

Popcorn-shaped polyethylene synthesised using highly active supported permethylindenyl metallocene catalyst systems

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Unsymmetrical permethylindenyl bent metallocene complexes have been synthesised and reacted with inorganic solid supports to afford catalysts for the slurry phase polymerisation of ethylene. Those supported on solid polymethylaluminoxane were both highly active catalysts and afforded polymer with a desirable, low aggregation, "popcorn" morphology.

Well-defined group 4 metallocenes have offered an important alternative technology to Ziegler-Natta and Philips catalysts.^{1,2} In contrast to these heterogeneous systems, metallocene catalysts produce polyethylene with narrow molecular weight distributions and the single-site nature of their active sites enables the polymer properties to be fine-tuned.³

Studies of bridged metallocene compounds have shown that slight variations of the ring substituents and bridging groups can dramatically influence the ethylene polymerisation activities.^{4,5} Electronic structure and steric encumbrance of the catalyst active site, influenced by ligand design, have profound effects on the microstructure of the polyethylene. We recently reported the synthesis of symmetrical permethylindenyl group 4 complexes.^{6,7}

Surface organometallic chemistry lies at the interface between traditional homogeneous and heterogeneous chemistry and preparation of 'single-site' catalysts on well-defined surfaces can offer many advantages over homogeneous analogues.^{8a} Support materials provide a convenient way to serve as a template for the growing polymer particle, with uniform particle morphology being crucial in an applied setting.^{8b,8c} Many materials have been tested as polymerisation supports including inorganic solids such as clays,⁹ ZrO₂,¹⁰ SiO₂,¹¹ and MgCl₂.² Silica (SiO₂) and modified silica materials are the most commonly used supports for immobilising metallocene complexes.¹¹⁻¹⁵

Recently, we developed a new generation of inorganic support for the slurry phase polymerisation of ethylene. Layered double hydroxides (LDHs) using an aqueous miscible solvent treatment (AMOST) method led to new AMO-LDH materials.¹⁸ An EXAFS study showed that the LDHs are well-ordered supports for slurry phase polymerisation of ethylene (Chart 1, A).¹⁹ We also demonstrated the study and uses of solid polymethylaluminoxane (solid MAO, sMAO) for the synthesis of polyethylene with very high activities (Chart 1, B).²⁰

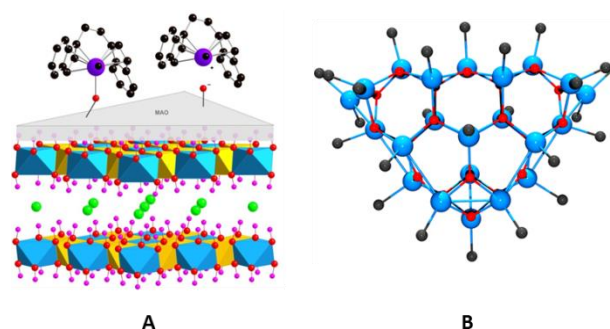


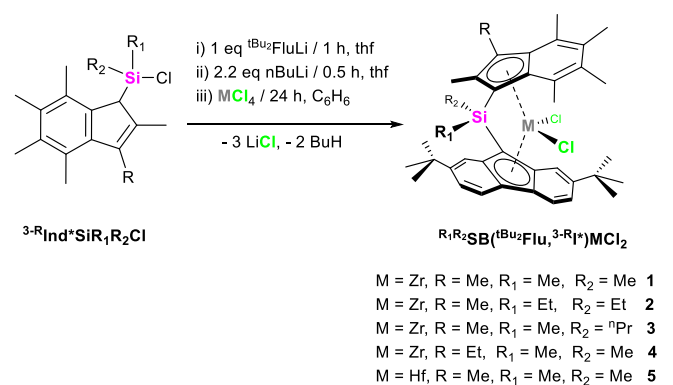
Chart 1. Illustration of layered double hydroxide dispersed in acetone and reacted with methylaluminoxane and *rac*-(EBI)ZrCl₂: AMO-LDHMAO-(EBI)ZrCl₂ (A, ref 19a) and solid polymethylaluminoxane cage structure, sMAO (B, ref 20a).

