meta- and *para*-Bis[zirconyl(IV)amino]cyclophanes; 1,3- or 1,4-$C_6H_4[\overline{N}(SiMe_3)]_2$ as bridging ligands†

Stephane Daniele, Peter B. Hitchcock and Michael F. Lappert*

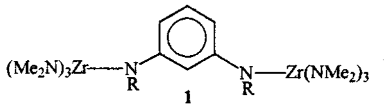
The Chemistry Laboratory, University of Sussex, Brighton, UK BN1 9QJ. E-mail: m.f.lappert@sussex.ac.uk

Received (in Basel, Switzerland) 17th May 1999, Accepted 17th July 1999

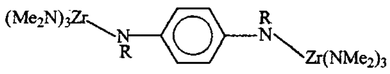
The structurally characterised *meta*- and *para*-dimetallacyclophanes $[R\overline{N(C_6H_4)N(R)Zr(NMe_2)_2N(R)(C_6H_4)N(R)Zr}(NMe_2)_2]$ (R = $SiMe_3$), obtained from $[\{Zr(NMe_2)_3(\mu\text{-}NMe_2)\}_2]$ and $C_6H_4[N(H)R]_2$-1,3 or -1,4 (2 mol), are catalysts (with methylaluminoxane) for the polymerisation of ethylene.

There has been much recent interest in chelating bis(amido) ligands in the context of zirconium(IV) or titanium(IV) chemistry, in part because of their ability to catalyse the polymerisation of olefins. Examples of such catalysts have been $[\overline{Zr(LL})(CH_2Ph)_2]$ with methylaluminoxane (MAO) [LL = 2,2′-$\{N(C_6H_4Bu^t\text{-}p)\}_2$-6,6′-$Me_2$-$(C_6H_3)_2$],[1] $[\overline{Ti(L'L'})Me_2]$ with $B(C_6F_5)_3$ [L′L′ = $N(R)(CH_2)_3NR$, R = $C_6H_3Me_2$-2,6];[2] for a review, see ref. 3. The *ortho*-*N*,*N*′-bis(silylated)amidobenzene ligands have also been employed as chelating moieties in group 14 metal and also zirconium(IV) complexes, as exemplified by $[(Sn\{N(SiMe_3)\}_2C_6H_4\text{-}1,2)_2(\mu\text{-tmen})]$[4] and $[Zr(\{N(SiPr^i_3)\}_2C_6H_4\text{-}1,2)_2]$.[5]

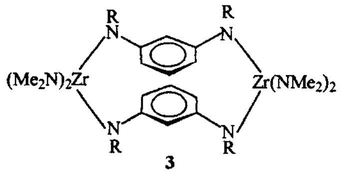
We now draw attention to the role of the isomeric *meta*- and *para*-*N*,*N*′-disilylated bis(amido)benzene ligands in zirconium chemistry. Of particular novelty is the discovery that their bonding mode differs from that of the chelating and terminally bonding *ortho* isomer. The *N*,*N*′-bis(trimethylsilyl)-1,3- or -1,4-diamidobenzene ligands behave in a bridging fashion, giving rise to binuclear derivatives such as **1**–**4**. These are either open chain molecules (**1** or **2**) or are macrocycles (**3** or **4**).



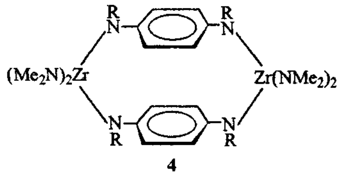
1



2



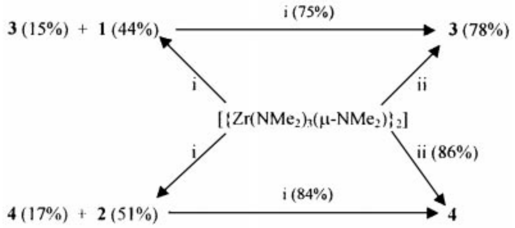
3



4

An alternative method of generating a binuclear $[Cu^{II}]$ amido-based cyclophane from 1,4-$C_6H_4(NH_2)_2$ has been reported: by cyclocondensation of the latter with ethylenediaminetetraacetic anhydride and successive treatment with Na_2CO_3 and $CuCl_2\cdot 2H_2O$.[6]

