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Cationic benzyl zirconium heteroscorpionates: synthesis and characterization of a novel ethylene polymerisation catalyst showing an unusual temperature dependent polymerisation mechanism

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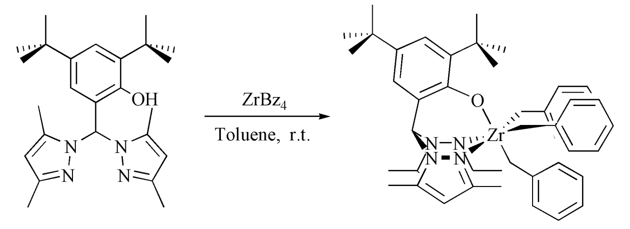
The reaction of (bpzmp)Zr(CH_2Ph)$_3$ with B(C_6F_5)$_3$ produces the active ethylene polymerisation catalyst [(bpzmp)Zr(CH_2Ph)$_2$]$^+$[$PhCH_2B(C_6F_5)_3$]$^-$ which showed a temperature dependent polymerisation mechanism identified by variable temperature ^{1}H NMR analysis of the catalyst solution.

One of the most attractive subjects in the organometallic chemistry of the group 4 metals is the synthesis of non-cyclopentadienyl complexes showing a chemical structure closely reminiscent of the active sites in the classical Ti based heterogeneous Ziegler–Natta catalysts.[1] Ligands containing nitrogen and/or oxygen donors have proved to be suitable and group 4 metal complexes bearing bis-phenoxyimine (FI) ligands are described as extremely active ethylene homogeneous polymerization catalysts with living properties at room temperature.[2]

Aiming to design novel homogeneous olefin polymerisation catalysts with octahedral co-ordination symmetry we considered the (3,5-^{t}Bu$_2$-2-hydroxyphenyl)bis(3,5-Me$_2$-pyrazolyl)-methane tridentate ligand (bpzmp). The corresponding monoanion is a six electron donating system with a phenoxydiimine skeleton and could be considered a suitable alternative to the classical cyclopentadienyl ligand where the Lewis basic properties of the nitrogen donors can be tuned and the bulkiness of the ligand and the symmetry properties of the resulting complexes modified introducing appropriated substituents in the 3-position *via* well established procedures.[3]

Here we report on the synthesis and solution structure of the zirconium complex (bpzmp)Zr(CH_2Ph)$_3$ **1** and of the corresponding ionic complex [(bpzmp)Zr(CH_2Ph)$_2$]$^+$-[$PhCH_2B(C_6F_5)_3$]$^-$ **2**. The latter was found to be active in ethylene polymerisation and a peculiar temperature dependent behaviour of the polydispersity of the polymer products *versus* polymerization temperature is herein presented and discussed in the light of the solution structure of **2**.

The ligand bpzmp was synthesised according to the literature[3] and the benzyl zirconium derivative readily obtained in good yields by reacting bpzmp with Zr(CH_2Ph)$_4$ (1 : 1 molar ratio) in toluene at room temperature (Scheme 1). † ^{1}H NMR monitoring of the reaction showed that this is fast and quantitative in few minutes. The addition of one more equivalent of bpzmp to **1** did not yield the bis-phenoxy derivative probably as a result of the relative bulkiness of the ligand and complex **1**. The molecular structure of **1** was defined by means of ^{1}H NMR, TOCSY, 1D NOE, ^{13}C NMR and gHMQC experiments.‡ **1** exhibits a pseudo-octahedral symmetry and the bpzmp ligand is κ^3-*N*,*N*,*O* co-ordinated to the metal centre. The single set of ^{1}H resonances observed for bpzmp in the temperature range 25–100 °C suggests an elevated co-ordination energy of the ligand to the metal centre and the absence of any fluxional equilibrium of the two N,N donors. The two *cis* methylene groups in the N,N plane produce an AB pattern consisting of two doublets at 2.78 and 2.67 ppm with a $^1J_{HH}$ of 11 Hz§ whereas the methylene protons of the benzyl *trans* to the oxygen are observed as a singlet at 2.84 ppm. No site-exchange reaction between the two types of benzyl groups was observed at room temperature or after heating of the toluene solution of **1** up to 100 °C.



