Synthesis of zirconocene complexes and their use in slurry-phase polymerisation of ethylene†

Phakpoom Angpanitcharoen, Jessica V. Lamb, Jean-Charles Buffet, Zoë R. Turner and Dermot O’Hare

A new family of zirconocene complexes of the type \((\text{Ind}^\text{R})_2\text{ZrX}_2\) (where Ind\(^R\) = C\(_8\)Me\(_3\)H and R = Me, Et and Ph) have been synthesised and fully characterised. Six new crystal structures have been reported \((\text{meso-}(\text{Ind}^\text{Me})_2\text{ZrBr}_2\), \((\text{meso-}(\text{Ind}^\text{Et})_2\text{ZrCl}_2\), \((\text{meso-}(\text{Ind}^\text{Et})_2\text{ZrBr}_2\), \((\text{meso-}(\text{Ind}^\text{Me})_2\text{ZrCl}_2\), \((\text{meso-}(\text{Ind}^\text{Me})_2\text{ZrBr}_2\) \((\text{meso-}(\text{Ind}^\text{Me})_2\text{ZrCl}_2\)). The complexes were studied for slurry-phase ethylene polymerisation when immobilised on solid polymethylaluminoxane (sMAO). Variation in the initiation group was found to have greater influence over polymerisation activity for \(\text{meso-}\) catalysts than \(\text{rac-}\) catalysts, with \(\text{meso-}\) alkyl catalysts showing higher polymerisation activities than \(\text{meso-}\) halide. Below 70 \(^\circ\)C, polymerisation activity follows the order \((\text{sMAO-}(\text{meso-}(\text{Ind}^\text{Me})_2\text{ZrCl}_2\), \((\text{sMAO-}(\text{meso-}(\text{Ind}^\text{Et})_2\text{ZrBr}_2\) \((\text{activities of 657, 561, and 452 kgPE mol}^{-1}\text{h}^{-1}\text{bar}^{-1}\)) respectively). \((\text{sMAO-}(\text{meso-}(\text{Ind}^\text{Me})_2\text{ZrBr}_2\) produces HDPE with the highest molecular weight, followed by \((\text{sMAO-}(\text{meso-}(\text{Ind}^\text{Me})_2\text{ZrCl}_2\) and \((\text{sMAO-}(\text{meso-}(\text{Ind}^\text{Me})_2\text{ZrBr}_2\) \((\text{activities of 657, 561, and 452 kgPE mol}^{-1}\text{h}^{-1}\text{bar}^{-1}\)) respectively). \((\text{M}_{\text{w}}\) of 503, 406, and 345 kg mol\(^{-1}\)), respectively, at 50 \(^\circ\)C. \((\text{sMAO-}(\text{meso-}(\text{Ind}^\text{Me})_2\text{ZrCl}_2\) produced HDPE with almost identical molecular weights to \((\text{sMAO-}(\text{meso-}(\text{Ind}^\text{Me})_2\text{ZrCl}_2\) (395 kg mol\(^{-1}\)) at 50 \(^\circ\)C.

Introduction

Group 4 metalloccenes are generally defined as \(d^5\) pseudo-tetrahedral organometallic compounds in which the transition metal atom bears two \(\sigma^5\)-cyclopentadienyl-based ligands and two \(\sigma\)-ligands.\(^1\) Upon the activation of group 4 metalloccenes by co-catalysts (e.g. MAO),\(^2\) the resulting highly electrophilic alkyl metalloccene cations, stabilised by non-nucleophilic, very weakly coordinating anions, are known to be the active species for \(\alpha\)-olefin polymerisation.\(^3\)–\(^5\) The stability of the cationic intermediate and the electron density, accessibility and geometry of the active site, all of which are influenced by ligand structure, are believed to be the main influencing factors towards reactivity and stereospecificity.\(^6\)

The discovery of ‘single-site’ metalloccene-based catalysts has revived \(\alpha\)-olefin polymerisation chemistry as these catalyst systems enable the production of (co)polyolefins with tuneable molecular structures, stereochemistries and molecular weight distributions (MWD, \(M_w/M_n\)).\(^7\)–\(^14\) Self-immobilisation of catalyst and co-catalysts for olefin polymerisation has shown that the high excess of MAO can reduced by more than 90%.\(^15\) Yet these catalysts are rarely used for industrial processes, with a few exceptions including Dowlex (Dow) and Sclairtech (Nova Chem. Corp.); due to the incompatibility with the existing gas or slurry phase olefin polymerisation processes. By immobilising metalloccene catalysts onto support materials, the processability problem is solved and the advantages of metalloccene catalysts, including narrow MWD, high activity, and precise control over polymer microstructure, are preserved to a great extent. Supporting metalloccene complexes also allows for the reduction of the ratio of MAO to metalloccene,\(^16\) and have an dramatic effect on the tacticity when polymerising \(\alpha\)-olefins.\(^17\) Many materials were tested as olefin polymerisation supports including inorganic solids such as silica,\(^17\) silicate clays,\(^18\) \(\text{MgCl}_2,\)\(^19\) and polymeric aluminoxanes.\(^20\) Various functionalised polymers have also been investigated as supports. Silica is the most commonly used support for heterogeneous metalloccene catalysts. Pre-contacting the silica surface with MAO was reported to increase catalyst loadings.\(^21\)–\(^24\) The use of layered double hydroxides (LDHs), a class of anionic clays consisting of positively charged Brucite-like layers with weakly bound anions intercalated between them, as catalyst supports for olefin polymerisation has been recently reported by the O’Hare group.\(^25\)–\(^27\) Heat treatment of MAO for a prolonged period was reported to increase polymerisation activity of up to 25%. This is believed to be caused by the aggregation of MAO to form larger particles which are insoluble in hydrocarbon solvents. This insoluble ‘solid MAO’ can act simultaneously as both co-catalyst and support in slurry phase ethylene polymerisation.\(^28\)–\(^29\)
Results and discussion

