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A new class of linked-bis(N,N'-dialkylamidinate) ligand: applications in the synthesis of bimetallic aluminium complexes

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Abstract

The 1,4-benzenebis(N,N'-dialkylamidine) compounds, 1,4-$C_6H_4[C\{NR\}\{NHR\}]_2$ (**1**, R = Cy; **2**, R = ^{i}Pr) were synthesised via addition of a stoichiometric amount of water to the 1,4-benzenebis(amidinate) species, generated from the in situ reaction between 1,4-$Li_2C_6H_4$ and the appropriate carbodiimide. Alternatively, the neutral silylated derivatives, 1,4-$C_6H_4[C\{NR\}\{N(SiMe_3)R\}]_2$ (**3**, R = Cy; **4**, R = ^{i}Pr) are synthesised by quenching the 1,4-benzenebis(amidinate) with excess Me_3SiCl. Structural characterisation of selected examples are reported, showing that the neutral NH compounds are monomeric with a *E-syn*:*E-syn* arrangement of the N-alkyl substituents, while in the silylated derivative **4**, the *E-anti:E-anti* form is present in the solid-state. Synthesis of the bimetallic aluminium compounds 1,4-$C_6H_4[C\{N^iPr\}_2AlMeX]_2$ (**5**, X = Cl; **6**, X = Me) was achieved from $AlMe_2Cl$ using **2** by either the direct protonolysis of an Al–C bond (**5**), or the trans-metallation reaction of the in situ generated dilithio-salt (**6**). Structural characterisation of **6** revealed a monomeric complex with a perpendicular arrangement of the amidinate units with respect to the C_6-group.

Keywords: Amidine; Amidinate; Linked; Silylated; Bimetallic; Aluminium; Crystal structures

1. Introduction

Amidinate anions, $[R'C\{NR\}_2]^-$, comprise a class of ligand currently finding many applications in coordination chemistry [1,2], and more recently as ancillary ligands in polymerisation catalysis [3]. The isolobal relationship with $[R'CO_2]^-$ has facilitated rapid development of this area, based upon the previously well established field of carboxylate chemistry [4]. A significant advantage of the amidinates is the ability to tailor the steric properties to satisfy specific requirements via derivitisation of the N-substituents, enabling a degree of control to be gained over the chemistry that occurs at the metal centre. Within the field of amidinate chemistry initial work focused primarily on the benzamidinate derivative $[PhC\{NSiMe_3\}_2]^-$ [2], synthesised from the reaction between $LiN(SiMe_3)_2$ and benzonitrile, first reported by Sanger in 1973 [5]. Subsequent developments in the field have expanded the number of ligand derivatives available through the use of various different N- and C-substituents, and a range of different synthetic protocols to metal amidinate complexes have been developed, including: (i) protonolysis reactions employing neutral amidines; (ii) insertion of carbodiimides into metal alkyl bonds; and (iii) salt metathesis routes between lithium amidinates (from reaction of alkyl lithium reagents with carbodiimides) and metal halide species.

The early benzamidinate work was extended to include the synthesis of multifunctional ligands that contain greater than one amidine group around the central C_6-ring. Thus, using analogous synthetic procedures, the bis- and tris-per(trimethylsilyl)amidine compounds, 1,4-$C_6H_4[C\{NSiMe_3\}\{N(SiMe_3)_2\}]_2$ [6] and 1,3,5-$C_6H_3[C\{NSiMe_3\}\{N(SiMe_3)_2\}]_3$ [7] were accessed. Despite the potential for the former ligand to act as a bridge between two metal fragments, applications within coordination chemistry have been limited to synthesis of the bis-trichlorotin complex, 1,4-$C_6H_4[C\{NSiMe_3\}_2SnCl_3(MeCN)]_2$ (**A**, Fig. 1) [8] and the dicationic

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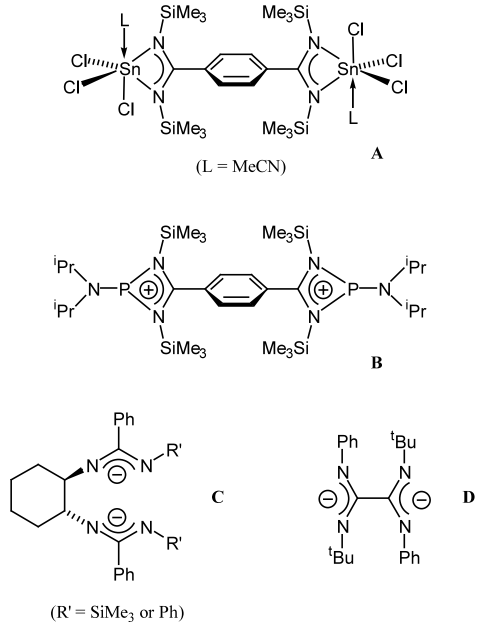


Fig. 1. Examples of linked amidinates: **A** [Ref. [8]]; **B** [Ref. [9]]; **C** [Ref. [10]] and **D** [Ref. [11]].

bis(1,3-diaza-2-phosphetine), $[1,4\text{-}C_6H_4[C\{NSiMe_3\}_2\text{-}PN^iPr_2]^{2+}$ (**B**, Fig. 1) [9]. Recently, new classes of linked bis-amidinates have been reported, based on the 1,2-disubstituted cyclohexyl framework (**C**, Fig. 1) [10] and the oxalic amidine, $[PhN{=}C(NH^tBu)]_2$ (**D**, Fig. 1) [11]. We have been interested in developing the ligand based on the 1,4-disubstituted benzamidinate framework, but avoiding the potentially labile nitrogen–silicon bonds present in the previously reported derivative [6]. We describe here the synthesis of two neutral ligand precursors, $1,4\text{-}C_6H_4[C\{NR\}\{NHR\}]_2$ and $1,4\text{-}C_6H_4[C\{NR\}\{N(SiMe_3)R\}]_2$ ($R = {}^iPr$ and Cy), and demonstrate their application in the synthesis of molecular aluminium derivatives.

2. Experimental

2.1. General experimental procedures

All manipulations were carried out under dry nitrogen using standard Schlenk and cannula techniques, or in a conventional, nitrogen-filled glovebox operating at less than 1 ppm oxygen. Solvents were dried over appropriate drying agents and degassed prior to use. Elemental analyses were performed by S. Boyer at the University of North London. The NMR spectra were recorded using a Bruker Avance DPX 300 at 300 (^1H), 75 (^{13}C) MHz and referenced internally to residual solvent resonances unless otherwise stated.

