DALTON
FULL PAPER

Synthesis, structures and catalytic properties of chelating *N*,*N*′-bis(silylated) 1,2-benzenediamidozirconium(IV) chlorides [and a titanium(IV) analogue] and dimethylamides†

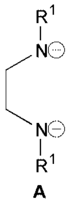
Stephane Danièle, Peter B. Hitchcock, Michael F. Lappert* and Philippe G. Merle

The Chemistry Laboratory, University of Sussex, Brighton, UK BN1 9QJ.
E-mail: m.f.lappert@sussex.ac.uk

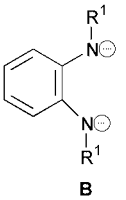
Received 11th August 2000, Accepted 3rd November 2000
First published as an Advance Article on the web 5th December 2000

Chelating diamido ligands of formula $[C_6H_4\{N(SiMe_2X)\}_2\text{-}1,2]^{2-}$, abbreviated as L'^{2-} ($X = CH{=}CH_2$) or L^{2-} ($X = Me$), were used to prepare di(amido)metal(IV) chlorides $[\{M(Cl)L'(\mu\text{-}Cl)(thf)\}_2]$ (M = Zr **2** or Ti **3**), $ZrCl_2(L')$ **5** and $[ZrCl_2(L)(tmen)]$ **6** and the heteroleptic amides $[\{Zr(NMe_2)(L^x)(\mu\text{-}NMe_2)\}_2]$ ($L^x = L'$ **4** or L **7**). Complexes **2** and **3** were obtained from equivalent proportions of Li_2L' (prepared *in situ* from H_2L' **1**) and the appropriate metal chloride $[MCl_4(thf)_2]$, while $[Li_2(L)(tmen)_2]$ and $ZrCl_4$ furnished **6**. Treatment of $Zr(NMe_2)_4$ with an equivalent portion of H_2L' or H_2L gave **4** and **7**, respectively. Complex **5** was obtained from **4** and $Si(Cl)Me_3$, and with thf yielded **2**. The crystal structures of **2**, **4**, **6** and **7** have been determined. Compounds **2** and **4**–**6**, unlike the less active titanium complex **3**, were active catalysts with methylaluminoxane $(AlMeO)_n$ for polymerisation of ethene and the resulting polymers were shown to have extremely high average molecular weights, as determined by viscosity measurements.

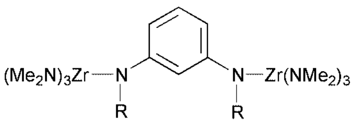
We have a long-standing interest in the chemistry of metal and non-metal amides,[1] including those of the Group 4 metals; for example, $[Ti(NMe_2)_4]$ was examined as an initiator of acrylonitrile polymerisation.[2] As an extension, we are exploring some aspects of the chemistry of complexes derived from diamido ligands. The first studies involved ligands such as **A** (R^1 = a primary alkyl or an unhindered aryl group), mainly in the context of derived carbene ligands $\overline{CN(R^1)(CH_2)_2N}R^1$.[3] The ligand **B** ($R^1 = SiMe_3 = R$; [$\equiv L^{2-}$]) was used to generate the compounds $[Mg(L)]_2$,[4] $[(SnL)_2(\mu\text{-tmen})]$[5] and Ge(L).[6] The related ligand **B**′ ($\equiv$ **B** with $R^1 = CH_2Bu^t$) having *N*,*N*′-neopentyl, rather than $SiMe_3$, substituents became prominent with the discovery of the thermally stable silylene Si**B**′;[7] isoleptic Group 14 element compounds E**B**′ (E = C, Ge, Sn or Pb) as well as their adducts C**B**′·E′**B**′ (E′ = Si, Ge, Sn or Pb) have also been obtained.[8] The 1,3 and 1,4 isomers of L^{2-} are being investigated; relevant to the present study are the zirconium(IV) complexes **C** and **D** and their 1,4 isomers.[9]



A

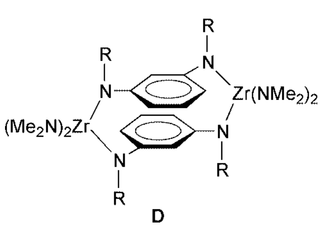


B



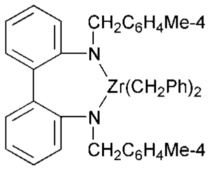
C

L^{2-} ($R^1 = SiMe_3 = R$)
L'^{2-} ($R^1 = SiMe_2Vi$)
B″ ($R^1 = SiPr^i_3$)

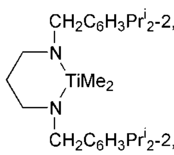


D

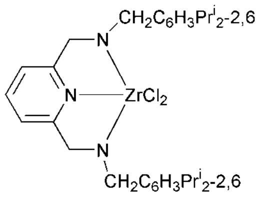
A recent review on new olefin polymerisation catalysts identified various types of spectator ligands, other than those of cyclopentadienyl type, many of which are nitrogen-centred.[10] In the context of the present paper, Group 4 metal complexes containing diamido ligands without (as in **E**[11] or **F**[12]) or with (as in **G**[13]) an additional donor site have been prominent (see also refs. 14–16), and several of them have been active polymerisation catalysts.[11–14] For example, **E**[11] or **G**[13] with methylaluminoxane $(AlMeO)_n$ (MAO) was a catalyst for both ethene and propene polymerisation, while **F** with $B(C_6F_5)_3$ induced the living polymerisation of hex-1-ene.[12]



E



F



G

A ligand **B**″ of type **B** ($R^1 = SiPr^i_3$) has featured in the complexes $[Ti(\mathbf{B}'')X_2]$ (X = Cl or Me) and $[Zr(\mathbf{B}'')X_2]$ ($X = OBu^t$, or $X_2 = \mathbf{B}''$),[16] while a ligand $[L'']^{2-}$ related to ligand L^{2-} has been a component of the complexes $[M(L'')\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}(\eta^3\text{-}C_3H_5)]$ {M = Zr or Hf; $[L'']^{2-} = [N(Ph)C(Me){=}C(Me)NPh]^{2-}$}.[17] The L^{2-} ligand has also been employed in the chemistry of Ta^V,[17] Mo^{VI},[18] and W^{VI}.[19]

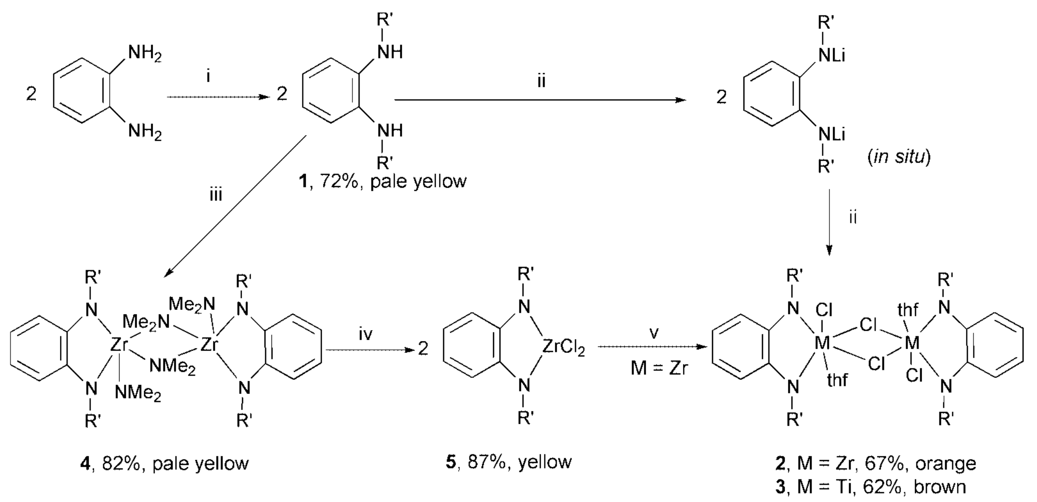
Results and discussion

Our initial aim was to obtain new chelated bis(amido)-zirconium(IV) and -titanium(IV) complexes, with a view to

---

† *In memoriam* Ron Snaith.

