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FULL PAPER

Synthesis and structures of dinuclear low-coordinate lithium and zirconium(IV) complexes derived from the diamido ligands 1,3-($CH_2\bar{N}C_6H_3R^1{}_2)_2C_6H_4$ (R^1 = Me or Pr^i)

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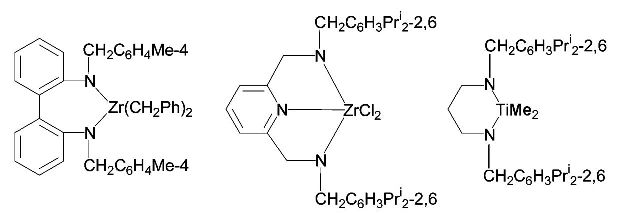
Treatment of 1,3-bis(bromomethyl)benzene with two equivalents of the appropriate compound Li[N(H)$C_6H_3R^1{}_2$-2,6] yielded the diamines 1,3-[CH_2N(H)$C_6H_3R^1{}_2$-2,6]$_2C_6H_4$ **1** [R^1 = Me, abbreviated as H_2(**D**)] or **2** [R = Pr^i, abbreviated as H_2(**D′**)]. The crystalline complex [Li_2(**D′**)]$_2$ **3** was obtained from **2** and 2 $LiBu^n$; the analogue from **1** and 2 $LiBu^n$ was an incompletely characterised oil. The binuclear, crystalline zirconium(IV) amides [{Zr(NMe_2)$_3$}$_2$(μ-**D′**)] **4**, its **D** analogue **5** and [{Zr(NMe_2)$_2$}$_2$(μ-**D**)$_2$] **6** were prepared from [{Zr(NMe_2)$_3$(μ-NMe_2)}$_2$] and H_2(**D′**) [or 2 H_2(**D′**)], H_2(**D**) and 2 H_2(**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 $\overline{LiNC_5NLiNC_5N}$ core with each of the two-coordinate lithium atoms part of the $\overline{LiNLiN}$ rhombus. The four-coordinate zirconium atoms in **4** are in an only slightly distorted tetrahedral environment, with the two Zr(NMe_2)$_3$ 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 amides[1] and in organic derivatives of the Group 4 metals.[2]

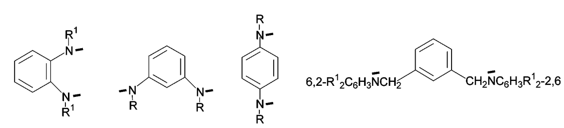
Bulky lithium amides $LiNR^1R^2$ are particularly useful reagents: as ligand transfer species and as powerful proton-abstractors, especially from acidic hydrocarbons, and as reagents for the synthesis of compounds containing C–C bonds;[1,3] homochiral lithium amides also have a role in asymmetric synthesis.[4]

Zirconium(IV) amides, or Ti(IV) analogues, are valuable as precursors for numerous M(IV) derivatives by virtue of their weak and polar $M^{\delta+}$–$N^{\delta-}$ 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(NMe_2)$_4$].[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(C_6F_5)$_3$ induced the living polymerisation of hex-1-ene.

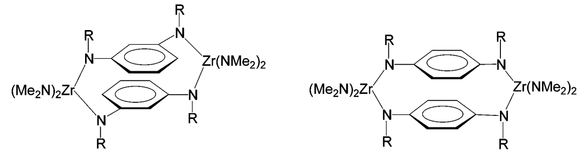


I **II** **III**

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=CH_2), **B** and **C**: [Li_2(μ-**A**)]$_2$,[9] [{Li(μ-**A**)(thf)}$_2${Li((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(**A**)Cl_2(tmen)],[11] [Zr(**A′**)Cl_2], [{Zr(**A″**)Cl(μ-Cl)(thf)}$_2$], [{Zr(**A** or **A″**)NMe_2(μ-NMe_2)}$_2$], [{Zr(NMe_2)$_3$}$_2$(μ-**B**)],[12] [{Zr(NMe_2)}$_2$(μ-**B**)$_2$] (**IV**), [{Zr(NMe_2)$_3$}$_2$(μ-**C**)] and [{Zr(NMe_2)}$_2$(μ-**C**)$_2$] (**V**); throughout R = $SiMe_3$. 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 R^1 = $SiMe_3$ = R **B** **C** **D** R^1 = Me
A′ R^1 = CH_2Bu^t **D′** R^1 = Pr^i
A″ R^1 = $SiMe_2Vi$



