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New and versatile routes to zirconium imido dichloride compounds

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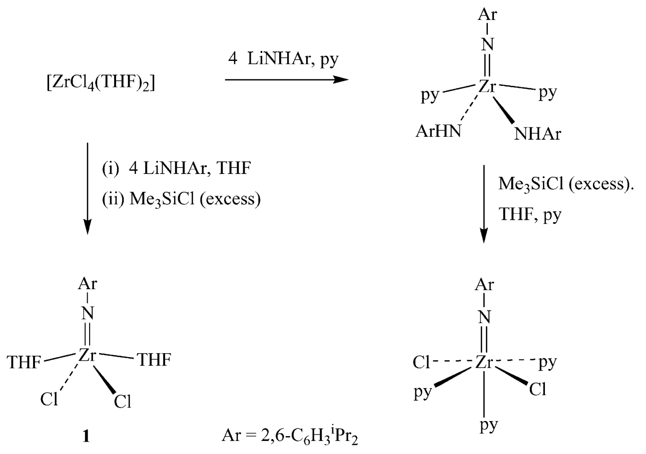
Received 12th January 2005, Accepted 14th February 2005
First published as an Advance Article on the web 10th March 2005

Reactions of zirconium dialkyl- or bis(amido)-dichloride complexes “$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$” or $[Zr(NMe_2)_2Cl_2(THF)_2]$ with primary alkyl and aryl amines are described. Reaction of “$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$” with RNH_2 in THF afforded dimeric $[Zr_2(\mu\text{-}NR)_2Cl_4(THF)_4]$ (R = 2,6-$C_6H_3{}^iPr_2$ (**1**), 2,6-$C_6H_3Me_2$ (**2**) or Ph (**3**)), $[Zr_2(\mu\text{-}NR)_2Cl_4(THF)_3]$ (R = ^tBu (**5**), ^iPr (**6**), CH_2Ph (**7**)), or the “ate” complex $[Zr_2(\mu\text{-}NC_6F_5)_2Cl_6(THF)_2\{Li(THF)_3\}_2]$ (**4**, the LiCl coming from the *in situ* prepared “$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$”). With $[Zr(NMe_2)_2Cl_2(THF)_2]$ the compounds $[Zr_2(\mu\text{-}NR)_2Cl_4(L)_x(L')_y]$ (R = 2,6-$C_6H_3{}^iPr_2$ (**8**), 2,6-$C_6H_3Me_2$ (**9**), Ph (**10**) or C_6F_5 (**11**); $(L)_x(L')_y$ = $(NHMe_2)_3(THF)$, $(NHMe_2)_2(THF)_2$ or undefined), $[Zr_2(\mu\text{-}N^tBu)_2Cl_4(NHMe_2)_3]$ (**12**) and insoluble $[Zr(NR)Cl_2(NHMe_2)]_x$ (R = ^iPr (**13**) or CH_2Ph (**14**)) were obtained. Attempts to form monomeric terminal imido compounds by reaction of **2** or **5** with an excess of pyridine led, respectively, to the corresponding dimeric adducts $[Zr_2(\mu\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(py)_4]$ (**15**) and $[Zr_2(\mu\text{-}N^tBu)_2Cl_4(py)_3]$ (**16**). The X-ray structures of **1**, **2**, **4**, **8**, **12** and **15** have been determined.

Introduction

Transition metal imido chemistry continues to be a topic of considerable interest.[1,2] Stoichiometric or catalytic reactions may occur at the metal–ligand multiple bond itself (for example, as in Bergman’s zirconocene systems[2c]), or the imido group might act as a supporting or ancillary ligand, as in Schrock’s Group 6 olefin metathesis catalysts[3] and imido-based Ziegler–Natta type olefin polymerisation catalysts.[1c] We have been interested in developing Group 4 imido chemistry,[2a,b,d] and found that the tris(pyridine) dichlorides[4] $[Ti(NR)Cl_2(py)_3]$ and the bis(dimethylamine) dichlorides[5] $[Ti(NR)Cl_2(NHMe_2)_2]$ (R = alkyl or aryl) are very useful entry points *via* chloride or/and Lewis base substitution reactions. The ease of synthesis (both yield and scale) of the compounds $[Ti(NR)Cl_2(py)_3]$ and $[Ti(NR)Cl_2(NHMe_2)_2]$ and the wide range of accessible imido N–R substituents are key factors in their usefulness. In zirconium imido chemistry there is still not yet a general *family* of “synthons” of this type which provide a base-stabilised $Zr(NR)Cl_2$ fragment which may be accessed by a *general* route. However, a number of classes of zirconium imido compounds $[(L_n)Zr(NR)]_x$ ((L_n) = supporting ligand or ligand set) have been prepared from precursors containing a pre-assembled $(L_n)Zr$ moiety.[1a,2c,6,7] Wigley and co-workers have previously reported[8] the compounds $[Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl_2(py)_3]$ and $[Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl_2(THF)_2]$ (**1**) (Scheme 1) but only for this specific imido N-substituent. Nonetheless, compound **1** was shown to be a precursor to other zirconium imido complexes, namely $[(\eta\text{-}C_8H_8)Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2Zr(\eta\text{-}C_8H_8)]$ and $[(\eta\text{-}C_5H_4Me)ClZr(\mu\text{-}N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2Zr(\eta\text{-}C_5H_4Me)Cl]$, and other research groups have also used Wigley’s compounds for the synthesis of 2,6-diisopropylphenyl imido complexes.[7,9,10,11] Given the versatility and success of the titanium imido systems $[Ti(NR)Cl_2(py)_3]$ and $[Ti(NR)Cl_2(NHMe_2)_2]$, and the promising results reported so far for $[Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl_2(L)_n]$ (L = THF, $n = 2$; L = py, $n = 3$) we decided to develop more general routes to zirconium imido dichloride compounds and this is the topic of our present contribution.



Scheme 1

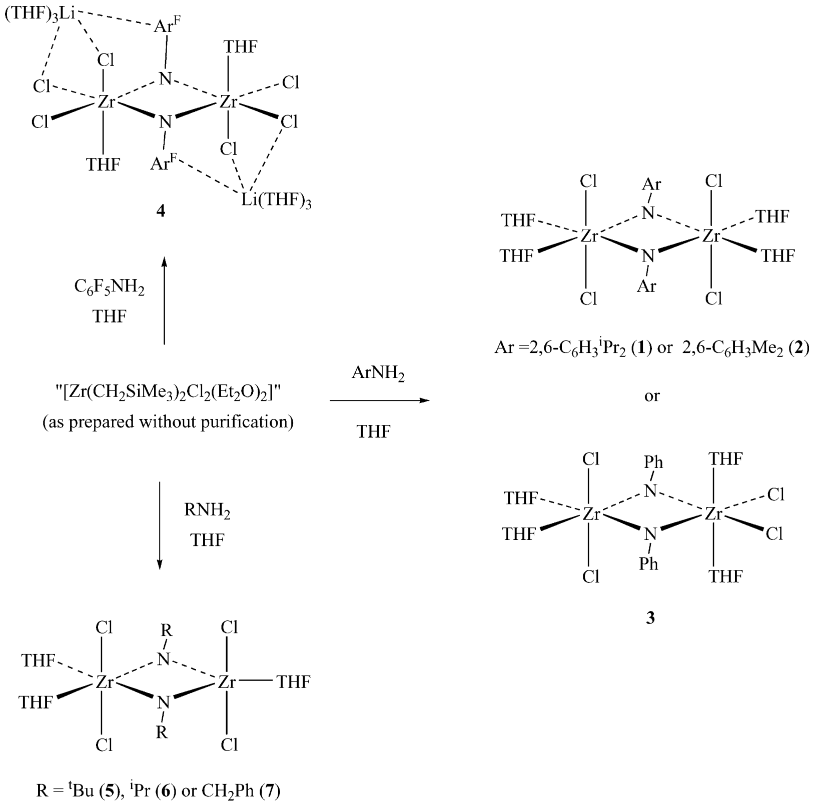
Results and discussion

Synthesis of zirconium imido complexes from “$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$”

Arnold’s previously-reported[12] alkyl-dichloride complex “$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$” was chosen as a likely entry point to new zirconium imido compounds as it is readily synthesised, and the anticipated by-product ($SiMe_4$) of protonolysis reactions with primary amines would be readily separated. It has been found previously that “$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$” is a useful source of the $\{ZrCl_2\}$ fragment by protonolysis reactions with R_2N–H and ArO–H functional groups.[13,14] The reactions of “$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$” with aryl and alkyl amines are summarised in Scheme 2

Reaction of “$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$” with one equivalent of $H_2N\text{-}2,6\text{-}C_6H_3{}^iPr_2$ in THF (rt for 10 h) followed by simple toluene–THF extraction and evaporation afforded **1** as a pure yellow solid in 85% yield. The ^1H and ^{13}C NMR data for complex **1** are identical to those reported by Wigley for “$[Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl_2(THF)_2]$”.[8] The previous synthesis of **1** *via* the two-step route mentioned above (Scheme 1) also goes in 85% overall yield, but takes three times as long and includes a low-temperature first-stage addition as well as a second-stage reflux and a crude separation/extraction of the proposed imido-bis(amide) intermediate. Corresponding reactions of “$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$” with one equivalent of H_2NAr (Ar = 2,6-$C_6H_3Me_2$ or Ph) gave the homologous compounds **2** and **3** in 74 and 61% isolated yields, respectively. The phenyl imido compound **3** has been reported previously[15] and was made by the *in situ* lithiation of *N*-allylaniline

DOI: 10.1039/b500507h



Scheme 2

(2 equiv.) followed by reaction with $ZrCl_4$ under reflux. Other than the crystal structure, no experimental yield or NMR or other characterising data were disclosed and so we provide all these data in the Experimental section. The compound **3** is in fact dimeric in the solid state having the imido-bridged structure represented in Scheme 2. Given the possibility that the *ortho*-substituted homologues **1** and **2** could also be dimeric, their X-ray crystal structures have been determined. The molecular structures are shown in Fig. 1 and selected distances and angles at zirconium are given in Table 1

Like **3**, the compounds **1** and **2** are both dimeric in the solid state. Molecules of **1** lie on crystallographic inversion centres and those of **2** on $2/m$ symmetry sites. The disorder in the THF molecules (see Experimental section) was satisfactorily modelled. In general terms the distances and angles associated with the compounds are within the normal limits.[16,17] Apart from **3**, a number of other imido bridged dizirconium compounds have been reported previously, including $[(Me_4taa)Zr(\mu\text{-}NR)_2Zr(NHR)_2]$ (R = ^tBu or 2,6-$C_6H_3Me_2$; H_2Me_4taa = tetramethyldibenzotetraaza[14]annulene),[18] $[Cp_2Zr(\mu\text{-}N\text{-}4\text{-}C_6H_4{}^tBu)_2ZrCp_2]$,[19] $[(\eta\text{-}C_5H_4Me)ClZr(\mu\text{-}N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2Zr(\eta\text{-}C_5H_4Me)Cl]$,[8] and $[(Me_2N)_2Zr(\mu\text{-}N^tBu)_2Zr(NMe_2)_2]$.[20]

While the overall structures and distances and angles for **1** and **2** are broadly comparable to the equivalent ones in **3**, there are some differences which are important to note. In particular the arrangement of the THF and Cl ligands in **3** differs from the two new structures in that only two Zr–Cl bonds are perpendicular to the $Zr_2(\mu\text{-}N)_2$ plane whereas in **1** and **2** all four are perpendicular to this plane (conversely all four THF O atoms lie in the $Zr_2(\mu\text{-}N)_2$ plane in **1** and **2**). This is attributed to the presence of the sterically more demanding (in comparison with H atoms) *ortho* substituents in the aryl imido ligand in **1** and **2**. The second point of interest is the somewhat pronounced asymmetry in the $Zr\text{–}N_{imide}$ bond distances in **1** ($Zr\text{–}N_{imid}$ = 2.115(5) and 2.018(5) Å) which is absent in **2** (all $Zr\text{–}N_{imide}$ distances (2.082(2) Å) are equivalent by crystallographically imposed symmetry) and negligible in **3** ($Zr\text{–}N_{imide}$ = 2.062(2) and 2.051(2) Å).[15] Asymmetrically bonded $M_2(\mu\text{-}NR)_2$ moieties are not without literature precedent,[8,21] although the distortions can be energetically rather "soft".[21] In the present instance, the greatest asymmetry is associated with the more sterically demanding imido N-substituent (2,6-$C_6H_3{}^iPr_2$) which might indicate that this dimeric structure is slightly less stable (with respect to the five-coordinate monomer) than those of **2** and **3**.

