Synthesis, characterisation and ethylene polymerisation performance of silyl bridged peralkylated bis(indenyl) zirconocenes

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Abstract

Six new peralkylated bis(indenyl) zirconocene complexes have been synthesised and fully characterised; *rac*- $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrX}_2$ and *meso*- $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrX}_2$ ($\text{X} = \text{Cl, Br and CH}_2\text{Ph}$). Solution-phase ethylene polymerisation using *rac*- $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ /methylaluminoxane (MAO) and slurry-phase ethylene polymerisation using *rac*- $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ immobilised on solid polymethylaluminoxane (sMAO), MAO modified layered double hydroxide (LDHMAO) and MAO modified silica (SSMAO) were studied. Polymerisation conditions were optimised for sMAO-*rac*- $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ and applied to the other catalysts. A 75:25 mixture of *rac*- and *meso*- $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{Zr}(\text{CH}_2\text{Ph})_2$ supported on sMAO showed the highest polymerisation activities ($4832 \text{ kg}_{\text{PE}} \text{ mol}_{\text{Zr}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ at 60°C), producing high density polyethylenes (HDPE) with modest molecular weight (M_w of 336 kg mol^{-1} at 60°C) and molecular weight distributions (M_w/M_n) less than 3.2. sMAO-*rac*- $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ was found to be responsive to H_2 in a high-throughput screening system, producing polyethylenes with low molecular weights (M_w of 41 kg mol^{-1} with 1.6% H_2). In the same high-throughput system, slurry-phase ethylene polymerisation in the presence of 1-hexene comonomer was shown to increase the polymerisation activity of sMAO-*rac*- $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ compared to polymerisation in the same system without 1-hexene.

Keywords

Zirconocenes, polymerisation, ethylene, solid polymethylaluminoxane, peralkylated bis(indenyl)

1 Introduction

Group 4 metallocenes are generally defined as d^0 , pseudo-tetrahedral organometallic compounds in which the transition metal atom bears two η^5 -cyclopentadienyl-based ligands

and two σ -ligands. Upon activation by co-catalysts (such as methylaluminoxane; MAO), the resulting electrophilic alkyl metallocene cations, stabilised by weakly coordinating anions, are highly active for α -olefin polymerisation.[1-5] *Ansa*-bridges can impart significant control over the activity and structure of metallocene catalysts, such as introducing additional stereochemistry, which is exemplified in the *rac*- and *meso*-isomers of bridged indenyl complexes.[6] Group 4 *ansa*-bridged indenyl and permethylindenyl complexes, such as *rac*-dichloro(dimethylsilylenebis(1-indenyl))zirconium(IV) (*rac*-^{Me}₂SBIZrCl₂) and *rac*-dichloro(dimethylsilylenebis(hexamethyl-1-indenyl))zirconium(IV) (*rac*-^{Me}₂SBI*ZrCl₂), have been shown to be very active for ethylene polymerisation.[7-10] Permethylation of the indenyl ring can lead to enhanced complex stability compared to the unsubstituted analogues, attributed to increased inductive donation and steric bulk around the metal centre.[11] It is proposed that this can lead to additional stabilisation of the cationic polymerisation intermediates and can therefore increase polymerisation activity. Furthermore, it has been shown that introducing alkyl groups at the 3-positions of unsubstituted indenyl ligands leads to increases in the stability and ethylene polymerisation activities of the corresponding complexes.[12-14]

These ‘single-site’ metallocene catalysts enable the production of polyolefins with tuneable molecular structures, stereochemistries and molecular weight distributions (MWD). Yet, they are rarely used for industrial polymer production due to their incompatibility with the existing slurry-phase or gas-phase olefin polymerisation infrastructure.[15] By immobilising metallocenes onto support materials this problem may be overcome, and the advantages of metallocene catalysts (including narrow MWD, high activity and precise control over polymer microstructure) are preserved.[16]

Silica (SiO₂) is the most common inorganic support for metallocene complexes.[15, 17] Impregnation of MAO, forming MAO modified silica (SSMAO), is required in order to activate the support.[10, 15, 18-21] Recently, aqueous miscible organic layered double hydroxides (AMO-LDHs), a class of anionic clays consisting of positively charged Brucite-like layers with weakly bound anions intercalated between them, activated with MAO (LDHMAO), have been reported as catalyst supports for olefin polymerisation.[10, 22, 23] AMO-LDH supports are simple to synthesise on a large scale, more cost-effective than silica and show no evidence of reactor fouling or catalyst leaching, making them viable options for industrial processes.[24] Solid polymethylaluminoxane (sMAO), an insoluble, oligomeric product of the incomplete hydrolysis of trimethylaluminium (TMA), has also recently been explored as a

support for metallocene complexes.[21, 25-27] sMAO can act a bifunctional activator and support without further modification,[28, 29] and has been found to be a very efficient support for metallocene catalysts.[27, 28, 30, 31]

Herein, we report the synthesis and characterisation of a new family of peralkylated bis(indenyl) group 4 metallocenes. Looking to improve the ethylene polymerisation activity of $\text{Me}_2\text{SBI}^*\text{ZrX}_2$ -type complexes, we have introduced ethyl groups at the 3-position of the permethylindenyl rings, forming complexes of the type $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{ZrX}_2$. The homogeneous ethylene polymerisation activities, and heterogeneous ethylene polymerisation activities of the complexes when immobilised on inorganic solid supports (SSMAO, LDHMAO and sMAO) are discussed. One catalyst is also evaluated for its potential industrial applications, including the synthesis of low molecular weight polyethylenes using dihydrogen (H_2) as a chain transfer agent, and linear low-density polyethylene (LLDPE) using 1-hexene as a comonomer.

2 Results and Discussion

2.1 Synthesis of $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{H}_2$

3-ethyl-2,4,5,6,7-pentamethylindenyl lithium ($^{3\text{-Et}}\text{Ind}^\# \text{Li}$) was synthesised according to a previously reported procedure.[20] One equivalent Me_2SiCl_2 was added to two equivalents $^{3\text{-Et}}\text{Ind}^\# \text{Li}$ at 0 °C and stirred at room temperature for 16 hours (Scheme 1). Following work-up, $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{H}_2$ was isolated as an off-white solid in 53% yield as a 50:50 mixture of *rac*- and *meso*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{H}_2$. The ^1H NMR spectrum shows that the two indenyl rings are magnetically equivalent for both isomers (Figure S1). For *rac*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{H}_2$, the two methyl groups on the silyl bridge appear as a singlet, indicating that they are enantiotopic and the isomer is racemic. However, for *meso*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{H}_2$, the methyl groups on the silyl bridge appear as two singlets and are therefore diastereotopic.

Scheme 1. Synthesis of *rac*- and *meso*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{ZrCl}_2$ (**1**) and *rac*- and *meso*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{ZrBr}_2$ (**2**) via $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{H}_2$.

Colourless crystals of $rac\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{H}_2$ suitable for a single crystal X-ray diffraction study were grown from Et_2O at $-30\text{ }^\circ\text{C}$ (Figure 1). The Flack parameter of 0.38(16) (near 0.5) indicates that the crystals are likely racemic. The crystal structure also confirms the position of the $\text{C}(2)=\text{C}(3)$ and $\text{C}(17)=\text{C}(18)$ double bonds with an average bond length of $1.351(6)\text{ \AA}$ (bond lengths of 1.54 and $1.34\text{ \AA}$ are expected for C–C single bonds and C=C double bonds, respectively). The structure displays a similar average Si–C_{Ind} bond length to $rac\text{-Me}_2\text{SBI}^*\text{H}_2$ ($1.934(4)$ and $1.939(6)\text{ \AA}$ respectively).[10]

Figure 1. Molecular structures of (a) $rac\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{H}_2$, (b) $rac\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (***rac*-1**), (c) $meso\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (***meso*-1**), (d) $rac\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrBr}_2$ (***rac*-2**), (e) $meso\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrBr}_2$ (***meso*-2**) and (f) $rac\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{Zr}(\text{CH}_2\text{Ph})_2$ (***rac*-3**). Hydrogen atoms omitted for clarity (except for stereocentres), ellipsoids drawn at 50% probability.

Table 4.1. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) for $rac\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (***rac*-1**), $meso\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (***meso*-1**), $rac\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrBr}_2$ (***rac*-2**), $meso\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrBr}_2$ (***meso*-2**) and $rac\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{Zr}(\text{CH}_2\text{Ph})_2$ (***rac*-3**).

	Complex	Zr–X	Zr–Cp _{cent}	α	δ	TA
<i>rac</i>-1	$rac\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$	2.4186(7) 2.4295(7)	2.2361(11) 2.2374(11)	58.21(13)	129.54(4)	144.92

<i>meso-1</i>	<i>meso</i> - ^{Me₂SB(3-EtI*)} ZrCl ₂	2.4136(6) 2.4357(7)	2.2513(11) 2.2410(11)	57.13(14)	130.53(4)	5.60
<i>rac-2</i>	<i>rac</i> - ^{Me₂SB(3-EtI*)} ZrBr ₂	2.5861(5) 2.5656(5)	2.2511(14) 2.2435(14)	59.65(18)	129.14(5)	144.99
<i>meso-2</i>	<i>meso</i> - ^{Me₂SB(3-EtI*)} ZrBr ₂	2.5635(8) 2.5945(9)	2.244(2), 2.2389(19)	57.9(3)	130.09(8)	2.89
<i>rac-3</i>	<i>rac</i> - ^{Me₂SB(3-EtI*)} Zr(CH ₂ Ph) ₂	2.273(4) 2.334(4)	2.2923(18) 2.3146(18)	63.2(2)	128.84(7)	146.78

2.2 Synthesis of ^{Me₂SB(3-EtI*)}ZrX₂ (X = Cl and Br)

One equivalent ^{Me₂SB(3-EtI*)}H₂ was deprotonated with two equivalents ⁿBuLi to yield ^{Me₂SB(3-EtI*)}Li₂ as a yellow solid, which was then reacted with one equivalent ZrX₄ (X = Cl and Br). Following work up, ^{Me₂SB(3-EtI*)}ZrCl₂ (**1**) was isolated as an orange solid in 24% yield as a 50:50 mixture of *rac*- and *meso*-^{Me₂SB(3-EtI*)}ZrCl₂ (***rac-1*** and ***meso-1***). Recrystallisation of the isomeric mixture in Et₂O at −30 °C yielded pure ***rac-1*** as orange crystals. Following work up, ^{Me₂SB(3-EtI*)}ZrBr₂ (**2**) was isolated as a red solid comprising of a 50:50 mixture of *rac*- and *meso*-^{Me₂SB(3-EtI*)}ZrBr₂ (***rac-2*** and ***meso-2***) and impurities. Recrystallisation of the isomeric mixture in Et₂O at −30 °C yielded ***rac-2*** as orange crystals in 1% yield.

