DALTON

Synthesis and structure of zirconium(IV) alkyl complexes with bi-, tri-, tetra- and penta-dentate amido ligands†

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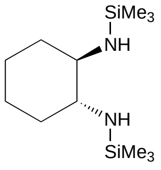
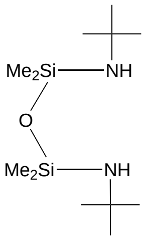
The reaction of $C_6H_{10}(NLiSiMe_3)_2$-1,2 (Li_2L^1) with $[ZrCl_4(thf)_2]$ (thf = tetrahydrofuran) afforded the tetraamide $[ZrL^1{}_2]$ **1**. Similarly treatment of $(RHNSiMe_2)_2O$ (H_2L^2, R = Bu^t; H_2L^3, R = cyclohexyl) with LiBu^n followed by $[ZrCl_4(thf)_2]$ led to $[ZrL^2{}_2]$ **2** and $[ZrL^3{}_2]$ **3**, respectively. Reaction of $Zr(CH_2Ph)_4$ with H_2L^3 gave the pale yellow zirconium dibenzyl compound $[Zr(CH_2Ph)_2L^3]$ **4**, while the analogous reaction with H_2L^4 (R = quinolin-8-yl) led to ruby-red $[Zr(CH_2Ph)_2L^4]$ **5**. In addition the bis(pyrrole) $[(2\text{-}C_4H_3NH)CH{=}NCH_2]_2$ (H_2L^5) reacted with $Zr(CH_2Ph)_4$ giving the complex $[Zr(CH_2Ph)_2L^5]$ **6**. The crystal structures of **1**, **4** and **5** have been determined. Compound **1** has a distorted tetrahedral structure. In **4** and **5** all available donor atoms co-ordinate to zirconium, including the silyl ether moiety, leading to a distorted trigonal bipyramidal structure for **4** and an approximately pentagonal bipyramidal geometry for **5**. Although L^3 and L^4 have flexible frameworks, in both **4** and **5** the heteroatom donors and the metal form an essentially coplanar arrangement. The zirconium–amido nitrogen distances proved to be highly variable, depending on the degree of electron deficiency and the co-ordination of the metal centres, and range from an average of 2.056 Å in **1** and 2.096 Å in **4** to 2.169 Å in **5**. Complexes **1** and **4** activated with methylaluminoxane gave high molecular weight polyethylene with moderate activity.

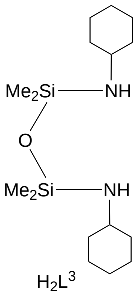
In recent years metallocene complexes of Group 4 metals have attracted considerable interest as highly efficient olefin polymerisation catalysts.[1] Appropriate ligand design has contributed much to this success, as in the example of stereoselective *ansa*-metallocenes of C_s and C_2 symmetry.[2] Increasing efforts are now being made to explore structure–reactivity relationships in alternative ligand systems. Complexes of chelating 'constant geometry' cyclopentadienylamido ligands $[C_5H_5{-}X{-}NR]^{2-}$ are highly active catalysts if $X = SiMe_2$[3] but are less effective if larger chelate rings are formed.[4] A number of non-C_5H_5 complexes with bidentate[5] and tridentate[6] amido ligands have been prepared, as well as complexes of tetradentate Schiff bases[7] and tetraaza macrocycles and porphyrins[8] which show little or no catalytic activity. By contrast, several recently reported complexes of bidentate amido ligands have been shown to polymerise ethene and higher alkenes.[9] We report here the synthesis and structures of new zirconium bis(amido) complexes with bi-, tri-, tetra- and penta-dentate ligands.



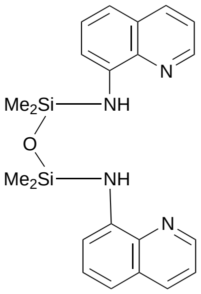
H_2L^1



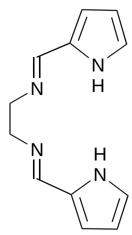
H_2L^2



H_2L^3



H_2L^4



H_2L^5

Results and Discussion

Synthesis of tetra(amido) complexes $[ZrL^n{}_2]$ (n = 1–3)

It was the aim of this work to explore the co-ordination chemistry of ligands with the potential to form chelate rings of varying sizes. Chelating diamines with silyl substituents are readily accessible by the reaction of dilithium diamides with chlorosilanes. For example, the reaction of *trans*-1,2-diaminocyclohexane with two equivalents of *n*-butyllithium followed by the addition of an excess of $SiMe_3Cl$ gives $C_6H_{10}(NHSiMe_3)_2$ (H_2L^1) in almost quantitative yield. Treatment of LiNHBu^t or $LiNH(C_6H_{11})$ with $O(SiMe_2Cl)_2$ affords the bis(aminosilyl) ethers $(RHNSiMe_2)_2O$ (H_2L^2, R = Bu^t; H_2L^3, R = cyclohexyl), respectively. Similarly, lithiation of 8-aminoquinoline followed by reaction with $O(SiMe_2Cl)_2$ gives the bis(aminoquinolinyl) derivative H_2L^4 as an off-white solid. The ligands are flexible; the range of possible co-ordination modes include five- and six-membered rings as well as four-membered ring structures if the Si–O–Si moiety were involved in co-ordination.

The reaction of Li_2L^1 with $[ZrCl_4(thf)_2]$ (thf = tetrahydrofuran) in diethyl ether leads to the isolation of the colourless tetraamide $[ZrL^1{}_2]$ **1**. In an analogous fashion the compounds $[ZrL^2{}_2]$ **2** and $[ZrL^3{}_2]$ **3** are obtained as colourless crystals. All three complexes are readily soluble in light petroleum and are purified by recrystallisation from this solvent (Scheme 1).

In none of these cases zirconium halides $[ZrCl_2L^n]$ (n = 1–4) could be obtained, irrespective of the Li_2L^n : Zr ratio. The comproportionation between compounds **1**–**3** and 1 equivalent of $[ZrCl_4(thf)_2]$ also proved unsuccessful. This behaviour matches earlier observations that mixed bis(amido)zirconium dihalides are not directly accessible or are too insoluble for reaction; Bürger and co-workers prepared a number of titanium[10] and zirconium[11] tetraamides of related but sterically less demanding N-methylamido ligands $[(MeNSiMe_2)_2Y]^{2-}$ (Y = CH_2, NMe or O) and found that complexes of the type $MCl_2(NR_2)_2$ were accessible only for M = Ti but not Zr.