Table 1 Selected bond lengths (Å) and angles (°) for $[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2Cl_4(THF)_4]$ (**1**) and $[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(THF)_4]$ (**2**)

	1	2
$Zr\text{–}N_{imide}$	2.115(5), 2.018(5)	2.082(2)
Zr–Cl	2.471(2), 2.468(2)	2.4643(4)
$Zr\text{–}O_{THF}$	2.329(4), 2.372(4)	2.387(2)
$Zr\text{–}N_{py}$	—	—
$N_{imide}\text{–}Zr\text{–}N_{imide}$	81.8(2)	80.49(9)
$O_{THF}\text{–}Zr\text{–}O_{THF}$	82.7(2)	100.65(7)
$N_{py}\text{–}Zr\text{–}N_{py}$	—	—
Cl–Zr–Cl	154.79(6)	150.49(2)

The solution ^1H and ^{13}C NMR data of **1** and **2** are consistent with the solid-state structures featuring a single set of resonances for the coordinated THF ligands and resonances attributable to 2,6-$C_6H_3R_2$ (R = ^iPr or Me) substituents. The spectra for **3** also feature the one set of THF resonances, whereas the solid-state structure shows the presence of two chemically distinct THF ligands. This implies that the THF ligands of **3** are in rapid exchange on the NMR timescale. The resonances for the THF ligands in all three compounds are rather broad at room temperature suggestive of one or more dynamic processes. The solution dynamic processes of other imido-bridged dizirconium complexes are discussed later on in this contribution.

Surprisingly, reaction of "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" with one equivalent of $H_2NC_6F_5$ (Scheme 2) consistently produced the crystallographically characterised "ate" complex $[Zr_2(\mu\text{-}NC_6F_5)_2Cl_6(THF)_2\{Li(THF)_3\}_2]$ (**4**) rather than the anticipated complex $[Zr_2(\mu\text{-}NC_6F_5)_2Cl_4(THF)_4]$ analogous to **1**–**3**. The compound **4** was obtained in 63% isolated yield on a preparative

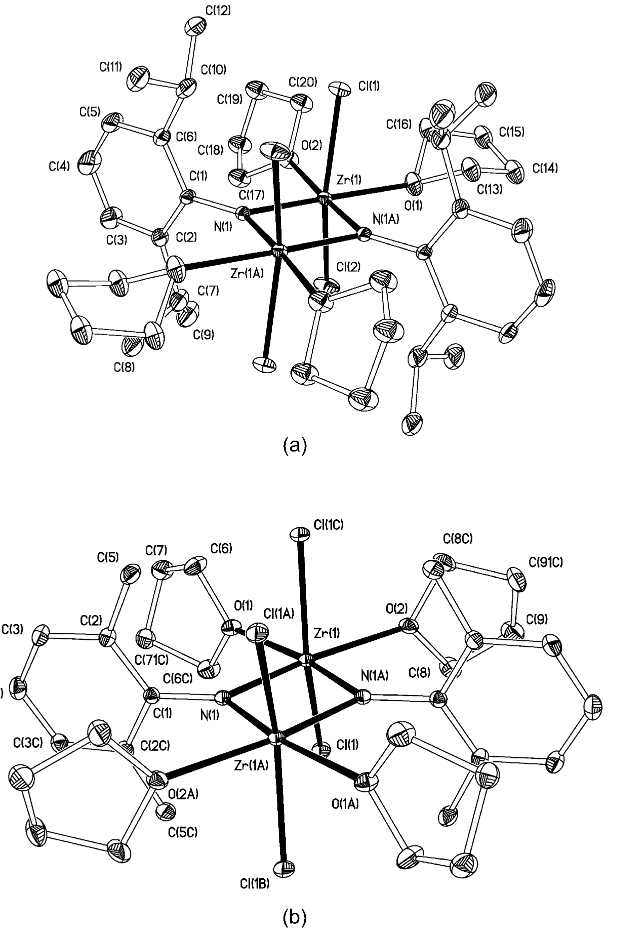


Fig. 1 Molecular structures of $[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2Cl_4(THF)_4]$ (**1**) (top) and $[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(THF)_4]$ (**2**) (bottom). Displacement ellipsoids drawn at the 25% probability level. H atoms omitted. Atoms carrying the suffix 'A' are related to their counterparts by the operators $[2 - x, -y, 2 - z]$ (for **1**) and $[x + 1/2, y + 1/2, z]$ (for **2**).

scale and formed quantitatively in NMR-tube scale experiments. Attempts to prepare a LiCl-free complex by treatment of **4** with hot (100 °C) toluene were unsuccessful.

It is believed that "ate" complex formation only occurs because of the highly electron-withdrawing C_6F_5 imido N-substituent which renders the zirconium centre more electron deficient (Lewis acidic) and also provides an additional site of attachment of the Li^+ cation (see below). The source of LiCl is thought to be from the starting material "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$"[12] prepared according to the literature method of reacting $LiCH_2SiMe_3$ (2 equiv.) with $ZrCl_4$ in Et_2O followed by a hexane–Et_2O extraction and evaporation of all volatiles. As described by Arnold,[12] "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" is fairly thermally sensitive and is not amenable to further work-up or purification. Our own analysis (Li and Cl elemental composition and ^{7}Li NMR) of "as prepared" $[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" suggests that it probably has the composition "$Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2\cdot LiCl$", at least in our hands. Throughout this present contribution we will refer to the material as "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$", although for the purposes of the molar calculations in the Experimental section we have assumed a molar mass appropriate for "$Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2\cdot LiCl$" which is *ca.* 10% greater than for the salt-free composition.

The molecular structure of **4** is shown in Fig. 2 and selected bond distances and angles are listed in Table 2. Molecules of **4** formally contain a dianionic $[Zr_2(\mu\text{-}NC_6F_5)_2Cl_6(THF)_2]^{2-}$ unit ligated by two $[Li(THF)_3]^+$ cations. The $[Zr_2(\mu\text{-}NC_6F_5)_2Cl_6(THF)_2]^{2-}$ fragment is broadly comparable to the neutral $[Zr_2(\mu\text{-}NAr)_2Cl_4(THF)_4]$ complexes **1–3** and has its two $Zr–O_{THF}$ bonds perpendicular to the $Zr_2(\mu\text{-}N)_2$ plane (*cf.* **3**). There is some asymmetry in the $Zr–N_{imide}$ bond distances (2.089(2) and 2.123(3) Å) which could easily be attributable to the rather asymmetric coordination environment about the Zr atoms. The Zr(1)–Cl(1) bond is 0.0626(8) Å longer than Zr(1)–Cl(2) and is attributed to the coordination of Li(1) to Cl(1). Each lithium cation in **4** is six-coordinate and ligated by three THF molecules, two Zr-bound Cl atoms and the *ortho* F atom of a C_6F_5 substituent. The coordination of solvated lithium cations to anionic metal complexes is very well precedented.[16,17] The *ortho* C–F bond assisted coordination of Li has also been reported previously.[22]

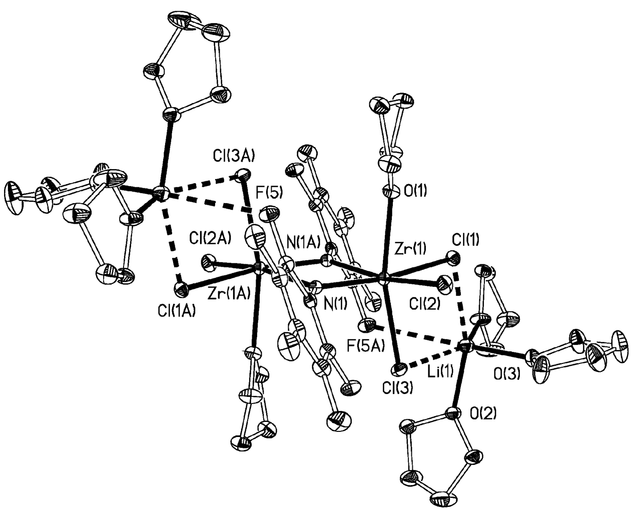


Fig. 2 Molecular structure of $[Zr_2(\mu\text{-}NC_6F_5)_2Cl_6(THF)_2\{Li(THF)_3\}_2]$ (**4**). Displacement ellipsoids drawn at the 25% probability level. H atoms omitted. Atoms carrying the suffix 'A' are related to their counterparts by the operator $[-x, -y, -z]$.

Table 2 Selected bond lengths (Å) and angles (°) for $[Zr_2(\mu\text{-}NC_6F_5)_2Cl_6(THF)_2\{Li(THF)_3\}_2]$ (**4**)

Zr(1)–N(1)	2.089(2)	Li(1)–Cl(1)	2.570(4)
Zr(1)–N(1A)	2.123(2)	Li(1)–Cl(3)	2.785(4)
Zr(1)–Cl(1)	2.5497(5)	Li(1)···F(5A)	2.843(5)
Zr(1)–Cl(2)	2.4871(6)	Li(1)–O(2)	1.996(4)
Zr(1)–Cl(3)	2.4674(6)	Li(1)–O(3)	1.963(5)
Zr(1)–O(1)	2.278(2)	Li(1)–O(4)	2.007(4)
N(1)–Zr(1)–N(1A)	79.48(7)	O(1)–Zr(1)–Cl(3)	165.79(4)
Cl(1)–Zr(1)–Cl(2)	96.07(2)		

The low-temperature (203 K) 500 MHz ^{1}H NMR spectrum of **4** in toluene-d_8 is consistent with the solid state structure (Fig. 2). In total, three sets of THF resonances are observed in a 2 : 1 : 1 ratio (*i.e*, those bound to the Li^+ cations are observed in a 2 : 1 "equatorial" : "axial" ratio). As the temperature is increased from 203 to 333 K all three sets of THF resonances broaden and coalesce to form a single set of resonances indicating that at high temperature all of the THF molecules are involved in rapid site-exchange. The low temperature ^{19}F NMR spectrum exhibits equivalent *ortho* F atoms indicating that rotation about the N–C_{ipso} bond (*ortho* C–F bond exchange) is still rapid at 203 K on the NMR timescale.