Herein, we report the facile and modular synthesis of C₁ symmetric permethylindenyl complexes and subsequent reactions with various inorganic supports (silica, LDH or sMAO) to afford solid catalysts for olefin polymerisation which can both demonstrate extremely high activities and result in desirable polymer morphology.

Peralkylindenyl dialkylchlorosilanes, ^{3-R}Ind*SiR₁R₂Cl (^{3-R}Ind*, ^{3-R}I*, C₉H₆ where R₁ or R₂ = CH₃, C₂H₅ and C₃H₇), were synthesised following modified literature procedures.²¹ The complexes were synthesised in a one pot synthesis over three steps (Equation 1). ^{3-R}Ind*SiR₁R₂Cl was reacted with *bis*(2,9-*t*Bu-fluorenyl)lithium (*t*Bu₂FluLi) in tetrahydrofuran, followed by dropwise addition of *n*-butyllithium and finally zirconium tetrachloride was added in benzene to afford the unsymmetrical peralkylindenyl

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metallocenes $R_1R_2SB(tBu_2Flu,^{3-R_1*})MCl_2$ ($R_1, R_2 = CH_3, C_2H_5, C_3H_7$ and $M = Zr$ or Hf ; **1–5**) as bright orange, microcrystalline solids.



Equation 1. Synthesis of unsymmetrical I^* group 4 complexes $R_1R_2SB(tBu_2Flu,^{3-R_1*})MCl_2$ where $M = Zr$ or Hf and R, R_1 and $R_2 = CH_3$ (Me), C_2H_5 (Et) and C_3H_7 (iPr).

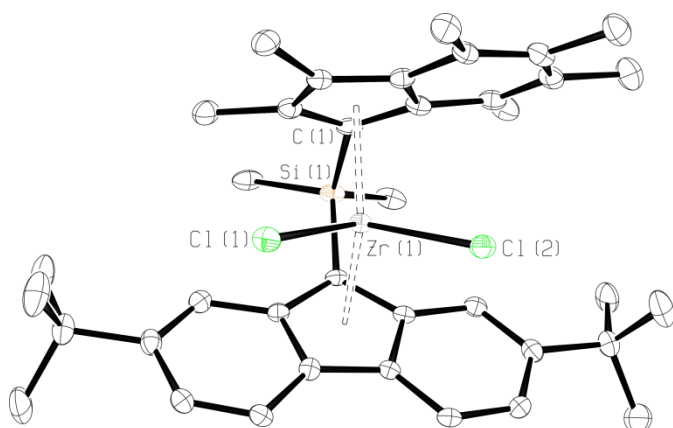


Fig. 1 Molecular structure of $Me_2SB(tBu_2Flu, I^*)ZrCl_2$ (**1**). Ellipsoids drawn at 30% and hydrogen are omitted for clarity.