Synthesis of \((3\text{-RInd}^\#)_2\text{ZrX}_2\) (R = Me, Et or Ph; X = Cl, Br or CH2Ph)

\(3\text{-PhInd}^\#\text{Li}\) was synthesised according to a modified literature procedure (Fig. S1–S10).\(^{38}\) Two equivalents \(3\text{-PhInd}^\#\text{Li}\) were reacted with one equivalent of ZrCl\(_4\) to afford a 50 : 50 mixture of \(\text{rac}\) and \(\text{meso}\)\((3\text{-PhInd}^\#)_2\text{ZrCl}_2\) (1) as an orange yellow solid in 45% yield (Scheme 1). The two sets of resonances corresponding to each isomer are indistinguishable in the \(^1\text{H}\) NMR spectrum; resonances between 6.90 and 7.90 ppm correspond to the phenyl protons, while two singlets at 5.86 and 6.52 ppm correspond to the cyclopentadienyl protons and singlets between 1.60 and 2.80 ppm correspond to the methyl groups on the indenyl rings (Fig. S11†).

\(3\text{-EtInd}^\#\text{Li}\) was synthesised according to a previously reported procedure.\(^{30}\) Two equivalents of \(3\text{-EtInd}^\#\text{Li}\) were reacted with one equivalent ZrBr\(_4\) to afford an orange solid comprising of a 40 : 60 mixture of \(\text{rac}\) and \(\text{meso}\)\((3\text{-EtInd}^\#)_2\text{ZrBr}_2\) after work-up. Recrystallisation of the isomeric mixture yielded \(\text{meso}\)\((3\text{-EtInd}^\#)_2\text{ZrBr}_2\) (meso-2) as orange crystals in 6% yield. Similar to 1, meso-2 shows diagnostic resonances corresponding to the cyclopentadienyl proton and methyl groups of the indenyl rings. meso-2 also shows two doublet of quartets at 2.69 and 3.22 ppm and a triplet at 1.05 ppm corresponding to the diastereotopic methylene and methyl protons of the ethyl groups respectively (Fig. S13†).

\(3\text{-MeInd}^\#\text{Li}\) was synthesised according to a literature procedure.\(^{30}\) They were reacted with two equivalents KCH2Ph to afford \(\text{rac}\)\((3\text{-MeInd}^\#)_2\text{Zr(CH}_2\text{Ph})_2\) (rac-4) and \(\text{meso}\)\((3\text{-MeInd}^\#)_2\text{Zr(CH}_2\text{Ph})_2\) (meso-4) as yellow solids, both in 93% yield after work-up. The \(\text{C}_2\)-symmetry of rac-4 results in magnetically equivalent indenyl rings and benzyl groups, as evidenced in the \(^1\text{H}\) NMR spectrum;
the phenyl protons are seen as a doublet, doublet of doublets, and triplet at 6.72, 7.08, and 6.80 ppm, respectively, while two doublets at 0.67 and 0.87 ppm correspond to the diastereotopic benzylic protons (Fig. S15†). Similar to meso-MeSBr(3-Et)\(^+\)Zr(CH\(_2\)Ph)\(_2\),\(^{33}\) the symmetry of meso-4 results in magnetically inequivalent benzyl groups in the 1H NMR spectrum; the ortho, meta, and para, and benzyl protons of one benzyl group are observed as a doublet at 6.46 ppm, a doublet of doublets at 7.04 ppm, a triplet at 6.75 ppm, and a singlet at 0.24 ppm, while for the other benzyl group they appear at 6.58, 7.06, 6.79, and 0.79 ppm (Fig. S17†). 3-MeS\(^+\)Li was synthesised according to a previously reported procedure.\(^{32}\) Two equivalents 3-MeS\(^+\)Li were reacted with one equivalent ZrBr\(_2\) to afford an orange solid comprising of a 20:80 mixture of rac- and meso-(3-MeS\(^+\)Ind\(^\#\))\(_2\)ZrBr\(_2\) (meso-5) as orange crystals in 6% yield. The 1H NMR spectrum of meso-5 shows that the two indenyl rings are magnetically equivalent, with diagnostic resonances corresponding to the cyclopentadienyl protons and indenyl methyl groups (Fig. S19†). One equivalent meso-5 was further reacted with two equivalents of KCH\(_2\)Ph to afford meso-(3-MeS\(^+\)Ind\(^\#\))\(_2\)Zr(CH\(_2\)Ph)\(_2\) (meso-6) as a yellow solid in 88% yield. Similar to meso-4, the C\(_r\)-symmetry of meso-6 results in magnetically inequivalent benzyl groups in the 1H NMR spectrum (Fig. S21†).

