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Tripodal amido-titanium and -zirconium complexes containing a trisilylsilane-derived ligand framework

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A series of amido-titanium and -zirconium complexes containing a tripodal amide with a trisilylsilane ligand framework has been prepared. The primary isolable products in the reaction of SiMe $(SiMe_2NHR)_3$ (R = $4-MeC_6H_4$, $2-FC_6H_4$ or $4-MeOC_6H_4$) with $LiBu^n$ and $ZrCl_4$ in diethyl ether are the $[Li(OEt_2)_2Cl]$ adducts of which the five-co-ordinate complex $[\{(4-MeOC_6H_4NSiMe_2)_3MeSi\}Zr(\mu-Cl)_2Li(OEt_2)_2]$ and the six-co-ordinate $[\{(2-FC_6H_4NSiMe_2)_3MeSi\}Zr(\mu-Cl)_2Li(OEt_2)_2]$ have been characterised by X-ray crystallography. In the latter one of the fluorine atoms of the peripheral $2-FC_6H_4$ groups is weakly co-ordinated to the metal. Stirring of the $(Et_2O)_2LiCl$ adducts in toluene generates the four-co-ordinate complexes $[Zr\{SiMe(SiMe_2NR)_3\}Cl]$. Upon reaction of $[M\{SiMe[SiMe_2N(C_6H_4F-2)]_3\}Cl]$ (M = Ti or Zr) with AgO_3SCF_3 the corresponding triflates were obtained which are sufficiently stable to be isolated. The halide ligand may be readily substituted to give the corresponding methyl, ethynyl and cyclopentadienyl complexes.

We have recently introduced a new class of tripodal amide ligands ('N_3 ligand') to the co-ordination chemistry of the early transition elements, in particular the titanium triad.[1,2] These provided the key to the stabilisation of unusual structural units involving the metal by virtue of an efficient shielding of most of the co-ordination sphere. An 'active site' of controllable size and geometry at which further functionalisation may occur thus remains at the metal centre.[3]

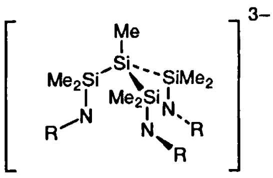
A particularly versatile ligand system $[SiMe(SiMe_2NR)_3]^{3-}$ contains a trisilylsilane backbone and co-ordinates to first-row as well as the second- and third-row metals equally well, thus being suitable for comparative studies.[4] In this paper we report an extension of our previous studies into the co-ordination chemistry of this particular ligand system. Emphasis is placed upon the way in which the key compounds of the general type (N_3 ligand)MX (M = Ti or Zr, X = halide) are being formed by reaction of the respective halide with the ligand-transfer reagent, a solvated or unsolvated lithium amide.

Results and Discussion

Synthesis of the tripodal ligands

The triamine precursors of the tripodal amides $SiMe(SiMe_2NHR)_3$ (R = $4-MeOC_6H_4$ **Ia**, 2-pyridyl **Ib** or $2-FC_6H_4$ **Ic**) were synthesised by condensation of $MeSi(SiMe_2Cl)_3$ with the respective primary amines as reported previously for several related systems [equation (1)].[4] The choice of the 2-pyridyl and 2-fluorophenyl groups in the ligand periphery was motivated by their potential to occupy additional co-ordination sites through their donor functions, thus kinetically stabilising otherwise elusive species.[3b] The $4-MeOC_6H_4$-substituted derivative was expected to display similar characteristics to those of the $4-MeC_6H_4$ derivative **Id**, which we reported previously.[4]

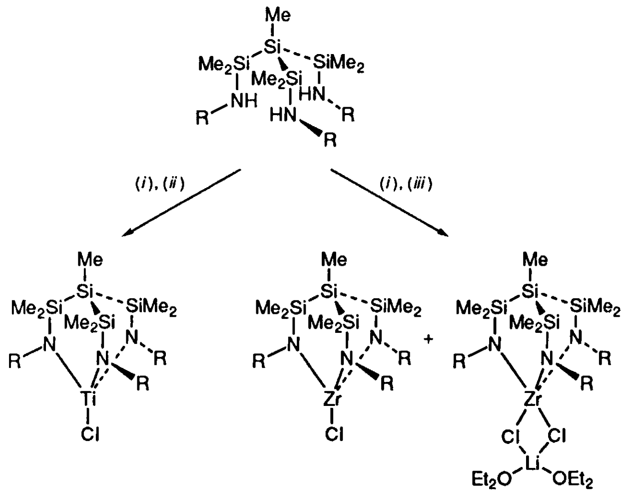
$$SiMe(SiMe_2Cl)_3 \xrightarrow[-3NEt_3HCl]{3NH_2R,3NEt_3} SiMe(SiMe_2NHR)_3 \quad (1)$$



Preparation of the tripodal titanium and zirconium amides

Whereas the reaction of $[TiX_4(thf)_2]$ (thf = tetrahydrofuran) with the appropriate amidolithium ligand-transfer reagent generates the four-co-ordinate target compound without isolable intermediates, the initial product of the analogous reaction with $ZrCl_4$ isolated from the reaction mixture depends very much upon the amide employed (Scheme 1).

The syntheses of the titanium compounds were carried out in solvent mixtures of pentane–diethyl ether (6:1), while the zirconium complexes were obtained using neat diethyl ether as solvent. These slightly different reaction conditions were dictated by the redox activity of the titanium salts in reactions with lithium amides which may be suppressed by choice of



Scheme 1 Synthesis of the tripodal amido-titanium and -zirconium complexes. (*i*) 3 $LiBu^n$; (*ii*) $[TiCl_4(thf)_2]$; (*iii*) $ZrCl_4$

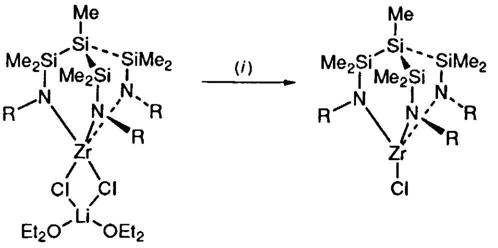
a non-polar reaction medium. The analytical data as well as the resonance patterns observed in the NMR spectra of the titanium compounds $[Ti\{SiMe(SiMe_2NR)_3\}X]$ (R = 4-$MeOC_6H_4$, X = Cl **1**; R = 2-FC_6H_4, X = Cl **2a** or Br **2b**; R = 4-MeC_6H_4, X = Cl **3a**[4] or Br **3b**[4]) and the zirconium complex $[Zr\{SiMe(SiMe_2NR)_3\}Cl]$ **4** (R = 2-pyridyl) are consistent with the three-fold symmetrical structures displayed in Scheme 1. The drastic shift of the ^{19}F NMR resonance of **2a** and **2b** (δ −119.6) in comparison to the free amide (δ −134.8) and the essentially temperature-independent nature of the NMR spectra of these compounds indicate that the peripheral fluorine atoms bind at least weakly to the titanium centres. This is similar to the situation established by X-ray crystallography for the trisilylmethane-derived complex $[Y\{CH[SiMe_2N(C_6H_4\text{-}F\text{-}2)]_3\}(OEt_2)]$ in which all three fluorine atoms are bound to the yttrium centre.[3b]

Isolation of $[\{(RNSiMe_2)_3MeSi\}Zr(\mu\text{-}Cl)_2Li(OEt_2)_2]$ as initial products and conversion to $[Zr\{SiMe(SiMe_2NR)_3\}Cl]$

The reaction of the trilithiated amines **Ia**, **Ic** and **Id** with $ZrCl_4$ in diethyl ether was found initially to yield the lithium chloride adducts $[\{(RNSiMe_2)_3MeSi\}Zr(\mu\text{-}Cl)_2Li(OEt_2)_2]$ (R = 4-$OMeC_6H_4$ **5**, 2-FC_6H_4 **6** or 4-MeC_6H_4 **7**), respectively, which were isolated from the ether solution as highly crystalline solids. The formulation of the compounds was established by elemental analysis while the NMR spectra indicated the co-ordination of an $(Et_2O)_2LiCl$ fragment to the amido zirconium halide complexes. Prolonged stirring of **5**–**7** in toluene or direct halide abstraction with $AgBPh_4$ yielded the corresponding four-co-ordinate compounds $[Zr\{SiMe[SiMe_2N(C_6H_4\text{-}OMe\text{-}4)]_3\}Cl]$ **8**, $[Zr\{SiMe[SiMe_2N(C_6H_4F\text{-}2)]_3\}Cl]$ **9** and $[Zr\{SiMe[SiMe_2N(C_6H_4Me\text{-}4)]_3\}Cl]$ **10**[4] (Scheme 2).

