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o-(Cyclohexyliminoethyl)(arylamido)benzene and related complexes of zirconium and titanium. The non-innocence of the ketimino functionality

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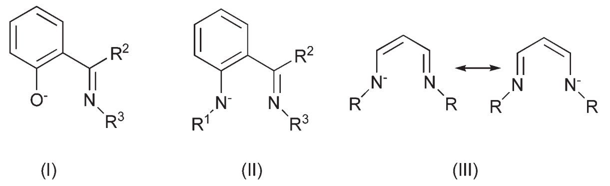
N-Arylamido complexes of zirconium in which the amido functional group is attached to an *o*-(alkyliminoethyl) substituted aromatic ring, have been synthesised by salt elimination reactions and characterised by spectroscopic and diffraction methods; they are analogous to the *N*-silylamido species recently reported (*Dalton Trans.*, 2002, 3290–3299). The ligands 2-[CyN=C(CH$_3$)]C$_6$H$_4$N(H)(xyl), L$^{\text{xyl}}$H, and 2-[CyN=C(CH$_3$)]C$_6$H$_4$N(H)(mes) L$^{\text{mes}}$H, Cy = C$_6$H$_{11}$, xyl = 3,5-Me$_2$C$_6$H$_3$ mes = 2,4,6-Me$_3$C$_6$H$_2$, were prepared in good yields by Buchwald–Hartwig amination of the arylbromides with 2-[CyN=C(CH$_3$)]C$_6$H$_4$NH$_2$. Reaction of L$^{\text{mes}}$Li with Zr(NEt$_2$)$_2$Cl$_2$(thf)$_2$ gave after chloride substitution the arylamido ketimino complex L$^{\text{mes}}$Zr(NEt$_2$)$_2$Cl **1**; variable amounts of the arylamido vinylamido complex **2** were also obtained. Interaction of L$^{\text{mes}}$Li or L$^{\text{xyl}}$Li with Ti(NMe$_2$)$_2$Cl$_2$ gave rise to the tripodal bis-amido amino complexes **5** and **6** possibly formed by ligand rearrangement involving migration of the dimethylamido group to the ketimino carbon.

Introduction

The recent search for non-cyclopentadienyl ‘spectator’ ligands for the early transition metals has focussed on chelating anionic amido and alkoxo or aryloxo ligands as well as mixed donor designs comprising anionic (amido, alkoxo *etc.*) linked with neutral functionalities.[1] Salicylaldiminato [2-R^{3}N=C(R^2)C$_6$H$_4$O$^-$ R^2 = H, (I in Scheme 1)] complexes[2] are well established across the periodic table, some of them exhibiting interesting catalytic properties. Salicylaldiminato complexes with group 4 metals have given rise to an important series of highly active titanium alkene polymerisation catalysts.[3,4]



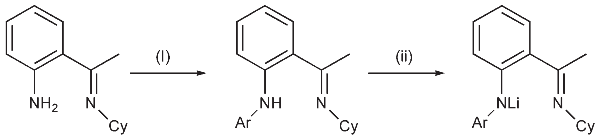
Scheme 1

We have recently embarked on an investigation of the isoelectronic amido analogues of the salicylaldiminato, (R^2 = H), and salicylketiminato, (R^2 = Me), ligands (II in Scheme 1, R^1 = SiMe$_3$).[5] These are related to the versatile β-diketiminato (nacnac) ligands[6] [(III) in Scheme 1] which are successful ‘spectators’ on many electrophilic metal centres. Our first paper described the synthesis of silylamido complexes of Ti and Zr *i.e.* {2-[R^{3}N=C(R^2)]C$_6$H$_4$NR^1}$^-$, R^1 = SiMe$_3$ or SiMe$_2$Bu^t, R^2 = H or Me, R^3 = Cy or Bu^t. In this paper we extend our studies to arylamido complexes of Ti and Zr {2-[R^{3}N=C(R^2)]C$_6$H$_4$NR^1}$^-$, R^1 = mesityl, 3,5-xylyl, R^2 = Me, R^3 = Cy. Recently, Piers *et al.* have described related ligands and their yttrium complexes.[7]

Results and discussion

Syntheses of ligands and ligand precursors

The synthesis of the substituted anilines L$^{\text{xyl}}$H and L$^{\text{mes}}$H used as precursors to the anionic arylamido ligands [(II) in Scheme 1, R^2 = Me, R^3 = cyclohexyl, R^1 = 3,5-xylyl, L$^{\text{xyl}}$; R^1 = mesityl, L$^{\text{mes}}$] is summarised in Scheme 2.



Scheme 2 The synthesis of ligand precursors. Reagents and conditions: (i) Ar = 3,5-xylyl, Pd(dba)$_2$, rac-BINAP, 3,5-Me$_2$C$_6$H$_3$Br, Bu^{t}ONa, xylenes, 140 °C; Ar = mesityl, Pd(dba)$_2$, 2,4,6-Me$_3$C$_6$H$_2$Br, Bu^{t}ONa, [*N*,*N*′-bis(2,6-Pr$^i_2$C$_6$H$_3$) imidazolinium] chloride, dioxane 100 °C. (ii) Bu^{n}Li/petroleum, −78 °C to RT.

The method involves palladium catalysed arylation[8] of the *o*-(1-cyclohexylimino-ethyl)-aniline,[5] which is easily available in multigram quantities. Using the sterically unhindered 3,5-xylylbromide the original Buchwald protocol [*rac*-BINAP, Pd(dba)$_2$, Bu^{t}ONa] worked well in hot (140 °C) xylenes. However, with the bulkier mesityl bromide the reaction was too slow to be of any synthetic use. In this case, we found that the catalytic system based on a palladium N-heterocyclic carbene active species [imidazolinium salt, Pd(dba)$_2$ Bu^{t}ONa, dioxane][9] gave quantitative conversion to the desired product after 3 days at 100 °C. Both arylations proceeded with high selectivity as evidenced by the absence of any side products (by GC/MS). Arylation with 2,4,6-Pr$^i_3$-C$_6$H$_2$Br following any of the previously mentioned protocols was not successful presumably due to steric reasons. Finally, arylation of the substituted aldimine [*i.e.* {2-[R^{3}N=C(H)]C$_6$H$_4$NH$_2$}] with 3,5-xylyl or mesityl bromides was not successful using either the N-heterocyclic carbene or the phosphine based catalytic systems under a variety of reaction conditions. The arylated aldimine (L$^{\text{ald}}$H) could be obtained by coupling of *o*-(cyclohexyliminomethyl)-bromobenzene with 2,4,6-trimethylaniline as described in the experimental section.

The lithiation of the new anilines was carried out cleanly with Bu^{n}Li in light petroleum. The lithium amides are yellow very air sensitive crystalline materials, which were characterised by analytical, spectroscopic and diffraction methods. The structure of L$^{\text{xyl}}$Li in the solid state as determined by single crystal X-ray diffraction is shown in Fig. 1a; the Li$_3$N$_3$ core is given in Fig. 1b with important bond lengths and angles in Table 1. The molecule exhibits a trimeric structure, with the amido nitrogen and lithium atoms occupying the corners of a distorted cyclohexane chair conformer. The lithium coordination sphere comprises one imino [2.026(10)–2.047(10) Å] and two amido [1.942(10)–2.048(10) Å] nitrogen atoms. Similar bond distances have been observed in the structures of the silylamido analogues.[5] The metrical data around the imine carbons indicate a planar geometry with C=N double bonds in the normal range [1.269(6)–1.291(6) Å]. In solution L$^{\text{xyl}}$Li exists as an equilibrium mixture of two species with differing degrees of aggregation (possibly dimeric and trimeric). This is evidenced by the ^{1}H, ^{13}C

