

# Surprising activity for Group 4 polyolefin catalysts [M{(OAr)<sub>2</sub>py}Cl<sub>2</sub>(thf)] (M = Zr, Ti) bearing tridentate pyridine-2,6-bis(aryloxy) ligands †

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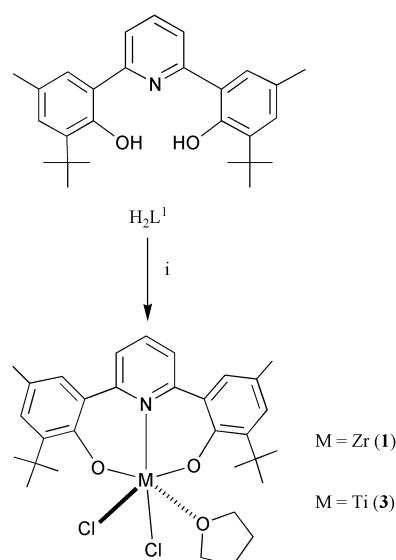
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Unexpectedly high ethylene polymerisation activity is observed for zirconium(IV) catalysts supported by a rigid tridentate pyridine-bis(phenolate) ligand in conjunction with MAO; a methodology towards analogues with unsymmetric ligands and the significance of the coordinated solvent molecule are described.

Many academic and industrial endeavours have been dedicated to the pursuit of new families of non-metallocene polyolefin catalysts, and considerable success for Group 4 metals has been achieved using dianionic chelating alkoxide-type spectator ligands.<sup>1</sup> While such species are isoelectronic with the [Cp<sub>2</sub>Zr] moiety, a diverse range of metal-ligand environments has been realised based on bidentate ([O,O] and [O,L]<sub>2</sub>) and tetradentate [O<sub>2</sub>L<sub>2</sub>] auxiliaries to yield novel catalysts with unprecedented activity and polymerisation capability.<sup>2,3</sup>

There is, however, a relative dearth in catalyst design incorporating tridentate [O,L,O] ancillary ligands.<sup>4</sup> Hence the criteria for active catalysts and the factors affecting polymerisation properties for these systems have not been elucidated. Kol and co-workers recently reported that bis(benzyl) Group 4 complexes with tetradentate ligands derived from amine-bis(phenolate) plus an extra donor arm can display extremely high activity in the polymerisation of 1-hexene.<sup>3</sup> One of the salient features of this work is that the pendant arm is essential for highly active catalysts, and tridentate analogues without the fourth donor show poor activity. These observations encouraged us to disclose our results for Group 4 complexes containing rigid tridentate pyridine-2,6-bis(phenolate) ligands. Despite similarities between the coordination characteristics of these and Kol's tridentate auxiliaries, we have observed unanticipated yet very high activity in our system for the polymerisation of ethylene.

The symmetric pyridine-bis(phenol) H<sub>2</sub>L<sup>1</sup> was prepared by the Ni-catalysed coupling reaction of the Grignard reagent derived from the substituted 2-bromoanisole with 2,6-dibromopyridine, followed by demethylation using molten pyridinium chloride.<sup>5</sup> Slow addition of Li<sub>2</sub>L<sup>1</sup> to ZrCl<sub>4</sub> in toluene/tetrahydrofuran at -78 °C afforded the thf-solvated complex **1** (Scheme 1) in 65% yield, but due care must be applied to this procedure to avoid generation of the bis-ligand species [Zr(L<sup>1</sup>)<sub>2</sub>].<sup>6</sup> Similarly, the Et<sub>2</sub>O adduct [Zr(L<sup>1</sup>)Cl<sub>2</sub>(OEt<sub>2</sub>)] (**2**) was formed using diethyl ether as the reaction solvent. A more convenient route to **1** (>80% yield) entails the reaction of Zr(CH<sub>2</sub>Ph)<sub>2</sub>Cl<sub>2</sub>(Et<sub>2</sub>O)<sub>n</sub> with H<sub>2</sub>L<sup>1</sup> in toluene/THF; the value of the THF donor is highlighted by the fact that in its absence, an intractable yellow precipitate is produced. The titanium(IV) complex [Ti(L<sup>1</sup>)Cl<sub>2</sub>(thf)] (**3**) readily precipitated from the reaction mixture containing TiCl<sub>4</sub>(thf)<sub>2</sub> and H<sub>2</sub>L<sup>1</sup> in Et<sub>2</sub>O/THF as a highly crystalline dark red solid.