We have also carried out reactions between the alkyl amines $^tBuNH_2$, $^iPrNH_2$ and $PhCH_2NH_2$ and "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" (Scheme 2). These yield the imido-bridged compounds $[Zr_2(\mu\text{-}NR)_2Cl_4(THF)_3]$ (R = ^{t}Bu (**5**), ^{i}Pr (**6**), Bz (**7**)) in somewhat lower (20–44%) isolated yields than for the aryl imido complexes **1–4**. According to the spectroscopic and analytical data these compounds possess only three THF ligands per dizirconium molecule, with one Zr being six-coordinate and the other five-coordinate. A structurally characterised tris(dimethylamine) analogue, namely $[Zr_2Cl_4(\mu\text{-}N^tBu)_2(HNMe_2)_3]$ (**12**), is discussed later on.

The ^1H NMR spectrum (and variable-temperature behaviour) of complexes **5–7** in $C_2D_2Cl_4$ are similar and only the details relating to **5** will be discussed. At 298 K the spectrum is rather complex, possibly suggesting the presence of structural isomers (*e.g.*, interchange of axial and equatorial coordination sites). The resonances are broad, indicating possible interconversion between isomers. As the temperature is raised above 298 K the spectrum becomes less complex and some of the resonances sharpen. At 363 K (the high temperature limit) a single sharp resonance is observed at 1.56 ppm (relative intensity 18H) assigned to the imido *tert*-butyl substituent, together with broad resonances at 4.89 (12H) and 1.93 (12H) ppm for three THF ligands. This high temperature spectrum is consistent with the structure proposed, but with all three THF ligands being labile and in rapid site-exchange. Cooling the sample down from 298 to 183 K in an attempt to observe a static structure afforded only a very complex spectrum consistent with the presence of several isomeric species.

Synthesis of zirconium imido complexes from $[ZrCl_2(NMe_2)_2(THF)_2]$

The use of "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" as a starting material allowed the general synthesis of a range of zirconium imido-dichloride complexes of the type $[Zr_2(\mu\text{-}NR)_2Cl_4(THF)_x]$ (R = alkyl or aryl, $x = 3$ or 4). Nonetheless, this synthetic route has certain drawbacks in that the starting dialkyl is of limited stability and cannot be stored for long periods of time, and that the desired products are often formed as waxy oils which require a time-consuming trituration step to produce crystalline samples. Bearing in mind that reaction of RNH_2 with $[Ti(NMe_2)_2Cl_2]$ affords excellent conversions to the imido complexes $[Ti(NR)Cl_2(NHMe_2)_2]$ for a wide range of alkyl and aryl amines,[5] an alternative synthetic route to zirconium imido compounds starting from the readily available and thermally stable $[ZrCl_2(NMe_2)_2(THF)_2]$[23] was investigated. Although $[ZrCl_2(NMe_2)_2(THF)_2]$ has not been used in the preparation of imido complexes, its use as a source of the $\{ZrCl_2\}$ fragment through $R_2N–H$ bond protonolysis reactions has been reported previously.[24]

The reactions of four different aryl amines with $[ZrCl_2(NMe_2)_2(THF)_2]$ in pentane for 1–2 h afforded the imido-bridged complexes $[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2Cl_4(NHMe_2)_x(THF)_y]$ (**8**, x and y are ill-defined, see below), $[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(NHMe_2)_2(THF)_2]$ (**9**) and $[Zr_2(\mu\text{-}NAr)_2Cl_4(NHMe_2)_3(THF)]$ (Ar = Ph (**10**) or C_6F_5 (**11**)). The products separate from solution under these conditions as yellow to off-white solids in *ca.* 70 to 80% isolated yields. The X-ray structure of **9** has been determined and confirms the dimeric structures proposed in Scheme 3. The molecular structure of **9** is shown in Fig. 3 and selected bond distances and angles are listed in Table 3.

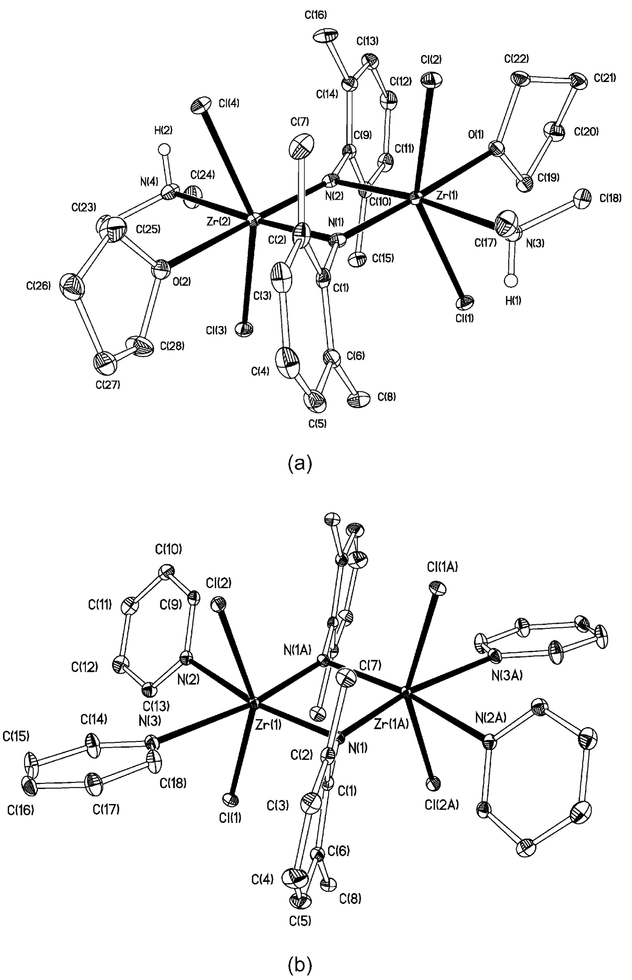
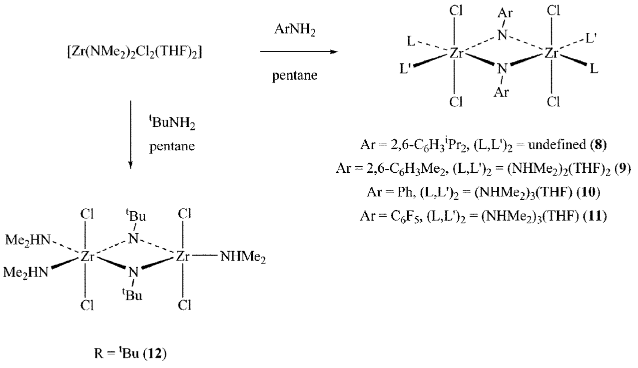


Fig. 3 Molecular structures of $[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(NHMe_2)_2(THF)_2]$ (**9**) (top), $[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(py)_4]$ (**15**) (bottom; atoms carrying the suffix 'A' are related to their counterparts by the operator $[-x, -y, -z]$). Displacement ellipsoids drawn at the 20% probability level. H atoms bound to carbon omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

Table 3 Selected bond lengths (Å) and angles (°) for $[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(NHMe_2)_2(THF)_2]$ (**9**)

Zr(1)–Cl(1)	2.4931(6)	Zr(2)–Cl(3)	2.4615(6)
Zr(1)–Cl(2)	2.4596(7)	Zr(2)–Cl(4)	2.5014(6)
Zr(1)–N(1)	2.017(2)	Zr(2)–N(1)	2.133(2)
Zr(1)–N(2)	2.156(2)	Zr(2)–N(2)	1.996(2)
Zr(1)–N(3)	2.455(2)	Zr(2)–N(4)	2.466(2)
Zr(1)–O(1)	2.407(2)	Zr(2)–O(2)	2.381(2)
N(1)–Zr(1)–N(2)	81.14(8)	N(1)–Zr(2)–N(2)	82.20(8)
N(3)–Zr(1)–O(1)	92.11(7)	N(4)–Zr(2)–O(2)	89.91(8)
Cl(1)–Zr(1)–Cl(2)	150.45(2)	Cl(3)–Zr(2)–Cl(4)	151.62(2)

The coordination geometry and average distances and angles for **9** are comparable to those of the tetrakis(THF) analogue $[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(THF)_4]$ (**2**), to which it is formally related by the replacement of two THF by two $NHMe_2$ ligands. However, unlike **2** which is constrained by $2/m$ crystallographic symmetry, molecules of **9** lie on general positions in the crystal lattice. There is quite a large variation in bond distances for chemically equivalent linkages, and in particular the Zr–Cl and $Zr–N_{imide}$ bond lengths, although the latter might be a consequence of the different donor atoms *trans* to the two $Zr–N_{imide}$ bonds. There are some intramolecular NH···Cl hydrogen bonds (NH···Cl = 2.79 and 2.89 Å; angles subtended at H = 126 and 138°; sum of the van der Waals radii for Cl and H = 2.95 Å[25] (H atoms placed in estimated positions, see Experimental section)) but these are at the long end of the range of such contacts that are deemed to be significant.[26] The solid state



Ar = 2,6-$C_6H_3{}^iPr_2$, $(L,L')_2$ = undefined (**8**)
Ar = 2,6-$C_6H_3Me_2$, $(L,L')_2$ = $(NHMe_2)_2(THF)_2$ (**9**)
Ar = Ph, $(L,L')_2$ = $(NHMe_2)_3(THF)$ (**10**)
Ar = C_6F_5, $(L,L')_2$ = $(NHMe_2)_3(THF)$ (**11**)

R = ^tBu (**12**)

Scheme 3

ν(N–H) stretching frequency of 3278 cm^{-1} for **9** is also indicative of a weak NH · · · Cl interaction according to our recent work on certain extensively NH · · · Cl hydrogen bonded five-coordinate titanium imido complexes [Ti(NR)Cl_2(NHMe$_2$)$_2$].[5] Here ν(N–H) values as low as 3220 cm^{-1} (associated NH · · · Cl distance 2.45 Å) were found. Note, however, that the presence of lower energy solid state ν(N–H) stretches in the other products **8**, **10** and **11** (*e.g.* 3264 cm^{-1} in **11**) indicates that in these cases more significant NH · · · Cl hydrogen bonding is present.[5]

It can be seen from Scheme 3 that the exact numbers of THF and NHMe$_2$ ligands associated with the aryl imido products **8–11** formed from [Zr(NMe$_2$)$_2$Cl$_2$(THF)$_2$] depend critically on the identity of the aniline aromatic ring substituents (and may be associated with NH · · · Cl hydrogen bonding possibilities as the products precipitate from the pentane solvent). Furthermore, the lability of these donor ligands on the NMR timescale differed, and in the case of **8** this even prevented the exact stoichiometry of the donor ligand set from being determined. In principle, however, it may be possible to convert the compounds **8–11** to the tetrakis(THF) analogues and we have shown this to be feasible for compound **9**. Thus a solution of [Zr$_2$(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$(HNMe$_2$)$_2$(THF)$_2$] (**9**) in THF was heated in an NMR tube at 50 °C for 16 h. Removal of all volatiles and redissolving in C$_6$D$_6$ showed that no dimethylamine remained and that [Zr$_2$(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$(THF)$_4$] (**2**) had been formed in quantitative yield.