The ¹H NMR spectrum of ***rac-1*** shows that the indenyl rings and silyl methyl groups are magnetically equivalent; five singlets at 1.90–2.60 ppm correspond to the methyl groups on the indenyl rings and a singlet at 1.14 ppm corresponds to the methyl groups on the silyl bridge (Figure S3). The diastereotopic methylene protons of the ethyl groups are observed as two doublet of quartets resonances at 2.71 and 3.30 ppm, while a triplet at 0.86 ppm corresponds to the methyl protons of the ethyl groups. The ¹H NMR spectrum of ***rac-2*** shows an identical pattern to ***rac-1*** (Figure S7). By subtracting the resonances corresponding to ***rac-1*** from the ¹H NMR spectrum of the 50:50 isomeric mixture of ***rac-1*** and ***meso-1***, the resonances corresponding to ***meso-1*** can be assigned (Figure S5).

Orange crystals of ***rac*-1** and ***meso*-1** suitable for single crystal X-ray diffraction studies were grown from the slow cooling of a hot pentane solution of the isomeric mixture and co-crystallised in the triclinic space group $P\bar{1}$. Orange crystals of ***rac*-2** and ***meso*-2** suitable for single crystal X-ray diffraction studies were grown by the slow evaporation of a Et₂O solution of ***rac*-2** or a chloroform-*d*₁ solution of 50:50 ***rac*-2** and ***meso*-2**, respectively. Both isomers crystallised in the monoclinic space group $P2_1/c$ (as a racemic mixture for ***rac*-2**). Molecular structures are depicted in Figure 1, with selected bond lengths and angles presented in Table 1.

The average Zr-X bond lengths of the *rac*- and *meso*-isomers are very similar; average Zr-Cl of 2.424 and 2.425 Å for ***rac*-1** and ***meso*-1** respectively and average Zr-Br of 2.576 and 2.579 Å for ***rac*-2** and ***meso*-2** respectively. The Zr-Br bond lengths are longer than Zr-Cl due to the increase in size of Br compared to Cl. The Zr-Cl bond lengths of ***rac*-1** are very similar to those of the permethylated analogue; average Zr-Cl of 2.424 and 2.423 Å for ***rac*-1** and *rac*-Me₂SBI*ZrCl₂, respectively.[10] The average Zr-Cp_{cent} distances for the *rac*- and *meso*-isomers of **1** (2.237 and 2.246 Å, respectively) and **2** (2.247 and 2.241 Å, respectively) are very similar and show good agreement with reported values for similar structures.[10, 30, 32-34]

The ring tilt angle (α) for ***rac*-1** is in close agreement with *rac*-Me₂SBI*ZrCl₂ (58.21 and 58.49° respectively), implying that the introduction of ethyl groups at the 3-position has no effect on ring tilt.[10] The torsion angles (the dihedral angle between the [C(2), Cp_{cent}, Cp'_{cent}] and [C(2)', Cp_{cent}, Cp'_{cent}] planes; TA) for ***rac*-1** and ***rac*-2** are very similar to *rac*-Me₂SBI*ZrCl₂ and *rac*-(SBI)ZrCl₂ (144.92, 144.99, 145.15 and 145.20° respectively)[9, 10] due to the geometric restriction of the silyl bridge. In comparison, when no restriction is present, the unbridged analogue *rac*-(Ind[#])₂ZrCl₂ adopts near perfect 'anti' conformation with a TA value of 175.82° in order to minimise steric interactions.[35] The same structural restriction can also be observed for ***meso*-1** and ***meso*-2** where TAs close to 0° are observed (5.60 and 2.89°, respectively), while TA of 37.16° is reported for unbridged *meso*-(Ind[#])₂ZrCl₂. [35]

2.3 Synthesis of Me₂SB(^{3-Et}I*)Zr(CH₂Ph)₂

One equivalent of a 50:50 mixture of *rac*- and *meso*-Me₂SB(^{3-Et}I*)ZrCl₂ (**1**) was reacted with two equivalents of KCH₂Ph (Equation 1). Following work up, Me₂SB(^{3-Et}I*)Zr(CH₂Ph)₂ (**3**) was isolated as a 75:25 mixture of *rac*- and *meso*-Me₂SB(^{3-Et}I*)Zr(CH₂Ph)₂ (***rac*-3** and ***meso*-3**) as an orange-yellow solid in 83% yield. The change in the isomeric ratio from the parent complex suggests differences in solubility of the two isomers.

Equation 1. Synthesis of $\text{rac-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{Zr}(\text{CH}_2\text{Ph})_2$ (**3**).

The two sets of resonances in the ^1H NMR spectrum of 75:25 *rac*- and *meso*-**3** can be distinguished by the difference in integration and 2D NMR spectroscopy correlations (Figure S9). For both isomers, the two indenyl rings are magnetically equivalent. However, the C_2 -symmetry of *rac*-**3** results in magnetically equivalent benzyl and silyl methyl groups, while the C_s -symmetry of *meso*-**3** results in two magnetically inequivalent benzyl groups.

Orange crystals of *rac*-**3** suitable for a single crystal X-ray diffraction study were grown from a pentane solution of the isomeric mixture at room temperature (Figure 1 and Table 1). The isomer crystallised in the triclinic space group $P\bar{1}$ as a racemic mixture. Comparison of *rac*-**3** with the parent complex *rac*-**1** highlights structure distortions caused by the bulky benzyl ligands; the α and TA values of *rac*-**3** (63.2 and 146.78°, respectively) are larger than for *rac*-**1** (58.21 and 144.92°, respectively). The increased steric bulk of benzyl compared to chloride also causes increases in the Zr-C_{pcent} distances of *rac*-**3** compared to *rac*-**1** (average Zr-C_{pcent} of 2.303 and 2.237 Å respectively); a trend also observed for $\text{Me}_2\text{SB}(\text{Cp}, \text{I}^*)\text{ZrX}_2$ and *meso*-EBI*ZrX₂ (X = Cl and CH₂Ph).[25, 30]

3. Ethylene polymerisation

3.1 Solution phase ethylene polymerisation

A 50:50 mixture of *rac*- $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ and *meso*- $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (**1**) was studied for homogeneous ethylene polymerisation in 150 mL ampoules with 0.5 mg **1**, methylaluminoxane (MAO) activator with an initial aluminium to zirconium ratio ($[\text{Al}_{\text{MAO}}]_0/[\text{Zr}]_0$) of 500, 50 mL hexane and 2 bar ethylene at 50–90 °C. Polymerisations were run until stirring ceased (approximately 2 minutes).

1 shows decreasing polymerisation activities with increasing temperatures, likely due to the lack of thermal stability of metallocene complexes (Figure S15 and Table S2).[36] **1** is significantly more active than the unbridged analogue *rac*-($^3\text{-EtInd}^\#$)₂ZrCl₂ under the same polymerisation conditions (activities of 12423 and 1421 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ respectively at

60 °C)[20] due to the *ansa*-bridge opening up the metal centre and increasing the ‘bite angle’ of the metallocene complex.[37] **1** also displays higher polymerisation activities than the unmethylated analogue (9150 and 7600 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ for *rac*-Me₂SB(^{3-Et}I)ZrCl₂ and *meso*-Me₂SB(^{3-Et}I)ZrCl₂, respectively, at 70 °C with [Al_{MAO}]₀/[Zr]₀ of 1000 and 2 bar ethylene)[38] due to the increased inductive donation of ^{3-Et}I* compared to ^{3-Et}I leading to increased stability. However, **1** shows lower polymerisation activities than the permethylated analogue Me₂SBI*ZrCl₂ (activity of 22622 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ at 60 °C under similar polymerisation conditions with [Al_{MAO}]₀/[Zr]₀ of 2000)[10] and related Me₂SB(ⁱBu₂Flu, ^{3-Et}I*)ZrCl₂ (activity of 17570 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ at 70 °C under similar polymerisation conditions with [Al_{MAO}]₀/[Zr]₀ of 2000).[27]

The molecular weights (*M_w*) of the polyethylenes produced using **1**, determined by gel permeation chromatography (GPC), decreased as polymerisation temperature increased due to increased rates of termination rate relative to the propagation (Figure S15 and Table S2). The morphologies of the polymers were analysed by scanning electron microscopy (SEM), which showed the formation of very inhomogeneous and aggregated polymer particles with poorly defined structures (Figure S17). The poor morphologies of the polymers led to reactor fouling, which hindered efficient stirring and limits the large-scale applications of these species.

3.2 Slurry-phase ethylene polymerisation

In order to avoid reactor fouling caused by hot spots in homogeneous processes while maintaining the high polymerisation activities of the metallocenes, it is beneficial to immobilise the active catalytic components onto a heterogeneous support.[15] A 50:50 mixture of *rac*- and *meso*-Me₂SB(^{3-Et}I*)ZrCl₂ (**1**) was immobilised on solid polymethylaluminoxane (sMAO)[25, 28, 29] (**1_{sMAO}**), MAO-modified silica (SSMAO)[10, 20, 30] (**1_{SSMAO}**) and MAO-modified aqueous miscible organic (AMO) layered double hydroxide (LDHMAO)[22, 23, 39, 40] (**1_{LDHMAO}**) according to a literature procedure,[20] with an initial aluminium to zirconium ([Al_{sMAO}]₀/[Zr]₀) loading of 200.