**Scheme 1** Reagents and solvents (all at -78 to 20 °C): i, for Zr, Method 1: (a) 2 <sup>n</sup>BuLi, toluene, (b) ZrCl<sub>4</sub>, toluene/THF; Method 2: Zr(CH<sub>2</sub>Ph)<sub>2</sub>Cl<sub>2</sub>(Et<sub>2</sub>O)<sub>n</sub>, toluene/THF; for Ti, TiCl<sub>4</sub>(thf)<sub>2</sub>, Et<sub>2</sub>O/THF.

The design of unsymmetric ligand systems and chiral catalytic species are fundamental to accomplishing the goal of stereospecific olefin polymerisation. We have devised a versatile methodology for the synthesis of unsymmetric pyridine-bis(phenol) substrates (Scheme 2). This is evolved from the preparation of pyridine-2,6-bis(2'-phenol),<sup>7</sup> which in essence involves the sequential coupling of two 2'-methoxyacetophenone molecules. The targeted H<sub>2</sub>L<sup>2</sup> ligand with different phenolic substituents can thus be obtained in moderate yield, and in principle, this strategy allows the synthesis of any unsymmetric pyridine-2,6-bis(phenol) molecule depending on the availability of the substituted 2'-methoxyacetophenones **A**<sup>1</sup> and **A**<sup>2</sup>. The Ti(IV) derivative **4** was generated by the interaction of TiCl<sub>4</sub>(thf)<sub>2</sub> with H<sub>2</sub>L<sup>2</sup> in Et<sub>2</sub>O/THF and was precipitated by slow addition of n-hexane. Synthesis of the Zr congener has been thwarted by the facile formation of [Zr(L<sup>2</sup>)<sub>2</sub>] and species bearing protonated pyridyl moieties (as observed by <sup>1</sup>H NMR).

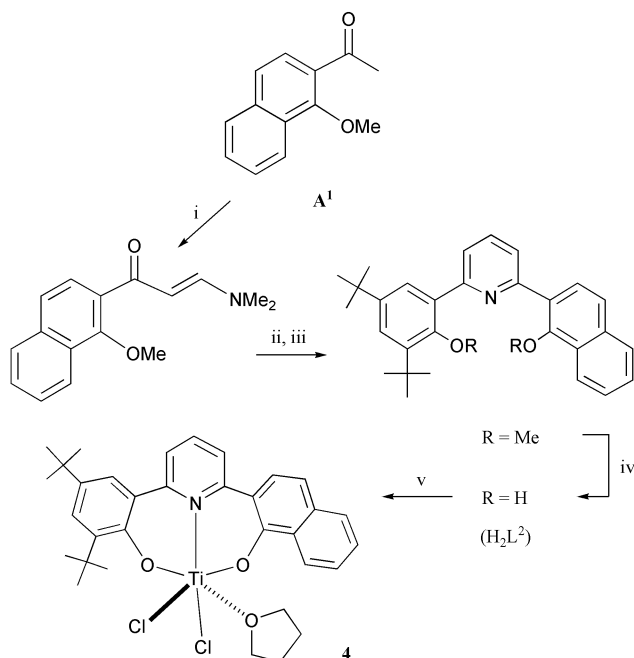
The molecular structures of complexes **1** (Fig. 1), **2** and **3** have been determined by X-ray crystallography. ‡ The pseudo-octahedral Zr centre in **1** is chelated by L<sup>1</sup> in a tridentate meridional fashion, with *cis*-chloride atoms and a thf group completing the coordination sphere. The Zr–O(thf) [2.247(3) Å] and Zr–OEt<sub>2</sub> [2.295(2) Å] distances in **1** and **2** respectively are significantly longer than the Ti–O(thf) bond length in **3** [2.148(3) Å]. The non-planar conformation of the pyridine-bis(phenolate) moiety and hence the two six-membered [M–N–O] metallacycles result in dihedral angles between the L<sup>1</sup> aromatic rings of 47 and 43° for **1**, 37 and 44° for **2**, and 33 and 45° for **3**. The *cis* configuration of the chloride ligands

† Electronic supplementary information (ESI) available: experimental and characterisation details. See <http://www.rsc.org/suppdata/dt/b2/b206328j/>