The ambient temperature solution ^{1}H NMR spectrum of complex **9** was consistent with the solid state structure determined by X-ray diffraction and contained sharp resonances assigned to the 2,6-C$_6$H$_3$Me$_2$ substituents and to the dimethylamine and THF ligands. The sharp nature of the resonances indicated that the structure was static on the NMR timescale at this temperature. The two complexes **10** and **11** displayed similar variable-temperature ^{1}H NMR behaviour and only **10** will be discussed. The ^{1}H NMR spectrum of **10** at 293 K showed two equivalent N-phenyl groups. The THF ligand appeared as broad resonances at 3.63 and 1.18 ppm and the NMe groups of the three dimethylamine ligands gave rise to a single very broad resonance at 2.44 ppm indicating rapid exchange. Upon heating the sample to 363 K this resonance sharpened as expected (fast exchange limit). Cooling to 223 K afforded the slow exchange limiting spectrum which was more complex and revealed the presence of two inequivalent phenyl imido groups, three distinct dimethylamine ligands and a THF ligand. Therefore the actual structure of **10** (and **11**) appears be completely non-symmetric. Unfortunately, the ^{1}H NMR spectrum of complex **8** was extremely broad even at all temperatures and a full assignment of the spectrum was not possible.

We have also examined reactions of [ZrCl$_2$(NMe$_2$)$_2$(THF)$_2$] with alkyl amines (Scheme 3). Addition of one equivalent of H$_2$N^{t}Bu in pentane afforded the complex [Zr$_2$Cl$_4$(μ-N^{t}Bu)$_2$(HNMe$_2$)$_3$] (**12**) as white powder which was isolated in 64% yield. The imido bridged dimeric structure (analogous to those proposed for [Zr$_2$Cl$_4$(μ-NR)$_2$(THF)$_3$] (**5–7**, Scheme 2) consisting of one five- and one six-coordinate zirconium centre was confirmed by single crystal X-ray diffraction analysis. The molecular structure and variable-temperature NMR behaviour are discussed below. The related complexes [Zr(NR)Cl$_2$(NHMe$_2$)]$_x$ (R = ^{i}Pr (**13**) or CH$_2$Ph (**14**)) were prepared in comparable yields using an analogous synthetic procedure but were totally insoluble in all non-donor solvents. The presence of only one NHMe$_2$ ligand per zirconium centre (according to elemental analysis) suggests the possible presence of vacant coordination sites, and the very insoluble nature of the compounds could be indicative of polymer formation. However, in the absence of structural data it is not possible to speculate further. The presence of low frequency ν(N–H) bands at 3180 (**13**) and 3194 cm^{-1} (**14**) suggest that NH · · · Cl intermolecular hydrogen bonding may also be a significant factor with regards to the insolubility of the compounds.

The molecular structure of [Zr$_2$Cl$_4$(μ-N^{t}Bu)$_2$(HNMe$_2$)$_3$] (**12**) is shown in Fig. 4 and selected distances and angles are summarised in Table 4. Molecules of **12** possess approximately trigonal bipyramidal (Zr(1)) and octahedral (Zr(2)) metals linked by bridging *tert*-butyl imido ligands. The Zr–Cl and Zr–N$_{imide}$ distances for Zr(2) are longer that those for Zr(1), consistent with the higher coordination number of Zr(2) (and for the Zr(2)–Cl bonds it should also be noted that these are *trans* to the labilising μ-imido nitrogens). In contrast the Zr(1)–N(3) (NHMe$_2$ ligand) distance is significantly longer than the Zr(2)–N(4) and Zr(2)–N(5) distances, even though the latter NHMe$_2$ ligands are associated with the more sterically crowded metal centre. The longer Zr–N$_{amine}$ distance for Zr(1) is in fact attributable to N(3) being more *trans* to the strongly labilising μ-NR donors whereas the two NHMe$_2$ ligands are only mutually *trans* to each other. A structurally characterised precedent for **12** (*i.e.*, containing a Zr$_2$(μ-NR)$_2$ unit with different ligand sets at each Zr) is [(Me$_4$taa)Zr(μ-NR)$_2$Zr(NHR)$_2$] (R = ^{t}Bu or 2,6-C$_6$H$_3$Me$_2$),[18] which feature six- and four-coordinate zirconium centres within the same imido-bridged dizirconium molecules.

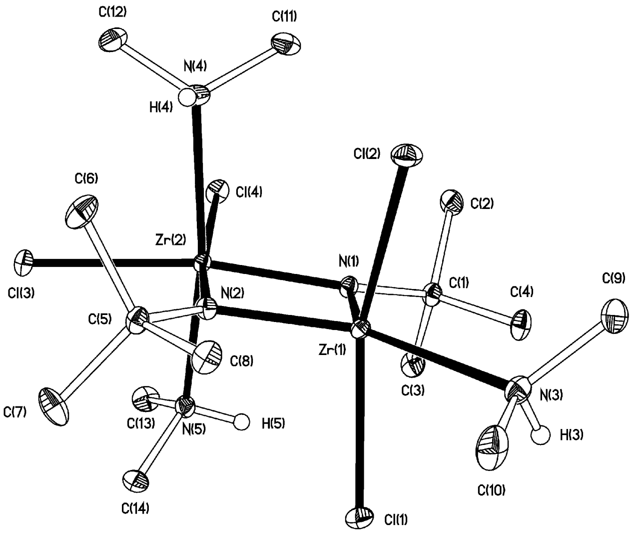


Fig. 4 Molecular structure of [Zr$_2$(μ-N^{t}Bu)$_2$Cl$_4$(NHMe$_2$)$_3$] (**12**). Displacement ellipsoids drawn at the 25% probablility level. H atoms bonded to C omitted; H atoms bonded to N drawn as spheres of arbitrary radius.

The solution dynamics of the complex [Zr$_2$Cl$_4$(μ-N^{t}Bu)$_2$(HNMe$_2$)$_3$] (**12**) are discussed with reference to the ^{1}H NMR spectra at 243, 293, 343 and 383 K (in toluene-d$_8$) shown in Fig. 5. The 293 K spectrum features a septet at 3.42 ppm assigned to the N–H protons of the dimethylamine groups bound to the six-coordinate zirconium centre, and a doublet at 2.75 ppm assigned to the corresponding methyl groups. The third dimethylamine group (bound to the five-coordinate zirconium) affords a broad resonance at 1.95 ppm indicating that it is labile at this temperature (consistent with the longer Zr(1)–N(3) distance mentioned above). On cooling to 243 K this broad resonance sharpens to afford a doublet at 1.82 ppm

Table 4 Selected bond lengths (Å) and angles (°) for [Zr$_2$(μ-N^{t}Bu)$_2$-Cl$_4$(NHMe$_2$)$_3$] (**12**)

Zr(1)–Cl(1)	2.4981(4)	Zr(2)–Cl(3)	2.5166(3)
Zr(1)–Cl(2)	2.4934(4)	Zr(2)–Cl(4)	2.5382(3)
Zr(1)–N(1)	2.0111(11)	Zr(2)–N(1)	2.0877(11)
Zr(1)–N(2)	2.0210(11)	Zr(2)–N(2)	2.0735(11)
Zr(1)–N(3)	2.4894(12)	Zr(2)–N(4)	2.3971(12)
		Zr(2)–N(5)	2.3809(12)
N(1)–Zr(1)–N(2)	83.20(4)	N(1)–Zr(2)–N(2)	80.08(4)
Cl(1)–Zr (1)–Cl(2)	156.107(13)	Cl(3)–Zr(2)–Cl(4)	91.816(12)
		N(4)–Zr(2)–N(5)	166.76(4)

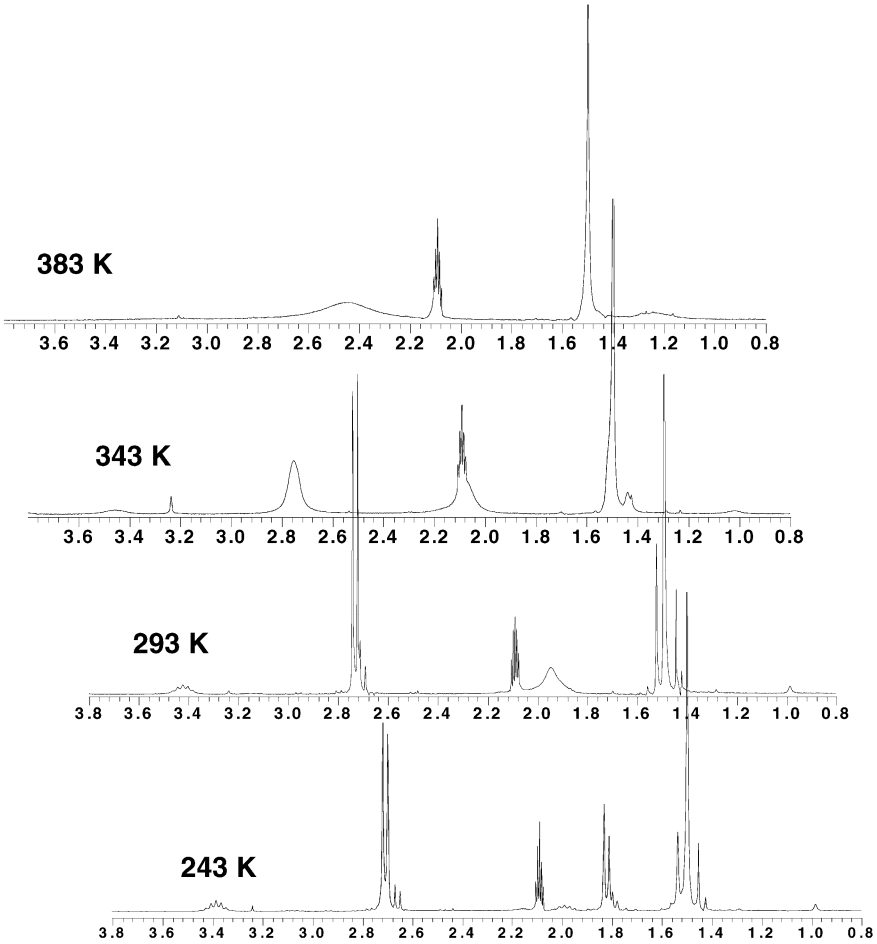
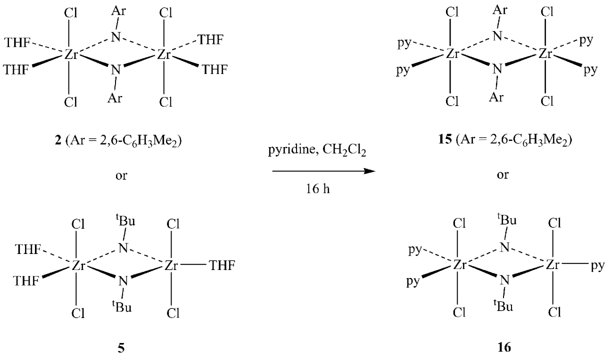


Fig. 5 Variable-temperature 500.1 MHz ^{1}H NMR spectra of [$Zr_2Cl_4(\mu\text{-}N^tBu)_2(HNMe_2)_3$] (**12**) in toluene-$d_8$. The multiplet at 2.10 ppm is attributed residual $C\mathit{H}D_2C_6D_5$.

with an associated septet ($N\mathit{H}Me_2$) at 1.99 ppm indicating that at this temperature the ligand is now firmly bound on the NMR timescale. These resonances are rather upfield in comparison with those of the other $NHMe_2$ ligands. Heating the sample to 343 K leads to a broadening of the resonances assigned to the two $NHMe_2$ ligands bound to the six-coordinate zirconium centre, indicating that these ligands are labile at this temperature. Finally, increasing the temperature to 383 K leads to total coalescence of all $NHMe_2$ methyl group resonances indicating that at this temperature rapid site-exchange is occurring. The additional minor peaks in the 243 and 293 K spectra are probably due to minor conformational isomers of the dimer which undergo exchange with the major isomer on heating.