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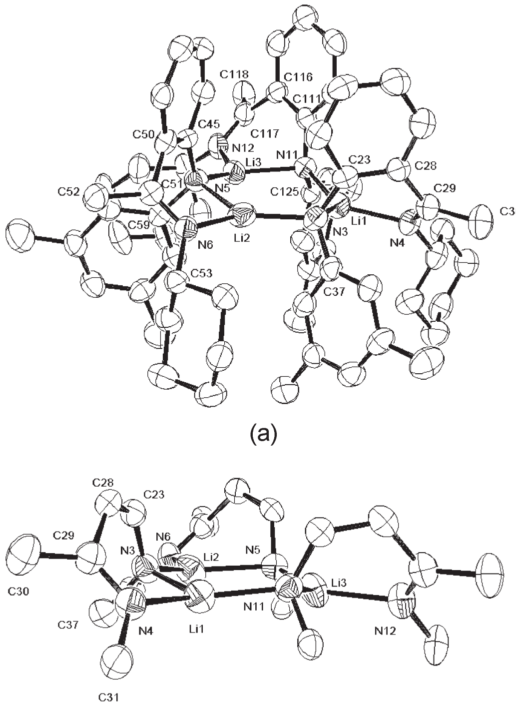
Table 1 Bond lengths (Å) and angles (°) for $L^{xyl}Li$

Li(1)–N(11)	1.943(9)	Li(1)–N(3)	2.042(9)
Li(1)–N(4)	2.029(10)	Li(1)–Li(2)	3.233(12)
Li(1)–Li(3)	3.181(12)	N(3)–C(23)	1.394(6)
C(23)–C(28)	1.425(7)	C(28)–C(29)	1.490(8)
N(4)–C(29)	1.275(6)	C(29)–C(30)	1.520(7)
N(3)–Li(1)–N(11)	128.0(5)	N(3)–Li(2)–N(5)	129.1(5)
N(5)–Li(3)–N(11)	130.6(5)	Li(1)–N(3)–Li(2)	108.5(4)
Li(2)–N(5)–Li(3)	106.7(4)	Li(3)–N(11)–Li(1)	106.0(4)
N(3)–Li(1)–N(4)	96.8(4)	C(23)–N(3)–Li(1)	91.7(4)
N(3)–C(23)–C(28)	125.5(5)	C(23)–C(28)–C(29)	122.8(5)
C(28)–C(29)–N(4)	119.1(5)	C(29)–N(4)–Li(1)	111.2(5)

Table 2 Bond lengths (Å) and angles (°) for $L^{mes}Li$

Li(1)–N(1)	1.950(8)	Li(1)–N(3)	2.071(9)
Li(2)–N(1)	2.178(9)	Li(2)–N(3)	1.924(8)
Li(1)–N(2)	1.952(8)	Li(2)–N(4)	1.974(9)
Li(1)–Li(2)	2.362(11)	N(1)–C(1)	1.389(5)
C(1)–C(6)	1.435(6)	C(6)–C(7)	1.487(6)
C(7)–C(8)	1.516(6)	N(2)–C(7)	1.306(5)
N(1)–Li(1)–N(3)	102.2(4)	N(1)–Li(2)–N(3)	99.5(4)
Li(1)–N(3)–Li(2)	72.4(3)	Li(1)–N(1)–Li(2)	69.6(3)
N(1)–Li(1)–N(2)	96.9(4)	N(3)–Li(2)–N(4)	96.4(4)
Li(1)–N(1)–C(1)	122.6(3)	N(1)–C(1)–C(6)	122.4(4)
C(1)–C(6)–C(7)	125.4(4)	C(6)–C(7)–N(2)	122.1(4)
C(7)–N(2)–Li(1)	125.1(4)		



(a)

(b)

Fig. 1 (a) ORTEP representing the crystal structure of $L^{xyl}Li$ (50% probability of thermal ellipsoids). Hydrogens are omitted for clarity. (b) ORTEP representing the Li_3N_3 ring from the crystal structure of $L^{xyl}Li$ (50% probability of thermal ellipsoids). Hydrogens are omitted for clarity.

and ^{7}Li-NMR of C_6D_6 solutions, which show two overlapping spectra of identical symmetry (4 : 1 ratio) and two Li environments, respectively.

The structure of $L^{mes}Li$ in the solid state determined crystallographically is shown in Fig. 2; important bond lengths and angles are given in Table 2. The molecule crystallises as a dimer, with the arylamido nitrogen atoms bridging the two lithium centres giving rise to an asymmetric puckered Li_2N_2 ring. Within this ring the shorter amido Li–N are those which are part of the amido imine chelate ring. The three-coordinate lithium atoms are distorted trigonal pyramidal, the third site being occupied by the imine nitrogens. The Li–N(amido) [1.924(8)–2.178(9) Å] and Li–N(imino) [1.952(8)–1.974(9) Å] bond lengths are comparable to the ones observed for the trimer and those previously reported.[5] In this structure too, the metrical data support a planar ketimine carbon [C=N = 1.293(5)–1.306(5) Å and C–C = 1.516(6)–1.524(6) Å]. In solution (C_6D_6) $L^{mes}Li$ exists as a single species (by ^{1}H, ^{13}C and ^{7}Li NMR spectroscopies) most likely dimeric. The positions of the observed peaks are only slightly shifted relative to the parent protonated compound, even though the band due to N–*H* is absent.

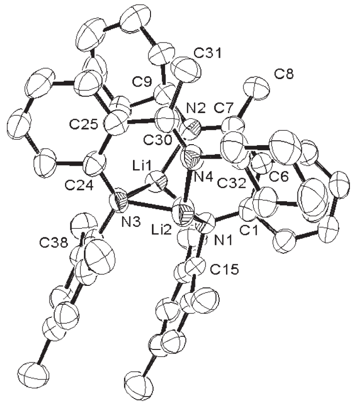
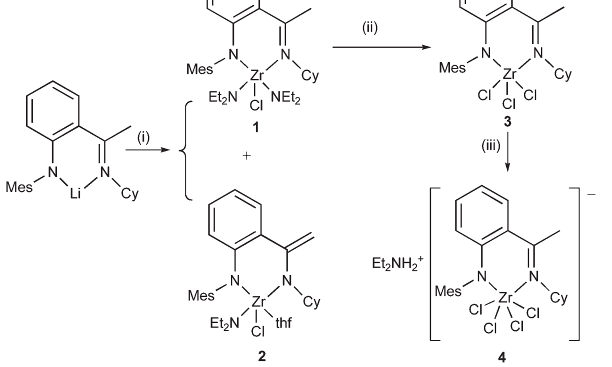


Fig. 2 ORTEP representing the crystal structure of $L^{mes}Li$ (50% probability of thermal ellipsoids). Hydrogens are omitted for clarity.

Zirconium complexes

The zirconium complexes described in the paper are summarised in Scheme 3.



Scheme 3 Reagents and conditions: (i) 1equiv. $ZrCl_2(NEt_2)_2(thf)_2$, thf, −78 °C to RT; (ii) Me_3SiCl, C_6H_6; (iii) see text.