Treatment of $[\{Zr(NMe_2)_3(\mu\text{-}NMe_2)\}_2]$ with 1,3- or 1,4-$C_6H_4[N(H)R]_2$ (R = $SiMe_3$) (2 mol) gave (ii in Scheme 1) yellow crystals of the cyclophane **3** or **4**, respectively, while the intermediates **1** and **2** were isolated (albeit with significant proportions of **3** and **4**) (i in Scheme 1) when equimolar quantities of these reagents were used. The conversion of each acyclic compound **1** or **2** into the macrocycle **3** or **4** was evidently faster than the formation of **1** or **2**, respectively. Complexes **3** or **4** were resistant to further transamination, when an excess of the appropriate diamine was employed.



Scheme 1 Synthesis of the crystalline complexes **1**–**4**. *Reagents and conditions*: $C_6H_4[N(H)SiMe_3]_2$-1,3 or -1,4 (i, 1 mol; ii, 2 mol), PhMe, 0 °C, 20 h and then crystallisation from *n*-pentane, 4 °C.

The new, pale yellow (**3** or **4**) or colourless (**1** or **2**), highly air-sensitive, readily aromatic hydrocarbon-soluble, crystalline compounds **1**–**4** gave satisfactory microanalyses (C, H, N), as well as multinuclear NMR spectra.‡ For each complex, the ^1H NMR spectra displayed single sets of sharp signals, consistent with the illustrated structures, and for **3** and **4** confirmed (X-ray) for the crystalline complexes.§ A common feature as between **3** and **4** on the one hand and **1** and **2** on the other, was that the aromatic and $SiMe_3$ ^1H NMR signals for the former were more shielded while the converse was the case for the NMe_2 signals.

The X-ray molecular structures of complexes **3** and **4** are shown in Figs. 1 (**3**) and 2 (**4**) and selected geometric parameters

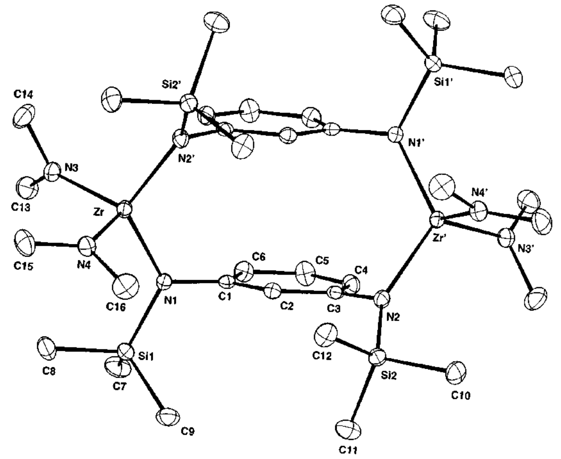


Fig. 1 The molecular structure of **3**.

---

† No reprints available.

Table 1 Selected geometric parameters for **3** and **4**

Compound	av. Zr–N$_{endo}$/Å	av. Zr–N$_{exo}$/Å	*endo*-N–Zr–N′/°	MeN–Zr–N′Me/°	C$_{ipso}$–N–Zr/°	Δ(C$_6$H$_4$–C$_6$H$_4$)[a]/Å	C$_6$H$_4$/C$_6$H$_4$ displ.[b]/Å
3	2.094(2)	2.031(2)	119.32(8)	105.29(10)	122.9(2), 103.7(2)	3.43	0.75
4	2.086(2)	2.026(2)	121.21(8)	102.11(9)	115.31(12), 107.27(12)	3.48	0.15

[a] This refers to the distance between the two C$_6$ planes. [b] This refers to the lateral displacement of the two C$_6$ planes.

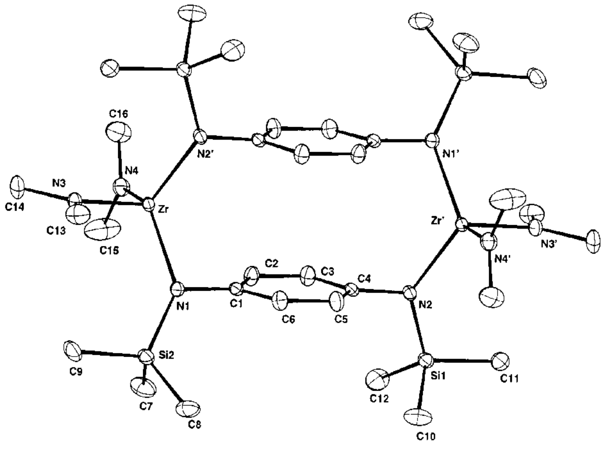


Fig. 2 The molecular structure of **4**.