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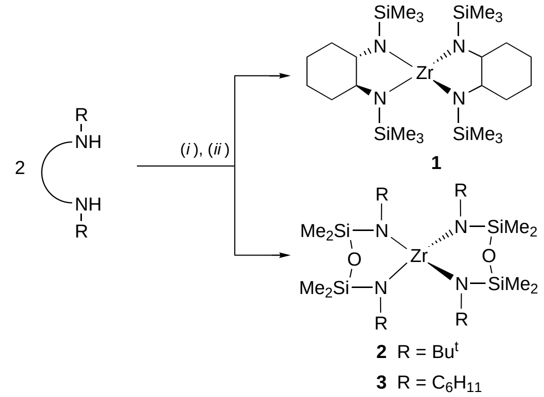
† *Non-SI unit employed:* bar = 101 325 Pa.

Table 1 Analytical data

Compound	Colour	Analysis* (%) C	H	N
1	White	47.6 (47.7)	9.2 (9.3)	9.4 (9.3)
2	White	45.1 (45.0)	9.7 (9.5)	8.4 (8.8)
3	White	51.5 (51.6)	9.4 (9.2)	7.2 (7.5)
4	Yellow	59.5 (60.0)	8.4 (8.1)	4.7 (4.7)
5	Ruby-red	62.5 (62.7)	5.9 (5.6)	8.2 (8.1)
6	Brick-red	64.1 (64.3)	5.6 (5.4)	11.1 (11.5)

* Calculated values in parentheses.



Scheme 1 (*i*) Et_2O, $2LiBu^n$, −78 °C; (*ii*) $[ZrCl_4(thf)_2]$

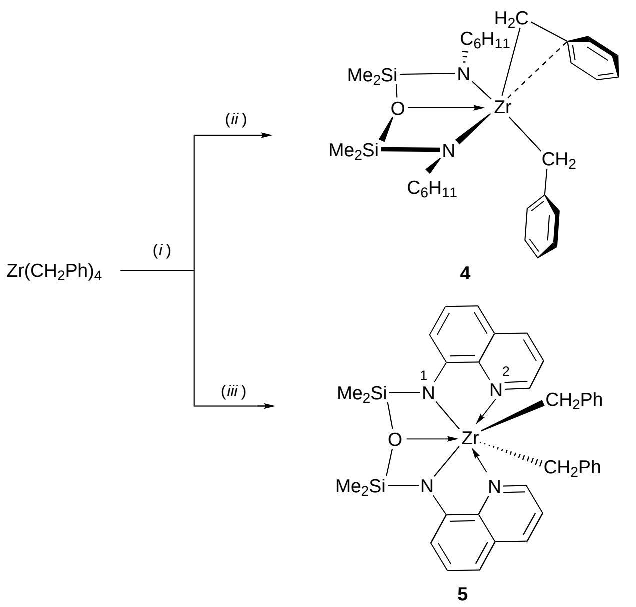
By contrast to the formation of compounds **1**–**3**, no product could be isolated from Li_2L^4 and $[ZrCl_4(thf)_2]$.

Synthesis of $[Zr(CH_2Ph)_2L^n]$ (n = 3 and 4)

Alkene elimination has proved to be a common method for the preparation of a wide variety of Group 4 metal complexes.[12] Bis(amido)zirconium dialkyls are obtained by protolysis of $Zr(CH_2Ph)_4$ with H_2L^3 or H_2L^4, to give the compounds $[Zr(CH_2Ph)_2L^3]$ **4** and $[Zr(CH_2Ph)_2L^4]$ **5** as yellow and deep red crystals, respectively (Scheme 2). Surprisingly, no product could be obtained from the reaction of $Zr(CH_2Ph)_4$ with the sterically very similar ligand H_2L^2. Compounds **4** and **5** are comparatively thermally stable and can be purified by recrystallisation from toluene. Crystalline **5** can be briefly handled in air without decomposition.

The tetradentate Schiff-base $[2\text{-}(C_4H_3NH)CH{=}NCH_2]_2$ H_2L^5 (C_4H_3NH = pyrrolyl), obtained by condensing pyrrole-2-carbaldehyde with ethane-1,2-diamine, reacts with $Zr(CH_2Ph)_4$ to eliminate toluene and form the dibenzyl complex $[Zr(CH_2Ph)_2L^5]$ **6** which can be isolated as a brick-red microcrystalline solid. Crystals suitable for X-ray determination have not yet been obtained. It is likely, however, that very similar constraints will control the geometry of **6** as those that act on **5** (see structural discussion below), with the tetraaza moiety and metal centre adopting an almost coplanar configuration. This would result in the benzyl groups adopting approximately *trans* positions similar to those previously described for Group 4 Schiff-base complexes.[7a]

All new compounds were characterised by ^1H and ^{13}C NMR spectroscopy and elemental analysis (Table 1). The benzyl complexes possess effective C_{2v} structure in solution on the NMR time-scale, with identical η^1-bonded benzyl ligands indicated by singlet resonances of the $SiMe_2$ and $ZrCH_2$ groups in the ^1H NMR for **4** and **5** and unremarkable C–H coupling constants [**4**, δ 0.16, 2.16; **5**, 0.32, 2.21; $ZrCH_2$, J_{CH} = 123.9 (**4**), 123.0 Hz (**5**)]. The NMR spectra of **4** are essentially unchanged on cooling to −90 °C. Only one signal in the ^{13}C NMR spectrum, corresponding to the *ipso*-carbon of the benzyl aromatic ring, was observed (in $[^2H_2]$dichloromethane) down to a temperature of 183 K, at chemical shift δ 143.7, as well as intermediate temperatures. This is unlikely to correspond with a benzyl group in an η^2-bonding mode since this exhibits typically high-field shifts of the *ipso*-carbon resonances.[13] The equivalence of the alkyl ligands in solution contrasts with the presence of inequivalent, η^1- and η^2-co-ordinate benzyl ligands in crystals of **4** (see below). Compound **6** also possesses a single resonance for the $ZrCH_2$ group (δ 2.18, J_{CH} = 135.8 Hz). In this case the value of J_{CH} might indicate η^2-co-ordinated benzyl groups but no direct solid-state structural evidence could be obtained.