Complex **1** was prepared by salt metathesis reactions in thf and isolated pure after crystallisation from petroleum. This purification is necessary in order to remove **2**, which is also formed in variable quantities during the reaction. Complexes **1** and **2** were fully characterised by ^{1}H and ^{13}C NMR spectroscopy; in addition, the structure of **1** was confirmed by diffraction methods. In both complexes the resonances assignable to the *o*-methyls and the aromatic protons in the 3- and 5-positions of the mesityl group appear as well-defined singlets. Furthermore, the diastereotopic methylene protons of the diethylamido groups appear as two multiplets. These observations are in agreement with the low symmetry of the molecules. The protons of the vinyl amido carbon in **2** appear as two broad singlets in the olefinic region. In contrast, the presence of the methyl on the ketimino carbon manifested by the appearance of a singlet at 2.0 ppm is characteristic of **1**. The structure of complex **1**, as determined by single crystal X-ray diffraction, is shown in Fig. 3; important bond lengths and angles are given in Table 3. The coordination geometry around the metal centre is best described as trigonal bipyramidal with axial chloride and arylamido ligands. The Zr–diethylamido bond [1.999(2)–2.027(2) Å] is shorter than the Zr–arylamido bond [2.180(2) Å]. The dative nature of the Zr–N(imino) bond is manifested by the observed bond length [2.315(2) Å]. Comparison of the structure of the *N*-mesitylamido **1** with the *N*-trimethylsilylamido analogue reported earlier[5] shows a preference for the occupation of

Table 3 Selected bond lengths (Å) and angles (°) for **1**

N(1)–Zr(1)	2.180(2)	N(2)–Zr(1)	2.315(2)
N(3)–Zr(1)	2.027(2)	N(4)–Zr(1)	1.999(2)
Cl(1)–Zr(1)	2.5228(9)	N(1)–C(1)	1.377(3)
C(1)–C(6)	1.424(4)	C(6)–C(7)	1.474(4)
N(2)–C(7)	1.300(3)	C(7)–C(8)	1.500(4)
N(1)–Zr(1)–N(2)	75.51(8)	N(4)–Zr(1)–N(2)	120.58(9)
N(2)–Zr(1)–N(3)	129.04(9)	N(3)–Zr(1)–N(4)	110.35(10)
N(1)–Zr(1)–Cl(1)	156.71(6)	C(1)–N(1)–Zr(1)	112.18(16)
N(1)–C(1)–C(6)	122.1(2)	C(1)–C(6)–C(7)	120.3(2)
C(6)–C(7)–N(2)	120.7(2)	C(7)–N(2)–Zr(1)	118.69(17)

an 'axial' site by the arylamido group in combination with a longer bond possibly due to reduced π-bonding. The preference may be of steric origin.

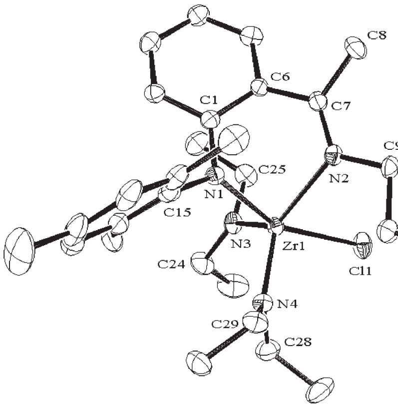
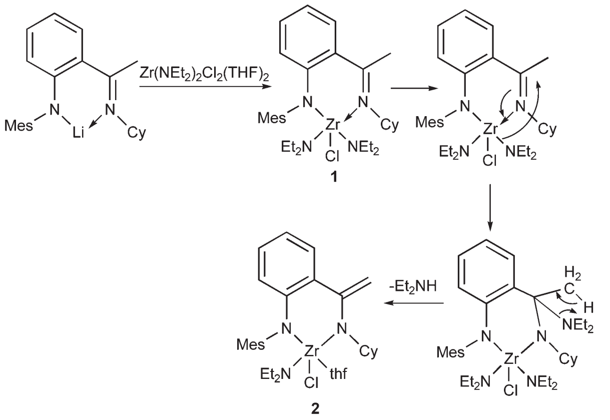


Fig. 3 ORTEP representing the crystal structure of **1** (50% probability of thermal ellipsoids). Hydrogens are omitted for clarity.

Attempts were made to understand the mechanism of formation of complex **2**. Plausible pathways that were considered included: (i) deprotonation of the $L^{mes}Li$ and formation of the vinyl amido dilithium prior to coordination to the zirconium centre, followed by salt metathesis; (ii) coordination of $L^{mes}Li$ and formation of **1** followed by deprotonation of the ketimino methyl by an excess of $L^{mes}Li$ present in solution during the initial stages of the reaction; (iii) coordination of $L^{mes}Li$, formation of **1** followed by insertion of imine (C=N) into the Zr–NEt$_2$ bond and elimination of Et$_2$NH (see Scheme 4).

A ^{1}H, ^{13}C and ^{7}Li NMR study of the solution of $L^{mes}Li$ in d^8-thf did not give any evidence of the presence of a second lithium species. In addition, when the reaction of ZrCl$_2$(NEt$_2$)$_2$(thf)$_2$ with $L^{mes}Li$ was carried out using excess of the lithium species the yield of **2** did not increase. In this case too, the major product was **1** together with unreacted $L^{mes}Li$. Heating a d^8-thf NMR sample of **1** at 75 °C showed consumption of the starting complex and formation of **2**. This suggests that **1** may be the intermediate leading to **2** following an intramolecular rearrangement (Scheme 4). Further evidence supporting the insertion of C=N into the metal amido bond was found by the isolation of the titanium complexes described in the following section. The migration of alkyl groups to the imino carbon of coordinated salicylaldiminato type ligands has been observed with early transition metals and lanthanides.[10a–c] Insertion of various 1,*n*-dipoles and heterocumulenes into amido-early transition metal bonds is also well established.[10d]



Scheme 4 Proposed mechanism leading to the formation of **2**.

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

N(1)–Zr(1)	2.118(4)	N(2)–Zr(1)	2.289(3)
Cl(1)–Zr(1)	2.4779(13)	Cl(2)–Zr(1)	2.5716(13)
Cl(3)–Zr(1)	2.4611(13)	Cl(4)–Zr(1)	2.4577(12)
N(1)–C(1)	1.389(5)	C(1)–C(6)	1.419(6)
C(6)–C(7)	1.495(6)	C(7)–C(8)	1.521(6)
C(7)–N(2)	1.293(5)		
N(1)–Zr(1)–N(2)	79.85(13)	Cl(1)–Zr(1)–Cl(3)	173.20(5)
N(1)–Zr(1)–Cl(2)	169.51(10)	N(2)–Zr(1)–Cl(4)	178.27(9)
Zr(1)–N(1)–C(1)	125.3(3)	N(1)–C(1)–C(6)	121.5(4)
C(1)–C(6)–C(7)	123.9(4)	C(6)–C(7)–N(2)	122.3(4)
C(7)–N(2)–Zr(1)	125.7(3)		

Treatment of **1** with Me$_3$SiCl in benzene resulted in substitution of the diethylamido groups by chlorides. Complex **3** was obtained in high yield as an air sensitive yellow solid, which precipitated out of the reaction mixture as it formed and was isolated by filtration. Minor impurities in the isolated product *i.e.* $L^{mes}H$, Me$_3$SiNEt$_2$ and C$_6$H$_6$ could not be removed by repeated washings with petroleum, hampering the isolation of analytically pure samples. Complex **3** had very low solubility in benzene and other non-polar solvents. However, it dissolved in d^8-thf, allowing characterisation by ^{1}H and ^{13}C NMR spectroscopy. Attempts to crystallise **3** by slow diffusion of petroleum into thf solution gave only a low yield of crystals of **4**, which were characterised by single crystal X-ray diffraction. The structure of the anion in **4** is shown in Fig. 4. Bond lengths and angles are given in Table 4. The geometry around the Zr in the anion is octahedral with two *cis* sites occupied by L^{mes}. The Zr–amido and Zr–imino bond lengths are slightly shorter than the analogous bonds in **1**. The presence of the Et$_2$NH$_2^+$ in the crystals of **4** can be rationalised by the possible slow hydrolysis of the Et$_2$NSiMe$_3$ impurity by adventitious moisture.