Orange crystals of meso-2, rac-4, and meso-4 were grown from pentane at room temperature, while crystals of rac-3, meso-5 and meso-6 were grown from a toluene solution at -30 °C and room temperature. The solid-state molecular structures are depicted in Fig. 1, with selected bond lengths and angles presented in Table 1.

For meso-2, the average Zr–Br bond length (2.598 Å) and Zr–Cp\(_{\text{cent}}\) distance (2.243 Å) are within the range of those reported for other unbridged dibromobisindenyl zirconocene complexes.\(^{16-18}\) The ring tilt angle (\(\alpha\) [52.44°]) and angle about the metal centre (\(\delta\) [131.93°]) are similar to meso-(3-MeS\(^+\)Ind\(^\#\))\(_2\)ZrCl\(_2\) (53.28° and 132.02°, respectively).\(^{32}\) The torsion angle (TA) measures the twist of the two indenyl rings relative to one another (Fig. S23†). The introduction of ethyl groups causes increased steric strain, resulting in meso-2 adopting ‘gauche’ conformation, which is reflected in the TA angle of 81.49° compared to 37.16° for meso-(3-MeInd\(^\#\))\(_2\)ZrCl\(_2\).\(^{32}\)

The average Zr–Cl bond length and Zr–Cp\(_{\text{cent}}\) distance of rac-3 (2.435 and 2.241 Å) are in good agreement with the 3-methyl analogue rac-(3-MeInd\(^\#\))\(_2\)ZrCl\(_2\) (2.421 and 2.228 Å).\(^{32}\) The \(\alpha\) and \(\delta\) values (Fig. S23†) of rac-3 (51.72° and 132.44°) are comparable to rac-(3-MeInd\(^\#\))\(_2\)ZrCl\(_2\) (51.58° and 133.59°) and rac-(3-EtInd\(^\#\))\(_2\)HFC\(_2\) (51.80° and 132.56°), as are the torsion angles (173.14, 171.31, and 173.01°), respectively, implying that the introduction of 3-ethyl groups has little-to-no impact on the molecular framework. Structure comparisons of rac-3 with the unmodified analog, rac-(3-EtInd\(^\#\))\(_2\)ZrCl\(_2\), show similar average Zr–Cl bond lengths (2.435 and 2.442 Å) and Zr–Cp\(_{\text{cent}}\) distances (2.241 and 2.233 Å).\(^{32}\) The \(\alpha\) and \(\delta\) values for rac-3 (51.72° and 132.44°) are slightly larger than for rac-(3-EtInd\(^\#\))\(_2\)ZrCl\(_2\) (120.02°) due to the increased steric of methylation. For meso-4, the average Zr–CH\(_2\)Ph bond length (2.318 Å) is similar to rac-4 (2.303 Å) and the hexamethylated analogue rac-(3-MeInd\(^\#\))\(_2\)Zr(CH\(_2\)Ph)\(_2\) (2.320 Å),\(^{32}\) and is slightly longer than (1,7-EtInd\(^\#\))\(_2\)Zr(CH\(_2\)Ph)\(_2\) (2.294 Å).\(^{33}\) Similar to meso-2, meso-4 has a TA value of 102.95°, adopting ‘gauche’ conformation to minimise the steric clash between the ethyl and benzyl groups. The average Zr–Br bond length and Zr–Cp\(_{\text{cent}}\) distances of meso-5 (2.594 and 2.251 Å) are similar to meso-2 (2.598 and 2.243 Å). The \(\alpha\) value for meso-5 (54.35°) is slightly larger than meso-(3-MeInd\(^\#\))\(_2\)ZrCl\(_2\) (53.28°) due to the larger Br ligands.\(^{32}\) The TA value of 35.46° for meso-5 is comparable to meso-(3-MeInd\(^\#\))\(_2\)ZrCl\(_2\) (37.16°), however, is significantly less than meso-2 (81.49°) due to the decrease in steric strain on exchanging ethyl for methyl. For meso-6, the average Zr–CH\(_2\)Ph bond length (2.323 Å) is comparable to rac-4 (2.303 Å) and rac-(3-MeInd\(^\#\))\(_2\)Zr(CH\(_2\)Ph)\(_2\) (2.320 Å).\(^{32}\) However, comparisons between the \(\alpha\) values of meso-6 and rac-4 are challenging because the complexes adopt different conformations, reflected in the TA values of 112.56° and 157.30°, in order to minimise the steric interactions between the indenyl and benzylligands.