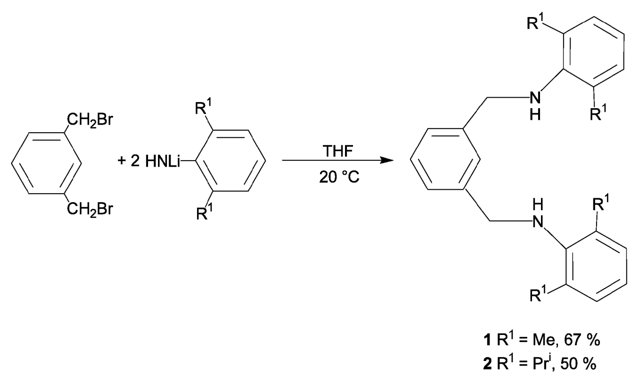
IV **V**

A previous collaboration between the Sussex and Greensboro groups related to aspects of the chemistry of compounds [Yb$Cp^x{}_2$] [Cp^x = η^5-C_5H_3(R^1)-1-{$CMe_2(CH_2)_nC_5H_4$N-2}-3; R^1 = 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 H_2(**D**) **1** and H_2(**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-$R^1{}_2C_6H_3NH_2$ and $LiBu^n$). 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** microanalysis.

Treatment of **2** with two equivalents of n-butyllithium furnished the hydrocarbon-soluble, pyrophoric, colourless, crystalline macrocycle [Li_2(**D′**)]$_2$ **3**. A similar experiment using **1** and 2 $LiBu^n$ 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 C_2-symmetric crystalline **3** (Fig. 1) has

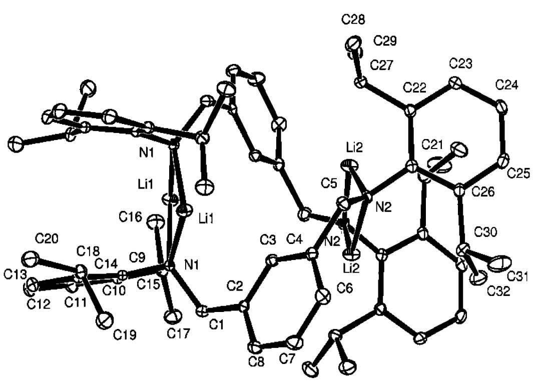


Fig. 1 Molecular structure of compound **3**.

a sixteen-membered twisted macrocyclic $\overline{LiNC_5NLiNC_5N}$ core; selected geometric parameters are in Table 1. Each of these two lithium atoms is part of a $\overline{LiNLiN}$ 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(l)–N(l)	1.909(4)	Li(l)–N(1)′	2.013(4)
Li(2)–N(2)	1.937(4)	Li(2)–N(2)′	1.988(4)
Li(l) ··· Li(l)′	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.

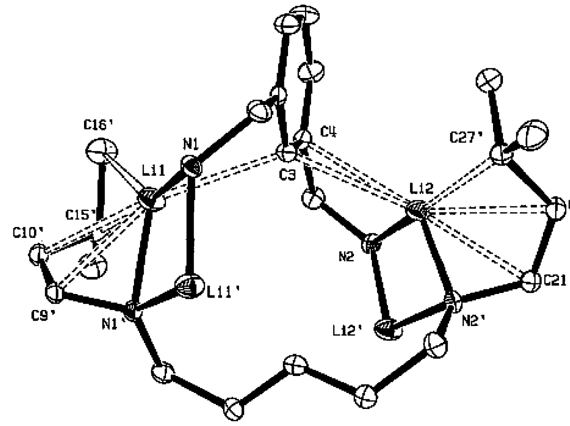
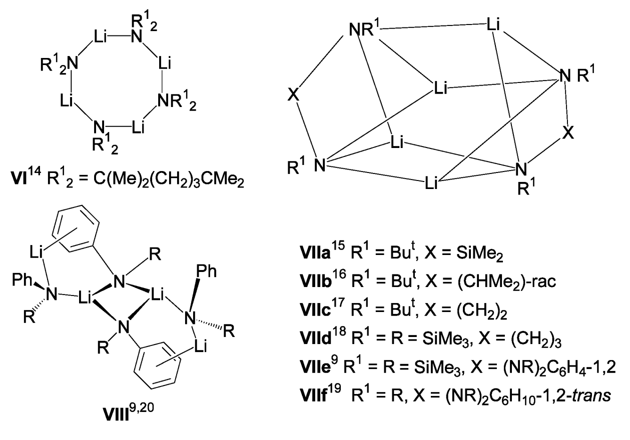


