

# (Alkyliminomethyl)phenylamido and related complexes of zirconium and titanium †

Robin M. Porter, Scott Winston, Andreas A. Danopoulos\* and Michael B. Hursthouse

Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ.  
E-mail: adl@soton.ac.uk

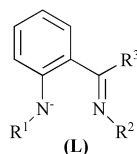
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A range of trialkylsilylamido complexes of zirconium in which the silylamido functional group is attached to an *o*-(alkyliminomethyl)- or an *o*-(alkyliminoethyl)-substituted aromatic ring have been synthesised by salt elimination or aminolysis reactions and characterised by spectroscopic and diffraction methods. The monoanionic ligands (L), formally isoelectronic to the cyclopentadienyl ligand, can be introduced to zirconium by reaction of LLi with ZrCl<sub>4</sub> under a variety of conditions giving rise to complexes of type LZrCl<sub>3</sub> and L<sub>2</sub>ZrCl<sub>2</sub>, by reaction of LLi with Zr(NMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub>, and Zr(NEt<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> giving rise to LZrCl(NMe<sub>2</sub>)<sub>2</sub>Cl and LZrCl(NEt<sub>2</sub>)<sub>2</sub>Cl, respectively, or by reaction of LH with Zr(NMe<sub>2</sub>)<sub>4</sub> giving rise to LZr(NMe<sub>2</sub>)<sub>3</sub>. LZr(NMe<sub>2</sub>)<sub>2</sub>Cl and LZr(NEt<sub>2</sub>)<sub>2</sub>Cl can be transformed to LZrCl<sub>3</sub> by reaction with Me<sub>3</sub>SiCl, while LZr(NMe<sub>2</sub>)<sub>3</sub> on heating rearranges to dimeric imido complexes by elimination of amidosilanes. Aminolysis of Zr(NMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> with LH results in a formal insertion of the imino C=N into the Zr-amido bond. The combination of enolisable imine and a bulky silyl amide gave rise to a new mixed donor ligand system comprising of one silylamido and one eneamido group. Finally aminolysis of Ti(NMe<sub>2</sub>)Cl<sub>2</sub> with LH resulted in the isolation of a C<sub>3</sub> symmetric triamido titanium complex.

## Introduction

There is currently great interest in the study of ligand architectures incorporating amido functional groups as non-metallocene spectators, especially in organometallic complexes of the early transition metals.<sup>1</sup> The well-known electronic characteristics of the amido group and its facile incorporation into tunable ligand backbones provides unique opportunities for the design of complexes with catalytic activity.<sup>1c,2</sup> Seminal contributions in this area have shown the viability of single site polymerisation catalysts based on chelating or functionalised amido ligands. The area has been recently reviewed.<sup>2</sup> Furthermore, organometallic complexes with Schiff bases, mainly salicylaldimines [6-RN=C(H)C<sub>6</sub>H<sub>4</sub>O<sup>-</sup>, R = alkyl or aryl] and their derivatives have been extensively explored. Some exhibit high activity or living behaviour in polymerisation reactions.<sup>3</sup> The attractive features of these ligands are easy synthetic accessibility and steric and electronic tuning by substitution of the aromatic ring or the imine carbon.<sup>3,4</sup> In contrast, the coordination chemistry of the anionic ligands that formally originate from salicylaldiminato by replacement of the PhO<sup>-</sup> group with the isoelectronic PhNR<sup>-</sup> have received less attention,<sup>5</sup> even though the tuning opportunities in this case are even broader (Scheme 1).



L<sup>1</sup>, R<sup>1</sup>=SiMe<sub>3</sub>, R<sup>2</sup>=Bu<sup>t</sup>, R<sup>3</sup>=H  
L<sup>2</sup>, R<sup>1</sup>=SiMe<sub>3</sub>, R<sup>2</sup>=Cy, R<sup>3</sup>=Me  
L<sup>3</sup>, R<sup>1</sup>=SiMe<sub>2</sub>Bu<sup>t</sup>, R<sup>2</sup>=Cy, R<sup>3</sup>=Me

Scheme 1

This is possibly due to the synthetic difficulties associated with the synthesis of this ligand system. We initiated a study in this area using the ligand backbones shown in Scheme 1. In the first of a series of papers we report on zirconium and titanium complexes with the *N*-silyl (R<sup>1</sup> = SiMe<sub>3</sub>, SiMe<sub>2</sub>Bu<sup>t</sup>) substituted analogues of L. As previously noted,<sup>5</sup> L is related to a wide family of β-diketiminato ligands.<sup>6</sup>

## Results and discussion

### Syntheses of ligands and ligand precursors

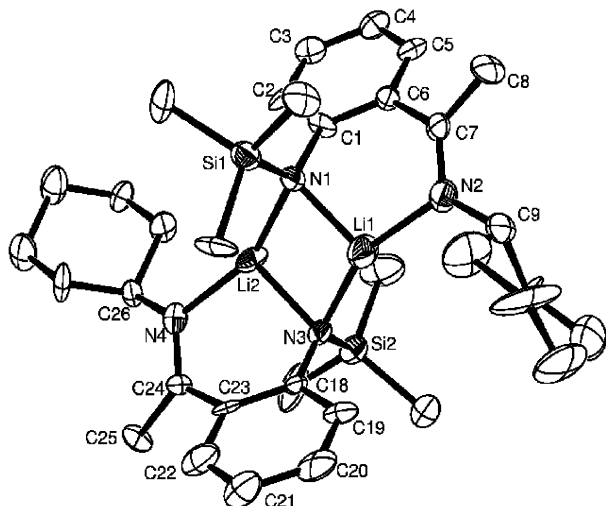
The *o*-[(*tert*-butyl)iminomethyl]aniline was synthesised by the literature method.<sup>5</sup> Following this method, condensation of Bu<sup>t</sup>NH<sub>2</sub> with the commercially available *o*-aminoacetophenone did not proceed even under forcing conditions and prolonged reaction times. However, reaction with cyclohexylamine in toluene in the presence of 4 Å molecular sieves afforded multigram quantities of the Schiff base in excellent yields. L<sup>1</sup>H, L<sup>2</sup>H and L<sup>3</sup>H were prepared by lithiation of the free anilines with Bu<sup>n</sup>Li in petrol, followed by quenching of the resulting lithium amides with SiMe<sub>3</sub>Cl and SiMe<sub>2</sub>Bu<sup>t</sup>Cl respectively. Deprotonation of the silylanilines with Bu<sup>n</sup>Li in petrol gave the lithium salts L<sup>1</sup>Li–L<sup>3</sup>Li as yellow, crystalline, extremely air sensitive materials. The structure of L<sup>2</sup>Li (**2**) in the solid state was determined by single crystal X-ray diffraction methods. The molecular structure of L<sup>2</sup>Li is given in Fig. 1. with selected bond lengths and angles in Table 1.

The molecule is a centrosymmetric dimer with bridging amido nitrogens. The coordination number around each lithium atom is three. The Li<sub>2</sub>N<sub>2</sub> ring is almost planar. The bridging amido group is tetrahedral. The lithium amido bond lengths [1.982(8), 2.000(7) Å] are in the range reported for bridging amido nitrogens.<sup>7</sup> The lithium–imino nitrogen bond length ([1.972(8), 1.977(8) Å] is almost equal to the Li–amido bond length, possibly due to the bridging nature of the amido ligands.

† Electronic supplementary information (ESI) available: ORTEP plots of **6** and **9**. See <http://www.rsc.org/suppdata/dt/b2/b202471c/>

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

C(1)–N(1)	1.407(5)	N(1)–Li(1)	1.989(8)
C(1)–C(6)	1.419(5)	N(1)–Li(2)	1.982(8)
C(6)–C(7)	1.491(5)	N(2)–Li(1)	1.970(8)
C(7)–N(2)	1.287(5)	Li(1)–Li(2)	2.415(9)
N(1)–C(1)–C(6)	123.7(4)	C(1)–N(1)–Li(2)	120.3(4)
C(1)–C(6)–C(7)	124.3(4)	Li(1)–N(1)–Li(2)	74.9(3)
N(2)–C(7)–C(6)	119.2(4)	C(7)–N(2)–Li(1)	117.1(3)
C(1)–N(1)–Li(1)	102.5(3)	N(2)–Li(1)–N(1)	99.6(4)

**Fig. 1** ORTEP representation of the crystal structure of **2** (50% probability thermal ellipsoids). Hydrogens are omitted for clarity.

### Zirconium complexes

The transformations leading to the zirconium complexes described in this paper are shown in Scheme 2.

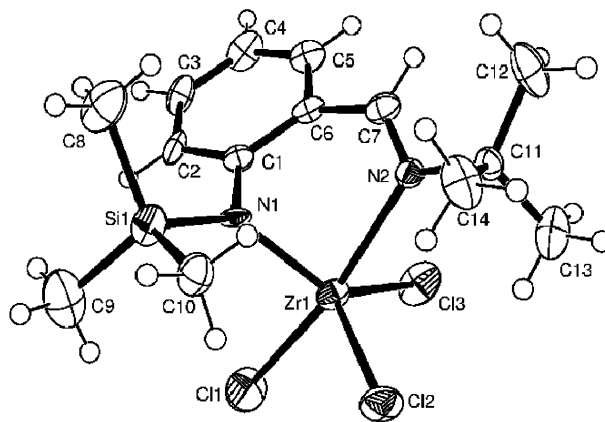
The nature of the zirconium complexes obtained by metathetical reactions involving lithium amido species and zirconium halide starting materials is strongly dependent on the reaction conditions, mainly, the reagents ratio, solvent, temperature of addition and the nature of the zirconium starting material used. Many products show reduced tendency to crystallise. This, in combination with their extreme sensitivity to moisture, reactivity with non-etheral polar solvents and their complicated  $^1\text{H}$  NMR spectra in solution rendered their full characterisation painstaking. Attempts to increase the crystallinity by using the bulkier and more lipophilic  $\text{SiMe}_2\text{Bu}^t$  were successful in some cases (see below). Furthermore, it became obvious that all three ligands *i.e.*  $\text{L}^1$ ,  $\text{L}^2$  and  $\text{L}^3$  were not completely inert, even under careful exclusion of moisture, undergoing insertion, elimination or deprotonation reactions as described below.

Reaction of  $\text{ZrCl}_4$  with one equivalent of  $\text{L}^1\text{Li}$  or  $\text{L}^2\text{Li}$  in toluene results in the isolation of **4** and **5** in moderate yields as extremely moisture sensitive, microcrystalline yellow powders. These show limited solubility in toluene, from dilute solutions of which **4** can be crystallised. The stoichiometry of **4** and **5** was established by analytical methods. The  $^1\text{H}$  NMR spectra show the presence of one type of resonance associated with the ligand backbone supporting the presence of a five-coordinate zirconium centre. A single crystal X-ray diffraction study of **4** supports the conclusions from the analytical and spectroscopic methods. A schematic diagram of the molecule is shown in Fig. 2, with selected bond lengths and angles in Table 2.