The support and catalyst morphologies were analysed by SEM. The morphology of the sMAO support was shown to resemble aggregated, ‘popcorn’ shaped particles, which was retained after complex immobilisation, although slightly less aggregated (Figure S18). The spherical morphology of the SSMAO support also became less aggregated after immobilisation (Figure S19). The unique morphology of AMOLDH has small platelets forming loose flower-shape agglomerates, which have a more exposed surface compared to the densely

stacked morphology of conventional LDHs (Figure S20).[24] LDHMAO also became less aggregated after complex immobilisation as a result of being dispersed in a hydrocarbon solvent (Figure S20).

Further characterisation of **1_sMAO** was achieved using solid-state NMR spectroscopy (SSNMR) (Figures S11–S13). The ¹³C CP/MAS SSNMR spectrum shows a broad resonance at –8 ppm corresponding to the methyl groups of the support, in addition to resonances consistent with features of the immobilised complex. The ²⁹Si CP/MAS SSNMR spectrum shows a singlet resonance at –13 ppm corresponding to the silyl bridge of the complex. The presence of a slight shoulder indicates the presence of at least two Si species, which is consistent with the 50:50 mixture of *rac*- and *meso*-isomers immobilised on the support surface.

Slurry-phase ethylene polymerisation studies with **1_sMAO**, **1_{ss}MAO** and **1_{LDH}MAO** were conducted in 150 mL ampoules with 50 mL hexane, 10 mg pre-catalyst and 2 bar ethylene at 50–90 °C for 30 minutes with triisobutylaluminium (TiBA, Al(CH₂CH(CH₃)₂)₃) scavenger with [Al_{scav}]₀/[Zr]₀ of 1000. **1_{ss}MAO** and **1_{LDH}MAO** displayed approximately constant activities across the temperature range (272–383 and 102–125 kg_{PE} mol_{Zr}^{–1} h^{–1} bar^{–1}, respectively), while **1_sMAO** displayed a maximum polymerisation activity at 60 °C (3507 kg_{PE} mol_{Zr}^{–1} h^{–1} bar^{–1}) (Figure 2 and Tables S3–S5). **1_sMAO** is significantly more active than **1_{ss}MAO** and **1_{LDH}MAO** (activities of 3507, 383 and 125 kg_{PE} mol_{Zr}^{–1} h^{–1} bar^{–1} respectively at 60 °C), a trend also observed for ^{Me}₂SB(^tBu₂Flu, I*)ZrCl₂ and ^{Me}₂SB(Cp^R, I*)ZrX₂ complexes immobilised on the same three supports.[27, 30] This may be because some –OH groups remain on the surface of the LDH and SiO₂ after calcination, which can hydrolyse MAO and reduce its performance as an activator.[41] Similar to the homogeneous polymerisation, **1_{ss}MAO** and **1_{LDH}MAO** display lower polymerisation activities than permethylated analogues, SSMAO-*rac*-^{Me}₂SBI*ZrCl₂ and LDHMAO-[*rac*-^{Me}₂SBI*ZrCl₂], under similar polymerisation conditions (383, 108, 611 and 9657 kg_{PE} mol_{Zr}^{–1} h^{–1} bar^{–1} respectively at 70 °C).[10] The activity of **1_{ss}MAO** is also significantly lower than SSMAO-*rac*-(EBI*)ZrCl₂ (2647 kg_{PE} mol_{Zr}^{–1} h^{–1} bar^{–1} at 70 °C) under similar polymerisation conditions,[10] and SSMAO-*rac*-EBIZrCl₂ (3111 kg_{PE} mol_M^{–1} h^{–1} bar^{–1} with [Al_{ssMAO}]₀/[Zr]₀ = 1700 at 40 °C and 1.3 bar ethylene).[42] However, **1_{ss}MAO** shows ethylene polymerisation activities approximately 2.5 times higher than SSMAO-(CpⁿBu)₂ZrCl₂ (activity of 226 kg_{PE} mol_{Zr}^{–1} h^{–1} bar^{–1} [Al_{ssMAO}]₀/[Zr]₀ of 148 at 80 °C with 8 bar ethylene).[43]

Figure 2. Slurry-phase ethylene polymerisation activity as a function of temperature of polymerisation using $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (**1**) supported on sMAO (**1**_{sMAO}; black square), SSMAO (**1**_{SSMAO}; red square) and LDHMAO (**1**_{LDHMAO}; blue square). Polymerisation conditions: ethylene (2 bar), pre-catalyst (10 mg), hexane (50 mL), $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0 = 200$, TiBA (1000 eq.) and 30 minutes.

The molecular weights (M_w) of the polyethylenes produced using **1**_{sMAO} and **1**_{SSMAO} were analysed by GPC (Figures S21–S23). **1**_{SSMAO} produced polyethylenes with significantly higher M_w than **1**_{sMAO}; 787 and 587 kg mol⁻¹ respectively at 50 °C), which is due to the presence of free TMA within MAO acting as a chain transfer agent.[28, 44] The polymers produced using **1**_{sMAO} show monomodal molecular weight distributions, although with wider dispersities than the polymers produced from homogeneous polymerisation using **1** (M_w/M_n of 4.4–6.1 and 2.3–2.5, respectively), suggesting the presence of two active sites resulting from the 50:50 mixture of *rac*- and *meso*-isomers. The polymers produced using **1**_{SSMAO} show an upper shoulder in the molecular weights distributions, accounting for the slightly larger dispersity values (M_w/M_n of 4.3–5.6). SEM images of the polyethylenes show that **1**_{SSMAO} and **1**_{LDHMAO} produced polyethylenes with very poor, undefined morphologies, while **1**_{sMAO} produced polyethylenes with uniform, ‘popcorn’ morphologies resembling that of the sMAO support (Figure 3). These differences in polymer morphologies are likely due to the templating effects of the solid support, whereby the morphology of the solid support is replicated in the final polymer with uniform particle size dependent on a high surface area, homogeneous distribution of catalytically active centres and ready availability of the innermost parts of the catalyst fragment to the incoming monomer.[15] Powder X-ray diffraction (PXRD) of the polyethylenes

produced using $\mathbf{1}_{\text{sMAO}}$ showed Bragg reflections at 21.5° and 24° corresponding to (110) and (200) planes of high-density polyethylene (HDPE), respectively (Figure S30),[45] with the sharp nature of the spectrum confirming high crystallinity.[46]

Figure 3. SEM images of the resulting polyethylenes of heterogeneous ethylene polymerisation using $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (**1**) supported on (a) sMAO ($\mathbf{1}_{\text{sMAO}}$), (b) SSMAO ($\mathbf{1}_{\text{SSMAO}}$) and (c) LDHMAO ($\mathbf{1}_{\text{LDHMAO}}$).

Due to the high polymerisation activity of $\mathbf{1}_{\text{sMAO}}$ compared to $\mathbf{1}_{\text{SSMAO}}$ and $\mathbf{1}_{\text{LDHMAO}}$, polymerisation conditions were optimised for this catalyst (scavenger, scavenger concentration and complex loading). All polymerisation reactions were conducted in 150 mL ampoules with 50 mL hexane, 10 mg pre-catalyst and 2 bar ethylene at 60°C for 30 minutes.

Trialkylaluminium reagents play an important role in ethylene polymerisation as impurity scavengers. They react with trace moisture or reactive functional groups present in the polymerisation setup and, hence, prevent decomposition of the metallocene.[47] However, they can also depress activity via the formation of dormant alkyl-bridged species, $[\text{Cp}_2\text{Zr}(\mu\text{-R})(\mu\text{-Me})\text{AlMe}_2]^+$, which block monomer coordination to the transition metal.[48-50] In order to determine the ideal scavenger for polymerisation, slurry-phase ethylene

polymerisation reactions were conducted using **1_sMAO** with four different scavengers (trimethylaluminium, TMA; triethylaluminium, TEA; triisobutylaluminium, TiBA; methylaluminoxane, MAO) with an initial scavenger to zirconium ($[Al_{scav}]_0/[Zr]_0$) ratio of 1000 and a complex loading of $[Al_{sMAO}]_0/[Zr]_0 = 200$.

TiBA was found to be the most effective scavenger followed by TEA and TMA (activities of 4533, 4390 and 3562 $kg_{PE} mol_{Zr}^{-1} h^{-1} bar^{-1}$ respectively), which is consistent with the tendency of the trialkylaluminium reagents to form the dormant alkyl-bridged species (TMA > TEA > TiBA) (Figure 4 and Table S6).[48-50] This trend in activity is also observed with $sMAO-Me_2SB(Cp,I^*)ZrCl_2$ under similar polymerisation conditions; activities of 5144, 4649 and 3013 $kg_{PE} mol_{Zr}^{-1} h^{-1} bar^{-1}$ for polymerisation using TiBA, TEA and TMA respectively.[32] Using MAO as the impurity scavenger caused leaching of the metallocene complex into the solution,[51] which initiated homogeneous polymerisation, disrupting stirring and leading to reduced activity (2393 $kg_{PE} mol_{Zr}^{-1} h^{-1} bar^{-1}$). The molecular weights (M_w) of the polyethylenes are consistent with the trends in activity (M_w of 131, 185 and 356 $kg mol^{-1}$ for TMA, TEA and TiBA respectively), with the higher M_w of the polymers produced using MAO (M_w of 451 $kg mol^{-1}$) caused by homogeneous polymerisation (Figures 4 and S24). The lower molecular weights of the polymers produced using TMA and TEA compared to TiBA and MAO can be attributed to the size of the alkyl group; the smaller the alkyl group of aluminium scavenger, the faster the rate of chain transfer and the lower polymer molecular weights. [52, 53] Overall, TiBA is the best performing impurity scavenger for this system.

Figure 4. Slurry-phase ethylene polymerisation activity using $\text{Me}_2\text{SB}(\text{}^{\text{3-Et}}\text{I}^*)\text{ZrCl}_2$ supported on sMAO ($\mathbf{1}_{\text{sMAO}}$) with MAO (orange), TMA (purple), TEA (teal) and TiBA (black) scavengers. M_w in parenthesis (kg mol^{-1}). Polymerisation conditions: ethylene (2 bar), pre-catalyst (10 mg), hexane (50 mL), $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0 = 200$, $[\text{Al}_{\text{scav}}]_0/[\text{Zr}]_0 = 1000$, 60 °C and 30 minutes.

