FULL PAPER

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

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A range of trialkylsilylamido complexes of zirconium in which the silylamido functional group is attached to 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 $ZrCl_4$ under a variety of conditions giving rise to complexes of type $LZrCl_3$ and L_2ZrCl_2 , by reaction of LLi with $Zr(NMe_2)_2Cl_2(THF)_2$, and $Zr(NEt_2)_2Cl_2(THF)_2$ giving rise to $LZrCl(NMe_2)_2Cl$ and $LZrCl(NEt_2)_2Cl$, respectively, or by reaction of LH with $Zr(NMe_2)_4$ giving rise to $LZr(NMe_2)_3$. $LZr(NMe_2)_2Cl$ and $LZr(NEt_2)_2Cl$ can be transformed to $LZrCl_3$ by reaction with Me_3SiCl , while $LZr(NMe_2)_3$ on heating rearranges to dimeric imido complexes by elimination of amidosilanes. Aminolysis of $Zr(NMe_2)_2Cl_2(THF)_2$ 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 $Ti(NMe_2)Cl_2$ with LH resulted in the isolation of a C_3 symmetric triamido titanium complex.

Introduction

There is currently great interest in the study of ligand architectures incorporating amido functional groups as nonmetallocene spectators, especially in organometallic complexes of the early transition metals.¹ 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.^{1c,2} 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.² Furthermore, organometallic complexes with Schiff bases, mainly salicylaldimines [6-RN=C(H)C₆H₄O⁻, R = alkyl or aryl] and their derivatives have been extensively explored. Some exhibit high activity or living behaviour in polymerisation reactions.³ 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.^{3,4} In contrast, the coordination chemistry of the anionic ligands that formally originate from salicylaldiminato by replacement of the PhO- group with the isoelectronic PhNR⁻ have received less attention,⁵ even though the tuning opportunities in this case are even broader (Scheme 1).



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 ($R^1 = SiMe_3$, $SiMe_2Bu^t$) substituted analogues of L. As previously noted,⁵ L is related to a wide family of β -diketiminato ligands.⁶

Results and discussion

Syntheses of ligands and ligand precursors

The o-[(tert-butyl)iminomethyl]aniline was synthesised by the literature method.⁵ Following this method, condensation of Bu^tNH₂ 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. L1H, L2H and L3H were prepared by lithiation of the free anilines with BuⁿLi in petrol, followed by quenching of the resulting lithium amides with SiMe₃Cl and SiMe₂-ButCl respectively. Deprotonation of the silylanilines with BuⁿLi in petrol gave the lithium salts L¹Li–L³Li as yellow, crystalline, extremely air sensitive materials. The structure of L²Li (2) in the solid state was determined by single crystal X-ray diffraction methods. The molecular structure of L²Li 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_2N_2 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.⁷ 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.

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

Table 1Selected 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-ethereal polar solvents and their complicated ¹H NMR spectra in solution rendered their full characterisation painstaking. Attempts to increase the crystallinity by using the bulkier and more lipophilic SiMe₂Bu^t were successful in some cases (see below). Furthermore, it became obvious that all three ligands *i.e.* L^1 , L^2 and L^3 were not completely inert, even under careful exclusion of moisture, undergoing insertion, elimination or deprotonation reactions as described below.

Reaction of $ZrCl_4$ with one equivalent of L^1Li or L^2Li 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 ¹H NMR spectra show the presence of one type of resonance associated with the ligand backbone supporting the presence of a five-cooordinate 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 Zr(1)–N(1) bond length of 2.029(7) Å is in the range for a planar amido nitrogen, while the

Table 2Selected 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).