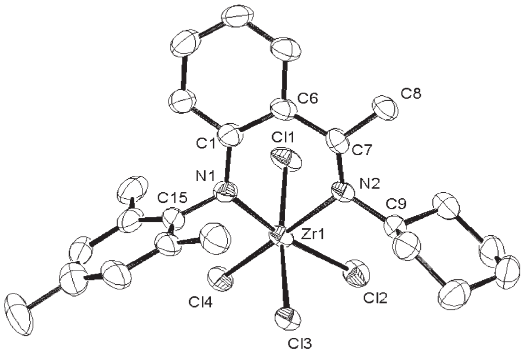
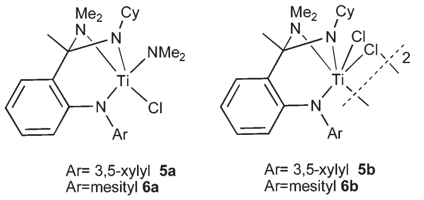


Fig. 4 ORTEP representing the crystal structure of the anion of **4** (50% probability of thermal ellipsoids). Hydrogens are omitted for clarity.

Titanium complexes

The titanium complexes described in the paper are shown in Scheme 5.

The complexes **5a** and **6a** were prepared by the reaction of Ti(NMe$_2$)$_2$Cl$_2$ with the lithium species $L^{xyl}Li$ and $L^{mes}Li$, respectively. From the reaction mixtures minor quantities of **5b** and **6b** were also isolated. All four compounds were characterised by spectroscopic methods. Their ^{13}C NMR spectra feature the quaternary



Scheme 5 Titanium complexes described in this paper.

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

Ti(1)–N(1)	1.954(3)	Ti(1)–N(2)	1.890(3)
Ti(1)–N(3)	2.224(3)	Ti(1)–Cl(1)	2.3185(11)
Ti(1)–Cl(2)	2.4968(11)	Ti(1)–Cl(2′)	2.5349(11)
N(1)–C(6)	1.415(5)	C(6)–C(1)	1.417(5)
C(1)–C(15)	1.514(5)	C(15)–N(2)	1.470(4)
C(15)–N(3)	1.535(4)	C(15)–C(22)	1.526(5)
N(1)–Ti(1)–N(2)	90.11(12)	N(2)–Ti(1)–N(3)	65.64(11)
N(1)–Ti(1)–N(3)	87.35(11)	N(3)–Ti(1)–Cl(1)	163.93(8)
N(1)–Ti(1)–Cl(2′)	165.27(9)	N(2)–Ti(1)–Cl(2)	153.93(9)
Cl(1)–Ti(1)–Cl(2′)	84.69(3)	Ti(1)–N(1)–C(6)	123.0(2)
N(1)–C(6)–C(1)	120.3(3)	C(6)–C(1)–C(15)	119.8(3)
C(1)–C(15)–N(2)	109.2(3)	C(15)–N(2)–Ti(1)	101.54(19)
C(15)–N(3)–Ti(1)	86.17(18)		

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

N(1)–Ti(1)	2.291(4)	N(2)–Ti(1)	1.914(4)
N(3)–Ti(1)	1.934(4)	N(4)–Ti(1)	1.918(4)
Cl(1)–Ti(1)	2.3757(15)	C(9)–N(3)	1.414(5)
C(8)–C(9)	1.416(6)	C(1)–C(8)	1.544(7)
C(1)–N(2)	1.480(6)	C(1)–C(23)	1.534(6)
C(1)–N(1)	1.524(6)		
N(3)–Ti(1)–N(2)	95.19(16)	N(3)–Ti(1)–N(1)	87.04(16)
N(2)–Ti(1)–N(1)	64.95(15)	N(4)–Ti(1)–N(1)	159.36(17)
N(4)–Ti(1)–N(3)	111.94(17)	N(2)–Ti(1)–Cl(1)	132.94(13)
C(9)–N(3)–Ti(1)	122.1(3)	N(3)–C(9)–C(8)	120.5(4)
C(9)–C(8)–C(1)	121.0(4)	C(8)–C(1)–N(2)	109.7(4)
C(1)–N(2)–Ti(1)	100.0(3)	N(1)–C(1)–C(8)	108.7(4)
C(1)–N(1)–Ti(1)	84.0(2)	N(1)–C(1)–N(2)	98.8(3)

chiral carbon formed during the reaction at 86 ppm. Its methyl substituent was shielded relative to $L^{mes}Li$. The diastereotopic methyls of the coordinated dimethylamino moiety appeared in the ^1H NMR spectra as singlets between 1.78 and 2.51 ppm. The structures of **6a** and **5b** were confirmed by single crystal X-ray diffraction. Diagrams of the molecules are shown in Figs. 5 and 6; important bond lengths and angles are in Tables 5 and 6.

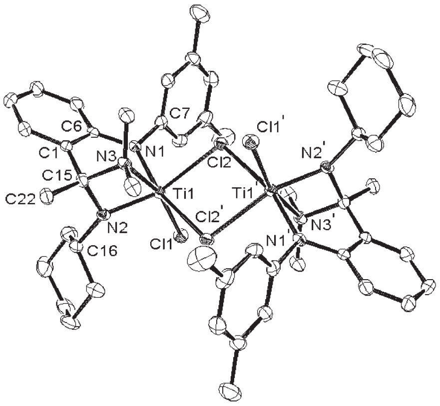


Fig. 5 ORTEP representing the crystal structure of **5b** (50% probability of thermal ellipsoids). Hydrogens are omitted for clarity.

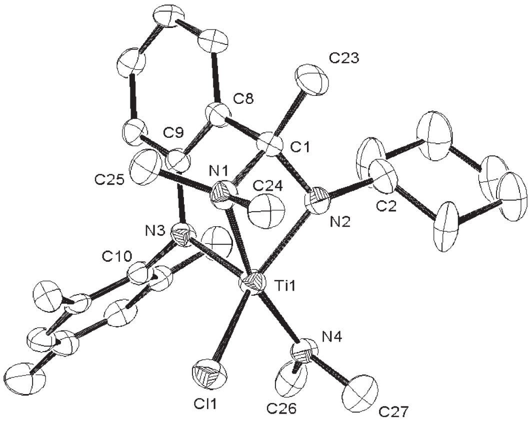
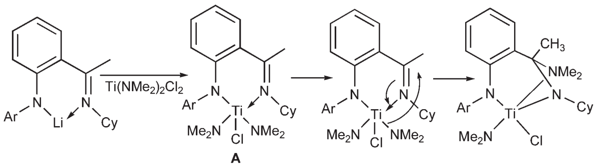


Fig. 6 ORTEP representing the crystal structure of **6a** (50% probability of thermal ellipsoids). Hydrogens are omitted for clarity.

In the centrosymmetric dimer **5b** the Ti centers are distorted octahedral. The cyclohexylalkyl amido–Ti is shorter than the aryl amido–Ti bond length [1.890(3) Å *vs* 1.954(3) Å], and shorter than the corresponding bond in **6a**.

In **6a** the coordination geometry around the Ti is best described as distorted square based pyramid with axial alkyldimethylamine donor. The basal sites are occupied by the diarylamido, the cyclohexylalkylamido, the dimethylamido and the chloride ligands. All three types of Ti–amido bond lengths lie within a narrow range [1.914(4)–1.934(4) Å], while the dative dimethylamine bond is much longer [2.291(4) Å]. The nonsymmetric nature of the tripodal ligand is further seen by the bite angles subtended on the titanium centre [95.19(16)°, 87.04(16)° and 64.95(15)°]. The observed geometrical distortions are possibly due to the constraints imposed by the ligand backbone

The formation of **5a** and **6a** can be rationalised by postulating the rearrangement of intermediate **A** (Scheme 6) to the observed product by migration of the dimethylamido group from the metal to the ketimino carbon.



Scheme 6 Mechanism leading to **5a** and **6a**.