Compound **4** is monomeric, comprising of a five-coordinate zirconium centre in a distorted trigonal bipyramidal geometry with the imine and chloride functions occupying the axial positions. The equatorial positions are occupied by the silylamide and the remaining chlorides. The  $\text{Zr}(1)\text{--N}(1)$  bond length of 2.029(7) Å is in the range for a planar amido nitrogen, while the

**Table 2** Selected bond lengths (Å) and angles (°) for **4**

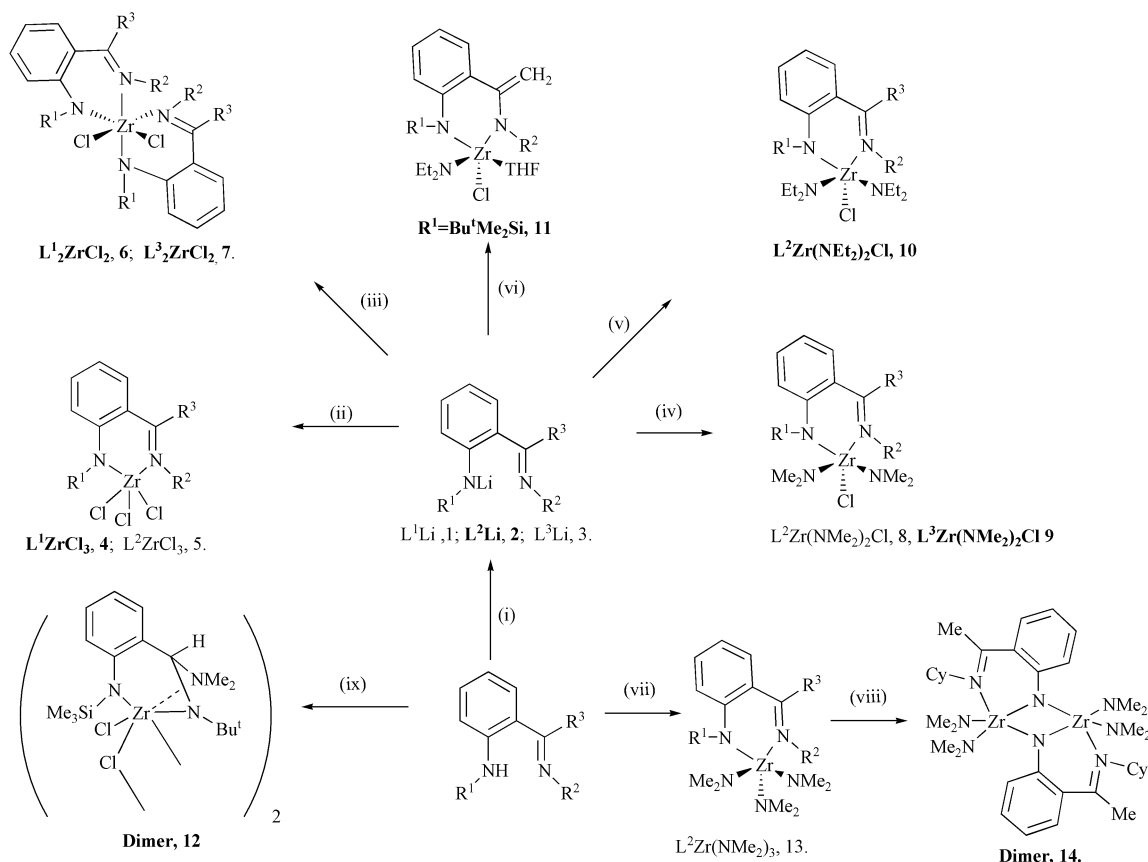
C(1)–N(1)	1.402(10)	Zr(1)–N(2)	2.336(9)
C(1)–C(6)	1.420(10)	Zr(1)–Cl(1)	2.434(6)
C(6)–C(7)	1.477(10)	Zr(1)–Cl(2)	2.386(6)
N(2)–C(7)	1.273(9)	Zr(1)–Cl(3)	2.415(8)
Zr(1)–N(1)	2.029(7)		
N(1)–C(1)–C(6)	120.8(7)	N(1)–Zr(1)–N(2)	81.19(2)
C(1)–C(6)–C(7)	122.5(8)	Cl(2)–Zr(1)–Cl(3)	112.9(2)
N(2)–C(7)–C(6)	124.81(8)	Cl(2)–Zr(1)–Cl(1)	95.49(2)
C(1)–N(1)–Zr(1)	101.03(5)	Cl(3)–Zr(1)–Cl(1)	91.13(14)
C(7)–N(2)–Zr(1)	108.12(5)		

**Fig. 2** ORTEP representation of the crystal structure of **4** (50% probability thermal ellipsoids).

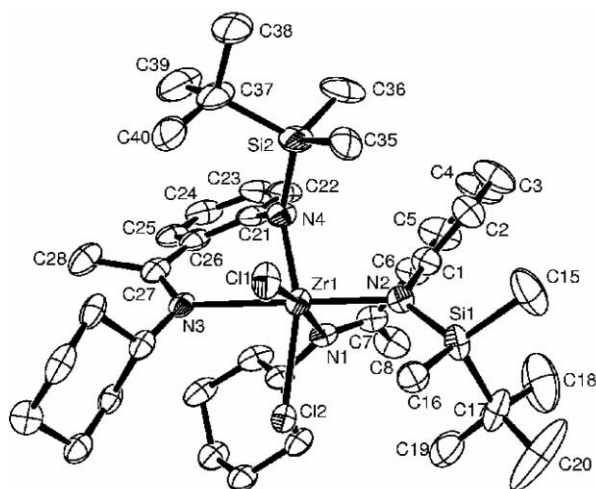
$\text{Zr}(1)\text{--N}(2)$  bond length of 2.336(9) Å is much longer; N(2) is also planar. The bite angle of the chelating ligand is 81.2° and the six-membered chelate ring is puckered. It is interesting to compare the metrical parameters of **4** with those observed for the isoelectronic  $\beta$ -diketiminato complexes;<sup>6</sup> the former features an asymmetrical chelate ring with unequal metal–nitrogen bond lengths, the shortest silylamido–Zr being almost 0.2 Å shorter and the longest Zr–N imino being 0.2 Å longer than the equal Zr–N lengths of the  $\beta$ -diketiminato chelate. In both cases the chelate rings are puckered. In **4** the C=N double bond character of the imino carbon is maintained after complexation and is shorter than the  $\text{C}_{\text{ipso}}\text{--N}(\text{Si})$ . This supports the fact that the presence of the aromatic ring inhibits delocalisation of electron density over the chelate. The aromatic carbon–carbon bonds are not strictly equal lying in the range 1.36 to 1.42 Å.

Reaction of  $\text{ZrCl}_4(\text{THT})_2$ , THT = tetrahydrothiophene, in etheral solvents with two equivalents of  $\text{L}^1\text{Li}$  or  $\text{L}^3\text{Li}$  resulted in the formation of  $\text{L}^1_2\text{ZrCl}_2$ , **6**, and  $\text{L}^3_2\text{ZrCl}_2$ , **7**, respectively. Both compounds can be crystallised from petroleum as yellow, very air sensitive crystals in moderate yields. Their  $^1\text{H}$  NMR spectra show the presence of two inequivalent ligands in a 1 : 1 ratio. This observation supports the presence in solution of a non-symmetric isomer. In **7** the ketimino methyl protons appear as a relatively broad singlet at 2.05 ppm. The non-symmetric nature of the complexes was established by single crystal X-ray diffraction studies of **6** and **7**. A schematic diagram of **7** is shown in Fig. 3 with selected bond lengths and angles in Table 3. (The structure of **6** is identical to **7**, the ORTEP plot is included as ESI, CCDC reference number 181537).

The zirconium centre has a six-coordinate distorted octahedral geometry with *cis* chlorides, while the arrangement of the chelates is such that the amido function of one is *trans* to a chloride and the amido function of the second is *trans* to the imino function of the first. This gives rise to a low symmetry  $C_1$  complex. The bond lengths observed reflect the relative *trans* influence of the functional groups involved *i.e.*  $\text{Zr}(1)\text{--Cl}(2)$  [*trans* to silylamide, 2.490(3) Å] is longer than  $\text{Zr}(1)\text{--Cl}(1)$  [*trans* to the imine, 2.414(3) Å] and  $\text{Zr}(1)\text{--N}(1)$  [*trans* to silylamide,



**Scheme 2** Compounds in bold have been structurally characterised. Reagents and conditions: (i) L<sup>1</sup>H, L<sup>2</sup>H or L<sup>3</sup>H, Bu<sup>n</sup>Li in petroleum (−78 °C to RT); (ii) L<sup>1</sup>Li or L<sup>2</sup>Li and ZrCl<sub>4</sub> in toluene (−78 °C to RT); (iii) L<sup>1</sup>Li or L<sup>3</sup>Li and ZrCl<sub>4</sub>(THF)<sub>2</sub> in diethyl ether (−78 °C to RT); (iv) L<sup>2</sup>Li and Zr(NMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> in THF (−78 °C to RT); (v) Zr(NEt<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> in THF (−78 °C to RT); (vi) L<sup>3</sup>Li and Zr(NEt<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> in THF (−78 °C to RT); (vii) L<sup>2</sup>H and Zr(NMe<sub>2</sub>)<sub>4</sub> in toluene 50 °C; (viii) heating at 100 °C for 24 h; (ix) Zr(NMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> and L<sup>1</sup>H in toluene at 100 °C for 72 h.



**Fig. 3** ORTEP representation of the crystal structure of **7** (50% probability thermal ellipsoids). Hydrogens are omitted for clarity.

2.486(7) Å] is slightly longer than Zr(1)–N(4) [*trans* to chloride, 2.456(6) Å]. As found in complex **4**, the localised bonding of the chelate ring in complexes **6** and **7** is maintained after complexation. The bite angle of the puckered chelate rings lies in the range 78–81°. There is no obvious reason why both **6** and **7** adopt the same geometry. The different size of the silyl substituents in the two complexes supports the fact that the observed geometry is sterically favoured.