| Complex | Zr-X | Zr-Cp\(_{\text{cent}}\) | \(\alpha\) | \(\delta\) | TA |
|---------|------|----------------|------|------|-----|
| meso-2  | meso-(3-EtInd\(^\#\))\(_2\)ZrBr\(_2\) | 2.6041(5) | 2.2425(11) | 52.44(14) | 131.93(4) | 81.49 |
|         |     | 2.5927(5) | 2.2430(11) |       |       |     |
| rac-3   | rac-(3-EtInd\(^\#\))\(_2\)ZrCl\(_2\) | 2.438(3) | 2.243(8) | 51.72(10) | 132.44(3) | 173.14 |
|         |     | 2.451(6) | 2.237(8) |       |       |     |
| meso-4  | meso-(3-MeInd\(^\#\))\(_2\)Zr(CH\(_2\)Ph)\(_2\) | 2.309(2) | 2.304(8) | 51.80(11) | 132.99(3) | 102.95 |
|         |     | 2.328(4) | 2.266(6) |       |       |     |
| rac-4   | rac-(3-MeInd\(^\#\))\(_2\)Zr(CH\(_2\)Ph)\(_2\) | 2.327(7) | 2.322(3) | 51.9(4) | 133.63(11) | 157.30 |
|         |     | 2.289(7) | 2.281(3) |       |       |     |
| meso-5  | meso-(3-MeInd\(^\#\))\(_2\)ZrBr\(_2\) | 2.6334(4) | 2.2500(10) | 54.35(13) | 133.62(4) | 35.46 |
|         |     | 2.5745(4) | 2.2525(10) |       |       |     |
| meso-6  | meso-(3-MeInd\(^\#\))\(_2\)Zr(CH\(_2\)Ph)\(_2\) | 2.3302(18) | 2.2763(9) | 53.66(10) | 133.92(3) | 112.56 |
|         |     | 2.3132(18) | 2.3419(10) |       |       |     |

\(\alpha\) = Br, Cl or CH\(_2\)Ph; \(\alpha\), \(\delta\) and TA: crystallographic parameters are defining in Fig. S23.
Looking at the meso-catalysts, below 70 °C polymerisation activity follows the order meso-4sMAO, meso-3sMAO, and meso-2sMAO (activities of 657, 561, and 452 kgPE mol\(^{-1}\) h\(^{-1}\) bar\(^{-1}\), respectively). This is likely due to faster formation of the active species, as catalysts containing halide initiation groups first need to be alkylated.\(^{26,27}\) meso-4sMAO shows less resilience to higher polymerisation temperatures and, as a result, the polymerisation activities converge to approximately 250 kgPE mol\(^{-1}\) h\(^{-1}\) bar\(^{-1}\) at 90 °C.

Reducing the steric bulk in the indenyl ligand leads to increases in polymerisation activities; the 3-methyl catalyst meso-5sMAO shows higher polymerisation activities than the corresponding 3-ethyl catalyst meso-2sMAO. (maximum activities of 927 kgPE mol\(^{-1}\) h\(^{-1}\) bar\(^{-1}\) at 70 °C and 503 kgPE mol\(^{-1}\) h\(^{-1}\) bar\(^{-1}\) at 50 °C, respectively). Unlike the other catalysts, which show continual decreases in activity with increasing temperature, meso-5sMAO shows a peak in activity at 70 °C (927 kgPE mol\(^{-1}\) h\(^{-1}\) bar\(^{-1}\) which could be related to the fact that meso-5sMAO possesses the largest gap aperture \(\alpha = 54.35(13)°\)\(^{28,29}\). meso-5sMAO displays lower polymerisation activity than the ethylene bridged analogue sMAO-meso-(EtInd)\(^2\)ZrCl\(_2\) activities of 874 and 1331 kgPE mol\(^{-1}\) h\(^{-1}\) bar\(^{-1}\) respectively at 60 °C (under similar polymerisation conditions with [Al]/[Zr] = 300),\(^25\) and lower than solution phase of well-known metalloocene complexes.\(^{40}\)

The molecular weights \(\left<M_w\right>\) and molecular weights distribution \((M_w/M_n)\) of the polyethylenes produced were analysed by gel permeation chromatography (GPC) (Fig. 3). rac-3sMAO and rac-4sMAO produce polymers with similar molecular weights; 391 and 381 kg mol\(^{-1}\) at 50 °C, which is expected due to their similar polymerisation activities. rac-3sMAO produces polymers with lower molecular weights than the dimethyl silyl bridged analog, \(M_w\) of 447 mol\(^{-1}\) at 50 °C for sMAO-rac-Me\(_2\)SB(1-R1)
ZrCl₂. rac-3-HF₅MAO produced polymers with the lowest molecular weights (297 kg mol⁻¹ at 50 °C). For the meso-3-ethyl catalysts, meso-2₅MAO produced polymers with the highest molecular weights, followed by meso-3₅MAO and meso-4₅MAO (M₉ of 503, 406, and 345 kg mol⁻¹, respectively, at 50 °C). meso-5₅MAO produced polymers with almost identical molecular weights to meso-3₅MAO (395 kg mol⁻¹ at 50 °C). All polymers show the expected decreases in polymer molecular weights with increasing polymerisation temperature, attributed to stronger chain transfer reactions at elevated temperatures.⁴¹ No long chain branching was observed by GPC or NMR spectroscopy, but very large molecular weights distribution were observed (M₉/M₈ around 5–8, Tables S₄–S₉) which will point towards several catalytic species on the surface.⁴²

Conclusions

A new family of unbridged bis(peralkylindenyl) zirconocene complexes of the type (⁺³Ind)₂ZrX₃ have been synthesised and fully characterised. Six new crystal structures have been reported.

When immobilised on solid polymethylaluminoxane (sMAO) these complexes produce HDPE in slurry-ethene polymerisations. The supported meso-alkyl catalysts showing higher polymerisation activities than meso-halide catalysts; polymerisation activity follows the order meso-4₅MAO, meso-3₅MAO, and meso-2₅MAO.