For all complexes, single crystals suitable for an X-ray crystallographic study were grown from benzene or pentane solutions. Molecular structures of pro-ligand $Me_2SB(tBu_2Flu, I^*)H_2$ and group 4 complexes $R_1R_2SB(tBu_2Flu,^{3-R_1*})MCl_2$ (**1–5**) are shown in Fig. 1 and Fig. S1–S6. Selected bond lengths and angles are given in Table S1 and crystallographic data in Tables S2 and S3. All the five complexes crystallised in the space group $P-1$ and are C_1 symmetric with a pseudo-tetrahedral geometry about the metal centres. The Zr-Cl bond lengths for **1** (2.4189(9) and 2.4120(9) Å), **2** (2.4193(5) and 2.4148(5) Å), **3** (2.4243(10) and 2.4164(11) Å) and **4** (2.4186(5) and 4.4041(5) Å), and Hf-Cl for **5** (2.3906(7) and 2.3862(7) Å) are within the literature ranges.^{7,22,23} All the metal to centroid distances $M-C_{pCent}$ and α angles (see ESI) are in a similar range for all complexes (with 2.205–2.235 Å for $M(1)-C_{pCent}(Ind)$ and 2.293–2.316 Å for $M(1)-C_{pCent}(Flu)$) and (with α of 62.00–63.63°). Geometry optimisation calculations were performed at BP86^{24,25} level of DFT for $Me_2SB(tBu_2Flu, I^*)ZrCl_2$ (**1**) and $Et_2SB(tBu_2Flu, I^*)ZrCl_2$ (**2**) and were found to reproduce the metrical data established experimentally (Fig. S7 and S8). The calculations indicated that the HOMO primarily consisted of $M-I^*$ π -bonding interactions. The 1H and $^{13}C\{^1H\}$ NMR spectra of $R_1R_2SB(tBu_2Flu,^{3-R_1*})MCl_2$ are

shown in Fig S9–S18. For all complexes, the 1H NMR spectra show six singlets corresponding to the indenyl ring methyl groups between 2.0–3.0 ppm, two singlets around 1.5 ppm corresponding to the tert-butyl groups and aromatic protons between 7.5–8.0 ppm.

We have investigated the use of these unsymmetrical permethylindenyl complexes in conjunction of three different catalyst supports: methylaluminoxane-activated silica (SSMAO) and AMO-LDH (LDHMAO),^{18,19} and solid polymethylaluminoxane (solid MAO or sMAO)^{20,26} for the slurry phase polymerisation of ethylene.^{7,19,20} After work-up, all the solids were afforded as coloured powders in good isolated yields (73–91%). Fig S19–S30 show solid state NMR spectra of the supported catalysts SSMAO- $Me_2SB(tBu_2Flu, I^*)ZrCl_2$ (**1_{SSMAO}**), LDHMAO- $Me_2SB(tBu_2Flu, I^*)ZrCl_2$ (**1_{LDHMAO}**), sMAO- $Me_2SB(tBu_2Flu, I^*)ZrCl_2$ (**1_{sMAO}**) and sMAO- $Et_2SB(tBu_2Flu, I^*)ZrCl_2$ (**2_{sMAO}**). The ^{29}Si CPMAS NMR spectra show one resonance for **1_{sMAO}**, indicating a well-defined, ordered material with only a single Si environment and hence catalytic site but several for **1_{SSMAO}** and **1_{LDHMAO}**. The ^{13}C CPMAS spectra highlight the presence of the complex on the solid support.

Preliminary solution phase polymerisations were carried out under ethylene (2 bar pressure), with 50 mL hexanes, 0.2 mg complex and with an Al:Zr ratio (MAO:complex) of 2000:1 for 5 minutes (Fig. S31). $Me_2SB(tBu_2Flu, I^*)ZrCl_2$ (**1**) demonstrated the highest activity (33 360 $kg_{PE}/mol_{Zr}/h/bar$ at 80 °C), two times faster than the symmetrical permethylindenyl zirconium dichloride (rac -(SBI *) $ZrCl_2$ 18 500 $kg_{PE}/mol_{Zr}/h/bar$)^{7d} in the same conditions which compares well with some of the zirconocenes with the highest reported activities.²⁷ The morphology of the obtained polyethylenes is poor and highly aggregated as indicated by SEM imaging; typical for solution phase polymerisation (Fig. S32–S34).