DOI: 10.1039/b006596j



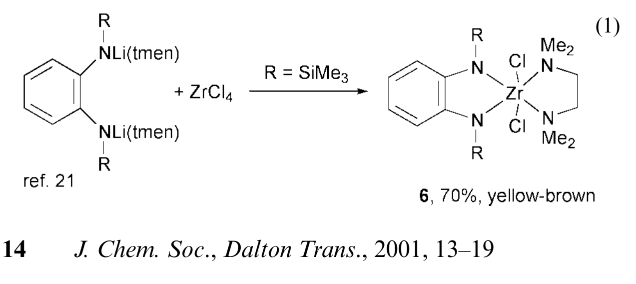
Scheme 1 Synthesis of compounds **1**–**5** (R′ = $SiMe_2Vi$). *Reagents*: i, successively $2LiBu^n$ and $2Si(Cl)Me_2Vi$; ii, successively $2LiBu^n$ and $[MCl_4(thf)_2]$; iii, $2Zr(NMe_2)_4$; iv, $4Si(Cl)Me_3$; v, thf (M = Zr, 100%).

employing them as procatalysts for alkene polymerisation. For this purpose, we first selected a ligand of type **B** ($[C_6H_4\text{-}(N\{SiMe_2(CH{=}CH_2)\})_2\text{-}1,2]^{2-} \equiv [L']^{2-}$), with R^1 chosen as a dimethylvinylsilyl group. The presence of a pendant vinyl (Vi) group was considered to have the potential to protect a zirconium atom site but readily be displaceable by an incoming untethered alkene. This strategy had been effective for hydrosilylation of terminal alkenes using various vinyl-silane- or -siloxy-rhodium(I), -nickel(0) and -platinum(0) catalysts.[20]

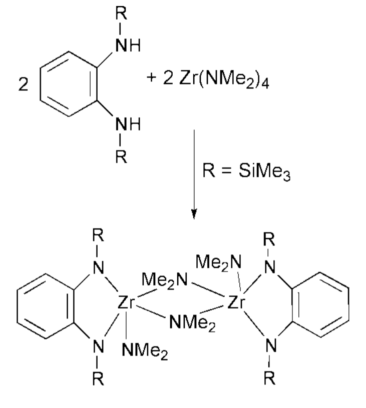
The syntheses in good yield of a number of L'^{2-} complexes of Ti^{IV} and Zr^{IV} are summarised in Scheme 1. 1,2-Bis[dimethylvinylsilylamino]benzene **1** was obtained (step i of Scheme 1) from 1,2-diaminobenzene by successive *N*,*N*′-dilithiation and quenching with the chlorosilane $Si(Cl)Me_2Vi$. The diamine **1** was converted (step ii of Scheme 1) into each of the binuclear complexes $[\{M(Cl)L'(\mu\text{-}Cl)(thf)\}_2]$ (M = Zr **2** or Ti **3**) by treatment successively with $2LiBu^n$ and the appropriate complex $[MCl_4(thf)_2]$. The diamine **1** with tetrakis(dimethylamido)zirconium gave (step iii of Scheme 1) the binuclear heteroleptic zirconium(IV) amide $[\{Zr(NMe_2)L'(\mu\text{-}NMe_2)\}_2]$ **4**, which in turn was transformed (step iv of Scheme 1) into the neutral donor-free zirconium(IV) chloride $ZrCl_2(L')$ **5**, by reaction with (chloro)trimethylsilane. Complex **5** with tetrahydrofuran provided (step v of Scheme 1) an alternative route to the dinuclear thf adduct **2**.

Attempts to make complex **5** directly from zirconium(IV) chloride and Li_2L' in toluene yielded a product which from microanalytical data was assigned as being a mixture of ZrL'_2 and $ZrCl_2(L')$ in a ratio of 0.6 : 1. This observation is consistent with the finding that $ZrCl_4$ and $Li_2(\mathbf{B}'')$ in benzene, irrespective of stoichiometry, had yielded $[Zr(\mathbf{B}'')_2]$.[16]

A further set of experiments relating to **B**-type zirconium(IV) complexes was undertaken using the ligand ($[C_6H_4(NSiMe_3)_2\text{-}1,2]^{2-} \equiv L^{2-}$). Thus, the crystalline diamidodilithium compound $[Li_2(L)(tmen)_2]$[21] with an equivalent portion of zirconium(IV) chloride in toluene at ambient temperature yielded the mononuclear zirconium(IV) chloride **6**, eqn. (1). By a procedure similar to that of step iii of Scheme 1 for the preparation of the amide **4**, its isoleptic analogue $[\{Zr(NMe_2)L(\mu\text{-}NMe_2)\}_2]$ **7** was obtained from $Zr(NMe_2)_4$ and H_2L in toluene at ambient temperature, eqn. (2).



(1)



(2)

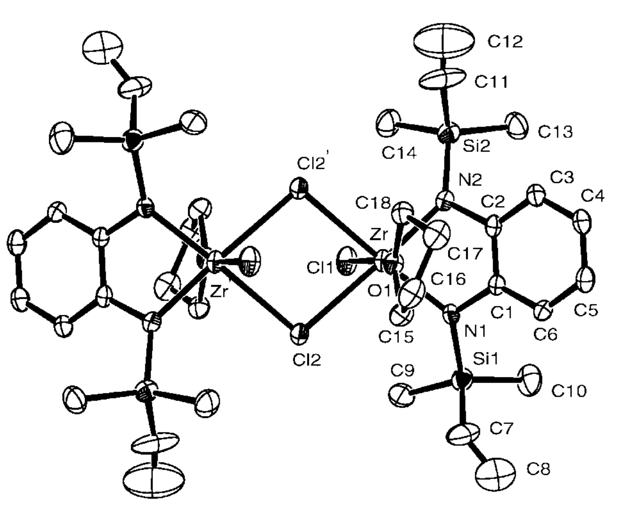


Fig. 1 Molecular structure of compound **2**.

Each of the yellow-to-brown (**2**–**6**) or colourless (**7**) crystalline metal(IV) complexes gave satisfactory microanalyses, as did the pale yellow liquid diamine **1**. The highest *m*/*z* peak in the EI mass spectrum corresponded to the monomeric molecular ion M^+ (**1**), $[M - 1]^+$ (**2**, **4** and **7**) or $[M - 2Cl]^+$ (**6**); for **5** a metal-containing fragment was not detected.

The molecular structure of the dinuclear zirconium(IV) chloride $[\{Zr(Cl)L'(\mu\text{-}Cl)(thf)\}_2]$ **2** is illustrated in Fig. 1. Selected geometric parameters are in Tables 1 and 2; the latter shows comparative data for the $ZrC_6H_4(NR^1)_2\text{-}1,2$ moiety ($R^1 = SiMe_2Vi$) of **2** and the related $Zr(\mathbf{B}'')$ of $[Zr(\mathbf{B}'')X_2]$[16] and ZrL'' of $[Zr(L'')\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}(\eta^3\text{-}C_3H_5)]$ **9** [L″ =

Table 1 Some important geometric data (bond lengths in Å, angles in °) on compound **2** (see also Table 2)