It is interesting to note that aminolysis of $Ti(NMe_2)_4$ with a phenoxy analogue of $L^{xyl}H$ and $L^{mes}H$ *i.e.* 6-[CyN=C(H)]-2-$Bu^tC_6H_3OH$, L′H leads to clean formation of $L'_2Ti(NMe_2)_2$ or $L'Ti(NMe_2)_3$ depending on the ratio of the reactants and reaction of one equivalent of L′Li with $Ti(NMe_2)_2Cl_2$ leads to clean formation of $L'Ti(NMe_2)_2Cl$. In none of the above cases rearrangement to tripodal ligands is observed.[11a] Recently, titanium mono salicylaldiminato complexes have also been reported.[11b] Finally, we have been unable to isolate or observe titanium analogues of **1** and **2** even though a zirconium analogue of **5a** and **5b** has already been reported by us.[5] Zirconium complexes of type $[(L^{xyl})_2ZrCl_2]$ have also been prepared and structurally characterised.[11a] All these facts may be accounted for by postulating that steric interactions are reduced by the formation of the pseudo tripodal ligand. This is expected to be more important with the smaller titanium centre substituted by the bulky arylamido (rather than phenoxy) functionalities.

Conclusions

In summary, we have prepared monoarylamido ketimino zirconium complexes by salt metathesis from $[Zr(NEt_2)_2Cl_2(thf)_2]$ and the appropriate lithium reagent. In most cases competing formation of the vinylamido complexes is observed. The latter reaction involves migration of the diethylamido group to the ketimino carbon followed by elimination of diethylamine rather than intermolecular enolisation by external bases. We have been unable to prepare the analogous titanium compounds. In this case complexes with the unsymmetrical tripodal diamido amine ligand were isolated. The formation of the new ligand has been rationalised by postulating intramolecular migration of the dimethylamido group to the ketimino carbon. This reaction is possibly driven by the release of steric strain in the coordination sphere of the metal and is more pronounced with the smaller Ti centre. All these reactivity patterns should be taken into consideration when designing new supporting imine ligands for the early transition and other electrophilic metals.

Experimental

Elemental analyses were carried out by the University College London Microanalytical Laboratory. NMR data were recorded on Bruker AMX-300, AM-300 and DPX-400 spectrometers, operating at 300 Mhz and 400 MHz, respectively (^1H). The spectra were referenced internally using the signal from the residual protio-solvent (^1H) or the signals of the solvent (^{13}C). All manipulations involving moisture sensitive materials were carried out under vacuum or N_2 using standard Schlenkware techniques. All solvents used were dried by continuous reflux under N_2 and distillation from suitable drying agents immediately prior to use; the light petroleum had bp 40–60 °C. Commercial chemicals were from Aldrich, Avocado and Lancaster. The following starting materials were prepared following literature methods: LH_2,[5] $Zr(NEt_2)Cl_2(thf)_2$,[12] $TiCl_2(NMe_2)_2$.[13]

2-(1-cyclohexylimino-ethyl)-*N*-(3,5-dimethylphenyl)-aniline, ($L^{xyl}H$)

A Schlenk flask was loaded with LH_2 (5.400 g, 25 mmol), $NaOBu^t$ (4.805 g, 50.0 mmol), $Pd(dba)_2$ (0.718 g, 1.25 mmol) and *rac*-BINAP (0.778 g, 1.25 mmol). Xylene (150 cm^3) was then added followed by 3,5-dimethylbromobenzene (3.5 cm^3, 25.5 mmol). The mixture was stirred at 140 °C for 5 days. After cooling, the xylene solution was filtered and the volatiles removed *in vacuo* to yield a dark brown residue, which was dissolved in diethyl ether (50 cm^3) and extracted with water (3 × 50 cm^3). The organic extract was dried with $MgSO_4$ and the volatiles were removed *in vacuo*. The resulting dark brown residue was transferred to a Kugelrohr apparatus and the product was distilled at 200 °C at 0.05 mm Hg to yield a bright yellow oil. Upon cooling to room temperature the product solidified as a pale yellow solid. Yield: 6.581 g, 82%. δ_H ($CDCl_3$) 1.20–1.90 (10H, m, cyclohexyl C*H*$_2$s), 2.30 (6H, s, xylyl methyls), 2.33 (3H, s, imino methyl), 3.60 (1H, m, cyclohexyl C*H* α to imino N), 6.63 (1H, s, xylyl aromatic), 6.77 (1H, t, aromatic), 6.85 (2H, s, xylyl aromatic), 7.18 (1H, t, aromatic), 7.42 (1H, d, aromatic), 7.75 (1H, d, aromatic), 11.90 (1H, br. s, N*H*). δ_C ($CDCl_3$) 16.59, 22.12 (methyls), 25.27, 26.48, 34.66 (cyclohexyl *C*H$_2$s), 59.59 (cyclohexyl *C*H α to imino N), 115.82, 117.57, 118.67, 124.09, 130.17, 130.35, 139.50, 142.92, 145.61 (aromatics), 165.80 (*C*=N). (Found: C, 81.8; H, 8.6; N, 8.2. $C_{22}H_{28}N_2$ requires C, 82.5; H, 8.8; N, 8.7%).

2-(1-cyclohexylimino-ethyl)-*N*-(2,4,6-trimethylphenyl)-aniline, ($L^{mes}H$)

A Schlenk flask was loaded with LH_2 (8.600 g, 39.8 mmol), $NaOBu^t$ (5.500 g, 57.0 mmol), $Pd(dba)_2$ (0.172 g, 0.30 mmol), and 1,3-bis-(2,6-diisopropyl-phenyl)-imidazolinium chloride (0.256 g, 0.60 mmol). 1,4-Dioxane (75 cm^3) was added followed by 2,4,6-trimethylbromobenzene (6.70 cm^3, 43.8 mmol). The Schlenk flask was then placed under reduced pressure and stirred at 105 °C for 3 days. After cooling, the solution was diluted with water (100 cm^3) and extracted with diethyl ether (3 × 100 cm^3). The organic extracts were combined and washed with a saturated brine solution before being dried with $MgSO_4$. The volatiles were then removed *in vacuo* to yield a brown residue, which was transferred to a Kugelrohr. The product was distilled at 250 °C at 0.05 mm Hg and isolated as a bright yellow oil. Yield: 10.99 g, 83%. δ_H ($CDCl_3$) 1.20–1.95 (10H, m, cyclohexyl C*H*$_2$s), 2.23 (6H, s, aromatic methyls), 2.38 (3H, s, methyl), 2.42 (3H, s, methyl), 3.60–3.80 (1H, m, cyclohexyl C*H* α to imino N), 6.27 (1H, d, aromatic), 6.67 (1H, t, aromatic), 7.02 (2H, s, aromatic), 7.10 (1H, t, aromatic), 7.66 (1H, d, aromatic), 11.71 (1H, br. s, N*H*). δ_C ($CDCl_3$) 15.22, 18.43, 20.87 (methyls), 24.68, 25.78, 34.23 (cyclohexyl *C*H$_2$s), 58.93 (cyclohexyl *C*H α to imino N), 112.28, 114.42, 119.82, 128.88, 129.36, 130.01, 134.82, 136.03, 136.18, 148.11 (aromatics), 165.23 (*C*=N). MS, M$^+$ calculated for $C_{23}H_{30}N_2$: 334.2409; found, 334.2405.