2.2. Synthesis

The compounds $1,4\text{-}Br_2C_6H_4$, $RN{=}C{=}NR$ ($R = {}^iPr$, Cy), Me_3SiCl (distilled) and $AlMe_2Cl$ (1.0 M solution in C_6H_{14}) were purchased from Aldrich and used without further purification, unless otherwise stated.

2.2.1. 1,4-Benzenebis(N,N'-dicyclohexylamidine) (1)

1,4-Dibromobenzene (5.0 g, 21.0 mmol) was dissolved in C_6H_{14} (100 ml) and 25.2 ml of ^{n}BuLi (2.5 M in C_6H_{14}, 63.0 mmol, three equivalents) was added at room temperature (r.t.). The mixture was heated at 80 °C for 12 h, affording a pale cream slurry of the dilithio-salt $1,4\text{-}Li_2C_6H_4$. The solvent was removed by filtration and the remaining solid was washed with C_6H_{14} (3×20 ml). The dilithio-salt was subsequently reslurried in THF (100 ml) and a solution of 1,3-dicyclohexylcarbodiimide (8.8 g, 42.4 mmol) in THF (20 ml) was added at 0 °C affording a beige slurry. The mixture was stirred for 12 h followed by the slow addition of a stoichiometric amount of distilled water (0.8 ml, 42.4 mmol) to afford a clear orange solution that was stirred at ambient temperature for 12 h. The solution was washed with water and the product was extracted with ether (3×20 ml). Removal of the volatiles in vacuo afforded crude **1** as an opaque yellow oil that was crystallised from Et_2O at −30 °C as colourless crystals (3.4 g, 33%).

Anal. Calc. for $C_{32}H_{50}N_4$: C, 78.32; H, 10.27; N, 11.42. Found: C, 78.88; H, 10.17; N, 11.35%. ^1H-NMR ($CDCl_3$, 298 K): δ 7.20 (m, br, 4H, C_6H_4), 3.10 (m, 4H, NCH), 1.82–0.84 (m, 40H, Cy), *. (*NH resonance not observed in ^1H-NMR). ^{13}C-NMR ($CDCl_3$, 298 K) δ 157.0 (CN$_2$), 137.0 ($C_6H_4\text{–}C_{ipso}$), 127.6 ($C_6H_4\text{–}C_{ortho}$), 56.3 (Cy), 53.2 ($Cy\text{–}C_1$), 35.3 (Cy), 34.7 (Cy), 34.1 (Cy), 26.1 (Cy), 25.6 (Cy), 25.3 (Cy). MS: m/z 490 $[M]^+$, 407 $[M-Cy]^+$. IR: (cm^{-1}) 3284w (N–H), 2119m, 1626s (C=N), 1610s, 1518s, 1343, 1316s, 1304s, 1279m, 1256m, 1238m, 1169m, 1150s, 1063m, 1050m, 1023m, 991m, 978m, 928m, 888m, 849m, 836m, 724m, 647m, 630m, 504m, 434m, 397m, 382m, 376s.

2.2.2. 1,4-Benzenebis(N,N'-diisopropylamidine) (2)

Compound **2** was prepared using the procedure described for **1**, using 1,4-dibromobenzene (5.0 g, 21.0 mmol), ^{n}BuLi (2.5 M in C_6H_{14}, 63.0 mmol), 1,3-diisopropylcarbodiimide (9.9 ml, 63.0 mmol) and water (0.8 ml, 42.4 mmol). Crystallisation from Et_2O afforded pure **2** as colourless crystals (3.0 g, 43% yield).

Anal. Calc. for $C_{20}H_{34}N_4$: C, 72.68; H, 10.37; N, 16.95. Found: C, 72.51; H, 10.48; N, 16.83%. ^1H-NMR ($CDCl_3$, 298 K) δ 7.33 (s, 4H, C_6H_4), 3.22 (sept, br, 4H, NCH), 1.03 (d, $^3J_{HH} = 5.1$ Hz, 24H, CHMe_2), *. (*NH resonance not observed in ^1H-NMR). ^{13}C-NMR ($CDCl_3$, 298 K) δ 156.0 (CN$_2$), 137.1 ($C_6H_4\text{–}C_{ipso}$), 127.6 ($C_6H_4\text{–}C_{ortho}$), 46.8 (CHMe$_2$), 24.4 (CHMe_2). MS: m/z 330 $[M]^+$, 315 $[M-CH_3]^+$, 287 $[M-{}^iPr]^+$.

IR: ($\mathrm{cm^{-1}}$) 3389m (N–H), 3351m (N–H), 1637s (C=N), 1510s, 1319s, 1282s, 1265s, 1171s, 1131s, 1102s, 1024s, 975m, 954m, 858s, 822m, 723m, 693m, 518m, 516m, 464m, 411m, 397m, 385m, 373m.

2.2.3. *1,4-Benzenebis(N,N′-dicyclohexyl-N-trimethylsilylamidine) (**3**)*

1,4-Dibromobenzene (5.0 g, 21.0 mmol) was dissolved in C_6H_{14} (100 ml) and 25.2 ml of ^{n}BuLi (2.5 M in C_6H_{14}, 63.0 mmol, three equivalents) was added at r.t. The mixture was heated at 80 °C for 12 h, affording a pale cream slurry of the dilithio-salt 1,4-$Li_2C_6H_4$. The solvent was removed by filtration and the remaining solid was washed with C_6H_{14} (3 × 20 ml). The dilithio-salt was subsequently reslurried in THF (100 ml) and a solution of 1,3-dicyclohexylcarbodiimide (8.8 g, 42.4 mmol) in THF (20 ml) was added dropwise at 0 °C, affording a beige slurry. Me_3SiCl (5.9 ml, 63.6 mmol) was added and the mixture was heated at reflux for 8 h, affording a clear yellow solution. Removal of the solvent in vacuo, and extraction with CH_2Cl_2 (3 × 30 ml) afforded an off-white solid that was crystallised from CH_2Cl_2, yielding colourless crystals (7.0 g, 52%). Anal. Calc. for $C_{38}H_{66}N_4Si_2$: C, 71.86; H, 10.47; N, 8.82. Found: C, 71.96, H, 10.57, N, 8.69%. ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.15 (s, 4H, C_6H_4), 2.74 (m, 4H, *Cy*), 1.43–1.63 (m, 32H, *Cy*), 0.88–0.96 (m, 8H, *Cy*), 0.64 (s, 18H, Si*Me*$_3$). ^{13}C-NMR ($CDCl_3$, 298 K): δ 162.2 (*C*N_2), 136.5 (C_6H_4–C_{ipso}), 127.6 (C_6H_6–C_{ortho}), 58.2 (*Cy*–C_1), 34.8 (*Cy*), 26.1 (*Cy*), 26.3 (*Cy*), 3.54 (Si*Me*$_3$). MS: *m*/*z* 634 $[M]^+$, 619 $[M-CH_3]^+$, 551 $[M-Cy]^+$, 561 $[M-SiMe_3]^+$, 490 $[M-2SiMe_3]^+$, 469 $[M-2Cy]^+$. IR: ($\mathrm{cm^{-1}}$) 1614s (C=N), 1504m, 1406m, 1338s, 1317s, 1304s, 1257s, 1242s, 1178s, 1156s, 1112s, 1072s, 1022s, 990s, 915m, 891m, 842s, 764m, 724m, 708m, 690m, 677m, 638m, 526m, 396m, 376s.