These metallocene complexes and their inorganic based supported catalysts show promising results for use as slurry-phase polymerisation catalysts. Further testing with hydrogen, co-monomers and z-olefins will be carried out.

Experimental section

General details, synthesis and characterisation of ligands precursors, NMR spectra, X-ray crystallography data and further polymerisation data are included in the ESI.†

Synthesis of (⁺³Ind)₂ZrCl₂ (1)

2.0 equivalents ¹⁻³Ind⁴Li (2.00 g, 7.45 mmol) and 1.0 equivalent ZrCl₄ (0.868 g, 3.73 mmol) were stirred in benzene (100 mL) for 16 hours at room temperature. The reaction mixture was allowed to settle, filtered and the resulting orange filtrate dried in vacuo to afford a 50:50 mixture of rac-(⁺³Ind)₂ZrCl₂ (rac-1) and meso-(⁺³Ind)₂ZrCl₂ (meso-1) as an orange-yellow solid in 45% yield (1.15 g, 1.68 mmol).¹ H NMR [chloroform-d₄, 400 MHz, 298 K] δ (ppm): 7.75 (Ph-H, 2H, JHH = 7.5 Hz), 7.56 (Ph-H, 2H, JHH = 7.5 Hz), 7.28 (Ph-H, 4H, m), 7.18 (Ph-H, 6H, m), 7.14 (Ph-H, 2H, m), 6.91 (Ph-H, 2H, m), 6.88 (Ph-H, 2H, m), 6.42 (Ind-H, 2H, s), 5.76 (Ind-H, 2H, s), 2.63 (Ind-CH₃, 6H, s), 2.19 (Ind-CH₃, 6H, s), 2.17 (Ind-CH₃, 12H, s), 2.11 (Ind-CH₃, 12H, s), 2.08 (Ind-CH₃, 6H, s), 1.92 (Ind-CH₃, 6H, s), 1.88 (Ind-CH₃, 6H, s), 1.54 (Ind-CH₃, 6H, s), 1.3 (C(CH₃)₃) NMR [chloroform-d₄, 101 MHz, 298 K] δ (ppm): 136.1 (Ind-Ph), 136.0 (Ind-Ph), 134.9 (Ind), 134.8 (Ind), 134.0 (Ph-H), 133.7 (Ind), 133.6 (Ind), 132.5 (Ind), 132.4 (Ph-H), 132.2 (Ph-H), 132.1 (Ph-H), 131.8 (Ind), 130.7 (Ind), 130.5 (Ind), 130.3 (Ind), 127.9 (Ph-H), 127.7 (Ph-H), 127.6 (Ind), 127.6 (Ind), 127.3 (Ph-H), 127.3 (Ph-H), 127.1 (Ph-H), 127.0 (Ph-H), 127.0 (Ph-H), 125.8 (Ind), 125.4 (Ind), 125.1 (Ind), 124.4 (Ind), 98.6 (Ind-H), 94.4 (Ind-H), 18.8 (Ind-CH₃), 18.5 (Ind-CH₃), 18.3 (Ind-CH₃), 17.1 (Ind-CH₃), 16.9 (Ind-CH₃), 16.8 (Ind-CH₃), 16.7 (Ind-CH₃), 16.7 (Ind-CH₃), 16.6 (Ind-CH₃), 15.1 (Ind-CH₃). CHN analysis (%): calculated C 74.95, H 6.68; observed C 75.13, H 6.72.

Synthesis of (⁺³Ind)⁴ZrBr₄ (meso-2)

2.0 equivalents ¹⁻³Ind⁴Li (2.00 g, 9.08 mmol) and 1.0 equivalent ZrBr₄ (1.87 g, 4.54 mmol) were stirred in benzene (100 mL) for 16 hours at room temperature. The reaction mixture was allowed to settle, filtered and the resulting orange filtrate dried in vacuo to afford a 40:60 mixture of rac-(⁺³Ind)³ZrBr₃ and meso-(⁺³Ind)³ZrBr₃ as an orange solid. Recrystallisation of the isomeric mixture in DCM at –30 °C yielded meso-1, 400 MHz, 298 K) δ (ppm): 6.25 (Ind-H, 2H, s), 3.22 (Ind-CH₂-CH₂, 2H, d, JHH = 15.0 Hz, JHH = 7.5 Hz), 2.69 (Ind-CH₂-CH₂, 2H, d, JHH = 15.0 Hz, JHH = 7.5 Hz), 2.54 (Ind-CH₂, 12H, s), 2.27 (Ind-CH₃, 6H, s), 2.23 (Ind-CH₃, 6H, s), 1.70 (Ind-CH₃, 6H, s), 1.5 (Ind-CH₂-CH₃, 6H, t, JHH = 7.5 Hz).¹ ¹³C(C(H)₃) NMR (chloroform-d₄, 101 MHz, 298 K) δ (ppm): 134.2 (Ind), 133.4 (Ind), 130.9 (Ind), 130.8 (Ind), 127.8 (Ind), 126.0 (Ind), 125.6 (Ind), 125.2 (Ind), 94.6 (Ind-H), 23.0 (Ind-CH₂-CH₂, 17.6 (Ind-CH₂-CH₂, 17.1 (Ind-CH₃), 16.8 (Ind-CH₃), 16.6 (Ind-CH₃), 15.6 (Ind-CH₂-CH₂), 14.6 (Ind-CH₃). CHN analysis (%): calculated C 56.71, H 6.25; observed C 56.61, H 6.33. HRMS (ESI): expected m/z 674.6095; observed 674.0724 [M⁺].

