A new diamido-amine ligand based on three-carbon atom "arms": synthesis, structures and polymerisation capability of zirconium derivatives of $MeN(CH_2CH_2CH_2NSiMe_3)_2$†

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Zirconium compounds of the new diamido-amine ligand $MeN(CH_2CH_2CH_2NSiMe_3)_2$ feature significantly different molecular structures and considerably improved olefin polymerisation characteristics in comparison with analogous compounds based on the two-carbon arm homologues.

Early transition metal complexes of polydentate amide ligands[1a,b] have been shown to be important in the polymerisation[1c] and, more recently, hydroamination[1d] of olefins. Most relevant to our present contribution are Group 4 (especially Zr) complexes of diamido-amine ligands (Chart 1).[2] Cloke[2a] and Horton[2b] first introduced the all-$SiMe_3$-substituted systems **I** ($N_2N^{C2,TMS}$) which were susceptible to intramolecular activation of the amide-bound $SiMe_3$ groups. Schrock has reported the living polymerisation of 1-hexene with the mesityl functionalised analogue **II**.[3a] The $SiMe_3$-centred deactivation reactions of complexes of **I** and the success of **II** and related[3b] non-$SiMe_3$ systems have led to the view[3c] that $SiMe_3$ amide *N*-substituents are incompatible with cationic olefin polymerisation catalysts. The flexible ligand **II** can bind with *fac* or *mer* coordination. To force the apparently more favourable *fac* diamide-donor mode, a recent focus has been on the tripod-like ligand **IV**[4a] which is a modification of Gade's original $SiMe_3$-functionalised ligand **III**.[4b] Despite the attractiveness of these latter ligands, their multistep syntheses involve organic azide intermediates and a high temperature and pressure autoclave first step.[4b] Here we report a new 3-carbon "arm" diamido-amine ligand that is available in multigram quantities from commercially available starting materials, and which exclusively affords *fac* coordination and exhibits promising olefin polymerisation behaviour, even with amide-$SiMe_3$ substituents.

Reaction of the commercially available $MeN(CH_2CH_2CH_2NH_2)_2$ with $ClSiMe_3$ (2 equiv.) in the presence of NEt_3 affords the protio ligand $MeN(CH_2CH_2CH_2N(H)SiMe_3)_2$ ($H_2N_2N^{C3}$, **1-H$_2$**) as a colourless oil in 84% yield (> 15 g isolated quantities) after a simple pentane extraction.† Reaction with BuLi (2 equiv.) gives the structurally characterised[5] dimer $[MeN(CH_2CH_2CH_2N(Li)SiMe_3)_2]_2$ (**1-Li$_2$**) in 91% yield. For the purposes of making a strict comparison of the 3-carbon arm N_2N^{C3} ligand with 2-carbon arm analogues under otherwise identical conditions we selected the ligand $N_2N^{C2,Me}$ **V** (Chart 1) reported by Bertrand in the context of main group chemistry.[6]

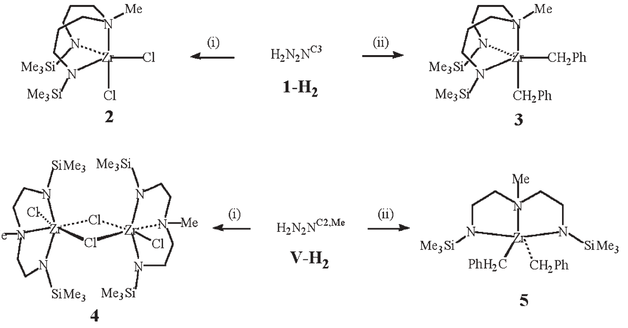
R' = R = $SiMe_3$ **I**; R' = Me, R = Mesityl **II** or $SiMe_3$ **V**

R = $SiMe_3$ **III** or Mesityl **IV**

Chart 1

The synthesis and structures of zirconium complexes of N_2N^{C3} and $N_2N^{C2,Me}$ are summarised in Scheme 1. The reactions all proceed in good yields. Alternatively, the dichloride **2** can be prepared from **1-Li$_2$** and $[ZrCl_4(THF)_2]$, and the dibenzyl **3** can be made from **2** and $PhCH_2MgBr$ (2 equiv.). The analogous reaction of **2** with MeMgBr (2 equiv.) yields $[Zr(N_2N^{C3})Me_2]$ **6**. The structures for **2**–**5** were confirmed by X-ray crystallography[5] and that of **3** is shown in Fig. 1 by way of example.†‡ Unlike certain Group 4 complexes of the two-carbon atom ligand **I**,[2a] the 300 MHz ^1H NMR spectra of **6** (toluene-d_8) show no evidence for dissociation of the amino NMe nitrogen on the NMR timescale up to 80 °C at which temperature thermal decomposition becomes significant.