Scheme 1

Treatment of **1** with B(C_6F_5)$_3$ or MAO produces active ethylene polymerisation catalysts with activity values in the range 100–700 g_{PE} $mmol_{CAT}^{-1}$ h^{-1} atm^{-1}.¶ These values are similar to those reported for (η^5-C_5Me_5)$ZrCl_3$ and Zr(CH_2Ph)$_4$[4] but higher than the heteroscorpionate complex (bdmpza)$TiCl_3$ (bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate) by Otero *et al.*[5] Note that the molecular weight distributions of the polyethylene samples (see Table 1) are monomodal and the polydispersity (M_w/M_n) is significantly lower than that found for the polyethylene samples by Cp′ZrX_3 (Cp′ = C_5H_5; $C_5(CH_3)_5$, X = Cl; Bz) and $ZrBz_4$.[6] Interestingly the M_w/M_n ratios decrease with polymerisation temperature and rank from 4.2 (at 50 °C) to 2.3 (at −40 °C); the latter value is very close to those found for single site catalysts.

To identify the active species responsible for this behavior the reaction of **1** with B(C_6F_5)$_3$ was monitored by variable temperature ^{1}H NMR spectroscopy. The formation of the expected ion pair [(bpzmp)Zr(CH_2Ph)$_2$]$^+$[$PhCH_2B(C_6F_5)_3$]$^-$ **2** was readily observed in CD_2Cl_2 at −80 °C where one set of ^{1}H signals for the bpzmp ligand and two sets of ^{1}H signals for two inequivalent benzyl groups bound to the zirconium were

Table 1 Ethylene polymerization catalyzed by **2**

Run[a]	Temp./°C	Yield/g	Activity[b]	M_w/M_n[c]
1	50	0.14	230	4.2
2	25	0.17	196	3.5
3	−20	0.77	340	2.8
4	−40	0.44	125	2.3

[a] Polymerization conditions: (bpzmp)Zr(CH_2Ph)$_3$ (38 mg, 50 μmol); B(C_6F_5)$_3$ (25 mg, 50 μmol); 40 ml of toluene; 0.3 mmol of $AlMe_3$ used as scavenger; polymerization time: 5 min; ethylene pressure: 1 bar. [b] Activity = g_{PE} $mmol_{CAT}^{-1}$ h^{-1} [C_2H_4]$^{-1}$. [c] Determined by GPC.

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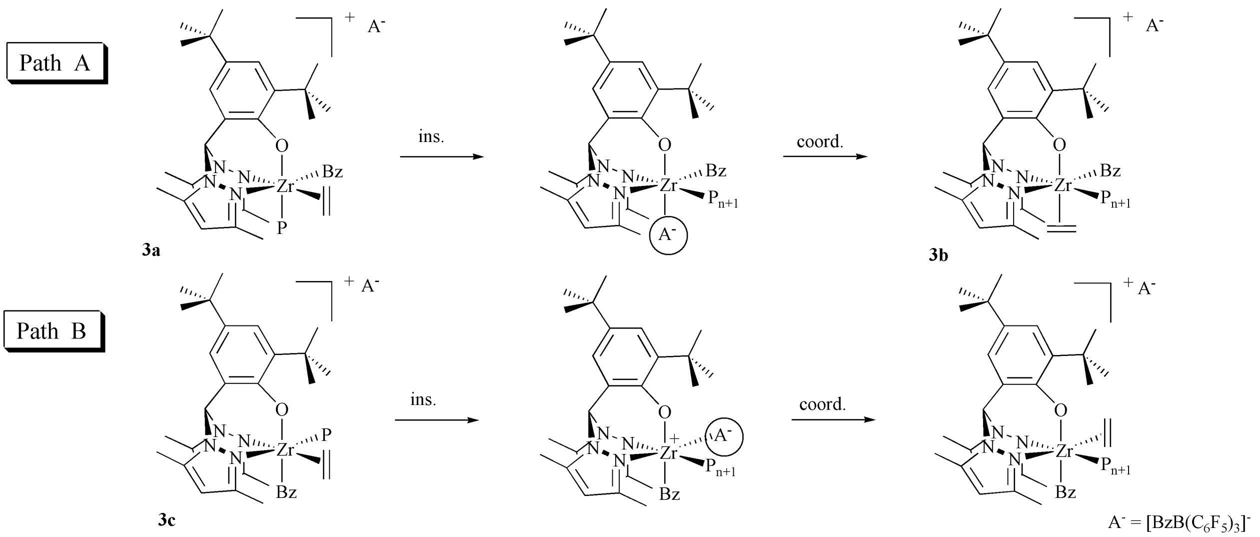