Lithium [2-(1-cyclohexylimino-ethyl)-*N*-(3,5-dimethylphenyl)-anilide], ($L^{xyl}Li$)

To a cooled (−78 °C), stirred solution of $L^{xyl}H$ (6.581 g, 20.57 mmol) in petroleum (100 cm^3) was added slowly *via* cannula Bu^nLi (9.3 cm^3 of 2.45 M solution in hexanes, 22.6 mmol). The mixture was stirred at −78 °C for 1 h, allowed to reach room temperature and stirred for 15 h. This produced a yellow/orange suspension. The product was isolated by filtration and dried *in vacuo* to yield an orange air sensitive solid. Yield: 5.50 g, 82%. X-ray quality crystals were grown from petroleum. δ_H (C_6D_6) 0.7–1.6 (10H, m, cyclohexyl C*H*$_2$s), 1.87 (3H, s, methyl), 2.00 (3H, s, methyl), 2.57 (3H, s, methyl), 2.8 (1H, m, cyclohexyl C*H* α to imino N), 6.0–6.3, (3H, m, aromatics), 6.8–7.2 (4H, m, aromatics). δ_C (C_6D_6) 17.87, 22.46, 22.53 (methyls), 26.12, 26.44, 26.68, 32.97, 33.56 (cyclohexyl *C*H$_2$s), 61.22 (cyclohexyl *C*H α to imino N), 112.43, 116.53, 117.45, 120.07, 128.12, 132.08, 136.47, 141.65, 152.93, 159.92 (aromatics), 170.12 (*C*=N). δ_{Li} (C_6D_6) 1.22 (minor), 1.77 (major). (Found: C, 79.9; H, 8.1; N, 8.5. $C_{22}H_{27}LiN_2$ requires C, 81.0; H, 8.3; N, 8.6%).

Lithium [2-(1-cyclohexylimino-ethyl)-*N*-(2,4,6-trimethylphenyl)-anilide], ($L^{mes}Li$)

To a cooled (−78 °C), stirred solution of $L^{mes}H$ (5.080 g, 15.19 mmol) in petroleum (100 cm^3) was added slowly *via* cannula Bu^nLi (6.8 cm^3 of 2.45 M solution in hexanes, 16.7 mmol). The mixture was stirred at −78 °C for 1 h, allowed to reach room temperature and stirred for 17 h. This produced a yellow/orange suspension. The product was isolated by filtration, washed with petrol (30 cm^3) and dried *in vacuo* to yield an orange air sensitive solid. Yield: 3.64 g, 70%. X-ray quality crystals were grown from petroleum. δ_H (C_6D_6) 0.80–1.8 (10H, m, cyclohexyl C*H*$_2$s), 1.99 (3H, s, methyl), 2.05 (6H, s, methyl), 2.23 (3H, s, methyl), 3.05 (1H, m, cyclohexyl C*H* α to imino N), 6.48 (1H, t, aromatic), 6.60 (1H, d, aromatic), 6.76 (2H, s, aromatic), 6.96 (1H, t, aromatic), 7.41 (1H, d, aromatic). δ_C 19.31, 19.83, 21.61 (methyls), 26.25, 26.33, 35.06 (cyclohexyl *C*H$_2$s), 61.10 (cyclohexyl *C*H α to imino N 112.54, 120.74, 124.74, 130.17, 130.72, 131.60, 132.50, 132.90, 152.37, 159.05 (aromatics), 170.88 (*C*=N). δ_{Li} (C_6D_6) 1.91. (Found: C, 80.3; H, 8.6, 7.8. $C_{23}H_{29}LiN_2$ requires C, 81.2; H, 8.6; N, 8.2%).

2-Cyclohexyliminomethyl-bromobenzene

A Schlenk flask was charged with 4 Å molecular sieves and toluene (50 cm^3) before the 2-bromobenzaldehyde and cyclohexylamine were added *via* syringe. The reaction was stirred at 100 °C for 80 hours before being filtered and the volatiles removed *in vacuo* to yield the product as a brown oil. Yield: 10.4 g, 72%. δ_H ($CDCl_3$) 1.00–2.10 (10H, m, cyclohexyl C*H*$_2$s), 3.20–3.40 (1H, m, cyclohexyl C*H* α to imino N), 7.17 (1H, t, aromatic), 7.23 (1H, t, aromatic), 7.50 (1H, d, aromatic), 8.02 (1H, d, aromatic), 8.66 (1H, s, C(*H*)=N).

2-Cyclohexyliminomethyl-*N*-(2,4,6-trimethylphenyl)-aniline, ($L^{ald}H$)

A Schlenk flask was loaded with *o*-(cyclohexyliminomethyl)-bromobenzene (0.532 g, 2.0 mmol), $NaOBu^t$ (0.28 g, 3.0 mmol), $Pd(dba)_2$ (0.057 g, 0.10 mmol), and 1,3-bis-(2,6-diisoproplyphenyl)-imidazolinium chloride (0.085 g, 0.20 mmol). 1,4-Dioxane (20 cm^3) was added before 2,4,6-trimethylaniline (0.31 cm^3, 2.2 mmol) was added to the resulting suspension. The Schlenk flask was placed under reduced pressure and stirred at 105 °C for 5 days. After cooling, the solution was diluted with water (20 cm^3) and extracted with diethyl ether (3 × 30 cm^3). The organic extracts were combined and washed with a saturated brine solution before being dried with $MgSO_4$. The volatiles were then removed *in vacuo* to yield a brown residue, which was transferred to a Kugelrohr. The product was distilled at 250 °C at 0.05 mm Hg and isolated as a dark yellow oil. Yield: 0.395 g, 62%. δ_H ($CDCl_3$) 1.15–1.90 (10H, m, cyclohexyl C*H*$_2$s), 2.19 (6H, s, methyl), 2.35 (3H, s, methyl), 3.10–3.25 (1H, m, cyclohexyl C*H* α to imino N), 6.23 (1H, d, aromatic), 6.67 (1H, t, aromatic), 6.99 (2H, s, aromatic), 7.11 (1H, t, aromatic), 7.27 (1H, d, aromatic), 8.47 (1H, s, C(*H*)=N), 10.70 (1H, s, N*H*). δ_C ($CDCl_3$) 18.33, 20.91 (methyls), 24.56, 25.74, 34.83 (cyclohexyl *C*H$_2$s), 69.54 (cyclohexyl *C*H α to imino N), 111.38, 114.95, 117.32, 128.93, 130.66, 133.32, 135.36, 135.71, 136.28, 147.97 (aromatic), 161.50 (*C*=N).

Lithium [(2-cyclohexyliminomethyl)-*N*-(2,4,6-trimethylphenyl)-anilide], ($L^{ald}Li$)

To a stirred and cooled (−78 °C) solution of $L^{ald}H$ (0.40 g, 1.25 mmol) in petroleum (30 cm^3) was added slowly *via* cannula

Bu^nLi (0.60 cm^3 of 2.45 M solution in hexanes, 1.5 mmol). The mixture was stirred at −78 °C for 1 h, allowed to reach room temperature and stirred for 17 h. This produced a yellow suspension that was isolated by filtration to yield an air sensitive yellow solid. Yield: 0.258 g, 64%. δ_H (C_6D_6) 0.7–1.7 (10H, m, cyclohexyl CH_2s), 2.11 (6H, s, mesityl methyls), 2.25 (3H, s, mesityl methyl), 2.67 (1H, br t, cyclohexyl C*H* α to imino N), 6.35–6.55 (2H, m, aromatics), 6.81 (2H, s, mesityl aromatics), 7.02 (1H, t, aromatic), 7.22 (1H, d, aromatic), 8.06 (1H, s, C(*H*)=N).

