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Polymethylaluminoxane supported zirconocene catalysts for polymerisation of ethylene

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A B S T R A C T

We report here the synthesis of two new ansa-bridged permethylindenyl zirconocenes, their reaction with solid polymethylaluminoxane (sMAO) and their use in slurry phase ethylene polymerisation. *Meso*-(EBI*)Zr(CH_2Ph)$_2$ and *meso*-(EBI*)Zr($CH_2\,^tBu$)Cl, (EBI* = ethylenebis[1-(2,3,4,5,6,7-hexamethylindenyl)]) were synthesised from *meso*-(EBI*)$ZrCl_2$ and KCH_2Ph and $LiCH_2\,^tBu$ respectively. The new zirconocenes were characterised by NMR spectroscopy and X-ray crystallography, and density functional theory calculations were carried out. Solid precatalysts were obtained when these compounds were reacted with the polymethylaluminoxane support. Ethylene polymerisation activities of up to 6000 $kg_{PE}/mol_{Zr}/h/bar$ were obtained in the slurry polymerisation of ethylene. The polyethylenes showed molecular weights, M_w, above 200 000 kg/mol and low polydispersities, $M_w/M_n < 3$.

1. Introduction

Group 4 metallocenes were discovered by Wilkinson and Birmingham in 1954 [1], and have recently been investigated for N_2 binding and functionalisation [2,3], as FLPs capable of activating small molecules such as CO_2 and H_2 [4–6], and for α-olefin polymerisation [7].

The polymerisation of ethylene is industrially significant with annual production in excess of 75 million tonnes [7]. It has also been a topic of academic importance and the focus of a number of reviews [8–11]. Slurry phase polymerisation (both Ziegler Natta or single-site type) is an extremely important aspect of the industrial polymerisation market [11–13]. For the immobilisation of single-site catalysts, the most commonly employed support material is silica but other inorganic materials such as zeolites and clays have also been investigated. Clays are typically ion exchanged, often with ammonium salts, before surface activation with alkylaluminium reagents [14]. They have been employed by Suga and co-workers as supports for zirconocenes [15], and were reported as active supports for Ziegler catalysts [16,17].

We recently reported the use of silica- [18], aqueous miscible organic layered double hydroxide- (AMO-LDH) [18–20], and core shell@LDH-supported indenyl metallocenes [21], for the slurry polymerisation of ethylene. Furthermore, we have demonstrated that a catalyst based on a tungsten imido complex supported on solid polymethylaluminoxane (sMAO) was much more active and selective for the dimerisation of ethylene than the silica and AMO-LDH analogues [22a]. Very recently, we observed that a sMAO-supported permethylpentalene zirconium complex (Pn*ZrCp^{Me}Cl$_{\text{s-MAO}}$) was superior in ethylene polymerisation activity relative to silica-supported methylaluminoxane (ssMAO) and MAO treated AMO-LDH (AMO-LDH-MAO) (5.3 and 2.3 times respectively). Significantly, the slurry-phase ethylene polymerisation activities using equivalent complexes supported on sMAO demonstrated enhanced performance compared to the solution phase [22b].

Here we report the synthesis and characterisation of two new ansa-bridged permethylindenyl zirconocene alkyl complexes, and the preparation of solid polymethylaluminoxane-supported complexes for evaluation of slurry phase ethylene polymerisation capability.

2. Materials and methods

2.1. General considerations

All reactions, unless specified otherwise, were performed under an atmosphere of nitrogen, using standard Schlenk techniques on a dual vacuum/inert gas manifold or within an MBraun UNIlab

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glovebox. Pentane, hexane, toluene and benzene were dried using an MBraun SPS-800 solvent purification system, stored in ampoules over a potassium mirror and degassed prior to use. Dichloromethane was stored over molecular sieves. Tetrahydrofuran was distilled from purple sodium/benzophenone ketyl radical and stored over molecular sieves. Benzene-d_6 (99.6%, Sigma Aldrich) was dried over Na/K. Tetrahydrofuran-d_8 (99.6%, Goss Scientific) was dried over calcium hydride. All deuterated solvents were vacuum transferred and freeze-pump-thaw degassed three times prior to use. Molecular sieves (3 Å, 8–12 mesh) were supplied from Acros Organics and were baked at 140 °C under vacuum ($<10^{-2}$ mbar) for at least 6 h before use.