To balance between the opposing effects of TiBA, such as the formation of dormant alkyl-bridged species, with the activity enhancement due to its scavenging properties, optimisation of catalyst activity with respect to TiBA loading was investigated. Slurry-phase ethylene polymerisation reactions were conducted using $\mathbf{1}_{\text{sMAO}}$ with $[\text{Al}_{\text{TiBA}}]_0/[\text{Zr}]_0$ of 100–2000 and $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0$ of 200. $[\text{Al}_{\text{TiBA}}]_0/[\text{Zr}]_0$ of 1000 was found to be the optimal concentration to remove impurities from the system without causing significant decreases in polymerisation activity; maximum activity of $4533 \text{ kg}_{\text{PE}} \text{ mol}_{\text{Zr}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ (Figure 5 and Table S6). In general, the M_w of the resulting polyethylenes decreased with increasing TiBA concentration (from 487 to 332 kg mol^{-1} with $[\text{Al}_{\text{TiBA}}]_0/[\text{Zr}]_0$ of 100 to 1500), which is likely due to TiBA acting as a chain transfer agent at higher concentrations.[54]

Figure 5. Slurry-phase ethylene polymerisation activity (black square) and molecular weights (M_w ; blue square) as a function of TiBA loading ($[\text{Al}_{\text{TiBA}}]_0/[\text{Zr}]_0$) using $\text{Me}_2\text{SB}(\text{}^{\text{3-Et}}\text{I}^*)\text{ZrCl}_2$ supported on sMAO ($\mathbf{1}_{\text{sMAO}}$). M_w/M_n in parenthesis. Polymerisation conditions: ethylene (2 bar), pre-catalyst (10 mg), hexane (50 mL), $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0 = 200$, 60 °C and 30 minutes.

The complex loading ($[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0$), inferring to the surface concentration of immobilised metallocene complex, was also optimised for $\mathbf{1}_{\text{sMAO}}$. As the loading decreased (increase in $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0$ ratio from 100 to 300), the ethylene polymerisation activity increased due to

the easier access to the monomer by each metallocene complex (Figure S16 and Table S7). Severn and Chadwick also observed higher polymerisation activities with lower catalyst loadings using Cp_2TiCl_2 and $^{\text{Me}_2}\text{Si}(^t\text{BuN}, \text{Cp}^*)\text{TiCl}_2$ immobilised on $\text{MgCl}_2(\text{Al}_{0.24})\text{Et}_{2.30}(\text{OEt})_{0.70}$; activities of 301 and 692 $\text{kg}_{\text{PE}} \text{mol}_{\text{Ti}}^{-1} \text{h}^{-1} \text{bar}^{-1}$ with catalyst loadings of 100 and 5 $\mu\text{mol g}^{-1}$ respectively (50 °C and 10 bar ethylene).[55] However, when productivity is considered, there is an optimal $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0$ ratio of 200, which maximises the polymerisation capability per gram of the catalyst (0.329 $\text{kg}_{\text{PE}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1} \text{bar}^{-1}$).

Following this, slurry-phase ethylene polymerisation using varied loadings of $\mathbf{1}_{\text{sMAO}}$ (5–20 mg) were carried out with $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0$ of 200. As expected, a catalyst loading of 20 mg resulted in lower activities than catalyst loadings of 10 mg (2809 and 4533 $\text{kg}_{\text{PE}} \text{mol}_{\text{Zr}}^{-1} \text{h}^{-1} \text{bar}^{-1}$, respectively) due to the physical limitations of the reactor. However, a catalyst loading of 5 mg surprisingly also yielded a slightly lower activity (3747 $\text{kg}_{\text{PE}} \text{mol}_{\text{Zr}}^{-1} \text{h}^{-1} \text{bar}^{-1}$). To study the effect of increased reaction volume, polymerisations were conducted in a 500 mL ampoule with a catalyst loading of 10 mg, 250 mL hexane, 2 bar ethylene and $[\text{Al}_{\text{TiBA}}]_0/[\text{Zr}]_0$ of 1000 at 60 °C for 30 minutes. Typically, an increase in activity with an increase in solvent volume is observed due to decreases in gas-liquid mass transfer limitations.[56] However, for $\mathbf{1}_{\text{sMAO}}$, a lower polymerisation activity was observed on the larger scale (activity of 3812 $\text{kg}_{\text{PE}} \text{mol}_{\text{Zr}}^{-1} \text{h}^{-1} \text{bar}^{-1}$). This is in contrast to $\text{sMAO-}^{\text{Me}_2}\text{SB}(\text{Cp}, \text{I}^*)\text{ZrCl}_2$ under similar condition, where an approximate 2-fold increase in activity was observed using 250 mL solvent compared to 50 mL.[30] It is therefore concluded that although the physical saturation of the reactor can lower the activity, for this system there is a minimum concentration of the catalyst loading per reaction volume required in order for ethylene polymerisation to function optimally. The lower polymerisation activity on the larger scale could also be due to the lower scavenger concentration; the larger volume of solvent is likely to contain increased quantities of impurities, which may lead to catalyst deactivation and decreases in polymerisation activity.

Using the optimised conditions, slurry-phase ethylene polymerisation was conducted using four different sMAO supported complexes. A 50:50 mixture of *rac*- and *meso*- $^{\text{Me}_2}\text{SB}(^3\text{-EtI}^*)\text{ZrCl}_2$ ($\mathbf{1}_{\text{sMAO}}$), *rac*- $^{\text{Me}_2}\text{SB}(^3\text{-EtI}^*)\text{ZrCl}_2$ (*rac*- $\mathbf{1}_{\text{sMAO}}$), *rac*- $^{\text{Me}_2}\text{SB}(^3\text{-EtI}^*)\text{ZrBr}_2$ (*rac*- $\mathbf{2}_{\text{sMAO}}$) and a 75:25 mixture of *rac*- and *meso*- $^{\text{Me}_2}\text{SB}(^3\text{-EtI}^*)\text{Zr}(\text{CH}_2\text{Ph})_2$ (**3**) were studied in 150 mL ampoules with 10 mg pre-catalyst, $[\text{Al}_{\text{TiBA}}]_0/[\text{Zr}]_0 = 1000$, 2 bar ethylene, $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0 = 200$ and 50 mL hexane for 30 minutes at 50–90 °C.

1_{sMAO}, ***rac*-1_{sMAO}** and ***rac*-2_{sMAO}** showed very similar polymerisation activities across the temperature range (3507, 3312 and 3971 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ respectively at 60 °C), which is consistent with the trend observed for ^{Me}₂SB(Cp,I*)ZrX₂ (X = Cl and Br) (Figure 6 and Tables S3, S8–S10).[30] **3_{sMAO}** consistently showed higher polymerisation activities (4832 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ at 60 °C), which may be because larger, more flexible benzyl ligands can weaken the interaction between the cationic catalyst and anionic counterion, allowing more space for ethylene monomers to coordinate (Figure 6).[57] **3_{sMAO}** also does not need to be alkylated, which likely leads to faster formation of the active species compared to **1_{sMAO}**, ***rac*-1_{sMAO}** and ***rac*-2_{sMAO}**, therefore leading to increases in the polymerisation activity.[58, 59] For solution-phase polymerisation using metallocene catalysts and MAO activator, it is known that chlorination of MAO can be detrimental for catalyst activation.[60] Similar effects may occur for sMAO and may reduce the polymerisation activities of **1_{sMAO}** and ***rac*-1_{sMAO}**.

An increase in ethylene polymerisation activity on moving from halide to alkyl initiation groups has also been observed for sMAO-*meso*-EBI*ZrX₂ and sMAO-^{Me}₂SB(^tBuN,I*)TiX₂, where X = CH₂Ph displayed optimum activities approximately double X = Cl; activities of 5179 and 2246 kg_{PE} mol⁻¹ h⁻¹ bar⁻¹ for sMAO-*meso*-EBI*ZrX₂,[25] and activities of 5793 and 3602 kg_{PE} mol⁻¹ h⁻¹ bar⁻¹ sMAO-^{Me}₂SB(^tBuN,I*)TiX₂.[31] The maximum activity of **3_{sMAO}** is similar to that of *meso*-EBI*Zr(CH₂Ph)₂; 4832 and 5179 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ respectively at 60 °C ([Zr]₀/[Al_{sMAO}]₀ of 300).[25]

A 50:50 mixture of *rac*- and *meso*-^{Me}₂SB(^{3-Et}I*)ZrCl₂ (**1_{sMAO}**) was found to be slightly more active than the pure *rac*-isomer (***rac*-1_{sMAO}**), implying that both isomers have similar activities. This is in contrast to the EBI*ZrCl₂ system, where *rac*-EBI*ZrCl₂ was found to have higher ethylene polymerisation activities than more sterically crowded *meso*-EBI*ZrCl₂; activities of 5006 and 1331 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ when supported on sMAO with [Al_{sMAO}]₀/[Zr]₀ of 200 and 300 respectively.[25] When directly compared to these catalysts, ***rac*-1_{sMAO}** shows lower polymerisation activities than sMAO-*rac*-EBI*ZrCl₂ (3144 and 5365 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ respectively at 50 °C).[25] However, a 50:50 mixture of the *rac*- and *meso*-isomers (**1_{sMAO}**) shows higher polymerisation activities than sMAO-*meso*-EBI*ZrCl₂ (3425 and 2246 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ respectively at 70 °C),[25] but lower activities than sMAO-*rac*-EBI*ZrCl₂ (3044 and 5365 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ respectively at 50 °C).[25]

Figure 6. Slurry-phase ethylene polymerisation activity as a function of temperature of polymerisation using sMAO supported $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (**1_{sMAO}**; black square), $\text{rac}\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (***rac*-1_{sMAO}**; blue circle), $\text{rac}\text{-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrBr}_2$ (**2_{sMAO}**; red triangle) and $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{Zr}(\text{CH}_2\text{Ph})_2$ (**3_{sMAO}**; green down triangle). Polymerisation conditions: ethylene (2 bar), pre-catalyst (10 mg), hexane (50 mL), $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0 = 200$, TiBA (1000 eq.) and 30 minutes.

