

Synthesis and structures of dinuclear low-coordinate lithium and zirconium(IV) complexes derived from the diamido ligands 1,3-(CH₂N⁻C₆H₃R¹)₂C₆H₄ (R¹ = Me or Prⁱ)

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Treatment of 1,3-bis(bromomethyl)benzene with two equivalents of the appropriate compound Li[N(H)C₆H₃R¹-2,6] yielded the diamines 1,3-[CH₂N(H)C₆H₃R¹-2,6]₂C₆H₄ **1** [R¹ = Me, abbreviated as H₂(**D**)] or **2** [R = Prⁱ, abbreviated as H₂(**D'**)]. The crystalline complex [Li₂(**D'**)]₂ **3** was obtained from **2** and 2 LiBuⁿ; the analogue from **1** and 2 LiBuⁿ was an incompletely characterised oil. The binuclear, crystalline zirconium(IV) amides [{Zr(NMe₂)₃}₂(μ-**D'**)] **4**, its **D** analogue **5** and [{Zr(NMe₂)₂}₂(μ-**D**)] **6** were prepared from [{Zr(NMe₂)₃(μ-NMe₂)₂}] and H₂(**D'**) [or 2 H₂(**D'**)], H₂(**D**) and 2 H₂(**D**), respectively. The single crystal X-ray molecular structures of complexes **3** and **4** have been elucidated.

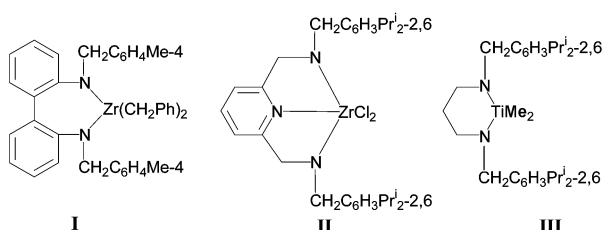
That of **3** comprises a sixteen-membered, twisted macrocyclic LiNC₅NLiNC₅N core with each of the two-coordinate lithium atoms part of the LiNLiN rhombus. The four-coordinate zirconium atoms in **4** are in an only slightly distorted tetrahedral environment, with the two Zr(NMe₂)₃ units arranged *trans* to one another across the central aromatic ring. None of **4–6**, with MAO, showed catalytic activity for ethylene polymerisation under ambient conditions.

Introduction

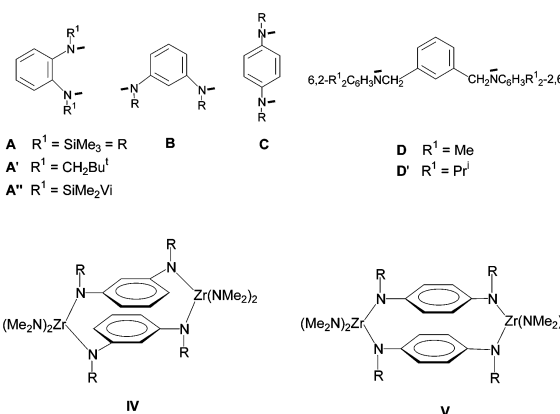
The results presented herein represent a continuation of our long-standing interest both in the chemistry of metal and metalloid amides¹ and in organic derivatives of the Group 4 metals.²

Bulky lithium amides LiNR¹R² are particularly useful reagents: as ligand transfer species and as powerful proton-abstractors, especially from acidic hydrocarbons, and as reagents for the synthesis of compounds containing C–C bonds;^{1,3} homochiral lithium amides also have a role in asymmetric synthesis.⁴

Zirconium(IV) amides, or Ti(IV) analogues, are valuable as precursors for numerous M(IV) derivatives by virtue of their weak and polar M^{δ+}–N^{δ-} bonds (M = Ti, Zr).^{1,2} Hence they are amenable both for reactions with protic species and as substrates for insertion reactions (*e.g.* of an isocyanate or carbon dioxide), with implications for their role as catalysts,^{1,2} as in the polymerisation of acrylonitrile by [Ti(NMe₂)₄].⁵ Group 4 metal complexes containing diamido ligands, such as **I**,⁶ **II**,⁷ and **III**⁸ have recently come to the fore as active olefin polymerisation procatalysts: **I** and **II** with methylaluminoxane (MAO) for both ethylene and propylene, while **III** with B(C₆F₅)₃ induced the living polymerisation of hex-1-ene.



