub> requires C, 62.08; H, 9.32; N, 11.43%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.26 (s, NSiMe<sub>3</sub>), 0.33 (s, NSiMe<sub>3</sub>), 0.82 (m, CH, 2H), 1.20 (m, CH, 2H), 1.48 (m, CH, 2H), 1.96 (m, CH, 2H), 2.66 (m, CH, 1H), 2.78 (m, CH, 1H), 7.19 (m, Ph, 2H), 7.50 (m, Ph, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.26 (s, SiMe<sub>3</sub>), 4.55 (s, SiMe<sub>3</sub>), 26.06 (s, NCCC), 27.02 (s, NCCC), 38.59 (s, NCC), 38.71 (s, NCC), 60.73 (s, CN), 65.73 (s, CPh).

Li<sub>2</sub>[(1*R*,2*R*)-(-)-1,2-{NC(Ph)N(SiMe<sub>3</sub>)}<sub>2</sub>C<sub>6</sub>H<sub>10</sub>] 5. PhCN (0.18 cm<sup>3</sup>, 1.77 mmol) was added by syringe to a solution of 3 (0.240 g, 0.89 mmol) in Et<sub>2</sub>O (*ca.* 25 cm<sup>3</sup>) at 0 °C. The mixture was slowly warmed to ambient temperature and stirred for 12 h. The solution was concentrated and a solid product obtained (0.38 g, 89%) (Found: C, 66.13; H, 8.18; N, 11.42. C<sub>26</sub>H<sub>38</sub>N<sub>4</sub>-Li<sub>2</sub>Si<sub>2</sub> requires C, 65.51; H, 8.04; N, 11.76%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.03 (s, NSiMe<sub>3</sub>), 0.59 (m, CH, 2H), 0.97 (m, CH, 4H), 1.71 (m, CH, 2H), 3.06 (m, CH, 2H), 6.59 (m, Ph, 2H), 6.97 (m, Ph, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.29 (s, SiMe<sub>3</sub>), 26.77 (s, NCCC), 37.07 (s, NCC), 64.80 (s, CN), 128.85–132.83 (m, C<sub>3</sub>H<sub>3</sub>), 143.49 (s, *C*C<sub>3</sub>H<sub>3</sub>), 181.68 (s, *C*Ph).

#### Crystal data and refinement details

Single crystals of complexes **2**, **3** and **4** were mounted in Lindemann capillaries under argon. Data were collected on an Bruker Smart 1000 diffractometer utilizing graphitemonochromatized Mo-K<sub>a</sub> radiation ( $\lambda = 0.71073$  Å) at room temperature. A total of N reflections were collected using an  $\omega$  scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption using multi-scans (SADABS).<sup>13</sup> The structure was solved by direct methods (SHELXS97).<sup>14</sup> Then the remaining non-hydrogen atoms were obtained from the successive difference fourier map. All non-H atoms were refined with anisotropic displacement parameters, while the H atoms were constrained to parent sites, using a riding model (SHELXTL).<sup>15</sup> Further details are given in Table 5. CCDC reference numbers 161938–161940.

See http://www.rsc.org/suppdata/dt/b1/b106992f/ for crystallographic data in CIF or other electronic format.

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