Metal β-diketiminates revisited: *ansa*-CH₂-bridged bis(β-diketiminate)s of lithium and aluminium having diverse structures

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Abstract
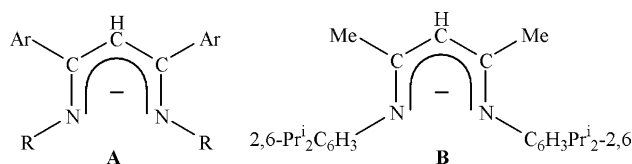
The metal β-diketiminato ligand-to-metal binding modes are briefly reviewed, with reference particularly to our previous work on metal complexes using the ligands $[\{N(R^1)C(R^2)\}_2CH]$ ($R^1 = SiMe_3 = R$ and $R^2 = Ph$; or $R^1 = C_6H_3Pr^i_2$-2,6 and $R^2 = Me$). The syntheses of the β-diketimines $H[\{N(R)C(Ar)\}_2CH]$ **1** (Ar = Ph) and **2** (Ar = C_6H_4Me-4) and the *ansa*-CH₂-bridged bis(β-diketimine)s **3** (Ar = Ph) and **4** (Ar = C_6H_4Me-4) are reported. Thus, from the appropriate compound $Li[\{N(R)C(Ar)\}_2CH]$ and H_2O, $(CH_2Br)_2$ or CH_2Br_2 the product was **2**, **3** or **4**. Compound **1** was prepared from $K[\{N(R)C(Ph)\}_2CH]$ and $(CH_2Br)_2$. Each of **3** or **4** with LiBuⁿ surprisingly yielded the bicyclic dilithium compound $Li_2[\{N(R)C(Ar)CC(Ar)NR\}_2(CH_2)]$ **5** (Ar = Ph) or **6** (Ar = C_6H_4Me-4) in which each of the β-diketiminato fragments is an *N,N′*-bridge between the two lithium atoms and the CH₂ moiety joins the two ligands through their central carbon atoms. However, **4** with AlMe₃ yielded the expected *ansa*-CH₂-bridged-bis[(β-diketiminato)(dimethyl)alane] **7**, which was also obtained from **6** and Al(Cl)Me₂. X-ray structures of the known compounds **2** and **3**, and of **5**, **6** and **7** are presented; the ¹H NMR spectra of **6** in toluene-d₈ show that there is restricted rotation about the NC–C_6H_4Me-4 bond. © 2004 Elsevier B.V. All rights reserved.

Keywords: β-Diketiminates; Lithium; Aluminium; *ansa*-bridged complexes

1. Introduction

β-Diketiminates have an increasing useful role in co-ordination chemistry especially as spectator ligands, by virtue of their strong binding to metals, their tuneable steric demands and their diversity of bonding modes. Our entry into this field dates back to our first publication in 1994 [1], when we introduced the *N N′*-bis-(tri- methylsilyl)-β-diketiminato ligands shown in **A** (R = SiMe₃) in the monoanionic delocalised mode (Ar = Ph or C_6H_4Me-4). Our published contributions to the chemistry of β-diketiminatometal complexes up to July 2002 were placed in the context of the develop-

ments elsewhere in a comprehensive review [2]. A ligand which has been much used is shown in delocalised form in **B**, and sometimes is abbreviated as Dipp₂nacnac.
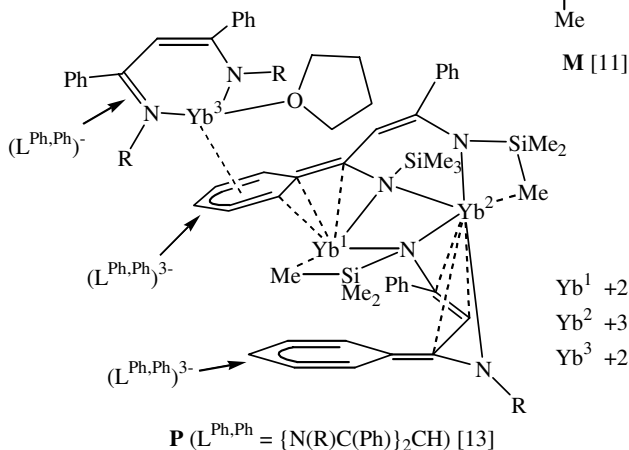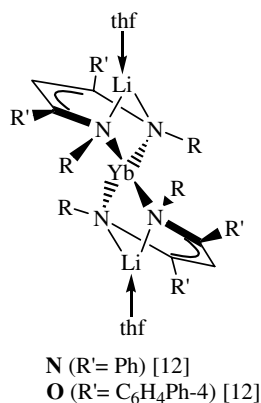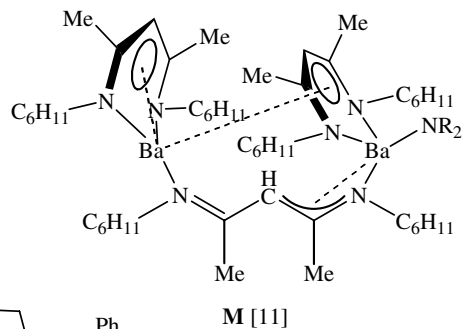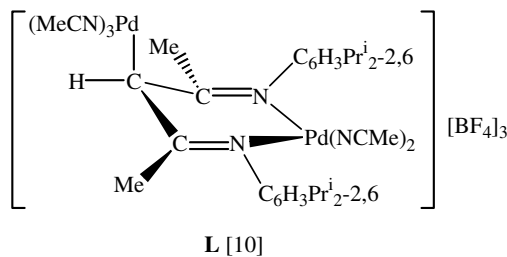

2. Bonding modes

The β-diketiminato ligand binds to metals in a terminal or bridging mode. The terminally bound ligand is

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usually *N,N'*-chelating and is attached to the metal either: (i) in a four-electron σ-bond fashion, the metallacycle being planar as in **C** [3], or has the metal out of the NCCCN plane as in **D** [4]; or (less usually) (ii) a six-electron $2\sigma + 4\pi$ η^5-fashion with the $\overline{\text{MNCCCN}}$ ring adopting a boat conformation as in **E** [1]. Rarer are the monodentate *N*- (as in

C [3]

D [4]

E [1]

Sn(**B**){N(C$_6$H$_3$Pr$^i_2$-2,6)C(Me)=CHC(Me)=NC$_6$H$_3$Pr$^i_2$-2,6}
F [5]

G (X = Cl) [6]
H (X = Ph) [7]

I [8]

J [1]

K [9]

L [10]

M [11]

N (R'= Ph) [12]
O (R'= C$_6$H$_4$Ph-4) [12]