are compared in Table 1. The aromatic rings are related by a crystallographic twofold axis for **3** and an inversion centre for **4**. They are parallel in both structures, the planes being separated by 3.43 (**3**) or 3.48 (**4**) Å but show a sideways displacement (**3** > **4**). The endocyclic N–Zr–N′ bond angle is somewhat wider in **4** than **3** but the converse is so for the Me$_2$N–Zr–N′Me$_2$ angle; while for each, the average endocyclic Zr–N bond length is significantly longer than the exocyclic, but both are unexceptional; for example, the average Zr–N bond lengths are 2.08 Å for [Zr({N(SiPr$^i_3$)}$_2$C$_6$H$_4$-1,2)$_2$],[5] and 2.06 Å for [Zr{η^5-C$_5$H$_4$C(Me)$_2$C$_9$H$_6$-η^5}(NMe$_2$)$_2$].[7] The sum of the angles at each nitrogen atom is close to 360°.

Each of the metallocyclophanes **3** and **4**, in the presence of MAO, was active as a catalyst for the polymerisation of ethylene, and this activity was substantially enhanced if **4** was pretreated with an excess (10 mol) of chlorotrimethylsilane to yield **5**; the polyethylenes had very high average molecular weights.¶ Complex **5** is tentatively formulated as RN(C$_6$H$_4$)N(R)Zr(Cl)$_2$N(R)(C$_6$H$_4$)N(R)ZrCl$_2$, an analogue of **4** (having only the terminal amido groups displaced by chloride ligands).

Compounds **1**–**4** are the first binuclear, four-coordinate zirconium(IV) amides and are also unusual in being heteroleptic. The cyclophanes **3** and **4** are of further interest in being macrocycles having both Lewis acid (Zr) and base [N(R) and C$_6$] sites and having parallel C$_6$ rings separated by distances close to that (3.35 Å) found in graphite. This ambiphilicity, as well as the catalytic properties of these compounds, are under further investigation as are comparisons of the use of these *meta*- and *para*-*N*,*N*′-bis(trimethylsilyl)bis(amido)benzene ligands in the context of complexes of other metals [for Ge^{II} and Sn^{II}, see refs. 8 and 9].

We thank the EU for the award of a Marie Curie fellowship to S. D. and to Dr M. Kristen and BASF (Ludwigshafen) for other support.

Notes and references

‡ *Selected spectroscopic data*: for **1**: ^{1}H NMR (300.1 MHz, 298 K, C$_6$D$_5$CD$_3$) δ 7.04 (t, *J* 7.2 Hz, 1H), 6.58 (d, *J* 7.2 Hz, 2H), 6.25 (s, 1H), 2.84 (s, NMe$_2$, 36H), 0.23 (s, SiMe$_3$, 18H). ^{13}C{^{1}H} NMR (75.5 MHz, 298 K, C$_6$D$_5$CD$_3$) δ 151.3, 132.0, 126.6, 122.9 (C$_6$H$_4$), 42.3 (NMe$_2$), 1.8 (SiMe$_3$). For **2**: ^{1}H NMR (300.1 MHz, 298 K, C$_6$D$_6$) δ 6.91 (s, 4H), 2.87 (s, NMe$_2$, 36H), 0.24 (s, SiMe$_3$, 18H). ^{13}C{^{1}H} NMR (75.5 MHz, 298 K, C$_6$D$_6$) δ 142.8, 128.9 (C$_6$H$_4$), 41.9 (NMe$_2$), 1.5 (SiMe$_3$). For **3**: ^{1}H NMR (300.1 MHz, 298 K, C$_6$D$_5$CD$_3$) δ 6.68 (t, *J* 7.0 Hz, 1H), 6.28 (d, *J* 7.0 Hz, 2H), 6.08 (s, 1H), 3.05 (s, NMe$_2$ 12H), 0.14 (s, SiMe$_3$, 18H). ^{13}C{^{1}H} NMR (75.5 MHz, 298 K, C$_6$D$_5$CD$_3$) δ 150.2, 130.9, 125.6, 121.8 (C$_6$H$_4$), 43.4 (NMe$_2$), 2.3 (SiMe$_3$). For **4**: ^{1}H NMR (300.1 MHz, 298 K, C$_6$D$_6$) δ 6.50 (s, 4H), 3.10 (s, NMe$_2$, 12H), 0.18 (s, SiMe$_3$, 18H). ^{13}C{^{1}H} NMR (75.5 MHz, 298 K, C$_6$D$_6$) δ 144.0, 127.9 (C$_6$H$_4$), 43.2 (NMe$_2$), 2.0 (SiMe$_3$).