We have extended our researches on metal amides to diamides. Relevant to the present paper are studies on the synthesis, structures and selected reactions of the crystalline lithium and zirconium complexes of the dianionic *N,N'*-disubstituted 1,2-, 1,3- and 1,4-benzenediamido ligands (**A**, **A'**, **A''**; Vi = CH=CH₂), **B** and **C**: [Li₂(μ-**A**)]₂,⁹ [Li(μ-**A**)(thf)]₂Li((μ-thf))₂, [Li(thf)₂(μ-**A**)Li(thf)], [Li(tmen)₂(μ-**A**)], [Li(μ-**A'**)(thf)]₂(μ-Li)₂, [Li(tmen)₂(μ-**A''**)], [Li(thf)₂(μ-**C**)],¹⁰ [Zr(μ-**A**)Cl₂(tmen)],¹¹ [Zr(μ-**A'**)Cl₂], [Zr(μ-**A''**)Cl(μ-Cl)(thf)]₂, [Zr(μ-**A** or μ-**A''**)NMe₂(μ-NMe₂)₂], [Zr(μ-**B**)],¹² [Zr(NMe₂)₂(μ-**B**)₂] (**IV**), [Zr(NMe₂)₃]₂(μ-**C**) and [Zr(NMe₂)₂(μ-**C**)₂] (**V**); throughout R = SiMe₃. The above Zr-**A''** compounds (like **IV** and **V**¹²) were shown to provide polyethylene of high average molecular weight when treated with MAO.¹¹

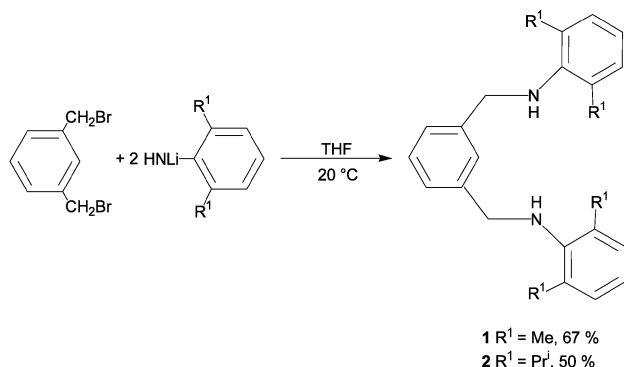


A previous collaboration between the Sussex and Greensboro groups related to aspects of the chemistry of compounds [YbCp^x]₂ [Cp^x = η⁵-C₅H₃(R¹)-1-{CMe₂(CH₂)_nC₅H₄N-2}-3; R¹ = H or R and n = 0 or 1].¹³

Results and discussion

The principal objective of the present study was to investigate the effects of a less rigid diamido ligand backbone than those of **A–C** on the preparation, structure and properties of lithium and zirconium derivatives. Hence attention focused on the ligands **D** and **D'**. The latter, in particular, resembles that present in **II**,⁷ but without incorporating the nitrogen heteroatom.

The diamines **H₂(D)** **1** and **H₂(D')** **2** were prepared (Scheme 1)



Scheme 1 Synthesis of compounds **1** and **2**.

by the metathetical reaction between 1,3-bis(bromomethyl)-benzene and two equivalents of the appropriate 2,6-dialkylbenzeneamidolithium (prepared *in situ* from 2,6-R¹₂C₆H₃NH₂ and LiBuⁿ). They were purified by column chromatography (**1**) or recrystallisation from light petroleum (**2**), as an orange oil (**1**) or a cream powder (**2**) and were characterised by NMR spectroscopy in solution, mass spectrometry and for **2** micro-analysis.

Treatment of **2** with two equivalents of *n*-butyllithium furnished the hydrocarbon-soluble, pyrophoric, colourless, crystalline macrocycle [Li₂(D')]₂ **3**. A similar experiment using **1** and 2 LiBuⁿ yielded a pyrophoric, labile compound, which was not adequately characterised.

The molecular structure of **3** was investigated both in the crystal by X-ray crystallography and in toluene solution by NMR spectroscopy. The C₂-symmetric crystalline **3** (Fig. 1) has

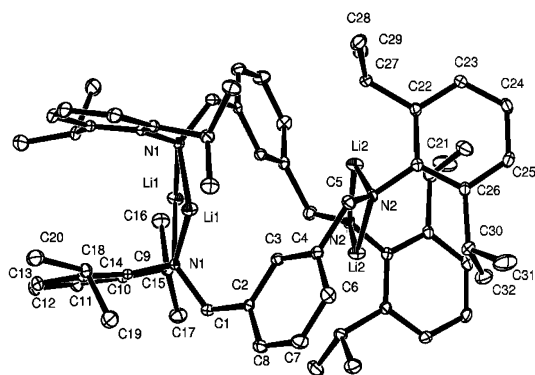


Fig. 1 Molecular structure of compound **3**.

a sixteen-membered twisted macrocyclic $\overline{\text{LiNC}_5\text{NLiNC}_5\text{N}}$ core; selected geometric parameters are in Table 1. Each of these two lithium atoms is part of a $\overline{\text{LiNLiN}}$ rhombus, with the angle at the lithium atoms [104.1(2)° at Li1 and 106.3(2)° at Li2] wider than those at the nitrogen atoms [75.1(2)° at N1 and 73.2(2)° at N2]. The inter-planar angles between Li1–N1–Li1' and Li1–N1'–Li1' or Li2–N2–Li2' and Li2–N2'–Li2' are 9.2 or 7.9°, respectively. The *N*-centred 2,6-diisopropylphenyl rings are orthogonal to the macrocycle, with average CNCC torsion angles of 90.1°.