Synthesis of rac-(⁺³Ind)²Zr(CH₂Ph)₂ (rac-4)

1.0 equivalent rac-(⁺³Ind)²ZrCl₂ (45.2 mg, 0.0768 mmol) and 2.0 equivalents KCH₂Ph (20.0 mg, 0.154 mmol) were stirred in benzene (1 mL) for 16 hours at room temperature. The reaction mixture was allowed to settle, filtered and the resulting yellow filtrate dried in vacuo to afford rac-(⁺³Ind)²Zr(CH₂Ph)₂ as a yellow solid in 93% yield (50.2 mg, 0.0717 mmol). Yellow crystals of rac-(⁺³Ind)²Zr(CH₂Ph)₂ suitable for a single crystal X-ray diffraction study were grown in pentane at ~30 °C.¹ H NMR (chloroform-d₄, 400 MHz, 298 K) δ (ppm): 7.08 (m-Ph-H, 4H, dd, JHH = 7.3, 7.4 Hz), 6.80 (p-Ph-H, 2H, t, JHH = 7.3 Hz), 6.62 (o-Ph-H, 4H, d, JHH = 7.4 Hz), 4.91 (Ind-H, 2H, s), 2.76 (Ind-CH₂-CH₂, 2H, d, JHH = 14.8 Hz, JHH = 7.4 Hz), 2.51 (Ind-CH₃, 6H, s), 2.45 (Ind-CH₂-CH₂, 2H, d, JHH = 14.8 Hz, JHH = 7.4 Hz), 2.28 (Ind-CH₃, 6H, s), 2.23 (Ind-CH₃, 6H, s), 2.01 (Ind-CH₃, 6H, s), 1.82 (Ind-CH₃, 6H, s), 0.99 (Ind-CH₂-CH₃, 6H, t, JHH = 7.4 Hz), 0.87 (Zr-CH₂Ph, 2H, d, JHH = 11.2 Hz), 0.67 (Zr-CH₂-Ph, 2H, d, JHH = 11.2 Hz).¹ ¹³C(C(H)₃) NMR (chloroform-d₄, 101 MHz, 298 K) δ (ppm): 152.8 (Zr-CH₂-Ph), 133.3 (Ind), 131.0 (Ind), 128.3 (Ind), 127.9 (Ind), 127.8 (Ind), 127.6 (m-Ph), 127.1 (o-Ph), 126.4 (Ind), 123.2 (Ind), 121.0 (p-Ph), 119.8 (Ind), 100.8 (Ind-H), 66.0 (Zr-CH₂Ph), 21.6 (Ind-CH₂-CH₂), 17.1 (Ind-CH₃), 16.8
Synthesis of meso-\((\text{Ind}^3\text{Et})_2\)Zr(\(\text{CH}_2\text{Ph}\)) \((\text{meso-4})\)

1.0 equivalent meso-\((\text{Ind}^3\text{Et})_2\)ZrCl\(_2\) (45.2 mg, 0.0768 mmol) and 2.0 equivalents KCH\(_2\)Ph (20.0 mg, 0.154 mmol) were stirred in benzene (1 mL) for 16 hours at room temperature. The reaction mixture was allowed to settle, filtered, and the resulting yellow filtrate dried in vacuo to afford meso-\((\text{Ind}^3\text{Et})_2\)Zr(\(\text{CH}_2\text{Ph}\)) \((\text{meso-6})\) as a yellow solid in 88% yield (45.6 mg, 0.0678 mmol). Yellow crystals of meso-\((\text{Ind}^3\text{Me})_2\)Zr(\(\text{CH}_2\text{Ph}\)) suitable for a single crystal X-ray diffraction study were grown in toluene at room temperature.

\(^1\text{H}\) NMR (chloroform-\(\text{d}_4\), 500 MHz, 298 K) \(\delta\) (ppm): 7.09 (\(\text{m-Ph}\)-H, 2H), dd, \(J_{HH} = 7.3, 7.6\) Hz, 7.04 (\(\text{m-Ph}\)-H, 2H), dd, \(J_{HH} = 7.3, 7.6\) Hz, 6.79 (\(\text{p-Ph}\)-H, 1H, t, \(J_{HH} = 7.3\) Hz), 6.75 (\(\text{p-Ph}\)-H, 1H, t, \(J_{HH} = 7.3\) Hz), 6.58 (\(\text{o-Ph}\)-H, 2H, d, \(J_{HH} = 7.6\) Hz), 6.46 (\(\text{o-Ph}\)-H, 2H, d, \(J_{HH} = 7.6\) Hz), 5.61 (\(\text{Ind-H}\)-H, 2H, s), 2.71 (\(\text{Ind-CH}_2\)\(-\text{CH}_2\)-H, 2H, dq, \(J_{HH} = 7.1, 7.4\) Hz), 2.45 (\(\text{Ind-CH}_2\)-H, 6H, s), 2.38 (\(\text{Ind-CH}_2\)\(-\text{CH}_2\)-H, 2H, dq, \(J_{HH} = 14.8, 7.4\) Hz), 2.22 (\(\text{Ind-CH}_3\)-H, 6H, s), 2.18 (\(\text{Ind-CH}_3\)-H, 6H, s), 2.10 (\(\text{Ind-CH}_3\)-H, 6H, s), 1.77 (\(\text{Ind-CH}_3\)-H, 6H, s), 0.95 (\(\text{Ind-CH}_3\)-H, 6H, t, \(J_{HH} = 7.4\) Hz), 0.79 (\(\text{Zr-CH}_2\)-H, 2H, s), 0.24 (\(\text{Zr-CH}_2\)-H, 2H, s), 1.11(\(\text{Zr-H}\)).