2.2.4. *1,4-Benzenebis(N,N′-diisopropyl-N-trimethylsilylamidine) (**4**)*

Compound **4** was prepared using the procedure described for **3**, using 1,4-dibromobenzene (5.0 g, 21.0 mmol), 25.2 ml of ^{n}BuLi (2.5 M solution in C_6H_{14}, 63.0 mmol, three equivalents), 1,3-diisopropylcarbodiimide (9.9 ml, 63.0 mmol) and Me_3SiCl (5.9 ml, 63.6 mmol). Crystallisation from CH_2Cl_2 afforded pure **4** as colourless crystals (6.2 g, 62% yield).

Anal. Calc. for $C_{26}H_{50}N_4Si_2$: C, 65.76; H, 10.71; N, 11.80. Found: C, 65.84; H, 10.70; N, 11.89%. ^{1}H-NMR ($CDCl_3$, 298 K) δ 7.12 (s, 4H C_6H_4), 3.22 (sept, $^{3}J_{HH}=$ 6.3 Hz, 4H, C*H*Me_2), 1.03 (d, $^{3}J_{HH}=6.5$ Hz, 24H, CH*Me*$_2$), 0.23 (s, 18H Si*Me*$_3$). ^{13}C-NMR ($CDCl_3$, 298 K): δ 161.3 (*C*N_2), 136.3 (C_6H_4–C_{ipso}), 127.9 (C_6H_4–C_{ortho}), 49.0 (*C*HMe_2), 24.5 (CH*Me*$_2$), 3.5 (Si*Me*$_3$). MS: *m*/*z* 474 $[M]^+$, 459 $[M-CH_3]^+$, 431 $[M-{}^{i}Pr]^+$, 401 $[M-SiMe_3]^+$. IR ($\mathrm{cm^{-1}}$): 1615s (C=N), 1505m, 1315s, 1245s, 1196m, 1169s, 1128s, 1051m, 1032m, 1013m, 945m, 884m, 847s, 769m, 729m, 690m, 675m, 636m, 526m, 447m, 376m.

2.2.5. *1,4-Benzenebis(N,N′-diisopropylamidinatocholromethylaluminium) (**5**)*

A solution of $AlMe_2Cl$ (5.6 ml of a 1 M solution in C_6H_{14}, 5.6 mmol) was further diluted with 20 ml of C_6H_{14}. A solution of **2** (1.6 g, 4.8 mmol) in 100 ml C_6H_{14} was added dropwise at r.t., resulting in the immediate formation of a pale yellow precipitate. The resultant mixture was stirred at r.t. for 12 h. Removal of the volatile components in vacuo afforded the crude product as an off-white solid, that was crystallised from hot $C_6H_5CH_3$ giving analytically pure **5** as pale yellow crystals (1.5 g, 63% yield).

Anal. Calc. for $C_{22}H_{38}Al_2Cl_2N_4$: C, 54.66; H, 7.92; N, 11.59. Found: C, 54.53; H, 7.98; N, 11.44%. ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.44 (s, 4H, C_6H_4), 3.23 (sept, $^{3}J_{HH}=6.5$ Hz, 4H, C*H*Me_2), 1.09 (d, $^{3}J_{HH}=6.3$ Hz, 12H, CH*Me*$_2$), 1.04 (d, $^{3}J_{HH}=6.3$ Hz, 12H CH*Me*$_2$), −0.39 (s, 6H, Al*Me*). ^{13}C-NMR ($CDCl_3$, 298 K): δ 174.9 (*C*N_2), 131.4 (C_6H_4–C_{ipso}), 127.6 (C_6H_4–C_{ortho}), 45.7 (*C*HMe_2), 25.0 (CH*Me*$_2$), −10.36 (Al*Me*). MS: *m*/*z* 482 $[M]^+$, 467 $[M-Me]^+$, 447 $[M-Cl]^+$, 405 $[M-AlMeCl]^+$.

2.2.6. *1,4-Benzenebis(N,N′-diisopropylamidinatodimethylaluminium) (**6**)*

^{n}BuLi (1.3 ml, 2.5 M in C_6H_{14}, 3.3 mmol) was added dropwise at r.t. to a solution of **2** (0.5 g, 1.5 mmol) in C_6H_{14}. The mixture was allowed to stir for 2 h during which time a thick white precipitate formed. The solvent was removed by filtration and the resultant solids were washed with C_6H_{14} (2 × 20 ml). The white solid was reslurried in C_6H_{14} and added dropwise to 3.2 ml $AlMe_2Cl$ (1.0 M in C_6H_{14}, 3.2 mmol) that had been further diluted in 30 ml of C_6H_{14}. The mixture was allowed to stir overnight, resulting in a thick white precipitate. The volatiles were removed in vacuo and the product was separated from lithium chloride by extraction with $C_6H_5CH_3$. Analytically pure **6** was obtained by cooling a warm, saturated $C_6H_5CH_3$ solution to r.t., affording colourless needles (1.2 g, 65% yield).

Anal. Calc. for $C_{24}H_{44}Al_2N_4$: C, 65.12; H, 10.02; N, 12.66. Found: C, 64.93; H, 9.92; N, 12.49%. ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.36 (s, 4H, C_6H_4), 3.18 (sept, $^{3}J_{HH}=6.3$ Hz, 4H, C*H*Me_2), 0.99 (d, $^{3}J_{HH}=6.4$ Hz, 24H, CH*Me*$_2$), −0.66 (s, 12H, Al*Me*$_2$). ^{13}C-NMR ($CDCl_3$, 298 K): δ 172.2 (*C*N_2), 131.9 (C_6H_4–C_{ipso}), 127.5 (C_6H_4–C_{ortho}), 45.5 (*C*HMe_2), 25.3 (CH*Me*$_2$), −10.0 (Al*Me*$_2$). MS: *m*/*z* 427 $[M-Me]^+$, 371 $[M-AlMe_2]^+$, 329 $[M-2AlMe_2]^+$.