Pyridine adducts

Wigley[8] has previously reported that the six-coordinate tris(pyridine) compound [$Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl_2(py)_3$] is monomeric (synthesised from [$Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(NH\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2(py)_2$] and $SiMe_3Cl$ and pyridine in THF). We have shown[10] that [$Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2Cl_4(THF)_4$] (**1**) can be converted to [$Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl_2(py)_3$] by addition of pyridine, and also to crystallographically characterised, monomeric six-coordinate [$Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl_2(Me_3[9]aneN_3)$] by addition of 1,4,7-trimethyltriazacyclononane ($Me_3[9]aneN_3$).[11] In related titanium imido chemistry,[4] the dimeric (chloride-bridged) titanium imido compounds [$Ti_2(NR)_2(\mu\text{-}Cl)_2Cl_2(py)_4$] (R = ^{t}Bu or aryl) can be converted to the monomeric tris(pyridine) homologues [$Ti(NR)Cl_2(py)_3$]. Reaction of certain complexes [$Ti(NR)Cl_2(NHMe_2)_2$] with an excess of pyridine also forms the corresponding [$Ti(NR)Cl_2(py)_3$] homologues.[5a] It was therefore of interest to see if some of the new zirconium imido complexes could also be converted to (monomeric) pyridine adducts.



(1)

Reaction of the THF adducts [$Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(THF)_4$] (**2**) and [$Zr_2(\mu\text{-}N^tBu)_2Cl_4(THF)_3$] (**5**) in dichloromethane with a very large excess of pyridine afforded the corresponding dimeric products [$Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(py)_4$] (**15**) and [$Zr_2(\mu\text{-}N^tBu)_2Cl_4(py)_3$] (**16**) as yellow solids in 35 and 60% isolated yields, respectively (Equation 1). It therefore appears that these particular imido N-substituents are insufficient with regards to forming monomeric pyridine adducts.

The NMR spectra of the new compounds are consistent with the proposed structures. In particular, the NMR spectra of **16** clearly show the presence of two different pyridine ligands in the ratio 2 : 1. Compound **15** has been crystallographically characterised. The molecular structure is shown in Fig. 3 and confirms the dimeric structure. Selected bond distances and angles are

Table 5 Selected bond lengths (Å) and angles (°) for $[Zr_2(\mu\text{-N-2,6-}C_6H_3Me_2)_2Cl_4(py)_4]$ (**15**)

Zr(1)–Cl(1)	2.4768(3)	Zr(1)–Cl(2)	2.4805(3)
Zr(1)–N(1)	2.0229(11)	Zr(1)–N(1A)	2.1227(11)
Zr(1)–N(2)	2.5004(12)	Zr(1)–N(3)	2.4822(12)
N(1)–Zr(1)–N(1A)	81.24(5)	N(2)–Zr(1)–N(3)	88.94(4)
Cl(1)–Zr (1)–Cl(2)	151.177(12)		

listed in Table 5 and these are rather similar to those discussed above for $[Zr_2(\mu\text{-N-2,6-}C_6H_3Me_2)_2Cl_4(THF)_4]$ (**2**) and $[Zr_2(\mu\text{-N-2,6-}C_6H_3Me_2)_2Cl_4(NHMe_2)_2(THF)_4]$ (**9**). The Zr–N_{imide} distances are slightly different (2.1231(13) and 2.0239(12) Å) but the average value is close to that in **2** and **9**, and the extent of asymmetry is less than in **9**. The Zr–Cl distances (av. 2.4787(4) Å) are slightly longer than in **2**, consistent with the better σ donor ability of pyridine in comparison to THF.

Summary

Protonolysis methodologies based on the reactions of "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" or $[Zr(NMe_2)_2Cl_2(THF)_2]$ with primary alkyl and aryl amines provide general entry points to dimeric zirconium imido dichloride compounds. The previously reported "$[Zr(N\text{-2,6-}C_6H_3{}^iPr_2)Cl_2(THF)_2]$" is dimeric, at least in the solid state. Two main structural types are formed depending on whether aryl or alkyl amines are used, namely $[Zr_2(\mu\text{-NAr})_2Cl_4(L)_4]$ or $[Zr_2(\mu\text{-NR})_2Cl_4(L)_3]$. The presence of LiCl in "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" is only a complication for the reaction with $H_2NC_6F_5$ in which case an "ate" complex is formed. $[Zr(NMe_2)_2Cl_2(THF)_2]$ is more convenient as a starting material in terms of its thermal stability, but it can give less well defined (or predictable) products. Attempts to cleave dimeric $[Zr_2(\mu\text{-2,6-}C_6H_3Me_2)_2Cl_4(THF)_4]$ or $[Zr_2(\mu\text{-N}^tBu)_2Cl_4(THF)_3]$ with pyridine yields only the corresponding dimeric pyridine adducts.

Experimental

General methods and instrumentation

All air- and moisture-sensitive manipulations were performed using standard Schlenk-line (Ar) and dry-box (N_2) techniques. Solvents were pre-dried over 4 Å molecular sieves, refluxed over the appropriate drying agents (CaH_2, sodium or potassium) under N_2, distilled at atmospheric pressure and stored in Teflon valve ampoules. Deuterated solvents were dried over sodium, potassium or CaH_2 as appropriate, distilled under reduced pressure and stored in Teflon valve ampoules. NMR samples were prepared in Wilmad 505-PS tubes fitted with J. Young NMR/5 valves. ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectra were recorded on Varian Unity Plus 500 and Varian Mercury-VX 300 spectrometers. ^1H and ^{13}C spectra are referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{19}F spectra were referenced externally to $CFCl_3$. Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. IR spectra were recorded on Perkin Elmer 1600 and Perkin Elmer 1710 spectrometers as Nujol mulls between KBr windows or as CH_2Cl_2 solutions in a 0.1 mm pathlength NaCl cell. All data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded on Micromass Autospec 500, AEI MS902, and Finnigan MAT 900 XLT spectrometers. All data are quoted in mass/charge ratio (m/z). Elemental analyses were carried out by the analytical laboratory at the Inorganic Chemistry Laboratory Oxford or Mikroanalytisches Labor Pascher, Germany.

Literature preparations

The compounds "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$"[12] and $[Zr(NMe_2)_2Cl_2(THF)_2]$[23] were prepared according to published methods. The actual structure of the complex previously reported as "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" is believed to be the "ate" complex "$Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2\cdot LiCl$". This assignment was supported by ^7Li NMR spectroscopy ($\delta = -0.2$ ppm) and elemental analysis of a sample quenched with water [found (calc. for $C_{16}H_{42}Cl_3LiO_2Si_2Zr$): Li 1.4 (1.3), Cl 22.4 (20.2)%]. All substances used in air- and moisture-sensitive manipulations were purified by standard techniques.[27] All other compounds and reagents were purchased from commercial chemical suppliers and used without further purification.

$[Zr_2(\mu\text{-N-2,6-}C_6H_3{}^iPr_2)_2Cl_4(THF)_4]$ (1). To a solution of "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" (0.865 g, 1.64 mmol) in THF (25 cm^3) was added $H_2N\text{-2,6-}C_6H_3{}^iPr_2$ (0.30 cm^3, 1.64 mmol) at rt. The pale yellow mixture was stirred at rt for 10 h to give a yellow solution. Removal of volatiles under reduced pressure gave a waxy yellow solid which was triturated with pentane (25 cm^3) and filtered to give a yellow powder. Extraction into toluene–THF (3 : 1, 40 cm^3) and removal of volatiles under reduced pressure afforded **1** as a yellow solid. 0.675 g, 85%. Diffraction-quality crystals were grown from a pentane solution at 0 °C. Characterising data were consistent with published values.[8]

$[Zr_2(\mu\text{-N-2,6-}C_6H_3Me_2)_2Cl_4(THF)_4]$ (2). To a solution of "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" (0.865 g, 1.64 mmol) in THF (25 cm^3) was added $H_2N\text{-2,6-}C_6H_3Me_2$ (0.20 cm^3, 1.64 mmol) at rt. The pale yellow mixture was stirred at rt for 10 h to give a yellow solution. Removal of volatiles under reduced pressure gave a waxy yellow solid which was triturated with pentane (25 cm^3) and filtered to gave a yellow powder. Extraction into toluene–THF (3 : 1, 40 cm^3) and removal of volatiles under reduced pressure afforded **2** as a yellow solid. Yield: 0.513 g (74%). Diffraction-quality crystals were grown from a THF–pentane mixture at 5 °C. ^1H NMR ($CDCl_3$, 500.1 MHz, 298 K): δ 6.91 (4H, d, ^3J = 10.5 Hz, $m\text{-}C_6H_3Me_2$), 6.62 (2H, t, ^3J = 10.5 Hz, $p\text{-}C_6H_3Me_2$), 3.70 (16H, br s, C_4H_8O), 2.75 (12H, s, $C_6H_3Me_2$), 1.52 (16H, br s, C_4H_8O). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz, 298 K): δ 151.1 ($o\text{-}C_6H_3Me_2$), 130.7 ($i\text{-}C_6H_3Me_2$), 128.2 ($m\text{-}C_6H_3Me_2$), 122.4 ($p\text{-}C_6H_3Me_2$), 72.3 (C_4H_8O), 25.0 (C_4H_8O), 21.3 ($C_6H_3Me_2$). IR (KBr plates, Nujol): 1402 (w), 1250 (m), 1190 (s), 1102 (m), 1044 (w), 1006 (m), 866 (m), 768 (m), 740 (m), 716 (w), 582 (s), 516 (s). Anal. found (calc. for $C_{32}H_{50}Cl_4N_2O_4Zr_2$): C 44.8 (45.2), H 5.6 (5.9), N 3.6 (3.3)%.

$[Zr_2(\mu\text{-NPh})_2Cl_4(THF)_4]$ (3). To a solution of "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" (0.865 g, 1.64 mmol) in THF (25 cm^3) was added $PhNH_2$ (0.15 cm^3, 1.64 mmol) at rt. The pale yellow mixture was stirred at rt for 10 h to give a yellow solution. Removal of volatiles under reduced pressure gave a yellow solid which was extracted into toluene–THF (3 : 1, 40 cm^3) and volatiles removed under reduced pressure to afford **3** as a yellow solid. Yield: 0.402 g (61%). ^1H NMR ($CDCl_3$, 300.1 MHz, 298 K): δ 7.18 (4H, app. t, ^3J = 8.4 Hz, $m\text{-}C_6H_5$), 7.09 (4H, d, ^3J = 8.1 Hz, $o\text{-}C_6H_5$), 6.76 (2H, t, ^3J = 7.5 Hz, $p\text{-}C_6H_5$), 3.91 (16H, br s, C_4H_8O), 1.79 (16H, br s, C_4H_8O). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, 298 K): δ 152.4 ($i\text{-}C_6H_5$), 128.0 ($m\text{-}C_6H_5$), 121.3 ($o\text{-}C_6H_5$), 120.6 ($p\text{-}C_6H_5$), 71.0 (C_4H_8O), 25.6 (C_4H_8O). IR (KBr plates, Nujol): 1582 (m), 1342 (w), 1228 (s), 1168 (w), 1042 (m), 868 (m), 754 (m), 694 (w), 622 (w), 578 (m). Anal. found (calc. for $C_{28}H_{42}Cl_4N_2O_4Zr_2$): C 41.8 (42.1), H 5.0 (5.3), N 3.2 (3.5)%.