[2-(1-cyclohexylimino-ethyl)-*N*-(2,4,6-trimethylphenyl)-anilido]-zirconium-bis-(diethylamido)-(chloride), 1, and [2-(1-cyclohexylamido-vinyl)-*N*-(2,4,6-trimethylphenyl)-anilido]-zirconium-(diethylamido)-(chloride)-tetrahydrofuran, 2

To a stirred and cooled (−78 °C) solution of $Zr(NEt_2)_2Cl_2(thf)_2$ (1.35 g, 3.0 mmol) in thf (50 cm^3) was added slowly *via* cannula a cooled (−78 °C) solution of $L^{mes}Li$ (1.02 g, 3.0 mmol) in thf (50 cm^3). The reaction was stirred at −78 °C for 1 h, allowed to reach room temperature and then stirred for 18 h. From the bright orange solution the volatiles were removed *in vacuo*, the residue extracted into petroleum (*ca.* 100 cm^3) and filtered through Celite. The bright orange filtrate was concentrated to *ca.* 15 cm^3 and cooled to −30 °C overnight to produce yellow, X-ray diffraction quality crystals of **1**. Yield: 0.90 g, 50%. (Found: C, 61.3; H, 8.3; N, 9.3. $C_{31}H_{49}ClN_4Zr$ requires C, 61.6; H, 8.2; N, 9.3%). δ_H (C_6D_6): 0.84 (12H, t, NCH_2CH_3), 1.10–2.80 (10H, m, cyclohexyl CH_2s), 2.02 (3H, s, imino methyl), 2.15 (6H, s, mesityl methyls), 2.24 (3H, s, mesityl methyl), 3.16–3.38 (8H, m, NCH_2CH_3), 3.74 (1H, br t, cyclohexyl C*H* α to imino N), 6.53 (1H, dt, aromatic), 6.62 (1H, d, aromatic), 6.86–6.95 (3H, m, mesityl aromatics and one aromatic), 7.24 (1H, dd, aromatic).

$^{13}C\{^1H\}$ δ_C (C_6D_6): 13.25 (NCH_2CH_3), 20.25 (mesityl methyls), 21.62 (mesityl methyl), 23.75 (imino methyl), 26.24, 27.02, 32.35 (cyclohexyl CH_2s), 41.48 (NCH_2CH_3), 65.85 (cyclohexyl *C*H α to imino N), 117.42, 120.50 (aromatic *C*Hs), 122.86, 129.07 (quaternary aromatics), 130.32, 131.77, 133.25 (aromatic CHs), 134.19, 135.61, 150.71 (quaternary aromatics), 169.75 (*C*=N).

By concentration of the supernatant solution **2** was isolated as yellow orange air sensitive powder in variable quantities depending on the scale of the reaction.

δ_H (C_6D_6) 0.75–1.80 (10H, cyclohexyl CH_2s), 0.90 (6H, t, $N(CH_2CH_3)_2$), 1.26 (4H, br t, thf), 2.19 (3H, s, mesityl methyl), 2.27 (3H, s, mesityl methyl), 2.56 (3H, s, mesityl methyl), 2.85–3.0 (2H, m, $N(CH_2CH_3)_2$), 3.10–3.25 (1H, m, cyclohexyl C*H* α to ene-amido N), 3.35–3.55 (2H, m, $N(CH_2CH_3)_2$), 3.78 (4H, br t, thf), 4.52 (1H, s, $C=CH_2$), 4.96 (1H, s, $C=CH_2$), 6.11 (1H, d, aromatic), 6.76 (1H, t, aromatic), 6.90–7.05 (3H, m, aromatics), 7.41 (1H, d, aromatic).

$^{13}C\{^1H\}$ δ_C (C_6D_6) 13.14 ($N(CH_2CH_3)_2$), 19.37, 19.74, 21.80 (mesityl methyls), 25.98 (thf), 26.24, 26.97, 35.18, 36.91, 37.12 (cyclohexyl CH_2s), 41.26 ($N(CH_2CH_3)_2$), 61.06 (cyclohexyl *C*H α to ene-amido N), 71.75 (thf), 102.77 ($C=CH_2$), 112.87 (aromatic *C*H), 113.48 (quaternary aromatic), 117.51, 128.08 (aromatic *C*Hs), 129.80 (quaternary aromatic), 130.25, 131.12, 131.25 (aromatic *C*Hs), 135.14, 142.61, 152.84, 155.92 (quaternary aromatics), 171.71 [$ArC(N)=CH_2$]. (Found: C, 61.5; H, 7.2; N, 6.5. $C_{31}H_{46}ClON_3Zr$ requires C, 61.7; H, 7.7; N, 6.7%).

[2-(1-cyclohexylimino-ethyl)-*N*-(2,4,6-trimethylphenyl)-anilido]-zirconium-(trichloride), 3

To a stirred solution of **1** (0.80 g, 1.33 mmol) in benzene (20 cm^3) was added trimethylchlorosilane (0.7 cm^3, 5.5 mmol). Upon addition the benzene solution became bright orange and after stirring for 30 min a bright yellow precipitate was produced. Stirring was continued for a total of 3 h when the product was collected by filtration, washed with petrol (*ca.* 50 cm^3) and dried *in vacuo* to yield a yellow solid. Yield: 0.590 g, 84%. δ_H (d^8-thf) 1.30–2.20 (10H, m, cyclohexyl CH_2s), 2.26 (3H, s, mesityl methyls), 2.39 (3H, s, methyl), 2.97 (3H, s, methyl), 5.08 (1H, br t, cyclohexyl C*H* α to imino N), 6.41 (1H, d, aromatic), 6.97–7.05 (3H, m, aromatic), 8.03 (1H, d, aromatic). $^{13}C\{^1H\}$ δ_C (d^8-thf) 21.24 (mesityl methyls), 22.26, 26.56 (methyls), 27.79, 28.70, 28.89, 32.18, 36.40 (cyclohexyl CH_2s) 66.17 (cyclohexyl *C*H α to imino N), 119.90, 121.35 (aromatic *C*Hs), 130.50 (quaternary aromatic), 131.53, 132.85, 134.39 (aromatic *C*Hs), 137.70, 137.86, 139.00, 151.54 (quaternary aromatics), 177.48 (*C*=N).

[2-(1-cyclohexylimino-ethyl)-*N*-(2,4,6-trimethylphenyl)-anilido]-zirconium-(tetrachloride) diethylammonium salt, 4

Complex **3** (100 mg) was dissolved in thf (10 cm^3) and layered with petroleum (10 cm^3) in a Schlenk tube. The tube was left to stand for *ca.* one week and afforded a small crop of yellow crystals of **4**.

[2-(1-cyclohexylamido-1-dimethylamino-ethyl)-*N*-(3,5-dimethylphenyl)-anilido]-titanium-(dimethylamido)-(chloride), 5a, and [2-(1-cyclohexylamido-1-dimethylamino-ethyl)-*N*-(3,5-dimethylphenyl)-anilido]-titanium-(dichloride), 5b

To a stirred, cooled (−78 °C) solution of $Ti(NMe_2)_2Cl_2$ (0.104 g, 0.5 mmol) in thf (15 cm^3) was added slowly a solution of $L^{xyl}Li$ (0.163 g, 0.5 mmol) in thf (15 cm^3). The dark red solution was allowed to reach room temperature over *ca.* 10 h and stirred for a further 2 h. Removal of the volatiles *in vacuo*, extraction of the residue into petroleum (2 × 30 cm^3), filtration through Celite, concentration of the bright red solution to *ca.* 20 cm^3 and cooling at −30 °C for 48 h gave an orange/red powder.

Major product 5a. δ_H (C_6D_6) 0.80–1.80 (10H, m, cyclohexyl CH_2s), 1.40 (3H, s, methyl α to cyclohexylamido and amino groups), 1.94 (3H, s, amino methyl), 2.18 (6H, s, xylyl methyls), 2.51 (3H, s, amino methyl), 3.17 (6H, s, dimethylamido $N(CH_3)_2$), 3.30–3.50 (1H, m, cyclohexyl C*H* α to cyclohexylamido N), 6.73 (1H, s, xylyl aromatic), 6.77–6.86 (2H, m, aromatics), 7.01 (1H, dt, aromatic), 7.13 (1H, dd, aromatic), 7.24 (2H, xylyl aromatics). (Found: C, 64.5; H, 7.8; N, 8.5. $C_{26}H_{39}ClN_3TiCl$ requires C, 65.5; H, 8.2; N, 8.8%).