Zr(1)–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 β-diketiminato complexes;⁶ 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 β-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 C_{ipso}–N(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 $ZrCl_4(THT)_2$, THT = tetrahydrothiophene, in ethereal solvents with two equivalents of L¹Li or L³Li resulted in the formation of L¹₂ZrCl₂, **6**, and L³₂ZrCl₂, **7**, respectively. Both compounds can be crystallised from petroleum as yellow, very air sensitive crystals in moderate yields. Their ¹H 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 nonsymmetric 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.* Zr(1)–Cl(2) [*trans* to silylamide, 2.490(3) Å] is longer than Zr(1)–Cl(1) [*trans* to silylamide, 2.414(3) Å] and Zr(1)–N(1) [*trans* to silylamide,



Scheme 2 Compounds in bold have been structurally characterised. Reagents and conditions: (i) L^1H , L^2H or L^3H , Bu^nLi in petroleum (-78 °C to RT); (ii) L^1Li or L^2Li and $ZrCl_4$ in toluene (-78 °C to RT); (iii) L^1Li or L^3Li and $ZrCl_4(THT)_2$ in diethyl ether (-78 °C to RT); (iv) L^2Li and $Zr(NMe_2)_2Cl_2(THF)_2$ in THF (-78 °C to RT); (v) $Zr(NEt_2)_2Cl_2(THF)_2$ in THF (-78 °C to RT); (vi) L^3Li and $Zr(NEt_2)_2Cl_2(THF)_2$ in toluene 50 °C; (viii) heating at 100 °C for 24 h; (ix) $Zr(NMe_2)_2Cl_2(THF)_2$ and L^1H 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 3Selected 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(27) - 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 $Zr(NMe_2)_2Cl_2(THF)_2$ with one equivalent of L^2Li or L^3Li in THF or reaction of $Zr(NEt_2)_2Cl_2(THF)_2$ with L^2Li in THF gave, after crystallisation from petroleum, pale yellow moisture sensitive crystals of **8**, **9** and **10** respectively in reasonable yields. The ¹H NMR spectra of these compounds showed inequivalent dialkylamido groups in addition to peaks assignable to L^2 or L^3 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 4Selected 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 π -bonding amido groups are in the equatorial plane; the two inequivalent dialkylamido groups are planar, indicating a strong π -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 Me₃SiCl were carried out in C_6D_6 as NMR scale experiments. In the reaction mixture peaks assignable to L^2ZrCl_3 and Me₃SiNMe₂ or Me₃SiNEt₂ can be observed. Scaling up of this reaction gave good yields of isolable L^2ZrCl_3 only in the case of 10 (see Experimental).

An unexpected result was obtained in an attempt to prepare $L^3ZrCl(NEt_2)_2$ by salt elimination reaction between $Zr(NEt_2)_2$ -Cl₂(THF)₂ and L^3Li 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 α to the nitrogen can be easily established from the ¹³C{¹H} 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 $L^{3}Li$ and $Zr(NEt_{2})_{2}Cl_{2}(THF)_{2}$ is not fully understood.

Table 5Selected 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 C_6D_6 any silylamido ene-amido dilithium impurity in the L³Li reagent used. This, in combination with the fact that the reaction of $Zr(NMe_2)_2Cl_2(THF)_2$ with L³Li and $Zr(NEt_2)_2Cl_2(THF)_2$ with L²Li 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 LiCH(SiMe_3)_2 with benzonitrile or isocyanides in the presence of tmed.⁸ 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 L¹H with $Zr(NMe)_2Cl_2(THF)_2$ 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 (CO₂, CS₂, RNCO *etc.*) are common in early transition metal amido complexes.⁹ 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 (X_2L_3) dianionic donor with one amido and one asymmetrically trisubstituted amidinato functional group. Functionalised amidinato complexes have recently appeared in the literature.¹⁰

Table 6 Selected	bond lengths (A	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 system¹¹ 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 $Zr(NMe)_2Cl_2(THF)_2$ and the ketimine L²H.

Attempts to introduce L^2 by transamination of $Zr(NMe_2)_4$ with one equivalent of L^2H in toluene resulted in clean formation of **13** as the only detectable product in an NMR scale reaction (C_6D_6). This was established by the disappearance of a peak at 10.4 ppm assignable to the NH of L^2H 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 L^2 by reaction with $Zr(NMe_2)_4$ using two equivalents of L^2H in toluene at 100 °C gave, after crystallisation, low yields of the dimer 14. We were unable to record a ¹H 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 7Selected bond lengths (Å) and angles (°) for 14

