High activity ethylene polymerisation catalysts based on chelating diamide ligands

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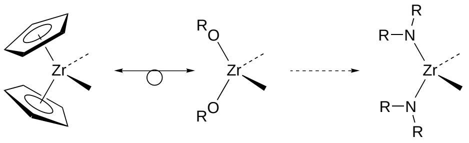
Treatment of $Zr(NMe_2)_4$ with $RNH(SiPh_2)NHR$ and $RNH(Me_2SiCH_2CH_2SiMe_2)NHR$ ($R = 2,6\text{-}Me_2C_6H_3$) affords the four- and seven-membered chelate complexes $\{Zr[RN(SiPh_2)NR](NMe_2)_2(HNMe_2)\}$ and $\{Zr[RN(Me_2SiCH_2CH_2SiMe_2)NR](NMe_2)_2\}$ respectively; a dramatic effect of chelate ring size on ethylene polymerisation activity and kinetic profile is found.

There is considerable interest in the development of new generation 'non-metallocene' catalysts for the polymerisation of α-olefins. Chelating diamide complexes of the Group 4 metals have recently become the focus of much attention,[1–10] partly because of their close relationship to the commercially significant half-sandwich metal amido 'constrained geometry' catalyst system,[11,12] and more generally due to a relationship to metallocenes that may be traced through alkoxide relatives (Scheme 1).† A potential advantage of the bis(amido)metal system relative to the constrained geometry half-sandwich metal amide catalyst family is a lower formal electron count [$(R_2N)_2Zr$ is formally a $10e^-$ fragment, *cf.* $12e^-$ for $CpZr(NR_2)$] which is likely to result in a more electrophilic and therefore potentially more active catalyst fragment. However, it must be recognised that the bis(amido)metal system is sterically more open and may need steric tuning to minimise deactivation processes.

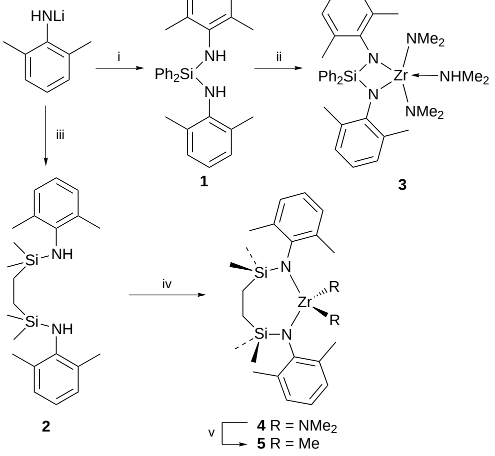


Scheme 1

We report a surprisingly active zirconium ethylene polymerisation catalyst system based on chelating diamide ligands. Of particular significance is the observation of dramatically enhanced activity and a more stable kinetic profile upon increase in the chelate ring size. Compounds **1** and **2** are readily synthesised in high yield *via* reaction of LiNHR ($R = 2,6\text{-}Me_2C_6H_3$) with the appropriate dichlorosilane (Scheme 2). Treatment of **1** and **2** with $Zr(NMe_2)_4$ in toluene at 90 °C leads to elimination of 2 equiv. of Me_2NH and formation of four- and seven-membered chelate complexes **3** and **4** in excellent yield.‡

The structures of **3** and **4** have been determined by X-ray crystallography.§ The structure of **3** reveals the formation of a distorted trigonal bipyramidal Zr complex (Fig. 1), the Zr being bonded to the bidentate chelating diamide **1**, two Me_2N groups and a molecule of Me_2NH. The equatorial plane is defined by N(2), N(6) and N(9), the axial positions being occupied by N(1) and N(3). The principal distortion in the coordination geometry is due to the small bite [71.3(1)°] of the chelating diamide, a consequence of which is 'reduced' steric congestion of the Zr centre allowing retention of three of the original four Me_2N ligands (rather than the expected two). The N_2SiZr chelate ring is planar to within 0.01 Å.