Zr···Zr′	4.078(6)			Cl(1)–Zr–Cl(2)	88.29(6)	Cl(2)–Zr–Cl(2)′	80.83(6)
Zr–Cl(1)	2.403(2)	Zr–Cl(2)	2.670(2)	N(1)–Zr–Cl(1)	101.53(14)	N(1)–Zr–Cl(2)′	167.72(13)
Zr–Cl(2)′	2.687(2)	Zr–O(1)	2.249(4)	N(1)–Zr–Cl(2)	99.37(13)	N(2)–Zr–Cl(2)′	94.26(13)
N(1)–C(1)	1.430(6)	C(1)–C(2)	1.405(8)	N(2)–Zr–Cl(1)	101.35(14)	N(1)–Zr–O(1)	87.9(2)
N(2)–C(2)	1.422(7)			N(2)–Zr–Cl(2)	169.29(13)	N(2)–Zr–O(1)	89.8(2)
N(1)–Si(1)	1.740(5)	N(2)–Si(2)	1.753(5)	Zr–Cl(2)–Zr′	99.17(6)	O(1)–Zr–Cl(2)	79.96(11)
				O(1)–Zr–Cl(1)	166.05(10)	O(1)–Zr–Cl(2)′	80.85(11)

Table 2 Some important geometric data (bond lengths in Å, angles in °) for the L^{2-}, L'^{2-}, **B**″ or L''^{2-} ligand in the compounds **2**, **4**, **6**, **7**, [Zr(**B**″)$_2$] **8**[16] and [Zr(L″){η^5-$C_5H_3(SiMe_3)_2$-1,3}(η^3-C_3H_5)] **9** [**B**″ = **B** with R^1 = $SiPr^i_3$; L″ = {N(Ph)C(Me)=C(Me)N(Ph)}][17]

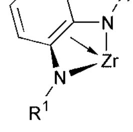
	2	**4**	**6**	**7**	**8**	**9**
Zr–N(1)	2.053(5)	2.112(4)	2.118(6)	2.1444(14)	2.072(6)	2.105(4)
Zr–N(2)	2.044(5)	2.116(4)	2.050(6)	2.0702(13)	2.087(6)	2.100(4)
N(1)–Zr–N(2)	83.4(2)	80.4(2)	82.0(2)	81.4(5)	86.1(2)	81.5(2)
Zr–N(1)–C(1)	102.9(3)	100.4(2)	100.6(4)	98.85(4)	92.8(2) 91.6(2)	92.9(3)
Zr–N(2)–C(2)	103.1(4)	100.2(3)	102.7(4)	98.64(9)	93.7(2) 94.8(2)	93.4(3)
Fold angle[a]	38	43	42	49	51 (53)	60

[a] The fold of the ligand L^{2-}, L'^{2-} or L''^{2-} along the N(1)···N(2) vector.

Table 3 Some important geometric data (bond lengths in Å, angles in °) on compound **4** (see also Table 2)

Zr(1)···Zr(2)	3.621(5)			Zr(1)–N(5)–Zr(2)	102.4(2)	Zr(1)–N(6)–Zr(2)	104.9(2)
Zr(1)–N(1)	2.112(4)	Zr(2)–N(3)	2.120(4)	N(5)–Zr(1)–N(6)	74.5(2)	N(5)–Zr(2)–N(6)	73.5(2)
Zr(1)–N(2)	2.116(4)	Zr(2)–N(4)	2.102(4)	N(1)–Zr(1)–N(2)	80.4(2)	N(3)–Zr(2)–N(4)	80.1(2)
Zr(1)–N(7)	2.021(5)	Zr(2)–N(8)	2.024(4)	N(1)–Zr(1)–N(6)	88.4(2)	N(3)–Zr(2)–N(6)	88.6(2)
Zr(1)–N(5)	2.276(4)	Zr(2)–N(5)	2.369(4)	N(2)–Zr(1)–N(5)	89.1(2)	N(4)–Zr(2)–N(5)	94.1(2)
Zr(1)–N(6)	2.304(4)	Zr(2)–N(6)	2.263(4)	N(7)–Zr(1)–N(1)	113.2(2)	N(8)–Zr(2)–N(3)	103.9(2)
N(1)–C(1)	1.409(7)	N(3)–C(15)	1.404(7)	N(7)–Zr(1)–N(2)	111.4(2)	N(8)–Zr(2)–N(4)	113.4(2)
N(2)–C(2)	1.405(7)	N(4)–C(16)	1.425(7)	N(7)–Zr(1)–N(5)	110.0(2)	N(8)–Zr(2)–N(5)	102.8(2)
N(1)–Si(1)	1.734(4)	N(2)–Si(2)	1.732(4)	N(7)–Zr(1)–N(6)	106.2(2)	N(8)–Zr(2)–N(6)	120.1(2)
N(3)–Si(3)	1.737(4)	N(4)–Si(4)	1.736(4)	N(2)–Zr(1)–N(6)	114.2(2)		
C(1)–C(2)	1.426(4)	C(15)–C(16)	1.432(4)				

{N(Ph)C(Me)=C(Me)N(Ph)}].[17] The molecule **2** lies on a crystallographic inversion centre having similar Zr–Cl(2) and Zr–Cl(2)′ bond lengths of 2.670(2) and 2.687(2) Å [compared with 2.403(2) Å for the terminal Zr–Cl(1) bond]; the endocyclic angles at the Cl atoms are wider [99.17(6)°] than those at the Zr atoms, 80.83(6)°. Each zirconium atom is at the centre of a distorted octahedron: N(1), N(2) and O(1) are *trans* to Cl(2)′, Cl(2) and Cl(1), respectively; the corresponding angles subtended at the Zr atom are 167.72(13), 169.29(13) and 166.05(10)°. The $[L']^{2-}$ ligand is folded along the N(1)···N(2) vector. Similar folding **H** (as also in that of **4**, **6** and **7**) has previously[16,17] been interpreted in terms of κ^4-bonding, which however we consider to be unlikely. The vinyl groups, as in **4**, are bent away from the Zr atoms.



H

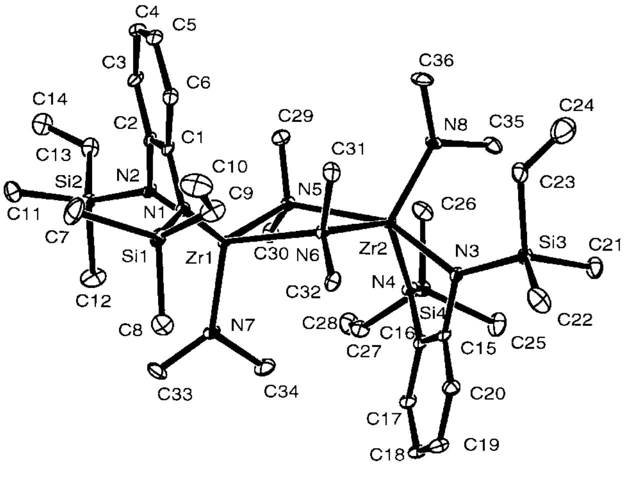


Fig. 2 Molecular structure of compound **4**.

The molecular structure of the binuclear zirconium(IV) amide [{Zr(NMe_2)L′(μ-NMe_2)}$_2$] **4** is shown in Fig. 2. Selected geometric parameters, other than those of the ZrL′ moiety (see Table 2), are listed in Table 3. The central Zr(1)N(5)Zr(2)N(6) ring is puckered; the mean Zr(1 or 2)–N(5 or 6) bond lengths range from 2.263(4) to 2.369(4) Å and the endocyclic angles at N(5) or N(6) are wider (103.5 ± 1.4°) than those at Zr(1) or Zr(2), 74.0 ± 0.5°. As for **2**, the vinyl groups in **4** are bent away from each of the five-co-ordinate Zr atoms, which are situated in an environment intermediate between trigonal bipyramidal (*TBPY*) and square pyramidal. On the basis of *TBPY*, the atoms N(1), N(5) and N(7) occupy the "equatorial" sites; the "axial" N(2) and N(6) atoms subtend an angle of 142.2(2)° at Zr(1). Angles at Zr(1) involving N(2) and N(5) or N(7) are 89.1(2) and 111.4(2)°, respectively, and those involving N(6) and N(7) or N(1) are 106.2(2) or 88.4(2)°, respectively. The Zr(2) environment is similar to that of Zr(1).