1.359(4)	N(1)–Zr(1)	2.217(3)
1.442(5)	N(2)-Zr(1)	2.306(3)
1.465(5)	N(3)-Zr(1)	2.065(3)
1.298(4)	N(4)-Zr(1)	2.064(3)
2.066(3)	$Zr(1) - Zr(1_3)$	3.3262(3)
125.7(3)	$C(7_3)-N(2)-Zr(1)$	133.2(2)
123.7(3)	N(4)-Zr(1)-N(3)	122.49(13)
121.0(3)	$N(4)-Zr(1)-N(1_3)$	119.78(13)
134.3(2)	$N(3)-Zr(1)-N(1_3)$	117.26(12)
122.5(2)	$N(1_3)-Zr(1)-N(1)$	78.16(12)
101.84(12)	N(1)-Zr(1)-N(2)	158.22(10)
123.6(3)		
	$\begin{array}{c} 1.359(4)\\ 1.442(5)\\ 1.465(5)\\ 1.298(4)\\ 2.066(3)\\ \end{array}$ $\begin{array}{c} 125.7(3)\\ 123.7(3)\\ 121.0(3)\\ 134.3(2)\\ 122.5(2)\\ 101.84(12)\\ 123.6(3)\\ \end{array}$	$\begin{array}{llllllllllllllllllllllllllllllllllll$



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 L² 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 Zr_2N_2 ring is highly asymmetric [Zr(1)-N(2) =2.2187(15) Å, $Zr(1)-N(2_3) = 2.0652(14)$ Å]. There is no evidence of any metal-metal interaction $[Zr(1)-Zr(1_3) =$ 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 π -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 Me₃SiNMe₂ 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 L¹H to titanium gave unexpected results. Reaction of Ti(NMe)₂Cl₂ with o-C₆H₄(NH₂)(CH=NBu^t)] in toluene at 100 °C gave complex **15** stabilised by a novel face-blocking C₃ symmetric trianionic macrocyclic amide as shown in Scheme 3. It was the only product detected by ¹H NMR spectroscopy in solution.

Air stable deep red crystals of **15** were isolated by crystallisation from diethyl ether solutions. The ¹H 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 π -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 of *o-tert*butyliminomethylaniline is necessary for the reaction to occur. This is shown by the inertness of the electronically richer $Ti(NMe_2)_4$ which fails to produce **15** by heating at 100 °C with *o-tert*-butyliminomethylaniline, possibly due to its reduced nucleophilicity.

The self-condensation of *o*-aminobenzaldehyde gives cyclic trimeric and tetrameric products, which were unambiguously characterised.¹² If the condensation is carried out in the presence of metal templates, macrocyclic complexes with the "faceblocking" 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.¹² Furthermore, complexes with **A** and **B** can react with strong nucleophiles (\mathbb{R}^- , \mathbb{RO}^- , \mathbb{RS}^- *etc.*) at the azomethine carbons giving derivatives with functionalised anionic macrocycles. A ruthenium complex incorporating **A** has recently been reported.¹³

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⁻¹ bar⁻¹ h⁻¹ 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 L¹ and L² 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 (¹H). The spectra were referenced internally using the signal from the residual protio-solvent (¹H) or the signals of the solvent (¹³C). All manipulations involving moisture sensitive materials were carried out under vacuum or N₂ using standard Schlenk techniques. All solvents used were dried by continuous reflux under N₂ 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: L¹H₂,⁵ ZrCl₄(THT)₂,¹⁴ Zr(NMe₂)₄,¹⁵ Zr(NMe₂)-Cl₂(THF)₂ and Zr(NEt₂)Cl₂(THF)₂,¹⁶ TiCl₂(NMe₂)₂.¹⁷