Table 1 Selected bond lengths [Å] and angles [°] for complex **3**

Li(1)–N(1)	1.909(4)	Li(1)–N(1')	2.013(4)
Li(2)–N(2)	1.937(4)	Li(2)–N(2')	1.988(4)
Li(1) ⋯ Li(1')	2.393(8)	Li(2) ⋯ Li(2')	2.341(8)
N(1)–C(9)	1.413(3)	N(1)–C(1)	1.467(3)
N(2)–C(21)	1.422(3)	N(2)–C(5)	1.470(3)
N(1)–Li(1)–N(1')	104.1(2)	N(2)–Li(2)–N(2)	106.3(2)
Li(1)–N(1)–Li(1')	75.1(2)	Li(2)–N(2)–Li(2')	73.2(2)

The lithium atoms are in a two-coordinate environment and range from 1.909(4) to 2.013(4) Å for Li2–N1 and Li1–N1', respectively. There are some close (< 2.80 Å) Li ⋯ C contacts (Fig. 2), but their relative spatial distribution is such that they are unlikely to have agostic implications.

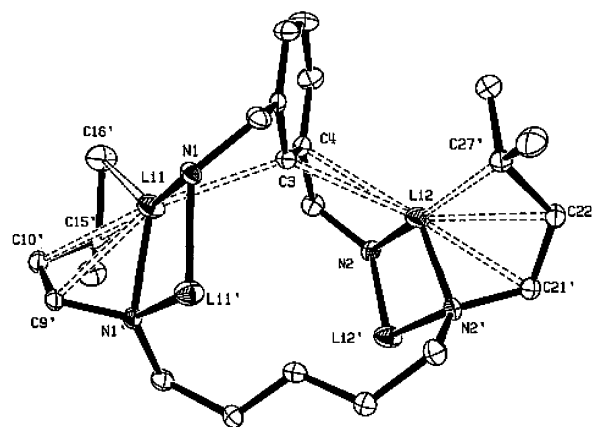
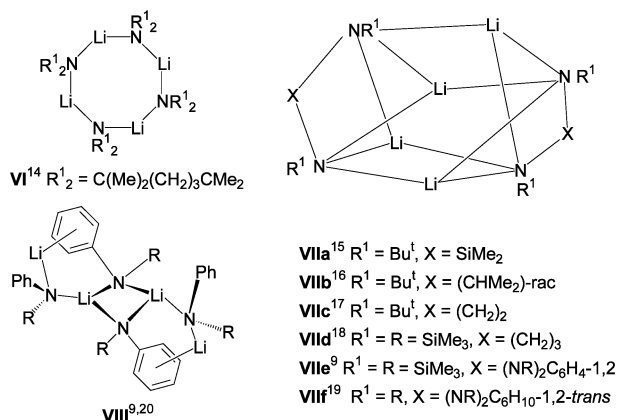


Fig. 2 Li environments showing shortest Li ⋯ C (< 2.80 Å) contacts for compound **3**: Li1 ⋯ C3 (2.649 Å), Li1 ⋯ C9' (2.378 Å), Li1 ⋯ C10' (2.629 Å), Li1 ⋯ C15' (2.579 Å), Li1 ⋯ C16' (2.786 Å), Li2 ⋯ C3 (2.652 Å), Li2 ⋯ C4 (2.726 Å), Li2 ⋯ C21' (2.477 Å), Li2 ⋯ C22' (2.707 Å), Li2 ⋯ C27' (2.667 Å).

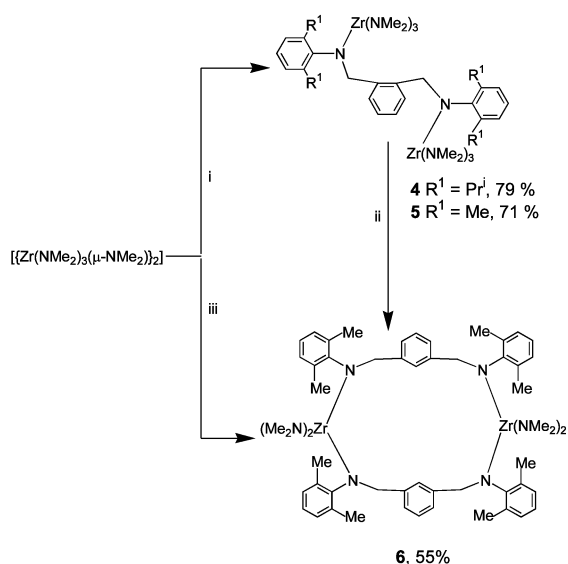
Although there appear to be eight previously published structures for tetranuclear lithium amides free from a neutral coligand, the structure of **3** is distinct and different from each. Complex **3** shares with just one of them **VI**¹⁴ the presence of two-coordinate lithium atoms, each bound to two nitrogen atoms. The presence of a pair of $\overline{\text{LiNLiN}}$ rhombi is a feature not only of complex **3** but also of the six complexes of the general formulae **VII**;^{15–19} however, in the latter each three-coordinate lithium atom is bound to three adjacent nitrogen atoms. Complex **VIII** also has two such Li₂ environments and a single but puckered [torsion angle 14.6(4)°] $\overline{\text{LiNLiN}}$ ring, and otherwise is unique.^{9,20} The average Li–N distance of 1.96 Å in **3** is shorter than in **VI** [2.00(2) Å],¹⁴ **VII** [average Li–N/ Å: 2.01 a,¹⁵ 2.06 b,¹⁶ 2.01 c,¹⁷ 2.06 d,¹⁸ 2.09 e,⁹ 2.06 f¹⁹] or **VIII** [2.12 Å for the central Li atoms].⁹ In the $\overline{\text{LiNLiN}}$ rings, as in **3**, the mean of angles subtended at the nitrogen atoms are narrower than those at the lithium atoms [average at N and Li: 68.4 and 101.3° (**VIIa**),¹⁵ 68.8 and 111° (**VIIb**),¹⁶ 70.6 and 109° (**VIIc**),¹⁷ 70.7 and 108.5° (**VIIId**),¹⁸ 82.5 and 108.7° (**VIIe**)⁹ and 71.7 and 108.7° (**VIIIf**)¹⁹].