Crystal structures of complexes 5 and 6

In order to establish the co-ordination geometry at Zr^{IV} in these initial products of the amide ligand transfer single-crystal X-ray structure analyses of **5** and **6** were carried out. The molecular structure of **5** depicted in Fig. 1 confirms the formulation based on the spectroscopic and analytical data. It may be viewed as a highly distorted trigonal bipyramid, with Cl(1) and N(2) at the apical positions [Cl(1)–Zr–N(2) 165.5°] and N(2), N(3) as well as Cl(2) occupying the equatorial co-ordination sites. The kind of distortion observed is closely related to the proposed transition-state geometry in 'turnstile rotations' of five-co-ordinate molecules containing tridentate ligands.[5] It should be noted that the N(2)–Zr 2.13(1) and Cl(1)–Zr 2.607(4) Å distances of the apical ligands are significantly longer than the corresponding values of the equatorial donors [Zr–N(1) 2.07(1), Zr–N(3) 2.03(1), Zr–Cl(2) 2.509(5) Å]. The overall arrangement of the donor atoms is dictated by the steric requirements of the tripodal amide ligand which is considerably distorted from the three-fold symmetry found in the four-co-ordinate complexes previously characterised [N(1)–Zr–N(2) 94.2, N(2)–Zr–N(3) 101.5, N(1)–Zr–N(3) 107.8°].[4] The almost planar quadrangular $ZrCl_2Li$ unit (angle between $ZrCl_2$ and $LiCl_2$ = 179°), of the type observed in other transition-metal and lanthanoid complexes,[6] has not previously been established for Zr.[7] The compound may thus be viewed as a contact ion pair of an anionic dichlorotriamidozirconium complex and an $[Li(OEt_2)_2]^+$ cation.



Scheme 2 Conversion of the LiCl adducts into the respective four-co-ordinate amidozirconium chlorides. (*i*) $AgBPh_4$ or heat

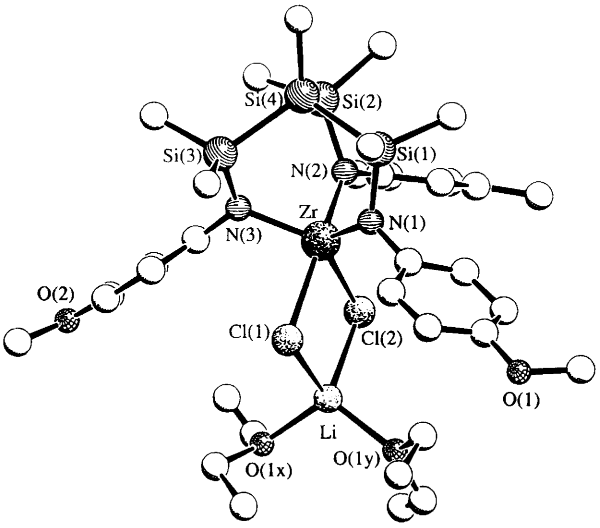


Fig. 1 Molecular structure of complex **5** in the crystal. The fractional coordinates are listed in Table 1, principal bond lengths and interbond angles in Table 2

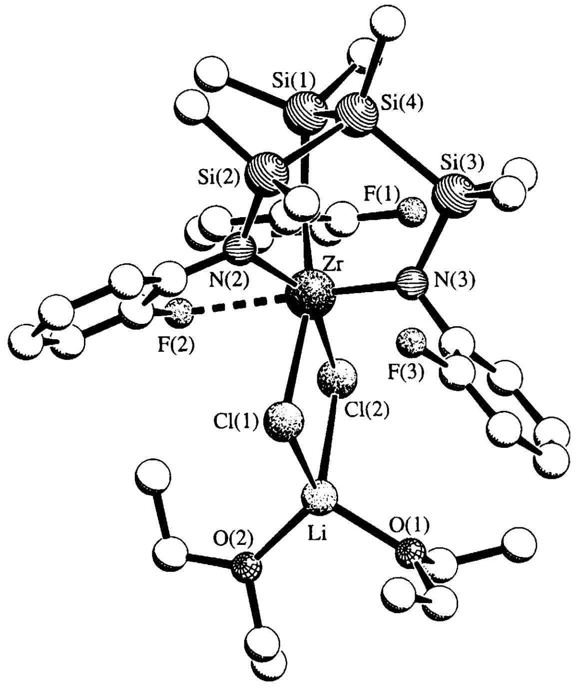


Fig. 2 Molecular structure of complex **6** in the crystal. The fractional coordinates are listed in Table 3, principal bond lengths and interbond angles in Table 4

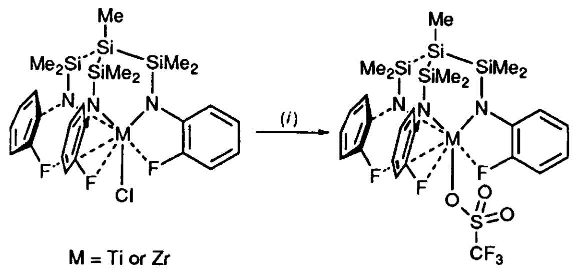
The X-ray analysis of complex **6** (Fig. 2) revealed a related structure to that of **5**, however one of the fluorine atoms of the 'ligand periphery' is involved in the co-ordination to the central metal atom. The latter displays six-fold co-ordination in a distorted-octahedral arrangement of donor atoms, with the amido-N atoms occupying three positions within the inner co-ordination sphere, while two chloride ligands and one of the *o*-fluorine atoms [F(2)] of the 2-fluorophenyl groups [Zr–F(2) 2.511(2) Å] are at the remaining three co-ordination sites. The other two *o*-fluorine atoms in the ligand periphery are unco-ordinated. Whereas the two unco-ordinated fluorophenyl groups are twisted into an almost orthogonal position to the Si–N bonds [dihedral angle between the phenyl plane and the Si–N vectors 91.1(3)° at N(1) and 89.4(3)° at N(3)], the corresponding torsion angle of the 2-fluorophenyl group at

Table 1 Atomic coordinates for complex **5**

Atom	*x*	*y*	*z*
Zr	0.771 53(3)	0.043 29(14)	0.107 52(6)
Cl(1)	0.797 6(2)	0.054 3(4)	0.005 4(1)
Cl(2)	0.702 2(3)	−0.141 7(4)	0.067 8(2)
Si(4)	0.823 9(2)	0.257 2(4)	0.218 2(2)
Si(1)	0.920 5(2)	0.206 2(4)	0.167 6(2)
Si(2)	0.793 8(2)	0.063 9(5)	0.247 8(2)
Si(3)	0.729 6(3)	0.321 2(4)	0.153 0(2)
N(1)	0.381 3(6)	0.075 4(10)	0.135 1(4)
N(2)	0.749 8(6)	−0.010 7(9)	0.187 0(4)
N(3)	0.721 5(6)	0.211 9(10)	0.098 6(4)
C(1)	0.851 8(8)	0.375 7(15)	0.274 9(6)
C(2)	1.007 0(8)	0.162 4(13)	0.213 2(6)
C(3)	0.939 1(8)	0.323 7(15)	0.115 6(6)
C(4)	0.729 2(8)	0.085 2(14)	0.298 3(6)
C(5)	0.878 9(8)	−0.023 3(14)	0.284 8(6)
C(6)	0.743 1(8)	0.480 8(13)	0.123 0(5)
C(7)	0.643 5(8)	0.328 2(14)	0.185 1(6)
C(11)	0.925 2(7)	−0.025 9(14)	0.120 2(5)
C(12)	0.977 0(7)	−0.003 3(13)	0.086 0(5)
C(13)	1.023 4(8)	−0.103 7(13)	0.073 4(6)
C(14)	1.012 5(9)	−0.216 9(16)	0.095 9(6)
C(15)	0.961 5(8)	−0.233 7(16)	0.129 5(6)
C(16)	0.917 9(8)	−0.142 4(14)	0.140 7(6)
O(1)	1.055 9(7)	−0.322 6(11)	0.088 9(5)
C(17)	1.115 2(11)	−0.299 1(20)	0.062 9(9)
C(21)	0.700 7(9)	−0.104 1(15)	0.199 9(6)
C(22)	0.724 9(9)	−0.215 8(14)	0.219 5(6)
C(23)	0.673 6(8)	−0.305 9(15)	0.233 2(6)
C(24)	0.604 1(9)	−0.282 5(15)	0.223 1(6)
C(25)	0.576 8(9)	−0.173 4(14)	0.200 4(6)
C(26)	0.625 4(8)	−0.083 9(14)	0.183 8(6)
O(2)	0.562 4(7)	−0.384 6(11)	0.236 8(4)
C(27)	0.486 1(10)	−0.367 5(18)	0.224 6(7)
C(31)	0.669 7(9)	0.250 6(14)	0.050 7(6)
C(32)	0.597 2(8)	0.213 1(14)	0.046 4(6)
C(33)	0.544 8(10)	0.260 9(17)	0.000 1(7)
C(34)	0.569 8(9)	0.336 1(16)	−0.035 5(7)
C(35)	0.641 3(9)	0.362 4(15)	−0.034 7(7)
C(36)	0.690 2(9)	0.317 7(14)	0.009 1(6)
O(3)	0.522 9(7)	0.385 6(11)	−0.082 9(5)
C(37)	0.446 7(10)	0.384 3(17)	−0.079 3(7)
O(1x)	0.638 2(7)	−0.093 0(13)	−0.080 1(5)
C(1x)	0.612 6(11)	0.032 6(23)	−0.087 7(9)
C(2x)	0.640 1(11)	0.089 5(19)	−0.136 4(8)
C(3x)	0.590 9(15)	−0.190 6(27)	−0.114 1(11)
C(4x)	0.610 0(13)	−0.311 6(24)	−0.100 2(10)
O(1y)	0.797 1(7)	−0.244 3(12)	−0.048 6(5)
C(1y1)	0.855 4(19)	−0.202 8(31)	−0.073 6(15)
C(1y2)	0.809 3(29)	−0.260 9(49)	−0.112 4(22)
C(2y)	0.816 4(11)	−0.139 1(20)	−0.129 6(8)
C(3y1)	0.801 6(27)	−0.384 5(46)	−0.015 2(21)
C(3y2)	0.858 4(27)	−0.288 1(46)	−0.004 3(20)
C(4y2)	0.884 7(23)	−0.397 7(51)	−0.004 4(22)
C(4y1)	0.842 2(37)	−0.373 1(62)	0.019 7(24)
Li	0.723 7(16)	−0.119 8(27)	−0.023 6(11)