(L^{Ph,Ph})$^-$

(L^{Ph,Ph})$^{3-}$

(L^{Ph,Ph})$^{3-}$

Yb^1 +2
Yb^2 +3
Yb^3 +2

P (L^{Ph,Ph} = {N(R)C(Ph)}$_2$CH) [13]
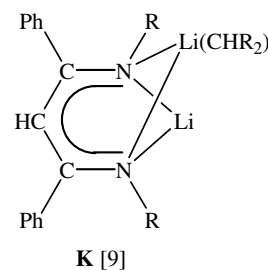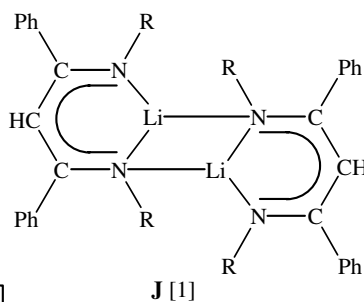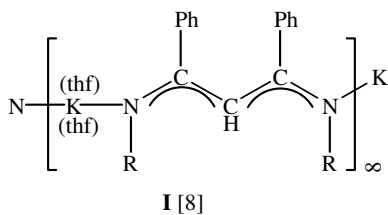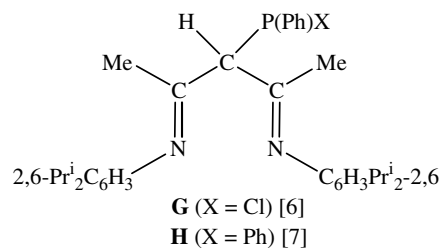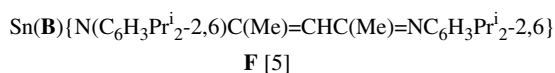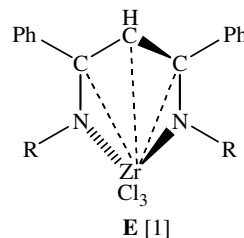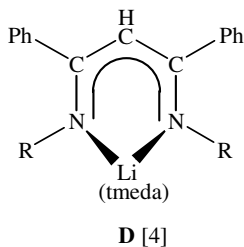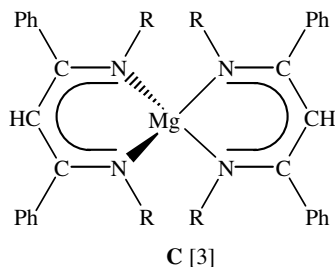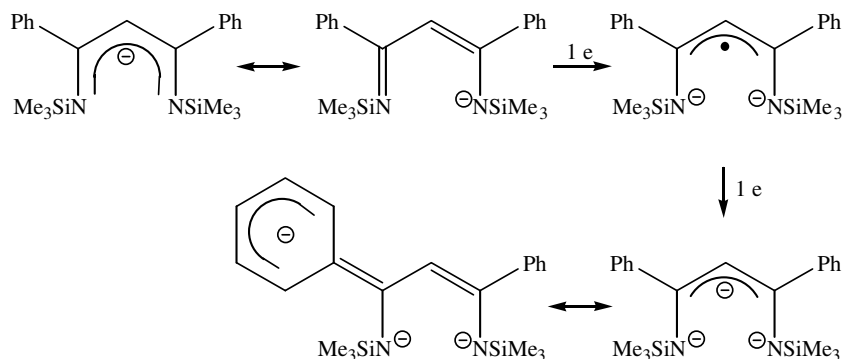
Scheme 1. Sucessive 1-electron reductions: $[L^{Ph,Ph}]^- \rightarrow [L^{Ph,Ph}]^{2-} \rightarrow [L^{Ph,Ph}]^{3-}$.

F [5] or *C*- (as in **G**, X = Cl [6] or **H**, X = Ph [7]) centered metal β-diketiminates. Similarly, the bridging β-diketiminates may be terminal as in **I** [8] or, more frequently, chelating as in **J** [1], **K** [9], **L** [10] or **M** [11].

Of the more than 500 known β-diketiminatometal complexes, in every case but three the ligand has been monoanionic. The exceptions were the ytterbium complexes **N** [12], **O** [12] and **P** [13]. In **N** and **O** the ligand [{N(R)C(Ph)}$_2$CH] ($\equiv L^{Ph,Ph}$) was regarded as dianionic. In **P** two of the ligands were assigned as trianionic, one bound to Yb(II) and the other to Yb(III), while the third β-diketiminate was attached to Yb(II); these features are indicated schematically in **P**. The X-ray data on the crystalline complexes **N–P** were consistent with the ligand charge distribution shown in valence bond terms in Scheme 1 [12,13]; particularly sensitive probes are the values of the C–N and C–C bond lengths. Structures **N–P** also illustrate thus far unique bonding modes: both *N, N′*-bridging and chelating in **N** and **O**, and multicentred chelating and bridging for the trianionic ligands in **P**.

3. Results and discussion

3.1. Objectives

In a preliminary publication, we described the synthesis of the β-diketimines **1** and **2** and the CH_2-bridged

bis(β-diketimine) **3**, Scheme 2 (R = $SiMe_3$) [1]. We now provide the experimental details and also X-ray data for the crystalline compounds **2** and **3**. The 4-tolyl analogue **4** of **3** is also reported.

The principal focus of this paper is on *ansa*-CH_2-bridged bis(β-diketiminato) ligands in the context of lithium and aluminium chemistry.