The ¹H and ¹³C{¹H} NMR spectra of **3** in toluene-*d*₈ displayed only one set of Prⁱ resonances and a singlet at δ 9.03 attributed to C(3)H and a broad feature at δ 0.8 (*w*_{1/2} = 112.5 Hz) assigned to CH(CH₃)₂. At 203 K, the latter split into a 1 : 1 : 1 : 1 multiplet and CH(CH₃)₂ protons give rise to four septets, consistent with the solid state structure (there are 8 Prⁱ groups of which 4 are unique). In addition, the CH₃ signal shifted from δ 4.34 to δ 4.93 at 203 K. The ⁷Li{¹H} NMR spectrum at 293 K showed a sharp signal at δ 1.84. From a heteronuclear ⁷Li{¹H} study, it is evident that at ambient temperature the ⁷Li nucleus interacted with both HCMe₂ and HC(3) ¹H nuclei, the ⁷Li



signal enhancements being 24 and 6% respectively. The $^1J[^{13}\text{C}(3)-^1\text{H}]$ was smaller for **3** (143 Hz) than in the parent diamine **2** (154 Hz). These features indicate that the close Li \cdots C contacts observed in the solid state may well also be present in solution.

The reactions between $[\{\text{Zr}(\text{NMe}_2)_3(\mu\text{-NMe}_2)\}_2]^{21}$ and the diamine H₂(**D**) **1** or H₂(**D'**) **2**, yielding the binuclear zirconium(IV) amides **4–6** are shown in Scheme 2. In the case of **1**, the



Scheme 2 Synthesis of compounds **4–6**. Reagents and conditions: (i) 1 equiv. of **1** or **2** in toluene at 20 °C; (ii) for R¹ = Me, 1 equiv. of **1** in toluene at 20 °C; (iii) 2 equiv. of **1** in toluene at 20 °C.

outcome was stoichiometry-dependent. Thus, using a 1 : 1 molar ratio of reagents, the product (i in Scheme 2) was the acyclic zirconium compound **5**; whereas from 2H₂(**D**), the macrocyclic complex **6** was obtained (iii in Scheme 2). By contrast, when employing a large excess of the bulkier diamine **2**, the acyclic zirconium(IV) amide **4** (i in Scheme 2), an analogue of **5**, was invariably formed. Presumably steric hindrance precluded a further reaction of **4** with more H₂(**D'**), as also evident from ^1H NMR spectroscopic data on **4** and **5**, *vide infra*.

The molecular structure of the acyclic binuclear zirconium(IV) amide **4** is illustrated in Fig. 3 and selected geometric parameters are listed in Table 2. The two zirconium atoms (each bound to three NMe₂ groups) are bridged by a $[\text{N}(\text{C}_6\text{H}_3\text{Pr}^i\text{-2,6})\text{CH}_2\text{C}_2\text{CH}]$ moiety; the three internal carbon atoms C14, C15 and C18 are members of the central benzene ring. The two Zr(NMe₂)₃ units are arranged *trans* to one another. The Zr–NMe₂ bond lengths range from 2.019(8) to 2.057(7) Å and are slightly shorter than the Zr–NC₆H₃Prⁱ-2,6 bonds of 2.093(7) and 2.098(7) Å. This is consistent with the previously observed

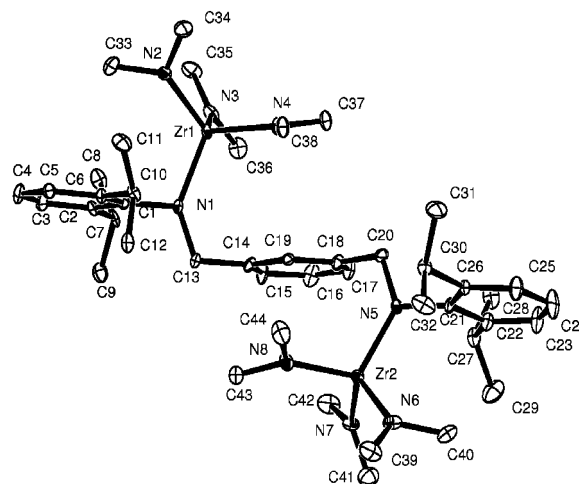


Fig. 3 Molecular structure of compound **4**.