Scheme 2

actually detected.[‖] In particular the methylene protons of the ZrC*H*$_2$Ph groups produce two broad signals at 2.37 and 2.47 ppm; the methylene protons of the benzylborate anion are observed as a broad signal at 2.76 ppm and the corresponding *ortho, para* and *meta* protons are found at 6.60, 6.76 and 6.82 ppm, respectively. When the temperature is raised to −20 °C, a rapid exchange of the two inequivalent benzyl groups becomes active producing a unique pattern of broad resonances for these groups and a significant broadening of the ^{1}H signal corresponding to the methyls of the pyrazolyl groups facing the metal center and the anion. Furthermore a small downfield shift of the aromatic protons of the anion resulting from the increased dissociation of the ion pair was observed with the *ortho, para* and *meta* protons actually detected at 6.69, 6.78 and 6.86 ppm, respectively.[7] We interpreted these results assuming that at low temperature (in the range from −80 to −40 °C) **2** adopts an octahedral geometry in which the anion is co-ordinated in one out of the two sites in the N,N plane. This hampers the isomerization process of the two inequivalent benzyl groups which, in contrast, becomes active at −20 °C as a result of the anion displacement. The olefin complex, assumed as the intermediate species in ethylene polymerisation, can thus exist in three forms: (**3a**) in which ethylene is in the N,N plane and the polymer chain in the axial site (opposite to the oxygen); (**3b**) with ethylene *trans* to the oxygen and polymer chain in the N,N plane and finally (**3c**) with ethylene and the growing polymer chain both in the *cis* sites of the N,N plane. Correspondingly two different pathways for the growth of the polymer chain can be drawn: in the pathway **A** of Scheme 2 the propagation step includes the polymer chain flipping between the axial and the equatorial sites (comprising the **3a** and **3b** intermediate species) whereas in pathway **B** the polymer chain flips between the two equatorial sites in the N,N plane.

At room or higher temperature both pathways are possible and a broader molecular weight distribution of the polymer products is obtained. At −40 °C the coordination of the anion produces an octahedral species and the incoming ethylene can replace the anion in the same N,N plane site followed by fast chain migratory insertion. Later on, the vacant site is readily occupied by the anion producing a resting state of the catalyst. In the frame of this picture only the pathway **B** is active at −40 °C or lower temperature producing a polymer with a narrow molecular weight distribution.

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Notes and references

[†] Synthesis of **1**: bpzmp (0.450 g, 1.1 mmol) dissolved in 50 ml toluene was added to a solution of ZrBz$_4$ (0.502 g; 1.1 mmol) in 20 ml of toluene at room temperature. The resulting yellow solution was stirred for 30 minutes, then concentrated to 10 ml and kept overnight at −20 °C yielding 0.450 g of a pale yellow solid (yield 53%).