Synthesis

[*o*-(*tert*-Butyl)iminomethyl]-*N*-(trimethylsilyl)aniline (L¹H). To a cooled (-78 °C), stirred solution of *o*-(*tert*-butyl)iminoaniline (5.0 g, 28.5 mmol) in ether (200 cm³) was added dropwise a solution of BuⁿLi (12.8 cm³ 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 °C and a solution of Me₃SiCl (3.40 g, 31.3 mmol) in ether (10 cm³) 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 × 100 cm³), 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 68–70 °C, 0.05 mmHg). Yield: 4.6 g, 65%. $\delta_{\rm H}$ (C₆D₆) 0.25 [9H, s, (CH₃)₃Si], 1.2 [9H, s, (CH₃)₃C], 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, (L¹Li), 1. To a solution of L¹H (3 g, 12 mmol) in petroleum (50 cm³) at -78 °C was added slowly via cannula BuⁿLi (5.4 cm³ of 2.45 M solution in hexanes, 13.2 mmol). The mixture was stirred at -78 °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 (L²H₂). 2-Aminoacetophenone (10.0 g, 74.1 mmol) was dissolved in toluene (100 cm³) and to the solution were added activated 4 Å molecular sieves and cyclohexylamine (63 cm³, 552 mmol). The resulting orange mixture was stirred at 100 °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%. $\delta_{\rm H}$ (CDCl₃) 1.25–1.90 (10H, m, cyclohexyl), 2.30 (3H, s, imino CH₃), 3.50–3.70 (1H, m, *H* on cyclohexyl C α to imino N), 6.55 (2H, br. s, NH₂), 6.65 (2H, m, aromatic), 7.10 (1H, t, aromatic), 7.50 (1H, d, aromatic). $\delta_{\rm C}$ (CDCl₃) 15.7 (imino CH₃), 24.9, 26.0, 34.3 (cyclohexyl), 59.3 (cyclohexyl C α to imino N), 116.0, 117.0, 121.7, 129.4, 129.9, 148.3 (aromatic), 165.1 (C=N).

(L²H). [o-(Cyclohexyl)iminoethyl]-N-(trimethylsilyl)aniline To a cooled (-78 °C), stirred solution of L²H₂ (5.90 g, 27.3 mmol) in diethyl ether (150 cm³), was added slowly via cannula BuⁿLi (12.3 cm³ of 2.45 M solution in hexanes, 30 mmol). After completion of addition, the bright yellow solution was stirred at -78 °C for 1 h, allowed to reach room temperature and stirred for 2 h. Trimethylchlorosilane (3.8 cm³, 30 mmol) was then added via syringe and the mixture was stirred for 15 h giving a light vellow suspension. Concentration to $ca. 50 \text{ cm}^3$, followed by addition of petroleum (150 cm³), 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 °C, 0.05 mm Hg). Yield: 6.74 g, 86%. $\delta_{\rm H}$ (CDCl₃) 0.35 (9H, s, SiMe₃), 1.10-1.90 (10H, m, cyclohexyl), 2.32 (3H, s, imino CH₃), 3.53–3.70 (1H, H on cyclohexyl C α 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). δ_C (CDCl₃) 0.3 (SiMe₃), 15.2 (imino CH₃), 24.9, 26.2, 35.0 (cyclohexyl), 59.2 (cyclohexyl C α 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, (L²Li), 2. To a cooled (-78 °C), stirred solution of L²H (4.58 g, 15.9 mmol) in petroleum (150 cm³) was added slowly *via* cannula BuⁿLi (7.1 cm³ of 2.45 M solution in hexanes, 17.5 mmol). The mixture was stirred at -78 °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 cm³ and cooled to -35 °C for 12 h giving a second crop (0.8 g). Yield: 4.0 g, 86%. $\delta_{\rm H}$ (C₆D₆) 0.06 (9H, s, SiMe₃), 1.10–1.90 (10H, m, cyclohexyl) 1.98 (3H, s, imino CH₃), 3.27–3.38 (1H, m, H on cyclohexyl C α to imino N), 6.82–6.88 (2H, m, aromatic), 7.21 (1H, d, aromatic), 7.31 (1H, d, aromatic). $\delta_{\rm C}$ (C₆D₆) 1.8 (SiMe₃), 19.6 (imino CH₃), 25.2, 25.2, 26.1, 34.4 (cyclohexyl), 60.2 (cyclohexyl C α 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 (L³H). To a cooled (-78 °C), solution of L²H₂ (4.00 g, 18.5 mmol) in diethyl ether (150 cm³), was added slowly via cannula BuⁿLi (8.3 cm³ of 2.45 M solution in hexanes, 20.4 mmol). The mixture was then stirred at -78 °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 cm³) 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 cm³ and petroleum (150 cm³) 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%. δ_H (CDCl₃) 0.29 (6H, s, SiMe₂), 1.01 (9H, s, SiBu^t), 1.2–1.9 (10H, m, cyclohexyl), 2.31 (3H, s, imino CH₃), 3.50-3.60 (1H, m, H on cyclohexyl C α 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). $\delta_{\rm C}$ (CDCl₃) -3.8 (SiMe₂), 16.0 (imino CH₃), 18.4 (SiBu^t), 25.3, 26.0 (cyclohexyl), 26.7 (SiBu^t), 34.5 (cyclohexyl), 60.0 (cyclohexyl C α to imino N), 115.4, 118.0, 122.7, 129.6, 129.9, 150.1 (aromatic), 166.0 (C=N).