1_{sMAO}, ***rac*-1_{sMAO}**, ***rac*-2_{sMAO}** and **3_{sMAO}** all showed maximum activities at 60 °C (3507, 3312, 3971 and 4832 $\text{kgPE molZr}^{-1} \text{h}^{-1} \text{bar}^{-1}$ respectively). The decreases in activity above 60 °C suggests deactivation or decomposition at elevated temperature, or that polymerisation activity is significantly affected by the decrease in the solubility of ethylene in hexane at higher temperatures.[61]

The molecular weights of the polyethylenes were characterised by GPC. All the catalysts showed modest molecular weights, which decreased as polymerisation temperature increased (Figures 7, S22, S25–27 and Tables S3 and S8–S10). ***rac*-2_{sMAO}** produced polyethylenes with lower molecular weights (M_w) than ***rac*-1_{sMAO}**, which may be due to its higher polymerisation activity (M_w of 326 and 477 kg mol^{-1} at 50 °C). The polymers produced using ***rac*-1_{sMAO}**, ***rac*-2_{sMAO}** and **3_{sMAO}** show relatively narrow dispersities with M_w/M_n of 4.1–4.9, 2.7–3.4 and 3.0–3.2 respectively. The polymers produced using **1_{sMAO}** show slightly larger dispersities (M_w/M_n of 4.4–6.1), which could be due to the 50:50 mix of *rac*- and *meso*-isomers (Table S3). The larger than expected dispersity values of these catalysts ($M_w/M_n > 3$) may be due to gas-to-liquid mass transfer limitations, which are likely present due to the high activities of the catalysts and the relatively small scale of the polymerisations (50 mL). Gas-to-liquid mass

transfer limitations are known to affect polymer properties, with higher molecular weight distributions shown to arise in the presence of gas-to-liquid mass transfer limitations for some systems.[62]

Figure 7. Molecular weights (M_w) as a function of temperature of polymerisation using sMAO supported $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (**1_{sMAO}**; black square), $\text{rac-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (***rac*-1_{sMAO}**; blue circle), $\text{rac-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrBr}_2$ (**2_{sMAO}**; red triangle) and $\text{Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{Zr}(\text{CH}_2\text{Ph})_2$ (**3_{sMAO}**; green down triangle). Polymerisation conditions: ethylene (2 bar), pre-catalyst (10 mg), hexane (50 mL), $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0 = 200$, TiBA (1000 eq.) and 30 minutes.

2.3 H₂ as a chain transfer agent

Dihydrogen (H₂) is a common chain transfer agent for α -olefins polymerisation using metallocene catalysts as it can decrease and control polymer molecular weights.[63, 64] $\text{rac-Me}_2\text{SB}(\text{}^3\text{-EtI}^*)\text{ZrCl}_2$ (***rac*-1_{sMAO}**) was tested for its response to H₂ in a high-throughput screening system, which makes use of miniaturised, automated, parallel reaction set-ups to allow for reduced time in the screening of different conditions.[65, 66] Polymerisations were conducted in a parallel pressure reactor (PPR) in 23 mL cells with 5 mL heptane, 10 μmol TiBA scavenger, 0.30–0.40 mg ***rac*-1_{sMAO}** with $[\text{Al}_{\text{sMAO}}]_0/[\text{Zr}]_0$ of 200, 8.3 bar ethylene and 0, 0.8% (0.07 bar) or 1.6% (0.13 bar) H₂ supplied by a mixed H₂/N₂ feed. Reactions were run at 80 °C for 1 hour or until 8.3 bar ethylene uptake was reached. Prior to polymerisation, the Zr content of the catalyst was measured by inductively coupled plasma (ICP) analysis to be 0.61 wt%, which is in good agreement with the expected value of 0.64 wt%.

The in-situ ethylene uptake rates reflect the rate of polymerisation (Figure 8). For all polymerisation runs the initial ethylene uptake rates are very high, which then sharply decline to low but stable rates. The ethylene uptake rates and polymerisation activities were observed to decrease as the amount of H₂ in the system increased; activities of 2100, 1100 and 640 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ with 0, 0.8 and 1.6% H₂. This effect has also been observed for sMAO-Me₂SB(Cp^R,I*)ZrX₂ and sMAO-Me₂SB(^{R'}N,^{3-R}I*)TiX₂ catalysts in the same system,[67, 68] and is likely due to formation of a metal hydride termination product, which requires reactivation by insertion of ethylene. This leads to reductions in polymerisation activity as the rate of insertion of ethylene into Zr–H is much slower than the rate of insertion into Zr–Me.[69-72]

Figure 8. Slurry-phase polymerisation ethylene uptake rate as a function of time of polymerisation using sMAO supported *rac*-Me₂SB(^{3-Et}I*)ZrCl₂ (*rac*-**1**_{sMAO}) with 0 (black), 0.8 (red) and 1.6% H₂ (blue). Polymerisation conditions: [Al_{sMAO}]₀/[Zr]₀ = 200, TiBA (10 μmol), ethylene (8.3 bar), pre-catalyst (0.05 mg), heptane (5 mL) and 80 °C. Reactions quenched at 8.3 bar ethylene uptake or after 1 hour.

As H₂ acts as a chain transfer agent, increases in H₂ partial pressure significantly lowers the molecular weights (*M_w*) of the resulting polyethylenes; 1009, 37 and 20 kg mol⁻¹ with 0, 0.8 and 1.6% H₂ (Figure S28). The decreases in *M_w* are similar to those observed using sMAO-Me₂SB(^{*t*Bu}N,I*)TiCl₂ (*M_w* of 2700 and 41 kg mol⁻¹ with 0 and 1.6% H₂ respectively).[68] *M_w*/*M_n* decreases slightly in the presence of H₂ (6.6, 2.8 and 3.2 with 0, 0.8 and 1.6% H₂ respectively), which suggests that one termination process dominates. As H₂ is a strong chain transfer agent,[73] it is likely that termination primarily occurs by chain transfer

to H₂ and other termination pathways (for example, termination by chain transfer to aluminium) are suppressed.

2.4 Ethylene/1-hexene copolymerisation

rac-Me₂SB(^{3-Et}I*)ZrCl₂ (***rac*-1_{sMAO}**) was also studied for its ethylene/1-hexene copolymerisation performance. High-throughput polymerisations were conducted in a PPR at 80 °C with 8.3 bar ethylene, 5 mL heptane, 10 μmol TiBA scavenger, 0.30–0.40 mg pre-catalyst ([Al_{sMAO}]₀/[Zr]₀ = 200) and 0, 125 or 250 μL 1-hexene for 1 hour or until 5.5 bar ethylene uptake was reached.

The ethylene uptake rate profiles show that the catalyst becomes more active as the amount of co-monomer in the system increases; activities of 2100, 2100 and 4000 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ with 0, 125 and 250 μL 1-hexene respectively (Figure 9). This is due to the comonomer effect, where incorporation of α-olefins decreases polymer crystallinity, which leads to an increase in polymer solubility and more easily accessible active sites.[74-76] It has also been proposed that the catalytically active sites may coordinate one ethylene and one 1-hexene monomer,[77] with the more electron rich α-olefin stabilising the active site and 'triggering' the insertion of ethylene, leading to an enhancement in activity.[78-80] Additionally, ethylene solubility is enhanced by up to 10% on the addition of 1-hexene, which could contribute to increases in polymerisation activity.[81] The rate enhancing effect of 1-hexene has also been observed in the solution phase for ethylene/1-hexene copolymerisation using unmethylated *rac*-EBIZrCl₂, where activity increased by 30% on the introduction of 0.5 mol L⁻¹ 1-hexene.[82]

Figure 9. Slurry-phase polymerisation ethylene uptake rate as a function of time of polymerisation using sMAO supported *rac*-Me₂SB(^{3-Et}I*)ZrCl₂ (***rac*-1_{sMAO}**) with 0 (black), 125 (red) and 250 μL 1-hexene (blue). Polymerisation conditions: [Al_{sMAO}]₀/[Zr]₀ = 200, TiBA

(10 μmol), ethylene (8.3 bar), pre-catalyst (0.05 mg), heptane (5 mL) and 80 °C. Reactions quenched at 5.5 bar ethylene uptake or after 1 hour.

The molecular weights (M_w) of the polyethylenes produced decrease with increasing 1-hexene concentration, likely resulting from chain termination following 1-hexene insertion and chain transfer to 1-hexene;[83, 84] M_w of 1009, 585 and 383 kg mol^{-1} with 0, 125 and 250 μL 1-hexene respectively (Figure S29). M_w/M_n also decreased with increasing 1-hexene concentration, indicating controlled copolymerisation (M_w/M_n of 6.6, 4.8 and 3.3 with 0, 125 and 250 μL 1-hexene respectively). The polyethylenes were determined by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy to have very low 1-hexene incorporation levels; 0.3 and 0.7 mol% with 125 and 250 μL 1-hexene, respectively. This is slightly lower than the incorporation levels recorded for related metallocene catalysts sMAO- $\text{Me}_2\text{SB}(\text{Cp}^R, \text{I}^*)\text{ZrX}_2$ (0.6–0.7 and 1.0–1.1 mol% with 125 and 250 μL 1-hexene respectively in the presence of 0.8% H_2),[67] and may be due to the increased steric bulk of $^{3\text{-Et}}\text{I}^*$ compared to Cp^R .

4. Conclusions

Six new zirconocene complexes of the type $\text{rac-}^{\text{Me}_2}\text{SB}(^{3\text{-Et}}\text{I}^*)\text{ZrX}_2$ and $\text{meso-}^{\text{Me}_2}\text{SB}(^{3\text{-Et}}\text{I}^*)\text{ZrX}_2$ ($\text{X} = \text{Cl, Br and CH}_2\text{Ph}$) have been synthesised and fully characterised by NMR spectroscopy and X-ray crystallography. The molecular structures show differences in sterics of the *rac*- and *meso*-isomers, with torsion angles of ~ 145 and $\sim 0^\circ$ reported respectively.