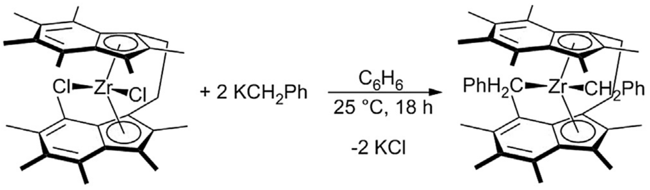
2.2. Complex syntheses

2.2.1. Preparation of meso-(EBI*)Zr(CH_2Ph)$_2$

Benzene (50 mL) was added to a mixture of *meso*-(EBI*)$ZrCl_2$ (600 mg, 1.03 mmol) and KCH_2Ph (295 mg, 2.27 mmol) and the reaction mixture was stirred for 18 h. Extraction with hexane (2 × 80 mL) and removal of the volatiles *in vacuo* afforded *meso*-(EBI*)Zr(CH_2Ph)$_2$ as a yellow solid in 64% yield (459 mg, 0.66 mmol). Single crystals were grown from a concentrated solution of hexane at −35 °C. ^1H NMR (400 MHz, 23 °C, benzene-d_6): δ −0.70 (s, 2H, $PhCH_2$), 1.83 (s, 2H, $PhCH_2$), 1.85 (s, 6H, Cp-Me), 2.01 (s, 6H, Ar-Me), 2.04 (s, 12H, Cp/Ar-Me), 2.41 (s, 6H, Ar-Me), 2.50 (s, 6H, Ar-Me), 3.07 (m, 2H, CH_2), 3.67 (m, 2H, CH_2), 6.39 (d, $^3J_{HH} = 7.5$ Hz, 2H, *o*-Ph), 6.58 (d, $^3J_{HH} = 7.5$ Hz, 2H, *o*-Ph), 6.80 (t, $^3J_{HH} = 7.2$ Hz, 1H, *p*-Ph), 6.95 (t, $^3J_{HH} = 7.3$ Hz, 1H, *p*-Ph), 7.04 (t, $^3J_{HH} = 7.6$ Hz, 2H, *m*-Ph), 7.16 (t, $^3J_{HH} = 7.6$ Hz, 2H, *m*-Ph). ^1H NMR (400 MHz, 23 °C, tetrahydrofuran-d_8): δ −1.01 (s, 2H, $PhCH_2$), 1.60 (s, 2H, $PhCH_2$), 2.04 (s, 6H, Cp-Me), 2.13 (s, 6H, Ar-Me), 2.15 (s, 6H, Ar-Me), 2.16 (s, 6H, Cp-Me), 2.39 (s, 6H, Ar-Me), 2.60 (s, 6H, Ar-Me), 3.44 (app. q, $^2J_{HH} = 6.8$ Hz, $^3J_{HH} = 6.2$ Hz, 2H, CH_2), 3.92 (app. q, $^2J_{HH} = 6.3$ Hz, $^3J_{HH} = 6.2$ Hz, 2H, CH_2), 6.07 (d, $^3J_{HH} = 7.6$ Hz, 2H, *o*-Ph), 6.26 (d, $^3J_{HH} = 7.5$ Hz, 2H, *o*-Ph), 6.50 (t, $^3J_{HH} = 7.3$ Hz, 1H, *p*-Ph), 6.66 (t, $^3J_{HH} = 7.2$ Hz, 1H, *p*-Ph), 6.77 (t, $^3J_{HH} = 7.5$ Hz, 2H, *m*-Ph), 6.86 (t, $^3J_{HH} = 7.4$ Hz, 2H, *m*-Ph). $^{13}C\{^1H\}$ NMR (100 MHz, 23 °C, benzene-d_6): δ 13.5 (Cp-Me), 15.4 (Cp-Me), 16.8 (Ar-Me), 17.0 (Ar-Me), 17.9 (Ar-Me), 18.7 (Ar-Me), 30.7 (C_2H_4), 64.7 (CH_2Ph), 69.4 (CH_2Ph), 110.6 (Ar), 115.8 (Ar), 121.0 (*p*-Ph), 121.9 (*p*-Ph), 125.6 (Ar), 126.4 (Ar), 127.2 (*o*-Ph), 127.2 (*m*-Ph), 127.7 (Ar), 127.9 (*m*-Ph), 128.7 (*o*-Ph), 129.0 (Ar), 129.6 (Ar), 132.3 (Ar), 133.3 (Ar), 151.4 (*i*-Ph), 151.6 (*i*-Ph). Unit cell data: monoclinic, $P2_1/n$, $a = 12.1915$ (3), $b = 19.1827$ (4), $c = 15.3626$ (3), $\alpha = \gamma = 90°$, $\beta = 93.2526$ (18). CCDC: 1451241. MS (EI): found 726.2760; calculated 726.3198. Major fragmentation peaks noted at 635, 544 and 91 corresponding to $[(EBI^*)Zr(CH_2Ph)]^+$, $[(EBI^*)Zr]^+$ and $[(CH_2Ph)]^+$ respectively. IR (KBr) (cm^{-1}): 2962, 1738, 1543, 1434, 1374, 1261, 1205, 1094, 1022, 802, 668.