Table 2 Selected bond lengths [Å] and angles [°] for complex **4**

Zr(1)–N(1)	2.098(7)	Zr(1)–N(2)	2.024(7)
Zr(1)–N(3)	2.057(7)	Zr(1)–N(4)	2.029(7)
Zr(2)–N(5)	2.093(7)	Zr(2)–N(6)	2.019(8)
Zr(2)–N(7)	2.043(7)	Zr(2)–N(8)	2.025(7)
N(1)–C(1)	1.447(10)	N(1)–C(13)	1.468(11)
N(5)–C(21)	1.437(10)	N(5)–C(20)	1.483(11)
N(1)–Zr(1)–N(2)	114.0(3)	N(1)–Zr(1)–N(3)	112.2(3)
N(1)–Zr(1)–N(4)	110.0(3)	N(2)–Zr(1)–N(3)	104.8(3)
N(2)–Zr(1)–N(4)	108.2(3)	N(3)–Zr(1)–N(4)	107.2(3)
N(5)–Zr(2)–N(6)	113.6(3)	N(5)–Zr(2)–N(7)	112.4(3)
N(5)–Zr(2)–N(8)	111.6(3)	N(6)–Zr(2)–N(7)	105.1(3)
N(6)–Zr(2)–N(8)	106.1(3)	N(7)–Zr(2)–N(8)	107.6(3)
Zr(1)–N(1)–C(1)	108.5(5)	Zr(1)–N(1)–C(13)	140.1(5)
C(1)–N(1)–C(13)	111.4(7)	Zr(2)–N(5)–C(20)	133.8(5)
Zr(2)–N(5)–C(21)	115.8(6)	C(20)–N(5)–C(21)	110.4(7)

trend in other Zr^{IV}(NMe₂)(NAr) compounds: in $[\{\text{Zr}(\text{A or A}')\text{NMe}_2(\mu\text{-NMe}_2)\}_2]$ the terminal Zr–NMe₂ bonds and lengths are 2.037(2) or 2.021(5) Å compared with mean Zr–N_{aryl} bond lengths of 2.107 or 2.114 Å, respectively;¹¹ while in **IV** and **V** the corresponding values are 2.031(2) or 2.026(2) Å and 2.094(2) or 2.086(2) Å.¹² The four-coordinate zirconium atoms are in an only slightly distorted tetrahedral environment, the N–Zr–N' angles ranging from 104.8(3) to 114.0(3)°, the angles to NC₆H₃Prⁱ-2,6 being the widest. Each nitrogen atom is in a distorted trigonal planar environment, the Zr–N–CH₂ angle being the widest, 140.1(5) for Zr1 and 133.8(5)° for Zr2. It is interesting that while **4** is a monomer, $[\{\text{Zr}(\text{NMe}_2)_3(\mu\text{-NMe}_2)\}_2]$ is a dimer with the Zr atoms in a distorted trigonal bipyramidal environment, the terminal equatorial and axial bond lengths being 2.050(5) and 2.104(5) Å, respectively.²¹

We propose, partly by analogy with structures of crystalline **4**, **IV**¹² and **V**, that **D** functions as a bridging ligand not only in **4** but also in **6** and thus differs from the chelating behaviour of the diamido ligands in **I**⁶ or **II**.⁷

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in toluene-d₈ or C₆D₆ (**6**) at 293 K were consistent with the structures shown in Scheme 2. The ^1H NMR spectra of the 2,6-dimethylphenylamides **5** and **6** showed singlets for the NMe₂ protons, indicative of there being unhindered rotation about the Zr–NMe₂ bonds on the NMR time scale. By contrast, the spectrum of the 2,6-diisopropylphenylamides **4** at ambient temperature showed the HCMe₂ signals as two separate 1 : 1 doublets.

Attempts to convert any of the amides **4–6** to chlorides by replacing NMe₂ groups by chlorides, using an excess of trimethyl(chloro)silane proved unsuccessful. Likewise none of **4–6**, with MAO, proved to be a catalyst for the polymerisation of ethylene under ambient conditions.

Experimental

General procedures

All manipulations were carried out under argon or dinitrogen (**1**, **2**) in flamed Schlenk-type glassware on a dual manifold Schlenk line. Solvents were dried over sodium wire. Hydrocarbons (pentane, hexane and toluene) or diethyl ether and tetrahydrofuran solvents were distilled from sodium/potassium alloy or sodium benzophenone, respectively, and stored over sodium mirrors. Deuteriated solvents (benzene- d_6 , toluene- d_8 and thf- d_8) were distilled and degassed prior to use. 2,6-Diisopropylaniline was purchased from Aldrich and was freshly vacuum-distilled. All other reagents (Aldrich) were used without further purification. The compound $[\{Zr(NMe_2)_3(\mu-NMe_2)\}_2]$ was prepared as described in the literature.²¹ NMR spectra were recorded on Bruker DPX 300 or AMX 500 instruments at 293 K unless otherwise stated, and were referenced internally (1H , ^{13}C) to residual solvent resonances or externally (7Li). The electron impact mass spectra were recorded on solid samples using a Kratos MS 80 or (**1**, **2**) a Fisons WG-Autospec instrument. Elemental analyses were carried out by Medac Ltd (UK) (**4-6**) or (**2**) Desert Analytics, Tucson, Arizona.