[o-(cyclohexyl)iminoethyl]-N-(tert-butyldimethyl-Lithium silyl)anilide, (L³Li), 3. To a cooled (-78 °C), stirred solution of L³H (2.74 g, 8.30 mmol) in petroleum (100 cm³) was slowly added via cannula BuⁿLi (3.6 cm³ of 2.45 M solution in hexanes, 8.7 mmol). The mixture was stirred at -78 °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 cm³ and cooled to -35 °C for 12 h giving a second crop (0.5 g). Yield 2.2 g, 79%. $\delta_{\rm H}$ (C₆D₆) -0.15 (3H, s, SiMe) -0.08 (3H, s, SiMe), 0.90 (9H, s, SiBu^t), 1.15-1.90 (10H, m, cyclohexyl), 1.95 (3H, s, imino CH₃), 3.20–3.40 (1H, m, H on cyclohexyl C α to imino N), 6.75 (1H, t, aromatic), 7.10 (1H, d, aromatic), 7.17 (1H, d, aromatic), 7.24 (1h, t, aromatic).

L¹ZrCl₃, 4. To a stirred, cooled (-78 °C) suspension of ZrCl₄ (0.233 g, 1 mmol) in toluene (50 cm³) was added a solution of L¹Li (0.255 g, 1 mmol) in toluene (50 cm³). 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 °C) gave the product as light yellow crystals. Yield: 0.12 g, 26%. $\delta_{\rm H}$ (C₆D₆) 0.25 [9H, s, (CH₃)₃Si], 1.25 [9H, s, (CH₃)₃C], 6.7–7.1 (4H, m, aromatic), 7.9 (1H, s, imino). (Found: C, 37.7; H, 5.4; N, 6.0. C₁₄H₂₃N₂SiCl₃Zr requires C, 37.8; H, 5.2; N, 6.3%).

L²ZrCl₃, 5. To a stirred, cooled (-78 °C) suspension of ZrCl₄ (0.233 g, 1 mmol) in toluene (50 cm³) was added slowly *via* cannula a solution of L²Li (0.294 g, 1 mmol) in toluene (50 cm³). After completion the reaction mixture was stirred at -78 °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 × 10 cm³) yielding the product as an orange solid. Yield: 0.11 g, 23%. $\delta_{\rm H}$ (CD₂Cl₂) 0.24 (9H, s, SiMe₃), 1.00–2.20 (10H, m, cyclohexyl), 2.26 (3H, s, imino CH₃), 3.45–3.60 (1H, m, H on cyclohexyl C α 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%).

L¹₂ZrCl₂, 6. To a stirred and cooled (-78 °C) solution of ZrCl₄(THT)₂ (0.30 g, 0.72 mmol) in diethyl ether (50 cm³) was added *via* cannula a solution of L¹Li (0.37 g, 1.45 mmol) in diethyl ether (50 cm³). The reaction was stirred at -78 °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 cm³). The extracts were filtered, concentrated and the solution cooled to -35 °C to produce pale yellow crystals. Yield: 0.15 g, 32%. $\delta_{\rm H}$ (C₆D₆) 0.25 (18H, s, SiMe₃), 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 CHNBu^t). (Found: C, 49.5; H, 7.5; N, 7.8. C₂₈H₄₆N₄Si₂Cl₂Zr requires C, 51.1; H, 7.0; N, 8.5%).