Table 2 Principal bond lengths (Å) and interbond angles (°) for complex **5**

Zr–Cl(1)	2.607(4)	Zr–Cl(2)	2.509(5)
Zr–N(1)	2.075(10)	Zr–N(2)	2.126(11)
Zr–N(3)	2.026(11)	Cl(1)–Li	2.32(3)
Cl(2)–Li	2.36(3)	Si(4)–C(1)	1.832(16)
Si(4)–Si(1)	2.321(7)	Si(4)–Si(2)	2.343(7)
Si(4)–Si(3)	2.335(6)	Si(1)–C(3)	1.904(17)
Si(1)–C(2)	1.360(14)	Si(2)–C(4)	1.879(16)
Si(1)–N(1)	1.722(11)	Si(2)–N(2)	1.763(11)
Si(2)–C(5)	1.367(14)	Si(3)–C(6)	1.894(15)
Si(3)–C(7)	1.390(17)	Si(3)–N(3)	1.764(12)
Cl(2)–Zr–Cl(1)	80.0(1)	N(1)–Zr–Cl(1)	88.6(3)
N(1)–Zr–Cl(2)	132.0(3)	N(2)–Zr–Cl(1)	165.5(3)
N(2)–Zr–Cl(2)	87.6(3)	N(2)–Zr–N(1)	94.2(4)
N(3)–Zr–Cl(1)	91.0(3)	N(3)–Zr–Cl(2)	118.8(3)
N(3)–Zr–N(1)	107.8(4)	N(3)–Zr–N(2)	101.5(4)
Li–Cl(1)–Zr	94.6(7)	Li–Cl(2)–Zr	96.2(7)
Si(1)–Si(4)–C(1)	117.0(5)	Si(2)–Si(4)–C(1)	115.3(5)
Si(2)–Si(4)–Si(1)	102.4(2)	Si(3)–Si(4)–C(1)	110.7(5)
Si(3)–Si(4)–Si(1)	106.1(2)	Si(3)–Si(4)–Si(2)	104.2(2)
Cl(2)–Zr–Cl(1)	80.0(1)	N(1)–Zr–Cl(1)	88.6(3)
N(1)–Zr–Cl(2)	132.0(3)	N(2)–Zr–Cl(1)	165.5(3)
N(2)–Zr–Cl(2)	87.6(3)	N(2)–Zr–N(1)	94.2(4)
N(3)–Zr–Cl(1)	91.0(3)	N(3)–Zr–Cl(2)	118.8(3)
N(3)–Zr–N(1)	107.8(4)	N(3)–Zr–N(2)	101.5(4)
Li–Cl(1)–Zr	94.6(7)	Li–Cl(2)–Zr	96.2(7)



Scheme 3 Synthesis of the amidotriflates of Ti and Zr. (*i*) AgO_3SCF_3

N(2) is significantly smaller [29.3(2)°] as a consequence of the metal-bound fluorine atom.

Dynamic behaviour of complexes 5–7

As mentioned above, the co-ordination geometry of complexes **5** and **7**, established in the solid state for **5**, bears close resemblence to the postulated transition state of the turnstile rotation.[5] This dynamic model is thought to be responsible for the rapid fluxional processes in solution observed by ^1H and ^{13}C NMR spectroscopy for both complexes **5** and **7** which confer effective three-fold symmetry upon the tripodal ligand unit as well as two-fold symmetry upon the $(Et_2O)_2Li$ unit at ambient temperature. The fact that although some exchange broadening is observed below 200 K, no low-temperature limit may be frozen out indicates the low activation barrier for this process. The observation that **6** displays a very similar dynamic behaviour in solution reflected in the patterns (representing effective three-fold symmetry) of the NMR spectra recorded at ambient temperature indicates that the bonding of the peripheral fluorine atom to the Zr is weak. Upon cleavage of the Zr–F bond a five-co-ordinate (highly fluxional) species is readily formed at room temperature. Unfortunately, the low-temperature limit spectrum of **6** could not be frozen out.

Substitution of the halide ligand in the tripodal amidohalide complexes

Halide abstraction from the titanum and zirconium complexes **2a** and **9** with AgO_3SCF_3 yields the corresponding triflato complexes $[M\{SiMe[SiMe_2N(C_6H_4F\text{-}2)]_3\}(O_3SCF_3)]$ (M = Ti **11** or Zr **12**) (Scheme 3). We previously reported the first example of a structurally characterised titanium amidotriflato complex, $[Ti\{N(CH_2CH_2NEt)_3\}(O_3SCF_3)]$,[8] in which the triflate is directly bonded to the metal. In view of the relatively small differences in the NMR spectral characteristics between **11** and **12** and their halide precursors, this situation is also thought to exist in these compounds. The chemical shifts of the ^{19}F nuclei in the NMR spectra of **11** and **12** indicate direct co-ordination of the fluorine donors to the metal, as noted for the halide complexes. This appears to stabilise the triflato complexes to an extent which enables their isolation as microcrystalline solids. We have not succeeded in the isolation

Table 3 Atomic coordinates (× 10^4) for complex **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zr	7 345(1)	2 599(1)	1 508(1)	O(1)	4 219(1)	3 566(2)	903(1)
Si(3)	7 620(1)	−21(1)	1 062(1)	F(3)	6 066(1)	49(2)	2 164(1)
Si(4)	8 926(1)	446(1)	1 535(1)	O(2)	4 897(1)	5 704(2)	1 515(1)
Cl(1)	6 033(1)	3 065(1)	2 094(1)	C(20)	6 022(2)	733(2)	1 221(1)
Si(1)	9 361(1)	2 078(1)	1 084(1)	C(25)	5 522(2)	901(3)	716(1)
Cl(2)	6 492(1)	3 845(1)	799(1)	C(21)	5 615(2)	219(3)	1 665(1)
Si(2)	8 604(1)	1 043(1)	2 451(1)	C(3)	9 650(3)	1 295(4)	2 868(2)
F(2)	7 814(1)	4 410(1)	1 976(1)	C(6)	7 264(3)	−1 423(3)	1 314(2)
F(1)	8 019(2)	2 810(2)	−157(1)	C(22)	4 766(2)	−145(3)	1 618(2)
N(2)	8 029(2)	2 286(2)	2 316(1)	C(10)	8 395(3)	4 691(4)	−295(2)
N(1)	8 415(2)	2 885(2)	1 013(1)	C(9)	8 309(2)	3 790(3)	67(1)
N(3)	6 910(1)	1 036(2)	1 272(1)	C(11)	8 683(3)	5 690(4)	−74(2)
C(16)	7 942(2)	5 155(3)	2 914(2)	C(24)	4 672(2)	546(3)	665(2)
C(13)	8 812(2)	4 869(3)	858(2)	C(12)	8 894(3)	5 777(4)	494(2)
C(8)	8 511(2)	3 839(3)	651(1)	Li	5 237(3)	4 135(5)	1 352(2)
C(15)	7 938(2)	4 242(3)	2 564(1)	C(29)	3 646(3)	2 774(4)	1 731(2)
C(2)	10 227(3)	2 870(4)	1 501(2)	C(30)	4 026(2)	6 109(3)	1 428(2)
C(14)	8 031(2)	3 136(3)	2 732(1)	C(23)	4 298(2)	28(3)	1 108(2)
C(18)	8 105(2)	3 895(3)	3 700(1)	C(28)	3 468(3)	3 051(4)	1 120(2)
C(7)	9 689(3)	−784(4)	1 537(3)	C(26)	4 069(3)	4 026(4)	334(2)
C(5)	7 657(3)	−82(4)	264(2)	C(32)	5 421(3)	6 574(4)	1 795(2)
C(17)	8 031(2)	4 974(3)	3 501(2)	C(33)	6 294(3)	6 153(4)	1 916(2)
C(4)	7 993(3)	−29(3)	2 853(2)	C(31)	3 916(3)	6 903(4)	936(2)
C(19)	8 107(2)	2 993(3)	3 329(1)	C(27)	3 932(6)	3 171(5)	−120(2)
C(1)	9 791(3)	1 727(4)	370(2)				