Table 4 Some important geometric data (bond lengths in Å, angles in °) on compound **7** (see also Table 2)

Zr–N(1)	2.0702(13)	Zr–N(3)	2.2528(14)	Zr–N(3)–Zr′	104.24(6)	N(3)–Zr–N(3)′	75.76(6)
Zr–N(2)	2.1444(14)	Zr–N(4)	2.0370(16)	N(1)–Zr–N(2)	81.14(5)		
N(1)–C(1)	1.419(2)	Zr–N(3)′	2.3551(14)	N(1)–Zr–N(3)	127.05(5)	N(2)–Zr–N(3)	89.75(5)
N(2)–C(2)	1.4080(19)			N(1)–Zr–N(3)′	89.22(5)	N(2)–Zr–N(3)′	152.69(5)
N(1)–Si(1)	1.7419(14)	N(2)–Si(2)	1.7358(14)	N(1)–Zr–N(4)	115.42(7)	N(2)–Zr–N(4)	106.44(6)
Zr · · · Zr′	3.638(2)	C(1)–C(2)	1.430(2)	N(4)–Zr–N(3)	117.18(7)	N(4)–Zr–N(3)′	100.78(6)

Table 5 Some important geometric data (bond lengths in Å, angles in °) on compound **6** (see also Table 2)

Zr–Cl(1)	2.537(2)	Zr–Cl(2)	2.432(2)	Cl–Zr–Cl(2)	86.41(8)		
Zr–N(1)	2.118(6)	Zr–N(3)	2.497(6)	N(1)–Zr–Cl(1)	173.01(16)	N(3)–Zr–Cl(1)	89.11(15)
Zr–N(2)	2.050(6)	Zr–N(4)	2.464(6)	N(1)–Zr–Cl(2)	95.13(17)	N(3)–Zr–Cl(2)	86.65(15)
N(1)–C(1)	1.438(9)	N(1)–Si(1)	1.753(6)	N(2)–Zr–Cl(1)	91.03(16)	N(4)–Zr–Cl(1)	83.06(15)
N(2)–C(2)	1.428(9)	N(2)–Si(2)	1.742(6)	N(2)–Zr–Cl(2)	103.37(16)	N(4)–Zr–Cl(2)	156.09(15)
C(1)–C(2)	1.412(10)			N(1)–Zr–N(2)	82.0(2)	N(2)–Zr–N(3)	165.0(2)
				N(1)–Zr–N(3)	97.8(2)	N(3)–Zr–N(4)	71.8(2)
				N(1)–Zr–N(4)	97.9(2)	N(4)–Zr–N(2)	93.3(2)

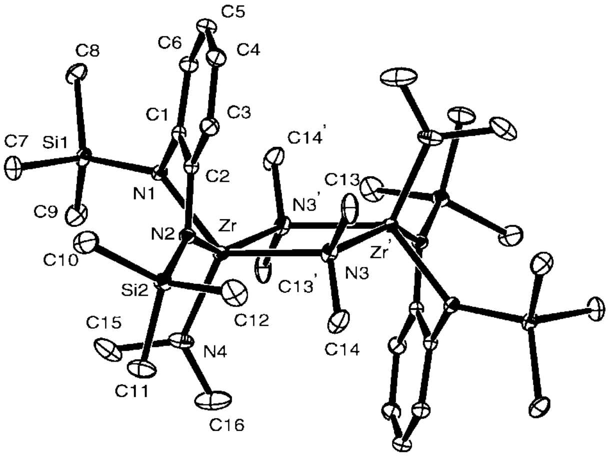


Fig. 3 Molecular structure of compound **7**.

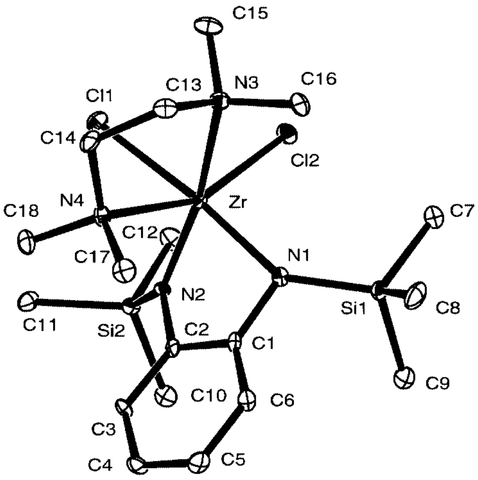


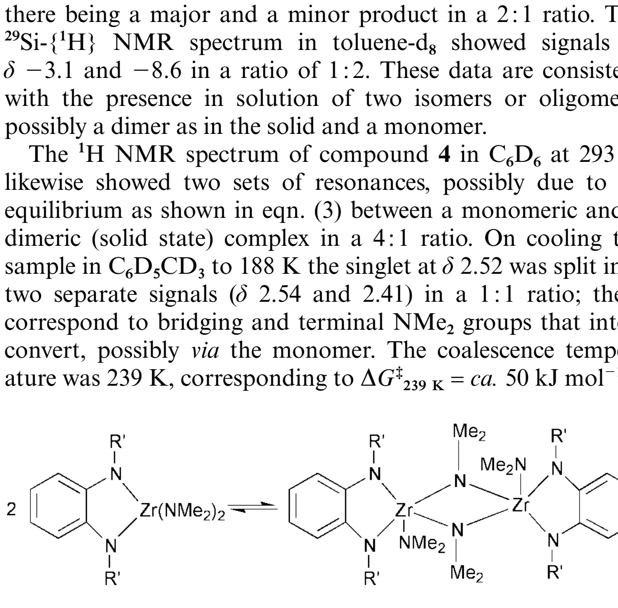
Fig. 4 Molecular structure of compound **6**.

Related to **4** is the isoleptic complex [{Zr(NMe$_2$)L(μ-NMe)}$_2$] **7**, see Fig. 3 and Tables 2 and 4. The two complexes are structurally similar except that the molecule **7** lies on an inversion centre, the midpoint of the ZrN(3)Zr′N(3)′ rhombus (*cf.* the puckered ring in **4**), having Zr–N bond lengths of 2.294 ± 0.041 Å [compared with 2.037(2) Å for the terminal Zr–N(4) bond distance]. The endocyclic angles at the N atoms are wider at 104.24(6)° than those at the Zr atoms, 75.76(6)°. Each zirconium atom is in a pseudo-*TBPY* environment, the atoms N(1), N(3) and N(4) being "equatorial"; the "axial" N(2) and N(3)′ atoms subtend an angle of 152.69(5)° at Zr. Angles at Zr involving N(2) and N(3) or N(4) are 89.75(5) or 106.44(6)°, respectively and those involving N(3)′ and N(1) or N(4) are 89.22(5) or 100.78(6)°, respectively.

The molecular structure of the mononuclear zirconium(IV) chloride [ZrCl$_2$(L)(tmen)] **6** is shown in Fig. 4. Selected geometric parameters are in Tables 2 and 5. There are three independent molecules in the unit cell, each of which is closely similar and hence data for only one are here cited. The molecule has the six-co-ordinate zirconium atom in a distorted octahedral environment: N(1), N(2) and N(4) are *trans* to Cl(1), N(3) and Cl(2), respectively; the corresponding angles subtended at the Zr atom are 173.01(16), 165.0(2) and 156.09(15)°, respectively. The Zr–N(1 or 2) or Zr–N(3 or 4) bond distances are 2.084 ± 0.034 or 2.481 ± 0.017 Å, respectively, the latter corresponding to the Zr–N(tmen) bonds. The Zr–Cl(1) bond of 2.537(2) Å is significantly longer than Zr–Cl(2) of 2.432(2) Å. The Zr–X bonds lengths indicate that the *trans*-influence order is $Cl^- > L^{2-} >$ tmen. The tmen bite angle at Zr, N(3)–Zr–N(4) of 71.8(2)°, and the N(2)–Zr–Cl(2) angle of 103.37(16)° deviate most markedly from the twelve idealised orthogonal angles of an octahedron; the others range from 83.06(15) [N(4)–Zr–Cl(1)] to 97.9(2)° [N(4)–Zr–N(1)].