2.3. X-ray structural determinations

Details of the crystal data, intensity collection and refinement are listed in Tables 1 and 6. Crystals were covered in oil and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97 [12].

2.3.1. 1,4-$C_6H_4[C\{NCy\}\{NHCy\}]_2$ (**1**)

Colourless crystals were isolated from an MeCN solution containing **1** that was cooled to −30 °C. Each of the two independent molecules lies on an inversion centre. The two molecules differ in the conformation of the C(11)–C(16) cyclohexyl ring relative to the rest of the molecule.

2.3.2. 1,4-$C_6H_4[C\{NCy\}\{NHCy\}]_2 \cdot 2(toluene)$ ($\mathbf{1}_{(\mathbf{tol})}$)

Colourless crystals were isolated from a $C_6H_5CH_3$ solution containing **1** that was cooled to −30 °C. The $C_6H_5CH_3$ solvate molecule is disordered and was refined with the C_6 ring as a rigid body.

2.3.3. 1,4-$C_6H_4[C\{N^iPr\}\{NH^iPr\}]_2$ (**2**)

Colourless crystals were isolated from a C_6H_{14} solution containing **2** that was cooled to 0 °C. There are two independent molecules, each lying across an inversion centre.

2.3.4. 1,4-$C_6H_4[C\{N^iPr\}\{NH^iPr\}]_2$ ($\mathbf{2}_{(\mathbf{tol})}$)

Colourless crystals were isolated by slow cooling of a hot (ca. 70 °C) $C_6H_5CH_3$ solution containing **2** to r.t. The molecule lies on an inversion centre.

2.3.5. 1,4-$C_6H_4[C\{N^iPr\}\{N(SiMe_3)^iPr\}]_2$ (**4**)

Colourless crystals were isolated from a CH_2Cl_2 solution containing **4** that was cooled to −30 °C.

2.3.6. 1,4-$C_6H_4[C\{N^iPr\}_2AlMe_2]_2$ (**6**)

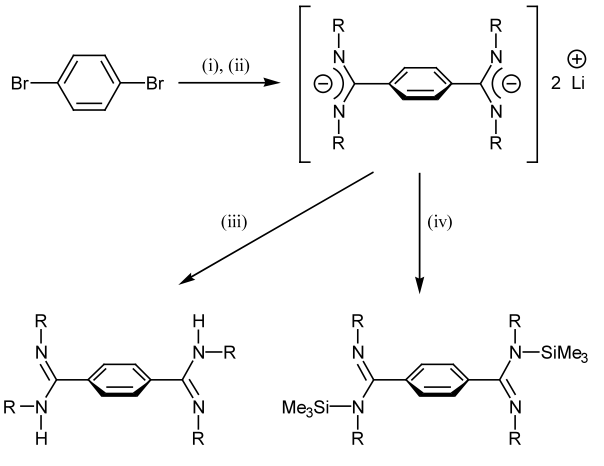
Colourless crystals were isolated by slow cooling of a hot (ca. 70 °C) $C_6H_5CH_3$ solution of **6** to r.t. The molecule lies on an inversion centre.

3. Results and discussion

Two types of neutral ligand precursor were synthesised in moderate to good yield using closely related synthetic procedures (Scheme 1). 1,4-Dibromobenzene was lithiated via addition of an excess of ^{n}BuLi in hexane, followed by heating at reflux for 12 h [13]. The dilithio-salt, 1,4-$Li_2C_6H_4$, which precipitated from solu-

Table 1
Crystal data for **1**, $\mathbf{1}_{(\mathbf{tol})}$, **2**, $\mathbf{2}_{(\mathbf{tol})}$ and **4**

	1	$\mathbf{1}_{(\mathbf{tol})}$	**2**	$\mathbf{2}_{(\mathbf{tol})}$	**4**
Empirical formula	$C_{32}H_{50}N_4$	$C_{46}H_{66}N_4$	$C_{20}H_{34}N_4$	$C_{20}H_{34}N_4$	$C_{26}H_{50}N_4Si_2$
Formula weight	490.76	675.03	330.51	330.51	474.88
Temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	10.3829(10)	12.9781(5)	9.4330(7)	5.8635(5)	10.3154(4)
b (Å)	10.7529(18)	20.2559(8)	10.1043(11)	7.6829(7)	11.7023(7)
c (Å)	14.074(2)	15.7556(3)	12.6424(14)	12.5231(12)	13.9879(9)
α (°)	107.764(5)	90	71.378(4)	105.664(5)	99.448(3)
β (°)	91.296(10)	90	71.722(6)	94.084(6)	94.660(4)
γ (°)	99.520(9)	90	73.590(6)	102.803(4)	110.228(3)
V (Å^3)	1471.3(4)	4141.9(2)	1061.8(2)	524.51(8)	1545.4(2)
Z	2	4	2	1	2
D_{calc} (Mg m^{-3})	1.11	1.08	1.03	1.05	1.02
Absorption coefficient (mm^{-1})	0.07	0.06	0.06	0.06	0.13
Crystal size (mm)	0.4 × 0.1 × 0.05	0.4 × 0.4 × 0.4	0.4 × 0.4 × 0.4	0.2 × 0.1 × 0.1	0.4 × 0.3 × 0.3
θ Range for data collection (°)	3.75–22.12	4.07–25.02	3.88–27.20	3.75–23.17	3.78–25.05
Reflections collected	7487	20 975	7539	3819	10 090
Independent reflections	3573 [$R_{int} = 0.095$]	3618 [$R_{int} = 0.062$]	4516 [$R_{int} = 0.046$]	1448 [$R_{int} = 0.050$]	5348 [$R_{int} = 0.053$]
Reflections with $I > 2\sigma(I)$	2308	2746	3391	1148	4165
Data/restraints/parameters	3573/0/331	3618/0/200	4516/0/225	1448/0/177	5348/0/289
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.066$, $wR_2 = 0.133$	$R_1 = 0.076$, $wR_2 = 0.201$	$R_1 = 0.054$, $wR_2 = 0.121$	$R_1 = 0.050$, $wR_2 = 0.123$	$R_1 = 0.083$, $wR_2 = 0.215$
R indices (all data)	$R_1 = 0.120$, $wR_2 = 0.155$	$R_1 = 0.099$, $wR_2 = 0.220$	$R_1 = 0.079$, $wR_2 = 0.135$	$R_1 = 0.068$, $wR_2 = 0.134$	$R_1 = 0.102$, $wR_2 = 0.225$
Goodness-of-fit on F^2	1.038	1.033	1.020	1.031	1.114
Largest difference peak and hole (e Å^{-3})	0.19 and −0.18	1.11 and −0.31	0.24 and −0.19	0.17 and −0.16	0.65 and −0.34