Scheme 2 (*i*) Toluene, 50 °C; (*ii*) 1 equivalent H_2L^3, 10 h; (*iii*) 1 equivalent H_2L^4, 14 h

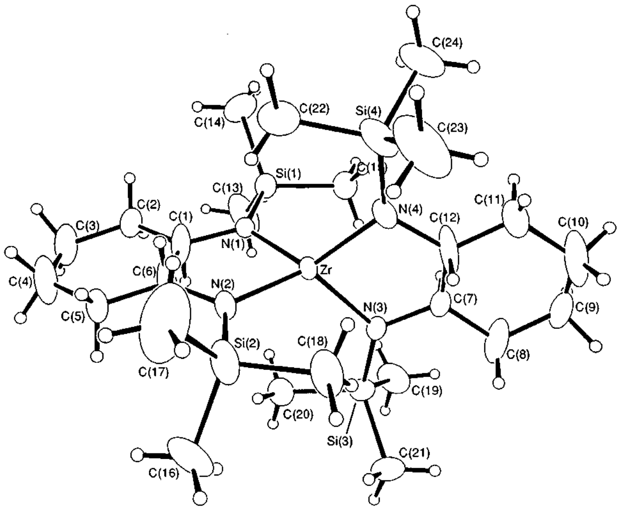


Fig. 1 Molecular structure of $[Zr\{1,2\text{-}(Me_3SiN)_2C_6H_{10}\}_2]$ **1** showing the atomic numbering scheme. Ellipsoids are drawn at 30% probability

Crystal structures

The crystal structures of compounds **1**, **4** and **5** were determined by X-ray crystallography. Crystal data are given in Table 5, selected bond lengths and angles in Table 2.

Complex **1** possesses a flattened tetrahedral structure (Fig. 1), with intraannular N–Zr–N angles significantly smaller than tetrahedral, average 86.7(2)°, while the N–Zr–N angles between the two chelate rings are larger, average 122.2(2)°. The average Zr–N distance of 2.056(5) Å is in line with those previously found for zirconium compounds with mono- and bi-dentate amido ligands.[14–16] Pertinent structural parameters are collected in Table 3 for comparison.

Table 2 Selected bond distances (Å) and angles (°) for compounds **1**, **4** and **5**

$[ZrL^1_2]$ **1**							
Zr–N(4)	2.050(5)	Zr–N(2)	2.055(4)	Si(3)–N(3)	1.724(5)	Si(4)–N(4)	1.716(6)
Zr–N(1)	2.059(5)	Zr–N(3)	2.062(4)	N(1)–C(1)	1.471(8)	N(2)–C(6)	1.455(8)
Si(1)–N(1)	1.717(5)	Si(2)–N(2)	1.722(5)	N(3)–C(7)	1.464(8)	N(4)–C(12)	1.489(9)
N(4)–Zr–N(2)	122.4(2)	N(4)–Zr–N(1)	122.0(2)	C(1)–N(1)–Zr	107.8(4)	C(6)–N(2)–Zr	109.1(4)
N(2)–Zr–N(1)	85.8(2)	N(4)–Zr–N(3)	87.7(2)	Si(1)–N(1)–Zr	124.5(2)	Si(2)–N(2)–Zr	124.0(3)
N(2)–Zr–N(3)	120.6(2)	N(1)–Zr–N(3)	122.5(2)				
$[Zr(CH_2Ph)_2L^3]$ **4**							
Zr–N(5)	2.092(3)	Zr–N(1)	2.099(3)	Zr–Si(4)	3.0213(10)	Zr–Si(2)	3.0214(10)
Zr–C(61)	2.297(3)	Zr–C(71)	2.299(3)	N(1)–Si(2)	1.698(3)	Si(4)–N(5)	1.703(3)
Zr–O(3)	2.381(2)	Zr–C(62)	2.608(3)	O(3)–Si(4)	1.668(3)	Si(2)–O(3)	1.662(3)
C(72)–C(71)–Zr	110.2(2)	C(62)–C(61)–Zr	84.9(2)	N(5)–Zr–C(62)	111.20(11)	N(1)–Zr–C(62)	113.45(11)
N(5)–Zr–N(1)	131.3(11)	N(5)–Zr–C(61)	102.31(12)	C(61)–Zr–C(62)	33.81(11)	C(71)–Zr–C(62)	89.98(12)
N(1)–Zr–C(61)	103.87(12)	N(5)–Zr–C(71)	98.51(13)	O(3)–Zr–C(62)	145.94(10)	O(3)–Si(4)–N(5)	93.62(13)
N(1)–Zr–C(71)	99.92(13)	C(61)–Zr–C(71)	123.79(12)	Si(2)–N(1)–Zr	104.94(14)	Si(4)–N(5)–Zr	105.05(14)
N(5)–Zr–O(3)	66.31(9)	N(1)–Zr–O(3)	65.99(9)	Si(4)–O(3)–Zr	94.86(11)	Si(2)–O(3)–Zr	95.04(11)
C(61)–Zr–O(3)	112.14(11)	C(71)–Zr–O(3)	124.05(11)	Si(2)–O(3)–Si(4)	160.5(2)		
$[Zr(CH_2Ph)_2L^4]$ **5**							
Zr–N(19)	2.168(3)	Zr–N(9)	2.169(3)	N(9)–Si(1)	1.707(3)	Si(1)–O	1.654(3)
Zr–C(25)	2.303(4)	Zr–C(32)	2.339(5)	Si(1)–C(22)	1.839(4)	Si(1)–C(21)	1.859(4)
Zr–O	2.442(3)	Zr–N(11)	2.445(3)	O–Si(2)	1.660(3)	N(11)–C(12)	1.328(5)
Zr–N(1)	2.470(3)	Zr–Si(1)	3.112(2)	N(11)–C(20)	1.371(5)	C(19)–N(19)	1.370(5)
Zr–Si(2)	3.115(2)	N(19)–Si(2)	1.705(3)	Si(2)–C(23)	1.845(4)	Si(2)–C(24)	1.851(4)
N(1)–C(2)	1.324(5)	N(1)–C(10)	1.377(5)				
C(33)–C(32)–Zr	108.4(3)	C(26)–C(25)–Zr	109.1(3)	N(9)–Zr–N(1)	69.60(12)	C(25)–Zr–N(1)	77.36(13)
N(19)–Zr–N(9)	127.04(12)	N(19)–Zr–C(25)	107.97(14)	C(32)–Zr(1)–N(1)	75.82(13)	O–Zr–N(1)	132.90(10)
N(9)–Zr–C(25)	92.09(14)	N(19)–Zr–C(32)	89.54(14)	N(11)–Zr–N(1)	94.53(11)	Si(1)–O–Si(2)	164.6(2)
N(9)–Zr–C(32)	106.62(13)	C(25)–Zr–C(32)	139.07(14)	Si(1)–O–Zr	96.99(13)	Si(2)–O–Zr	96.96(12)
N(19)–Zr–O(1)	63.60(11)	N(9)–Zr–O	63.60(11)	C(20)–N(11)–Zr	112.9(2)	C(19)–N(19)–Zr	122.9(2)
C(25)–Zr–O	108.54(13)	C(32)–Zr–O	112.37(12)	C(9)–N(9)–Zr	124.0(3)	C(10)–N(1)–Zr	112.9(2)
N(19)–Zr–N(11)	69.98(11)	N(9)–Zr–N(11)	162.36(11)	O–Si(2)–N(19)	93.0(2)	O–Si(1)–N(9)	93.1(2)
C(25)–Zr–N(11)	76.44(13)	C(32)–Zr–N(11)	75.49(12)	Si(1)–N(9)–Zr	106.2(2)	Si(2)–N(19)–Zr	106.5(2)
O–Zr–N(11)	132.55(10)	N(19)–Zr–N(1)	161.16(12)				