Slurry-phase ethylene polymerisation studies showed that when immobilised on solid polymethylaluminumoxane, a 50:50 isomeric mixture of $\text{rac-}^{\text{Me}_2}\text{SB}(^{3\text{-Et}}\text{I}^*)\text{ZrCl}_2$ and $\text{meso-}^{\text{Me}_2}\text{SB}(^{3\text{-Et}}\text{I}^*)\text{ZrCl}_2$ displayed higher polymerisation activities than when immobilised on MAO modified silica or MAO modified LDH, and produced HDPE (confirmed by PXRD) with industrially desirable, ‘popcorn’ morphologies. Polymerisation conditions were optimised for this system and the slurry-phase ethylene polymerisation activities of sMAO supported $\text{rac-}^{\text{Me}_2}\text{SB}(^{3\text{-Et}}\text{I}^*)\text{ZrCl}_2$ (***rac-1***_{sMAO}), $\text{rac-}^{\text{Me}_2}\text{SB}(^{3\text{-Et}}\text{I}^*)\text{ZrBr}_2$ (***rac-2***_{sMAO}) and a 75:25 mixture of $\text{rac-}^{\text{Me}_2}\text{SB}(^{3\text{-Et}}\text{I}^*)\text{Zr}(\text{CH}_2\text{Ph})_2$ and $\text{meso-}^{\text{Me}_2}\text{SB}(^{3\text{-Et}}\text{I}^*)\text{Zr}(\text{CH}_2\text{Ph})_2$ (***3***_{sMAO}) evaluated. ***3***_{sMAO} was found to show the highest polymerisation activities (4832 $\text{kg}_{\text{PE}} \text{mol}_{\text{Zr}}^{-1} \text{h}^{-1} \text{bar}^{-1}$ at 60 °C), with modest molecular weights (336 kg mol^{-1} at 60 °C) and molecular weight distributions with $M_w/M_n < 3.2$.

In a high-throughput screening system, ***rac-1***_{sMAO} was found to be responsive to H_2 , maintaining reasonable activities (640 $\text{kg}_{\text{PE}} \text{mol}_{\text{Zr}}^{-1} \text{h}^{-1} \text{bar}^{-1}$ with 1.6% H_2) and producing

polymers with low molecular weights (M_w of 41 kg mol⁻¹ with 1.6%). **rac-1_sMAO** was also shown to experience increases in polymerisation activity for ethylene/1-hexene copolymerisation compared to ethylene homopolymerisation (4000 kg_{PE} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ with 250 μL 1-hexene), although displayed low 1-hexene incorporation levels (maximum incorporation of 0.7 mol%).

5. Experimental

Synthesis of Me₂SB(^{3-Et}I)H₂*

2.0 equivalents ^{3-Et}Ind[#]Li (2.00 g, 9.08 mmol) were dissolved in THF (100 mL), forming a dark brown solution. 1.0 equivalent Me₂SiCl₂ (0.586 g, 4.54 mmol) diluted in THF (50 mL) was added dropwise to the ^{3-Et}Ind[#]Li solution at 0 °C. The reaction was allowed to warm up to room temperature and stirred for 16 hours. The pale yellow solution was dried *in vacuo*, extracted with DCM (200 mL) and the resulting pale yellow filtrate dried *in vacuo* to yield a 50:50 mixture of *rac*-Me₂SB(^{3-Et}I*)H₂ and *meso*-Me₂SB(^{3-Et}I*)H₂ as an off-white solid in 53% yield (1.16 g, 2.39 mmol). Colourless crystals of *rac*-Me₂SB(^{3-Et}I*)H₂ suitable for a single crystal X-ray diffraction study were grown from Et₂O at -30 °C. CHN analysis (%): calculated C 84.23, H 9.98; observed C 84.10, H 10.15. MS (EI): expected *m/z* 484.35; observed 484.35. *rac*-Me₂SB(^{3-Et}I*)H₂: ¹H NMR (chloroform-*d*₁, 400 MHz, 298 K): δ (ppm) 3.74 (Ind-**H**, 2H, s), 2.74 (Ind-**CH**₂-CH₃, 4H, q, ³*J*_{HH} = 7.5 Hz), 2.46 (Ind-**CH**₃, 6H, s), 2.27 (Ind-**CH**₃, 6H, s), 2.20 (Ind-**CH**₃, 6H, s), 2.16 (Ind-**CH**₃, 12H, s), 1.17 (Ind-CH₂-**CH**₃, 6H, t, ³*J*_{HH} = 7.5 Hz), -0.63 (Si-**CH**₃, 6H, s). ¹³C{¹H} NMR (chloroform-*d*₁, 101 MHz, 298 K): δ (ppm) 142.6 (**Ind**), 140.6 (**Ind**), 139.6 (**Ind**), 139.4 (**Ind**), 132.4 (**Ind**), 129.8 (**Ind**), 127.2 (**Ind**), 125.8 (**Ind**), 47.2 (**Ind**-H), 21.0 (Ind-CH₂-CH₃), 19.2 (Ind-CH₃), 16.4 (Ind-CH₃), 16.4 (Ind-CH₃), 16.0 (Ind-CH₃), 15.7 (Ind-CH₃), 14.8 (Ind-CH₂-CH₃), -4.0 (Si-CH₃). *meso*-Me₂SB(^{3-Et}I*)H₂: ¹H NMR (chloroform-*d*₁, 400 MHz, 298 K): δ (ppm) 3.60 (Ind-**H**, 2H, s), 2.67 (Ind-**CH**₂-CH₃, 4H, q, ³*J*_{HH} = 7.5 Hz), 2.46 (Ind-**CH**₃, 6H, s), 2.21 (Ind-**CH**₃, 6H, s), 2.17 (Ind-**CH**₃, 12H, s), 1.98 (Ind-**CH**₃, 6H, s), 1.12 (Ind-CH₂-**CH**₃, 6H, t, ³*J*_{HH} = 7.5 Hz), -0.43 (Si-**CH**₃, 3H, s), -0.61 (Si-**CH**₃, 3H, s). ¹³C{¹H} NMR (chloroform-*d*₁, 101 MHz, 298 K): δ (ppm) 143.0 (**Ind**), 140.5 (**Ind**), 140.1 (**Ind**), 139.0 (**Ind**), 132.3 (**Ind**), 129.8 (**Ind**), 127.0 (**Ind**), 125.8 (**Ind**), 47.1 (**Ind**-H), 20.9 (Ind-CH₂-CH₃), 19.1 (Ind-CH₃), 16.4 (Ind-CH₃), 16.4 (Ind-CH₃), 15.9 (Ind-CH₃), 15.0 (Ind-CH₃), 14.8 (Ind-CH₂-CH₃), -2.1 (Si-CH₃), -2.6 (Si-CH₃). CCDC number: 2024131.

Synthesis of $^{Me_2SB(3-EtI^*)ZrCl_2}$ (**1**)

1.0 equivalent $^{Me_2SB(3-EtI^*)H_2}$ (2.64 g, 5.45 mmol) was dissolved in THF (100 mL) to form a pale yellow solution. 2.2 equivalents nBuLi (2.5 M in hexanes, 4.79 mL, 12.0 mmol) were added dropwise at 0 °C and the reaction stirred for 30 minutes. The resulting dark brown solution was dried *in vacuo* to form $^{Me_2SB(3-EtI^*)Li_2}$ as a yellow solid, which was then washed with Et_2O (50 mL) and pentane (2×50 mL). 1.0 equivalent $ZrCl_4$ (1.27 g, 5.45 mmol) was added to $^{Me_2SB(3-EtI^*)Li_2}$ and stirred in benzene (100 mL) for 16 hours at room temperature, resulting in a red solution. The reaction mixture was allowed to settle before being filtered. The red filtrate was dried *in vacuo* to afford an orange solid which was washed with Et_2O (50 mL) to yield a 50:50 mixture of $^{rac-Me_2SB(3-EtI^*)ZrCl_2}$ and $^{meso-Me_2SB(3-EtI^*)ZrCl_2}$ (**1**) as an orange solid in 24% yield (0.850 g, 1.32 mmol). Orange crystals of $^{rac-Me_2SB(3-EtI^*)ZrCl_2}$ (**rac-1**) and $^{meso-Me_2SB(3-EtI^*)ZrCl_2}$ (**meso-1**) suitable for single crystal X-ray diffraction studies were grown from the slow cooling of a hot pentane solution of 50:50 $^{rac-Me_2SB(3-EtI^*)ZrCl_2}$ and $^{meso-Me_2SB(3-EtI^*)ZrCl_2}$. CHN analysis (%): calculated C 63.32, H 7.19; observed C 63.16, H 7.29. MS (EI): expected m/z 642.18; observed 642.18. $^{rac-Me_2SB(3-EtI^*)ZrCl_2}$: 1H NMR (benzene- d_6 , 400 MHz, 298 K) δ (ppm): 3.30 (Ind- CH_2-CH_3 , 2H, dq, $^2J_{HH} = 15.2$ Hz, $^3J_{HH} = 7.6$ Hz), 2.71 (Ind- CH_2-CH_3 , 2H, dq, $^2J_{HH} = 15.2$ Hz, $^3J_{HH} = 7.6$ Hz), 2.54 (Ind- CH_3 , 6H, s), 2.35 (Ind- CH_3 , 6H, s), 2.24 (Ind- CH_3 , 6H, s), 2.04 (Ind- CH_3 , 6H, s), 1.92 (Ind- CH_3 , 6H, s), 1.14 (Si- CH_3 , 6H, s), 0.86 (Ind- CH_2-CH_3 , 6H, t, $^3J_{HH} = 7.6$ Hz). $^{13}C\{^1H\}$ NMR (benzene- d_6 , 101 MHz, 298 K) δ (ppm): 135.2 (**Ind**), 134.6 (**Ind**), 134.3 (**Ind**), 131.0 (**Ind**), 129.9 (**Ind**), 128.7 (**Ind**), 128.2 (**Ind**), 127.9 (**Ind**), 79.2 (**Ind-Si**), 23.0 (Ind- CH_2-CH_3), 22.4 (Ind- CH_3), 17.5 (Ind- CH_3), 17.0 (Ind- CH_3), 16.7 (Ind- CH_3), 15.3 (Ind- CH_3), 15.0 (Ind- CH_2-CH_3), 10.8 (Si- CH_3). $^{meso-Me_2SB(3-EtI^*)ZrCl_2}$: 1H NMR (chloroform- d_1 , 400 MHz, 298 K) δ (ppm): 3.15 (Ind- CH_2-CH_3 , 2H, dq, $^2J_{HH} = 15.2$ Hz, $^3J_{HH} = 7.6$ Hz), 2.67 (Ind- CH_2-CH_3 , 2H, dq, $^2J_{HH} = 15.2$ Hz, $^3J_{HH} = 7.6$ Hz), 2.48 (Ind- CH_3 , 6H, s), 2.42 (Ind- CH_3 , 6H, s), 2.19 (Ind- CH_3 , 6H, s), 2.16 (Ind- CH_3 , 6H, s), 2.06 (Ind- CH_3 , 6H, s), 1.44 (Si- CH_3 , 3H, s), 1.31 (Si- CH_3 , 3H, s), 1.02 (Ind- CH_2-CH_3 , 6H, t, $^3J_{HH} = 7.6$ Hz). $^{13}C\{^1H\}$ NMR (benzene- d_6 , 101 MHz, 298 K) δ (ppm): 134.9 (**Ind**), 134.5 (**Ind**), 134.2 (**Ind**), 134.1 (**Ind**), 133.5 (**Ind**), 130.6 (**Ind**), 129.4 (**Ind**), 128.8 (**Ind**), 78.2 (**Ind-Si**), 22.8 (Ind- CH_3), 22.7 (Ind- CH_2-CH_3), 17.3 (Ind- CH_3), 16.6 (Ind- CH_3), 16.6 (Ind- CH_3), 15.6 (Ind- CH_3), 14.2 (Ind- CH_2-CH_3), 14.0 (Si- CH_3), 9.6 (Si- CH_3). CCDC number: 2024132.