Preparations

1,3-Bis(2',6'-dimethylphenylaminomethyl)benzene 1. n-Butyllithium (18.9 cm³ of a 2.0 mol dm⁻³ solution in hexane, 37.9 mmol) was added to 2,6-dimethylaniline (2.77 g, 37.9 mmol) in thf (75 cm³) at 0 °C with stirring. The mixture was brought to room temperature and was stirred for 30 min, then transferred into a dropping funnel, from which it was added dropwise to 1,3-bis(bromomethyl)benzene (5.00 g, 18.9 mmol) in thf (100 cm³) at 0 °C. The mixture was set aside at room temperature for ca. 48 h. Water (100 cm³) was added and the mixture was extracted with diethyl ether (2 × 50 cm³). The ethereal layer was dried and volatiles were removed *in vacuo*. Purification was carried out using an alumina chromatography column with light petroleum (bp 40–60 °C) as eluant. Removal of volatiles from the eluate yielded **1** (4.37 g, 67.1%) as an orange oil. 1H NMR (CDCl₃): δ 2.40 (s, 12 H, CH₃), 3.29 (s, 2 H, NH), 4.29 (s, 4 H, CH₂), 7.45–6.90 (m, 10 H, aromatic). MS (m/z): 344 [**1**]⁺.

1,3-Bis(2,6-diisopropylphenyl)aminomethyl)benzene 2. Using a procedure similar to that described for **1** [from n-butyllithium (15.2 cm³ of a 2.5 mol dm⁻³ solution in hexane, 37.9 mmol), 2,6-diisopropylaniline (7.0 cm³, 37.9 mmol), thf (100 cm³) and 1,3-bis(bromomethyl)benzene (5.00 g, 18.9 mmol)], there was obtained a light orange oil which, upon crystallisation from a light petroleum solution, yielded **2** (4.29 g, 50%) (Found: C, 83.75; H, 9.60; N, 6.01. C₃₂H₄₄N₂ requires C, 84.2; H, 9.71; N, 6.31%). 1H NMR (CDCl₃): δ 1.15 [d, $^3J(H-H) = 6.85$, 24 H, CH₃], 3.07 [s, 2 H, NH], 3.29–3.19 [sept, $^3J(H-H) = 6.85$, 4 H, CH], 3.97 [s, 4 H, CH₂], 7.27–7.01 [m, $^1J(H-^{13}C(3)) = 154$ Hz, 10 H, aromatic]. $^{13}C\{^1H\}$: δ 24.8 (CH₃), 28.3 (CH), 56.6 (CH₂), 124.2, 124.7, 127.4, 127.9, 129.4, 141.1, 143.3 and 143.4 (aromatic). MS (m/z): 456 [**2**]⁺.

The dinuclear macrocyclic lithium amide 3. n-Butyllithium (1.6 cm³ of a 1.6 mol dm⁻³ solution in hexane, 2.59 mmol) was added dropwise by syringe to the 1,3-di(arylphenylaminomethyl)benzene **2** (0.591 g, 1.30 mmol) in hexane (10 cm³) at 0 °C. The mixture was brought to room temperature with stirring for 2 h, yielding a white precipitate and a green supernatant liquor. The mixture was filtered and the precipitate was dissolved in warm (80 °C) toluene (15 cm³). Cooling to room temperature afforded colourless crystals of **3** (0.54 g, 88%). 1H NMR (toluene- d_8): δ 0.8 [br s, $w_{1/2} = 112.5$ Hz, 24 H, CH₃], 3.26 [sept, $^3J(H-H) = 6.5$, 4 H, CH], 4.34 [s, 4 H, CH₂], 6.88–7.08 [m, $^1J(H-^{13}C(3)) = 143$, 9 H, aromatic], 9.03 [s, 1 H, *o*-CH];

1H NMR (toluene- d_8 , 203 K): δ 0.31 [d, $^3J(H-H) = 6.5$, 6 H, CH₃], 0.61 [d, $^3J(H-H) = 6.5$, 6 H, CH₃], 1.23 [d, $^3J(H-H) = 6.5$, 6 H, CH₃], 1.37 [d, $^3J(H-H) = 6.5$, 6 H, CH₃], 3.13 [sept, $^3J(H-H) = 6.5$, 1 H, CH], 3.22 [sept, $^3J(H-H) = 6.5$, 1 H, CH], 3.68 [sept, $^3J(H-H) = 6.5$, 1 H, CH], 3.79 [sept, $^3J(H-H) = 6.5$ Hz, 1 H, CH], 4.93 [s, 4 H, CH₂], 6.94–7.11 [m, 9 H, aromatic], 9.11 [s, 1 H, CH]; $^{13}C\{^1H\}$ NMR (toluene- d_8): δ 25.0 [br, $w_{1/2} = 187$ Hz, CH₃], 27.8 (CH), 63.2 (CH₂), 120.0, 123.0, 124.4, 127.4, 132.4, 146.8, 148.2 and 153.7 (aromatic); $^7Li\{^1H\}$ NMR (toluene- d_8): δ 1.84 (br, $w_{1/2} = 97$ Hz).