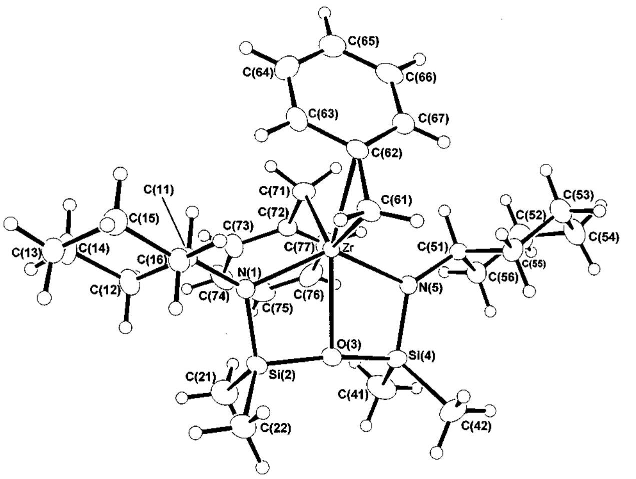


Fig. 2 Molecular structure of $[Zr(CH_2Ph)_2\{(C_6H_{11}NSiMe_2)_2O\}]$ **4** showing the atomic numbering scheme. Ellipsoids are drawn at 30% probability

The benzyl complex **4** has a distorted trigonal bipyramidal geometry (Fig. 2). The ZrN_2O unit is approximately planar. The two amido-nitrogens occupy approximately axial positions; the N–Zr–N unit deviates significantly from linearity, however, with an angle of 131.31(11)°. The Zr–N bond lengths of 2.092(3) and 2.099(3) Å are rather longer than in **1**. In addition, there is co-ordination of the Si–O–Si bridge to the metal centre, with a Zr–O bond length of 2.381(2) Å. This Zr–O interaction is comparatively weak and may be compared to the $Zr–OC_4H_8$ distance of 2.200(4) Å in the thf complex $[Zr(\eta\text{-}C_5H_5)_2(OBu^t)(thf)]BPh_4$.[17] The $Zr–OSi_2$ donor interaction requires only little distortion of the ligand framework, and the Si–O–Si bridge remains almost linear, 160.5(2)°. A number of related compounds $[M\{MeN(SiMe_2)_2Y\}_2]$ (Y = NMe or O) have been reported some time ago and formulated as spiro compounds with six-ring chelate structures; the possibility of co-ordination to the O or NMe units was apparently not recognised.[10,11,14] Weak M · · · O interactions have also been found in complexes of the $[L^2]^{2-}$ dianion with later transition metals, such as $[(ML^2)_2]$ (M = Mn, Fe, Co or Zn), although in these cases the Si–O–Si angles are significantly more acute and the M–O bonding interactions much weaker (*e.g.* Mn–O 2.512 Å).[18]

The two benzyl ligands in compound **4** form a C–Zr–C angle 123.79(12)°. The two Zr–C distances are almost identical, although one of the benzyl ligands shows η^2 co-ordination, with a distance between Zr and the phenyl *ipso*-C of 2.608(3) Å, whereas the other is η^1-co-ordinate. The difference in bonding modes is strongly reflected in the bond angles, with an acute Zr–C–C angle of only 84.9(2)° for the first and a normal angle of 110.2(2)° for the second benzyl ligand. For comparison, the cationic 16-electron complex $[Zr(\eta\text{-}C_5H_5)_2(\eta^2\text{-}CH_2Ph)(NCMe)]BPh_4$ shows a slightly longer $Zr–C_{ipso}$ distance of 2.648(6) Å and a Zr–C–C angle of 84.9(4)°.[19] Variations in the bonding modes of benzyl ligands have, for example, been found in $[Zr(CH_2Ph)_3\{\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3\}]$ which contains three different benzyl ligands, with Zr–C–C angles of 82.7, 103.9 and 121.1°.[20]

The geometry of compound **5** (Fig. 3) resembles that of **4**, although in this case there are two additional donor inter-

Table 3 Comparison of Zr–N bond lengths (Å) and N–Zr–N (°) of zirconium amido complexes

Compound	*r*(Zr–N)	N–Zr–N	Ref.
1	2.056 (average)	85.8(2), 87.7(2), 122.4(2), 122.0(2)	
4	2.092(3), 2.099(3)	131.3(1)	
5	2.168(3), 2.169(3)	127.0(1)	
$[Zr\{(Bu^tN)_2SiMe_2\}_2]$	2.054(3), 2.051(3)	77.9(1), 129.8(2), 126.5(1)	14
$[Zr\{\eta^4\text{-}(Pr^i_3SiN)_2C_6H_4\}_2]$	2.080 (average)	86.8(2), 85.3(2). 136.3(2), 118.1(2)	5[c]
$[ZrCl\{N(SiMe_3)_2\}_3]$	2.070(3)	114.1(1)	15
$[Zr_2(NMe_2)_8]$	2.050(3) (equatorial) 2.108(3) (axial) 2.224(3), 2.451(3) (bridging)	93.54(14), 92.55(12), 118.50(14), 119.42(13) (terminal)	16

Table 4 Ethene polymerisation

Run no.	Catalyst	C_2H_4 pressure (bar)	Yield (mg)	10^{-5} M_w	10^{-5} M_n	M_w/M_n	Activity/ kg mol^{-1} catalyst bar^{-1} h^{-1})
1[a]	**1**	1	80	*b*			16
2[a]	**4**	1	200	5.91	2.11	2.8	40
3[c]	**1**	6	2490	*b*			50
4[c]	**3**	6	1100	*b*			22
5[c]	**4**	6	600	1.25	0.01	125	12
6[c]	**5**	6	260	*b*			5.2

[a] Ambient temperature over 60 min, 5 μmol catalyst, MAO cocatalyst, Al : Zr ratio *ca*. 1200, solvent toluene. [b] Sample proved insufficiently soluble in refluxing dichlorobenzene for reliable GPC measurements to be obtained. [c] 50 °C over 50 min, 10 μmol catalyst, MAO cocatalyst, Al : Zr ratio *ca*. 1200, solvent toluene.