Fig. 2 Li environments showing shortest Li ··· C (< 2.80 Å) contacts for compound **3**: Li1 ··· C3 (2.649 Å), Li1 ··· C9′ (2.378 Å), Li1 ··· C10′ (2.629 Å), Li1 ··· C15′ (2.579 Å), Li1 ··· C16′ (2.786 Å), Li2 ··· C3 (2.652 Å), Li2 ··· C4 (2.726 Å), Li2 ··· C21′ (2.477 Å), Li2 ··· C22′ (2.707 Å), Li2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

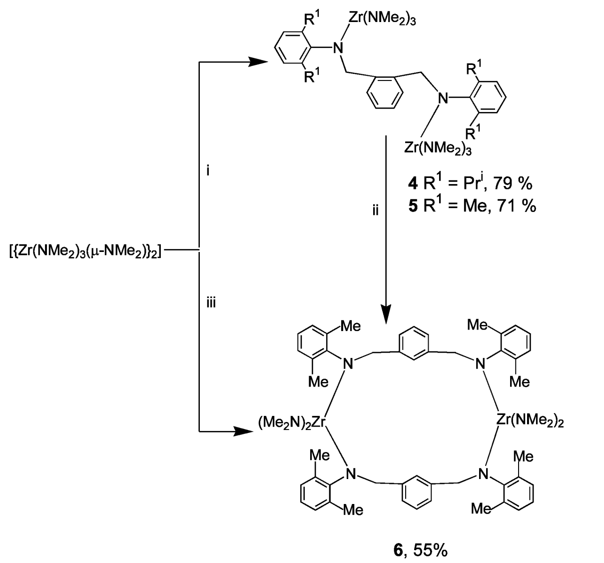
Although there appear to be eight previously published structures for tetranuclear lithium amides free from a neutral coligand, the structure of **3** is distinct and different from each. Complex **3** shares with just one of them **VI**[14] the presence of two-coordinate lithium atoms, each bound to two nitrogen atoms. The presence of a pair of $\overline{LiNLiN}$ 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 LiN_3 environments and a single but puckered [torsion angle 14.6(4)°] $\overline{LiNLiN}$ 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 **f**[19]] or **VIII** [2.12 Å for the central Li atoms].[9] In the $\overline{LiNLiN}$ 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° (**VIId**),[18] 82.5 and 108.7° (**VIIe**)[9] and 71.7 and 108.7° (**VIIf**)[19]].

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** in toluene-d_8 displayed only one set of Pr^i 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 $CH(CH_3)_2$. At 203 K, the latter split into a 1 : 1 : 1 : 1 multiplet and $CH(CH_3)_2$ protons give rise to four septets, consistent with the solid state structure (there are 8 Pr^i groups of which 4 are unique). In addition, the CH_2 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 $HCMe_2$ and $HC(3)$ ^1H nuclei, the ^7Li



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

The reactions between [{Zr(NMe$_2$)$_3$(μ-NMe$_2$)}$_2$][21] and the diamine H$_2$(**D**) **1** or H$_2$(**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 R^1 = Me, 1 equiv. of **1** in toluene at 20 °C; (iii) 2 equiv. of **1** in toluene at 20 °C.

outcome was stochiometry-dependent. Thus, using a 1 : 1 molar ratio of reagents, the product (i in Scheme 2) was the acyclic zirconium compound **5**; whereas from 2H$_2$(**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 H$_2$(**D′**), as also evident from ^{1}H 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 NMe$_2$ groups) are bridged by a [N(C$_6$H$_3$Pr$^i_2$-2,6)CH$_2$C]$_2$CH moiety; the three internal carbon atoms C14, C15 and C18 are members of the central benzene ring. The two Zr(NMe$_2$)$_3$ units are arranged *trans* to one another. The Zr–NMe$_2$ bond lengths range from 2.019(8) to 2.057(7) Å and are slightly shorter than the Zr–NC$_6$H$_3$Pr$^i_2$-2,6 bonds of 2.093(7) and 2.098(7) Å. This is consistent with the previously observed