The dinuclear open-chain zirconium(IV) amide 4. The diamine **2** (0.844 g, 1.85 mmol) in toluene (10 cm³) was added dropwise during ca. 10 min to a solution of $[\{Zr(NMe_2)_3(\mu-NMe_2)\}_2]$ (0.59 g, 1.85 mmol) in toluene (30 cm³) at 0 °C. The deep yellow mixture was stirred at room temperature for ca. 20 h, whereafter solvent was removed *in vacuo* and pentane (30 cm³) was added. The mixture was filtered. The filtrate was concentrated (to ca. 10 cm³) and set aside at –35 °C. Three crops of the pale yellow, crystalline complex **4** (1.15 g, 79%) (Found: C, 58.2; H, 8.39; N, 12.51. C₄₄H₇₄N₈Zr₂ requires C, 58.9; H, 8.31; N, 12.48%) were isolated by filtration and drying *in vacuo*. 1H NMR (toluene- d_8): δ 1.12 [d, $^3J(H-H) = 6.5$, 12 H, CCH₃], 1.21 [d, $^3J(H-H) = 6.5$, 12 H, CCH₃], 2.75 [s, 36 H, NCH₃], 3.59 [sept, $^3J(H-H) = 6.5$ Hz, 4 H, CH], 4.48 [s, 4 H, CH₂], 7.04–7.21 [m, 10 H, aromatic]; $^{13}C\{^1H\}$ NMR (toluene- d_8): δ 24.6 and 25.7 (CCH₃), 28.1 (CH), 41.7 (NCH₃), 61.6 (CH₂), 124.3, 125.8, 126.2, 128.8, 131.7, 141.2, 144.0 and 148.1 (aromatic C). MS (m/z (%), assignment): 855 (53, [M – Pr]⁺); 812 (39, [M – 2Pr]⁺).

The dinuclear open-chain zirconium(IV) amide 5. Using a procedure similar to that described for **4** [from the diamine **1** (0.31 g, 0.9 mmol) and $[\{Zr(NMe_2)_3(\mu-NMe_2)\}_2]$ (0.48 g, 0.9 mmol) in toluene (6 cm³)] there were obtained two crops of yellow crystals of **5** (0.53 g, 71%) (Found: C, 57.55; H, 6.82; N, 13.47. C₄₀H₅₈N₈Zr₂ requires C, 57.7; H, 6.97; N, 13.45%), mp 112 °C. 1H NMR (toluene- d_8): δ 2.19 [s, 12 H, CCH₃], 2.74 [s, 36 H, NCH₃], 4.35 [s, 4 H, CH₂], 6.81 [t, $^3J(H-H) = 7.37$ Hz, 3 H, aromatic], 6.92–7.06 [m, 7 H, aromatic]; $^{13}C\{^1H\}$ NMR (toluene- d_8 , 293K): δ 18.8 (CCH₃), 41.0 (NCH₃), 58.4 (CH₂), 123.6, 125.8, 127.7, 128.4, 130.3, 136.7, 141.9 and 148.8 (aromatic). MS (m/z (%), assignment): 344 (100, [**1**]⁺).

The dinuclear macrocyclic zirconium(IV) amide 6. Using a procedure similar to that described for **4** [from the diamine **1** (1.48 g, 4.32 mmol) and $[\{Zr(NMe_2)_3(\mu-NMe_2)\}_2]$ (1.16 g, 2.16 mmol) in toluene (15 cm³)] there were obtained two crops of yellow crystals of **6** (1.03 g, 55%) (Found: C, 64.2; H, 7.16; N, 10.88. C₂₈H₃₈N₄Zr requires C, 64.4; H, 7.34; N, 10.73%), mp 125–126 °C. 1H NMR (toluene- d_8): δ 2.12 [s, 12 H, CCH₃], 2.62 [s, 12 H, NCH₃], 4.61 [s, 4 H, CH₂], 6.56 [s, 1 H, aromatic], 6.85–7.01 [m, 9 H, aromatic]; $^{13}C\{^1H\}$ NMR (toluene- d_8): δ 19.5 (CCH₃), 41.6 (NCH₃), 56.5 (CH₂), 124.2, 128.0, 128.9, 129.3, 130.9, 136.0, 140.6 and 147.6 (aromatic). MS (m/z (%), assignment): 344 (100, [**1**]⁺).

Crystallography

Data sets for **3** and **4** were collected on an Enraf-Nonius CAD4 diffractometer at 173 K using monochromated Mo- $K\alpha$ radiation. A single crystal was coated in mineral oil and cooled in a stream of nitrogen gas. Corrections for absorption were made using ψ -scan measurements. Structure solutions were made using SHELXS-86.²² Refinement was based on F^2 , with H atoms in riding mode, using SHELXL-97²³ with $U_{iso}(H)$ of 1.2 $U_{eq}(C)$ or 1.5 $U_{eq}(C)$ for methyl groups. Further details for **3** and **4** are found in Table 3.

CCDC reference numbers 187959 (**3**) and 187960 (**4**).