Slurry phase polymerisation using methylaluminoxane-modified silica (SSMAO) and AMO-LDH (LDHMAO) catalysts were carried out under similar conditions but with 10 mg of solid catalysts and 150 mg of triisobutylaluminium used as scavenger instead. Complex $Me_2SB(tBu_2Flu, I^*)ZrCl_2$ (**1**) supported on SSMAO (**1_{SSMAO}**) demonstrated the highest activity at 80 °C (1342 $kg_{PE}/mol_{Zr}/h/bar$), twice more than SSMAO- rac -(SBI *) $ZrCl_2$) and four times more than its hafnium analogue (**5_{SSMAO}**) (759 and 414 $kg_{PE}/mol_{Zr}/h/bar$ respectively, Fig. S35–S36). However, when supported on LDHMAO, **2_{LDHMAO}** led to the highest activity at 70 °C (1522 $kg_{PE}/mol_{Zr}/h/bar$) (Fig. S38–S39). These values were thirty times slower than the solution activities (notably, these are carried out for only 5 minutes) but higher than previously reported zirconocenes supported on silica.^{7c,28} The morphologies for the synthesised polyethylenes mimicked their support materials; spherical particles which still showed some significant aggregation and rough surfaces (silica-based, Fig. S37) and highly aggregated particles which were not uniform (AMO-LDH-based, Fig. S40–S41).

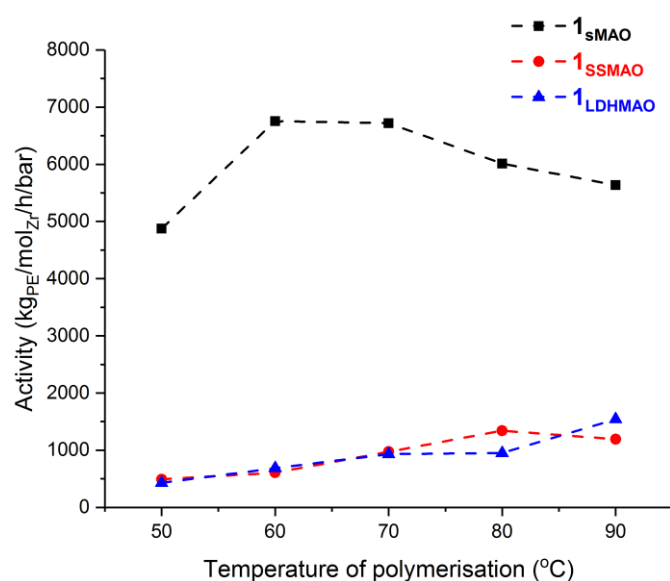


Fig. 2 Slurry phase polymerisation of ethylene activity as a function of temperature using $\text{sMAO-Me}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ (**1_{sMAO}**) (black square), $\text{SSMAO-Me}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ (**1_{SSMAO}**) (red circle) and $\text{LDHMAO-Me}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ (**1_{LDHMAO}**) (blue triangle). Polymerisation conditions: 10 mg catalyst, 2 bar ethylene, 50 mL hexanes, 30 minutes and 150 mg triisobutylaluminium.