The ^{1}H and ^{13}C-{^{1}H} NMR spectra of compound **2** in aromatic solvents were more complicated than expected. Thus the ^{1}H NMR spectrum in C_6D_6 at 293 K displayed two sets of resonances for each of the C_6H_4, CH=CH$_2$, and the diastereotopic SiMe$_2$ groups and the thf ligand, consistent with there being a major and a minor product in a 2 : 1 ratio. The ^{29}Si-{^{1}H} NMR spectrum in toluene-d$_8$ showed signals at δ −3.1 and −8.6 in a ratio of 1 : 2. These data are consistent with the presence in solution of two isomers or oligomers, possibly a dimer as in the solid and a monomer.

The ^{1}H NMR spectrum of compound **4** in C_6D_6 at 293 K likewise showed two sets of resonances, possibly due to an equilibrium as shown in eqn. (3) between a monomeric and a dimeric (solid state) complex in a 4 : 1 ratio. On cooling the sample in $C_6D_5CD_3$ to 188 K the singlet at δ 2.52 was split into two separate signals (δ 2.54 and 2.41) in a 1 : 1 ratio; these correspond to bridging and terminal NMe$_2$ groups that interconvert, possibly *via* the monomer. The coalescence temperature was 239 K, corresponding to $\Delta G^{\ddagger}_{239\ \mathrm{K}} = ca.$ 50 kJ mol^{-1}.



(3)

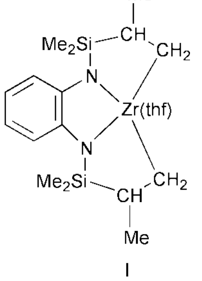
Table 6 Data for polymerisation of ethene

Entry	Catalyst/mg	Conditions	Yield of polymer/mg	Activity × 10^3/g polymer (mol cat)$^{-1}$ h^{-1} bar^{-1}	Viscosity number/ ×10^3 cm^3 g^{-1}
1	**2** (53)	*a*	1250	20.0	750
2	**4** (61)	*a*	1020	12.7	500
3	**5** (36)	*a*	705	14.2	450
4	**3** (26)	*a*	26	1.1	2000
5	**2** (20)	*b*	505	21.6	
6	**2** (7)	*c*	50	6.2	
7	**2** (34)	*d*	146	5.9	
8	**2** (19)	*e*	1700	5.4	900
9	**2** (11)	*f*	49	3.8	
10	$[Zn(\eta^5\text{-}C_5H_5)_2Cl_2]$	*a*	13100	266	

[a] Unless otherwise stated, the Al : Zr ratio was 500 : 1, the Al being provided in the form of MAO as a 10% solution in toluene; [catalyst] = 6×10^{-4} mol l^{-1}; pressure of C_2H_4 2.4 bar; $t = 15$ min. [b] As *a*, but Al : Zr 1200 : 1. [c] As *a*, but [cat] = 10^{-4} mol l^{-1}. [d] As *a*, but pressure of C_2H_4 1.4 bar. [e] As *d*, but $t = 6$ h. [f] As *a*, but CH_2Cl_2–C_6H_5Me (6 : 1).

The ^{1}H NMR spectrum of complex **7** in C_6D_6 at 293 K gave only one set of resonances; the broad signal at δ 2.53 is attributed to the NMe_2 groups, although the ^{13}C-{^{1}H} spectrum under the same conditions showed the two expected signals at δ 45.0 and 41.9 for the terminal and the bridging NMe_2 units, respectively.

Attempts to obtain a dialkyl derivative containing the Zr(L′) moiety were carried out using, in the first instance, the standard methylating reagent LiMe or Mg(Cl)Me with [{Zr(Cl)L′(μ-Cl)(thf)}$_2$] **2**. Elemental analysis of the product was consistent with the composition Zr(L′)Me_2(thf). The ^{1}H NMR spectrum in C_6D_6 revealed the absence of vinyl resonances suggesting that an intermediate Zr(L′)Me_2 complex had undergone a bis(cyclometallation); thus the product is tentatively formulated as **I**. Similarly, a dibenzyl complex was not obtained from the equimolar reaction between $[Zr(CH_2C_6H_5)_4]$ and H_2L'.



I

Details of ethene polymerisation experiments, using compounds **2**–**5** activated by an excess of methylaluminoxane as catalyst, are shown in Table 6. In a typical reaction (footnote *a* in Table 6) a solution of metal complex (6×10^{-4} mol l^{-1} in toluene) and MAO (500 : 1 Al : Zr ratio) at 20 °C was pressurised with ethene (2.4 bar) for 15 min. The polymerisation was quenched by addition of a methanolic hydrogen chloride (MeOH–concentrated aqueous HCl 1 : 1 by volume) solution. The polymer was filtered off, washed and dried; its insolubility precluded examination by GLC, but viscosity measurements showed that the average molecular weight of the polymer was very high.

The new zirconium catalysts showed lower activity (entries 1–3 in Table 6) than $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ by an order of magnitude (entry 10) under similar conditions, but similar to those of related bis(amido)zirconium(IV) complexes;[11,14] they were significantly more active than the titanium catalyst **3** (entry 4). The catalyst derived from [{Zr(Cl)L′(μ-Cl)(thf)}$_2$] **2** was next examined under changed conditions. Its catalytic activity remained relatively constant as a function of (i) time [up to 6 h; entry 8; *cf.* zirconocene(IV) chloride generally loses its activity after *ca.* 1 h] and (ii) use of an excess of MAO (entry 5); but was adversely affected by lowering (iii) the concentration of **2** (entry 6) or (iv) pressure of C_2H_4 (entry 7). Using a mixed CH_2Cl_2–C_6H_5Me solvent system (entry 9) drastically reduced the catalytic activity. Items (i)–(iv) and the high average molecular weight of the polymers are indicative of there being a low concentration of active species.

Experimental

All experiments were carried out under argon in flamed Schlenk-type glassware on a dual manifold Schlenk line. Solvents were pre-dried over sodium wire. Hydrocarbons (pentane, hexane and toluene) and thf were distilled from sodium–potassium alloy and sodium–benzophenone, respectively, and stored over potassium mirrors or molecular sieves. Deuteriated solvents (benzene-d_6, toluene-d_8 and thf-d_8) were distilled or dried on molecular sieves and degassed prior to use. n-Butyllithium in hexanes (1.6 mol dm^{-3}), 1,2-diaminobenzene, MCl_4 (M = Ti or Zr), $Si(Cl)Me_2(CH{=}CH_2)$ and $Si(Cl)Me_3$ were purchased from Aldrich and used without further purification. The compounds $Zr(NMe_2)_4$[22] and $B(C_6F_5)_3$[23] were prepared according to literature methods. The NMR spectra were recorded on Bruker, DPX 300 or AMX 500 instruments at 293 K unless otherwise stated, and were referenced internally (^{1}H and ^{13}C) to residual solvent resonances or externally (^{29}Si) to $SiMe_4$. The IR spectra were measured on solid samples as "Nujol" mulls using a Perkin-Elmer 1720 instrument, electron impact mass spectra using a Kratos MS 80 RF instrument (*M* denotes the mass number of the monomeric compound). Elemental analyses were carried out by Medac Ltd, UK. Average molecular weights of polyethylene were determined by BASF (Ludwigshafen).