Synthesis of \((\text{Ind}^3\text{Et})_2\)ZrBr\(_2\) \((\text{meso-5})\)

2.0 equivalents Ind\(^3\)Li (2.00 g, 9.70 mmol) and 1.0 equivalent ZrBr\(_4\) (1.99 g, 4.85 mmol) were stirred in benzene (100 mL) for 16 hours at room temperature. The reaction mixture was allowed to settle, filtered, and the red filtrate dried in vacuo to afford orange solid comprising of a 20:80 mixture of rac-\((\text{Ind}^3\text{Me})_2\)ZrBr\(_2\) and meso-\((\text{Ind}^3\text{Et})_2\)ZrBr\(_2\) and impurities. Recrystallisation of the isomeric mixture in toluene at \(-30^\circ\text{C}\) yielded meso-\((\text{Ind}^3\text{Et})_2\)ZrBr\(_2\) \((\text{meso-5})\) as orange crystals, suitable for a single crystal X-ray diffraction study, in 6% yield (0.180 g, 0.277 mmol). \(^1\text{H}\) NMR (chloroform-\(\text{d}_4\), 400 MHz, 298 K) \(\delta\) (ppm): 5.90 (\(\text{Ind-H}\)-H, 2H, s), 2.64 (\(\text{Ind-CH}_3\)-H, 6H, s), 2.55 (\(\text{Ind-CH}_2\), 6H, s), 2.17 (\(\text{Ind-CH}_3\)-H, 6H, s), 2.12 (\(\text{Ind-CH}_2\)-H, 6H, s), 0.97 (\(\text{Ind-CH}_3\)-H, 6H, s), 0.24 (\(\text{Ind-CH}_2\)-H, 2H, s), 1.11(\(\text{Zr-H}\)).

Synthesis of \((\text{Ind}^3\text{Me})_2\)Zr(\(\text{CH}_2\text{Ph}\)) \((\text{meso-6})\)

1.0 equivalent meso-\((\text{Ind}^3\text{Et})_2\)ZrBr\(_2\) (49.9 mg, 0.0768 mmol) and 2.0 equivalents KCH\(_2\)Ph (20.0 mg, 0.154 mmol) were stirred in benzene (1 mL) for 16 hours at room temperature. The reaction mixture was allowed to settle, filtered, and the resulting yellow filtrate dried in vacuo to afford meso-\((\text{Ind}^3\text{Me})_2\)Zr(\(\text{CH}_2\text{Ph}\)) \((\text{meso-6})\) as a yellow solid in 88% yield (45.6 mg, 0.0678 mmol). Yellow crystals of meso-\((\text{Ind}^3\text{Me})_2\)Zr(\(\text{CH}_2\text{Ph}\)) suitable for a single crystal X-ray diffraction study were grown in toluene at room temperature.
Acknowledgements

P. A., J. V. L., J.-C. B., and Z. R. T. (SCG Research Fellowship) would like to thank SCG Chemicals Co., Ltd (Thailand) for financial support; Chemical Crystallography (University of Oxford) for the use of the diffractometers; and Ms Liv Thobru (Norner AS, Norway) for GPC analysis.