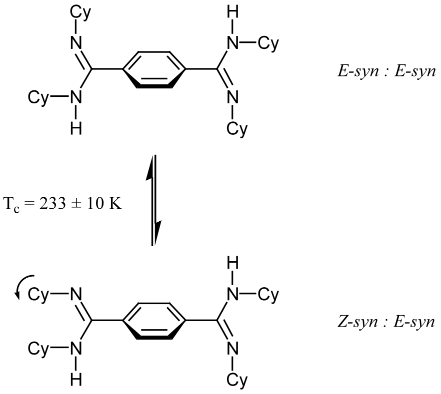


(**1**, R = Cy; **2**, R = ^{i}Pr) (**3**, R =Cy; **4**, R = ^{i}Pr)

Scheme 1. (i) Excess ^{n}BuLi, hexane, reflux, 12 h; (ii) two equivalents RN=C=NR, THF, 12 h; (iii) two equivalents H_2O, 12 h; (iv) three equivalents Me_3SiCl, reflux, 8 h.

tion, was isolated by filtration and washed with hexane to remove any unreacted starting materials. The salt was subsequently slurried in THF and a solution of carbodiimide RN=C=NR (R = ^{i}Pr, Cy) was added, to produce the lithium salt of the 1,4-benzenebis(amidinate), '1,4-$C_6H_4[C\{NR\}_2Li(THF)_x]_2$' in situ. For storage and handling purposes, the neutral bis-amidine species were synthesised by quenching the lithium salts with a stoichiometric amount of water to afford 1,4-$C_6H_4[C\{NR\}\{NHR\}]_2$ (**1**, R = Cy; **2**, R = ^{i}Pr). Alternatively, the silylated derivatives, 1,4-$C_6H_4[C\{NR\}\{N(SiMe_3)R\}]_2$ (**3**, R = Cy; **4**, R = ^{i}Pr), were synthesised by quenching the respective lithium-amidinate compounds with an excess of trimethylsilyl chloride. The bis(amidine) compounds **1** and **2** are best purified by crystallisation from Et_2O at −30 °C, while the silyl derivatives **3** and **4** can be crystallised under the same conditions using CH_2Cl_2 as solvent.

Recent NMR studies of amidinate ligands that incorporate bulky substituents have indicated the presence of different isomers and tautomers in solution [14,15]. It was noted in our work that the room temperature ^{1}H-NMR spectrum of an analytically pure sample of **1** consists of resonances from two separate species in solution, in a ratio of ca. 24:1. The major component exhibits a singlet resonance in the aromatic region of the spectrum, indicating a symmetrical species which, on the basis of crystallographic data (vide infra), we assign as the *E-syn*:*E-syn* isomer. The minor component consists of a non-symmetric structure with doublet resonances for the aromatic protons which, on the basis of the loss of a nOe between the Cy-substituent and the aromatic protons, we assign as the *Z-syn*:*E-syn* isomer arising from isomerisation of one of the 'C=NCy' double bonds (Scheme 2). In contrast, the non-symmetrical *Z-syn*:*E-syn* isomer is not observed for **2** at low temperature (193 K), presumably due to the smaller steric demand of the $N-{}^i$Pr versus the $N-$Cy substituent. The silylated derivatives, **3** and **4**, exist as single species in solution at room temperature.



Scheme 2. Fluctional process occurring in **1** in solution.

During the course of our studies into the application of these ligands in coordination chemistry, several crystal structures of the neutral bis-amidine compounds have been obtained. These data are reported here as they illustrate several differences associated with the metrical parameters within the ligand framework that depend on the nature of the nitrogen substituent, in addition to the solvent from which the compound is crystallised. These are compared with and contrasted to the crystal structure of the neutral, silylated derivative **4**. Thus, the molecular structures of compounds **1**, **2** and **4** are illustrated in Figs. 2–4, crystal data is summarised in Table 1 and selected bond lengths and angles are collected in Tables 2–4.

Compound **1** crystallises from acetonitrile with two independent molecules in the unit cell [**1a** and **1b**], each of which lie on an inversion centre. In contrast, crystallisation from toluene gives a structure with a single molecule in the unit cell, present as the bis-solvate [$\mathbf{1_{(tol)}}$]. Molecules **1a** and **1b** differ from each other in the orientation of one of the cyclohexyl groups (Fig. 2a and b); thus, in **1a** the cyclohexyl substituents are attached to the amidine nitrogen atoms via an equatorial [C(5)–C(10)] and an axial [C(11)–C(16)] linkage, while in **1b**, both C–N bonds are equatorial with respect to the cyclohexyl ring. Each amidine moiety is present in the *E-syn*:*E-syn* form, as observed in the previously structurally characterised *N*,*N'*-diphenyl- and *N*,*N'*-di(*p*-tolyl)benzamidine derivatives [16], and the bulky terphenyl compound, [2,4,6-$Ph_3C_6H_2C\{N^iPr\}\{NH^iPr\}$] [17]. In contrast with the former two structures however, no hydrogen bonding is present between neighbouring molecules, presumably due to the steric bulk of the *N*-substituents. The angle between the CN_2 amidine units and the C_6-plane of the phenyl group (α) varies considerably for each molecule, with values of 80.3 and 62.4° for **1a** and **1b**, respectively (see Table 5). The