Preparations

$C_6H_4(NH\{SiMe_2(CH{=}CH_2)\})_2$-1,2] (≡ H_2L') 1. n-Butyllithium (60 cm^3, 96 mmol in hexanes) was added dropwise during *ca.* 20 min at 0 °C to 1,2-diaminobenzene (5.40 g, 50 mmol) in thf (100 cm^3). The mixture was warmed to room temperature and stirred for *ca.* 20 h. The resulting green suspension was cooled to 0 °C and a solution of $Si(Cl)Me_2(CH{=}CH_2)$ (15 cm^3, 109 mmol) in thf (20 cm^3) added dropwise during *ca.* 30 min. The mixture was refluxed for 2 h and stirred at room temperature for *ca.* 20 h. The solvent was removed *in vacuo* and pentane (100 cm^3) added to give an orange solution and a white precipitate. Filtration and evaporation of the solvent from the filtrate led to an orange oil. Distillation at bp *ca.* 90 °C/ 0.5 mmHg gave pale yellow oil **1** (9.5 g, 72%). ^{1}H NMR (C_6D_6): δ 6.96 (m, 2 H, C_6H_4), 6.81 (m, 2 H, C_6H_4), 6.19 (dd, 2 H, $^3J_{HHtrans}$ 20.0, $^3J_{HHcis}$ 14.8, C*H*=CH$_2$), 5.92 (dd, 2 H, $^3J_{HHcis}$ 14.7, $^2J_{HH}$ 4.0, CH=C*H*$_2$), 5.75 (dd, 2 H, $^3J_{HHtrans}$ 20.0, $^2J_{HH}$ 4.0 Hz, CH=C*H*$_2$), 3.05 (s, 2 H, NH), 0.18 and 0.17 (s, 12 H, $SiMe_2$). ^{13}C-{^{1}H} NMR (C_6D_6): δ 138.8, 137.5, 132.8 (C_6H_4), 121.1 (*C*H=CH$_2$) 120.7 (CH=*C*H$_2$) and −1.8 (SiMe$_2$). ^{29}Si-{^{1}H} NMR (C$_6$D$_6$): δ −6.6. IR: 3370m [ν(N–H)], 1599m, 1584w [ν(C=C)], 1251s cm^{-1} [ν(Si–C)]. MS: *m*/*z* 276 (100, [*M*]$^+$), 261 (17, [*M* − Me]$^+$) and 234 (11%, [*M* − Me − Vi]$^+$).

[{Zr(Cl)L′(μ-Cl)(thf)}$_2$] 2. *Procedure a.* A mixture of compound **1** (0.77 g, 2.6 mmol) and LiBu^n (3.2 cm^3 of a 1.6 mmol dm^{-3} solution in hexanes, 5.12 mmol) was added dropwise during *ca.* 30 min at 0 °C to a solution of [ZrCl$_4$(thf)$_2$] (1.0 g, 2.65 mmol) in thf (100 cm^3). The mixture changed from colourless to deep orange. It was allowed to warm to room temperature and stirred for 20 h. Solvent was removed *in vacuo* and hexane (80 cm^3) added. The resulting suspension was stirred for 4 h at ambient temperature and filtered. The filtrate was concentrated and cooled at −35 °C to give deep orange crystals of compound **2** (0.90 g, 67%).

Procedure b. Complex **2** (Found: C, 41.75; H, 5.80; N, 5.75. C$_{18}$H$_{30}$Cl$_2$N$_2$OSi$_2$Zr requires C, 42.5; H, 5.91; N, 5.51%) was obtained quantitatively by dissolving [ZrCl$_2$(L′)] **5** (see below) in thf and removing excess of thf *in vacuo*. ^{1}H NMR (C$_6$D$_6$): δ 7.06–6.96 (m, 5 H, C$_6$H$_4$), 6.85 (m, 1 H, C$_6$H$_4$), 6.52 (m, 2 H, C*H*=CH$_2$), 6.21 (m, 1 H, C*H*=CH$_2$), 6.00–5.75 (m, 6 H, CH=C*H*$_2$), 4.15 (br s, 2 H, OC*H*$_2$CH$_2$), 3.69 (br s, 4 H, OCH$_2$C*H*$_2$), 1.30 (br s, 4 H, OCH$_2$C*H*$_2$), 1.09 (br s, 2 H, OCH$_2$C*H*$_2$), 0.84 (s, 6 H, SiMe$_2$), 0.52 (s, 6 H, SiMe$_2$), 0.28 (s, 3 H, SiMe$_2$) and 0.18 (s, 3 H, SiMe$_2$). ^{29}Si-{^{1}H} NMR (C$_6$D$_6$): δ −3.1 and −8.6. MS: *m*/*z* 436 (15, [*M* − 1]$^+$), 386 (12, *M* − 1 − MeCl)$^+$] and 360 (74%, [*M* − Ph]$^+$).

[{Ti(Cl)L′(μ-Cl)(thf)}$_2$] 3. Deep brown crystals of complex **3** (0.66 g, 62%) (Found: C, 45.85; H, 6.22; N, 5.96. C$_{18}$H$_{30}$Cl$_2$N$_2$OSi$_2$Ti requires C, 46.45; H, 6.45; N, 6.02%) were obtained from the diamine **1** (0.63 g, 2.28 mmol) and LiBu^n (5.56 mmol) in hexanes (30 cm^3) and [TiCl$_4$(thf)$_2$] (0.76 g, 2.28 mmol) at −35 °C, using a procedure similar to that of (*a*) for complex **2**. ^{1}H NMR (C$_5$D$_6$CD$_3$): δ 6.92–6.71 (m, 8 H, C$_6$H$_4$), 6.13 (m, 4 H, C*H*=CH$_2$), 6.01–5.62 (m, 8 H, CH=C*H*$_2$), 3.53 (br s, 4 H, OC*H*$_2$CH$_2$), 3.24 (br s, 4 H, OC*H*$_2$CH$_2$) 1.59 (br s, 4 H, OCH$_2$C*H*$_2$), 1.40 (br s, 4 H, OCH$_2$C*H*$_2$), 1.24 (br s, 3 H, SiMe$_2$), 0.82 (s, 3 H, SiMe$_2$), 0.21, 0.19 (s, 15 H, SiMe$_2$), 0.14, 0.10 (s, 3 H, SiMe$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_5$CD$_3$): δ 139.1, 133.4, 132.5, 131.9 (C$_6$H$_4$), 124.5, 120.9, 120.6, 119.8 (CH=CH$_2$), 70.4 (O*C*H$_2$CH$_2$), 26.8 (OCH$_2$*C*H$_2$), 1.4, 0.9, 0.4, −2.1 (SiMe$_2$). ^{29}Si-{^{1}H} NMR (C$_6$D$_5$CD$_3$): δ −4.4 and −7.6. MS: *m*/*z* 367 (15, [*M* − Vi]$^+$).

[{Zr(NMe$_2$)L′(μ-NMe$_2$)}$_2$] 4. The diamine **1** (0.72 g, 2.61 mmol) in toluene (20 cm^3) was added dropwise at 0 °C during *ca.* 10 min to Zr(NMe$_2$)$_4$ (0.70 g, 2.62 mmol) in toluene (30 cm^3). The mixture became orange. It was stirred at room temperature for *ca.* 20 h. The solvent was removed *in vacuo* and pentane (30 cm^3) added. After filtration, the volume of the filtrate was reduced to *ca.* 5 cm^3 and cooled to 4 °C. The pale yellow crystalline complex **4** (0.97 g, 82%) (Found: C, 46.7 (duplicate analyses); H, 7.36; N, 11.91. C$_{18}$H$_{34}$N$_4$Si$_2$Zr requires C, 47.6; H, 7.55; N, 12.34%) was isolated by filtration and dried *in vacuo*. ^{1}H NMR (C$_5$D$_6$CD$_3$): δ 7.16 (m, 4 H, C$_6$H$_4$), 6.87 (m, 4 H, C$_6$H$_4$), 6.73 (m, 1 H, C$_6$H$_4$), 6.62 (m, 1 H, C$_6$H$_4$), 6.31 (m, 4 H, C*H*=CH$_2$), 6.05 (m, 1 H, C*H*=CH$_2$), 5.74 (m, 8 H, CH=C*H*$_2$), 5.77 (m, 2 H, CH=C*H*$_2$), 2.58 (s, 6 H, NMe$_2$), 2.52 (s, 24 H, NMe$_2$), 0.30 (s, 6 H, SiMe$_2$), 0.27 (s, 12 H, SiMe$_2$) and 0.25 (s, 12 H, SiMe$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_5$CD$_3$): δ 142.0, 137.4, 134.6, 131.0 (C$_6$H$_4$), 124.8, 122.5, 118.7, 116.1 (CH=CH$_2$), 45.1, 42.1, 41.4 (NMe$_2$), 0.9, 0.4, −0.6 (SiMe$_2$). ^{29}Si-{^{1}H} NMR (C$_6$D$_5$CD$_3$): δ −10.8 and −18.3. MS: *m*/*z* 452 (100, [*M* − 1]$^+$), 407 (65, [*M* − 2 − NMe$_2$]$^+$) and 364 (50%, [*M* − 1 − 2NMe$_2$]$^+$).