Minor product 5b. δ_H (C_6D_6) 0.70–2.70 (10H, m, cyclohexyl CH_2s), 1.26 (3H, s, methyl α to cyclohexylamido and amino groups), 1.92 (3H, amino methyl), 2.13 (6H, s, xylyl methyls), 2.25 (3H, s, amino methyl), 2.40–2.60 (1H, m, cyclohexyl C*H* α to cyclohexylamido N), 6.35 (1H, dd, aromatic), 6.70 (2H, s, xylyl aromatics), 6.79 (1H, dt, aromatic), 6.87 (1H, dt, aromatic), 6.99 (1H, dd, aromatic), 7.15 (1H, s, xylyl aromatic).

$^{13}C\{^1H\}$: δ_C (C_6D_6) 16.26 (methyl α to cyclohexylamido and amino groups), 21.90 (xylyl methyls), 26.30, 27.05, 27.30, 35.07, 37.19 (cyclohexyl CH_2s), 40.52, 43.24 (amino methyls), 67.30 (cyclohexyl *C*H α to cyclohexylamido N), 86.12 (carbon α to cyclohexylamido and amino groups), 112.47, 123.64, 128.03, 129.00 (aromatic *C*Hs), 129.68 (quaternary aromatic), 129.84, 130.46 (aromatic *C*Hs), 140.75, 144.90, 151.56 (quaternary aromatics). (Found: C, 61.0; H, 6.8; N, 5.6. $C_{24}H_{33}Cl_2N_2Ti$ requires C, 61.6; H, 7.1; N, 6.0%). X-ray quality crystals were grown from diethyl ether.

[2-(1-cyclohexylamido-1-dimethylamino-ethyl)-*N*-(2,4,6-trimethylphenyl)-anilido]-titanium-(dimethylamide)-(chloride), 6a, and [2-(1-cyclohexylamido-1-dimethylamino-ethyl)-*N*-(2,4,6-trimethylphenyl)-anilido]-titanium-(dichloride), 6b

These were prepared following a method similar to the above from $Ti(NMe_2)_2Cl_2$ (0.104 g, 0.5 mmol) and $L^{mes}Li$ (0.170 g, 0.5 mmol) in thf (15 cm^3).

Major product 6a. δ_H (C_6D_6) 0.80–1.65 (10H, m, cyclohexyl CH_2s), 1.47 (3H, s, methyl α to cyclohexylamido and amino groups), 1.96 (3H, s, amino methyl), 2.12 (3H, s, mesityl methyl), 2.22 (3H, s, mesityl methyl), 2.46 (3H, s, mesityl methyl), 2.49 (3H, s, amino methyl), 3.13 (6H, s, dimethylamido $N(CH_3)_2$),

Table 7 Crystal structure determination data

	$\mathbf{L^{xyl}Li}$	$\mathbf{L^{mes}Li}$	**1**	**4**	**5b**	**6a**
Chemical formula	$C_{66}H_{81}Li_3N_6$	$C_{46}H_{58}Li_2N_4$	$C_{31}H_{49}Cl_1N_4Zr_1$	$C_{27}H_{41}Cl_4N_3Zr_1$	$C_{48}H_{66}Cl_4N_6Ti_2$	$C_{27}H_{41}Cl_1N_4Ti_1$
Formula weight	979.19	680.84	604.41	640.65	964.67	504.99
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*-1	*Pbca*	$P2_1/c$	$P2_1/c$	*P*-1	$P2_1/c$
a/Å	13.9493(8)	14.6329(7)	17.199(7)	19.245(3)	8.6874(12)	14.891(2)
b/Å	19.9645(8)	17.3919(7)	12.774(5)	11.4615(19)	11.0077(15)	19.812(3)
c/Å	23.3181(15)	31.7930(18)	14.655(4)	17.391(3)	15.197(2)	9.1479(7)
α/°	109.670(2)	90	90	90	96.648(3)	90
β/°	104.223(2)	90	98.410(10)	112.964(4)	98.987(4)	100.210(8)
γ/°	90.457(4)	90	90	90	108.334(4)	90
V/ Å^3	5898.2(6)	8091.1(7)	3185(2)	3532.0(10)	1341.3(3)	2656.1(6)
Z	4	8	4	4	1	4
T/K	120	120	120	120	120	120
μ/mm^{-1}	0.063	0.064	0.454	0.632	0.533	0.445
No. data collected	35444	11147	13616	31784	7610	13708
No. unique data	11225	5978	7191	5670	2271	4295
R_{int}	0.1188	0.0902	0.0479	0.0853	0.0376	0.1296
Final $R(\|F\|)$ for $F_0 > 2\sigma(F_0)$	0.0751	0.0848	0.0456	0.0528	0.0337	0.0728
Final $R(F^2)$ for all data	0.1793	0.1968	0.0952	0.1360	0.0937	0.1496

3.27 (1H, tt, cyclohexyl C*H* α to cyclohexylamido N), 6.08 (1H, dd, aromatic), 6.81 (1H, dt, aromatic), 6.87–6.98 (3H, m, mesityl aromatics and one aromatic), 7.13 (1 h, dd, aromatic). $^{13}C\{^1H\}$ δ_C (C_6D_6) 17.87 (methyl α to cyclohexylamido and amino groups), 19.88, 20.34, 21.70 (mesityl methyls), 27.02, 27.33, 27.60, 36.34, 37.66 (cyclohexyl *C*H$_2$s), 39.58, 42.56 (amino methyls), 46.46 (dimethylamido N(*C*H$_3$)$_2$), 66.66 (cyclohexyl *C*H α to cyclohexylamido N), 86.59 (carbon α to cyclohexylamido and amino groups), 110.91, 121.34, 128.00, 129.53 (aromatic *C*Hs), 129.74 (quaternary aromatic), 130.50, 131.89 (aromatic *C*Hs), 135.69, 137.36, 138.17, 140.24, 148.71 (quaternary aromatics). (Found: C, 65.5; H, 8.5; N, 8.5. $C_{27}H_{41}N_3TiCl$ requires C, 66.0; H, 8.6; N, 8.6%). X-ray quality crystals were grown from petroleum.

Minor product 6b. δ_H (C_6D_6) 0.80–2.00 (10H, m, cyclohexyl C*H*$_2$s), 1.29 (3H, s, methyl), 1.78 (3H, s, methyl), 2.13 (3H, s, methyl), 2.19 (3H, s, methyl), 2.25 (3H, s, methyl), 2.28 (3H, s, methyl), 3.05 (1H, tt, cyclohexyl C*H* α to cyclohexylamido N), 6.00 (1H, dd, aromatic), 6.75–6.90 (4H, m, mesityl aromatics and two aromatics), 7.01 (1H, dd, aromatics). (Found: C, 62.0; H, 7.0.; N, 5.5. $C_{25}H_{35}Cl_2N_2Ti$ requires C, 62.3; H, 7.3; N, 5.8%).

Crystallography

A summary of the crystal data, data collection and refinement for compounds $\mathbf{L^{xyl}Li}$, $\mathbf{L^{mes}Li}$, **1**, **4**, **5b** and **6a** is given in Table 7. All data sets were collected on a Enraf Nonius Kappa CCD area detector diffractometer with rotating anode FR591 and an Oxford Cryosystems low-temperature device, operating in omega scanning mode with phi scans to fill the Ewald sphere. The crystals were isolated under dinitrogen, covered with Fomblin vacuum oil and mounted on a glass fibre with silicon grease. Structures were solved and refined using SHELX[14] and WinGX[15] software packages. Non-hydrogen atoms were refined with anisotropic thermal parameters. The crystals of all compounds except **1** were small, giving rise to weak diffraction and data of low quality. However, the solutions obtained are satisfactory for the purposes of this paper. Compound **4** crystallises with one molecule of thf and compound **5b** crystallises with one molecule of diethyl ether per dimer; in both cases, these were highly disordered and were handled using the PLATON SQUEEZE procedure.[16]

CCDC reference numbers 234200–234205.

See http://www.rsc.org/suppdata/dt/b4/b404173a/ for crystallographic data in CIF or other electronic format.

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