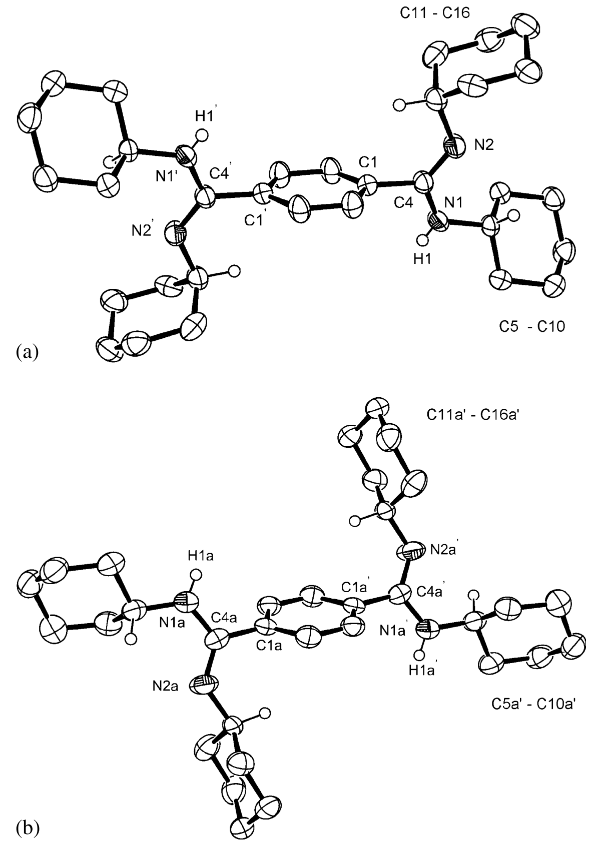


Fig. 2. (a) Molecular structure of **1a** showing 50% thermal ellipsoids. Hydrogen atoms, except N–*H* and cyclohexyl α-hydrogens, omitted for clarity. (b) Molecular structure of **1b** showing 50% thermal ellipsoids. Hydrogen atoms, except N–*H* and cyclohexyl α-hydrogens, omitted for clarity.

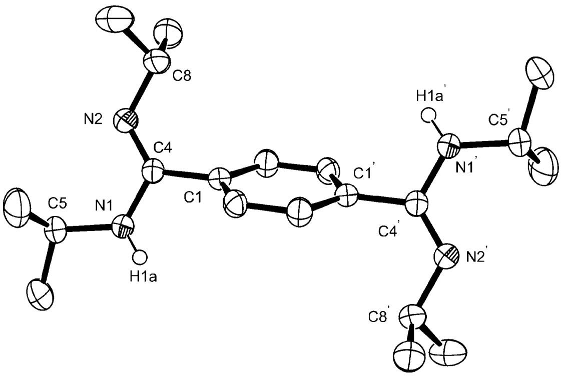


Fig. 3. Molecular structure of **2a** showing 50% thermal ellipsoids. Hydrogen atoms, except N–*H*, omitted for clarity.

molecular structure of $\mathbf{1}_{\mathbf{(tol)}}$ also lies on an inversion centre, with the gross structure being similar to that of **1b**. Thus the *E*-*syn*:*E*-*syn* form is present, with both of the *N*-cyclohexyl bonds in the equatorial position, and a value of 63.3° for α, close to the observed value for **1b**.

The structure of the *iso*-propyl analogue, when crystallised from hexane, also consists of a pair of independent molecules [**2a** and **2b**] that each lie on an inversion centre, with no interactions between neighbouring molecules (one of the independent molecules, **2a**, is illustrated in Fig. 3). Crystallisation from toluene however [$\mathbf{2}_{\mathbf{(tol)}}$] generates a unit cell that contains one independent molecule, with no included solvent molecules. In all cases, the amidine units exist as the *E*-*syn*:*E*-*syn* isomer. The angle between the amidines and the phenyl ring are 66.2 (**2a**) and 63.0° (**2b**) with a slightly larger value of 68.9° for $\mathbf{2}_{\mathbf{(tol)}}$.

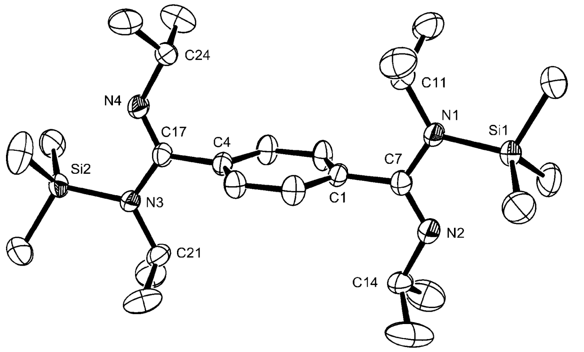


Fig. 4. Molecular structure of **4** showing 50% thermal ellipsoids. Hydrogen atoms, omitted for clarity.

Comparison of the α-value between the different structures of compounds **1** and **2** shows a significant variation (62.4–80.3°, Table 5), with none of the angles small enough to suggest any conjugation to the phenyl ring. This is markedly different from isoelectronic phenyl carboxylic acids, where α approaches 0° and an appreciable shortening of the C–C bond between the phenyl ring and the CO_2H moiety is observed [18]. The larger values of α for the amidine structures are attributable to the presence of the nitrogen substituents. However, as no trend can be rationalised between the different values for the structures of **1** and **2**, these variations are ascribed to the different ways in which the molecules pack within the crystal.

Inspection of the $C{=}N_{imino}$ and $C{-}N_{amino}$ bond lengths (Table 5), using the previously described Δ_{CN} value [where $\Delta_{CN} = d(C{-}N) - d(C{=}N)$] [19], show a range of values from 0.008 (**1b**) to 0.108 Å (**2a**). Previously, low Δ_{CN} values have been ascribed to disorder between the *Z*-*anti* and *E*-*syn* tautomers, that differ only in the location of the N–*H* atom [14]. Investigation of the electron-density map of **1b**, however, did not indicate that such disorder was present, leading us to propose that the low Δ_{CN} is therefore likely to result from a greater delocalisation of electron density across the 'CN_2' moiety. As with the different values for α, no clear trend can be deduced for the different Δ_{CN} values, again suggesting that variations may be the result of packing effects.