actions involving the quinoline nitrogen atoms which form comparatively long Zr–N bonds of 2.470(3) and 2.445(3) Å. As a result the complex is electronically more saturated, and, if one admits full π contribution from the lone electron pairs of the two amido nitrogens, achieves an electron count of 18. In consequence all the zirconium–ligand bonds are elongated in comparison with **4**. The Zr–C bonds are least affected, with an average Zr–C distance of 2.321(5) Å, compared to an average of 2.298(3) Å in **4**. There is however no indication of an η^2-type bonding, and the Zr–C–C angles are very close to tetrahedral, 108.4(3) and 109.1(3)°. The two benzyl ligands are best described as *trans*, occupying the axial positions of a distorted pentagonal bipyramid, with a C–Zr–C angle of 139.07(14)°, while the N_4O macrocycle occupies the equatorial positions. The N_4O arrangement is almost planar and only slightly twisted to accommodate the benzylic phenyl substituents [Fig. 3(*b*)].

The most pronounced structural difference concerns the zirconium–amido nitrogen distances which are elongated to 2.168(3) and 2.169(3) Å (*cf.* Table 3). The data underline that the Zr–N (amide) distances in compound **5** are at the upper limit for non-bridging amido ligands. As in **4**, there is coordination to the oxygen of the silyl ether bridge, though the Zr–O bond is even longer [2.442(3) Å] and the Si–O–Si bridge is more linear [164.6(2)°]. Zirconium–oxygen bonds are, on average, *ca*. 2.2 Å which shortens to *ca*. 1.9 Å if π bonding leads to double-bond character.[17,21] The siloxymethyl complex $[Zr(\eta\text{-}C_5Me_5)Cl_2(CH_2SiMe_2OSiMe_3)]$,[22] by comparison, possesses a Zr–O bond length of 2.427(3) Å, only slightly shorter than that in **5**. In that case, however, the Si–O–Si angle is significantly more acute at 131.10(16)°.

Olefin polymerisations

Compounds **1** and **4** in the presence of methylaluminoxane (MAO) as activator show moderate activity as ethene polymerisation catalysts, while **5** is almost inactive even at elevated pressure. The results of reactions under 1 and 6 bar ethene pressure are given in Table 4. The polymer formed by reaction at 1 bar C_2H_4 for complex **4** has relatively high molecular weight ($M_w = 590\,000$) and narrow polydispersity (2.8). In most of the other polymerisations the polyethylene produced proved to be very insoluble even in refluxing dichlorobenzene. Gel permeation chromatography (GPC) traces could only be obtained on the small amount of soluble fraction and are thus unrepresentative of the bulk polymer. This solubility behaviour is consistent with the formation of very high molecular weight material, possibly resulting from a low concentration of active species.

A successful ethylene polymerisation system based on zirconium amides has recently been developed, employing a bis(silylamido)zirconium dihalide complex $[ZrCl_2\{N(SiMe_3)_2\}_2]$, activated with MAO.[23] The systems we report differ by being halide free in nature. The activation of tetraamido complexes such as **1**–**3** by MAO requires the removal of one diamido ligand by the aluminium reagent, to give active species $[(N\text{–}N)ZrR]^+$. It is therefore not surprising that the concentration of active species in the case of tetraamido species is low and that the complexes show little productivity at ambient pressure. At higher pressure, however, the best results were achieved for **1**, with **3** also showing some activity. The reasons for the inactivity of **2** under these conditions are not clear. This complex has proved more prone to decomposition than its cyclohexyl analogue **3**, and it is possible that at the elevated temperatures of the higher pressure experiments the compound decomposes to a wholly inactive material.

The dibenzyl complexes **4** and **5** have shown very little activity under either ambient or high-pressure conditions. Compound **5** has only low activity perhaps as a consequence of the *trans* orientation of the alkyl groups in these complexes, which to a lesser degree is also true of **4** (C–Zr–C 123.79°); compound **6** is inactive. The productivity of **4** is comparable to that exhibited by cationic zirconium half-sandwich complexes under comparable conditions.[24]

Conclusion

Zirconium complexes of chelating bis(amido) ligands are readily accessible, with differing chelate ring sizes and varying

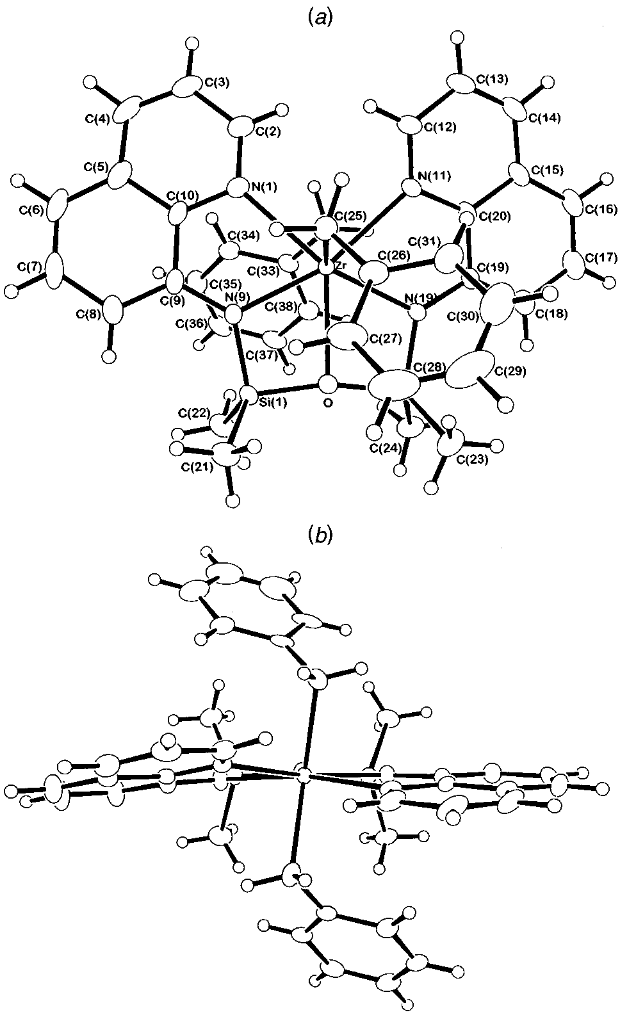


Fig. 3 Molecular structure of $[Zr(CH_2Ph)_2\{(NC_9H_6NSiMe_2)_2O\}]$ **5**: (*a*) top view showing the atomic numbering scheme; (*b*) side view illustrating the planarity of the ZrN_4O core and the conformation of the benzyl ligands

degrees of electron deficiency. The wide range of the Zr–N (amido) distances in such complexes underlines the ability of amido ligands to act as one- to three-electron ligands. With polydentate ligands a meridional geometry of the heteroatom donors and a transoid arrangement of the benzyl ligands is favoured, *i.e.* a geometry which could be expected to disfavour alkene insertion and chain growth by the accepted Ziegler mechanism.[1,2] The polyethylene produced with amido complexes in this study was, however, in most cases of unusually high molecular weight, indicative of the formation of catalytically highly active centres, albeit in low concentrations. Bis(amido) ligands leading to five-membered rings appear preferable to ligands with additional donor functions. The ability of even weakly basic silyl ether bridges to co-ordinate to zirconium centres may be seen as an illustration of the way in which oxidic supports are able to interact with catalyst precursors.