[‡] ^{1}H NMR data (400 MHz, CD$_2$Cl$_2$, 25 °C) for **1**: δ 1.34 (s, 9H, 5-^{t}*Bu*-Ar), 1.52 (s, 9H, 3-^{t}*Bu*-Ar), 2.05 (s, 6H, 3-C*H*$_3$-Pz), 2.48 (s, 6H, 5-C*H*$_3$-Pz), 2.67 (d, 2H, J = 11 Hz, eq-C*H*$_2$Ph), 2.78 (d, 2H, J = 11 Hz, eq-C*H*$_2$Ph), 2.84 (s, 2H, ax-C*H*$_2$Ph), 5.85 (s, 2H, Pz-*H*), 6.36 (d, 2H, ax-*o*-Ph), 6.58 (t, 1H, ax-*p*-Ph), 6.75 (t, 2H, ax-*m*-Ph), 6.79 (t, 2H, eq-*p*-Ph), 6.84 (d, 4H, eq-*o*-Ph), 7.03 (t, 4H, eq-*m*-Ph), 7.10 (d, 1H, J = 2 Hz, 6-*H*-Ar), 7.14 (s, 1H, =N)$_2$-C*H*(ArO)-), 7.47 (d, 1H, J = 2 Hz, 4-*H*-Ar).

[§] The methylene carbons of three benzyl groups show a $^1J_{\mathrm{CH}}$ coupling constant of 114 Hz, in the range expected for carbon atoms with sp^3 hybridisation.

[¶] The highest activity value was achieved with the MAO activated catalyst (A = 700 g$_{\mathrm{PE}}$ mmol$_{\mathrm{CAT}}{}^{-1}$ h^{-1} atm^{-1}) under the following polymerisation conditions: **1** (7.7 mg, 10 µmol); MAO (5 mmol, Al/Zr molar ratio = 500); toluene (100 ml); 0.3 mmol of AlMe$_3$ used as scavenger; polymerization temperature = 50 °C, ethylene pressure = 5 bar; polymerization time: 5 min. Under similar conditions the **1**–B(C$_6$F$_5$)$_3$ catalyst (**1** = 50 µmol; B/Zr molar ratio = 1:1) showed an activity value of 250 g$_{\mathrm{PE}}$ mmol$_{\mathrm{CAT}}{}^{-1}$ h^{-1} atm^{-1} and the corresponding polyethylene a polydispersity index ($M_{\mathrm{w}}/M_{\mathrm{n}}$) of 4.2.

[‖] ^{1}H NMR data (400 MHz, CD$_2$Cl$_2$, −80 °C) for **2**: δ 1.28 (s, 9H, 5-^{t}*Bu*-Ar), 1.42 (s, 9H, 3-^{t}*Bu*-Ar), 1.92 (s, 6H, 3-C*H*$_3$-Pz), 2.42 (s, 6H, 5-C*H*$_3$-Pz), 2.37 (s, 2H, C*H*$_2$Ph), 2.47 (s, 2H, C*H*$_2$Ph), 2.76 (s, 2H, B-C*H*$_2$Ph), 5.91 (s, 2H, Pz-*H*), 6.36 (d, 2H, ax-*o*-Ph), 6.60 (d, 2H, BCH$_2$-*o*-Ph), 6.74 (d, 2H, *o*-Ph), 6.76 (t, 1H, BCH$_2$-*p*-Ph), 6.82 (t, 2H, BCH$_2$-*m*-Ph), 7.15 (m, 10H, Zr-CH$_2$C$_6$*H*$_5$, 6-*H*-Ar, =N)$_2$-C*H*(ArO)-), 7.47 (s, 1H, 4-*H*-Ar).

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6 Unpublished data from our laboratory.

7 For comparison, the chemical shifts of the aromatic protons in the "free" anion [PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ were observed at 6.88 (*m*), 6.78 (*p*), 6.74 (*o*) ppm (CD$_2$Cl$_2$, 25 °C). See *e.g.* A. D. Horton and J. de With, *Chem Commun.*, 1996, 1375.