Attempts to substitute the chlorides in **4**, **5**, **6** and **7** with alkyls or amides using lithium or Grignard reagents gave only intractable mixtures. In order to access these compounds we reacted simple homoleptic zirconium dialkylamido or

**Table 3** Selected bond lengths (Å) and angles (°) for **7**

C(1)–C(6)	1.405(7)	N(2)–Zr(1)	2.111(4)
C(1)–N(2)	1.419(6)	N(3)–Zr(1)	2.459(4)
C(6)–C(7)	1.495(7)	N(4)–Zr(1)	2.090(4)
C(7)–N(1)	1.272(6)	Cl(1)–Zr(1)	2.4417(13)
N(1)–Zr(1)	2.366(4)	Cl(2)–Zr(1)	2.4938(13)
C(6)–C(1)–N(2)	123.0(5)	N(2)–Zr(1)–N(1)	81.06(14)
C(1)–C(6)–C(7)	123.9(5)	N(4)–Zr(1)–Cl(1)	99.47(11)
N(1)–C(7)–C(6)	119.9(4)	N(1)–Zr(1)–Cl(1)	171.78(10)
C(7)–N(1)–Zr(1)	123.0(3)	N(4)–Zr(1)–N(3)	78.06(15)
C(1)–N(2)–Zr(1)	112.0(3)	N(2)–Zr(1)–N(3)	174.70(13)
C(7)–N(3)–Zr(1)	123.8(3)	Cl(1)–Zr(1)–Cl(2)	90.23(5)
C(21)–N(4)–Zr(1)	115.6(3)		

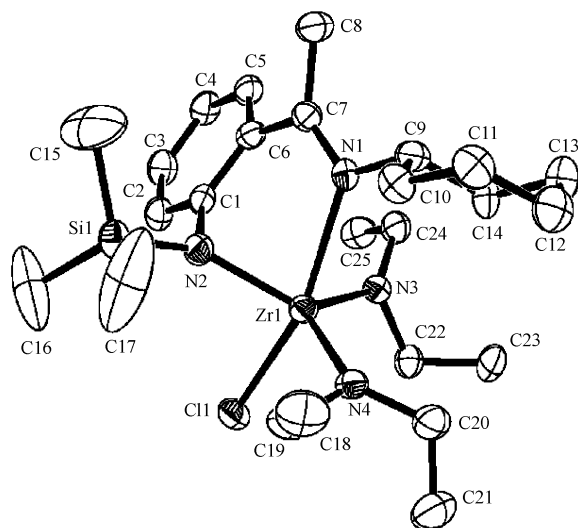
dialkylamido halide complexes with LH or LLi, by transamination or salt elimination reactions, respectively.

Reaction of Zr(NMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> with one equivalent of L<sup>2</sup>Li or L<sup>3</sup>Li in THF or reaction of Zr(NEt<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> with L<sup>2</sup>Li in THF gave, after crystallisation from petroleum, pale yellow moisture sensitive crystals of **8**, **9** and **10** respectively in reasonable yields. The <sup>1</sup>H NMR spectra of these compounds showed inequivalent dialkylamido groups in addition to peaks assignable to L<sup>2</sup> or L<sup>3</sup> backbones in a 2 : 1 ratio. This data supports a trigonal bipyramidal structure in which the dialkylamido groups are occupying inequivalent positions. The solution structures were maintained in the solid state as confirmed by single crystal X-ray diffraction studies of **9** and **10**. Both molecules adopt identical geometries. Fig. 4 shows the molecular structure of **10** with selected bond lengths and angles in Table 4. (The structure of **9** is included as ESI, CCDC reference number 181539).

The molecules adopt a five-coordinate distorted trigonal bipyramidal geometry with the imino and chloride groups

**Table 4** Selected bond lengths (Å) and angles (°) for **10**

C(1)–C(6)	1.414(7)	N(2)–Zr(1)	2.112(4)
C(1)–N(2)	1.426(7)	N(3)–Zr(1)	2.047(4)
C(6)–C(7)	1.494(8)	N(4)–Zr(1)	2.054(5)
C(7)–N(1)	1.285(7)	Cl(1)–Zr(1)	2.5021(13)
N(1)–Zr(1)	2.460(4)		
C(2)–C(1)–N(2)	121.1(5)	N(3)–Zr(1)–N(2)	128.42(18)
C(1)–C(6)–C(7)	121.0(5)	N(4)–Zr(1)–N(2)	119.53(17)
N(1)–C(7)–C(6)	118.5(4)	N(3)–Zr(1)–Cl(1)	96.79(12)
C(7)–N(1)–Zr(1)	116.8(4)	N(4)–Zr(1)–Cl(1)	95.20(12)
C(1)–N(2)–Zr(1)	98.5(3)	N(2)–Zr(1)–Cl(1)	89.63(12)
N(3)–Zr(1)–N(4)	110.78(17)	N(1)–Zr(1)–Cl(1)	162.13(11)

**Fig. 4** ORTEP representation of the crystal structure of **10** (50% probability thermal ellipsoids). Hydrogens are omitted for clarity.

occupying the axial positions. The stronger  $\pi$ -bonding amido groups are in the equatorial plane; the two inequivalent dialkylamido groups are planar, indicating a strong  $\pi$ -bonding interaction with the metal. The Zr–silylamido and Zr–imino bond lengths are comparable to those observed in the other complexes reported in this paper.

Attempts to substitute the dialkylamido groups with chlorides by reaction of **8** or **10** with  $\text{Me}_3\text{SiCl}$  were carried out in  $\text{C}_6\text{D}_6$  as NMR scale experiments. In the reaction mixture peaks assignable to  $\text{L}^2\text{ZrCl}_3$  and  $\text{Me}_3\text{SiNMe}_2$  or  $\text{Me}_3\text{SiNEt}_2$  can be observed. Scaling up of this reaction gave good yields of isolable  $\text{L}^2\text{ZrCl}_3$  only in the case of **10** (see Experimental).

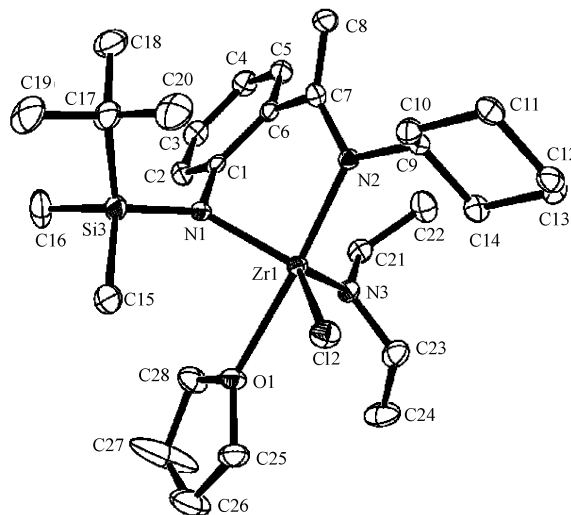
An unexpected result was obtained in an attempt to prepare  $\text{L}^3\text{ZrCl}(\text{NET}_2)_2$  by salt elimination reaction between  $\text{Zr}(\text{NET}_2)_2\text{Cl}_2(\text{THF})_2$  and  $\text{L}^3\text{Li}$  in THF. The only product that could be isolated reproducibly in good yields was the air sensitive **11** in which the chelating ligand can be best formulated as the dianionic ene-amido silyl amide. The presence of the methylene group on the carbon  $\alpha$  to the nitrogen can be easily established from the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (at 88.7 ppm) and DEPT 135 experiment. The structure of **11** was studied by single crystal X-ray diffraction. A diagram of the molecule is shown in Fig. 5 with selected bond lengths and angles in Table 5.

Here the ligands on the five-coordinate trigonal bipyramidal Zr are the dianionic ene-iminato silyl amide, one diethylamido, one chloride and one THF. The axial positions are occupied by the ene-iminato nitrogen and the THF molecule. The Zr(1)–N(1)(silylamido) distance is the same as the other complexes described here; the ene-iminato bond length of 2.1290(19) Å is much shorter than the C=N–Zr bonds in complexes previously studied. The chelate ring is puckered and the bite angle of the new ligand is 89.5°.

The reason behind the preferential formation of **11** by reaction of  $\text{L}^3\text{Li}$  and  $\text{Zr}(\text{NET}_2)_2\text{Cl}_2(\text{THF})_2$  is not fully understood.

**Table 5** Selected bond lengths (Å) and angles (°) for **11**

C(1)–C(6)	1.416(3)	N(2)–Zr(1)	2.1290(19)
C(1)–N(1)	1.426(3)	N(3)–Zr(1)	2.019(2)
C(1)–Zr(1)	2.768(3)	Cl(2)–Zr(1)	2.4503(7)
C(6)–C(7)	1.499(4)	Zr(1)–O(1)	2.3625(16)
C(7)–N(2)	1.392(3)	C(7)–C(8)	1.348(3)
N(1)–Zr(1)	2.052(2)		
C(6)–C(1)–N(1)	120.5(2)	N(3)–Zr(1)–N(2)	99.18(8)
C(1)–C(6)–C(7)	123.1(2)	N(1)–Zr(1)–N(2)	89.54(8)
N(2)–C(7)–C(6)	115.1(2)	N(3)–Zr(1)–Cl(2)	122.11(7)
C(1)–N(1)–Zr(1)	104.00(15)	N(1)–Zr(1)–Cl(2)	119.55(6)
C(7)–N(2)–Zr(1)	118.02(16)	N(2)–Zr(1)–Cl(2)	98.03(6)
N(3)–Zr(1)–N(1)	115.42(9)		

**Fig. 5** ORTEP representation of the crystal structure of **11** (50% probability thermal ellipsoids). Hydrogens are omitted for clarity.

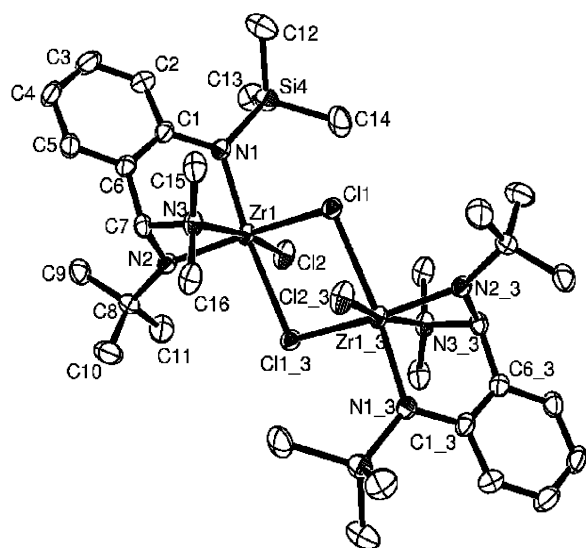
We were unable to detect by NMR spectroscopy in  $\text{C}_6\text{D}_6$  any silylamido ene-amido dilithium impurity in the  $\text{L}^3\text{Li}$  reagent used. This, in combination with the fact that the reaction of  $\text{Zr}(\text{NMe}_2)_2\text{Cl}_2(\text{THF})_2$  with  $\text{L}^3\text{Li}$  and  $\text{Zr}(\text{NET}_2)_2\text{Cl}_2(\text{THF})_2$  with  $\text{L}^2\text{Li}$  produce the anticipated products, points to a possible competing intermolecular deprotonation of the enolisable imine by the excess of bulky lithium silylamide. Lappert has observed lithium ene-amides in the reaction of  $\text{LiCH}(\text{SiMe}_3)_2$  with benzonitrile or isocyanides in the presence of tmed.<sup>8</sup> In this case products are sensitive to the stoichiometry, the nature of the organic group on the (iso)nitrile and the presence of tmed.