Table 4 Principal bond lengths (Å) and interbond angles (°) for complex **6**

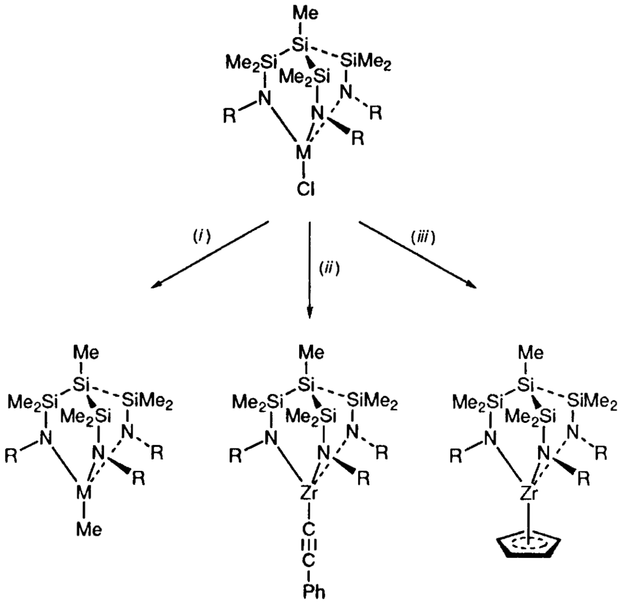
Zr–N(3)	2.049(2)	Cl(2)–Li	2.421(6)	Si(3)–Si(4)	2.324(2)	O(1)–C(28)	1.435(4)
Zr–N(1)	2.103(2)	Si(2)–N(2)	1.752(2)	Si(4)–C(7)	1.887(4)	O(1)–C(26)	1.446(4)
Zr–N(2)	2.148(2)	Si(2)–C(3)	1.874(4)	Si(4)–Si(1)	2.3317(13)	O(1)–Li	1.968(6)
Zr–F(2)	2.511(2)	Si(2)–C(4)	1.875(4)	Si(4)–Si(2)	2.333(2)	F(3)–C(21)	1.343(4)
Zr–Cl(2)	2.5445(12)	F(2)–C(15)	1.391(3)	Cl(1)–Li	2.436(5)	O(2)–C(30)	1.439(4)
Zr–Cl(1)	2.5755(14)	F(1)–C(9)	1.349(4)	Si(1)–N(1)	1.757(3)	O(2)–C(32)	1.453(5)
Si(3)–N(3)	1.763(2)	N(2)–C(14)	1.404(4)	Si(1)–C(2)	1.873(4)	O(2)–Li	1.988(6)
Si(3)–C(5)	1.867(4)	N(1)–C(8)	1.430(4)	Si(1)–C(1)	1.877(4)		
Si(3)–C(6)	1.868(4)	N(3)–C(20)	1.424(4)				
N(3)–Zr–N(1)	104.98(9)	N(1)–Si(1)–Si(4)	103.86(9)	C(6)–Si(3)–Si(4)	109.3(2)	C(9)–C(8)–N(1)	121.6(3)
N(3)–Zr–N(2)	102.66(9)	C(2)–Si(1)–Si(4)	113.8(2)	C(7)–Si(4)–Si(3)	110.3(2)	C(13)–C(8)–N(1)	122.7(3)
N(1)–Zr–N(2)	98.26(10)	C(1)–Si(1)–Si(4)	109.9(2)	C(7)–Si(4)–Si(1)	117.0(2)	C(16)–C(15)–C(14)	126.6(3)
N(3)–Zr–F(2)	169.75(7)	Li–Cl(2)–Zr	98.16(13)	Si(3)–Si(4)–Si(1)	104.58(5)	C(16)–C(15)–F(2)	118.3(3)
N(1)–Zr–F(2)	83.09(8)	N(2)–Si(2)–C(3)	112.1(2)	C(7)–Si(4)–Si(2)	113.6(2)	C(14)–C(15)–F(2)	115.1(2)
N(2)–Zr–F(2)	69.47(7)	N(2)–Si(2)–C(4)	113.6(2)	Si(3)–Si(4)–Si(2)	106.53(5)	C(15)–C(14)–N(2)	119.7(2)
N(3)–Zr–Cl(2)	101.76(7)	C(3)–Si(2)–C(4)	107.2(2)	Si(1)–Si(4)–Si(2)	103.93(5)	C(19)–C(14)–N(2)	126.6(3)
N(1)–Zr–Cl(2)	86.89(8)	N(2)–Si(2)–Si(4)	103.14(9)	Li–Cl(1)–Zr	96.94(14)	C(28)–O(1)–C(26)	113.2(3)
N(2)–Zr–Cl(2)	152.76(7)	C(3)–Si(2)–Si(4)	107.6(2)	N(1)–Si(1)–C(2)	110.2(2)	C(28)–O(1)–Li	127.2(3)
F(2)–Zr–Cl(2)	84.77(5)	C(4)–Si(2)–Si(4)	113.0(2)	N(1)–Si(1)–C(1)	112.0(2)	C(26)–O(1)–Li	116.3(3)
N(3)–Zr–Cl(1)	94.65(7)	C(15)–F(2)–Zr	109.1(2)	C(2)–Si(1)–C(1)	107.1(2)	C(30)–O(2)–C(32)	108.8(3)
N(1)–Zr–Cl(1)	158.14(7)	C(14)–N(2)–Si(2)	120.4(2)	C(30)–O(2)–Li	123.1(3)	F(1)–C(9)–C(8)	118.2(3)
N(2)–Zr–Cl(1)	86.47(8)	C(14)–N(2)–Zr	117.7(2)	C(32)–O(2)–Li	127.7(3)	O(1)–Li–O(2)	102.3(3)
F(2)–Zr–Cl(1)	78.61(5)	Si(2)–N(2)–Zr	121.82(12)	C(21)–C(20)–C(25)	116.2(3)	O(1)–Li–Cl(2)	108.3(2)
Cl(2)–Zr–Cl(1)	79.68(5)	C(8)–N(1)–Si(1)	112.2(2)	C(21)–C(20)–N(3)	122.0(3)	O(2)–Li–Cl(2)	117.8(3)
N(3)–Si(3)–C(5)	111.0(2)	C(8)–N(1)–Zr	124.4(2)	C(25)–C(20)–N(3)	121.8(3)	O(1)–Li–Cl(1)	124.0(3)
N(3)–Si(3)–C(6)	110.6(2)	Si(1)–N(1)–Zr	122.71(13)	F(3)–C(21)–C(20)	118.5(3)	O(2)–Li–Cl(1)	119.1(3)
C(5)–Si(3)–C(6)	107.8(2)	C(20)–N(3)–Si(3)	114.4(2)	F(3)–C(21)–C(22)	118.1(3)	Cl(2)–Li–Cl(1)	85.0(2)
N(3)–Si(3)–Si(4)	103.82(9)	C(20)–N(3)–Zr	123.9(2)	C(20)–C(21)–C(22)	123.4(3)	O(2)–C(30)–C(31)	113.0(4)
C(5)–Si(3)–Si(4)	114.28(14)	Si(3)–N(3)–Zr	121.61(12)	F(1)–C(9)–C(10)	118.6(3)	O(2)–C(32)–C(33)	109.4(3)

of the corresponding complexes containing tripodal amide ligands with an 'inactive' ligand periphery.

The tripodal titanium and zirconium amides may be useful starting materials in the synthesis of organometallic zirconium compounds as exemplified by the synthesis of [M{SiMe(SiMe$_2$NR)$_3$}Me] (M = Ti, R = 4-MeC$_6$H$_4$ **13a** or 2-FC$_6$H$_4$ **13b**; M = Zr, R = 4-MeC$_6$H$_4$ **14a** or 2-FC$_6$H$_4$ **14b**), [Zr{SiMe(SiMe$_2$NR)$_3$}(C$_2$Ph)] (R = 4-MeC$_6$H$_4$ **15a** or 2-FC$_6$H$_4$ **15b**) and [Zr{SiMe(SiMe$_2$NR)$_3$}(η^5-C$_5$H$_5$)] (R = 4-MeC$_6$H$_4$ **16a** or 2-FC$_6$H$_4$ **16b**) (Scheme 4). The observation of ^{19}F–^{13}C coupling in the signals (split as quartets) of the C$_\alpha$ carbons of **13b**–**15b** [^2J(^{19}F–^{13}C) = 3.5, 15.5, 16.7 Hz, respectively] indicates the involvement of the peripheral F atoms in the co-ordination of the ligand to the metal. On the other hand, the absence of such coupling and steric considerations applicable to **16a** and **16b** support the notion that the fluorine atoms are not interacting with the central metal atom.

Conclusion

This study has extended our previous work on trisilylsilane-derived tripodal amide ligands. It has been possible for the first time to isolate five- and six-co-ordinate precursors of the four-



Scheme 4 Synthesis of organo-titanium and -zirconium amido complexes. (*i*) LiMe; (*ii*) Li(C≡CPh); (*iii*) Li[C_5H_5]

co-ordinate target molecules which formally are contact ion pairs of an ether-solvated lithium cation and an anionic amide halide complex, shedding new light upon the way the neutral tripodal complexes are being formed. The co-ordination site at the metal which is not occupied by the polyfunctional ligand may be readily derivatised by substitution with appropriate nucleophiles, and, for example, abstraction with silver trifluoromethanesulfonate generates the reactive triflato complexes. The chemical reactivity of the latter, in particular the use as building blocks in the synthesis of polynuclear complexes containing highly polar metal–metal bonds, is currently being investigated.

Experimental

All manipulations were performed under an inert-gas atmosphere of dried argon in standard (Schlenk) glassware which was flame dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuteriated solvents used for the NMR spectroscopic measurements were degassed by three successive freeze–pump–thaw cycles and dried over 4 Å molecular sieves.

The ^{1}H, ^{13}C, ^{29}Si and ^{19}F NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable-temperature unit (at 200.13, 50.32, 39.76 and 188.31 MHz, respectively) with tetramethylsilane and $CFCl_3$ as references. Infrared spectra were recorded on Perkin-Elmer 1420 and Bruker IRS 25 FT-spectrometers.

Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at Würzburg. The compounds $SiMe(SiMe_2Cl)_3$ and $SiMe[SiMe_2NH(C_6H_4Me\text{-}4)]_3$ **Id** were prepared according to the procedures reported previously, as were complexes **3a**, **3b** and **10**.[4] The arylamines employed in the amide synthesis were distilled before use. All other starting materials were obtained commercially and used without further purification.