L³₂**ZrCl**₂, **7.** To a stirred and cooled (−78 °C) solution of ZrCl₄(THT)₂ (0.205 g, 0.5 mmol) in diethyl ether (50 cm³) was added *via* cannula a solution of L³Li (0.336 g, 1 mmol) in diethyl ether (50 cm³). The reaction was stirred at −78 °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 cm³). The extracts were filtered, concentrated to *ca.* 25 cm³ and the solution cooled to −35 °C to produce pale yellow crystals. Yield: 0.11 g, 27%. mp 197–205 °C. $\delta_{\rm H}$ (C₆D₆) −0.45–0.25 (12H, br. s, SiMe₂), 0.64 (18H, s, SiBu¹), 1.10–1.90 (20H, m, cyclohexyl), 2.00–2.20 (6H, br. s, imino *CH*₃), 2.6–2.8 (2H, m, *H* on cyclohexyl C *a* to imino N), 6.6–7.5 (8H, m, aromatic *H*). (Found: C, 57.3; H, 8.0; N, 6.7. C₄₀H₆₆N₄Si₂Cl₂Zr requires C, 58.5; H, 8.1; N, 6.8%).

L²Zr(NMe₂)₂Cl, 8. To a cooled (-78 °C) solution of Zr-(NMe₂)₂Cl₂(THF)₂ (0.790 g, 2 mmol) in THF (80 cm³), was added slowly a solution of L²Li (0.588 g, 2 mmol) in THF (40 cm³). The light yellow mixture was stirred at -78 °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 cm³ and cooling at -35 °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 120–127 °C. $\delta_{\rm H}$ (C₆D₆) 0.33 (9H, s, SiMe₃), 1.05–1.95 (10H, m, cyclohexyl), 1.72 (3H, s, imino CH₃), 2.86 (6H, s, NMe₂), 2.97 (6H, s, NMe₂), 3.32-3.45 (1H, m, H on cyclohexyl C a to imino N), 6.70 (1H, t, aromatic), 7.06 (2H, m, aromatic), 7.28 (1H, d, aromatic). δ_C (C₆D₆) 2.5 (SiMe₃), 11.6 (imino CH₃), 20.6, 22.7, 25.5, 25.7, 32.2 (cyclohexyl), 43.0 (NMe₂), 43.7 (NMe₂), 63.7 (cyclohexyl C α 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. C₂₁H₃₉N₄SiClZr requires C, 50.2; H, 7.8; N, 11.2%).

Conversion of L²Zr(NMe₂)₂Cl to L²ZrCl₃. Compound **8** (0.032 g, 0.07 mmol) was dissolved in *d*⁶-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 °C for 48 h during which period the progress of the reaction was monitored by ¹H 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*⁶-benzene. $\delta_{\rm H}$ (C₆D₆) 0.25 (9H, s, SiMe₃), 0.90–1.50 (10H, m, cyclohexyl), 1.60 (3H, s, imino CH₃), 3.30–3.50 (1H, m, *H* on cyclohexyl C α to imino N), 6.90 (1H, t, aromatic), 6.95–7.10 (2H, m, aromatic), 7.18 (1H, d, aromatic).

 $L^{3}Zr(NMe_{2})_{2}Cl$, 9. This was prepared as above from Zr-(NMe₂)₂Cl₂(THF)₂ (0.198 g, 0.5 mmol) and L³Li (0.168 g,

0.5 mmol) in THF. X-Ray diffraction quality crystals were obtained by cooling petroleum solutions. Yield: 0.05 g, 18%. $\delta_{\rm H}$ (C₆D₆) -0.05 (3H, s, SiMe) 0.13 (3H, s, SiMe), 0.85 (9H, s, SiBu^t), 1.10–1.90 (10H, m, cyclohexyl), 1.85 (3H, s, imino CH₃), 2.80 (6H, s, NMe₂), 2.96 (6H, s, NMe₂), 3.30–3.45 (1H, m, H on cyclohexyl C *a* to imino N), 6.90–7.40 (4H, m, aromatic). $\delta_{\rm C}$ (C₆D₆) -0.7 (SiMe₂), 0.5 (SiMe₂), 11.6, (SiBu^t), 20.6 (imino CH₃), 21.9, 25.4, 25.8, (cyclohexyl), 27.2 (SiBu^t), 32.0, 32.6 (cyclohexyl), 42.9 (NMe₂), 43.3 (NMe₂), 64.1 (cyclohexyl C *a* 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. C₂₄H₄₅N₄Si-ClZr requires C, 52.95; H, 8.33; N, 10.29%).