Attempts to transaminate dimethylamido for silylamido groups by reaction of  $\text{L}^1\text{H}$  with  $\text{Zr}(\text{NMe}_2)_2\text{Cl}_2(\text{THF})_2$  in toluene at 100 °C resulted in the isolation of low yields of **12** as one component of a complicated reaction mixture. **12** is formally formed by insertion of the *tert*-butylimino group into the Zr–dimethylamido bond. Insertion reactions, especially of cumulenes ( $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{RNCO}$  etc.) are common in early transition metal amido complexes.<sup>9</sup> However, insertion of the imine into metal–amido bonds is rare. The structure of **12** was determined by a single crystal X-ray diffraction study. A diagram of the molecule is shown in Fig. 6 with selected bond lengths and angles in Table 6.

**12** is a dimer with bridging chlorides. The Zr centres are formally six-coordinate with one face occupied by the ‘tripodal’ ligand. The Zr–nitrogen bond lengths and the bond angles around the nitrogens support the presence of two mono-anionic amido groups [Zr(1)–N(1) = 2.0882(18), Zr(1)–N(2) = 2.0122(17) Å] and one dative amine [Zr(1)–N(3) = 2.3582(17) Å] functional groups. This makes the ligand a ten electron ( $\text{X}_2\text{L}_3$ ) dianionic donor with one amido and one asymmetrically trisubstituted amidinato functional group. Functionalised amidinato complexes have recently appeared in the literature.<sup>10</sup>

**Table 6** Selected bond lengths (Å) and angles (°) for **12**

N(1)–C(1)	1.424(3)	Zr(1)–N(1)	2.0882(18)
C(7)–N(2)	1.480(3)	Zr(1)–N(3)	2.3582(17)
C(7)–C(6)	1.500(3)	Zr(1)–Cl(2)	2.4395(7)
C(7)–N(3)	1.507(3)	Zr(1)–Cl(1)	2.6142(7)
C(6)–C(1)	1.413(3)	Zr(1)–Cl(1_3)	2.7067(8)
Zr(1)–N(2)	2.0122(17)		
C(1)–N(1)–Zr(1)	120.66(14)	C(7)–N(3)–Zr(1)	83.60(11)
N(2)–C(7)–C(6)	112.59(17)	N(2)–Zr(1)–N(1)	92.01(7)
N(2)–C(7)–N(3)	101.01(16)	N(2)–Zr(1)–N(3)	63.07(7)
C(6)–C(7)–N(3)	113.08(17)	N(1)–Zr(1)–N(3)	84.70(7)
C(7)–N(2)–Zr(1)	97.72(12)	N(3)–Zr(1)–Cl(2)	169.92(5)
C(1)–C(6)–C(7)	121.17(19)	N(2)–Zr(1)–Cl(1)	142.23(5)
C(6)–C(1)–N(1)	120.61(19)	N(1)–Zr(1)–Cl(1_3)	172.23(5)

**Fig. 6** ORTEP representation of the crystal structure of **12** (50% probability thermal ellipsoids). Hydrogens are omitted for clarity.

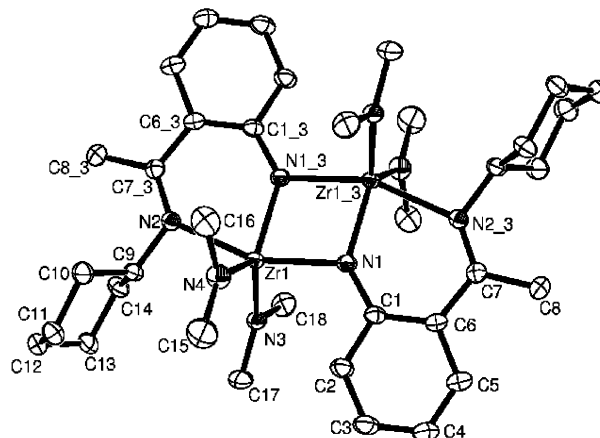
Attempts to independently synthesise this ligand system<sup>11</sup> are under way. The exact mechanism of formation of **12** is unclear. Although transamination of one dimethylamido functional group by silylamide followed by insertion of the imine to the second dimethylamide is plausible, an intermolecular pathway involving nucleophilic attack of dimethylamide followed by transamination cannot be eliminated. The observed reactivity of the imino group in the presence of highly electrophilic early transition metals has to be taken into account when using salen type ligands as spectators. It is interesting to notice that a similar reaction is not observed between  $\text{Zr}(\text{NMe}_2)_2\text{Cl}_2(\text{THF})_2$  and the ketimine  $\text{L}^2\text{H}$ .

Attempts to introduce  $\text{L}^2$  by transamination of  $\text{Zr}(\text{NMe}_2)_4$  with one equivalent of  $\text{L}^2\text{H}$  in toluene resulted in clean formation of **13** as the only detectable product in an NMR scale reaction ( $\text{C}_6\text{D}_6$ ). This was established by the disappearance of a peak at 10.4 ppm assignable to the NH of  $\text{L}^2\text{H}$  and the simultaneous appearance of signals assignable to free dimethylamine and the product. **13** can be isolated as a very moisture sensitive oil making its characterisation by analytical methods difficult. However, the identity of the compound is easily established by NMR spectroscopy (see Experimental) where a peak at 3 ppm is assignable to the dimethylamido functions; furthermore peaks assignable to the ligand framework are also observed.

Introduction of a second  $\text{L}^2$  by reaction with  $\text{Zr}(\text{NMe}_2)_4$  using two equivalents of  $\text{L}^2\text{H}$  in toluene at 100 °C gave, after crystallisation, low yields of the dimer **14**. We were unable to record a  $^1\text{H}$  NMR spectrum of **14** because of its poor solubility in inert solvents. However, **14** was characterised by a single crystal X-ray diffraction study. A diagram of the molecule is shown in Fig. 7 with selected bond lengths and angles in Table 7.

**Table 7** Selected bond lengths (Å) and angles (°) for **14**

C(1)–N(1)	1.359(4)	N(1)–Zr(1)	2.217(3)
C(1)–C(6)	1.442(5)	N(2)–Zr(1)	2.306(3)
C(6)–C(7)	1.465(5)	N(3)–Zr(1)	2.065(3)
C(7)–N(2_3)	1.298(4)	N(4)–Zr(1)	2.064(3)
N(1)–Zr(1_3)	2.066(3)	Zr(1)–Zr(1_3)	3.3262(3)
N(1)–C(1)–C(6)	125.7(3)	C(7_3)–N(2)–Zr(1)	133.2(2)
C(1)–C(6)–C(7)	123.7(3)	N(4)–Zr(1)–N(3)	122.49(13)
N(2_3)–C(7)–C(6)	121.0(3)	N(4)–Zr(1)–N(1_3)	119.78(13)
C(1)–N(1)–Zr(1_3)	134.3(2)	N(3)–Zr(1)–N(1_3)	117.26(12)
C(1)–N(1)–Zr(1)	122.5(2)	N(1_3)–Zr(1)–N(1)	78.16(12)
Zr(1_3)–N(1)–Zr(1)	101.84(12)	N(1)–Zr(1)–N(2)	158.22(10)
C(7_3)–N(2)–C(9)	123.6(3)		

**Fig. 7** ORTEP representation of the crystal structure of **14** (50% probability thermal ellipsoids). Hydrogens are omitted for clarity.

Compound **14** is a centrosymmetric dimer in which  $\text{L}^2$  acts as a bridging ligand *via* an imido function. The coordination sphere of each Zr centre is completed by one imino and two dimethylamido groups, giving a total coordination number of five. The  $\text{Zr}_2\text{N}_2$  ring is highly asymmetric [ $\text{Zr}(1)–\text{N}(2) = 2.2187(15)$  Å,  $\text{Zr}(1)–\text{N}(2_3) = 2.0652(14)$  Å]. There is no evidence of any metal–metal interaction [ $\text{Zr}(1)–\text{Zr}(1_3) = 3.3262(3)$  Å]. Both imido and amido nitrogens are planar with the Zr imido bond distance almost equal to the Zr dimethylamido distances. An interesting feature of **14** is the planarity of the chelate ring. This is to be contrasted with the puckered conformation of the chelate rings described earlier. It could be ascribed to increased  $\pi$ -interaction of the imido with the metal centre. The mechanism of formation of **14** probably involves an initial transamination step followed by intra- or inter-molecular  $\text{Me}_3\text{SiNMe}_2$  elimination resulting in the formation of the imido group. If the elimination is intramolecular dimerisation gives rise to **14**.

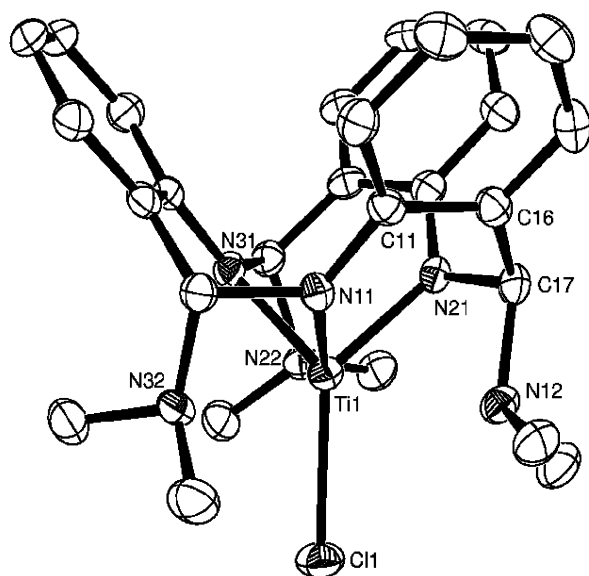
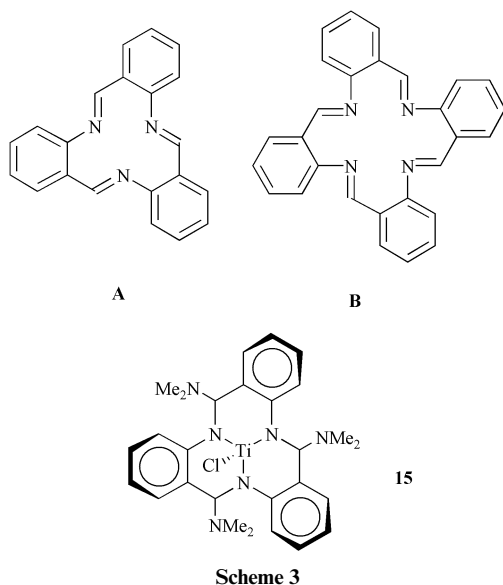
### Titanium macrocyclic complex

Preliminary attempts to extend the chemistry of  $\text{L}^1\text{H}$  to titanium gave unexpected results. Reaction of  $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$  with  $o\text{-C}_6\text{H}_4(\text{NH}_2)(\text{CH}=\text{NBU}^t)$  in toluene at 100 °C gave complex **15** stabilised by a novel face-blocking  $\text{C}_3$  symmetric trianionic macrocyclic amide as shown in Scheme 3. It was the only product detected by  $^1\text{H}$  NMR spectroscopy in solution.