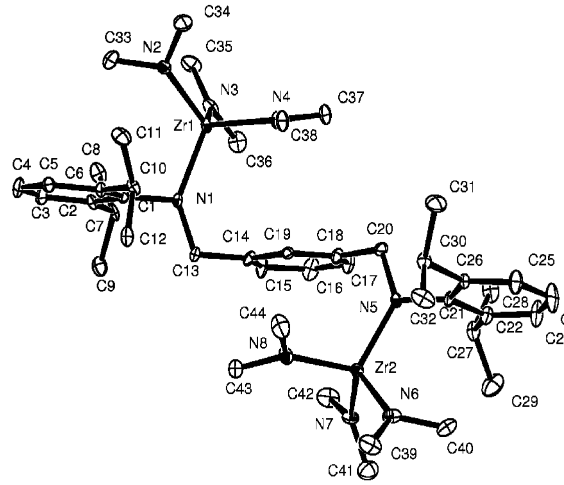


Fig. 3 Molecular structure of compound **4**.

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}(NMe$_2$)(NAr) compounds: in [{Zr(**A** or **A′**)NMe$_2$(μ-NMe$_2$)}$_2$] the terminal Zr–NMe$_2$ 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 NC$_6$H$_3$Pr$^i_2$-2,6 being the widest. Each nitrogen atom is in a distorted trigonal planar environment, the Zr–N–CH$_2$ angle being the widest, 140.1(5) for Zr1 and 133.8(5)° for Zr2. It is interesting that while **4** is a monomer, [{Zr(NMe$_2$)$_3$(μ-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 ^{1}H and $^{13}C\{^1H\}$ NMR spectra in toluene-d$_8$ or C$_6$D$_6$ (**6**) at 293 K were consistent with the structures shown in Scheme 2. The ^{1}H NMR spectra of the 2,6-dimethylphenylamides **5** and **6** showed singlets for the NMe$_2$ protons, indicative of there being unhindered rotation about the Zr–NMe$_2$ bonds on the NMR time scale. By contrast, the spectrum of the 2,6-diisopropylphenylamides **4** at ambient temperature showed the HC*Me*$_2$ signals as two separate 1 : 1 doublets.

Attempts to convert any of the amides **4**–**6** to chlorides by replacing NMe$_2$ 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 $[\{Zr(NMe_2)_3(\mu\text{-}NMe_2)\}_2]$ 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 cm^3 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 cm^3) 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 cm^3) at 0 °C. The mixture was set aside at room temperature for *ca.* 48 h. Water (100 cm^3) was added and the mixture was extracted with diethyl ether (2 × 50 cm^3). 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 ($CDC1_3$): δ 2.40 (s, 12 H, CH_3), 3.29 (s, 2 H, NH), 4.29 (s, 4 H, CH_2), 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 cm^3 of a 2.5 mol dm^{-3} solution in hexane, 37.9 mmol), 2,6-diisopropylaniline (7.0 cm^3, 37.9 mmol), thf (100 cm^3) 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. $C_{32}H_{44}N_2$ requires C, 84.2; H, 9.71; N, 6.31%). ^1H NMR ($CDC1_3$): δ 1.15 [d,$^3J(^1H–^1H)$ = 6.85, 24 H, CH_3], 3.07 [s, 2 H, NH], 3.29–3.19 [sept, $^3J(^1H–^1H)$ = 6.85, 4 H, CH], 3.97 [s, 4 H, CH_2], 7.27–7.01 [m, $^1J(^1H–^{13}C(3))$ = 154 Hz, 10 H, aromatic]. $^{13}C\{^1H\}$: δ 24.8 (CH_3), 28.3 (CH), 56.6 (CH_2), 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 cm^3 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 cm^3) 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 cm^3). 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, CH_3], 3.26 [sept, $^3J(^1H–^1H)$ = 6.5, 4 H, CH], 4.34 [s, 4 H, CH_2], 6.88–7.08 [m, $^1J(^1H–^{13}C(3))$ = 143, 9 H, aromatic], 9.03 [s, 1 H, *o*-CH]; ^1H NMR (toluene-d_8, 203 K): δ 0.31 [d, $^3J(^1H–^1H)$ = 6.5, 6 H, CH_3], 0.61 [d, $^3J(^1H–^1H)$ = 6.5, 6 H, CH_3], 1.23 [d, $^3J(^1H–^1H)$ = 6.5, 6 H, CH_3], 1.37 [d, $^3J(^1H–^1H)$ = 6.5, 6 H, CH_3], 3.13 [sept, $^3J(^1H–^1H)$ = 6.5, 1 H, CH], 3.22 [sept, $^3J(^1H–^1H)$ = 6.5, 1 H, CH], 3.68 [sept, $^3J(^1H–^1H)$ = 6.5, 1 H, CH], 3.79 [sept, $^3J(^1H–^1H)$ = 6.5 Hz, 1 H, CH], 4.93 [s, 4 H, CH_2], 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, CH_3], 27.8 (CH), 63.2 (CH_2), 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 cm^3) was added dropwise during *ca.* 10 min to a solution of $[\{Zr(NMe_2)_3(\mu\text{-}NMe_2)\}_2]$ (0.59 g, 1.85 mmol) in toluene (30 cm^3) 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 cm^3) was added. The mixture was filtered. The filtrate was concentrated (to *ca.* 10 cm^3) 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. $C_{44}H_{74}N_8Zr_2$ 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, $^3J(^1H–^1H)$ = 6.5, 12 H, CCH_3], 1.21 [d, $^3J(^1H–^1H)$ = 6.5, 12 H, CCH_3], 2.75 [s, 36 H, NCH_3], 3.59 [sept, $^3J(^1H–^1H)$ = 6.5 Hz, 4 H, CH], 4.48 [s, 4 H, CH_2], 7.04–7.21 [m, 10 H, aromatic]; $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 24.6 and 25.7 ($C\mathit{C}H_3$), 28.1 (CH), 41.7 (NCH_3), 61.6 (CH_2), 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^i]$^+$); 812 (39, [M − 2Pr^i]$^+$).