$[Zr_2(\mu\text{-NC}_6F_5)_2Cl_6(THF)_2\{Li(THF)_3\}_2]$ (4). To a solution of "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" (0.865 g, 1.64 mmol) in THF (10 cm^3) was added a solution of $H_2NC_6F_5$ (0300 g, 1.64 mmol) in THF (10 cm^3) at rt. The pale yellow mixture was stirred at rt for 10 h to give a pale yellow solution and a white solid. The reaction mixture was filtered to afford **4** as a white solid. Yield: 0.614 g (63%). ^1H NMR (C_7D_8, 500.1 MHz, 203 K): δ 4.89 (8H, br m, C_4H_8O–Zr), 3.60 (16H, br m, C_4H_8O–Li), 3.48 (8H, br m, C_4H_8O–Li), 1.35 (16H, br m, C_4H_8O–Li), 1.27 (8H, br m, C_4H_8O–Li), 0.80 (8H, br m, C_4H_8O–Zr). $^{13}C\{^1H\}$ NMR (C_7D_8, 75.5 MHz, 203 K): δ 68.1 (C_4H_8O), 25.7 (C_4H_8O). ^{19}F NMR (C_7D_8, 282.5 MHz, 203 K): δ 145.5 (4F, d, $^3J = 24.2$ Hz, *o*- or *m*-C_6F_5N), 161.21 (4F, t, $^3J = 24.2$ Hz, *o*- or *m*-C_6F_5N), 164.6 (2F, t, $^3J = 24.2$ Hz, *p*-C_6F_5N). ^7Li NMR (C_6D_6, 116.5 MHz, 298 K): δ 0.25 (fwhm = 9.39 Hz). IR (KBr plates, Nujol): 1524 (m), 1260 (m), 1098 (m), 1018 (m), 948 (w), 802 (m). Anal. found (calc. for $C_{44}H_{64}Cl_6F_{10}Li_2N_2O_4Zr_2$): C 39.0 (39.2), H 4.6 (4.8), Cl 16.5 (15.8), Li 1.4 (1.0), N 2.0 (2.3)%.

$[Zr_2Cl_4(\mu\text{-}N^tBu)_2(THF)_3]$ (5). To a solution of "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" (0.327 g, 0.62 mmol) in THF (20 cm^3) was added $^tBuNH_2$ (65 µl, 0.62 mmol) at rt. The pale yellow mixture was stirred at rt for 10 h. Removal of volatiles under reduced pressure gave a waxy pale yellow solid which was triturated with pentane (15 cm^3) and filtered to give a pale yellow powder. Extraction into toluene–THF (3 : 1, 40 cm^3) and removal of volatiles under reduced pressure afforded **5** as a pale yellow solid. Yield: 0.091 g (43%). ^1H NMR ($C_2D_2Cl_4$, 500.1 MHz, 363 K): δ 4.89 (12H, br s, C_4H_8O), 1.93 (12H, br s, C_4H_8O), 1.56 (18H, s, N^tBu). IR (KBr plates, Nujol): 1362 (m), 1218 (m), 1176 (s), 1042 (s), 972 (s), 916 (w), 894 (m), 858 (m). Anal. found (calc. for $C_{20}H_{42}Cl_4N_2O_3Zr_2$): C 34.9 (35.2), H 6.2 (6.2), N 4.0 (4.1)%. This complex decomposes slowly at high temperatures in $C_2D_2Cl_4$ so ^{13}C NMR data were not recorded.

$[Zr_2Cl_4(\mu\text{-}N^iPr)_2(THF)_3]$ (6). To a solution of "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" (0.474 g, 0.90 mmol) in THF (20 cm^3) was added $^iPrNH_2$ (77 µl, 0.90 mmol) at rt. The pale yellow mixture was stirred at rt for 16 h to give an orange solution. Removal of volatiles under reduced pressure gave a waxy orange solid which was triturated with pentane (30 cm^3) and filtered to give a sandy coloured powder. Extraction into toluene–THF (3 : 1, 40 cm^3) and removal of volatiles under reduced pressure afforded **6** as a sandy coloured solid. Yield: 0.058 g (20%). ^1H NMR ($C_2D_2Cl_4$, 500.1 MHz, 393 K): δ 4.19 (12H, br s, C_4H_8O), 1.99 (12H, br s, C_4H_8O), 1.37 (12H, br m, $CH\mathit{Me}_2$), $C\mathit{H}Me_2$ resonance not observed. IR (KBr plates, Nujol): 1261 (m), 1161 (w), 1114 (w), 1042 (m), 917 (w), 848 (m), 722 (w). Anal.: found (calc. for $C_{18}H_{38}Cl_4N_2O_3Zr_2$): C 32.6 (33.0), H 5.4 (5.8), N 4.0 (4.3)%. This complex decomposes slowly at high temperatures in $C_2D_2Cl_4$ so ^{13}C NMR data were not recorded.

$[Zr_2Cl_4(\mu\text{-}NCH_2Ph)_2(THF)_3]$ (7). To a solution of "$[Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2]$" (0.474 g, 0.90 mmol) in THF (20 cm^3) was added $PhCH_2NH_2$ (98 µl, 0.90 mmol) at rt. The pale yellow mixture was stirred at rt for 20 h to give a dark red/brown solution. Removal of volatiles under reduced pressure gave a dark red–brown waxy solid which was triturated with pentane (30 cm^3) and filtered to give a brown powder. Extraction into toluene–THF (3 : 1, 40 cm^3) and removal of volatiles under reduced pressure afforded **7** as a brown solid. Yield: 0.150 g (44%). ^1H NMR ($C_2D_2Cl_4$, 500.1 MHz, 353 K): δ 7.38 (10H, br m, overlapping *o*-, *m*-, *p*-C_6H_5), 3.91 (12H, br s, C_4H_8O), 1.92 (12H, br s, C_4H_8O), $C\mathit{H}_2C_6H_5$ resonance not observed. IR (KBr plates, Nujol): 1588 (w), 1299 (w), 1261 (m), 1094 (w), 1071 (w), 1041 (m), 916 (w), 850 (w), 801 (m), 699 (m). Anal. found (calc. for $C_{26}H_{38}Cl_4N_2O_3Zr_2$): C 41.1 (41.6), H 5.3 (5.1), N 3.7 (3.7)%. This complex decomposes slowly at high temperatures in $C_2D_2Cl_4$ so ^{13}C NMR data were not recorded.

"$[Zr_2Cl_4(\mu\text{-}N\text{-}2,6\text{-}C_6H_3{}^iPr_2)_2(NHMe_2)_x(THF)_y]$" (8). To a stirred suspension of $[ZrCl_2(NMe_2)_2(THF)_2]$ (0.209 g, 0.53 mmol) in pentane (20 cm^3) was added H_2N-2,6-$C_6H_3{}^iPr_2$ (100 µl, 0.53 mmol) at rt. The pale yellow–green suspension became deep yellow almost instantly. The suspension was stirred at rt for 1 h and filtered to afford **8** as a lemon coloured powder which was dried under reduced pressure. Yield 0.132 g. A meaningful percentage yield cannot be calculated since the formula weight is uncertain. Elemental analysis was not consistent with a meaningful formula. The ^1H NMR spectrum of isolated **8** was extremely broad and an assignment was not possible. Therefore, ^1H and ^{13}C NMR data are reported for the complex prepared *in situ* in an NMR tube without removal of volatiles. ^1H NMR (C_6D_6, 500.1 MHz, 293 K): δ 7.21 (4H, d, $^3J = 7.6$ Hz, *m*-$NC_6\mathit{H}_3{}^iPr_2$), 6.95 (2H, t, $^3J = 7.6$ Hz, *p*-$NC_6\mathit{H}_3{}^iPr_2$), 4.78 (4H, sept., $^3J = 7.1$ Hz, $ArC\mathit{H}Me_2$), 3.61 (16H, m, $OC\mathit{H}_2CH_2$) 2.11 (24H, br s, $HN\mathit{Me}_2$), 1.53 (24H, d, $^3J = 7.1$ Hz, $ArCH\mathit{Me}_2$), 1.30 (16H, m, $OCH_2C\mathit{H}_2$). Resonance for $\mathit{H}NMe_2$ not observed. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 293 K): δ 151.9 (*i*-$N\mathit{C}_6H_3{}^iPr_2$), 143.4 (*o*-$N\mathit{C}_6H_3{}^iPr_2$), 122.4 (*m*-$N\mathit{C}_6H_3{}^iPr_2$), 120.3 (*p*-$N\mathit{C}_6H_3{}^iPr_2$), 68.8 ($O\mathit{C}H_2CH_2$), 40.2 ($HN\mathit{Me}_2$), 27.8 ($Ar\mathit{C}HMe_2$), 25.5 ($OCH_2\mathit{C}H_2$) 24.6 ($ArCH\mathit{Me}_2$). IR (KBr plates, Nujol): 3254 (w), 3230 (w), 3148 (w), 1422 (m), 1356 (w), 1334 (m), 1282 (w), 1102 (w), 1016 (w), 992 (w), 944 (w), 756 (w). Anal. found C 48.3 H 7.0, N 5.1%.

$[Zr_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4(NHMe_2)_2(THF)_2]$ (9). To a stirred suspension of $[ZrCl_2(NMe_2)_2(THF)_2]$ (0.224 g, 0.57 mmol) in pentane (20 cm^3) was added H_2N-2,6-$C_6H_3Me_2$ (70 µl, 0.57 mmol) at rt. The pale yellow–green suspension became deep yellow almost instantly. The suspension was stirred at rt for 1 h and filtered to afford **9** as a dark yellow powder which was dried under reduced pressure. Yield: 0.178 g (79%). Diffraction-quality crystals were grown by slow diffusion of pentane into a toluene solution of **9** at rt. ^1H NMR (C_6D_6, 300.1 MHz, 293 K): δ 6.98 (4H, d, $^3J = 7.9$ Hz, *meta*-$NC_6\mathit{H}_3Me_2$), 6.73 (2H, t, $^3J = 7.9$ Hz, *para*-$NC_6\mathit{H}_3Me_2$), 3.70 (8H, app. t, app. $^3J = 6.6$ Hz, C_4H_8O), 3.18 (12H, s, $NC_6H_3\mathit{Me}_2$), 1.76 (12H, s, $HN\mathit{Me}_2$), 0.96 (8H, m, C_4H_8O), resonance for $\mathit{H}NMe_2$ not observed. $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 293 K): δ 151.8 (*ipso*-$N\mathit{C}_6H_3Me_2$), 130.1 (*meta*-$N\mathit{C}_6H_3Me_2$), 128.6 (*ortho*-$N\mathit{C}_6H_3Me_2$), 122.1 (*para*-$N\mathit{C}_6H_3Me_2$), 73.4 (C_4H_8O) 38.9 ($HN\mathit{Me}_2$), 25.2 (C_4H_8O), 22.3 ($NC_6H_3\mathit{Me}_2$). Mass spectrum (EI$^+$, *m*/*z*): 561 $[M - 2THF - 2HNMe_2]^+$ 5%. IR (KBr plates, Nujol): 3278 (w), 1580 (w), 1402 (w), 1252 (m), 1196 (s), 1102 (m), 996 (m), 888 (m), 570 (m), 496 (m) cm^{-1}. Anal. found (calc. for $C_{28}H_{48}Cl_4N_4O_2Zr_2$): C 39.8 (42.2), H 6.1 (6.1), N 7.6 (7.0)%. Recrystallisations did not lead to an improved %C figure for this crystallographically characterised compound.