The presence of an N–$SiMe_3$ group in **4** compared with the N–*H* of **1** and **2** (Fig. 4) causes the N-alkyl substituents to adopt the *E*-*anti* configuration, due to

Table 2
Selected bond lengths (Å) and angles (°) for **1a**, **1b** and **1**$_{(tol)}$

1a		**1b**		**1**$_{(tol)}$	
Bond lengths					
C(4)–N(1)	1.334(5)	C(4a)–N(1a)	1.328(4)	C(1)–N(2)	1.372(3)
C(4)–N(2)	1.305(4)	C(4a)–N(2a)	1.320(5)	C(1)–N(1)	1.274(3)
C(1)–C(4)	1.504(5)	C(1a)–C(4a)	1.491(5)	C(1)–C(2)	1.507(3)
N(1)–C(5)	1.462(4)	N(1a)–C(5a)	1.465(5)	N(2)–C(11)	1.457(3)
N(2)–C(11)	1.472(4)	N(2a)–C(11a)	1.472(5)	N(1)–C(5)	1.461(3)
Bond angles					
C(1)–C(4)–N(1)	114.0(3)	C(1a)–C(4a)–N(1a)	116.7(3)	C(2)–C(1)–N(2)	112.0(2)
C(1)–C(4)–N(2)	123.3(3)	C(1a)–C(4a)–N(2a)	122.1(3)	C(2)–C(1)–N(1)	127.5(2)
N(1)–C(4)–N(2)	122.6(3)	N(1a)–C(4a)–N(2a)	121.1(3)	N(1)–C(1)–N(2)	120.5(2)
C(4)–N(1)–C(5)	121.8(3)	C(4a)–N(1a)–C(5a)	121.3(3)	C(1)–N(2)–C(11)	123.1(2)
C(4)–N(2)–C(11)	121.8(3)	C(4a)–N(2a)–C(11a)	121.8(3)	C(1)–N(1)–C(5)	121.0(2)

Symmetry elements for **1a**/**1b**: $' = -x, -y, -z+1$; $'' = -x+1, -y, -z+1$. Symmetry elements for **1**$_{(tol)}$: $' = -x, -y, -z$.

Table 3
Selected bond lengths (Å) and angles (°) for **2a**, **2b** and **2**$_{(tol)}$

2a		**2b**		**2**$_{(tol)}$	
Bond lengths					
C(4)–N(1)	1.3807(19)	C(14)–N(3)	1.3695(19)	C(4)–N(1)	1.362(3)
C(4)–N(2)	1.2724(18)	C(14)–N(4)	1.281(2)	C(4)–N(2)	1.272(2)
C(1)–C(4)	1.5022(19)	C(11)–C(14)	1.5046(18)	C(1)–C(4)	1.503(3)
N(1)–C(5)	1.4664(19)	N(3)–C(15)	1.4591(19)	N(1)–C(5)	1.461(3)
N(2)–C(8)	1.467(2)	N(4)–C(18)	1.459(2)	N(2)–C(8)	1.463(3)
Bond angles					
C(1)–C(4)–N(1)	112.70(12)	C(11)–C(14)–N(3)	113.14(12)	C(1)–C(4)–N(1)	112.21(17)
C(1)–C(4)–N(2)	126.96(13)	C(11)–C(14)–N(4)	126.71(13)	C(1)–C(4)–N(2)	127.06(17)
N(1)–C(4)–N(2)	120.29(13)	N(3)–C(14)–N(4)	120.15(13)	N(1)–C(4)–N(2)	120.72(18)
C(4)–N(1)–C(5)	121.99(13)	C(14)–N(3)–C(15)	122.11(14)	C(4)–N(1)–C(5)	124.66(19)
C(4)–N(2)–C(8)	120.16(13)	C(14)–N(4)–C(18)	121.01(13)	C(4)–N(2)–C(8)	119.71(16)

Symmetry elements for **2a**/**2b**: $' = -x, -y+1, -z+1$; $'' = -x-2, -y+2, -z+1$. Symmetry elements for **2**$_{(tol)}$: $' = -x+1, -y+1, -z+1$.

the increased bulk of the silyl group. The Δ_{CN} values [0.111 and 0.109 Å] are consistent with a more localised C–N single and C=N double bond within the amidine unit, and the α-values [83.6 and 75.6°] are also larger when compared to the parent amidines, also reflecting the larger silyl substituent.

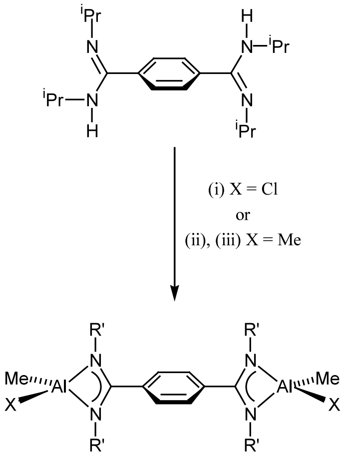
Table 4
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths			
C(7)–N(1)	1.386(5)	C(17)–N(3)	1.388(5)
C(7)–N(2)	1.275(5)	C(17)–N(4)	1.279(5)
C(1)–C(7)	1.498(5)	C(4)–C(17)	1.500(5)
N(1)–Si(1)	1.780(3)	N(3)–Si(2)	1.775(3)
N(1)–C(11)	1.485(5)	N(3)–C(21)	1.489(5)
N(2)–C(14)	1.462(5)	N(4)–C(24)	1.467(5)
Bond angles			
C(1)–C(7)–N(1)	119.4(3)	C(4)–C(17)–N(3)	119.2(3)
C(1)–C(7)–N(2)	124.0(3)	C(4)–C(17)–N(4)	123.9(3)
N(1)–C(7)–N(2)	116.6(3)	N(3)–C(17)–N(4)	116.8(3)
C(7)–N(1)–Si(1)	112.8(2)	C(17)–N(3)–Si(2)	114.2(2)
C(11)–N(1)–Si(1)	126.8(2)	C(21)–N(3)–Si(2)	126.6(2)
C(7)–N(1)–C(11)	119.3(3)	C(17)–N(3)–C(21)	119.0(3)
C(7)–N(2)–C(14)	122.0(3)	C(17)–N(4)–C(24)	122.0(3)

To demonstrate that the 1,4-benzenebis(amidine) compounds described above can be used in the synthesis of coordination complexes, a brief study into the application of **2** as a ligand precursor in aluminium chemistry was conducted. The reaction between the neutral amidine $1,4\text{-}C_6H_4[C\{N^iPr\}\{NH^iPr\}]_2$ (**2**) and $AlMe_2Cl$ in toluene proceeded via protonolysis of the Al–C bond to afford the bis(aluminiumchloromethyl) complex, $1,4\text{-}C_6H_4[C\{N^iPr\}_2AlMeCl]_2$ (**5**, Scheme 3). The mass spectrum and elemental analysis were consistent with two 'AlMeCl' units attached to the central bis(amidinate) ligand. The ^{1}H-NMR spectrum of **5** showed one septet for the *iso*-propyl methine hydrogen and two doublets (1:1 ratio), as predicted for a non-symmetrically substituted Al-centre and restricted rotation about the N–^{i}Pr bonds. An X-ray structural analysis of crystals of **5** confirmed the formulation as $1,4\text{-}C_6H_4[C\{N^iPr\}_2AlMeCl]_2$. However, disorder between the methyl and chloride sites prevented satisfac-