Preparations

Tripodal amines. The aminolysis of $SiMe(SiMe_2Cl)_3$ with 2-aminopyridine, 2-fluoroaniline as well as *p*-anisidine, the work-up of the reaction mixtures and isolation of the products was carried out as described previously for related amines.[2b,3b,4]

$SiMe[SiMe_2NH(C_6H_4OMe\text{-}4)]_3$ **Ia**. Yield 75%, m.p. 52 °C. NMR ($CDCl_3$, 295 K): ^{1}H (200 MHz), δ 0.33 (s, $SiCH_3$), 0.37 [s, $Si(CH_3)_2$], 3.71 (s, OCH_3), 6.48 [d, ^3J(HH) = 8.8 Hz, H^2] and 6.69 (d, H^3); ^{13}C-{^{1}H} (50.3 MHz), δ −10.8 ($SiCH_3$), 1.5 [$Si(CH_3)_2$], 55.6 (OCH_3), 114.7 (C^2), 117.2 (C^3), 140.8 (C^4) and 152.1 (C^1). IR (benzene): 3388m, 2935s, 2880m, 2820m, 1628s, 1368s, 1243s (br), 1180s, 1110m, 1035m, 898s, 836m and 775m cm^{-1} (Found: C 57.75; H, 7.90; N, 7.45. Calc. for $C_{28}H_{45}N_3O_3Si_4$: C, 57.60; H, 7.75; N, 7.20%).

$SiMe[SiMe_2NH(2\text{-}C_5H_4N)]_3$ **Ib**. Yield 72%, m.p. 111 °C (decomp.). NMR ($CDCl_3$, 295 K): ^{1}H (200 MHz), δ 0.32 (s, $SiCH_3$), 0.35 [s, $Si(CH_3)_2$], 6.30 [d, ^3J(HH) = 8.4, H^6], 6.53 [ddd, ^3J(HH) = 6.3, H^4], 7.30 [ddd, ^3J(HH) = 7.7, ^4J(HH) = 1.8, H^5] and 8.08 [dd, ^3J(HH) = 5.1, ^4J(HH) = 1.8 Hz, H^3]; ^{13}C-{^{1}H} (50.3 MHz), δ −10.7 ($SiCH_3$), 1.0 [$Si(CH_3)_2$], 110.0 (C^2), 112.7 (C^4), 137.1 (C^3), 148.0 (C^5) and 160.2 (C^6). IR (benzene): 3405m, 2955m, 2900w, 1603vs, 1568m, 1452vs, 1375m, 1320m, 1280w, 1250m, 1150m, 986w, 895m, 835m, 779s, 736m and 650w cm^{-1} (Found: C, 53.40; H, 7.10; N, 17.10. Calc. for $C_{22}H_{36}N_6Si_4$: C, 53.20; H, 7.30; N, 16.90).

$SiMe[SiMe_2NH(C_6H_4F\text{-}2)]_3$ **Ic**. Yield 53%, m.p. 51 °C. NMR (C_6D_6, 295 K): ^{1}H (200 MHz), δ 0.27 [s, $Si(CH_3)_2$], 0.34 (s, $SiCH_3$) and 6.42–6.87 (m, aromatic protons); ^{13}C-{^{1}H} (50.3 MHz), δ −10.2 ($SiCH_3$), 1.3 [$Si(CH_3)_2$], 115.3 (C^5), 117.1 (C^6), 118.3 (C^3), 124.6 (C^4), 136.0 (C^1) and 153.3 [d, ^1J(CF) = 237.2 Hz, C^2]; ^{19}F-{^{1}H} (188.3 MHz), δ −134.9. IR (pentane): 3405m, 3050w, 1612s, 1305s, 1243s, 1205m, 1184m, 1094m, 899m and 831m cm^{-1} (Found: C, 55.05; H, 6.50; N, 7.55. Calc. for $C_{25}H_{36}F_3N_3Si_4$: C, 54.80; H, 6.60; N, 7.65).

Tripodal amidotitanium complexes. To a solution of $SiMe(SiMe_2NHR)_3$ **Ia**–**Ic** (3.17 mmol) in pentane (45 cm^3) and diethyl ether (5 cm^3) was added *n*-butyllithium (3.88 cm^3 of 2.5 mol dm^{-3} solution in hexanes, 9.49 mmol) at −50 °C. The mixture was warmed to 0 °C and stirred at this temperature for 1 h. After cooling to −70 °C, [$TiX_4(thf)_2$] (X = Cl or Br) (3.17 mmol) was added to the stirred solution. After warming to room temperature the mixture was stirred for 72 h, the LiX generated was then filtered off through a G3 frit and the filtrate concentrated to *ca.* 10 cm^3. Storage of the solution at −30 °C for several days led to crystallisation of the products which were filtered off.

[Ti{$SiMe[SiMe_2N(C_6H_4OMe\text{-}4)]_3$}Cl] **1**. Yield 25%, m.p. 54 °C. NMR (C_6D_6, 295 K): ^{1}H (200 MHz), δ 0.24 (s, $SiCH_3$), 0.50 [s, $Si(CH_3)_2$], 3.25 (s, OCH_3), 6.78 [d, ^3J(HH) = 8.8 Hz, H^2] and 7.09 (d, H^3); ^{13}C-{^{1}H} (50.3 MHz), δ −13.8 ($SiCH_3$), 2.1 [$Si(CH_3)_2$], 54.9 (OCH_3), 114.9 (C^2), 125.3 (C^3), 142.8 (C^4) and 157.2 (C^1). IR (benzene): 3039m, 2983w, 2921w, 1563s, 1551s, 1496m, 1303s, 1298s, 946s, 906s, 882s, 813s, 778s and 762m cm^{-1} (Found: C, 50.95; H, 6.50; N, 6.60. Calc. for $C_{28}H_{42}ClN_3O_3Si_4Ti$: C, 50.60; H, 6.35; N, 6.35%).

[Ti{$SiMe[SiMe_2N(C_6H_4F\text{-}2)]_3$}Cl] **2a**. Yield 53%, m.p. 51 °C. NMR (C_6D_6, 295 K): ^{1}H (200 MHz), δ 0.73 [s, $Si(CH_3)_2$], 0.76 (s, $SiCH_3$) and 6.99–7.30 (m, aromatic protons); ^{13}C-{^{1}H} (50.3 MHz), δ −14.4 ($SiCH_3$), 1.7 [$Si(CH_3)_2$], 115.3 (C^3), 124.6 (C^6), 125.6 (C^4), 126.0 (C^5), 136.4 (C^1) and 154.8 [d, ^1J(CF) = 241.0 Hz, C^2]; ^{19}F-{^{1}H} (188.3 MHz), δ −119.6. IR (benzene): 2947w, 2890w, 1610m, 1498s, 1447w, 1383w, 1305m, 1242s, 1183m, 1095m, 882s, 830s, 743m and 704m cm^{-1} (Found: C, 47.60; H, 5.50; N, 6.95. Calc. for $C_{25}H_{33}ClF_3N_3Si_4Ti$: C, 47.80; H, 5.30; N, 6.70%).

[Ti{$SiMe[SiMe_2N(C_6H_4F\text{-}2)]_3$}Br] **2b**. Yield 52%. NMR (C_6D_6, 295 K): ^{1}H (200 MHz), δ 0.16 (s, $SiCH_3$), 0.51 [s, $Si(CH_3)_2$] and 6.62–7.52 (m, aromatic protons); ^{13}C-{^{1}H} (50.3 MHz), δ −14.2 ($SiCH_3$), 1.7 [$Si(CH_3)_2$], 116.4 (C^3), 124.6 (C^6), 125.9 (C^4), 126.5 (C^5), 137.6 (C^1) and 154.8 [d, ^1J(CF) = 242.2 Hz, C^2]; ^{19}F-{^{1}H} (188.3 MHz), δ −119.2. IR (benzene): 2943m, 2885m, 1609m, 1594m, 1566w, 1497s, 1444m, 1396m, 1240s, 1181s, 1095s, 930m, 889s (br), 825s (br), 748s, 700m and

614m cm^{-1} (Found: C, 44.85; H, 5.10; N, 6.40. Calc. for $C_{25}H_{33}BrF_3N_3Si_4Ti$: C, 44.65; H, 4.95; N, 6.25%).

Complexes 4, 8 and 9. To a solution of $SiMe(SiMe_2NHR)_3$ (1.69 mmol) in diethyl ether (20 cm^3) at −70 °C was added *n*-butyllithium (2.03 cm^3 of a 2.5 mol dm^{-3} solution in hexanes, 5.07 mmol). The mixture was warmed to room temperature, stirred for 2 h and then recooled to −70 °C. Solid $ZrCl_4$ (2.00 mmol, 0.480 g) was added and the solution was warmed to room temperature over a period of 12 h and then evaporated to dryness. The residue was extracted with toluene (20 cm^3), the LiCl filtered off, the filtrate concentrated to 5 cm^3 and stored at −30 °C to yield bright yellow (**4**) or pale yellow (**8–10**) crystals of the zirconium complex. The solid product was filtered off and dried *in vacuo*.