Experimental

All manipulations were carried out by standard anaerobic Schlenk-line techniques. Elemental analyses were obtained by the University of East Anglia Microanalysis Laboratory and the University of Leeds Microanalysis Laboratory. Gel permeation chromatography measurements of polymer samples were carried out using Plgel mixed bed-B, 10 μm, 30 cm columns at 140 °C in dichlorobenzene. The NMR spectra were obtained using Bruker ARX250, JEOL FX-270 or Bruker Avance DPX300 spectrometers. Solvents were freshly distilled from sodium–benzophenone (Et_2O and thf) and sodium metal [light petroleum (b.p. 40–60 °C) and toluene]. Zirconium tetrachloride was sublimed and converted into $[ZrCl_4(thf)_2]$ by the standard literature procedure;[25] $Zr(CH_2Ph)_4$ was prepared as described.[26] 1,3-Dichlorotetramethyldisiloxane, *trans*-1,2-diaminocyclohexane, 8-aminoquinoline and pyrrole-2-carbaldehyde were used as purchased.

Syntheses

***trans*-1,2-$(Me_3SiNH)_2C_6H_{10}$ (H_2L^1).** *trans*-1,2-Diaminocyclohexane (5.0 g, 43.8 mmol) was dissolved in freshly distilled Et_2O (100 cm^3) and stirred at −78 °C for the dropwise addition of $LiBu^n$ (35 cm^3, 1.6 mol dm^{-3}). The solution was allowed to warm to room temperature for an hour before recooling in an ice–water bath for the addition of an excess of $SiMe_3Cl$ (15 cm^3, 0.12 mol) in Et_2O (50 cm^3). The mixture was stirred for 48 h at room temperature during which time a white precipitate was produced. The solution was concentrated to *ca.* half volume *in vacuo* and filtered. The solvent was removed from the filtrate *in vacuo* leaving a yellow oil which could be used without further purifaction. Yield 10.9 g, 96%. ^1H NMR (270 MHz, $CDCl_3$, 25 °C): δ 0.01 [d, 18 H, *J* = 1 Hz, $Si(CH_3)_3$], 0.68 (br, 2 H, cyclohexyl CH_2), 1–1.56 (br m, 6 H, cyclohexyl CH_2), 1.82 (br, m, 2 H cyclohexyl CH) and 2.14 (br, 2 H, NH).

$O(SiMe_2NHBu^t)_2$ (H_2L^2). *tert*-Butylamine (2.9 g, 40 mmol) was placed in a flame-dried flask and dissolved in light petroleum (30 cm^3). A solution of $O(SiMe_2Cl)_2$ (2.0 g, 9.8 mmol) in light petroleum (20 cm^3) was added dropwise to the stirred solution at 0–5 °C. The mixture was stirred for 12–24 h before filtration and evaporation to dryness leaving an oily product. Yield 2.1 g, 77%. ^1H NMR (270 MHz, $CDCl_3$, 25 °C): δ 0.03 [s, 12 H, $Si(CH_3)_2$], 0.90 (br, 2 H, NH) and 1.13 [s, 18 H, $C(CH_3)_3$].

$O(SiMe_2NHC_6H_{11})_2$ (H_2L^3). Cyclohexylamine (3.9 g, 39 mmol) was placed in a flame-dried flask and dissolved in light petroleum (40 cm^3). A solution of $O(SiMe_2Cl)_2$ (2.0 g, 9.8 mmol) in light petroleum (20 cm^3) was added dropwise to the stirred amine solution at *ca.* 0–5 °C. A white precipitate rapidly formed. After stirring for 12 h the solid was filtered off, washed with further light petroleum (4 × 20 cm^3) and the filtrate evaporated to dryness giving a colourless oil. Yield 3.13 g, 97%. ^1H NMR (270 MHz, $CDCl_3$, 25 °C): δ −0.01 [s, 12 H, $Si(CH_3)_2$], 0.75–1.80 (br, m, 22 H, cyclohexyl CH and CH_2) and 2.58 (br s, 2 H, NH).

$O[SiMe_2NH(C_9H_6N)]_2$ (H_2L^4). 8-Aminoquinoline (2.0 g, 13.9 mmol) was dissolved in freshly distilled Et_2O (40 cm^3) and stirred at −78 °C. Upon addition of $LiBu^n$ (8.7 cm^3, 1.6 mol dm^{-3}) the solution turned rapidly from green to red-brown. The mixture was allowed to stir at room temperature for *ca.* 14 h before the addition of $O(SiMe_2Cl)_2$ (1.4 g, 7 mmol) in Et_2O (20 cm^3) to the cooled solution. The mixture was stirred at room temperature for 24 h during which time a light precipitate formed. The solution was filtered and the solvent removed *in vacuo* leaving an off-white solid product. Yield 2.30 g, 79%. ^1H NMR (250 MHz, $CDCl_3$): δ 0.39 [s, 12 H, $Si(CH_3)_2$], 6.39 (br s, 2 H, NH), 7.06 (d, 4 H, quinolinyl aromatic CH), 7.22 (dd, 2 H, quinolinyl aromatic CH), 7.32 (dd, 2 H, quinolinyl aromatic CH), 8.02 (dd, 2 H, quinolinyl aromatic CH) and 8.68 (dd, 2 H, quinolinyl aromatic CH).