$[Zr_2Cl_4(\mu\text{-}NPh)_2(HNMe_2)_3(THF)]$ (10). To a stirred suspension of $[ZrCl_2(NMe_2)_2(THF)_2]$ (0.217 g 0.55 mmol) in pentane (20 cm^3) was added H_2NPh (50 µl, 0.55 mmol) at rt. Shortly after addition, the pale yellow–green suspension became pale yellow. The suspension was stirred at rt for 2 h and filtered to afford **10** as a pale yellow powder which was dried under reduced pressure. Yield: 0.162 g (83%). ^1H NMR (C_6D_6, 300.1 MHz, 293 K): δ 7.24 (8H, app. d, app. $^3J = 4.1$ Hz, overlapping *ortho* and *meta*-$NC_6\mathit{H}_5$), 6.80 (2H, app. quin., app. $^3J = 4.1$ Hz, *para*-$NC_6\mathit{H}_5$), 3.63 (4H, app. t, app. $^3J = 6.3$ Hz, C_4H_8O), 2.44 (18H, br s, $HN\mathit{Me}_2$), 1.18 (4H, br s, C_4H_8O), resonance for $\mathit{H}NMe_2$ not observed. ^1H NMR (toluene-d_8, 300.1 MHz, 223 K): δ 7.4 – 7.2 (8H, m, *ortho* and *meta*-$NC_6\mathit{H}_5$), 6.9–6.7 (2H, m, *para*-$NC_6\mathit{H}_5$), 3.58 (4H, m, C_4H_8O), 3.37 (1H, sept., $^3J = 5.9$ Hz, $\mathit{H}NMe_2$), 2.70 (6H, d, $^3J = 5.9$ Hz, $HN\mathit{Me}_2$), 2.48 (1H, sept., $^3J = 5.9$ Hz, $\mathit{H}NMe_2$), 2.17 (6H, d, $^3J = 5.9$ Hz, $HN\mathit{Me}_2$) 1.90 (1H, sept., $^3J = 5.9$ Hz, $\mathit{H}NMe_2$), 1.61 (6H, d, $^3J = 5.9$ Hz, $HN\mathit{Me}_2$), 1.38 (2H, m, C_4H_8O), 0.69 (2H, m, C_4H_8O). IR (KBr plates, Nujol): 3250 (w), 1582 (s), 1470 (s), 1228 (s), 1170 (m), 1068 (w), 1000 (m), 888 (s), 832 (m), 756 (s), 698 (m), 612 (w), 578 (s), 500 (m), 472 (w), 448 (w). Anal. found (calc. for $C_{22}H_{39}Cl_4N_5OZr_2$): C 36.0 (37.0), H 5.5 (5.5), N 9.8 (9.8)%. Recrystallisations did not lead to an improved %C figure.

[Zr$_2$Cl$_4$(μ-NC$_6$F$_5$)$_2$(HNMe$_2$)$_3$(THF)] (11). To a stirred suspension of [ZrCl$_2$(NMe$_2$)$_2$(THF)$_2$] (0.209 g, 0.53 mmol) in pentane (20 cm^3) was added a solution of H$_2$NC$_6$F$_5$ (0.097 g, 0.53 mmol) in pentane (10 cm^3) at rt. Following addition, the mixture became slightly darker. The suspension was stirred at rt for 2 h and filtered to afford **11** as an off-white powder which was dried under reduced pressure. Yield: 0.160 g (68%). ^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 293 K): δ 3.59 (4H, app. t, C$_4$H$_8$O), 2.8–1.8 (18H, 2 br s, HNMe_2), 1.24 (4H, br s, C$_4$H$_8$O), resonance for HNMe$_2$ not observed. ^{19}F NMR (C$_6$D$_6$, 252.2 MHz, 293 K): δ −162.45 (4F, dd, ^3J = 16.6 Hz, ^4J = 7.6 Hz, *ortho*-NC$_6F_5$), −165.00 (4F, dd, ^3J(*ortho-meta*) = 16.6 Hz, ^3J(*meta-para*) = 22.7 Hz, *meta*-NC$_6F_5$), −173.65 (2F, tt, ^3J = 22.7 Hz, ^4J = 7.6 Hz, *para*-NC$_6F_5$). ^{1}H NMR (C$_7$D$_8$, 300.1 MHz, 203 K): δ 3.73 (2H, br s, (HNMe$_2$)$_2$Zr), 3.44 (4H, br s, C$_4$H$_8$O), 2.61 (12H, app. t, (HNMe_2)$_2$Zr), 1.92 (1H, m, (HNMe$_2$)(THF)Zr), 1.41 (6H, d, ^3J = 5.9 Hz, (HNMe_2)(THF)Zr), 0.56 (4H, br s, C$_4$H$_8$O). ^{19}F NMR (C$_7$D$_8$, 252.2 MHz, 203 K): δ −150.68 (2F, app. d, app. ^3J = 22.7 Hz, *ortho*-NC$_6F_5$), −151.43 (2F, app. d, app. ^3J = 22.7 Hz, *ortho*-NC$_6F_5$), −164.15 (2F, app. t, app. ^3J = 22.7 Hz, *meta*-NC$_6F_5$), −164.76 (2F, app. t, app. ^3J = 22.7 Hz, *meta*-NC$_6F_5$), −167.80 (1F, app. t, app. ^3J = 22.7 Hz, *para*-NC$_6F_5$), −169.08 (1F, app. t, app. ^3J = 22.7 Hz, *para*-NC$_6F_5$). IR (KBr plates, Nujol): 3320 (w), 3302 (w), 3264 (w), 2664 (w), 2422 (w), 1644 (w), 1622 (w), 1586 (w), 1494 (s), 1444 (s), 1298 (m), 1248 (w), 1210 (w), 1158 (s), 1124 (w), 1108 (w), 1016 (s), 1000 (s), 978 (s), 928 (w), 850 (w), 780 (w), 676 (w), 652 (m), 532 (w). Anal. found (calc. for C$_{22}$H$_{29}$Cl$_4$F$_{10}$N$_5$OZr$_2$): C 29.2 (29.6), H, 3.7 (3.3), N 7.8 (7.8)%.

[Zr$_2$Cl$_4$(μ-N^{t}Bu)$_2$(HNMe$_2$)$_3$] (12). To a stirred suspension of [ZrCl$_2$(NMe$_2$)$_2$(THF)$_2$] (0.334 g, 0.85 mmol) in pentane (20 cm^3) was added H$_2$N^{t}Bu (89 μl, 0.85 mmol) at rt. The suspension was stirred for 3 d at rt, during which time the mixture became milky white. The reaction mixture was filtered to afford **12** as a white powder which was dried under reduced pressure. Yield: 0.162 g (64%). Diffraction-quality crystals were grown from a pentane solution at rt. ^{1}H NMR (C$_7$D$_8$, 300.1 MHz, 293 K): δ 3.42 (2H, sept., ^3J = 5.9 Hz, (Me$_2$NH)$_2$Zr), 2.75 (12H, d, ^3J = 5.9 Hz, (Me_2NH)$_2$Zr), 1.95 (6H, br s, (Me_2NH)Zr), 1.49 (18H, s, N^tBu), resonance for (Me$_2$NH)Zr not observed. ^{1}H NMR (C$_7$D$_8$, 300.1 MHz, 243 K): δ 3.39 (2H, sept., ^3J = 5.9 Hz, (Me$_2$NH)$_2$Zr), 2.70 (12H, d, ^3J = 5.9 Hz, (Me_2NH)$_2$Zr), 1.99 (1H, sept., ^3J = 5.9 Hz, (Me$_2$NH)Zr), 1.82 (6H, d, ^3J = 5.9 Hz, (Me_2NH)Zr), 1.50 (18H, s, N^tBu). ^{13}C{^{1}H} NMR (C$_7$D$_8$, 75.5 MHz, 243 K): δ 63.1 (NCMe$_3$), 42.2 ((Me_2NH)$_2$Zr), 38.5 ((Me_2NH)Zr), 31.3 (NCMe_3). IR (KBr plates, Nujol): 3280 (w), 1466 (s), 1354 (m), 1250 (w), 1220 (w), 1176 (s), 1108 (w), 1016 (m), 992 (s), 956 (s), 884 (s), 778 (w), 644 (s), 498 (w). Anal.: found (calc. for C$_{14}$H$_{39}$Cl$_4$N$_5$Zr$_2$): C 27.1 (27.9), H 6.5 (6.5), N 11.0 (11.6)%. Recrystallisations did not lead to improved %C or N figures for this crystallographically characterised compound.

[Zr(N^{i}Pr)Cl$_2$(NHMe$_2$)]$_x$ (13). To a stirred suspension of [ZrCl$_2$(NMe$_2$)$_2$(THF)$_2$] (0.250 g, 0.63 mmol) in pentane (20 cm^3) was added H$_2$N^{i}Pr (54 μl, 0.63 mmol) at rt. The suspension was stirred for 15 h at rt. The reaction mixture was filtered to afford **13** as a white powder which was dried under reduced pressure. Yield: 0.162 g (64%). The product was insoluble in all standard (non-coordinating) solvents and NMR data could not be obtained. IR (KBr plates, Nujol): 3180 (s), 1260 (w), 1158 (w), 1112 (m), 1022 (w), 982 (w), 894 (m), 802 (w). Anal.: found (calc. for {C$_5$H$_{14}$Cl$_2$N$_2$Zr}$_x$): C 22.6 (22.7), H 6.5 (5.3), N 11.4 (10.6)%.

[ZrCl$_2$(NCH$_2$Ph)(HNMe$_2$)]$_x$ (14). To a stirred suspension of [ZrCl$_2$(NMe$_2$)$_2$(THF)$_2$] (0.250 g, 0.63 mmol) in pentane (25 cm^3) was added H$_2$NCH$_2$Ph (69 μl, 0.63 mmol) at rt. The suspension was stirred for 5 h at rt and filtered to afford **14** as a white powder which was dried under reduced pressure. Yield: 0.103 g (52%). The product was insoluble in all standard (non-coordinating) solvents and NMR data could not be obtained. IR (KBr plates, Nujol): 3194 (s), 1600 (w), 1344 (w), 1260 (w), 1112 (w), 1046 (s), 1026 (s), 888 (s), 804 (w), 698 (s). Anal. found (calc. for {C$_9$H$_{14}$Cl$_2$N$_2$Zr}$_x$): C 33.7 (34.6), H 5.4 (4.5), N 9.4 (9.0)%.