By contrast, the structure of **4** (Fig. 2) reveals a slightly distorted tetrahedral coordination at Zr, comprising the bidentate disilyldianilide [bite angle 109.2(1)°] and just two Me_2N ligands. An important effect of increasing the size of the chelate ring in **4** (now seven-membered, *cf.* four-membered in **3**) is for the two aryl rings to partially envelop the Zr centre and one of the Me_2N ligands [N(10)]. The geometry of the seven-membered chelate ring appears to be somewhat strained, the internal angles at the N (131°) and C (117°) centres being significantly enlarged from normal trigonal and tetrahedral geometries, respectively. The reason(s) for these distortions are not immediately evident, although they are clearly a factor in the envelopment of the Zr centre described above. Complex **4** is readily converted to complex **5** upon reaction with excess $AlMe_3$.[13]



Scheme 2 *Reagents and conditions*: i, Cl_2SiPh_2 (0.5 equiv.), Et_2O, room temp., 12 h, 79%; ii, $Zr(NMe_2)_4$, toluene, 90 °C, 12 h, 98%; iii, $ClSi(Me)_2CH_2CH_2Si(Me)_2Cl$ (0.5 equiv.), Et_2O, room temp., 12 h, 74%; iv, $Zr(NMe_2)_4$, toluene, 90 °C, 12 h, 97%; $AlMe_3$ (5.0 equiv.), toluene, room temp., 30 min, 98%

The results of preliminary studies on their activities for ethylene polymerisation are collected in Table 1. For the mono-silyl bridged species **3**, pretreatment with Bu^nLi, to remove the bound Me_2NH, and prealkylation with excess $AlMe_3$, followed

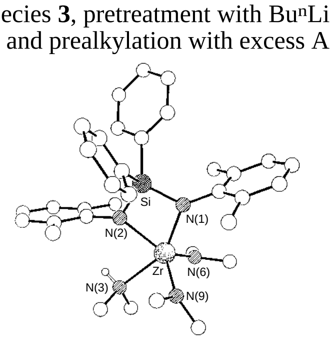


Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Zr–N(1) 2.158(2), Zr–N(2) 2.159(2), Zr–N(3) 2.426(2), Zr–N(6) 2.025(3), Zr–N(9) 2.057(3), Si–N(1) 1.709(2), Si–N(2) 1.725(2); N(6)–Zr–N(9) 108.5(1), N(6)–Zr–N(1) 106.1(1), N(9)–Zr–N(1) 105.2(1), N(6)–Zr–N(2) 128.1(1), N(9)–Zr–N(2) 122.4(1), N(1)–Zr–N(2) 71.3(1), N(6)–Zr–N(3) 91.8(1), N(9)–Zr–N(3) 89.2(1), N(1)–Zr–N(3) 151.6(1), N(2)–Zr–N(3) 80.3(1), N(1)–Si–N(2) 94.2(1), Si–N(1)–Zr 97.5(1), Si–N(2)–Zr 97.0(1).

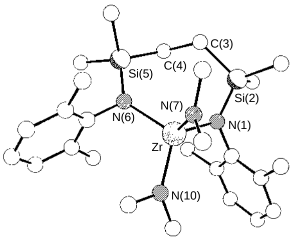


Fig. 2 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Zr–N(10) 2.024(4), Zr–N(7) 2.032(4), Zr–N(1) 2.084(4), Zr–N(6) 2.105(4), N(1)–Si(2) 1.735(4), Si(2)–C(3) 1.874(5), C(3)–C(4) 1.535(7), C(4)–Si(5) 1.869(5), Si(5)–N(6) 1.746(4); N(10)–Zr–N(7) 104.7(2), N(10)–Zr–N(1) 116.0(2), N(7)–Zr–N(1) 108.2(2), N(10)–Zr–N(6) 111.1(2), N(7)–Zr–N(6) 107.2(2), N(1)–Zr–N(6) 109.2(1), Si(2)–N(1)–Zr 129.0(2), N(1)–Si(2)–C(3) 107.8(2), C(4)–C(3)–Si(2) 116.8(4), C(3)–C(4)–Si(5) 116.6(4), N(6)–Si(5)–C(4) 110.8(2), Si(5)–N(6)–Zr 131.7(2).