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 $[\{Zr(NMe_2)_3(\mu\text{-}NMe_2)\}_2]$ (0.48 g, 0.9 mmol) in toluene (6 cm^3)] there were obtained two crops of yellow crystals of **5** (0.53 g, 71%) (Found: C, 57.55; H, 6.82; N, 13.47. $C_{40}H_{58}N_8Zr_2$ requires C, 57.7; H, 6.97; N, 13.45%), mp 112 °C. ^1H NMR (toluene-d_8): δ 2.19 [s, 12 H, CCH_3], 2.74 [s, 36 H, NCH_3], 4.35 [s, 4 H, CH_2], 6.81 [t, $^3J(^1H–^1H)$ = 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 ($C\mathit{C}H_3$), 41.0 (NCH_3), 58.4 (CH_2), 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 $[\{Zr(NMe_2)_3(\mu\text{-}NMe_2)\}_2]$ (1.16 g, 2.16 mmol) in toluene (15 cm^3)] there were obtained two crops of yellow crystals of **6** (1.03 g, 55%) (Found: C, 64.2; H, 7.16; N, 10.88. $C_{28}H_{38}N_4Zr$ 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, CCH_3], 2.62 [s, 12 H, NCH_3], 4.61 [s, 4 H, CH_2], 6.56 [s, 1 H, aromatic], 6.85–7.01 [m, 9 H, aromatic]; $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 19.5 ($C\mathit{C}H_3$), 41.6 (NCH_3), 56.5 (CH_2), 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-Kα 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-97[23] with U_{iso}(H) of $1.2U_{eq}$(C) or $1.5U_{eq}$(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	$C_{64}H_{84}Li_4N_4$	$C_{44}H_{74}N_8Zr_2$
Formula weight	937.1	897.5
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c* (no.15)	$P\bar{1}$ (no.2)
a/Å	21.045(6)	11.315(4)
b/Å	15.874(3)	12.706(6)
c/Å	18.651(3)	18.040(7)
a/°	90	75.53(4)
β/°	115.79(2)	77.94(3)
γ/°	90	84.97(3)
U/Å³	5610(2)	2454(2)
μ/mm^{-1}	0.06	0.46
Z	4	2
Unique reflections, R_{int}	3688, 0.017	6799
Reflections with $I > 2\sigma(I)$	2564	4020
Final *R* indices (for $I > 2\sigma(I)$)	$R_1 = 0.048$, w$R_2 = 0.104$	$R_1 = 0.068$, $R_w = 0.139$
R indices (all data)	$R_1 = 0.079$, w$R_2 = 0.118$	$R_1 = 0.136$, w$R_2 = 0.168$

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