3.2. β-Diketimines and ansa-CH$_2$-bridged bis(β-diketimine)s

Treatment of the potassium β-diketiminate K[{N(R)C(Ph)}$_2$CH] with an equimolar portion of 1,2-dibromoethane yielded ((i) in Scheme 2) yellow needles of the β-diketimine **1** in essentially quantitative yield. Using a 0.5 molar portion of $(CH_2Br)_2$ gave **1** in ca. 50% yield, with the K salt not fully consumed; it is assumed that the coproduct was bromoethene which was unreactive under the mild reaction conditions. Alternatively, **1** was obtained from the potassium β-diketiminate by hydrolysis, but less satisfactorily; it is noteworthy that the *N*-SiMe$_3$ bonds were not cleaved. The hydrolysis method gave an almost quantitative yield of **2** ((ii) in Scheme 2) by bubbling moist air through a hexane solution of Li[{N(R)C(C$_6$H$_4$Me-4)}$_2$CH]. Heating the latter salt, or the phenyl analogue, under reflux with dibromomethane in refluxing hexane gave ((iii) in Scheme 2) the pale yellow crystalline complex **4** or **3**, in ca. 40% yield.
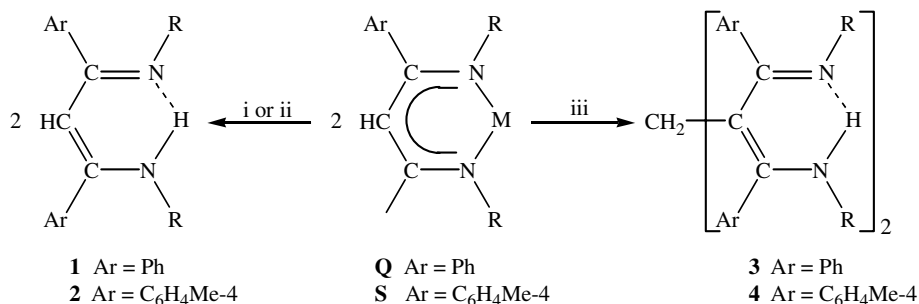
Scheme 2. Synthesis of β-diketimines (**1,2**) and *ansa*-CH$_2$-bridged bis(β-diketimine)s (**3,4**) Reagents and conditions: (i) (for **1**) **S** (M = K), $(CH_2Br)_2$, C$_6$H$_4$, C$_6$H$_{14}$, 5 h, 50 °C; (ii) (for **2**) **S** (M = Li), H$_2$O, C$_6$H$_{14}$; (iii) (M = Li) **Q** (for **3**) or **S** (for **4**), CH$_2$Br$_2$, C$_6$H$_{14}$, reflux.

The pale yellow crystalline compounds **1–4** melted without decomposition [at 120–124 °C (**1**), 85–87 °C (**2**), 193–198 °C (**3**), 196 °C (**4**)] and gave satisfactory microanalyses and ^1H and ^{13}C NMR spectra, which showed that at ambient temperature in C_6D_6 there was rapid exchange of the proton between its two adjacent nitrogen atoms.

The X-ray molecular structures of crystalline **2** and **3** show that each is a monomer. Selected bond lengths and an angle are sketched schematically in **2′** and **3′**, and illustrated in greater detail in the Supplementary Information. The mean endocyclic bond angles in **3′** are 121.0(8), 122.9(9), and 121.1(9)° at C, C(NR), and C[N(H)R], respectively.


2′

3′
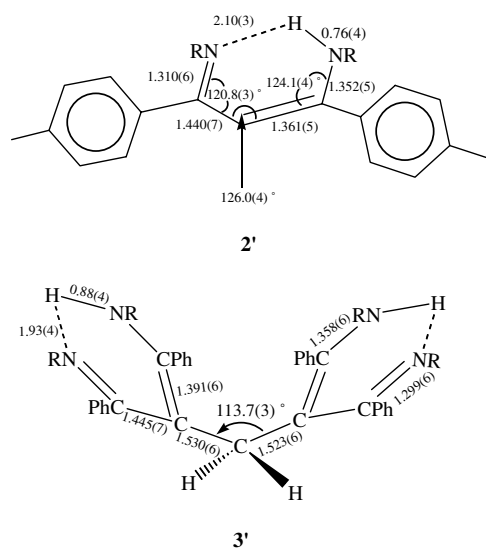
The phenyl rings are twisted out of the NCCCN plane by ca. 45° in **2′**, but are nearly orthogonal to each such plane in **3′**. In the latter, the four nitrogen atoms are located in such a way as to offer a potentially tetradentate donor site to a metal or metals.

### 3.3. Lithium and aluminium ansa-CH₂-bridged bis(β-diketiminate)s

Treatment of the appropriate *ansa*-CH₂-bridged bis(β-diketimine) **3** or **4** with two equivalents of *n*-butyllithium yielded ((i) in Scheme 3) crystals of the monomeric dilithium CH₂-bridged bis(β-diketiminate) in good yield: the orange **5**, m.p. 157–160 °C and the deep yellow **6**, m.p. 158–160 °C. Likewise, from **4** and two equivalents of trimethylalane yellow crystals of the *ansa*-CH₂-bridged bis[β-diketiminato(dimethyl)alane] **7** were obtained ((ii) in Scheme 3) in excellent yield. Compound **7** was also synthesised ((iii) in Scheme 3) in nearly quantitative yield from the dilithio precursor **6** and two equivalents of chlorodi(methyl)alane. Each of **5–7** gave satisfactory analyses and multinuclear NMR spectra in

C_6D_6 (**5**, **7**) or C_7D_8 (**6**); the EI mass spectrum of **7** showed as the parent ion $[M - Me]^+$. Additionally, the molecular structures of crystalline **5** (Fig. 1), **6** (Fig. 2), and **7** (Fig. 3) were determined by X-ray diffraction.

The molecule of crystalline **5** is a 4,8-dilithio-3,5,7,9-tetraazabicyclo[5.5.1]tridecane derivative, in which each of the two ligands N1C4C1C14N4 and N2C24 C3C34N3 acts as an *N,N′*-bridge between the two lithium atoms. The central carbon atoms C1 and C3 of each ligand are joined through a methylene bridge. The 3,5,7,9 nitrogen positions correspond to N1, N2, N3 and N4, respectively of Fig. 1, while the 4- and 8-lithium positions refer to Li1 and Li2, respectively. The atom Li1 has short contacts to C1, C2, and C4, whereas Li2 is close to C2 and C(13)′of an adjacent molecule. It is evident from the key bond distances sketched schematically in **5′** and bond angles (Fig. 1) that (i) there is significant π-delocalisation over the five skeletal atoms of each ligand; (ii) the environments at Li1 and Li2 are disparate, which is reflected in the very different endocyclic angles: 158.4(4)° at Li1 and 127.6(3)° at Li2; (iii) the environment at C2 is severely distorted tetrahedral; and (iv) whereas the sum of the bond angles at each of N2, N3 and N4 is 359.7 ± 0.2°, at N1 it is 352.7°. The structure of the *p*-tolyl homologue **6** of **5** is very similar; Fig. 2 provides two different views, in order to indicate the conformations of the Li1-(a) and Li2-(b)-containing rings.