by exposure to ethylene (10 atm) in the presence of MAO (750 equiv.) at 50 °C gave an active, although short-lived (< 15 min) catalyst; 450 mg of polyethylene was isolated, corresponding to an activity of 3 g mmol^{-1} h^{-1} bar^{-1}. By contrast, under identical conditions of temperature, pressure and cocatalyst concentration (entry 2), complex **4** afforded a steady uptake of ethylene over the 60 min duration of the run at an activity of 490 g mmol^{-1} h^{-1} bar^{-1}. Increasing the temperature (entries 2–4) gave a corresponding increase in activity, although a noticeable deactivation occurs over the course of the 60 min run at 50 °C, which becomes even more enhanced at 75 °C. The effect of MAO cocatalyst concentration can be seen from entries 3, 5 and 6, the more MAO the higher the activity and also the more stable the kinetic profile. If the procatalyst is not pre-alkylated with $AlMe_3$ (entry 7) reduced activity is found, consistent with the necessity for efficient alkylation of the Me_2N complex;[13] MAO on its own is known to be a relatively poor alkylating agent. The molecular weights of the polyethylenes generated using the most active catalysts are in the region of 10^5 (M_w) with relatively broad molecular weight distributions (PDIs 5–9). These will be discussed in more detail in a future publication.

Treatment of dimethylzirconium procatalyst **5** with trityltetrakis(pentafluorophenyl)borate at 50 °C initially gives a highly active catalyst that rapidly deactivates over 10 min. The same procatalyst in the presence of MAO gives a much more stable kinetic profile and an activity figure of merit comparable to prealkylated **4** (entry 3). This is consistent with the general stabilising effect found for MAO with metallocene catalyst systems.

The dramatically more favourable activity and kinetic profile characteristics found for **4** relative to **3** may be attributed to the steric protection of the zirconium centre by the bulky aryl substituents of the large ring chelate ligand. Not only do these prevent the binding of small base molecules such as Me_2NH, they also undoubtedly lend protection to the active catalyst site.

Table 1 Ethylene polymerisation characteristics[a] for **3**–**5**

Entry	Procatalyst	Cocatalyst (equiv.)	T/°C	Activity/ g mmol^{-1} h^{-1} bar^{-1}
1	**3**	MAO (750)	50	3[b]
2	**4**	MAO (750)	25	250[c]
3	**4**	MAO (750)	50	490[d]
4	**4**	MAO (750)	75	680[e]
5	**4**	MAO (100)	50	140[b]
6	**4**	MAO (2000)	50	990[d]
7	**4**	MAO (750)[f]	50	70
8	**5**	$[Ph_3C][B(C_6F_5)_4]$	50	60[b]
9	**5**	MAO (750)	50	400[d]

[a] General conditions: procatalyst dissolved in toluene for runs 1–7 and 9, CH_2Cl_2 for run 8, pretreatment with excess $AlMe_3$ (10 equiv.) for runs 1–6, 1 litre autoclave, 10 atm ethylene pressure, isobutane solvent, $AlMe_3$ scavenger, runs carried out over 60 min. [b] Rapid deactivation. [c] Stable ethylene uptake over 1 h duration of run. [d] Slow deactivation over 1 h duration of run. [e] Deactivation more rapid than in footnote (*d*). [f] No prealkylation.

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Notes and References

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† The similar 1σ,2π bonding characteristics of the cyclopentadienide and alkoxide ligands affords a direct isolobal relationship. It should be noted that, whilst closely related to the alkoxide moiety, the amide ligand is formally a 1σ,1π unit and therefore is not strictly isolobal; as a 1σ,1π ligand it also donates two fewer electrons to the metal centre.