Notes and references

1. L. Resconi, L. Cavallo, A. Fait and F. Piemontesi, Chem. Rev., 2000, 100, 1253–1346.
2. W. Kaminsky and H. Sinn, Adv. Polym. Sci., 2013, 258, 1–28; Methylaluminoxane: Key Component for New Polymerization Catalysts, ed. W. Kaminsky, Springer. Polyolefins: 50 years after Ziegler and Natta II.
3. N. Schneider, M. E. Huttenloch, U. Stehling, R. Kirsten, F. Schaper and H. H. Brintzinger, Organometallics, 1997, 16, 3413–3420.
4. M. Bochmann, Adv. Polym. Sci., 2000, 100, 1347–1376.
5. B. Wang, Coord. Chem. Rev., 2006, 250, 242–258.
6. O. Olabisi, M. Atiquullah and W. Kaminsky, J. Macromol. Sci., Part C, 1997, 37, 519–554.
7. W. Kaminsky and H. Winkelbach, Top. Catal., 1999, 7, 61–67.
8. W. Kaminsky, Catal. Today, 1994, 20, 257–271.
9. W. Kaminsky, J. Chem. Soc., Dalton Trans., 1998, 1413–1418.
10. W. Kaminsky, Adv. Catal., 2001, 46, 89–159.
11. W. Kaminsky and A. Laban, Appl. Catal., A, 2001, 222, 47–61.
12. W. Kaminsky, J. Polym. Sci., Polym. Chem., 2004, 42, 3911–3921.
13. W. Kaminsky, A. Funck and H. Hähnse, Dalton Trans., 2009, 8803–8810.
14. H. G. Alt, Dalton Trans., 2005, 3271–3276.
15. W. Kaminsky, Macromol. Symp., 1995, 97, 79–89.
16. C. Janiak and B. Rieger, Angew. Chem., 1994, 215, 47–57.
17. P. A. Zapata, C. Belver, R. Quijada, P. Aranda and E. Ruiz-Hitzky, App. Catal. A Gen., 2013, 433, 142–150.
18. D. Bianchini, J. H. Z. dos Santos, T. Uozumi and T. Sano, J. Mol. Catal. A Chem., 2002, 185, 223–235.
19. C. Janiak, B. Rieger, R. Voelkel and H.-G. Braun, J. Polym. Sci., Polym. Chem., 1993, 31, 2959–2968.
20. H. Cramail, K. Radhakrishnan and A. Deffieux, Compt. Rend., 2002, 5, 49–52.
21. T. Dalet, H. Cramail and A. Deffieux, Macromol. Chem. and Phys., 2004, 205, 1394–1401.
22. M. M. Mortazavi, S. Ahmadjo, J. H. Z. Dos Santos, H. Arabi, M. Nekoonanesh, G. H. Zohuri, R. Brambilla and G. B. Galland, J. Appl. Polym. Sci., 2013, 130, 4568–4575.
23. F. Silveira, M. D. C. Martins Alves, F. C. Stedile, S. B. Pergher and J. H. Z. dos Santos, J. Mol. Catal. A Chem., 2010, 315, 213–220.
24. J.-C. Buffet, Z. R. Turner, R. T. Cooper and D. O’Hare, Polym. Chem., 2015, 6, 2493–2503.
25. J.-C. Buffet, N. Wanna, T. A. Q. Arnold, E. K. Gibson, P. P. Wells, Q. Wang, J. Tantirungrotechai and D. O’Hare, Chem. Mater., 2015, 27, 1495–1501.
26. J. C. Buffet, C. F. H. Byles, R. Felton, C. P. Chen and D. O’Hare, Chem. Commun., 2016, 52, 4076–4079.
27. A. F. R. Kilpatrick, J.-C. Buffet, P. Norby, N. H. Rees, N. P. Funnell, S. Sriplotongnak and D. O’Hare, Chem. Mater., 2016, 28, 7444–7450.
28. A. F. R. Kilpatrick, N. H. Rees, S. Sriplotongnak, J.-C. Buffet and D. O’Hare, Organometallics, 2018, 37, 156–164.
29. P. Angpanitcharoen, G. Hay, J.-C. Buffet, Z. R. Turner, T. A. Q. Arnold and D. O’Hare, Polycryst., 2016, 116, 216–222.
30. P. Angpanitcharoen, J. V. Lamb, Z. R. Turner, J.-C. Buffet and D. O’Hare, Mol. Catal., 2020, 498, 111275.
31. T. A. Q. Arnold, J.-C. Buffet, Z. R. Turner and D. O’Hare, J. Organomet. Chem., 2015, 792, 55–65.
32. N. E. Grimmer, N. J. Coville, C. B. de Koning, J. M. Smith and L. M. Cook, J. Organomet. Chem., 2000, 616, 112–127.
33. N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sironi and M. Moret, Organometallics, 1990, 9, 3098–3105.
34. A. F. R. Kilpatrick, N. H. Rees, S. Sriplotongnak, J.-C. Buffet and D. O’Hare, J. Organomet. Chem., 2015, 792, 55–65.
35. T. A. Q. Arnold, Z. R. Turner, J.-C. Buffet and D. O’Hare, J. Organomet. Chem., 2016, 822, 85–90.
36. T. K. Trefz, M. A. Henderson, M. Linnolahti, S. Collins and J. S. McNidoe, Chem. Eur. J., 2015, 21, 2980–2991.
37. S. Collins, M. Linnolahti, M. G. Zamora, H. S. Zijlstra, M. T. Rodriguez Hernández and O. Perez-Camacho, Macromolecules, 2017, 50, 8871–8884.
38. C. Janiak, K. C. H. Lange, U. Versteeg, D. Lentz and P. H. M. Budzelaar, Chem. Ber., 1996, 129, 1517–1529.
39. C. Janiak, U. versteeg, K. C. H. Lange, R. Weimann and E. Hahn, J. Organomet. Chem., 1995, 501, 219–234.
40. W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck and J. Rohrmann, Makromol. Chem., 1992, 193, 1643–1651.
41. M. A. Parvez, M. Rahaman, M. A. Suleiman, J. B. P. Soares and I. A. Hussein, Int. J. Polym. Sci., 2014, 1–10.
42. A. Malmborg, J. Liimata, A. Lehtinen and B. Löfgren, Macromolecules, 1999, 32, 6687–6696.
43. M. Pollard, K. Klimke, R. Graf, H. W. Spiess, M. Wilhelm, O. Sperber, C. Piel and W. Kaminsky, Macromolecules, 2004, 37, 813–825.
44. A. Ahlers and W. Kaminsky, Makromol. Chemie, Rapid. Commun., 1988, 9, 457–461.