Air stable deep red crystals of **15** were isolated by crystallisation from diethyl ether solutions. The  $^1\text{H}$  NMR spectrum of **15** showed signals at 2.3 and 2.8 ppm assignable to the diastereotopic dimethylamino methyl groups, and signals due to azomethine and aromatic protons. There was no evidence for the formation of more than one diastereomer. The identity of **15** was established by a single crystal X-ray diffraction study. A diagram of the molecule is given in Fig. 8 with selected bond lengths and angles in Table 8.

**Table 8** Selected bond lengths (Å) and angles (°) for **15**

Ti(1)–N(11)	1.975(2)	Ti(1)–N(12)	2.385(2)
Ti(1)–N(31)	1.979(2)	N(11)–C(11)	1.387(3)
Ti(1)–N(21)	1.981(2)	N(12)–C(17)	1.498(3)
Ti(1)–N(32)	2.366(2)	C(17)–N(21)	1.460(4)
Ti(1)–Cl(1)	2.3722(10)	C(17)–C(16)	1.500(4)
Ti(1)–N(22)	2.380(2)	C(11)–C(16)	1.416(4)
N(11)–Ti(1)–N(31)	87.35(9)	C(11)–N(11)–Ti(1)	130.44(18)
N(11)–Ti(1)–N(21)	87.18(9)	N(21)–C(17)–N(12)	98.3(2)
N(31)–Ti(1)–N(21)	87.75(9)	N(21)–C(17)–C(16)	111.5(2)
N(11)–Ti(1)–Cl(1)	127.23(7)	N(11)–C(11)–C(16)	116.2(2)
N(31)–Ti(1)–Cl(1)	126.36(7)	C(17)–N(21)–Ti(1)	102.67(16)
N(21)–Ti(1)–Cl(1)	127.60(7)		

**Fig. 8** ORTEP representation of the crystal structure of **15** (50% probability thermal ellipsoids). Hydrogens are omitted for clarity.

The coordination geometry around the titanium can be best described as a tricapped trigonal pyramid. The macrocyclic ligand adopts a cone conformation reminiscent of the cone conformation found in calixarenes. The three shorter titanium–nitrogen distances [Ti(1)–N(11), Ti(1)–N(21) and Ti(1)–N(31), average 1.978 Å] fall in the long end of the bond range characteristic of titanium(IV) amido bonds. The geometry of these nitrogens is almost planar (average angle sum 354.4°). The slight deviation from planarity can be ascribed to competition of N–C and N–Ti  $\pi$ -bonding, or due to constraints imposed by

the ligand backbone. The pyramidal nitrogen atoms of the dimethylamino groups [N(12), N(22), N(32)] interact only weakly with the metal centre [average Ti(1)–N distance 2.37 Å].

Although the mechanism of the formation of **15** is not clear and still under investigation, there is evidence that it involves a metal directed condensation. Pre-coordination of the *o*-*tert*-butyliminomethyl-aniline is necessary for the reaction to occur. This is shown by the inertness of the electronically richer Ti(NMe<sub>2</sub>)<sub>4</sub> which fails to produce **15** by heating at 100 °C with *o*-*tert*-butyliminomethyl-aniline, possibly due to its reduced nucleophilicity.

The self-condensation of *o*-aminobenzaldehyde gives cyclic trimeric and tetrameric products, which were unambiguously characterised.<sup>12</sup> If the condensation is carried out in the presence of metal templates, macrocyclic complexes with the “face-blocking” trimer **A** or the planar “porphyrin-like” tetramer **B** (Scheme 3) are obtained; the first compounds of this type were realised and characterised in 1965 by Busch.<sup>12</sup> Furthermore, complexes with **A** and **B** can react with strong nucleophiles (R<sup>−</sup>, RO<sup>−</sup>, RS<sup>−</sup> etc.) at the azomethine carbons giving derivatives with functionalised anionic macrocycles. A ruthenium complex incorporating **A** has recently been reported.<sup>13</sup>

To the best of our knowledge this is the first time that a selective cyclotrimerisation of an *o*-aminobenzaldehyde derivative has been achieved in non-polar solvents using a transition metal amide as template. This method could open a new route to template-directed macrocyclisation reactions. The use of early transition metals could prove beneficial in the isolation of the demetallated macrocycle under mild conditions. Attempts to extend this synthetic methodology to other main group and transition metals, the preparation of organometallic derivatives of **15** and the use of *o*-aminobenzaldehyde derived macrocycles as spectators in catalyst design will be reported in a forthcoming paper.

### Ethylene polymerisation studies

The activity of **7** and **8** for the polymerisation of ethylene in the presence of MAO was studied. They show medium polymerisation activity, 3.0 and 8.8 g mmol<sup>−1</sup> bar<sup>−1</sup> h<sup>−1</sup> respectively, at room temperature. This fact is not surprising in view of the generally inferior activity reported for silylamides (‘silicon effect’). The synthesis and polymerisation activity of *N*-aryl substituted analogues of L<sup>1</sup> and L<sup>2</sup> will be reported shortly in a forthcoming paper.

### Experimental

Elemental analyses were carried out by the University College London Microanalytical Laboratory. NMR data were recorded on Bruker AMX-300 and AM-300 spectrometers, operating at 300 MHz (<sup>1</sup>H). The spectra were referenced internally using the signal from the residual protio-solvent (<sup>1</sup>H) or the signals of the solvent (<sup>13</sup>C). All manipulations involving moisture sensitive materials were carried out under vacuum or N<sub>2</sub> using standard Schlenk techniques. All solvents used were dried by continuous reflux under N<sub>2</sub> and distillation from suitable drying agents immediately prior to use; the light petroleum had bp 40–60 °C. Commercial chemicals were from Aldrich and Avocado. The following starting materials were prepared following literature methods: L<sup>1</sup>H,<sup>5</sup> ZrCl<sub>4</sub>(THT)<sub>2</sub>,<sup>14</sup> Zr(NMe<sub>2</sub>)<sub>4</sub>,<sup>15</sup> Zr(NMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> and Zr(NEt<sub>2</sub>)Cl<sub>2</sub>(THF)<sub>2</sub>,<sup>16</sup> TiCl<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>.<sup>17</sup>

### Synthesis

**[*o*-*tert*-Butyl]iminomethyl]-*N*-(trimethylsilyl)aniline (L<sup>1</sup>H).** To a cooled (−78 °C), stirred solution of *o*-*tert*-butylimino-aniline (5.0 g, 28.5 mmol) in ether (200 cm<sup>3</sup>) was added dropwise a solution of Bu<sup>n</sup>Li (12.8 cm<sup>3</sup> of 2.45 M solution in hexanes, 31.3 mmol). The mixture was stirred for 15 min then allowed to reach room temperature and stirred for 2 h. The

resulting yellow suspension was cooled again to  $-30\text{ }^{\circ}\text{C}$  and a solution of  $\text{Me}_3\text{SiCl}$  (3.40 g, 31.3 mmol) in ether ( $10\text{ cm}^3$ ) was added dropwise from a syringe. After stirring at room temperature for 12 h the majority of the ether was removed under reduced pressure, the resulting residue was extracted with petroleum ( $2 \times 100\text{ cm}^3$ ), the organic extracts were filtered through Celite and evaporated to dryness. The remaining oily residue gave after distillation under vacuum the product as a colourless oil (bp  $68\text{--}70\text{ }^{\circ}\text{C}$ ,  $0.05\text{ mmHg}$ ). Yield: 4.6 g, 65%.  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 0.25 [9H, s,  $(\text{CH}_3)_3\text{Si}$ ], 1.2 [9H, s,  $(\text{CH}_3)_3\text{C}$ ], 6.6–7.2 (4H, m, aromatic), 8.2 (1H, s, imino), 9.9 (1H, s, NH).

**Lithium [*o*-(*tert*-butyl)iminomethyl]-*N*-(trimethylsilyl)anilide, ( $\text{L}^1\text{Li}$ ), **1**.** To a solution of  $\text{L}^1\text{H}$  (3 g, 12 mmol) in petroleum ( $50\text{ cm}^3$ ) at  $-78\text{ }^{\circ}\text{C}$  was added slowly *via* cannula  $\text{Bu}^n\text{Li}$  ( $5.4\text{ cm}^3$  of 2.45 M solution in hexanes, 13.2 mmol). The mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, allowed to reach room temperature and stirred for 12 h. This produced a light yellow suspension. The product precipitate was isolated by filtration as a light yellow, extremely air sensitive solid. Yield: 2.2 g, *ca.* 71%.

**[*o*-(Cyclohexyl)iminoethyl]aniline ( $\text{L}^2\text{H}_2$ ).** 2-Aminoacetophenone (10.0 g, 74.1 mmol) was dissolved in toluene ( $100\text{ cm}^3$ ) and to the solution were added activated 4 Å molecular sieves and cyclohexylamine ( $63\text{ cm}^3$ , 552 mmol). The resulting orange mixture was stirred at  $100\text{ }^{\circ}\text{C}$  in a closed vessel under reduced pressure for 4 days. After completion, filtration of the sieves and removal of the volatiles under reduced pressure gave a light brown solid, which was crystallised from petroleum as white solid that was washed with cold petroleum. Yield: 10.12 g, 63%.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.25–1.90 (10H, m, cyclohexyl), 2.30 (3H, s, imino  $\text{CH}_3$ ), 3.50–3.70 (1H, m, *H* on cyclohexyl C  $\alpha$  to imino N), 6.55 (2H, br. s,  $\text{NH}_2$ ), 6.65 (2H, m, aromatic), 7.10 (1H, t, aromatic), 7.50 (1H, d, aromatic).  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 15.7 (imino  $\text{CH}_3$ ), 24.9, 26.0, 34.3 (cyclohexyl), 59.3 (cyclohexyl C  $\alpha$  to imino N), 116.0, 117.0, 121.7, 129.4, 129.9, 148.3 (aromatic), 165.1 (C=N).