2.2.2. Preparation of meso-(EBI*)Zr($CH_2\,{}^tBu$)Cl

A solution of $LiCH_2\,{}^tBu$ (53.5 mg, 0.69 mmol) in benzene (10 mL) was added to a solution of *meso*-(EBI*)$ZrCl_2$ (200 mg, 0.34 mmol) in benzene (40 mL). The reaction mixture was stirred for 1 h before drying under reduced pressure to yield a pale orange solid. Extraction into hexane and subsequent removal of the volatiles *in vacuo* afforded *meso*-(EBI*)Zr($CH_2\,{}^tBu$)Cl as a pale orange powder in 21% yield (44.5 mg, 0.07 mmol). Very small, pale orange crystalline blocks were grown from a hexane solution at −35 °C. ^1H NMR (400 MHz, 23 °C, benzene-d_6): δ −2.23 (s, 2H, $CH_2\,{}^tBu$), 0.74 (s, 9H, CMe_3), 1.92 (s, 6H, Cp-Me), 2.07 (s, 6H, Ar-Me), 2.14 (s, 6H, Ar-Me), 2.44 (s, 6H, Ar-Me), 2.47 (s, 6H, Ar-Me), 2.53 (s, 6H, Ar-Me), 3.16 (m, 2H, CH_2), 3.63 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, 23 °C, benzene-d_6): δ 14.1 (Ar-Me), 16.3 (Ar-Me), 16.8 (Ar-Me), 16.9 (Ar-Me), 17.7 (Ar-Me), 18.8 (Ar-Me), 30.9 (CH_2), 35.0 (CMe_3), 77.2 ($CH_2\,{}^tBu$) 111.8 (Cp), 116.9 (Cp), 125.2 (Ar), 127.5 (Ar), 128.0 (Ar), 129.5 (Cp), 130.3 (Ar), 132.5 (Ar), 133.7 (Ar). Unit cell data: triclinic, *P*, $a = 11.4222$ (5), $b = 15.9204$ (6), $c = 19.5395$ (7), $\alpha = 92.805$ (3), $\beta = 90.490$ (3), $\gamma = 108.372$ (4). CCDC: 1451242. MS (EI): no molecular ion peak was found. Major fragmentation peaks at 592 and 551, corresponding to $[(EBI^*)Zr(CH_2\,{}^tBu)]^+$ and $[(EBI^*)ZrCl]^+$ respectively. IR (KBr) (cm^{-1}): 3386 (b), 2962, 1640, 1459, 1261, 1095, 1020, 801.



Scheme 1. Synthesis of *meso*-(EBI*)Zr(CH_2Ph)$_2$.

2.3. Polymerisation study

2.3.1. Preparation of polymethylaluminoxane-supported zirconocene catalysts

The quantity of catalyst immobilised on the surface of the support is given in terms of the Al:Zr ratio of the polymethylaluminoxane component to the organometallic complex. This was typically 300:1. In the glovebox, the support and the complex were weighed out into a Schlenk tube. Toluene (50 mL) was added and the reaction mixture swirled at 60 °C for 1 h. The coloured solid was allowed to settle from the clear, colourless solution which was decanted, and the solid dried *in vacuo* (40 °C, 1×10^{-2} mbar).

2.3.2. Ethylene polymerisation procedure

A typical slurry-phase laboratory polymerisation run was performed as follows: TIBA (150 mg) and hexane (10 mL) were added to a 150 mL Rotaflo ampoule containing a stirrer bar. The supported complex (10 mg) was added to the ampoule and washed in with further hexane (40 mL). The vessel was sealed and degassed under reduced pressure. The slurry was brought to temperature using an oil bath and the stirring speed was set at 1000 rpm. The stopcock was opened to ethylene at a pressure of 2 bar. On completion of the run, the vessel was closed to ethylene and degassed, before filtration through a glass sintered frit (porosity 3) and washing with pentane (50 mL). The resultant polymer was dried in the vacuum oven at 50 °C overnight.

3. Results and discussion

3.1. Synthesis and characterisation of meso-(EBI*)Zr(CH_2Ph)$_2$

meso-(EBI*)Zr(CH_2Ph)$_2$ was prepared by addition of benzene directly to a mixture of *meso*-(EBI*)$ZrCl_2$ and KCH_2Ph, followed by stirring at room temperature for 18 h. After work-up, *meso*-(EBI*)Zr(CH_2Ph)$_2$ was obtained as a yellow microcrystalline solid in 64% yield, Scheme 1.

Crystals of *meso*-(EBI*)Zr(CH_2Ph)$_2$ suitable for an X-ray diffraction study were grown from hexane at −35 °C (Fig. 1). *meso*-(EBI*)Zr(CH_2Ph)$_2$ was found to crystallise in the monoclinic spacegroup $P2_1/n$. The value for the torsion angle TA′[1] agrees well with that measured for *meso*-(EBI*)$ZrCl_2$ (18.97°) [23], suggesting either that

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[1] Definitions of structural parameters are defined in the supporting information (Figs. S15 and S16).