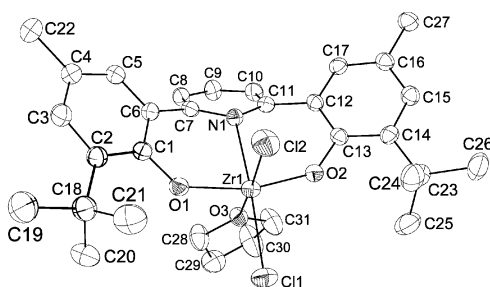
**Table 1** Polymerisation data<sup>a</sup>

Compound <b>1</b> /μmol	<i>T</i> /°C	Time/min	Yield/g	Activity/g mol <sup>-1</sup> h <sup>-1</sup> atm <sup>-1</sup>	<i>T</i> <sub>m</sub> /°C
6.29	20	1	0.29	2.74 × 10 <sup>6</sup>	128
4.72	20	2	0.92	5.85 × 10 <sup>6</sup>	129
4.72	1	2	0.23	1.45 × 10 <sup>6</sup>	134
4.72	65	2	0.31	2.00 × 10 <sup>6</sup>	111
7.86	20	4 <sup>b</sup>	2.09	3.99 × 10 <sup>6</sup>	125
4.72	20	6 <sup>b</sup>	3.32	7.03 × 10 <sup>6</sup>	127

<sup>a</sup> Conditions: 50 mL toluene, 1 atm pressure of ethylene, 1000 equiv. MAO co-catalyst. <sup>b</sup> A rapid exotherm was observed.



**Scheme 2** Reagents and conditions: i, (MeO)<sub>2</sub>CHNMe<sub>2</sub>; ii, 2-COMe-4,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OMe (**A**<sup>2</sup>) + KO<sup>*t*</sup>Bu; iii, NH<sub>4</sub>OAc; iv, molten pyHCl; v, TiCl<sub>4</sub>(thf)<sub>2</sub>, Et<sub>2</sub>O/THF.



**Fig. 1** Perspective view of [Zr(L)<sup>1</sup>Cl<sub>2</sub>(thf)] (**1**, 30% ellipsoids). Selected bond lengths (Å) and angles (°): Zr(1)–O(1) 1.958(3), Zr(1)–O(3) 2.247(3), Zr(1)–Cl(1) 2.4199(13), Zr(1)–Cl(2) 2.4033(12), Zr(1)–N(1) 2.422(3); O(1)–Zr(1)–O(2) 158.96(11), Cl(1)–Zr(1)–Cl(2) 99.49(5).

in **1–3** are important for their employment as polyolefin catalysts.

The ability of complexes **1–4** to mediate the polymerisation of ethylene in association with MAO has been investigated. Firstly, it is clear that **1** is a particularly active catalyst (Table 1). Exotherms were quickly observed (up to ~60 °C for extended runs), hence the duration of some experiments were restricted to ensure that the rates were not mass transport-limited. Catalytic rates were apparently reduced at 1 and 65 °C. At 20 °C, the higher activity for the 6 min run suggests that the polymerisation efficiency of **1** is enhanced after the appearance of the exotherm. The lower activity of the 4 min run at high catalyst concentration is indicative of a diffusion-controlled process. The highest observed activity of 7.03 × 10<sup>6</sup> g(PE) (mol catalyst)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup> corresponds to a turnover frequency value of 2.51 × 10<sup>5</sup> h<sup>-1</sup> atm<sup>-1</sup>.

The very high activity of complex **1**/MAO is intriguing given the presence of the thf ligand. This can be compared to the well-documented suppression in catalytic efficiency for the solvated [Cp<sub>2</sub>ZrMe(L)]<sup>+</sup> cations (L = thf, amine).<sup>8</sup> A report on highly effective polyethylene catalysts bearing such donor solvents appeared very recently for cationic iron and cobalt pyridine-2,6-bis(imino) derivatives,<sup>9</sup> but activity of this magnitude for the highly oxophilic Zr(IV) centre in **1** is surprising. Insight into the role of the O-donor may be acquired from the catalytic ability of the Et<sub>2</sub>O-bound analogue **2**, in which the Zr–O(donor) interaction is expected to be somewhat weaker. However, we observed comparable ethylene polymerisation activity for **1** and **2** under identical conditions (difference < 10%). Hence it is unclear at present whether the thf/Et<sub>2</sub>O ligand remains actively involved during catalysis (*i.e.* act as the ‘fourth’ donor arm *à la* Kol<sup>3</sup>). We have witnessed that the polymerisation process is totally inhibited upon addition of THF.