[Zr$_2$(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$Cl$_4$(py)$_4$] (15). [Zr$_2$(μ-N-2,6-C$_6$H$_3$-Me$_2$)$_2$Cl$_4$(THF)$_4$] (**2**, 1.490 g, 1.75 mmol) was slurried into CH$_2$Cl$_2$ (40 cm^3) and pyridine (30 cm^3) was added. The resulting yellow solution was stirred at rt for 16 h and concentrated under reduced pressure to a volume of 40 cm^3, giving an orange solution and a bright yellow precipitate. Filtration yielded **15** as a yellow powder which was washed with CH$_2$Cl$_2$ (2 × 10 cm^3) and dried under reduced pressure Yield: 0.562 g (35%). Diffraction-quality crystals were grown by layering a CH$_2$Cl$_2$ solution of **15** (containing a few drops of pyridine to solubilise the compound) with pentane at room temperature. ^{1}H NMR (CDCl$_3$, 500.1 MHz, 298 K): δ 8.42 (8 H, br s, *o*-NC$_5$H$_5$), 7.58 (4 H, br t, ^3J = 6.83, *p*-NC$_5$H$_5$), 7.03 (8 H, br m, *m*-NC$_5$H$_5$), 6.69 (4 H, d, ^3J = 7.32 *m*-C$_6H_3$Me$_2$), 6.56 (2 H, t, ^3J = 7.32, *p*-C$_6H_3$Me$_2$), 2.59 (12 H, s, C$_6$H$_3$$Me_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.5 MHz, 298 K): δ 150.4 (overlapping *o*-C_6H$_3$Me$_2$ and *o*-NC$_5$H$_5$), 137.0 (*p*-NC$_5$H$_5$), 132.5 (*i*-C_6H$_3$Me$_2$), 127.8 (*m*-C_6H$_3$Me$_2$), 123.26 (*m*-NC$_5$H$_5$), 121.9 (*p*-C_6H$_3$Me$_2$), 21.2 (C$_6$H$_3$$Me_2$). IR (CH$_2Cl_2$, cm^{-1}): 3944 (w), 3756 (w), 3728 (w), 3692 (w), 3066 (s), 3048 (s), 2986 (s), 2830 (w), 2686 (m), 2522 (w), 2410 (w), 2304 (s), 2156 (w), 2126 (w), 2054 (w), 1970 (w), 1604 (w), 1550 (w), 1422 (s, br), 1284 (s), 1268 (s), 1250 (s), 1200 (s), 1156 (m), 1100 (w), 1064 (w), 1082 (w), 1008 (w), 986 (w), 822 (s), 788 (s), 754 (s), 744 (s), 742 (s), 682 (s), 576 (m), 538 (m), 526 (m), 508 (s), 498 (s), 478 (s), 416 (s). EIMS: m/z 280 [1/2M − py − Cl]$^+$. Anal. found (calc. for C$_{36}$H$_{38}$Cl$_4$N$_6$Zr$_2$·0.3CH$_2$Cl$_2$): C 48.1 (48.2), H 4.4 (4.3), N 9.5 (9.3)%.

[Zr$_2$(μ-N^{t}Bu)$_2$Cl$_4$(py)$_3$] (16). To a slurry of [Zr$_2$(μ-N^{t}Bu)$_2$Cl$_4$(THF)$_3$] (**5**, 1.512 g, 2.21 mmol) in CH$_2$Cl$_2$ (30 cm^3) was added pyridine (40 cm^3) to give a yellow solution which was stirred at rt for 16 h. Volatiles were removed under reduced pressure and the resulting yellow oil was triturated with pentane (40 cm^3) and filtered to yield **16** as a yellow solid. Yield: 0.928 g (60%). ^{1}H NMR (CDCl$_3$, 500.1 MHz, 298 K): δ 9.67 (2 H, br s, *o*-C$_5$H$_5$N), 8.69 (4 H, br s, *o*-C$_5$H$_5$N), 7.89 (1 H, br m, *p*-C$_5$H$_5$N), 7.67 (2 H, m, br m, *p*-C$_5$H$_5$N), 7.50 (2 H, br m, *m*-C$_5$H$_5$N), 7.29 (4 H, br m, *m*-C$_5$H$_5$N), 1.48 (18 H, s, ^{t}Bu). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.5 MHz, 298 K): δ 152.3 (*o*-C$_5$H$_5$N), 150.1 (*o*-C$_5$H$_5$N), 139.3 (*p*-C$_5$H$_5$N), 136.5 (*p*-C$_5$H$_5$N), 124.1 (*m*-C$_5$H$_5$N), 123.8 (*m*-C$_5$H$_5$N), 64.0 (CMe$_3$), 30.6 (CMe_3). IR (CH$_2$Cl$_2$, cm^{-1}): 3944 (m), 3758 (w), 3726 (w), 3962 (w), 3060 (s), 3048 (s), 2982 (s), 2830 (w), 2696 (m), 2522 (w), 2410 (w), 2304 (s), 2156 (w), 2126 (w), 2054 (w), 1970 (w), 1608 (w), 1582 (w), 1550 (w), 1426 (s), 1284 (s), 1276 (s), 1250 (s), 1156 (m), 1102 (w), 1104 (w), 1070 (w), 1030 (w), 1012 (w), 1104 (w), 1070 (w), 1030 (w), 1012 (w), 992 (w), 958 (w), 892 (s), 784 (s), 740 (s), 716 (s), 700 (s), 680 (s), 666 (s), 586 (m), 570 (m), 554 (m), 520 (s), 490 (s), 466 (s), 456 (s), 440 (s), 424 (s). Anal. found (calc. for C$_{23}$H$_{33}$Cl$_4$N$_5$Zr$_2$·0.5C$_5$H$_{12}$): C, 41.5 (41.4); H 4.7 (5.3); N, 9.6 (9.5)%.

Crystal structure determinations of [Zr$_2$(μ-N-2,6-C$_6$H$_3$^{i}Pr$_2$)$_2$Cl$_4$(THF)$_4$] (1), [Zr$_2$(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$Cl$_4$(THF)$_4$] (2), [Zr$_2$(μ-NC$_6$F$_5$)$_2$Cl$_6$(THF)$_2${Li(THF)$_3$}$_2$] (4), [Zr$_2$(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$Cl$_4$(NHMe$_2$)$_2$(THF)$_2$] (9), [Zr$_2$(μ-N^{t}Bu)$_2$Cl$_4$(NHMe$_2$)$_3$] (12) and [Zr$_2$(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$Cl$_4$(py)$_4$] (15)

Crystal data collection and processing parameters are given in Table 6. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Enraf-Nonius

Table 6 X-ray data collection and processing parameters for $[Zr_2(\mu\text{-N-2,6-}C_6H_3{}^iPr_2)_2Cl_4(THF)_4]$ (**1**), $[Zr_2(\mu\text{-N-2,6-}C_6H_3Me_2)_2Cl_4(THF)_4]$ (**2**), $[Zr_2(\mu\text{-}NC_6F_5)_2Cl_6(THF)_2\{Li(THF)_3\}_2]$ (**4**), $[Zr_2(\mu\text{-N-2,6-}C_6H_3Me_2)_2Cl_4(NHMe_2)_2(THF)_2]$ (**9**), $[Zr_2(\mu\text{-N}{}^tBu)_2Cl_4(NHMe_2)_3]$ (**12**) and $[Zr_2(\mu\text{-N-2,6-}C_6H_3Me_2)_2Cl_4(py)_4]$ (**15**)

	1	**2**	**4**	**9**	**12**	**15**
Formula	$C_{40}H_{66}Cl_4N_2O_4Zr_2$	$C_{32}H_{50}Cl_4N_2O_4Zr_2$	$C_{44}H_{64}Cl_6F_{10}Li_2N_2O_8Zr_2$	$C_{28}H_{48}Cl_4N_4O_2Zr_2$	$C_{14}H_{39}Cl_4N_5Zr_2$	$C_{36}H_{38}Cl_4N_6Zr_2$
Formula weight	963.22	851.00	1348.02	796.97	601.75	878.99
Crystal system	Monoclinic	Orthorhombic	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/n$	$Cmca$	$P\bar{1}$	$Pca2_1$	$P\bar{1}$	$P2_1/n$
a/Å	11.1206(4)	12.7820(3)	10.3615(2)	9.4672(1)	10.0181(1)	12.2186(1)
b/Å	15.9555(6)	17.5806(5)	11.7620(2)	17.0837(3)	10.0274(1)	12.4098(2)
c/Å	12.6383(5)	15.5901(4)	11.9942(2)	21.1400(3)	14.3986(2)	12.2628(2)
α/°	—	—	93.973(1)	—	97.5478(6)	—
β/°	93.200(2)	—	97.234(1)	—	101.1935(6)	105.0415(7)
γ/°	—	—	106.1726(8)	—	110.7356(6)	—
V/Å^3	2239.0(1)	1722.4(1)	1384.35(4)	3419.1(1)	1295.05(3)	1795.70(4)
Z	2	4	1	4	2	2
μ/mm^{-1}	0.74	0.92	11874	14507	1.23	0.914
Total reflections	8483	4063	0.749	0.95	11080	7336
R^a	0.0644	0.0271,	0.0350	0.0231	0.0194	0.0232
$R_w{}^a$ $[I > 3\sigma(I)]$	0.0487	0.0326	0.0278	0.0267	0.0093	0.0253

^{a} $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $R_w = \sqrt{\{\sum w(|F_o| - |F_c|)2/\sum(w|F_o|2\}}$.

Kappa-CCD diffractometer equipped with an Oxford Cryosystems low-temperature device. Data were collected at low temperature using Mo-Kα radiation; equivalent reflections were merged and the images were processed with the DENZO and SCALEPACK programs.[28] Corrections for Lorentz-polarisation effects and absorption were performed and the structures were solved by direct methods using SIR92.[29] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were placed geometrically (N–H = 0.87 Å; C–H = 1.0 Å. Extinction corrections were applied as required.[30] Crystallographic calculations were performed using SIR92 and CRYSTALS.[31]

Molecules of $[Zr_2(\mu\text{-N-2,6-}C_6H_3{}^iPr_2)_2Cl_4(THF)_4]$ (**1**) lie across crystallographic inversion centres. Both of the unique THF molecules were disordered over two sites with equal chemical occupancies. The disorder was modelled satisfactorily and the non-H atoms of these ligands were positionally and isotropically refined subject to vibrational restraints, and similarity restraints on the O–C and C–C distances and associated internal ring angles.

Molecules of $[Zr(N\text{-2,6-}C_6H_3Me_2)_2Cl_4(THF)_4]$ (**2**) lie across crystallographic $2/m$ symmetry sites with the $Zr_2N_2O_4$ coordination cores lying on the mirror planes and perpendicular twofold axes bisecting the Zr···Zr vectors. The THF molecules were disordered over two sites with equal chemical occupancies, and this disorder was modelled satisfactorily.

CCDC reference numbers 260433–260438.

See http://www.rsc.org/suppdata/dt/b5/b500507h/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the EPSRC, DSM Research and Millennium Pharmaceuticals for support.

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