Table 5
α (°) and Δ_{CN} (Å) values for **1**, $\mathbf{1}_{(tol)}$, **2**, $\mathbf{2}_{(tol)}$, **4** and **6**

Compound	d(C–N) Å	d(C=N) (Å)	Δ_{CN} (Å)	α (°)
1a	1.334(5)	1.305(4)	0.029	80.3
1b	1.328(4)	1.320(5)	0.008	62.4
$\mathbf{1}_{(tol)}$	1.372(3)	1.274(3)	0.098	63.3
2a	1.3807(19)	1.2724(18)	0.108	66.2
2b	1.3695(19)	1.2810(2)	0.089	63.0
$\mathbf{2}_{(tol)}$	1.362(3)	1.272(2)	0.090	68.9
4	1.386(5)	1.275(5)	0.111	83.6
	1.388(5)	1.279(5)	0.109	75.6
6	1.332(4)	1.331(4)	0.001	89.3



(**5**, X = Cl; **6**, X = Me)

Scheme 3. (i) Two equivalents $AlMe_2Cl$, hexane, 12 h; (ii) two equivalents ^{n}BuLi, hexane, 2 h; (iii) two equivalents $AlMe_2Cl$, hexane, 12 h.

tory refinement of the data set, precluding a detailed discussion of bond lengths and angles.

To avoid the possibility of such disorder, the symmetrical bis(aluminiumdimethyl) compound was synthesised. Thus, a sample of **2** was deprotonated to generate the dilithio-salt in situ, [20] which reacted smoothly with $AlMe_2Cl$ to afford 1,4-$C_6H_4[C\{N^{i}Pr\}_2AlMe_2]_2$ as colourless crystals (**6**, Scheme 3). The spectroscopic data were again consistent with a bi-metallic complex, which was subsequently confirmed by X-ray analysis. The molecular structure is illustrated in Fig. 5; crystal data is summarised in Table 6 and selected bond lengths and angles are collected in Table 7.

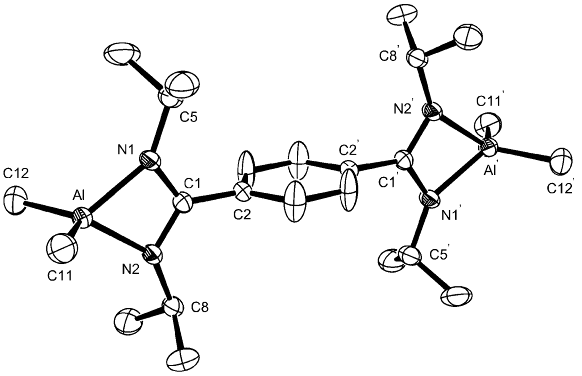


Fig. 5. Molecular structure of **6** showing 30% thermal ellipsoids. Hydrogen atoms omitted for clarity.

Table 6
Crystal data for **6**

	6
Empirical formula	$C_{24}H_{44}Al_2N_4$
Formula weight	442.59
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	10.6225(14)
b (Å)	8.7187(8)
c (Å)	16.195(2)
α (°)	90
β (°)	105.269(5)
γ (°)	90
V (Å^3)	1447.0(3)
Z	2
D_{calc} (Mg m^{-3})	1.02
Absorption coefficient (mm^{-1})	0.12
Crystal size (mm)	0.2 × 0.2 × 0.1
θ Range for data collection (°)	4.14–22.96
Reflections collected	7376
Independent reflections	1993 [$R_{int} = 0.082$]
Reflections with $I > 2\sigma(I)$	1440
Data/restraints/parameters	1993/0/136
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.066$, $wR_2 = 0.146$
R indices (all data)	$R_1 = 0.097$, $wR_2 = 0.160$
Goodness-of-fit on F^2	1.045
Largest difference peak and hole (e Å^{-3})	0.21 and −0.16

Compound **6** is monomeric, with the distorted tetrahedral aluminium atom coordinated by a dihapto-amidinate ligand and two methyl groups. The Al–N and Al–C bond lengths and angles are comparable to related aluminium amidinate species [17,21], where the bite angle of the ligand is relatively acute [N(1)–Al–N(2) = 68.86(12)°], and is compensated for by an increase in the N–Al–C angles [114.8° average]. The 'CN$_2$' fragment is symmetrically delocalised in each C–N bond [$\Delta_{CN} = 0.001$ Å] with a perpendicular arrangement of the amidinate and phenyl substituents [$\alpha = 89.3°$].

In summary, a new class of neutral, linked-bis(N,N'-dialkylamidine) ligand has been developed and the application in coordination chemistry investigated. Synthetic routes to the N–H and N–SiMe$_3$ derivatives are described, and the solid-state structure of selected representatives is discussed. It has been shown that the N–H derivative **2** may be utilised in the synthesis of di-aluminium complexes using $AlMe_2Cl$, via protonolysis of an Al–C bond, or transmetallation of the in situ generated lithium salt. Further studies into the applica-

Table 7
Selected bond lengths (Å) and angles (°) for **6**

Bond lengths	
C(1)–N(1)	1.332(4)
C(1)–N(2)	1.331(4)
C(1)–C(2)	1.492(4)
N(1)–Al	1.925(3)
N(2)–Al	1.939(3)
Al–C(11)	1.946(4)
Al–C(12)	1.943(4)
N(1)–C(5)	1.459(4)
N(2)–C(8)	1.453(4)
Bond angles	
N(1)–C(1)–N(2)	110.3(3)
C(1)–N(1)–Al	90.7(2)
C(1)–N(2)–Al	90.1(2)
N(1)–Al–N(2)	68.86(12)
C(11)–Al–N(1)	115.23(18)
C(11)–Al–N(2)	116.14(16)
C(12)–Al–N(1)	113.97(17)
C(12)–Al–N(2)	113.94(17)
C(11)–Al–C(12)	118.8(2)

Symmetry elements for **6**: $' = -x+1, -y+1, -z$.

tion of these ligands in the synthesis of molecular species and extended arrays are ongoing within the group.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 190074–190079 for compounds **1**, **1**$_{\mathbf{(tol)}}$, **2**, **2**$_{\mathbf{(tol)}}$, **4**, and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

5. Note added in proof

A new class of linked bis(amidine) molecule, and application in the synthesis of a bis(aluminium) complex was reported during the preparation of this manuscript [22].

Acknowledgements

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