$[(C_4H_3NH)CH{=}NCH_2]_2$ (H_2L^5). This compound was made by a modification of a literature procedure.[27] Pyrrole-2-carbaldehyde (3.80 g, 40 mmol) was dissolved in EtOH (40 cm^3) and stirred for the addition of ethane-1,2-diamine (1.20 g, 20 mmol) followed by a drop of acetic acid. A white solid was quickly formed. After *ca.* 2 h the solid was filtered off, washed with further cold EtOH and dried *in vacuo*. Yield 3.35 g, 78%. ^1H NMR (300 MHz, $CDCl_3$): δ 3.78 (s, 4 H, NCH_2CH_2N), 6.22

Table 5 Crystal data of zirconium amide complexes **1**, **4** and **5**

	1	**4**	**5**
Empirical formula	$C_{24}H_{56}N_4Si_4Zr$	$C_{30}H_{48}N_2OSi_2Zr$	$C_{36}H_{38}N_4OSi_2Zr$
M	604.31	600.10	690.10
T/K	200(2)	200(2)	160(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	10.6696(10)	9.7408(7)	11.2795(12)
b/Å	17.443(2)	17.179(2)	12.077(2)
c/Å	18.6615(10)	19.0983(13)	12.8233(14)
α/°	—	—	87.890(10)
β/°	93.255(8)	100.098(7)	87.787(10)
γ/°	—	—	81.737(9)
U/Å^3	3467.2(5)	3146.3(4)	1706.7(3)
λ/Å	0.710 73	0.710 73	1.541 84
Z	4	4	4
D_c/Mg m^{-3}	1.16	1.27	1.34
F(000)	1296	1272	716
Crystal size/mm	0.38 × 0.30 × 0.22	0.65 × 0.365 × 0.08	0.60 × 0.41 × 0.25
μ/mm^{-1}	0.473	0.450	3.574
Maximum, minimum transmission	0.904, 0.832	0.887, 0.818	0.607, 0.170
θ_{min},θ_{max}/°	1.60, 25.0	1.61, 24.99	3.49, 64.57
h_{min},h_{max}; k_{min},k_{max}; l_{min},l_{max}	−12, 12; 0, 20; 0, 22	−11,11; −20,20; −22,22	−12,12; −13,14; 0.15
No. data collected	6114	8750	5379
No. unique data, n	6114	5518	5379
R_{int}[a]	—	0.0338	—
R_{sig}[b]	0.0478	0.0434	0.0128
No. data with $F^2 > 2\sigma F^2$	4904	4753	5229
No. parameters, p	310	325	402
No. restraints	0	0	32
$R1$[c]	0.0766	0.0505	0.0394
$wR2$[c]	0.1577	0.0968	0.1135
Weighting parameters a,b[e]	0.0389, 11.0013	0.0286, 3.1362	0.0547, 4.2115
Goodness of fit, S[f]	1.138	1.203	1.091
Extinction parameter, x	—	—	0.000 61(13)
Largest Δ/σ	0.001	0.002	0.003
Maximum and minimum difference peak	0.585, −0.658	0.297, −0.357	0.791, −0.623

[a] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$. [b] $R_{sig} = \Sigma[\sigma(F_o^2)]/\Sigma F_o^2$. [c] $R1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2\}^{\frac{1}{2}}$. [e] $w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [f] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{\frac{1}{2}}$.

(dd, 2 H, pyrrole CH), 6.49 (dd, 2 H, pyrrole CH), 6.90 (m, 2 H, pyrrole CH), 8.03 (s, 2 H, CH=N); NH not observed.

$Zr[(Me_3SiN)_2C_6H_{10}]_2$ 1. The compound $(Me_3SiNH)_2C_6H_{10}$ (4.14 g, 16 mmol) was dissolved in freshly distilled Et_2O (40 cm^3) and stirred at −78 °C for the dropwise addition of $LiBu^n$ (12.8 cm^3, 2.5 mol dm^{-3}). After allowing the mixture to stir at room temperature for 1 h the solution was recooled and solid $[ZrCl_4(thf)_2]$ (3.0 g, 8 mmol) was added. The mixture was stirred for 16 h and then filtered. The solvent was removed from the filtrate *in vacuo* and the residue extracted with light petroleum (3 × 12 cm^3). The solution was stored at −20 °C and large colourless crystals were deposited. Yield 3.72 g, 81%. These were suitable for single-crystal X-ray determination. NMR (C_6D_6, 25 °C): ^{1}H (270 MHz), δ 0.34 [s, 36 H, $Si(CH_3)_3$] and 1.2–1.8 (br, m, 20 H, cyclohexyl CH and CH_2); ^{13}C-{^{1}H} (67.9 MHz), δ 2.33 [$Si(CH_3)_3$], 25.70 (cyclohexyl, $C^{4,5}$), 36.45 (cyclohexyl $C^{3,6}$) and 65.89 (cyclohexyl $C^{1,2}$).

$Zr[O(SiMe_2NBu^t)_2]_2$ 2. A solution of $O(SiMe_2NHBu^t)_2$ (2.20 g, 8 mmol) in Et_2O (50 cm^3) was cooled to −78 °C for the addition of $LiBu^n$ (10 cm^3, 1.6 mol dm^{-3}). The mixture was stirred at room temperature for 1 h before recooling for the addition of solid $[ZrCl_4(thf)_2]$ (1.50 g, 4 mmol). The mixture was stirred at room temperature for 16 h before concentration to *ca.* half volume *in vacuo* and filtration. The solvent was removed from the filtrate leaving an oily solid which could be purified by recrystallisation from light petroleum giving colourless crystals. Yield 1.43 g, 56%. NMR (C_6D_6, 25 °C): ^{1}H (300 MHz), δ 0.35 [s, 24 H, $Si(CH_3)_2$] and 1.28 [s, 36 H, $C(CH_3)_3$]; ^{13}C-{^{1}H} (75.5 MHz), δ 7.71 [$Si(CH_3)_2$], 37.92 [$C(CH_3)_3$] and 50.01 (CMe_3).

$Zr[O(SiMe_2NC_6H_{11})_2]_2$ 3. A solution of $O(SiMe_2NHC_6H_{11})_2$ (3.5 g, 10.6 mol) in freshly distilled Et_2O (40 cm^3) was cooled to −78 °C for the addition of $LiBu^n$ (8.5 cm^3, 2.5 mol dm^{-3}). The mixture was stirred for 1 h at room temperature before the addition of solid $[ZrCl_4(thf)_2]$ (2.0 g, 5.3 mmol). After stirring at room temperature for 16 h and precipitation of LiCl the solution was filtered and the solvent removed from the filtrate *in vacuo*. The white solid was recrystallised from light petroleum giving colourless crystals. Yield 2.32 g, 59%. NMR (C_6D_6, 25 °C): ^{1}H (270 MHz), δ 0.39 [s, 24 H, $Si(CH_3)_2$], 1.05–1.80 (br m, 40 H, cyclohexyl CH_2) and 2.20 (m, 4 H, cyclohexyl CH); ^{13}C-{^{1}H} (67.9 MHz), δ 5.07 [$Si(CH_2)_2$], 26.44 (cyclohexyl C^4), 26.87 (cyclohexyl $C^{3,5}$), 39.83 (cyclohexyl $C^{2,6}$) and 57.58 (cyclohexyl C^1).