**[*o*-(Cyclohexyl)iminoethyl]-*N*-(trimethylsilyl)aniline ( $\text{L}^2\text{H}$ ).** To a cooled ( $-78\text{ }^{\circ}\text{C}$ ), stirred solution of  $\text{L}^2\text{H}_2$  (5.90 g, 27.3 mmol) in diethyl ether ( $150\text{ cm}^3$ ), was added slowly *via* cannula  $\text{Bu}^n\text{Li}$  ( $12.3\text{ cm}^3$  of 2.45 M solution in hexanes, 30 mmol). After completion of addition, the bright yellow solution was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, allowed to reach room temperature and stirred for 2 h. Trimethylchlorosilane ( $3.8\text{ cm}^3$ , 30 mmol) was then added *via* syringe and the mixture was stirred for 15 h giving a light yellow suspension. Concentration to *ca.*  $50\text{ cm}^3$ , followed by addition of petroleum ( $150\text{ cm}^3$ ), filtration of the precipitated LiCl and removal of the volatiles under reduced pressure gave a dark orange oil which was purified by vacuum distillation. The product was collected as bright yellow oil (bp  $140\text{ }^{\circ}\text{C}$ ,  $0.05\text{ mmHg}$ ). Yield: 6.74 g, 86%.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.35 (9H, s,  $\text{SiMe}_3$ ), 1.10–1.90 (10H, m, cyclohexyl), 2.32 (3H, s, imino  $\text{CH}_3$ ), 3.53–3.70 (1H, *H* on cyclohexyl C  $\alpha$  to imino N), 6.70 (1H, t, aromatic), 6.83 (1H, m, aromatic), 7.17 (1H, t, aromatic), 7.54 (1H, d, aromatic), 10.0 (1H, s, NH).  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 0.3 ( $\text{SiMe}_3$ ), 15.2 (imino  $\text{CH}_3$ ), 24.9, 26.2, 35.0 (cyclohexyl), 59.2 (cyclohexyl C  $\alpha$  to imino N), 115.7, 117.7, 122.8, 130.0, 130.2, 150.6 (aromatic), 165.9 (C=N).

**Lithium [*o*-(cyclohexyl)iminoethyl]-*N*-(trimethylsilyl)anilide, ( $\text{L}^2\text{Li}$ ), **2**.** To a cooled ( $-78\text{ }^{\circ}\text{C}$ ), stirred solution of  $\text{L}^2\text{H}$  (4.58 g, 15.9 mmol) in petroleum ( $150\text{ cm}^3$ ) was added slowly *via* cannula  $\text{Bu}^n\text{Li}$  ( $7.1\text{ cm}^3$  of 2.45 M solution in hexanes, 17.5 mmol). The mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, allowed to reach room temperature and stirred for 15 h. This produced a light yellow suspension. From this the product was isolated by filtration as a white, extremely air sensitive solid (3.2 g), which was dried *in vacuo*. The mother liquor was reduced to *ca.*  $30\text{ cm}^3$  and cooled to  $-35\text{ }^{\circ}\text{C}$  for 12 h giving a second crop (0.8 g). Yield: 4.0 g, 86%.  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 0.06 (9H, s,  $\text{SiMe}_3$ ), 1.10–1.90 (10H, m,

cyclohexyl) 1.98 (3H, s, imino  $\text{CH}_3$ ), 3.27–3.38 (1H, m, *H* on cyclohexyl C  $\alpha$  to imino N), 6.82–6.88 (2H, m, aromatic), 7.21 (1H, d, aromatic), 7.31 (1H, d, aromatic).  $\delta_{\text{C}}$  ( $\text{C}_6\text{D}_6$ ) 1.8 ( $\text{SiMe}_3$ ), 19.6 (imino  $\text{CH}_3$ ), 25.2, 25.2, 26.1, 34.4 (cyclohexyl), 60.2 (cyclohexyl C  $\alpha$  to imino N), 117.2, 129.8, 129.9, 130.7, 132.3, 156.7 (aromatic), 170.1 (C=N).

**[*o*-(Cyclohexyl)iminoethyl]-*N*-(*tert*-butyldimethylsilyl)aniline ( $\text{L}^3\text{H}$ ).** To a cooled ( $-78\text{ }^{\circ}\text{C}$ ), solution of  $\text{L}^2\text{H}_2$  (4.00 g, 18.5 mmol) in diethyl ether ( $150\text{ cm}^3$ ), was added slowly *via* cannula  $\text{Bu}^n\text{Li}$  ( $8.3\text{ cm}^3$  of 2.45 M solution in hexanes, 20.4 mmol). The mixture was then stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, allowed to reach room temperature and stirred for a further 2 h. To this, was added *via* cannula a solution of *tert*-butyldimethylchlorosilane (3.07 g, 20.4 mmol) in diethyl ether ( $20\text{ cm}^3$ ) and stirring was continued for a further 15 h resulting in the formation of a brown solution and LiCl precipitate. The mixture was concentrated to *ca.*  $50\text{ cm}^3$  and petroleum ( $150\text{ cm}^3$ ) was added to induce complete precipitation of LiCl. Filtration and removal of the volatiles *in vacuo* gave the product as a light brown solid. Yield: 4.71 g, 77%.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.29 (6H, s,  $\text{SiMe}_2$ ), 1.01 (9H, s,  $\text{SiBu}^t$ ), 1.2–1.9 (10H, m, cyclohexyl), 2.31 (3H, s, imino  $\text{CH}_3$ ), 3.50–3.60 (1H, m, *H* on cyclohexyl C  $\alpha$  to imino N), 6.64 (1H, t, aromatic), 6.83 (1H, d, aromatic), 7.10 (1H, t, aromatic), 7.50 (1H, d, aromatic), 9.77 (1H, br. s, NH).  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ )  $-3.8$  ( $\text{SiMe}_2$ ), 16.0 (imino  $\text{CH}_3$ ), 18.4 ( $\text{SiBu}^t$ ), 25.3, 26.0 (cyclohexyl), 26.7 ( $\text{SiBu}^t$ ), 34.5 (cyclohexyl), 60.0 (cyclohexyl C  $\alpha$  to imino N), 115.4, 118.0, 122.7, 129.6, 129.9, 150.1 (aromatic), 166.0 (C=N).

**Lithium [*o*-(cyclohexyl)iminoethyl]-*N*-(*tert*-butyldimethylsilyl)anilide, ( $\text{L}^3\text{Li}$ ), **3**.** To a cooled ( $-78\text{ }^{\circ}\text{C}$ ), stirred solution of  $\text{L}^3\text{H}$  (2.74 g, 8.30 mmol) in petroleum ( $100\text{ cm}^3$ ) was slowly added *via* cannula  $\text{Bu}^n\text{Li}$  ( $3.6\text{ cm}^3$  of 2.45 M solution in hexanes, 8.7 mmol). The mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, allowed to reach room temperature and stirred for 15 h. This produced a light yellow suspension. From this the product was isolated by filtration as a white, extremely air sensitive solid (1.7 g), which was dried *in vacuo*. The mother liquor was reduced to *ca.*  $30\text{ cm}^3$  and cooled to  $-35\text{ }^{\circ}\text{C}$  for 12 h giving a second crop (0.5 g). Yield 2.2 g, 79%.  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ )  $-0.15$  (3H, s,  $\text{SiMe}$ )  $-0.08$  (3H, s,  $\text{SiMe}$ ), 0.90 (9H, s,  $\text{SiBu}^t$ ), 1.15–1.90 (10H, m, cyclohexyl), 1.95 (3H, s, imino  $\text{CH}_3$ ), 3.20–3.40 (1H, m, *H* on cyclohexyl C  $\alpha$  to imino N), 6.75 (1H, t, aromatic), 7.10 (1H, d, aromatic), 7.17 (1H, d, aromatic), 7.24 (1H, t, aromatic).

**$\text{L}^1\text{ZrCl}_3$ , **4**.** To a stirred, cooled ( $-78\text{ }^{\circ}\text{C}$ ) suspension of  $\text{ZrCl}_4$  (0.233 g, 1 mmol) in toluene ( $50\text{ cm}^3$ ) was added a solution of  $\text{L}^1\text{Li}$  (0.255 g, 1 mmol) in toluene ( $50\text{ cm}^3$ ). The suspension was allowed to reach room temperature, when it started developing a yellow colouration, and was stirred at this temperature for 24 h. Filtration through Celite, concentration of the extracts and cooling ( $-20\text{ }^{\circ}\text{C}$ ) gave the product as light yellow crystals. Yield: 0.12 g, 26%.  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 0.25 [9H, s,  $(\text{CH}_3)_3\text{Si}$ ], 1.25 [9H, s,  $(\text{CH}_3)_3\text{C}$ ], 6.7–7.1 (4H, m, aromatic), 7.9 (1H, s, imino). (Found: C, 37.7; H, 5.4; N, 6.0.  $\text{C}_{14}\text{H}_{23}\text{N}_2\text{SiCl}_3\text{Zr}$  requires C, 37.8; H, 5.2; N, 6.3%).

**$\text{L}^2\text{ZrCl}_3$ , **5**.** To a stirred, cooled ( $-78\text{ }^{\circ}\text{C}$ ) suspension of  $\text{ZrCl}_4$  (0.233 g, 1 mmol) in toluene ( $50\text{ cm}^3$ ) was added slowly *via* cannula a solution of  $\text{L}^2\text{Li}$  (0.294 g, 1 mmol) in toluene ( $50\text{ cm}^3$ ). After completion the reaction mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, allowed to reach room temperature and the resulting yellow solution was stirred for 24 h after which period it turned to an orange suspension. The supernatant was filtered and the toluene removed *in vacuo*. The residue was washed with petroleum ( $5 \times 10\text{ cm}^3$ ) yielding the product as an orange solid. Yield: 0.11 g, 23%.  $\delta_{\text{H}}$  ( $\text{CD}_2\text{Cl}_2$ ) 0.24 (9H, s,  $\text{SiMe}_3$ ), 1.00–2.20 (10H, m, cyclohexyl), 2.26 (3H, s, imino  $\text{CH}_3$ ), 3.45–3.60 (1H, m, *H* on cyclohexyl C  $\alpha$  to imino N), 6.50–7.90 (4H, m,

aromatic). (Found: C, 42.4; H, 6.0; N, 6.4.  $C_{17}H_{27}N_2SiCl_3Zr$  requires C, 42.1; H, 5.6; N, 5.8%).

**$L^1_2ZrCl_2$ , 6.** To a stirred and cooled ( $-78^\circ C$ ) solution of  $ZrCl_4(THT)_2$  (0.30 g, 0.72 mmol) in diethyl ether ( $50\text{ cm}^3$ ) was added *via* cannula a solution of  $L^1Li$  (0.37 g, 1.45 mmol) in diethyl ether ( $50\text{ cm}^3$ ). The reaction was stirred at  $-78^\circ C$  for 1 h, allowed to reach room temperature and stirred for 24 h. Removal of the diethyl ether under reduced pressure was followed by extraction of the residue into petroleum (*ca.*  $150\text{ cm}^3$ ). The extracts were filtered, concentrated and the solution cooled to  $-35^\circ C$  to produce pale yellow crystals. Yield: 0.15 g, 32%.  $\delta_H$  ( $C_6D_6$ ) 0.25 (18H, s, SiMe<sub>3</sub>), 1.25 and 1.35 (18H, s, inequivalent *tert*-butyl groups), 6.5–7.0 (8H, m, aromatic), 8.0 and 8.2 (two singlets, 1H each, inequivalent imino *CHN*Bu<sup>t</sup>). (Found: C, 49.5; H, 7.5; N, 7.8.  $C_{28}H_{46}N_4Si_2Cl_2Zr$  requires C, 51.1; H, 7.0; N, 8.5%).