$[Zr\{SiMe[SiMe_2N(2\text{-}C_5H_4N)]_3\}Cl]$ **4**. Yield 39%, m.p. 112 °C (decomp.). NMR (C_6D_6, 295 K): ^1H (200 MHz), δ 0.16 (s, $SiCH_3$), 0.44 [s, $Si(CH_3)_2$], 6.03 [ddd, $^2J(HH)$ = 6.9, $^2J(HH)$ = 5.3,$^3J(HH)$ = 0.8,H^4],6.13[dd,$^2J(HH)$ = 9.2,H^6], 6.86 [ddd, $^3J(HH)$ = 2.1, H^3] and 7.65 [ddd, $^4J(HH)$ = 1.1 Hz, H^5]; $^{13}C\text{-}\{^1H\}$ (50.3 MHz), δ −14.6 ($SiCH_3$), 2.4 [$Si(CH_3)_2$], 111.6 (C^2), 113.4 (C^4), 140.2 (C^3) 142.8 (C^5) and 169.3 (C^1). IR (benzene): 3045w, 2892m, 2827w, 1626s, 1594w, 1566m, 1478s, 1463s, 1391w, 1324s, 1264s, 1171m, 1132m, 1049m, 1032s, 964s, 912m, 845s, 794s, 754m, 706w and 657m cm^{-1} (Found: C, 42.25; H, 5.20; N, 13.70. Calc. for $C_{22}H_{33}ClN_6Si_4Zr$: C, 42.60; H, 5.35; N, 13.55%).

$[Zr\{SiMe[SiMe_2N(C_6H_4OMe\text{-}4)]_3\}Cl]$ **8**. Yield 22%, m.p. 70 °C (decomp.). NMR (C_6D_6, 295 K): ^1H (200 MHz), δ 0.27 (s, $SiCH_3$), 0.49 [s, $Si(CH_3)_2$], 3.24 (s, OCH_3), 6.77 [d, $^3J(HH)$ = 8.6 Hz, H^2] and 7.05 (d, H^3); $^{13}C\text{-}\{^1H\}$ (50.3 MHz), δ −15.7 ($SiCH_3$), 1.9 [$Si(CH_3)_2$], 54.9 (OCH_3), 115.5 (C^2), 127.3 (C^3), 138.6 (C^4) and 157.2 (C^1). IR (benzene): 2990w, 2954m, 2895w, 2834w, 1615m, 1583w, 1501s, 1472m, 1446m, 1372w, 1286m, 1248s, 1226s, 1187m, 1109m, 1043s, 938m, 907s, 856s, 832s, 785s, 748m, 717m and 662w cm^{-1} (Found: C, 47.85; H, 5.90; N, 5.90. Calc. for $C_{28}H_{42}ClN_3O_3Si_4Zr$: C, 47.50; H, 6.00; N, 5.95%).

$[Zr\{SiMe[SiMe_2N(C_6H_4F\text{-}2)]_3\}Cl]$ **9**. Yield 51%, m.p. 94 °C (decomp.). NMR (C_6D_6, 295 K): ^1H (200 MHz), δ 0.19 (s, $SiCH_3$), 0.45 [s, $Si(CH_3)_2$] and 6.48–6.80 (m, aromatic protons); $^{13}C\text{-}\{^1H\}$ (50.3 MHz), δ −16.2 ($SiCH_3$), 1.5 [$Si(CH_3)_2$], 114.9 (m, C^3), 121.6 (m, C^6), 123.2 (C^4), 125.5 (C^5), 139.3 (m, C^1) and 158.4 [d, $^1J(FC)$ = 227 Hz, C^2]; $^{19}F\text{-}\{^1H\}$ (188.3 MHz), δ −121.2. IR (toluene): 2820w, 1617m, 1493w, 1486m, 1447m, 1298m, 1271s, 1246s, 1183m, 1145w, 1092s, 1030w, 936m, 917s, 887s, 822s, 782s, 732m, 685m, 651m and 617w cm^{-1} (Found: C, 44.30; H, 5.00; N, 6.35. Calc. for $C_{25}H_{33}ClF_3N_3Si_4Zr$: C, 44.70; H, 4.95; N, 6.25%).

Complexes 5–7. To a solution of $SiMe(SiMe_2NHR)_3$ (R = 4-MeC_6H_4, 2-FC_6H_4 or 4-$MeOC_6H_4$) (2.00 mmol) in diethyl ether (75 cm^3) was added *n*-butyllithium (2.40 cm^3 of 2.5 mol dm^{-3} solution in hexanes, 6.00 mmol) at −50 °C. The mixture was warmed to room temperature and stirred for 1 h, recooled to −70 °C after which $ZrCl_4$ (2.20 mmol, 0.512 g) was added. After warming to room temperature the mixture was stirred for 10 h, the LiCl generated was filtered off through a G3 frit and the filtrate concentrated to *ca.* 10 cm^3. Storage at −30 °C for several days led to crystallisation of the reaction products **5–7** which were filtered off. The supernatant solution mainly contained complexes **8–10** which were isolated as described above.

$[\{(4\text{-}MeOC_6H_4NSiMe_2)_3MeSi\}ZrCl_2Li(OEt_2)_2]$ **5**. Yield 16%. NMR (C_6D_6, 295 K): ^1H (200 MHz), δ 0.28 (s, $SiCH_3$), 0.50 [s, $Si(CH_3)_2$], 1.10 {t, $^3J(HH)$ = 6.9, $Li[O(CH_2C\mathit{H}_3)_2]_2$}, 3.22 {q, $Li[O(C\mathit{H}_2CH_3)_2]_2$}, 3.28 (s, OCH_3), 6.80 [d, $^3J(HH)$ = 8.7, H^2] and 7.06 (d, H^3); $^7Li\text{-}\{^1H\}$ (77.8 MHz), δ −2.70 (Found: C, 48.90; H, 6.85; N, 4.80. Calc. for $C_{36}H_{62}Cl_2LiN_3O_5Si_4Zr$: C, 48.15; H, 6.95; N, 4.70%).

$[\{(2\text{-}FC_6H_4NSiMe_2)_3MeSi\}ZrCl_2Li(OEt_2)_2]$ **6**. Yield 36%. NMR (C_6D_6, 295 K): ^1H (200 MHz), δ 0.19 ($SiCH_3$), 0.46 [$Si(CH_3)_2$], 1.09 {s, br, $Li[O(CH_2C\mathit{H}_3)_2]_2$}, 3.25 {s, br, $Li[O(C\mathit{H}_2CH_3)_2]_2$} and 6.46–6.89 (m, aromatic protons); $^{13}C\text{-}\{^1H\}$ (50.3 MHz), δ −16.7 ($SiCH_3$), 1.5 [$Si(CH_3)_2$], 15.1 {$Li[O(CH_2\mathit{C}H_3)_2]_2$}, 66.0 {$Li[O(\mathit{C}H_2CH_3)_2]_2$}, 115.1 (m, C^3), 121.6 (m, C^6), 123.2 (C^4), 125.4 (C^5), 139.2 (m, C^1) and 158.3 [d, $^1J(FC)$ = 224 Hz, C^2]; $^7Li\text{-}\{^1H\}$ (77.8 MHz), δ −2.0; $^{19}F\text{-}\{^1H\}$ (188.3 MHz), δ −121.1; $^{29}Si\text{-}\{^1H\}$ (39.7 MHz), δ −3.0 [$Si(CH_3)_2$] and −99.3 ($SiCH_3$) (Found: C, 45.85; H, 6.30; N, 4.90. Calc. for $C_{33}H_{53}Cl_2F_3LiN_3O_2Si_4Zr$: C, 45.95; H, 6.20; N, 4.85%).

$[\{(4\text{-}MeC_6H_4NSiMe_2)_3MeSi\}ZrCl_2Li(OEt_2)_2]$ **7**. Yield 26%. NMR (C_6D_6, 295 K): ^1H (200 MHz), δ 0.24 ($SiCH_3$), 0.48 [$Si(CH_3)_2$], 0.98 {t, $^3J(HH)$ = 6.8, $Li[O(CH_2C\mathit{H}_3)_2]_2$}, 2.05 ($C\mathit{H}_3C_6H_4$), 3.23 {q, $Li[O(C\mathit{H}_2CH_3)_2]_2$}, 6.96 [d, $^3J(HH)$ = 7.1 Hz, H^2] and 7.06 (d, H^3); $^{13}C\text{-}\{^1H\}$ (50.3 MHz), δ −15.8 ($SiCH_3$), 1.9 [$Si(CH_3)_2$], 15.0 {$Li[O(CH_2\mathit{C}H_3)_2]_2$}, 20.8 ($\mathit{C}H_3C_6H_4$), 65.8 {$Li[O(\mathit{C}H_2CH_3)_2]_2$}, 126.1 ($C^2$), 130.7 ($C^4$), 133.5 ($C^3$) and 143.7 ($C^1$); $^7Li\text{-}\{^1H\}$ (77.8 MHz), δ −2.28; $^{29}Si\text{-}\{^1H\}$ (39.7 MHz), δ −2.6 [$Si(CH_3)_2$] (the resonance of the apical Si was not observed) (Found: C, 51.00; H, 7.40; N, 4.90. Calc. for $C_{36}H_{62}Cl_2LiN_3O_2Si_4Zr$: C, 50.85; H, 7.35; N, 4.95%).

Conversion of complexes 5–7 into 8–10. *Method A.* A suspension of complex **5**, **6** or **7** (1.23 mmol) in toluene (25 cm^3) was stirred at 35 °C for 24 h. The mixture was cooled to room temperature and filtered through a G3 frit. The filtrate was concentrated to *ca.* 10 cm^3 and stored for several days at −30 °C to yield pale yellow crystals of **8**, **9** or **10** which were filtered off and dried *in vacuo*.