‡ Satisfactory elemental analyses have been obtained. *Selected data* for **1**: $\delta_H(C_6D_6$, 298 K) 2.10 (s, 12 H, Ph*Me*$_2$), 3.39 (br s, 2 H, NH), 6.80–6.91 (overlapping m, aryl H), 7.04–7.10 (overlapping m, aryl H), 7.66–7.84 (overlapping m, aryl H); $\delta_C(C_6D_6$, 298 K) 20.44, 122.13, 129.05, 130.10, 130.72, 134.81, 135.02, 136.82, 142.90. For **2**: $\delta_H(C_6D_6$, 298 K) 0.76 (s, 12 H, Si*Me*$_2$), 0.51 (s, 4 H, $(CH_2SiMe_2)_2$), 2.18 (s, 12 H, Ph*Me*$_2$), 6.85 (t, 2 H, $^3J_{HH}$ 6.7, *p*-C_6H_3), 7.00 (d, 4 H, $^3J_{HH}$ 6.7, *m*-C_6H_3); $\delta_C(C_6D_6$, 298 K) -1.10, 9.75, 19.85, 122.01, 128.70, 131.45, 143.80. For **3**: $\delta_H(C_6D_6$, 298 K) 1.42 (br s, 1 H, *H*NMe$_2$), 1.68 (d, 6 H, $^3J_{HH}$ 5.9, HN*Me*$_2$), 2.26 (br s, 6 H, Ph*Me*), 2.42 (br s, 6 H, Ph*Me*), 2.79 (s, 12 H, N*Me*$_2$), 7.07–7.11 (overlapping m, aryl H), 7.61–7.64 (overlapping m, aryl H); $\delta_C(C_6D_6$, 298 K) 21.15, 39.43, 41.95, 120.99, 127.22, 128.65, 135.64, 142.83. For **4**: $\delta_H(C_6D_6$, 298 K) 0.13 (s, 12 H, Si*Me*$_2$), 1.21 (s, 4 H, Me_2SiCH_2), 2.39 (s, 12 H, Ph*Me*$_2$), 2.48 (s, 12 H, N*Me*$_2$), 6.83 (t, 2 H, $^3J_{HH}$ 7.3, aryl H), 7.06 (d, 4 H, $^3J_{HH}$ 7.3, aryl H); $\delta_C(C_6D_6$, 298 K) 1.06, 10.72, 20.61, 42.42, 123.21, 128.95, 135.36, 146.13. For **5**: $\delta_H(C_6D_6$, 298 K) 0.12 (s, 12 H, Si*Me*$_2$), 0.23 (s, 6 H, Zr*Me*$_2$), 1.08 (s, 4 H, Me_2SiCH_2), 2.37 (s, 12 H, $C_6H_3Me_2$), 6.89–6.95 (m, 2 H, *p*-aryl H), 7.00–7.03 (m, 4 H, *m*-aryl H); $\delta_C(C_6D_6$, 298 K) 0.18 ($SiMe_2$), 9.38 ($C_6H_3Me_2$), 20.75 ($C_6H_3Me_2$), 43.07 ($ZrMe_2$), 125.48 (C_6H_3-C_m), 129.51 (C_6H_3-C_p), 137.00 (C_6H_3-C_o), 137.94 (C_6H_3-C_{ipso}).

§ *Crystal data* for **3**: $C_{34}H_{47}N_5SiZr$, $M = 645.1$, monoclinic, $P2_1/n$ (no. 14), $a = 11.425(1)$, $b = 19.501(1)$, $c = 15.423(3)$ Å, $\beta = 97.58(1)°$, $V = 3406.1(7)$ Å^3, $Z = 4$, $D_c = 1.26$ g cm^{-3}, μ(Cu-Kα) = 32.0 cm^{-1}, $F(000) = 1360$. A clear prism of dimensions 0.35 × 0.23 × 0.10 mm was used. For **4**: $C_{26}H_{46}N_4Si_2Zr$, $M = 562.1$, monoclinic, $P2_1/c$ (no. 14), $a = 9.403(2)$, $b = 33.301(6)$, $c = 10.640(2)$ Å, $\beta = 113.02(1)°$, $V = 3066(1)$ Å^3, $Z = 4$, $D_c = 1.22$ g cm^{-3}, μ(Mo-Kα) = 4.6 cm^{-1}, $F(000) = 1192$. A clear prism of dimensions 0.67 × 0.57 × 0.57 mm was used. For **3** (**4**), 5590 (4306) independent reflections were measured on a Siemens P4/PC diffractometer at 183 K (293 K) with graphite monochromated Cu-Kα—rotating anode source—(Mo-Kα) radiation using ω-scans. The structures were solved by direct methods and all the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.036$ (0.046), $wR_2 = 0.095$ (0.099) for 5084 (3093) independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 128°$ (50°)] and 351 (299) parameters respectively. The N–H hydrogen atom in **3** was located from a ΔF map and refined isotropically subject to an N–H distance constraint (0.90 Å). CCDC 182/700.

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