See <http://www.rsc.org/suppdata/dt/b2/b206508h/> for crystallographic data in CIF or other electronic format.

Table 3 Crystal data and refinement for complexes **3** and **4**

	3	4
Formula	C ₆₄ H ₈₄ Li ₄ N ₄	C ₄₄ H ₇₄ N ₈ Zr ₂
Formula weight	937.1	897.5
Crystal system	Monoclinic	Triclinic
Space group	C2/c (no.15)	P $\bar{1}$ (no.2)
<i>a</i> /Å	21.045(6)	11.315(4)
<i>b</i> /Å	15.874(3)	12.706(6)
<i>c</i> /Å	18.651(3)	18.040(7)
α /°	90	75.53(4)
β /°	115.79(2)	77.94(3)
γ /°	90	84.97(3)
<i>U</i> /Å ³	5610(2)	2454(2)
μ /mm ⁻¹	0.06	0.46
<i>Z</i>	4	2
Unique reflections, <i>R</i> _{int}	3688, 0.017	6799
Reflections with <i>I</i> > 2 σ (<i>I</i>)	2564	4020
Final <i>R</i> indices (for <i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.048, <i>wR</i> ₂ = 0.104	<i>R</i> ₁ = 0.068, <i>R</i> _w = 0.139
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.079, <i>wR</i> ₂ = 0.118	<i>R</i> ₁ = 0.136, <i>wR</i> ₂ = 0.168

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References

- M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, in *Metal and Metalloid Amides*, Horwood-Wiley, Chichester, 1980.
- D. J. Cardin, M. F. Lappert and C. L. Raston, *Chemistry of Organo-zirconium and -hafnium compounds*, Horwood-Wiley, Chichester, 1986.
- (a) B. J. Wakefield, *Best Synthetic Methods: Organolithium Methods*, Academic Press, London, 1988; (b) L. Brandsma and H. Verkuijsse, *Preparative Polar Organometallic Chemistry 1*, Springer, Berlin, 1987; (c) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1624; (d) G. Boche, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 277; (e) V. Snieckus, *Chem. Rev.*, 1990, **90**, 879; (f) A. M. Sapse, P. v. R. Schleyer (Editors), *Lithium Chemistry*, Wiley, New York, 1994.
- (a) P. J. Cox and N. S. Simpkins, *Tetrahedron Asymmetry*, 1991, **2**, 1; (b) P. Beak, A. Basu, D. J. Gallagher, Y. S. Park and S. Thayumanavan, *Acc. Chem. Res.*, 1996, **29**, 552; (c) D. Hoppe and T. Hense, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2282; P. O'Brien, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1439; P. O'Brien, *J. Chem. Soc., Perkin Trans. 1*, 2001, 95.
- A. D. Jenkins, M. F. Lappert and R. C. Srivastava, *Eur. Polym. J.*, 1971, **7**, 289.
- F. G. N. Cloke, T. J. Geldbach, P. B. Hitchcock and J. B. Love, *J. Organomet. Chem.*, 1996, **506**, 343.
- F. Guérin, D. H. McConville and J. J. Vittal, *Organometallics*, 1996, **15**, 5586.
- J. D. Scollard and D. H. McConville, *J. Am. Chem. Soc.*, 1996, **118**, 10008.
- S. Daniele, C. Drost, B. Gehrhus, S. M. Hawkins, P. B. Hitchcock, M. F. Lappert, P. G. Merle and S. G. Bott, *J. Chem. Soc., Dalton Trans.*, 2001, 3179.
- L. J.-M. Pierssens, D. Phil Thesis, University of Sussex, 1997.
- S. Daniele, P. B. Hitchcock, M. F. Lappert and P. G. Merle, *J. Chem. Soc., Dalton Trans.*, 2001, 13.
- S. Daniele, P. B. Hitchcock and M. F. Lappert, *Chem. Commun.*, 1999, 1909.
- J. R. van den Hende, P. B. Hitchcock, M. F. Lappert and T. A. Nile, *J. Organomet. Chem.*, 1994, **472**, 79.
- M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers and R. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302.
- D. J. Brauer, H. Bürger and G. R. Liewald, *J. Organomet. Chem.*, 1984, **308**, 119.
- M. G. Gardiner and C. L. Raston, *Inorg. Chem.*, 1995, **34**, 4206.
- M. G. Gardiner and C. L. Raston, *Inorg. Chem.*, 1996, **35**, 4047.
- K. W. Hellmann, A. Bergner, L. H. Gade, I. J. Scowen and M. McPartlin, *J. Organomet. Chem.*, 1999, **573**, 156.
- J.-F. Li, L.-H. Weng, X.-H. Wei and D.-S. Liu, *J. Chem. Soc., Dalton Trans.*, 2002, 1401.
- F. Antolini, P. B. Hitchcock, M. F. Lappert and P. G. Merle, *Chem. Commun.*, 2000, 1301.
- M. H. Chisholm, C. E. Hammond and J. C. Huffman, *Polyhedron*, 1988, **7**, 2515.
- G. M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structures, University of Göttingen, 1986.
- G. M. Sheldrick SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.