Scheme 1 clearly shows how the 3-carbon arm N_2N^{C3} ligand favours *fac*-coordination. It also illustrates that, with this ligand, dichloride **2** remains monomeric whereas the otherwise identical 2-carbon arm ligand $N_2N^{C2,Me}$ leads to binuclear **4**. The binuclear structure of **4** parallels that formed with the all-$SiMe_3$ ligand **I**;[2] the *mer*-coordination found for $N_2N^{C2,Me}$ in **5** is paralleled by the coordination of the *N*-mesityl ligand **II** in its dialkyl zirconium derivatives.[3a] Points of note in the structure of **3** include the well-defined trigonal bipyramidal geometry at Zr with the longer ligand arms allowing the metal to be more fully embraced. The



Scheme 1 (i) $[ZrCl_2(NMe_2)_2(THF)_2]$, yields 52% (for **2**) and 77% (for **4**); (ii) $[Zr(CH_2Ph)_4]$, yields 70% (for **3**) and 45% (for **5**).

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† Electronic supplementary information (ESI) available: characterising data for the new compounds. See http://www.rsc.org/suppdata/cc/b4/b412381f/

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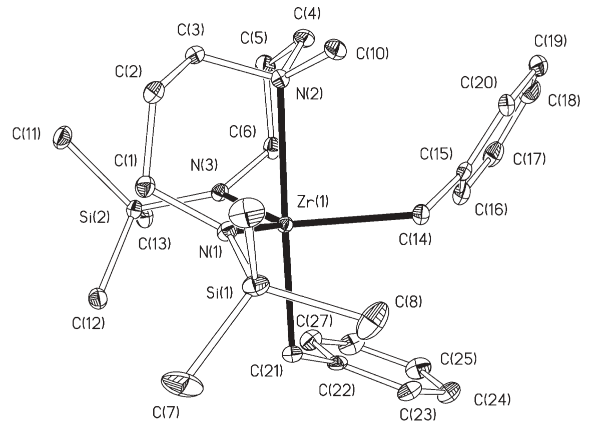

Fig. 1 Molecular structure of $[Zr(N_2N^{C3})(CH_2Ph)_2]$ **3**. Selected data: Zr(1)–N(1) 2.039(2), Zr(1)–N(2) 2.517(2), Zr(1)–N(3) 2.053(2), Zr(1)–C(14) 2.319(2), Zr(1)–C(21) 2.327(3) Å.

conformations of the two C_3 arms are different such that one $SiMe_3$ group (Si(1)) orientates towards the equatorial benzyl ligand and the other one is orientated away. The Zr–N distances for **3** are comparable to those reported for the compounds of the diamido-pyridine ligands **III** and **IV**.

With regard to olefin polymerisation catalysis, evidence of well-defined alkyl cations is essential. Dimethyl $[Zr(N_2N^{C3})Me_2]$ **6** reacts cleanly with $[CPh_3][B(C_6F_5)_4]$ (TB, 1 : 1 ratio) in C_6D_5Br to form $[Zr(N_2N^{C3})Me]^+$ $\mathbf{7}^+$. There is no evidence for $SiMe_3$ activation at room temperature, and all data point to $\mathbf{7}^+$ being fully solvent-separated from the anion. We note that the analogous reaction with ligand **IV** gives a self-trapped binuclear μ-methyl cation with a $\{Zr_2Me_2(\mu\text{-}Me)\}$ unit,[4a] highlighting again how the new ligand N_2N^{C3} helps enforce the formation of mononuclear species.

All three compounds $[Zr(N_2N^{C3})X_2]$ (X = Cl **2**, CH_2Ph **3**, Me **6**) are active for the polymerisation of ethylene (Table 1) with very favourable polydispersities as indicated by the gel permeation chromatography (GPC) data (Fig. 2). Selected data for $[Zr(N_2N^{C2,Me})X_2]_n$ (X = Cl, n = 2 **4**; X = CH_2Ph, n = 1 **5**) and the previously reported[2] $[Zr(N_2N^{C2,TMS})Cl_2]_2$ **8** under the same conditions are presented for comparison.

On MAO activation (Al : Zr ratio = 1500 : 1), the dichloride **2** (3-carbon arm) has an activity that is about two orders of magnitude higher than that for the 2-carbon arm analogue **4**. A very similar position emerges for the previously reported **8**. With TB activation, the dibenzyl **3** is again considerably more active than the 2-carbon analogue **5** under identical conditions. The dimethyl compound **6** has a lower activity than that of the dibenzyl **3** (but similar polymer is formed, Fig. 2). This perhaps points to an activator effect[4a] where, in the poorly polar toluene medium used for the polymerisation, there may in fact be some self-trapping of the $\mathbf{7}^+$ prior to enchainment of monomer. Alternatively, $\mathbf{7}^+$ could interact more strongly with the Al^iBu_3 scavenger present than the cation derived from **3** does. Such factors will be the subject of future studies.