5′
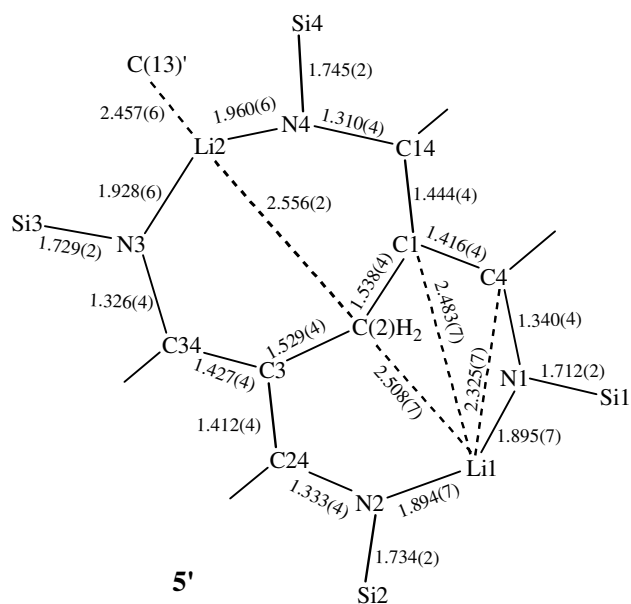
The NMR spectra of **6** in toluene-d₈ at 248 K showed that its solution structure is consistent with that found in the crystal. Thus, there were two $^{29}Si\{^1H\}$ NMR spectral signals at δ −6.90 and δ −6.19. Due to restricted rotation about the C–C_6H_4Me-4 bond, each of the pairs of *o*- and *m*-protons
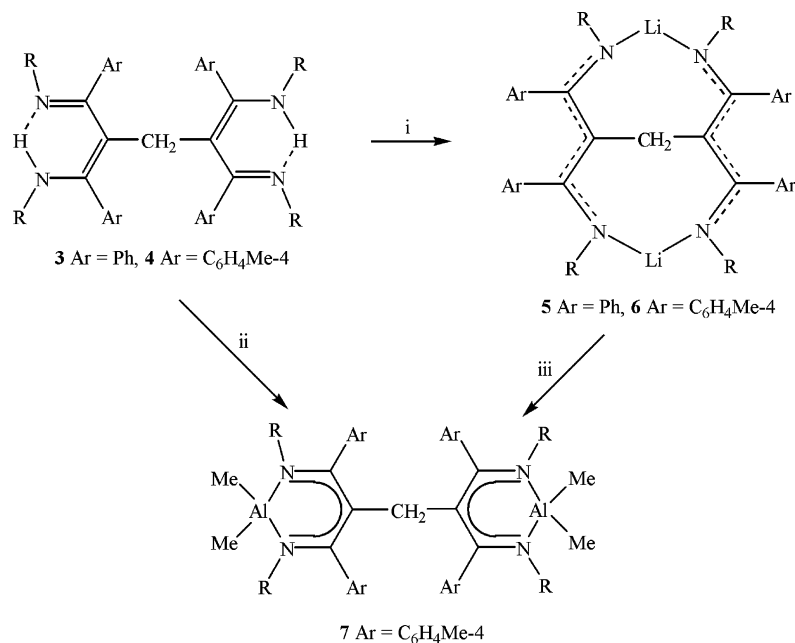
Scheme 3. Synthesis of lithium (5,6) and dimethylaluminium (7) bis(β-diketiminate)s. Reagents and conditions: (i) 2 LiBu^n, C_6H_{14}, −78 °C; (ii) 2 AlMe$_3$, C_6H_{14}, −78 °C; (iii) 2 Al(Cl)Me$_2$, PhMe, −20 °C.
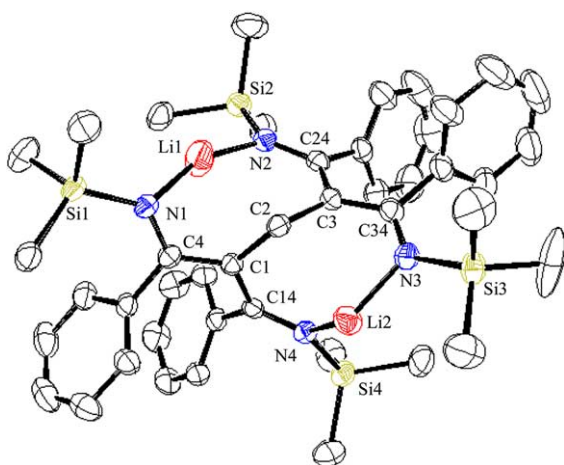

Fig. 1. Molecular structure of 5 with selected bond angles (°): N1–Li1–N2 158.4(4), N3–Li2–N4 127.6(3), Li1–N1–C4 90.2(3), Li1–N2–C24 121.1(2), N1–C4–C1 122.5(3), N2–C24–C3 122.2(3), C4–C1–C14 122.0(2), C4–C1–C2 118.9(2), C24–C3–C34 123.4(3), C24–C3–C2 118.3(2), C1–C2–C3 119.6(2), C2–C1–C14 119.0(2), C2–C3–C34 118.0(2), C1–C14–N4 122.1(3), C3–C34–N3 122.6(3), C14–N4–Li2 113.9(3), C34–N3–Li2 106.5(2).

is magnetically inequivalent, with two distinct aryl rings. For each ring, the *o*- and *m*-protons on one side were at higher frequency and well separated (δ 7.1 and δ 6.7) whereas those on the other side were not resolved and appeared at lower frequency (δ 6.3). This is consistent with the notion that the two rings are interleaved (Fig. 4), so that the protons designated "H$_a$" experience a ring current from the neighbouring ring and hence H$_a$ signals are at lower frequency than those

labelled "H$_b$". The central methylene group in both 5 and 6 is characterised by a somewhat high frequency ^{1}H signal, indicative of rather acidic protons.

The crystalline *ansa*-CH$_2$-bridged bis[β-diketiminato(dimethyl)alane] molecule 7 is C_2 symmetric. Each of the β-diketiminato-Al six-membered rings has the boat conformation (cf. E), the Al and C2 atoms being 1.027 and 0.299 Å, respectively, out of the almost planar N1N2C1C3 moiety. The aluminium atom is in a distorted tetrahedral environment; the ring bite angle N1–Al–N2 is the smallest, 91.83(11)°. There is significant π-delocalisation in the β-diketiminato ligands, which does not extend to the phenyl substituents. The angle subtended at the methylene carbon atom C4 is 116.7(3)°. The angle between the N1N2C1C3 plane and the C1C2C3 or N1AlN2 plane is 24.68(35)° or 50.30(12)°, respectively. The metric parameters for 7 (Fig. 3) may be compared with those for Al(Me)$_2$[{N(R)C(Ph)}$_2$CH]: av. Al–CH$_3$ 1.960(5), av. Al–N 1.921(4), av. C–C 1.400(6) Å; H$_3$C–Al–CH$_3$ 111.3(2)°, N1–Al–N2 97.1(2)°, Al–N–CH$_3$ 107.3(2)° and 116.3(2)°, av. Al–N–C 109.2(3)°, C1–C2–C3 126.8(4)°; and the angle between the N1N2C1C3 plane and the C1C2C3 or N1AlN2 plane is 11.22(17)° or 48.44(21)°, respectively [14].

The ^{1}H, ^{13}C, ^{27}Al, and ^{29}Si NMR spectra of 7 in C$_6$D$_6$ at 333 K were fully consistent with the structure of the crystalline molecule. The bridging CH$_2$ group ^{1}H NMR spectral chemical shift was unexceptional at δ 2.83, in contrast to the higher frequency shifts recorded for 5 and 6.