**$L^3_2ZrCl_2$ , 7.** To a stirred and cooled ( $-78^\circ C$ ) solution of  $ZrCl_4(THT)_2$  (0.205 g, 0.5 mmol) in diethyl ether ( $50\text{ cm}^3$ ) was added *via* cannula a solution of  $L^3Li$  (0.336 g, 1 mmol) in diethyl ether ( $50\text{ cm}^3$ ). The reaction was stirred at  $-78^\circ C$  for 1 h, allowed to reach room temperature and then stirred for 24 h. From the pale yellow suspension the diethyl ether was removed *in vacuo* and the residue was extracted into petroleum (*ca.*  $150\text{ cm}^3$ ). The extracts were filtered, concentrated to *ca.*  $25\text{ cm}^3$  and the solution cooled to  $-35^\circ C$  to produce pale yellow crystals. Yield: 0.11 g, 27%. mp  $197\text{--}205^\circ C$ .  $\delta_H$  ( $C_6D_6$ )  $-0.45\text{--}0.25$  (12H, br. s, SiMe<sub>2</sub>), 0.64 (18H, s, SiBu<sup>t</sup>), 1.10–1.90 (20H, m, cyclohexyl), 2.00–2.20 (6H, br. s, imino *CH*<sub>3</sub>), 2.6–2.8 (2H, m, *H* on cyclohexyl C  $\alpha$  to imino N), 6.6–7.5 (8H, m, aromatic *H*). (Found: C, 57.3; H, 8.0; N, 6.7.  $C_{40}H_{66}N_4Si_2Cl_2Zr$  requires C, 58.5; H, 8.1; N, 6.8%).

**$L^2Zr(NMe_2)_2Cl$ , 8.** To a cooled ( $-78^\circ C$ ) solution of  $Zr(NMe_2)_2Cl_2(THF)_2$  (0.790 g, 2 mmol) in THF ( $80\text{ cm}^3$ ), was added slowly a solution of  $L^2Li$  (0.588 g, 2 mmol) in THF ( $40\text{ cm}^3$ ). The light yellow mixture was stirred at  $-78^\circ C$  for 1 h, allowed to reach room temperature and stirred for 15 h giving an orange solution. The THF was removed *in vacuo* and the residue extracted into petroleum ( $3 \times 50\text{ cm}^3$ ). Filtration, concentration of the extracts to *ca.*  $25\text{ cm}^3$  and cooling at  $-35^\circ C$  for 15 h gave an orange solid (0.4 g). Further concentration of the supernatant and cooling gave further product (0.12 g). Yield: 0.52 g, 52%. mp  $120\text{--}127^\circ C$ .  $\delta_H$  ( $C_6D_6$ ) 0.33 (9H, s, SiMe<sub>3</sub>), 1.05–1.95 (10H, m, cyclohexyl), 1.72 (3H, s, imino *CH*<sub>3</sub>), 2.86 (6H, s, NMe<sub>2</sub>), 2.97 (6H, s, NMe<sub>2</sub>), 3.32–3.45 (1H, m, *H* on cyclohexyl C  $\alpha$  to imino N), 6.70 (1H, t, aromatic), 7.06 (2H, m, aromatic), 7.28 (1H, d, aromatic).  $\delta_C$  ( $C_6D_6$ ) 2.5 (SiMe<sub>3</sub>), 11.6 (imino *CH*<sub>3</sub>), 20.6, 22.7, 25.5, 25.7, 32.2 (cyclohexyl), 43.0 (NMe<sub>2</sub>), 43.7 (NMe<sub>2</sub>), 63.7 (cyclohexyl C  $\alpha$  to imino N), 121.2, 129.1, 131.1, 131.4, 145.5 (aromatic), 168.4 (C=N). (Found: C, 49.7; H, 7.8; N, 10.0.  $C_{21}H_{39}N_4SiClZr$  requires C, 50.2; H, 7.8; N, 11.2%).

**Conversion of  $L^2Zr(NMe_2)_2Cl$  to  $L^2ZrCl_3$ .** Compound **8** (0.032 g, 0.07 mmol) was dissolved in *d*<sup>6</sup>-benzene and placed in an NMR tube fitted with a Youngs PTFE tap. Trimethylchlorosilane (8 drops) was added to the solution and the closed NMR tube was heated at  $50^\circ C$  for 48 h during which period the progress of the reaction was monitored by <sup>1</sup>H NMR. After completion the volatiles were removed *in vacuo* to yield the product as a yellow oil which was characterised by NMR after redissolving in *d*<sup>6</sup>-benzene.  $\delta_H$  ( $C_6D_6$ ) 0.25 (9H, s, SiMe<sub>3</sub>), 0.90–1.50 (10H, m, cyclohexyl), 1.60 (3H, s, imino *CH*<sub>3</sub>), 3.30–3.50 (1H, m, *H* on cyclohexyl C  $\alpha$  to imino N), 6.90 (1H, t, aromatic), 6.95–7.10 (2H, m, aromatic), 7.18 (1H, d, aromatic).

**$L^3Zr(NMe_2)_2Cl$ , 9.** This was prepared as above from  $Zr(NMe_2)_2Cl_2(THF)_2$  (0.198 g, 0.5 mmol) and  $L^3Li$  (0.168 g,

0.5 mmol) in THF. X-Ray diffraction quality crystals were obtained by cooling petroleum solutions. Yield: 0.05 g, 18%.  $\delta_H$  ( $C_6D_6$ )  $-0.05$  (3H, s, SiMe) 0.13 (3H, s, SiMe), 0.85 (9H, s, SiBu<sup>t</sup>), 1.10–1.90 (10H, m, cyclohexyl), 1.85 (3H, s, imino *CH*<sub>3</sub>), 2.80 (6H, s, NMe<sub>2</sub>), 2.96 (6H, s, NMe<sub>2</sub>), 3.30–3.45 (1H, m, *H* on cyclohexyl C  $\alpha$  to imino N), 6.90–7.40 (4H, m, aromatic).  $\delta_C$  ( $C_6D_6$ )  $-0.7$  (SiMe<sub>2</sub>), 0.5 (SiMe<sub>2</sub>), 11.6, (SiBu<sup>t</sup>), 20.6 (imino *CH*<sub>3</sub>), 21.9, 25.4, 25.8, (cyclohexyl), 27.2 (SiBu<sup>t</sup>), 32.0, 32.6 (cyclohexyl), 42.9 (NMe<sub>2</sub>), 43.3 (NMe<sub>2</sub>), 64.1 (cyclohexyl C  $\alpha$  to imino N), 120.8, 129.6, 131.1, 131.8, 133.7, 145.5 (aromatic), 168.9 (C=N). (Found: C, 53.25; H, 8.57; N, 10.87.  $C_{24}H_{45}N_4SiClZr$  requires C, 52.95; H, 8.33; N, 10.29%).

**$L^2Zr(NEt_2)_2Cl$ , 10.** This was prepared as above from  $Zr(NEt_2)_2Cl_2(THF)_2$  (0.225 g, 0.5 mmol) and  $L^2Li$  (0.147 g, 0.5 mmol) in THF. X-Ray diffraction quality crystals were obtained by cooling petroleum solutions. Yield: 0.150 g, 54%.  $\delta_H$  ( $C_6D_6$ ) 0.35 (9H, s, SiMe<sub>3</sub>), 0.90 (6H, t, NEt<sub>2</sub>), 1.07 (6H, t, NEt<sub>2</sub>), 1.10–1.80 (10H, m, cyclohexyl), 1.78 (3H, s, imino *CH*<sub>3</sub>), 3.0–3.75 (9H, m, *H* on cyclohexyl C  $\alpha$  to imino N) and two inequivalent NEt<sub>2</sub> groups), 6.75 (1H, t, aromatic), 7.00 (1H, d, aromatic), 7.04 (1H, t, aromatic), 7.30 (1H, d, aromatic).  $\delta_C$  ( $C_6D_6$ ) 2.5 (SiMe<sub>3</sub>), 13.6, 13.7 (NEt<sub>2</sub>), 21.1 (imino *CH*<sub>3</sub>), 25.5, 25.9, 26.0, 31.6, 32.1 (cyclohexyl), 42.0, 42.4 (NEt<sub>2</sub>), 63.7 (cyclohexyl C  $\alpha$  to imino N), 121.2, 128.8, 131.1, 131.8, 134.0, 145.8 (aromatic), 168.8 (C=N). (Found: C, 54.05; H, 8.60; N, 10.15.  $C_{25}H_{47}N_4SiClZr$  requires C, 53.77; H, 8.48; N, 10.03%).

**Conversion of  $L^2Zr(NEt_2)_2Cl$  to  $L^2ZrCl_3$ .** To a solution of **10** (0.200 g, 0.36 mmol) in benzene at room temperature was added *via* syringe trimethylchlorosilane (0.110 g, 1.00 mmol). The bright yellow solution was stirred for 15 h resulting in a very pale orange solution. The volatiles were removed *in vacuo* to yield the product as a pale orange powder. Yield: 0.165 g, 94%.  $\delta_H$  ( $C_6D_6$ ) 0.25 (9H, s, SiMe<sub>3</sub>), 0.90–1.65 (10H, m, cyclohexyl), 1.58 (3H, s, imino *CH*<sub>3</sub>), 3.38–3.52 (1H, m, *H* on cyclohexyl C  $\alpha$  to imino N), 6.85 (1H, t, aromatic), 6.95–7.05 (2H, m, aromatic), 7.18 (1H, d, aromatic).

**Silylamido(ene-iminato)zirconium complex, 11.** To a cooled ( $-78^\circ C$ ), stirred solution of  $Zr(NEt_2)_2Cl_2(THF)_2$  (0.225 g, 0.5 mmol) in THF ( $20\text{ cm}^3$ ) was added slowly a solution of  $L^3Li$  (0.168 g, 0.5 mmol) in THF ( $20\text{ cm}^3$ ). The light yellow mixture was stirred at  $-78^\circ C$  for 1 h, allowed to reach room temperature and stirred for 15 h giving a yellow solution. Removal of the THF *in vacuo* was followed by extraction of the residue into petroleum ( $50\text{ cm}^3$ ). The supernatant solution was then filtered and concentrated to *ca.*  $20\text{ cm}^3$  before cooling to  $-35^\circ C$  for 15 h gave orange, X-ray diffraction quality crystals. Yield: 0.135 g, 45%.  $\delta_H$  ( $C_6D_6$ ) 0.29 (3H, s, SiMe), 0.45 (3H, s, SiMe), 0.79 (6H, t, NEt<sub>2</sub>), 1.02 (9H, s, SiBu<sup>t</sup>), 1.20–2.40 (10H, m, cyclohexyl), 1.30–1.35 (4H, m, THF), 2.8–3.1 (4H, m, NEt<sub>2</sub>), 3.27–3.43 (1H, m, *H* on cyclohexyl C  $\alpha$  to ene-iminato N), 3.69 (4H, t, THF), 4.27 (1H, s, C=CH<sub>2</sub>), 4.44 (1H, s, C=CH<sub>2</sub>), 6.90–7.02 (2H, m, aromatic), 7.10 (1H, t, aromatic), 7.67 (1H, d, aromatic).  $\delta_C$  ( $C_6D_6$ )  $-2.0$  (SiMe<sub>2</sub>), 12.0 (SiBu<sup>t</sup>), 14.1 (NEt<sub>2</sub>), 25.3 (THF), 25.9, 26.1 (cyclohexyl), 27.0 (SiBu<sup>t</sup>), 32.7, 34.1 (cyclohexyl), 42.5 (NEt<sub>2</sub>), 62.9 (cyclohexyl C  $\alpha$  to ene-iminato N), 69.7 (THF), 88.7 (C=CH<sub>2</sub>), 123.9, 127.9, 128.7, 131.5, 135.0, 142.0, (aromatic), 174.0 (C(N)=CH<sub>2</sub>). (Found: C, 56.36; H, 8.54; N, 7.15.  $C_{28}H_{50}N_3SiOClZr$  requires C, 56.10; H, 8.41; N, 7.01%).