Table 1 Polymerisation activities for $[Zr(N_2N^{C3})X_2]$ (X = Cl **2**, CH_2Ph **3**, Me **6**), $[Zr(N_2N^{C2,Me})X_2]_n$ (X = Cl **4**, CH_2Ph **5**) and $[Zr(N_2N^{C2,TMS})Cl_2]_2$ **8**[a]

Dichloride pre-catalyst[c]	Activity[b] (avg. M_w)	Dialkyl pre-catalyst[d]	Activity[b] (avg. M_w)
2	110 (1.81×10^5)	**3**	164 (2.48×10^5)
4	1.3 (7.52×10^5)	**5**	0.8 (not measured)
8	4.0 (1.46×10^6)	**6**	47 (1.29×10^4)

[a] Conditions: 10 or 20 μmol precatalyst, 250 cm^3 toluene; 5 bar ethylene; run time 60 min; T_o 22 ± 3 °C. [b] In kg(PE)/mol(Zr)/h/bar. [c] 1500 equiv. MAO. [d] 1 equiv. TB and 250 equiv. Al^iBu_3.

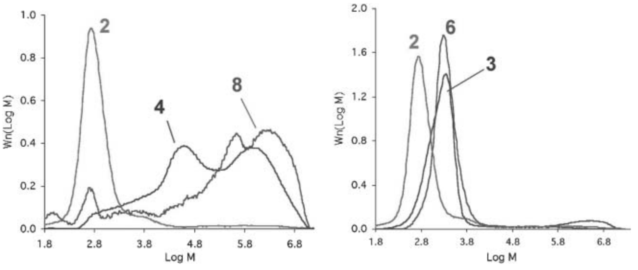

Fig. 2 GPC traces for polyethylene produced by $[Zr(N_2N^{C3})X_2]$ (X = Cl **2**, CH_2Ph **3**, Me **6**), $[Zr(N_2N^{C2,Me})Cl_2]_2$ **4** and $[Zr(N_2N^{C2,TMS})Cl_2]_2$ **8**.

The ^1H and ^{13}C NMR data (100 °C, $C_6D_4Cl_2$) for the soluble portion of the solid, free-flowing polymers formed by the new catalysts suggest they are non-branched and without detectable vinyl end-groups. No significant levels of hydrocarbon or other impurity were detected. The GPC data (Fig. 2) show that all three catalyst systems **2**/MAO, **3**/TB and **6**/TB produce rather similar polymers containing low and high molecular weight fractions. Under identical conditions the polymers formed for the 2-carbon chain analogues are very broad and multimodal. Although the polymers formed by **2**/MAO and **3**/TB each have a high molecular weight fraction, the prominent low molecular weight components have polydispersity indices (PDIs) between 1.5 (**6**/TB; $M_w = 2.6 \times 10^3$) and 1.8 (**2**/MAO; M_w = 890). We believe that the larger PDIs for the more active **2**/MAO and **3**/TB systems can be attributed to the non-isothermal experimental conditions (ΔT_{max} between 20 and 50 °C were recorded). Indeed, preliminary results show that diluting the catalyst solution (and reducing the exotherm output) for **2**/MAO (at constant Zr : Al ratio) retains the lower molecular weight component and significantly reduces the higher molecular weight material. Further work on these aspects are in progress as well as extending the studies to α-olefins.

Although the data in Table 1 and Fig. 2 show that the silylated system N_2N^{C3} has considerable merit and promise for future development (with the added benefit of the inexpensive and facile introduction of different SiR_3 amide *N*-substituents), it is clear from the literature that one should also have access to *N*-arylated homologues. Therefore we also report here our preliminary results that arylation of $MeN(CH_2CH_2CH_2NH_2)_2$ with mesityl bromide using standard procedures[7] affords $MeN(CH_2CH_2CH_2N(mesityl)H)_2$ in *ca.* 50% isolated yield.† Complexation reactions of this ligand are underway, together with polymerisation studies of the compounds so formed. We will report on this work in due course.

In conclusion, we have introduced a new, simple and readily-available diamido-donor ligand, established its capability in areas of current interest and have demonstrated how its chemistry and applications may be developed in the future.

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Notes and references

‡ Crystal data for [Zr{MeN($CH_2CH_2CH_2NSiMe_3)_2$}($CH_2Ph)_2$] (**3**): $C_{27}H_{47}N_3Si_2Zr_1$, M_w = 561.09, orthorhombic, *Pna* 21, *a* = 20.9927(4), *b* = 12.0115(2), *c* = 12.1022(2) Å, α = 90.00, β = 90.00, γ = 90.00°, *U* = 3051.6(1) $Å^3$, *Z* = 4, *F*(000) = 1180.68, *T* = 150 K, Nonius Kappa CCD, Mo-Kα radiation, $2.91 \leqslant 2\theta \leqslant 27.48°$, 6677 independent reflections, 5525 reflections $I > 3\sigma(I)$, *R* = 0.0273, R_w = 0.0262. The structure was solved using the CRYSTALS software suite.[8] Notes on refinement: the refined Flack parameter of 0.50(3) is indicative of an intimately twinned structure since Friedel pairs were collected but not merged. CCDC 247514. See http://www.rsc.org/suppdata/cc/b4/b412381f/ for crystallographic data in .cif or other electronic format.

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