The reaction pathway for the formation of the bicyclic dilithio compound 5 or 6 from the *ansa*-CH$_2$-bridged
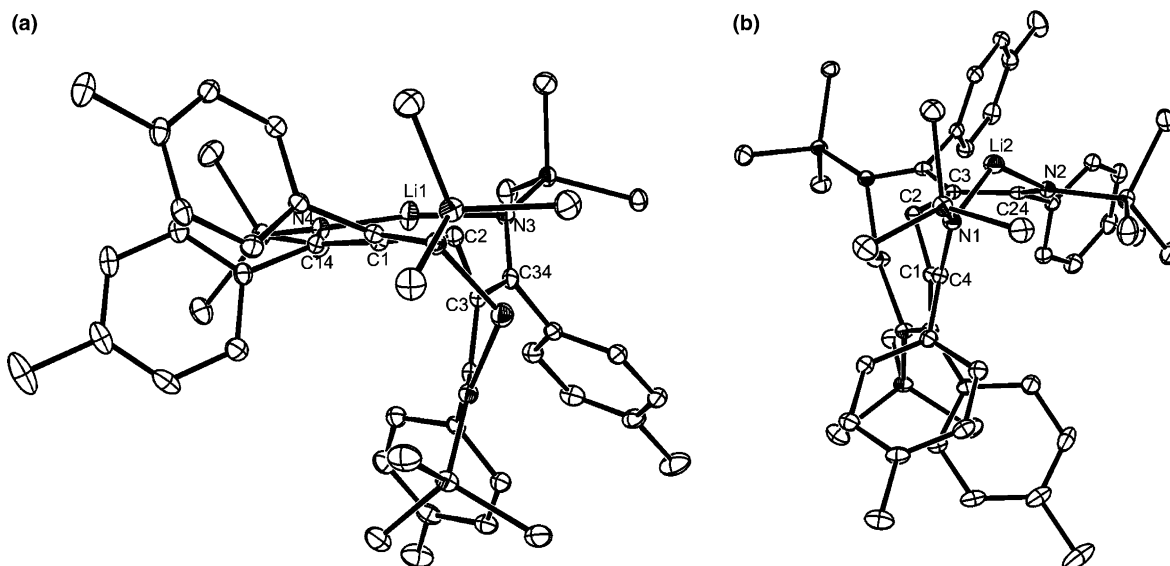
Fig. 2. Molecular structure of **6**, showing two alternative views (a and b, ellipsoid probability 20%), with selected bond lengths (Å) and angles (°): Li1–N3 1.897(2), Li1–N4 1.910(5), Li2–N1 1.919(5), Li2–N2 1.961(5), Li1...C2 2.514(5), Li1...C3 2.439(5), Li1–C34 2.279(5), Li2...C4 2.617(5), Li2...C2 2.541(5), Li2–C(41)′ 2.427(5), N3–C34 1.339(3), N4–C14 1.331(3), N1–C4 1.335(3), N2–C24 1.311(3), C34–C3 1.418(3), C14–C1 1.422(3), C1–C4 1.418(3), C3–C24 1.452(3), C1–C2 1.528(3), C3–C2 1.535(3) Å; N3–Li1–N4 160.9(3), N1–Li2–N2 126.7(3), Li1–N3–C34 88.2(2), Li1–N4–C14 121.1(2), Li2–N1–C4 105.8(2), Li2–N2–C24 115.1(2), N3–C34–C3 122.4(2), N4–C14–C1 122.2(2), N1–C4–C1 123.2(2), N2–C24–C3 121.0(2), C4–C1–C2 119.2(2), C24–C3–C2 118.7(2), C1–C2–C3 119.7(2)°.
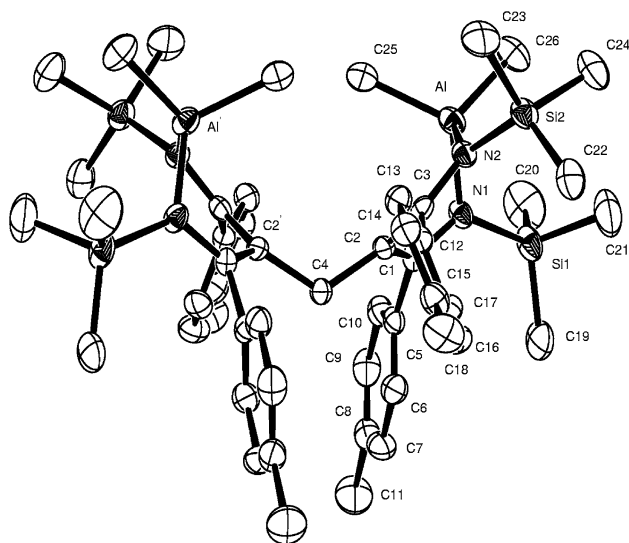
Fig. 3. Molecular structure of **7** with selected bond lengths (Å) and angles (°): Al–N1 1.895(3), Al–N2 1.949(3), Al–C25 1.956(3), Al–C26 1.971(3), N1–Si1 1.763(2), N2–Si2 1.784(2), N1–C1 1.363(3), N2–C3 1.333(4), C1–C2 1.397(4), C2–C3 1.437(4), C2–C4 1.530(3) Å; N1–Al–N2 91.83(11), N1–Al–C25 117.67(13), N1–Al–C26 112.17(14), N2–Al–C25 106.10(12), N2–Al–C26 123.62(14), Al–N1–C1 110.4(2), Al–N2–C3 111.1(2), N1–C1–C2 123.2(2), N2–C3–C2 124.4(3), C1–C2–C3 119.1(2), C1–C2–C4 120.0(2), C2–C4–C2′ 116.7(3).

bis(β-diketimine) **3** or **4** is suggested to follow the route shown in Scheme 4 (R = SiMe$_3$, Ar = Ph or C$_6$H$_4$Me-4). The formation of **7** from **4** and AlMe$_3$, on the other hand, is unexceptional since no rearrangement is implicated. However, that **7** is also obtained from Al(Cl)Me$_2$

Fig. 4.

and **6** indicates that the isomer **7′** is thermodynamically less favoured than **7** and if **7′** is first formed then its rearrangement into **7** may require a process similar in reverse of the final two steps of Scheme 4 with the lithium atoms replaced by AlMe$_2$ moieties in **7′**.