L²Zr(NEt₂)₂Cl, 10. This was prepared as above from Zr-(NEt₂)₂Cl₂(THF)₂ (0.225 g, 0.5 mmol) and L²Li (0.147 g, 0.5 mmol) in THF. X-Ray diffraction quality crystals were obtained by cooling petroleum solutions. Yield: 0.150 g, 54%. $\delta_{\rm H}$ (C₆D₆) 0.35 (9H, s, SiMe₃), 0.90 (6H, t, NEt₂), 1.07 (6H, t, NEt₂), 1.10–1.80 (10H, m, cyclohexyl), 1.78 (3H, s, imino CH₃), 3.0–3.75 (9H, m, H on cyclohexyl C α to imino N and two inequivalent NEt₂ groups), 6.75 (1H, t, aromatic), 7.00 (1H, d, aromatic), 7.04 (1H, t, aromatic), 7.30 (1H, d, aromatic). $\delta_{\rm c}$ (C₆D₆) 2.5 (SiMe₃), 13.6, 13.7 (NEt₂), 21.1 (imino CH₃), 25.5, 25.9, 26.0, 31.6, 32.1 (cyclohexyl), 42.0, 42.4 (NEt₂), 63.7 (cyclohexyl C α 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. C₂₅H₄₇N₄SiClZr requires C, 53.77; H, 8.48; N, 10.03%).

Conversion of L²Zr(NEt₂)₂Cl to L²ZrCl₃. 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%. $\delta_{\rm H}$ (C₆D₆) 0.25 (9H, s, SiMe₃), 0.90–1.65 (10H, m, cyclohexyl), 1.58 (3H, s, imino CH₃), 3.38–3.52 (1H, m, H on cyclohexyl C α 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 °C), stirred solution of Zr(NEt₂)₂Cl₂(THF)₂ (0.225 g, 0.5 mmol) in THF (20 cm³) was added slowly a solution of L³Li (0.168 g, 0.5 mmol) in THF (20 cm³). The light yellow mixture was stirred at -78 °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 cm³), The supernatant solution was then filtered and concentrated to ca. 20 cm³ before cooling to -35 °C for 15 h gave orange, X-ray diffraction quality crystals. Yield: 0.135 g, 45%. $\delta_{\rm H}$ (C₆D₆) 0.29 (3H, s, SiMe), 0.45 (3H, s, SiMe), 0.79 (6H, t, NEt₂), 1.02 (9H, s, SiBut), 1.20-2.40 (10H, m, cyclohexyl), 1.30-1.35 (4H, m, THF), 2.8-3.1 (4H, m, NEt₂), 3.27-3.43 (1H, m, H on cyclohexyl C a to ene-iminato N), 3.69 (4H, t, THF), 4.27 (1H, s, C=CH₂), 4.44 (1H, s, C=CH₂), 6.90-7.02 (2H, m, aromatic), 7.10 (1H, t, aromatic), 7.67 (1H, d, aromatic). $\delta_{\rm C}$ (C₆D₆) -2.0 (SiMe₂), 12.0 (SiBu^t), 14.1 (NEt₂), 25.3 (THF), 25.9, 26.1 (cyclohexyl), 27.0 (SiBut), 32.7, 34.1 (cyclohexyl), 42.5 (NEt₂), 62.9 (cyclohexyl C α to ene-iminato N), 69.7 (THF), 88.7 (C=CH₂), 123.9, 127.9, 128.7, 131.5, 135.0, 142.0, (aromatic), 174.0 (C(N)=CH₂). (Found: C, 56.36; H, 8.54; N, 7.15. C₂₈H₅₀N₃SiOClZr requires C, 56.10; H, 8.41; N, 7.01%).