$[Zr(CH_2Ph)_2\{(C_6H_{11}NSiMe_2)_2O\}]$ 4. The compound $Zr(CH_2Ph)_4$ (1.45 g, 2.85 mmol) was dissolved in freshly distilled toluene (40 cm^3) and heated to *ca.* 50 °C whilst protecting the reaction vessel from light. A solution of $O(SiMe_2NHC_6H_{11})_2$ (1.05 g, 2.85 mmol) in toluene (10 cm^3) was added and the mixture stirred at 50 °C for 10 h. The solvent was removed *in vacuo* to leave, initially, an amber oil which solidified on extensive pumping to give a canary-yellow powder. Crude yield 1.5 g, 79%. Crystals suitable for single-crystal X-ray determination were obtained by recrystallising from fresh toluene at −20 °C. NMR (C_6D_6, 25 °C): ^{1}H (270 MHz), δ 0.16 [s, 12 H, $Si(CH_3)_2$], 0.82–1.90 (br, 22 H, cyclohexyl CH and CH_2) 2.16 (s, 4 H, $ZrCH_2$), 6.89 (m, 4 H, *ortho* CH) and 6.94–7.12 (m, 6 H, *meta* and *para* CH); ^{13}C (67.9 MHz), δ 4.71 [$Si(CH_3)_2$], 26.10 (cyclohexyl, C^4), 26.74 (cyclohexyl $C^{3,5}$), 39.02 (cyclohexyl $C^{2,6}$), 55.78 (cyclohexyl CHN), 62.11 ($ZrCH_2$), 122.27 (benzyl, *para*), 127.08 (benzyl, *ortho*), 129.85 (benzyl, *meta*) and 144.78 (benzyl, *ipso*).

$[Zr(CH_2Ph)_2\{(NC_9H_6NSiMe_2)_2O\}]$ 5. A solution of $Zr(CH_2Ph)_4$ (1.20 g, 2.6 mmol) in freshly distilled toluene (35 cm^3) was stirred at *ca.* 50 °C. The compound $O[SiMe_2NH(C_9H_6N)]_2$ (1.10 g, 1.7 mmol) was dissolved in toluene (10 cm^3) and added to the solution. The reaction was maintained at 50 °C for 14 h before the solvent was removed *in vacuo*. The residue was extracted into fresh toluene (10 cm^3) and stored at −20 °C resulting in the formation of ruby-red crystals suitable for single-crystal X-ray determination. Yield 1.0 g, 56%. NMR (C_6D_6, 25 °C): ^1H (300 MHz), δ 0.32 [s, 12 H, $Si(CH_3)_2$], 2.21 (s, 4 H, $ZrCH_2$), 6.09 (d, 4 H, benzyl *ortho*-H), 6.47 (dd, 2 H, quinolinyl aromatic CH), 6.56 (t, 2 H, benzyl *para*-H), 6.70 (t, 4 H, benzyl *meta*-H), 6.80 (dd, 2 H, quinolinyl aromatic CH), 6.94 (dd, 2 H, quinolinyl aromatic CH), 7.26 (t, 2 H, quinolinyl aromatic CH), 7.63 (dd, 2 H, quinolinyl aromatic CH) and 8.58 (dd, 2 H, quinolinyl aromatic CH); $^{13}C-\{^1H\}$ (75.5 MHz), δ 64.34 ($ZrCH_2$), 119.50 (benzyl, *para*), 125.71 (benzyl, *ortho*), 127.62 (benzyl, *meta*), 144.63 (benzyl, *ipso*), 113.15, 115.2, 120.99, 129.45, 130.55, 137.90, 145.98, 150.99, 151.12 (quinolinyl C).

$[Zr(CH_2Ph)_2\{(2\text{-}C_4H_3NHCH{=}NCH_2)_2\}]$ 6. The compound $Zr(CH_2Ph)_4$ (1.07 g, 2.35 mmol) was dissolved in freshly distilled toluene (40 cm^3) and stirred for the addition of H_2L^5 (0.50 g, 2.35 mmol) in toluene (30 cm^3). The mixture was stirred for 10 h at room temperature before removal of the solvent *in vacuo* and washing with light petroleum (2 × 5 cm^3) to give a brick-red solid. Yield 0.85 g, 75%. NMR (C_6D_6, 25 °C): ^1H (300 MHz), 2.18 (s, 4 H, $ZrCH_2$), 3.36 (s, 4 H, NCH_2CH_2N), 6.46 (d, 4 H, benzyl, *ortho*), 6.49 (dd, 2 H, pyrrole, CH), 6.57 (t, 2 H, benzyl, *para*), 6.67 (d, 2 H, pyrrole CH), 6.77 (t, 4 H, benzyl, *meta*), 7.09 (m, 2 H, pyrrole CH) and 7.75 (s, 2 H, CH=N); $^{13}C-\{^1H\}$ (75.5 MHz), δ 55.47 (NCH_2CH_2), 67.98 ($ZrCH_2$), 113.81 (pyrrole), 118.72 (pyrrole), 122.28 (benzyl, *para*), 129.10 (benzyl, *ortho*), 130.64 (benzyl, *meta*), 138.51 (pyrrole), 140.55 (benzyl, *ipso*), 140.95 (pyrrole) and 159.80 (C_4H_3-NHCH=N).

Crystallography

Crystal data, data collection and structure refinement details are summarised in Table 5. Data for all three complexes were collected on a Stoe STADI4 diffractometer operating in the ω–θ scan mode. In each case the cell dimensions were refined from the values of 40 selected reflections (+ their Friedel opposites) measured at ±2θ in order to minimise systematic errors. Intensity data of all three complexes were corrected for absorption semiempirically using azimuthal ψ scans. None of the data sets displayed any significant signs of intensity decay.

The structures of all three complexes were solved by heavy-atom methods using SHELXS 86[28] and refined by full-matrix least squares (against all the unique F^2 data) using SHELX 93.[29] The non-hydrogen atoms of each complex were refined with anisotropic displacement parameters. Restraints were applied to the phenyl rings of **5** such that they remained flat with overall C_{2v} symmetry. In all three cases all hydrogen atoms were constrained to idealised positions with a riding model including free rotation of methyl groups. In the case of **5** an isotropic extinction coefficient multiplied F_c by $k[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-\frac{1}{4}}$. Final $wR2$ and goodness of fit values were based on F^2 values for all data; the conventional R ($R1$ in Table 5) is based on F values with $F_o^2 > 2\sigma(F_o^2)$ for comparison with refinements based on F.

Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 187/539.

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