7′

4. Experimental

4.1. Synthesis of H[{N(R)C(Ph)}$_2$CH] (1) (R = SiMe$_3$)

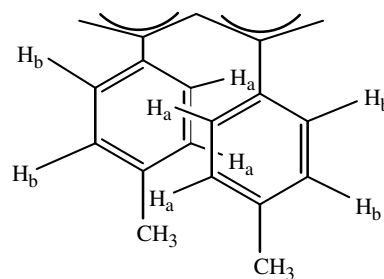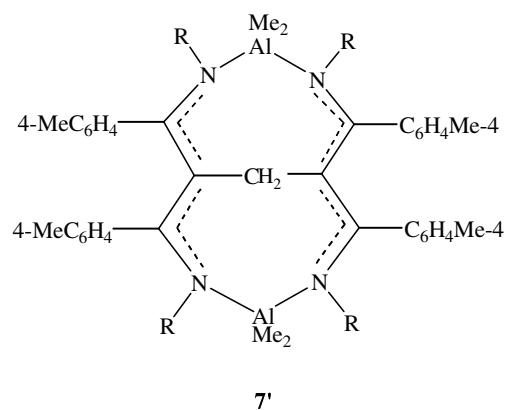$(CH_2Br)_2$ (0.01 mL, 0.82 mmol) was added by syringe to a solution of [K{N(R)C(Ph)}$_2$CH] (0.41 g, 1.01 mmol) in hexane (ca. 20 mL). The mixture was heated at 50 °C for 5 h. The white precipitate formed was filtered off and evaporation of the solvent from the filtrate in vacuo produced yellow needles of compound 1 (0.36 g, 97%), m.p. 85–87.5 °C.

By using the potassium compound and $(CH_2Br)_2$ in the proportion 2:1, the reaction, even under reflux in hexane for 10 h, led only to 1 and unreacted potassium complex.

^{1}H NMR (360.1 MHz, toluene-d$_8$, 298 K) δ 0.04 (s, 18 H, SiMe$_3$), 5.39 (s, 1 H, CH), 6.99–7.21 (m, 10 H, C$_6$H$_5$), 12.38 (s, 1 H, NH); ^{13}C NMR (62.9 MHz, C$_6$D$_6$, 298 K) δ 1.9 (SiMe$_3$), 102.8 (CH), 128.9 (CN), 127.4, 132.8, 143.7, 170.6 (C$_6$H$_5$). Elemental analysis for C$_{21}$H$_{30}$N$_2$Si$_2$, found % (calculated %), C 68.9 (68.8), H 8.25 (8.25), N 7.82 (7.64).

4.2. Synthesis of H[{N(R)C(Ar)}$_2$CH] (2) (R = SiMe$_3$, Ar = C$_6$H$_4$Me-4)

A suspension of [Li{N(R)C(Ar)}$_2$CH]$_2$ (0.33 g, 0.44 mmol) in hexane (ca. 10 mL) was stirred until nearly all the solid had dissolved; there was a change in colour from red to yellow. Slow evaporation of the solvent in vacuo afforded yellow crystals of 2 (0.31 g, 96%), m.p. 120–124 °C. ^{1}H NMR (360.1 MHz, CDCl$_3$, 298 K) δ 0.06 (s, 18 H, SiMe$_3$), 2.39 (s, 6 H, CH$_3$–C$_6$H$_4$), 5.28 (s, 1 H, CH), 7.16 and 7.28 (d, 8 H, C$_6$H$_4$Me-4), 12.08 (s, 1 H, NH); ^{13}C NMR (62.9 MHz, CDCl$_3$, 298 K) δ 1.8 (SiMe$_3$), 21.3 (CH$_3$–C$_6$H$_4$), 102.1 (CH), 128.6 (CN), 127.2, 138.1, 140.5, 170.5 (C$_6$H$_4$). Elemental analysis for C$_{23}$H$_{34}$N$_2$Si$_2$, found % (calculated %), C 70.1 (70.0), H 9.17 (8.78), N 7.22 (7.10).

4.3. Synthesis of [H{N(R)C(Ph)}$_2$C]$_2$CH$_2$ (3) (R = SiMe$_3$)

CH_2Br_2 (0.34 g, 1.95 mmol) was added to a solution of [Li{N(R)C(Ph)}$_2$CH]$_2$ (1.32 g, 1.77 mmol) in hexane (ca. 20 mL). The mixture was refluxed for 10 h and the white precipitate formed was then filtered off. Concentrating the filtrate by slow evaporation of solvent in vacuo afforded yellow crystals of 3 which were washed with hexane (ca. 5 mL) and dried in vacuo (0.57 g, 43%), m.p. 193–198 °C. ^{1}H NMR (360.1 MHz, toluene-d$_8$, 298 K) δ 0.08 (s, 36 H, SiMe$_3$), 2.65 (s, 2 H, CH$_2$), 6.76–7.01 (m, 20 H, C$_6$H$_5$), 11.80 (s, 2 H, NH); ^{13}C NMR (62.9 MHz, toluene-d$_8$, 298 K) δ 2.0 (SiMe$_3$), 33.0 (CH$_2$), 110.5 (NCCCN), 128.4 (CN), 127.6, 129.3, 142.9, 170.1 (C$_6$H$_5$). Elemental analysis for C$_{43}$H$_{60}$N$_4$Si$_4$, found % (calculated %), C 67.9 (69.3), H 8.44 (8.12), N 7.41 (7.52).

4.4. Synthesis of [H{N(R)C(Ar)}$_2$C]$_2$CH$_2$ (4) (R = SiMe$_3$, Ar = C$_6$H$_4$Me-4)

The same method as for the synthesis of 3 was used to prepare 4. CH_2Br_2 (0.42 g, 2.42 mmol) added to a solution of [Li{N(R)C(Ar)}$_2$CH]$_2$ (1.79 g, 4.47 mmol) in hexane (ca. 30 mL). After refluxing for 13 h yellow crystals of 4 (0.71 g, 40%), m.p. 196–198 °C, were obtained. ^{1}H (300.13 MHz, C$_6$D$_6$, 293 K) δ 0.04 (s, 36 H, SiMe$_3$), 2.14 (s,12 H, CH$_3$–C$_6$H$_4$), 2.90 (s, 2 H, CH$_2$); 6.79–6.95 (m, 16 H, C$_6$H$_4$), 11.50 (s, 2 H, NH); ^{13}C (75.46 MHz, C$_6$D$_6$, 293 K) δ 2.1 (SiMe$_3$), 21.2 (CH$_3$–C$_6$H$_4$), 33.3 (CH$_2$), 110.6 (NCCCN), 128.4, 128.7, 136.8, 140.2 (C$_6$H$_4$), 170.2 (NCAr). Elemental analysis for C$_{47}$H$_{68}$N$_4$Si$_4$, found % (calculated %), C 70.0 (70.4), H 8.44 (8.55), N 7.29 (6.99).