Synthesis of $^{rac-Me_2SB(3-EtI^*)ZrBr_2}$ (**rac-2**)

1.0 equivalent $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{H}_2$ (3.30 g, 6.81 mmol) was dissolved in THF (100 mL) to form a pale yellow solution. 2.2 equivalents $n\text{BuLi}$ (2.5 M in hexanes, 5.99 mL, 15.0 mmol) were added dropwise to the solution at 0 °C and the reaction stirred for 30 minutes at 0 °C. The resulting dark brown solution was dried *in vacuo* to form a yellow solid, which was washed with Et_2O (50 mL) and pentane (2×50 mL). 1.0 equivalent ZrBr_4 (2.80 g, 6.81 mmol) was mixed with $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{Li}_2$ (yellow solid) and stirred in benzene (100 mL) for 16 hours at room temperature, resulting in a red solution. The reaction mixture was allowed to settle, filtered and dried *in vacuo* to afford a red solid comprising of a 50:50 mixture of *rac*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{ZrBr}_2$, *meso*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{ZrBr}_2$ and impurities. Recrystallisation of the isomeric mixture in Et_2O at -30 °C yielded *rac*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{ZrBr}_2$ (**rac-2**) as orange crystals in 1% yield (68.6 mg, 0.0935 mmol). Orange crystals of *rac*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{ZrBr}_2$ suitable for single crystal X-ray diffraction were grown by slow evaporation of a Et_2O solution of the isomer. Orange crystals of *meso*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{ZrBr}_2$ suitable for single crystal X-ray diffraction were grown by the slow evaporation of a chloroform- d_1 solution of the isomeric mixture. *rac*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{ZrBr}_2$: ^1H NMR (chloroform- d_1 , 400 MHz, 298 K) δ (ppm): 3.23 (Ind- $\text{CH}_2\text{-CH}_3$, 2H, dq, $^2J_{\text{HH}} = 15.2$ Hz, $^3J_{\text{HH}} = 7.6$ Hz), 2.65 (Ind- $\text{CH}_2\text{-CH}_3$, 2H, dq, $^2J_{\text{HH}} = 15.2$ Hz, $^3J_{\text{HH}} = 7.6$ Hz), 2.46 (Ind- CH_3 , 6H, s), 2.45 (Ind- CH_3 , 6H, s), 2.35 (Ind- CH_3 , 6H, s), 2.15 (Ind- CH_3 , 6H, s), 1.86 (Ind- CH_3 , 6H, s), 1.35 (Si- CH_3 , 6H, s), 0.91 (Ind- $\text{CH}_2\text{-CH}_3$, 6H, t, $^3J_{\text{HH}} = 7.6$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (chloroform- d_1 , 101 MHz, 298 K): δ (ppm) 135.7 (**Ind**), 135.6 (**Ind**), 134.8 (**Ind**), 134.2 (**Ind**), 131.3 (**Ind**), 130.2 (**Ind**), 128.6 (**Ind**), 128.4 (**Ind**), 77.4 (**Ind**-Si), 24.0 (Ind- $\text{CH}_2\text{-CH}_3$), 22.3 (Ind- CH_3), 17.6 (Ind- CH_3), 17.0 (Ind- CH_3), 16.7 (Ind- CH_3), 15.7 (Ind- CH_3), 15.3 (Ind- $\text{CH}_2\text{-CH}_3$), 11.1 (Si- CH_3). CCDC number: 2024133.

Synthesis of $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{Zr}(\text{CH}_2\text{Ph})_2$ (**3**)

1.0 equivalent $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{ZrCl}_2$ (49.5 mg, 0.0768 mmol) and 2.0 equivalents KCH_2Ph (20.0 mg, 0.154 mmol) were mixed in benzene (1 mL) and stirred for 16 hours at room temperature. The reaction mixture was allowed to settle before being filtered. The orange filtrate was dried *in vacuo* to afford a 75:25 mixture of *rac*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{Zr}(\text{CH}_2\text{Ph})_2$ and *meso*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{Zr}(\text{CH}_2\text{Ph})_2$ (**3**) as an orange-yellow solid in 83% yield (48.4 mg, 0.0640 mmol). Orange crystals of *rac*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{Zr}(\text{CH}_2\text{Ph})_2$ (**rac-3**) suitable for a single crystal X-ray diffraction study were grown from a pentane solution of the isomeric mixture at room temperature. *rac*- $\text{Me}_2\text{SB}^{(3\text{-EtI}^*)}\text{Zr}(\text{CH}_2\text{Ph})_2$: ^1H NMR (chloroform- d_1 , 400 MHz, 298 K) δ (ppm): 7.00 (*m*-Ph-**H**, 4H, dd, $^3J_{\text{HH}} = 7.3$, 7.4 Hz), 6.73 (*p*-Ph-**H**, 2H, t, $^3J_{\text{HH}} = 7.3$ Hz), 6.46 (*o*-Ph-**H**, 4H, d, $^3J_{\text{HH}} = 7.4$ Hz), 2.49 (Ind- CH_3 , 6H, s), 2.31 (Ind- CH_3 , 6H, s), 2.30 (Ind- CH_3 ,

6H, s), 2.26 (Ind-CH₃, 6H, s), 1.92 (Ind-CH₂-CH₃, 4H, q, ³J_{HH} = 7.4 Hz), 1.84 (Ind-CH₃, 6H, s), 1.22 (Si-CH₃, 6H, s), 0.65 (Zr-CH₂-Ph, 2H, d, ²J_{HH} = 11.5 Hz), 0.62 (Ind-CH₂-CH₃, 6H, t, ³J_{HH} = 7.4 Hz), -0.29 (Zr-CH₂-Ph, 2H, d, ²J_{HH} = 11.5 Hz). ¹³C{¹H} NMR (chloroform-*d*₁, 101 MHz, 298 K) δ (ppm): 152.4 (Zr-CH₂-Ph), 134.01 (Ind), 133.7 (Ind), 133.2 (Ind), 129.6 (Ind), 128.9 (Ind), 128.8 (Ind), 128.7 (Ind), 128.5 (Ind), 127.5 (*m*-Ph), 126.5 (*o*-Ph), 121.0 (*p*-Ph), 76.4 (Ind-Si), 69.9 (Zr-CH₂-Ph), 22.2 (Ind-CH₃), 19.9 (Ind-CH₂-CH₃), 17.6 (Ind-CH₃), 16.8 (Ind-CH₃), 16.7 (Ind-CH₃), 15.8 (Ind-CH₂-CH₃), 14.5 (Ind-CH₃), 11.4 (Si-CH₃). *meso*-Me₂SB(³-EtI*)Zr(CH₂Ph)₂: ¹H NMR (chloroform-*d*₁, 400 MHz, 298 K) δ (ppm): 6.95 (*m*-Ph-H, 2H, dd, ³J_{HH} = 7.3, 7.6 Hz), 6.86 (*m*-Ph-H, 2H, dd, ³J_{HH} = 7.3, 7.6 Hz), 6.75 (*p*-Ph-H, 1H, t, ³J_{HH} = 7.3 Hz), 6.63 (*p*-Ph-H, 1H, t, ³J_{HH} = 7.3 Hz), 6.25 (*o*-Ph-H, 2H, d, ³J_{HH} = 7.6 Hz), 6.05 (*o*-Ph-H, 2H, d, ³J_{HH} = 7.6 Hz), 2.49 (Ind-CH₂-CH₃, 2H, m, ³J_{HH} = 7.4 Hz), 2.41 (Ind-CH₃, 6H, s), 2.38 (Ind-CH₃, 6H, s), 2.32 (Ind-CH₂-CH₃, 2H, m, ³J_{HH} = 7.4 Hz), 2.22 (Ind-CH₃, 6H, s), 2.12 (Ind-CH₃, 6H, s), 2.09 (Ind-CH₃, 6H, s), 1.79 (Zr-CH₂-Ph, 2H, s), 1.27 (Si-CH₃, 3H, s), 1.17 (Si-CH₃, 3H, s), 0.91 (Ind-CH₂-CH₃, 6H, t, ³J_{HH} = 7.4 Hz), -1.03 (Zr-CH₂-Ph, 2H, s). ¹³C{¹H} NMR (chloroform-*d*₁, 101 MHz, 298 K) δ (ppm): 152.0 (Zr-CH₂-Ph), 150.0 (Zr-CH₂-Ph), 133.7 (Ind), 133.4 (Ind), 132.7 (Ind), 131.2 (Ind), 130.7 (Ind), 129.9 (Ind), 129.2 (Ind), 128.8 (Ind), 127.4 (*o*-Ph), 127.2 (*m*-Ph), 126.9 (*m*-Ph), 126.7 (*o*-Ph), 121.2 (*p*-Ph), 120.7 (*p*-Ph), 76.6 (Ind-Si), 67.4 (Zr-CH₂-Ph), 65.5 (Zr-CH₂-Ph), 23.1 (Ind-CH₃), 21.6 (Ind-CH₂-CH₃), 17.4 (Ind-CH₃), 17.3 (Ind-CH₃), 16.8 (Ind-CH₃), 15.2 (Ind-CH₃), 14.8 (Si-CH₃), 14.6 (Ind-CH₂-CH₃), 10.4 (Si-CH₃). CCDC number: 2024135.