Method B. To a suspension of complex **5**, **6** or **7** (0.25 mmol) in benzene (20 cm^3) was added $AgBPh_4$ (0.25 mmol, 106 mg). After stirring at room temperature for 30 min the mixture was filtered through a G3 frit and the solvent removed *in vacuo*. Complexes **8–10** were isolated as pale yellow solids in quantitative yield.

Complexes 11 and 12. Solid $[M\{SiMe[SiMe_2N(C_6H_4F\text{-}2)]_3\}Cl]$ (M = Ti or Zr) (1.0 mmol) and solid AgO_3SCF_3 (1.0 mmol) were weighed in a Schlenk tube. To the mixture C_6H_6 (10 cm^3) was added with the aid of a cannula at room temperature. The reaction mixture was stirred for 30 min, the AgCl formed was filtered off through a G3 frit and the filtrate evaporated to dryness. The analytically pure but exceedingly moisture-sensitive triflato complexes remained as yellow (**11**) or colourless (**12**) residues. The yields were quantitative.

$[Ti\{SiMe[SiMe_2N(C_6H_4F\text{-}2)]_3\}(O_3SCF_3)]$ **11**. NMR (C_6D_6, 295 K): ^1H (200 MHz), δ 0.16 (s, $SiCH_3$), 0.43 [s, $Si(CH_3)_2$] and 6.61–7.05 (m, aromatic protons); $^{13}C\text{-}\{^1H\}$ (50.3 MHz), δ −14.0 ($SiCH_3$), 1.6 [$Si(CH_3)_2$], 116.4 (C^3), 122.3 [d, $^1J(FC)$ =263.5, CF_3], 123.2 (C^6), 125.4 (C^4), 126.0 (C^5), 136.5 (m, C^1) and 154.6 [d, $^1J(CF)$ = 239.4 Hz, C^2]; $^{19}F\text{-}\{^1H\}$ (188.3 MHz), δ −74.4 (CF_3) and −118.1 (2-FC_6H_4). IR (benzene): 2950w, 1605w, 1505m, 1480s, 1376m, 1303m, 1245s, 1200s, 1155m, 1100m, 1025m, 980s, 938m, 898s, 833s, 752m, 708m and 635s cm^{-1} (Found: C, 42.80; H, 4.90; N, 5.70. Calc. for $C_{26}H_{33}F_6N_3O_3SSi_4Ti$: C, 42.10; H, 4.50; N, 5.65%).

$[Zr\{SiMe[SiMe_2N(C_6H_4F\text{-}2)]_3\}(O_3SCF_3)]$ **12**. NMR (C_6D_6, 295 K): ^1H (200 MHz), δ 0.17 (s, $SiCH_3$), 0.41 [s, $Si(CH_3)_2$] and 6.80–6.95 (m, aromatic protons); $^{13}C\text{-}\{^1H\}$ (50.3 MHz), δ −16.2 ($SiCH_3$), 1.4 [$Si(CH_3)_2$], 115.4 (m, C^3), 124.4 (m, C^6), 125.2 [d, $^1J(FC)$ = 245, CF_3], 125.4 (C^4), 128.3 (C^5), 137.9 (m, C^1) and 158.6 [d, $^1J(FC)$ = 228 Hz, C^2]; $^{19}F\text{-}\{^1H\}$ (188.3 MHz), δ −77.42 (CF_3) and −121.89 (2-FC_6H_4). IR (toluene): 2882w, 1612m, 1589m, 1473s, 1394s, 1299s, 1241s, 1203s, 1147m, 1089m, 1075m, 1031s, 932m, 834s, 764s and 647s cm^{-1} (Found: C, 40.00; H, 4.30; N, 5.40. Calc. for $C_{26}H_{33}F_6N_3O_3SSi_4Zr$: C, 39.75; H, 4.25, N, 5.35%).

Complexes 13a, 13b, 14a and 14b. To a solution of [M{SiMe(SiMe$_2$NR)$_3$}Cl] (M = Ti or Zr; R = 4-MeC$_6$H$_4$ or 2-FC$_6$H$_4$) (1.72 mmol) in diethyl ether (25 cm^3) was added methyllithium (2.03 cm^3 of a 1.6 mol dm^{-3} solution in diethyl ether, 1.72 mmol) at −78 °C. After warming to room temperature, stirring was continued for 30 min. The LiCl formed was filtered off through a G3 frit and the filtrate evaporated to dryness leaving a yellow (**13a, 13b**) or pale yellow (**14a, 14b**) residue.

[Ti{SiMe[SiMe$_2$N(C$_6$H$_4$Me-4)]$_3$}Me] **13a**. Yield 91%. NMR (C$_6$D$_6$, 295 K): ^{1}H (200 MHz), δ 0.18 (s, SiCH$_3$), 0.49 [s, Si(CH$_3$)$_2$], 0.87 (s, TiCH$_3$), 2.07 (s, 4-*C*H$_3$C$_6$H$_4$), 6.99 [d, ^3J(HH) = 7.6 Hz, H^2] and 7.17 (d, H^3); ^{13}C-{^{1}H} (50.3 MHz), δ −14.9 (SiCH$_3$), 1.8 [Si(CH$_3$)$_2$], 20.8 (4-*C*H$_3$C$_6$H$_4$), 74.6 (TiCH$_3$), 125.4 (C^4), 130.4 (C^2), 132.7 (C^3) and 146.4 (C^1); ^{29}Si-{^{1}H} (39.7 MHz), δ −97.7 (SiCH$_3$) and −1.2 [Si(CH$_3$)$_2$]. IR (pentane): 3010w, 1493s, 1235s, 1215s, 1123m, 938m, 895s, 850s, 795m, 783m and 705m cm^{-1} (Found: C, 58.65; H, 7.80; N, 7.30. Calc. for C$_{29}$H$_{45}$N$_3$Si$_4$Ti: C, 58.45; H, 7.60; N, 7.05%).

[Ti{SiMe[SiMe$_2$N(C$_6$H$_4$F-2)]$_3$}Me] **13b**. Yield 71%, m.p. 92 °C. NMR (C$_6$D$_6$, 295 K): ^{1}H (200 MHz), δ 0.15 (s, SiCH$_3$), 0.50 [s, Si(CH$_3$)$_2$], 1.08 [q, ^3J(HF) = 2.2, TiCH$_3$] and 6.61–7.37 (m, aromatic protons); ^{13}C-{^{1}H} (50.3 MHz), δ −15.1 (SiCH$_3$), 1.6 [Si(CH$_3$)$_2$], 77.2 [q, ^3J(CF) = 3.5, TiCH$_3$], 116.5 (m, C^3), 124.2 (m, C^6), 124.7 (C^4), 126.5 (C^5), 138.0 (C^1) and 156.3 [d, ^1J(CF) = 241.3 Hz, C^2]; ^{19}F-{^{1}H} (188.3 MHz), δ −120.8 (2-FC$_6$H$_4$). IR (benzene): 2960w, 1626m, 1498s, 1300m, 1247m, 1202m, 893m, 834m, 772m, 742s and 648m cm^{-1} (Found: C 51.55; H, 6.15; N, 7.10. Calc for C$_{26}$H$_{36}$F$_3$N$_3$Si$_4$Ti: C 51.40; H, 5.95 N, 6.90%).

[Zr{SiMe[SiMe$_2$N(C$_6$H$_4$Me-4)]$_3$}Me] **14a**. Yield 93%. NMR (C$_6$D$_6$, 295 K): ^{1}H (200 MHz), δ 0.26 (s, SiCH$_3$), 0.49 (s, ZrCH$_3$), 0.51 [s, Si(CH$_3$)$_2$], 2.05 (s, *C*H$_3$C$_6$H$_4$), 6.96 [d, ^3J(HH) = 7.6 Hz, H^2] and 7.05 (d, H^3); ^{13}C-{^{1}H} (50.3 MHz), δ −16.2 (SiCH$_3$), 1.9 [Si(CH$_3$)$_2$], 20.8 (*C*H$_3$C$_6$H$_4$), 126.8 (C^4), 130.9 (C^2), 132.9 (C^3) and 142.3 (C^1) (Found: C, 54.20; H, 7.00; N, 6.45. Calc. for C$_{29}$H$_{45}$N$_3$Si$_4$Zr: C, 54.50; H, 7.10; N, 6.55%).

[Zr{SiMe[SiMe$_2$N(C$_6$H$_4$F-2)]$_3$}Me] **14b**. Yield 92%. NMR (C$_6$D$_6$, 295 K): ^{1}H (200 MHz), δ 0.19 (s, SiCH$_3$), 0.48 [s, Si(CH$_3$)$_2$], 0.58 [q, ^3J(HF) = 7.8 Hz, ZrCH$_3$] and 6.48–6.87 (m, aromatic protons); ^{13}C-{^{1}H} (50.3 MHz), δ −15.7 (SiCH$_3$), 1.5 [Si(CH$_3$)$_2$], 50.6 [q, ^3J(CF) = 15.5], 114.3 (m, C^3), 120.8 (m, C^6), 125.5 (C^4), 127.6 (C^5), 139.1 (m, C^1) and 158.6 [d, ^1J(FC) = 229 Hz, C^2]; ^{19}F{^{1}H} (188.3 MHz), δ −124.16 (Found: C, 47.65; H, 5.35; N, 6.35. Calc. for C$_{26}$H$_{36}$F$_3$N$_3$Si$_4$Zr: C, 47.95; H, 5.55; N, 6.45%).