### 4.5. Synthesis of Li$_2$[{N(R)C(Ar)$\overline{CC(Ar)NR}$}$_2$(CH$_2$)] (5) (R=SiMe$_3$, Ar = C$_6$H$_5$)

LiBu^n (1.6 M in hexane, 0.70 mL, 1.12 mmol) was added dropwise to a solution of 3 (0.4 g, 0.54 mmol) in Et$_2$O (ca. 10 mL) at −78 °C. An immediate change of colour from yellow to orange was observed. The solution was stirred for a further 30 min more at low temperature, then allowed to warm up slowly and stirred at room temperature for 4 h. Solvents were removed in vacuo from the dark green-yellow solution to give a yellow-brown powder. Orange crystals of 5 (0.25 g, 61%), m.p. 157–160 °C, were obtained from a hot hexane/toluene solution by cooling slowly to room temperature. ^{1}H (300.13 MHz, C$_6$D$_6$, 333 K) δ −0.05 (s broad, 36 H, SiMe$_3$), 4.78 (s, 2 H, CH$_2$), 6.60–6.91 (m broad, 20 H, C$_6$H$_5$); ^{1}H (C$_6$D$_6$, 300.13 MHz, 293 K) δ −0.13 (s, 18 H, SiMe$_3$), 0.05 (s, 18 H, SiMe$_3$), 4.79 (s, 2 H, CH$_2$), 6.65–6.80 (m, 20 H, C$_6$H$_5$); ^{13}C (75.46 MHz, C$_6$D$_6$, 293 K) δ 2.4 (SiMe$_3$), 2.7 (SiMe$_3$), 35.3 (CH$_2$), 114.5 (NCCCN), 126.2, 127.1, 128.4, 128.5, 142.7, 148.7, 149.7 (C$_6$H$_5$), 182.1 (NCC$_6$H$_5$), 185.9 (NCC$_6$H$_5$); ^{7}Li (116.6 MHz, C$_6$D$_6$, 293 K) δ 0.40; ^{29}Si (99.36 MHz, C$_6$D$_6$, 298 K) δ −6.65 (SiMe$_3$), −6.15 (SiMe$_3$); MS (EI, 70 eV) m/z 496 ([M − (2Li + 3Me$_3$Si + NC)]$^+$, 35%), 190 ([Me$_3$SiNCC$_6$H$_5$]$^+$, 82%). Elemental analysis for C$_{43}$H$_{58}$Li$_2$N$_4$Si$_4$, found % (calculated %), C 67.27 (68.21), H 7.63 (7.67), N 7.45 (7.40).

4.6. Synthesis of Li$_2$[{N(R)C(Ar)$\overline{CC(Ar)NR}$}$_2$(CH$_2$)] (6) (R = SiMe$_3$, Ar = C$_6$H$_4$Me-4)

The method used for the synthesis of 5 was applied for the synthesis of 6, from LiBu^n (1.6 M in hexane, 3.2 mL, 5.12 mmol), 4 (2.05 g, 2.56 mmol) in a mixture Et$_2$O (42 mL)/hexane (6 mL). Deep yellow crystals of 6 (1.42 g, 68%), m.p. 158–160 °C, were isolated. ^{1}H (300.13 MHz, toluene-d$_8$, 293 K) δ −0.16 (s, 18 H, SiMe$_3$), 0.08 (s, 18 H, SiMe$_3$), 2.07 (s,12 H,
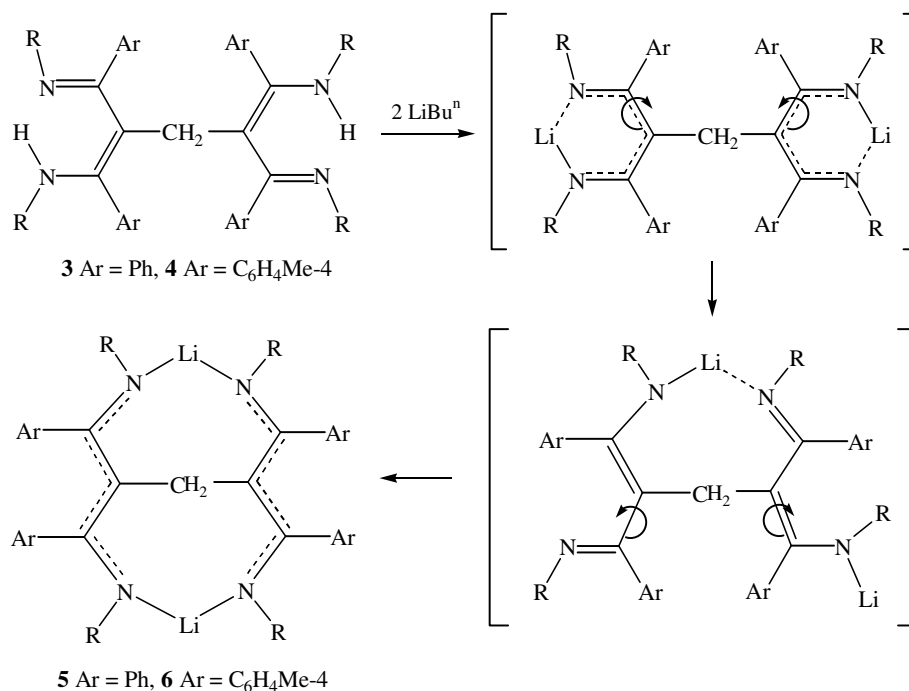
Scheme 4.

CH_3—C_6H_4), 4.65 (s, 2 H, CH_2), 6.42–6.77 (m, 16 H, C_6H_4); ^{13}C (75.46 MHz, toluene-d_8, 293 K) δ 2.1 (SiMe$_3$), 2.7 (SiMe$_3$), 21.0 (CH_3-C_6H_4), 35.4 (CH_2), 114.7 (NCCCN), 124.8–147.3 (C_6H_4), 182.0 (NCC$_6$H$_4$Me-4), 186.2 (NCC$_6$H$_4$Me-4); ^7Li (116.6 MHz, toluene-d_8, 293 K) δ 0.38; ^{29}Si (99.36 MHz, toluene-d_8, 298 K) δ −6.92 (SiMe$_3$), −6.38 (SiMe$_3$). Elemental analysis for $C_{47}H_{66}Li_2N_4Si_4$, found % (calculated %), C 71.2 (69.4), H 8.29 (8.18), N 6.50 (6.89).