The activity of the titanium derivatives **3** and **4** were low (4.4 × 10<sup>3</sup> and 1.8 × 10<sup>3</sup> g mol<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup>, respectively) and runs at 1 °C yielded similar rates. In order to probe whether these results were a consequence of presumably stronger Ti–O(thf) chelation (*cf.* Zr), the thf ligand in **3** was removed by heating the complex *in vacuo* at 100 °C for 24 hours. However, the activity of the resultant compound did not noticeably improve.

The catalytic activity of **1**/MAO represents one of the best reported for alkoxide-type derivatives using such MAO concentrations at atmospheric pressure.<sup>10</sup> Compared to previously investigated aliphatic congeners,<sup>3,4</sup> the tridentate pyridine-2,6-bis(phenolate) moiety is a particularly rigid and robust ligand framework that is resistant to decomposition/rearrangement processes.<sup>4c</sup> We also note that calculations by Froese, Musaev and Morokuma,<sup>11</sup> inspired by related 2,2′-thiobis(4-methyl-6-*tert*-butylphenolate) Ti complexes,<sup>4a</sup> predicted lower ethylene insertion barriers and higher activity as a consequence of stronger binding by the central donor in tridentate bis(alkoxide) catalysts. The excellent activity of complex **1** is therefore consistent with the expected strong pyridine coordination to the Zr centre.

In conclusion, despite the conventional perception regarding the detrimental effects of a chelating solvent upon the reactivity of Group 4 polyolefin catalysts, we have demonstrated that the solvent-bound tridentate pyridine-2,6-bis(aryloxy) Zr system is highly active for the polymerisation of ethylene. Moreover, the O-donor is required for complex isolation and solubility. Studies on stereospecific polymerisation and the effect of replacing the thf ligand in **1** with N- and P-type donors upon catalytic efficiency are continuing.

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## Notes and references

† Crystal data for 1·2C<sub>6</sub>H<sub>6</sub>: C<sub>45</sub>H<sub>55</sub>NO<sub>3</sub>Cl<sub>2</sub>Zr, *M* = 820.02, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 14.466(3), *b* = 16.874(3), *c* = 18.241(4) Å, *a* = *γ* = 90, *β* = 91.36(3)°, *U* = 4451.4(16) Å<sup>3</sup>, *T* = 293(2) K, *Z* = 4, *D*<sub>c</sub> = 1.224 g cm<sup>-3</sup>, *μ* = 0.404 mm<sup>-1</sup>, 2*θ*<sub>max</sub> = 51°, 6330 independent reflections (*R*<sub>int</sub> = 0.0404), 440 parameters, *R*<sub>1</sub> = 0.0423 [*I* > 2σ(*I*)], *wR*<sub>2</sub> = 0.1136.

For  $2 \cdot C_6D_6$ :  $C_{37}H_{41}NO_3Cl_2D_6Zr$ ,  $M = 721.91$ , orthorhombic,  $Pbca$ ,  $a = 15.485(3)$ ,  $b = 18.357(4)$ ,  $c = 26.266(5)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $U = 7466(3)$  Å<sup>3</sup>,  $T = 301(2)$  K,  $Z = 8$ ,  $D_c = 1.284$  g cm<sup>-3</sup>,  $\mu = 0.471$  mm<sup>-1</sup>,  $2\theta_{max} = 51^\circ$ , 6225 independent reflections ( $R_{int} = 0.0397$ ), 397 parameters,  $R_1 = 0.0336$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.0877$ .

For  $3 \cdot C_7H_8$ :  $C_{38}H_{47}NO_3Cl_2Ti$ ,  $M = 684.57$ , monoclinic,  $P2_1/n$ ,  $a = 15.904(3)$ ,  $b = 15.026(3)$ ,  $c = 16.426(3)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 110.49(3)^\circ$ ,  $U = 3677.0(12)$  Å<sup>3</sup>,  $T = 293(2)$  K,  $Z = 4$ ,  $D_c = 1.237$  g cm<sup>-3</sup>,  $\mu = 0.413$  mm<sup>-1</sup>,  $2\theta_{max} = 51^\circ$ , 4771 independent reflections ( $R_{int} = 0.0530$ ), 405 parameters,  $R_1 = 0.0477$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1193$ . CCDC reference numbers 185372–185374. See <http://www.rsc.org/suppdata/dt/b2/b206328j/> for crystallographic data in CIF or other electronic format.

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