ZrCl$_2$(L′) 5. The zirconium(IV) amide **4** (0.85 g, 1.9 mmol) was dissolved in hexane (100 cm^3), an excess of chloro(trimethyl)silane (2.4 cm^3, 19 mmol) was added dropwise at room temperature and the mixture stirred overnight. A fine yellow precipitate began to appear after *ca.* 10 min. The precipitate was collected by filtration and washed with pentane. The residue, a yellow microcrystalline powder after recrystallisation from toluene at 4 °C, was identified as complex **5** (0.72 g, 87%) (Found: C, 38.35; H, 4.91; N, 6.99. C$_{14}$H$_{22}$Cl$_2$N$_2$Si$_2$Zr requires C, 38.5; H, 5.08; N, 6.41%). ^{1}H NMR (C$_5$D$_6$CD$_3$): δ 6.87 (m, 2 H, C$_6$H$_4$), 6.73 (m, 2 H, C$_6$H$_4$), 6.13 (m, 2 H, C*H*=CH$_2$), 5.79 (m, 4 H, CH=C*H*$_2$), 0.49 (br s, 3 H, SiMe$_2$), 0.19 to −0.02 (5 peaks, 9 H, SiMe$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_5$CD$_3$): δ 138.9, 137.5, 133.9, 132.8 (C$_6$H$_4$), 121.1 (*C*H=CH$_2$), 120.8 (CH=*C*H$_2$), 1.4, −1.6 (SiMe$_2$). No ^{29}Si-{^{1}H} NMR signals were observed due to the low solubility of the compound in toluene. MS: *m*/*z* 276 (100, [H$_2$L′]$^+$).

[ZrCl$_2${C$_6$H$_4$(NSiMe$_3$)$_2$-1,2}(tmen)] 6. Zirconium(IV) chloride (1.17 g, 5.03 mmol) was added in portions during *ca.* 10 min to an orange solution of [Li$_2${C$_6$H$_4$(NSiMe$_3$)$_2$-1,2}(tmen)$_2$][21] (1.62 g, 3.26 mmol) in toluene (20 cm^3). The resulting mixture initially contained a green solid, which became yellow after *ca.* 12 h. Volatiles were removed *in vacuo*. The residual brown solid was extracted into pentane (20 cm^3). The extract was filtered and the filtrate evaporated *in vacuo*, yielding a yellow-brown solid which, upon crystallisation from toluene, gave at −30 °C yellow-brown crystals of complex **6** (1.73 g, 70%) (Found: C, 39.2; H, 7.02; N, 10.61. C$_{18}$H$_{38}$Cl$_2$N$_4$Si$_2$Zr requires C, 40.9; H, 7.19; N, 10.60%), mp 260–264 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.02 (br s, 4 H, C$_6$H$_4$), 2.18 (s, 12 H, NMe), 1.73 (s, 4 H, CH$_2$N) and 0.53 (s, 18 H, SiMe$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$): δ 136.8 (*ipso*-C), 125.4 (*m*-C), 123.4 (*o*-C), 58.4 (NMe), 50.6 (CH$_2$N) and 2.7 (SiMe$_3$). ^{29}Si-{^{1}H} NMR (C$_6$D$_6$): δ −2.6. MS: *m*/*z* 459 (20, [*M* − 2Cl]$^+$), 385 (25, [*M* − tmen − 2Me]$^+$), 315 (20, [*M* − tmen − 2Me − 2Cl]$^+$), 281 (30), 323 (60), 197 (75), 73 (60, [SiMe$_3$]$^+$) and 58 (100, [SiMe$_2$]$^+$).

[Zr(NMe$_2$){C$_6$H$_4$(NSiMe$_3$)$_2$-1,2}(μ-NMe$_2$)] 7. A solution of the diamine C$_6$H$_4$(NHSiMe$_3$)$_2$-1,2 (2.76 g, 10.90 mmol) in toluene (20 cm^3) was added dropwise during *ca.* 10 min to Zr(NMe$_2$)$_4$ (2.84 g, 10.78 mmol) in toluene (80 cm^3) at 0 °C. The mixture was set aside at ambient temperature for *ca.* 12 h. Volatiles were removed *in vacuo*. The residual solid was extracted into pentane (100 cm^3). The extract was filtered; concentration of the filtrate to *ca.* 30 cm^3 yielded colourless crystals of compound **7** (4.40 g, 95%) (Found: C, 42.8; H, 7.70; N, 12.58. C$_{16}$H$_{34}$N$_4$Si$_2$Zr requires C, 41.9; H, 7.97; N, 13.04%), mp 197–199 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.01–7.19 (m, 2 H, *m*-H), 6.97–7.00 (m, 2 H, *o*-H), 2.53 (s, 12 H, NMe$_2$) and 0.29 (s, 18 H, SiMe$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$): δ 137.7 (*ipso*-C), 124.9 (*m*-C), 122.4 (*o*-C), 45.0 and 41.9 (NMe$_2$) and 2.8 (SiMe$_3$). ^{29}Si-{^{1}H} NMR (C$_6$D$_6$): δ −1.8. MS: *m*/*z* 428 (100, [*M* − H]$^+$), 383 (90, [*M* − NMe$_2$]$^+$), 368 (25, [*M* − NMe$_2$ − Me]$^+$), 340 (40), 323 (30), 307 (60), 252 (30, [H$_2$L]$^+$), 149 (20), 73 (55, [SiMe$_3$]$^+$) and 58 (100, [SiMe$_2$]$^+$).

Reaction of LiMe with [{Zr(Cl)L′(μ-Cl)(thf)}$_2$] 2. Methyllithium (4.7 cm^3 of a 1.6 mmol dm^{-3} solution in diethyl ether, 7.0 mmol) was added dropwise at 0 °C during *ca.* 10 min to complex **2** (1.33 g, 3.53 mmol) in thf (50 cm^3). The mixture, which became deep orange, was stirred at ambient temperature for *ca.* 48 h. Volatiles were removed *in vacuo* and hexane (80 cm^3) was added. After filtration, the filtrate was concentrated and cooled at −25 °C. An orange amorphous solid (0.80 g) was separated and dried *in vacuo*. It is believed to have been a compound of composition Zr(L′)Me$_2$(thf) (Found: C, 50.35; H, 7.77; N, 5.36. C$_{20}$H$_{36}$Cl$_2$N$_2$OSi$_2$Zr requires C, 51.4; H, 7.70; N, 5.99%). MS: the highest peak observed had *m*/*z* 276 (100%).