Dimeric zirconium complex, 12. To a solution of $L^{1}H$ (0.20 g, 0.8 mmol) in toluene (5 cm³) was added a solution of Zr-(NMe₂)₂Cl₂(THF)₂ (0.33 g) in toluene (10 ml) and the reaction mixture stirred at 95 °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 cm³) 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. $\delta_{\rm H}$ (C₆D₆) 0.27 [9H, s, Si(CH₃)₃], 1.14 [9H, s, C(CH₃)₃], 1.53 [6H, s, N(CH₃)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).

L²Zr(NMe₂)₃, 13. Zr(NMe₂)₄ (0.067 g, 0.25 mmol) and L²H (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. $\delta_{\rm H}$ (C₆D₆) 0.26 (9H, s, SiMe₃), 1.00–1.80 (10H, m, cyclohexyl), 1.84 (3H, s, imino CH₃), 2.99 (18H, t, NMe₂), 3.30–3.45 (1H, m, H on cyclohexyl C α to imino N), 6.72 (1H, t, aromatic), 7.05–7.12 (2H, m, aromatic), 7.25 (1H, d, aromatic).

Dimeric zirconium complex, 14. $Zr(NMe_2)_4$ (0.134 g, 0.5 mmol) was dissolved in toluene (15 cm³) and added *via* cannula to L²H (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 TiCl₂-(NMe₂)₂ (0.074 g, 0.36 mmol) in toluene (10 cm³) was added *via* cannula a solution of *o*-(*tert*-butyliminomethyl)aniline (0.127 g, 0.72 mmol) in toluene (5 cm³). 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%. $\delta_{\rm H}$ (C₆D₆) 2.3 (9H, s, N–CH₃), 2.8 (9H, s, N–CH₃), 5.3 (3H, s, Ph–CHNMe–N), 6.0 (3H, d, aromatic), 6.5 (3H, t, aromatic), 6.7 (3H, t, aromatic), 7.0 (3H, d, aromatic). ¹³C{¹H} $\delta_{\rm c}$ 41.5, 49.2 (N–CH₃), 87.2, 106.4, 118.1, 128.3, 129.4, 130.0 (aromatic *C*), 174.2 [Ph–CHN(CH₃)₂].

Ethylene polymerization catalysis.¹⁸ 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, 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 mmol⁻¹ bar⁻¹ 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 $3.02 \text{ g mmol}^{-1} \text{ bar}^{-1} \text{ h}^{-1}$. 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 determined	ermination data							
	2	4	L	10	П	12	14	15
	SIN: LI U	E B D N H O	E S D N H C		E BOND H D	T S D N H C	EN II C	
	C34II54LI2IN43I2	C14 ^{T1} 23 ^{TN} 2 ^{C1} 3 ^{S1} 1 ^{LT} 1		C25H47U11N4SH2ET	C281150Cl11N3Cl2l1LL1	C16/1/29/N3/C12/SH1/LF1	C18113014211	C31T43IN6C11U111
rormula weight	10.000	C 41	821.27	C4.0CC	14.660	c0.cct	00.060	00.660
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$Pna2_1$	$P2_{n/n}$	P2,ln	$P2_1/n$	P2,ln	$P2_1/n$	P2,ln	$P\overline{l}$
	30.959(6)	15.31(5)	10.494 (2)	17.2365(7)	14.4679(4)	9.1721(18)	8.7107(2)	10.205(2)
Å/Å	9.919(2)	8.01(3)	31.860(6)	9.3683(5)	12.2609(3)	13.137(3)	18.7443(4)	10.252(2)
з/Å	11.8838(4)	17.37(4)	14.365(3)	18.9138(13)	18.0837(6)	17.476(4)	11.8704(2)	14.980(3)
<i>x</i> /°	90	90	90	90	90	90	06	87.61(3)
g/°	90	108.5(2)	106.39(3)	106.866(2)	104.3480(10)	93.88(3)	103.130(1)	84.12(3)
v/°	90	90	90	90	90	90	06	76.98(3)
$V/Å^3$	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	5
T/K	150	150	150	150	150	150	150	150
u/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
Rint	0.1083	0.136	0.1328	0.0745	0.0506	0.0778	0.0396	0.0655
Final $R(F)$ for $F_{a} > 2\sigma(F_{a})$	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,19 Ortep-320 for Windows and Platon²¹ 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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