Complexes 15a and 15b. Solid [Zr{SiMe(SiMe$_2$NR)$_3$}Cl] (1.23 mmol) and solid Li(C≡CPh) (1.23 mmol) were weighed in a Schlenk tube. Diethyl ether (20 cm^3) was added with the aid of a cannula at room temperature. The reaction mixture was stirred for 30 min, the LiCl formed was filtered off through a G3 frit and the filtrate evaporated to dryness to yield a yellow solid.

[Zr{SiMe[SiMe$_2$N(C$_6$H$_4$Me-4)]$_3$(C≡CPh)] **15a**. Yield 96%. NMR (C$_6$D$_6$, 295 K): ^{1}H (200 MHz), δ 0.28 (s, SiCH$_3$), 0.53 [s, Si(CH$_3$)$_2$] 2.05 (s, C*H*$_3$C$_6$H$_4$), 6.77 (s, br, Ph), 6.97 [d, ^3J(HH) = 8.4 Hz, H^2] and 7.08 (d, H^3); ^{13}C-{^{1}H} (50.3 MHz), δ −15.4 (SiCH$_3$), 2.5 [Si(CH$_3$)$_2$], 20.9 (*C*H$_3$C$_6$H$_4$), 113.5 (ZrC≡*C*Ph), 125.0 (C^1 of Ph), 125.3 (C^4 of Ph), 127.2 (C^2 of tolyl), 127.5 (C^3 of Ph), 129.6 (C^3 of tolyl), 130.1 (C^2 of Ph), 133.2 (C^4 of tolyl), 146.9 (Zr*C*≡CPh) and 149.6 (C^1 of tolyl) (Found: C, 59.25; H, 6.50; N, 5.85. Calc. for C$_{36}$H$_{47}$N$_3$Si$_4$Zr: C, 59.60; H, 6.55; N, 5.80%).

[Zr{SiMe[SiMe$_2$N(C$_6$H$_4$F-2)]$_3$}(C≡CPh)] **15b**. Yield 94%. NMR (C$_6$D$_6$, 295 K): ^{1}H (200 MHz), δ 0.23 (s, SiCH$_3$), 0.50 [s, Si(CH$_3$)$_2$] and 6.48–6.98 (m, aromatic protons); ^{13}C-{^{1}H} (50.3 MHz), δ −16.0 (SiCH$_3$), 1.7 [Si(CH$_3$)$_2$], 99.3 (ZrC≡*C*Ph), 114.9 (m, C^3 of FC$_6$H$_4$), 121.3 (m, C^6 of FC$_6$H$_4$), 123.6 (C^4 of FC$_6$H$_4$), 124.3 (C^1 of Ph), 125.4 (C^5 of FC$_6$H$_4$), 127.2 (C^4 of Ph), 127.6 (C^3 of Ph), 132.62 (C^2 of Ph), 138.2 (m, C^1 of FC$_6$H$_4$), 147.8 [q, J(FC) = 16.7, Zr*C*≡CPh] and 158.8 [d, ^1J(FC) = 229 Hz, C^2 of FC$_6$H$_4$]; ^{19}F-{^{1}H} (188.3 MHz), δ −122.24 (Found: C, 53.55; H, 5.05; N, 5.75. Calc. for C$_{33}$H$_{38}$F$_3$N$_3$Si$_4$Zr: C, 53.75; H, 5.20; N, 5.70%).

Complexes 16a and 16b. Solid [Zr{SiMe(SiMe$_2$NR)$_3$}Cl] (1.0 mmol) and solid Li[C$_5$H$_5$] (1.0 mmol) were weighed in a Schlenk tube. Benzene (10 cm^3) was added with the aid of a cannula at room temperature. The mixture was stirred for 30 min, the LiCl formed was filtered off through a G3 frit and the filtrate evaporated to dryness. The analytically pure, only moderately air and moisture-sensitive cyclopentadienide complexes remained as colourless residues. The yields were quantitative.

[Zr{SiMe[SiMe$_2$N(C$_6$H$_4$Me-4)]$_3$}(η^5-C$_5$H$_5$)] **16a**. NMR (C$_6$D$_6$, 295 K): ^{1}H (200 MHz), δ 0.24 (s, SiCH$_3$), 0.40 [s, Si(CH$_3$)$_2$], 2.20 (s, 4-C*H*$_3$C$_6$H$_4$), 5.57 (s, C$_5$H$_5$), 6.90 [d, ^3J(HH) = 8.2 Hz, H^2] and 7.05 (d, H^3); ^{13}C-{^{1}H} (50.3 MHz), δ −16.0 (SiCH$_3$), 2.3 [Si(CH$_3$)$_2$], 20.8 (4-*C*H$_3$C$_6$H$_4$), 116.4 (C$_5$H$_5$), 126.4 (C^2), 129.6 (C^3), 131.1 (C^4) and 154.6 (C^1). IR (benzene): 3024w, 2962m, 2921w, 2901w, 1621w, 1527m, 1497s, 1446w, 1376w, 1287w, 1239m, 1218s, 1174m, 1109m, 1026m, 947m, 892s, 871s, 854s, 825s (br), 789m, 742m and 711m cm^{-1} (Found: C, 57.60; H, 6.90; N, 6.20. Calc. for C$_{33}$H$_{47}$N$_3$Si$_4$Zr: C, 57.50; H, 6.85; N, 6.10%).

[Zr{SiMe[SiMe$_2$N(C$_6$H$_4$F-2)]$_3$}(η^5-C$_5$H$_5$)] **16b**. NMR (C$_6$D$_6$, 295 K): ^{1}H (200 MHz) δ 0.21 (s, SiCH$_3$), 0.42 [s, Si(CH$_3$)$_2$], 5.43 (m, C$_5$H$_5$) and 6.42–6.91 (m, aromatic protons); ^{13}C-{^{1}H} (50.3 MHz), δ −16.8 (SiCH$_3$), 2.3 [Si(CH$_3$)$_2$], 106.3 (C$_5$H$_5$), 115.3 (m, C^3), 124.1 (m, C^6), 124.8 (C^4), 125.9 (C^5), 137.2 (m, C^1) and 158.0 [d, ^1J(FC) = 223 Hz, C^2]; ^{19}F-{^{1}H} (188.3 MHz), δ −122.7 (Found: C, 51.10; H, 5.40; N, 5.95. Calc. for C$_{30}$H$_{38}$F$_3$N$_3$Si$_4$Zr: C, 51.40; H, 5.45; N, 6.00%).

Crystallography

The clear colourless, block-shaped crystals of complexes **5** and **6** were mounted under argon in Lindemann capillaries. Data collection for **5** in the range θ 3–25° with a scan width of 0.80° was carried out at 293 K using a Philips PW110 diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å) employing techniques described previously.^{9} Data for **6** were collected at 223 K with an Enraf-Nonius CAD4 diffractometer and Mo-Kα radiation. Unit-cell parameters were determined by least-squares analysis of 25 automatically centred reflections in the range of 10 < θ < 15°. Data were collected in the range θ = 3–25°.

Crystal data. C$_{36}$H$_{62}$Cl$_2$LiN$_3$O$_5$Si$_4$Zr **5**, M = 898.8, monoclinic, space group $P2_1/c$, a = 18.574(4), b = 10.840(3), c = 24.313(5) Å, β = 99.35(3)°, U = 4830.25 Å^3, Z = 4, F(000) = 1888, D_c = 1.235 g cm^{-3}, μ(Mo-Kα) = 0.45 mm^{-1}, 2319 unique reflections [$I/\sigma(I)$ > 3].

C$_{33}$H$_{53}$Cl$_2$F$_3$LiN$_3$O$_2$Si$_4$Zr **6**, M = 862.2, monoclinic, space group $P2_1/c$, a = 15.537(9), b = 11.925(2), c = 23.374(15) Å, β = 93.08(3)°, U = 4324.96 Å^3, Z = 4, F(000) = 1792, D_c = 1.325 g cm^{-3}, μ(Mo-Kα) = 0.53 mm^{-1}, 7160 unique reflections [$I/\sigma(I)$ > 3].

Structure solution and refinement were carried out with the programs SHELX 76^{10} (**5**) and SHELXS 86/SHELXL 93^{11} (**6**). For **6** the coordinates of the zirconium and one chlorine atom were deduced from a Patterson synthesis. The remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. Extended regions of electron density were observed in the vicinity of one diethyl ether molecule of the complex and were resolved into two sites of equal occupancy for three of the four carbons. A Fourier-difference-synthesis calculated using low-angle data (sin θ < 0.35) revealed the positions of ten methyl hydrogen atoms. The remaining hydrogens of the amide ligand were included in idealised positions (C–H 1.08 Å) and all hydrogens were assigned a fixed thermal parameter of $U = 0.10$ Å^2. They were included in the structure-factor calculations although their positions were not refined. After refinement with isotropic thermal parameters for all non-hydrogen atoms an empirical absorption correction[12] (maximum 1.066, minimum 0.885) was applied. Individual weights of $1/\sigma^2(F)$ were assigned to each reflection and in the final cycles of full-matrix least-squares refinement, anisotropic thermal parameters were assigned to the zirconium, nitrogen and silicon atoms. Refinement converged at $R = 0.0678$ and $R' = 0.0648$ for 271 parameters.

For complex **6** the coordinates of the zirconium atom were obtained by the Patterson method and the remaining non-hydrogen atoms located from Fourier-difference-syntheses. The positions of all the C-bound hydrogen atoms were located in electron-density difference maps, and the data allowed their isotropic refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters and full-matrix least-squares refinement converged at $R_1 = 0.0312$, $wR_2 = 0.0783$ for 654 parameters.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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