Table 7 Crystal data and refinement for compounds **2**, **4**, **6** and **7**

	2	**4**	**6**	**7**
Formula	$C_{36}H_{60}Cl_4N_4O_2Si_4Zr_2$	$C_{36}H_{68}N_8Si_4Zr_2$	$C_{18}H_{38}Cl_2N_4Si_2Zr$	$C_{32}H_{68}N_8Si_4Zr_2$
M	1017.5	907.8	528.8	859.7
T/K	293(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	Cc (no. 9)	$C2/c$ (no. 15)
a/Å	9.836(4)	18.596(11)	30.39(2)	25.7431(4)
b/Å	13.669(4)	10.248(4)	18.203(5)	10.1941(2)
c/Å	18.534(7)	25.869(13)	14.315(5)	18.7501(4)
β/°	93.90(3)	111.00(4)	102.52(4)	116.877(1)
U/Å^3	2486(2)	4603(4)	7731(6)	4389.0(1)
Z	2	4	12	4
μ/mm^{-1}	0.76	0.59	0.74	0.615
Unique reflections, R_{int}	3449, 0.03	6398, 0.05	5487	5216, 0.04
Reflections with $I > 2\sigma(I)$	2212	5575	4994	4722
$R1$ ($I > 2\sigma(I)$)	0.048	0.070	0.033	0.026
$wR2$ (all data)	0.107	0.200	0.072	0.069

Crystallography

Data were collected on an Enraf-Nonius CAD4 (compounds **2**, **4** and **6**) or KappaCCD (**7**) diffractometer using monochromated Mo-Kα radiation [λ 0.71073 Å]. Crystals were either sealed in a Lindemann capillary under argon (**2**) or else directly mounted on the diffractometer under a stream of cold nitrogen gas. Refinement was based on all F^2 using SHELXL 93[24] (**2** and **4**) or SHELXL 97[25] (**6** and **7**). Further details are in Table 7.

CCDC reference number 186/2264.

See http://www.rsc.org/suppdata/dt/b0/b006596j/ for crystallographic files in .cif format.

Acknowledgements

We thank the European Commission for the award of Marie Curie fellowships to P. G. M. and S. D., BASF (Ludwigshafen) for polymer evaluation and EPSRC for other support.

References

1 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood-Wiley, Chichester, 1980.

2 A. D. Jenkins, M. F. Lappert and R. C. Srivastava, *Eur. Polym. J.*, 1971, **7**, 289.

3 For a review, see M. F. Lappert, *J. Organomet. Chem.*, 1988, **358**, 185.

4 A. W. Duff, P. B. Hitchcock, M. F. Lappert, R. G. Taylor and J. A. Segal, *J. Organomet. Chem.*, 1985, **293**, 271.

5 H. Braunschweig, B. Gehrhus, P. B. Hitchcock and M. F. Lappert, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1922.

6 J. Pfeiffer, W. Maringgele, M. Noltemeyer and A. Meller, *Chem. Ber.*, 1989, **122**, 245.

7 B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. Heinicke, R. Boese and D. Bläser, *J. Organomet. Chem.*, 1996, **521**, 211.

8 B. Gehrhus, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 2000, 3094.

9 S. Danièle, P. B. Hitchcock and M. F. Lappert, *Chem. Commun.*, 1999, 1909.

10 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.

11 F. G. N. Cloke, T. J. Geldbach, P. B. Hitchcock and J. B. Love, *J. Organomet. Chem.*, 1996, **506**, 343.

12 J. D. Scollard and D. H. McConville, *J. Am. Chem. Soc.*, 1996, **118**, 10008.

13 F. Guérin, D. H. McConville and J. J. Vittal, *Organometallics*, 1996, **15**, 5586.

14 H. Mack and M. S. Eisen, *J. Organomet. Chem.*, 1996, **525**, 81; A. D. Horton and J. de With, *Organometallics*, 1997, **16**, 5424; V. C. Gibson, B. S. Kimberley, A. J. P. White, D. J. Williams and P. Howard, *Chem. Commun.*, 1998, 313; Y.-M. Jeon, S. J. Park, J. Heo and K. Kim, *Organometallics*, 1998, **17**, 3161; C. H. Lee, Y.-H La, S. J. Park and J. W. Park, *Organometallics*, 1998, **17**, 3648.

15 N. A. H. Male, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1997, 2487; A. D. Horton, J. de With, A. J. van der Linden and H. van de Weg, *Organometallics*, 1996, **15**, 2672; R. R. Schrock, F. Schattenmann, M. Aizenberg and W. M. Davis, *Chem. Commun.*, 1998, 199; R. Baumann, W. M. Davis and R. R. Schrock, *J. Am. Chem. Soc.*, 1997, **119**, 3830; F. J. Schattenmann, R. R. Schrock and W. M. Davis, *Organometallics*, 1998, **17**, 989; B. Tsuie, D. C. Swenson, R. F. Jordan and J. L. Petersen, *Organometallics*, 1997, **16**, 1392; H. Fuhrmann, S. Brenner, P. Arndt and R. Kempe, *Inorg. Chem.*, 1996, **35**, 6742; S. Friedrich, L. H. Gade, I. J. Scowen and M. McPartlin, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1338; H. C. S. Clark, F. G. N. Cloke, P. B. Hitchcock, J. B. Love and A. P. Wainwright, *J. Organomet. Chem.*, 1995, **501**, 333; F. G. N. Cloke, P. B. Hitchcock and J. B. Love, *J. Chem. Soc., Dalton Trans.*, 1995, 25; S. Friedrich, L. H. Gade, I. J. Scowen and M. McPartlin, *Organometallics*, 1995, **14**, 5344; S. Tinkler, R. J. Deeth, D. J. Duncalf and A. McCamley, *Chem. Commun.*, 1996, 2623; J. D. Scollard, D. H. McConville and S. J. Rettig, *Organometallics*, 1997, **17**, 1810; S. A. A. Shah, H. Dorn, A. Voigt, H. W. Roesky, E. Parisini, H.-G. Schmidt and M. Noltemeyer, *Organometallics*, 1996, **15**, 3176; S. Pritchett, P. Gantzel and P. J. Walsh, *Organometallics*, 1997, **16**, 5130; C. H. Lee, Y.-H. La and J. W. Park, *Organometallics*, 2000, **19**, 344; Y.-M. Jeon, J. Heo, N. M. Lee, T. Chang and K. Kim, *Organometallics*, 1999, **18**, 4107.

16 K. Aoyagi, P. K. Gantzel, K. Kalai and T. D. Tilley, *Organometallics*, 1996, **15**, 923.

17 G. J. Pindado, M. Thornton-Pett and M Bochmann, *J. Chem. Soc., Dalton Trans.*, 1998, 393.

18 C. G. Ortiz, K. A. Abboud and J. M. Boncella, *Organometallics*, 1999, **18**, 4253.

19 D. D. VanderLende, K. A. Abboud and J. M. Boncella, *Organometallics*, 1994, **13**, 3378; J. M. Boncella, S.-Y. S. Wang, D. D. VanderLende, R. L. Huff, K. A. Abboud and W. M. Vaughn, *J. Organomet. Chem.*, 1996, **530**, 59; R. L. Huff, S.-Y. S. Wang, K. A. Abboud and J. M. Boncella, *Organometallics*, 1997, **16**, 1779; S.-Y. S. Wang, K. A. Abboud and J. M. Boncella, *J. Am. Chem. Soc.*, 1997, **119**, 11990; S.-Y. S. Wang, D. D. VanderLende, K. A. Abboud and J. M. Boncella, *Organometallics*, 1998, **17**, 2628.

20 C. J. Cardin, P. B. Hitchcock, C. MacBeath and N. J. W. Warhurst, *J. Organomet. Chem.*, 1999, **584**, 366; and references therein.

21 S. Danièle, C. Drost, B. Gehrhus, S. M. Hawkins, P. B. Hitchcock, M. F. Lappert and P. G. Merle, *J. Chem. Soc., Dalton Trans.*, to be submitted.

22 M. H. Chisolm, C. E. Hammond and J. C. Huffman, *Polyhedron*, 1988, **7**, 2515.

23 A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1966, **5**, 218.

24 G. M. Sheldrick, SHELXL 93, Program for Crystal Structures Refinement, University of Göttingen, 1993.

25 G. M. Sheldrick, SHELXL 97, Program for Crystal Structures Refinement, University of Göttingen, 1997.