§ *Crystal data*: for **3**, C$_{32}$H$_{68}$N$_8$Si$_4$Zr$_2$, M = 859.7, T = 173(2) K, space group $C2/c$ (no. 15), a = 14.234(2), b = 17.771(4), c = 18.860(4) Å, β = 109.55(2)°, U = 4496(2) Å^3, Z = 4, μ(Mo-Kα) = 0.60 mm^{-1}, specimen 0.40 × 0.30 × 0.30 mm, 4123 reflections collected for $2 < \theta < 25°$, 3963 independent ($R_{\rm int}$ = 0.0167), R_1 = 0.031 for 3288 reflections with $I > 2\sigma(I)$, wR_2 = 0.077 for all data. For **4**, C$_{32}$H$_{68}$N$_8$Si$_4$Zr$_2$, M = 859.7, T = 173(2) K, space group $P\bar{1}$ (no. 2), a = 9.005(4), b = 10.128(8), c = 13.168(9) Å, α = 69.17(6), β = 80.33(4), γ = 78.63(5)°, U = 1094(1) Å^3, Z = 1, μ(Mo-Kα) = 0.62 mm^{-1}, specimen 0.3 × 0.3× 0.3 mm, 6379 reflections collected for $2 < \theta < 25°$, all independent, R_1 = 0.031 for 5617 reflections with $I > 2\sigma(I)$, wR_2 = 0.082 for all data. CCDC 182/1351. See http://www.rsc.org/suppdata/cc/1999/1909/ for crystallographic files in .cif format.

¶ *Polymerisation data*: an aliquot (25 cm^3) of a solution (**3** or **4**), or a suspension (**5**) in toluene [6×10^{-4} mol l^{-1} catalyst, MAO (3×10^{-1} mol) in toluene (1 l)] was pressurised with C$_2$H$_4$ (2.4 bar) at 20 °C for 15 min, whereafter the mixture was quenched by addition of methanolic HCl. The polymer was filtered off, washed with successively 1 M aq. HCl, water and MeOH and then dried at 80 °C. The activity corresponded to 0.11 (**3**) [or 0.15 (**4**) or 14.72 (**5**)] × 10^3 g polymer bar^{-1} h^{-1} (mol cat)$^{-1}$. The polymer had high average molecular weight ($\approx 2 \times 10^6$ g mol^{-1}), determined by viscosity determinations; solubility problems excluded the use of traditional GPC experiments.

1 F. G. N. Cloke, T. J. Geldbach, P. B. Hitchcock and J. B. Love, *J. Organomet. Chem.*, 1996, **506**, 343.
2 J. D. Scollard and D. H. McConville, *J. Am. Chem. Soc.*, 1996, **118**, 10 008.
3 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 428.
4 H. Braunschweig, B. Gehrhus, P. B. Hitchcock and M. F. Lappert, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1922.
5 K. Aoyagi, P. K. Gantzel, K. Kalai and T. D. Tilley, *Organometallics*, 1996, **15**, 923.
6 M. B. Inoue, E. F. Velazquez, F. Medrano, K. L. Ochoa, J. C. Galvez, M. Inoue and Q. Fernando, *Inorg. Chem.*, 1998, **37**, 4070.
7 W. A. Herrmann, M. J. A. Morawietz and T. Priermei, *J. Organomet. Chem.*, 1996, **506**, 351.
8 H. Braunschweig, C. Drost, P. B. Hitchcock, M. F. Lappert and L. J.-M. Pierssens, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 261.
9 H. Braunschweig, P. B. Hitchcock, M. F. Lappert and L. J.-M. Pierssens, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1156.

Communication 9/03921J