4.7. Synthesis of [Me$_2$Al{N(R)C(Ar)}$_2$C]$_2$CH$_2$ (7) (R = SiMe$_3$, Ar = C$_6$H$_4$Me-4)

AlMe$_3$ (2 M in hexanes, 0.6 mL, 1.2 mmol, 30% excess) was added dropwise to a suspension of **3** (0.37 g, 0.46 mmol) in hexane (ca. 20 mL) at −78 °C. After 30 min at −78 °C the yellow solution was allowed to warm up slowly and stirred for 1 h at room temperature. The solvents were then removed in vacuo to afford **7** (0.38 g,

Table 1

Compound	**2**	**3**	**5**	**6**	**7**
Empirical formula	C$_{23}$H$_{34}$N$_2$Si$_2$	C$_{43}$H$_{60}$N$_4$Si$_4$	C$_{43}$H$_{58}$Li$_2$N$_4$Si$_4$·(C$_5$H$_{12}$)	C$_{47}$H$_{66}$Li$_2$N$_4$Si$_4$	C$_{51}$H$_{78}$Al$_2$N$_4$Si$_4$·(C$_6$H$_{14}$)
Formula weight	394.7	745.3	829.32	813.28	999.7
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c (No. 15)	P$\bar{1}$ (No. 2)	P$\bar{1}$ (No. 2)	P2$_1$/c (No. 14)	C2/c (No. 15)
a (Å)	48.282(8)	12.285(4)	12.0755(3)	12.3070(4)	19.461(4)
b (Å)	6.144(9)	14.186(4)	12.6880(3)	11.6518(4)	23.237(4)
c (Å)	16.887(4)	14.182(4)	19.5345(5)	35.7160(13)	13.954(2)
α (°)	90	89.15(2)	78.286(2)	90	90
β (°)	106.46(2)	75.00(3)	75.507(2)	99.666(2)	97.75
γ (°)	90	75.82(2)	63.528(2)	90	90
V Å^3	4804.0(3)	2311.3(3)	2579.4(1)	5048.9(3)	6253(2)
Z	8	2	2	4	4
μ (mm^{-1})	0.15	0.15	0.15	0.15	0.16
Reflections collected	4694	5630	27390	26994	5656
Independent reflections, [R (int)]	4650, [0.03]	5630	8961, [0.043]	8784, [0.065]	5492, [0.033]
Reflections with $I > 2\sigma(I)$	2172	3166	7000	6270	3862
Final R indices ($I > 2\sigma(I)$)	R$_1$ 0.062	R$_1$ 0.057	R$_1$ 0.064, wR_2 0.183	R$_1$ 0.054, wR_2 0.122	R$_1$ 0.055, wR_2 0.136
R indices (all data)	–	–	R$_1$ 0.083, wR_2 0.200	R$_1$ 0.086, wR_2 0.137	R$_1$ 0.088, wR_2 0.161

90%), m.p. 198 °C, as a yellow solid which was washed with pentane. Crystals for X-ray structure determination were obtained from hexane at 4 °C. ^{1}H (300.13 MHz, C_6D_6, 333 K) δ −0.02 (s, 12 H, $AlMe_2$), 0.06 (s, 36 H, $SiMe_3$), 2.07 (s, 12 H, CH_3−C_6H_4), 2.83 (s, 2 H, CH_2), 6.68–6.82 (m, 16 H, C_6H_4); ^{13}C (75.46 MHz, C_6D_6, 333 K) δ −1.1 ($AlMe_2$), 4.0 ($SiMe_3$), 21.2 (CH_3−C_6H_4), 36.1 (CH_2), 116.7 (NC$C(CH_2)CN$), 128.5, 129.9, 137.6, 134.0 (C_6H_4), 177.8 (NCAr); ^{29}Si (99.36 MHz, C_6D_6, 333 K) δ 4.77 ($SiMe_3$); ^{27}Al (130.31 MHz, C_6D_6, 333 K) δ 151.4 ($\Delta_{1/2}$ ~5.5 KHz); MS (EI, 70 eV) m/z 897 ($[M − Me]^+$, 53%). Elemental analysis for $C_{51}H_{78}Al_2N_4Si_4.(C_6H_{14})$, found % (calculated %), C 68.2 (68.5), H 9.1 (9.2), N 5.8 (5.6).

4.8. Crystallographic data and structure refinement for **2**, **3**, **5**, **6** and **7**

Diffraction data for **2** and **3** were collected on an En-raf Nonius CAD4 diffractometer at room temperature with crystals sealed in capillaries. These structures were refined on F using reflections with $I > 2\sigma(I)$ with the En-raf Nonius MolEN programs.

Crystallographic data for **5**, **6** and **7** were collected at 173(2) K on a CAD4 diffractometer. The structures were refined with full-matrix, least-squares on all F^2 (SHELXL 93 for **5** and **7**, SHELXL 97 for **6**). The poorly defined pentane solvate was refined isotropically with distance constraints and no H atoms for **5**. In **7**, all non-hydrogen atoms were anisotropic, and hydrogen atoms were included in the riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$ for Me groups. The *para*-methyl groups were included with disordered H atoms. There is a molecule of hexane solvate disordered across an inversion centre for which C atoms were left isotropic and H atoms were omitted.

Data are summarised in Table 1.

5. Conclusions

We have very briefly reviewed the bonding modes adopted by β-diketiminato ligands in their binding to metals, with an emphasis on our published work largely with the ligands $[\{N(R)C(Ar)\}_2CH]^-$ (R = $SiMe_3$) or $[\{N(C_6H_3Pr^i_2\text{-}2,6)C(Me)\}_2CH]^-$. Using the former ligand, as the lithium derivative, the synthesis of the β-diketimines $[H\{N(R)C(Ar)\}_2CH]$ **1** (Ar = Ph) and **2** (Ar = C_6H_4Me-4) is described. From **1** or **2** and successively KBz or LiBu^n and then dibromomethane, the *ansa*-CH_2-bridged bis(β-diketimine)s CH_2-[{CC(Ar)-N(R)}$_2$H]$_2$ **3** (Ar = Ph) or **4** (Ar = C_6H_4Me-4) were obtained. Each of **3** or **4** when treated with LiBu^n yielded the 4,8-dilithio-3,5,7,9-tetraazabicyclo[5.5.1]tridecane derivative $Li_2[\{N(R)C(Ar)CC(Ar)NR\}_2(CH_2)]$ **5** (Ar = Ph) or **6** (Ar = C_6H_4Me-4), in which each of the β-diketimi-

nato fragments behaves as an N,N'-bridge between the two lithium atoms. By contrast, from **4** and $AlMe_3$ the product was the *ansa*-CH_2-bridged-bis[β-diketimina-to(dimethyl)alane] **7**. The X-ray structures of **2**, **3**, **5**, **6** and **7** are described. The ^{1}H NMR spectrum of **6** in tol-uene at 248 K showed that there is restricted rotation about the C–Ar bond.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 236280 and 236281 for **2** and **3**, respectively and 237141–237143 for **5**–**7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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