Synthesis of methylaluminoxane modified silica (SSMAO)

2.0 equivalents silica (SiO₂, 2.00 g, 33.3 mmol) were dispersed in toluene (25 mL) to form a colourless slurry. 1.0 equivalent MAO (0.966 g, 16.6 mmol) was dissolved in toluene (25 mL) to form a colourless solution which was then quickly added to the silica slurry at room temperature. The reaction mixture was heated to 80 °C for 2 hours with occasional swirling. The resulting colourless slurry was cooled to room temperature and dried *in vacuo* to afford the product as a white solid in 88% yield (2.62 g, 14.7 mmol).

Synthesis of methylaluminoxane modified layered double hydroxide (LDHMAO)

2.0 equivalents aqueous miscible organic layered double hydroxide (AMO-LDH) (Mg_{0.75}Al_{0.25}(OH)₂(CO₃)_{0.125}, 2.00 g, 30.1 mmol) were dispersed in toluene (25 mL) to form a colourless slurry. 1.0 equivalent MAO (0.873 g, 15.0 mmol) was dissolved in toluene (25 mL) to form a colourless solution which was then quickly added to the AMO-LDH slurry at room

temperature. The reaction mixture was heated to 80 °C for 2 hours with occasional swirling. The resulting colourless slurry was cooled to room temperature and dried *in vacuo* to afford the product as a white solid in 92% yield (2.64 g, 13.8 mmol).

Synthesis of SSMAO-^{Me}₂SB(^{3-Et}I)ZrCl₂ (**I**_{SSMAO})*

200 equivalents SSMAO (0.300 g, 1.68 mmol) were dispersed in toluene (25 mL) to form a colourless slurry. 1.0 equivalent of a 50:50 mixture of *rac*-^{Me}₂SB(^{3-Et}I*)ZrCl₂ and *meso*-^{Me}₂SB(^{3-Et}I*)ZrCl₂ (5.4 mg, 0.00842 mmol) was dissolved in toluene (25 mL) to form an orange solution which was then quickly added to the SSMAO slurry at room temperature. The reaction mixture was heated to 60 °C for 2 hours with occasional swirling. The orange solid was allowed to settle from the clear, colourless solution which was decanted, and the solid was dried *in vacuo* to afford the product as a pale orange solid in 90% yield (0.276 g).

Synthesis of LDHMAO-^{Me}₂SB(^{3-Et}I)ZrCl₂ (**I**_{LDHMAO})*

200 equivalents LDHMAO (0.300 g, 1.57 mmol) was dispersed in toluene (25 mL) to form a colourless slurry. 1.0 equivalent of a 50:50 mixture of *rac*-^{Me}₂SB(^{3-Et}I*)ZrCl₂ and *meso*-^{Me}₂SB(^{3-Et}I*)ZrCl₂ (5.1 mg, 0.00785 mmol) was dissolved in toluene (25 mL) to form an orange solution which was then quickly added to the LDHMAO at room temperature. The reaction mixture was heated to 60 °C for 2 hours with occasional swirling. The yellow solid was allowed to settle from the clear, colourless solution which was decanted, and the solid was dried *in vacuo* to afford the product as an off-white solid in 94% yield (0.288 g).

*Synthesis of solid polymethylaluminoxane (sMAO) solid catalysts (**I**_{sMAO}, **rac-I**_{sMAO}, **rac-2**_{sMAO} and **3**_{sMAO})*

200 equivalents sMAO (39.7 or 41.1% wt_{Al}; 0.300 g, 4.41 or 4.57 mmol_{Al}) were dispersed in toluene (25 mL) to form a colourless slurry. 1.0 equivalent metallocene complex (0.0221 or 0.0229 mmol) was dissolved in toluene (25 mL) to form a coloured solution which was then quickly added to the sMAO at room temperature. An initial aluminium to zirconium ratio ([Al]_{sMAO}/[Zr]₀) of 200 was used unless stated otherwise. The reaction mixture was heated to 60 °C for 2 hours with occasional swirling. The coloured solid was allowed to settle from the clear, colourless solution, which was decanted and the solid dried *in vacuo* to give the product as a faintly coloured powder in 73–92% yield. sMAO-^{Me}₂SB(^{3-Et}I*)ZrCl₂ (**I**_{sMAO}): ¹³C CP/MAS SSNMR: δ (ppm) –8 (CH₃ in sMAO), 15 (Ind-**R**), 21 (Ind-**R**), 128 (**Ind**), 131 (**Ind**), 136 (**Ind**). ²⁷Al Hahn-echo MAS SSNMR: δ (ppm) –92 (**Al** in sMAO). ²⁹Si CP/MAS SSNMR: δ (ppm)

–13 (**Si-CH₃**). sMAO-^{Me₂SB}(^{3-Et}I*)Zr(CH₂Ph)₂ (**3_{sMAO}**): ¹³C CP/MAS SSNMR: δ (ppm) –8 (CH₃ in sMAO), 16 (**Ind-R**), 21 (**Ind-R**), 128 (**Ind**), 131 (**Ind**), 136 (**Ind**). ²⁷Al Hahn-echo MAS SSNMR: δ (ppm) –91 (**Al** in sMAO). ²⁹Si CP/MAS SSNMR: δ (ppm) –15 (**Si-CH₃**), –13 (**Si-CH₃**).

50 mL ethylene polymerisation

For homogeneous ethylene polymerisation, a metallocene complex (0.5 mg, 1.0 equivalent), MAO (500 equivalents) and hexane (50 mL) were added to a 150 mL Rotaflo ampoule containing a stirrer bar. For heterogeneous ethylene polymerisation, a supported metallocene catalyst (10 mg, 1.0 eq_{complex}), TiBA (1000 eq.) and hexane (50 mL) were added. The ampoule was sealed and degassed before being heated to the desired temperature with a stirring speed of 1000 rpm. The ampoule was then opened to ethylene gas (2 bar). On completion, the ampoule was closed to ethylene and degassed. The resulting polyethylene was filtered on a glass sintered frit, washed with pentane (2 × 25 mL) and dried. All polymerisations were carried out, at least, in duplicate and run for 30 minutes, unless stated otherwise. The activities were reported as an average with ± 1 ESD error.

250 mL slurry-phase ethylene polymerisation

A supported metallocene catalyst (10 mg, 1.0 eq_{complex}), TiBA (1000 eq.) and hexane (250 mL) were added to a 500 mL Rotaflo ampoule containing a stirrer bar. The ampoule was sealed and degassed before being heated to the desired temperature with a stirring speed of 1000 rpm. The ampoule was then opened to ethylene gas (2 bar). On completion, the ampoule was closed to ethylene and degassed. The resulting polyethylene was filtered on a glass sintered frit, washed with pentane (2 × 25 mL) and dried. All polymerisations were carried out, at least, in duplicate and run for 30 minutes. Activities were reported as an average with ± 1 ESD error.

High-throughput ethylene polymerisation

Polymerisation experiments were conducted by Dr Alessio Mingione under the supervision of Prof. Vincenzo Busico at HTExplore (University of Naples, Italy) in a Freeslate Parallel Pressure Reactor (PPR) platform consisting of 48 reaction cells contained within a triple MBraun LabMaster Glovebox. The cells (geometric volume ~23 mL, working volume 5 mL) were individually controlled with monitoring of temperature and pressure. Slurry-phase polymerisations were run in semi-continuous mode. Two Vortex stir plates fitted with 6 × 8 racks held the catalyst system components (pre-catalyst and scavenger). The injection system

consisted of a dual-arm robot with specialised needles and injectors. Liquid solvents, diluents, and monomers were fed through syringe pumps, with gaseous monomers and diluents fed through direct lines with solenoid valves to individual cells.[85] Heptane solvent (5 mL) and TiBA scavenger (10 μ mmol) were added to the PPR via robotic syringes, which were then heated to 80 °C and pressurized to 8.3 bar with ethylene. When required, H₂ was added to the reaction vessel via a 0.8 or 1.6% mixed H₂/N₂ feed. Pre-catalyst (0.30–0.40 mg in heptane slurry) and 1-hexene (when required) were injected with robotic syringes and chased by a certain amount of heptane solvent. The reactions were run for 1 hour or until a certain ethylene uptake was reached (8.3 bar for ethylene homopolymerisation and 5.5 bar for ethylene/1-hexene copolymerisation), following which the reaction was quenched with an excess of dry air. The polymer samples were transferred to a Genevac EZ-Plus centrifugal evaporator to remove volatiles and then dried under vacuum overnight. Inductively coupled plasma (ICP) analysis, ¹³C{¹H} NMR spectroscopy and gel permeation chromatography (GPC) were carried out at HTExplore, Italy.

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