**Dimeric zirconium complex, 12.** To a solution of  $L^1H$  (0.20 g, 0.8 mmol) in toluene ( $5\text{ cm}^3$ ) was added a solution of  $Zr(NMe_2)_2Cl_2(THF)_2$  (0.33 g) in toluene (10 ml) and the reaction mixture stirred at  $95^\circ C$  under partial vacuum for 3 days. The solution was then filtered, the solvent removed *in vacuo* and the resulting solid crystallised by dissolving in ether ( $3\text{ cm}^3$ ) and standing overnight at room temperature. Two types of crystal



were formed, one yellow and one orange which could not be separated by chemical means. The crystal structure obtained was that of the yellow crystal.  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 0.27 [9H, s,  $\text{Si}(\text{CH}_3)_3$ ], 1.14 [9H, s,  $\text{C}(\text{CH}_3)_3$ ], 1.53 [6H, s,  $\text{N}(\text{CH}_3)_2$ ], 3.31 (1H, d, aromatic), 6.71 (1H, t, aromatic), 6.88 (1H, d, aromatic), 7.01 (1H, t, aromatic), 8.21 (1H, s, N-CH-N).

**$\text{L}^2\text{Zr}(\text{NMe}_2)_3$ , 13.**  $\text{Zr}(\text{NMe}_2)_4$  (0.067 g, 0.25 mmol) and  $\text{L}^2\text{H}$  (0.072 g, 0.25 mmol) dissolved in  $d^6$ -benzene were placed in an NMR tube fitted with a Youngs PTFE tap. The tube was heated at 50 °C for 72 h during which period the progress of the reaction was monitored by NMR. After completion the volatiles were removed *in vacuo* and the product was obtained as an orange oil which was characterised by NMR after redissolving in  $d^6$ -benzene.  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 0.26 (9H, s,  $\text{SiMe}_3$ ), 1.00–1.80 (10H, m, cyclohexyl), 1.84 (3H, s, imino  $\text{CH}_3$ ), 2.99 (18H, t,  $\text{NMe}_2$ ), 3.30–3.45 (1H, m,  $H$  on cyclohexyl C  $\alpha$  to imino N), 6.72 (1H, t, aromatic), 7.05–7.12 (2H, m, aromatic), 7.25 (1H, d, aromatic).

**Dimeric zirconium complex, 14.**  $\text{Zr}(\text{NMe}_2)_4$  (0.134 g, 0.5 mmol) was dissolved in toluene (15  $\text{cm}^3$ ) and added *via* cannula to  $\text{L}^2\text{H}$  (0.288 g, 1.0 mmol). The reaction was heated at 100 °C for 24 hours and the toluene removed *in vacuo*. X-Ray diffraction quality crystals were grown from a saturated petroleum solution. Once the crystals were formed it was not possible to dissolve them in inert deuterated solvents in order to obtain spectroscopic data.

**Titanium macrocyclic complex, 15.** To a solution of  $\text{TiCl}_2(\text{NMe}_2)_2$  (0.074 g, 0.36 mmol) in toluene (10  $\text{cm}^3$ ) was added *via* cannula a solution of *o*-(*tert*-butyliminomethyl)aniline (0.127 g, 0.72 mmol) in toluene (5  $\text{cm}^3$ ). The mixture was heated at 95 °C overnight before the resulting dark red solution was filtered and the toluene removed *in vacuo*. The resulting solid was recrystallised from diethyl ether at room temperature to give dark red, X-ray diffraction quality crystals. Yield: 0.082 g, 43%.  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 2.3 (9H, s, N- $\text{CH}_3$ ), 2.8 (9H, s, N- $\text{CH}_3$ ), 5.3 (3H, s, Ph- $\text{CHNMe-N}$ ), 6.0 (3H, d, aromatic), 6.5 (3H, t, aromatic), 6.7 (3H, t, aromatic), 7.0 (3H, d, aromatic).  $^{13}\text{C}\{^1\text{H}\}$   $\delta_{\text{C}}$  41.5, 49.2 (N- $\text{CH}_3$ ), 87.2, 106.4, 118.1, 128.3, 129.4, 130.0 (aromatic C), 174.2 [Ph- $\text{CHN}(\text{CH}_3)_2$ ].

**Ethylene polymerization catalysis.<sup>18</sup> 8** (0.050 g, 0.09 mmol) was dissolved in toluene (100 ml) in a glass pressure bottle. MAO (10% weight in toluene) (66.3 ml, 100 mmol) was added to the solution of **8**. This was stirred for 30 minutes at room temperature. The toluene solution was then saturated with ethylene at a pressure of 7 bar for 2 hours. A white solid was formed in the toluene solution during the catalysis run. After 2 hours the ethylene was blown off the system and the polymerization quenched by the addition of ethanol (5 ml). The polymeric solid that was produced was filtered away from the toluene solution and stirred overnight in a 20 vol% ethanolic hydrochloric acid solution, then washed with water and ethanol and dried *in vacuo*.

Average yield of polyethylene produced: 9.068 g. This corresponds to a catalyst activity of *ca.* 8.8 g  $\text{mmol}^{-1} \text{bar}^{-1} \text{h}^{-1}$ . The melting point of the polyethylene was 210–220 °C.

This procedure was followed for **7** but on half the scale. The yield of polyethylene was 2.114 g. This corresponds to a catalyst activity of 3.02 g  $\text{mmol}^{-1} \text{bar}^{-1} \text{h}^{-1}$ . The melting point of the polyethylene was 217–230 °C.

#### Crystal structure determinations of compounds 2, 4, 7, 10, 11, 12, 14, 15

A summary of the crystal data, data collection and refinement for compounds **2**, **4**, **7**, **10**, **11**, **12**, **14**, **15** is given in Table 9. All data sets were collected on an Enraf Nonius Kappa CCD area detector diffractometer with rotating anode FR591 and an

Table 9 Crystal structure determination data

	2	4	7	10	11	12	14	15
Chemical formula	$\text{C}_{34}\text{H}_{54}\text{Li}_2\text{N}_4\text{Si}_2$	$\text{C}_{14}\text{H}_{23}\text{N}_2\text{Cl}_3\text{Si}_1\text{Zr}_1$	$\text{C}_{40}\text{H}_{66}\text{N}_4\text{Cl}_2\text{Si}_2\text{Zr}_1$	$\text{C}_{25}\text{H}_{47}\text{Cl}_1\text{N}_4\text{Si}_1\text{Zr}_1$	$\text{C}_{28}\text{H}_{50}\text{Cl}_1\text{N}_3\text{O}_1\text{Si}_1\text{Zr}_1$	$\text{C}_{16}\text{H}_{29}\text{N}_3\text{Cl}_2\text{Si}_1\text{Zr}_1$	$\text{C}_{18}\text{H}_{30}\text{N}_4\text{Zr}_1$	$\text{C}_{31}\text{H}_{43}\text{N}_6\text{Cl}_1\text{O}_1\text{Ti}_1$
Formula weight	588.87	445	821.27	558.43	599.47	453.63	393.68	599.06
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$Pnca_2$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P1$
$a/\text{\AA}$	30.959(6)	15.31(5)	10.494 (2)	17.2365(7)	14.4679(4)	9.1721(18)	8.7107(2)	10.205(2)
$b/\text{\AA}$	9.919(2)	8.01(3)	31.860(6)	9.3683(5)	12.2609(3)	13.137(3)	18.7443(4)	10.252(2)
$c/\text{\AA}$	11.8838(4)	17.37(4)	14.365(3)	18.9138(13)	18.0837(6)	17.476(4)	11.8704(2)	14.980(3)
$a^\circ$	90	90	90	90	90	90	90	87.61(3)
$\beta^\circ$	90	108.5(2)	106.39(3)	106.866(2)	104.3480(10)	93.88(3)	103.130(1)	84.12(3)
$\gamma^\circ$	90	90	90	90	90	90	90	76.98(3)
$V/\text{\AA}^3$	3649.4(10)	2021(11)	4607.6(16)	2922.8(3)	3107.80(15)	2101.0(7)	1187.48(7)	1518.7(5)
Z	4	4	4	4	4	4	4	2
T/K	150	150	150	150	150	150	150	150
$\mu/\text{mm}^{-1}$	0.124	0.95	0.436	0.527	0.502	0.404	0.588	0.404
No. of data collected	17720	7052	45007	9956	12852	48258	27335	13977
No. of unique data	4403	2892	9212	6424	7048	4293	4320	5918
$R_{\text{int}}$	0.1083	0.136	0.1328	0.0745	0.0506	0.0778	0.0396	0.0655
Final $R(I)$ for $F_o > 2\sigma(F_o)$	0.0482	0.0358	0.0667	0.0722	0.0419	0.0305	0.0269	0.0518
Final $R(F^2)$ for all data	0.1002	0.0858	0.1685	0.2078	0.0912	0.0743	0.0834	0.1352

Oxford Cryosystems low-temperature device, operating in the omega scanning mode with phi scans to fill the Ewald sphere. The only exception is compound **4** was collected using a FAST TV area detector and due to this has a small goodness of fit due to underestimation of esds by the machine. The crystals were isolated under dinitrogen, covered with Flombin vacuum oil and mounted on a glass fibre with silicon grease. All solutions and refinements were performed using the WinGX,<sup>19</sup> Ortep-3<sup>20</sup> for Windows and Platon<sup>21</sup> software packages. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model. Structure **7** contains a highly disordered molecule of diethyl ether which has not been completely modelled due to the extent of the disorder. Structure **10** has a residual peak which does not represent an atom and is located within 0.8 Å of the zirconium centre and is caused by a heavy metal ripple effect.

CCDC reference numbers 181535, 181536, 181538 and 181540–181544.

See <http://www.rsc.org/suppdata/dt/b2/b202471c/> for crystallographic data in CIF or other electronic format.

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