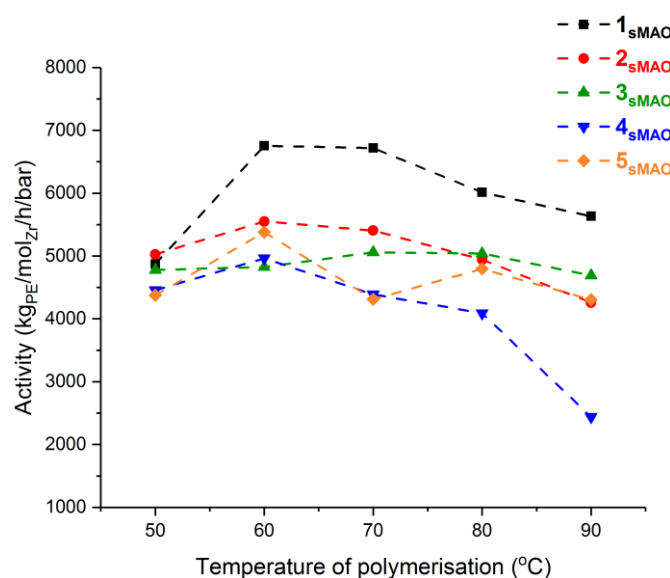


Fig. 3 Slurry phase ethylene polymerisation activity as a function of the temperature of polymerisation using $\text{sMAO-Me}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ (**1_{sMAO}**) (black square), $\text{sMAO-Et}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ (**2_{sMAO}**) (red circle), $\text{sMAO-Me}_2\text{PropSB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ (**3_{sMAO}**) (green triangle), $\text{sMAO-Me}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*,\text{Et}^*)\text{ZrCl}_2$ (**4_{sMAO}**) (blue down triangle) and $\text{sMAO-Me}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{HfCl}_2$ (**5_{sMAO}**) (orange diamond). Polymerisation conditions: 10 mg catalyst, 2 bar ethylene, 50 mL hexanes, 30 minutes and 150 mg triisobutylaluminium.

$\text{Me}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ supported on **1_{sMAO}** demonstrated the highest activity over all temperatures; ten times the activities obtained when the same complex was supported on **SSMAO** and **LDHMAO** (Fig. 2; 6755 vs. 606 and 687 kgPE/molZr/h/bar respectively at 60 °C for 30 minutes).

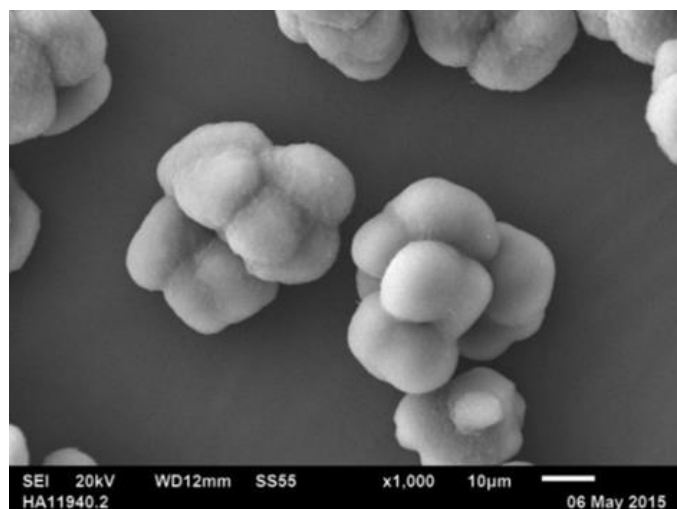


Fig. 4. SEM images of the polyethylene synthesised using $\text{sMAO-Me}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ (**1_{sMAO}**). Polymerisation conditions: 10 mg catalyst, 2 bar ethylene, 50 mL hexanes, 30 minutes and 150 mg triisobutylaluminium.

The catalyst **1_{sMAO}** is also 20–40% more active than the four other solid polymethylaluminoxane catalysts (**2–5_{sMAO}**), with activities between 4826 to 5550 kgPE/molZr/h/bar at 60 °C for 30 minutes (Fig. 3). The activities decreased with increasing time of polymerisation (9145 to 5981 kgPE/molZr/h/bar for 5 to 60 minutes), consistent with literature reports.²⁹ Notably, the morphology of the polymer is not compromised despite the high activity obtained for all polyethylene synthesised using the **1_{sMAO}** support; smooth popcorn-like particles with low levels of aggregation are indicated (Fig. 4 and S43–S44). High molecular weights (M_w above 500 kg/mol at 70 °C for 30 minutes) and low polydispersities (M_w/M_n around 2–3) were obtained with all supports indicating rapid and controlled polymerisation likely resulting from single-site catalytic behaviour in these heterogeneous systems (Fig. S45–S47). The highest molecular weights were obtained with **5_{LDHMAO}** (1168 kg/mol).

In conclusion, new unsymmetrical permethylindenyl complexes have been synthesised and characterised. Heterogeneous olefin polymerisation systems of these complexes immobilised onto methylaluminoxane-modified silica, layered double hydroxide and solid polymethylaluminoxane have been prepared and characterised by solid-state NMR spectroscopy demonstrating the presence of the complex on the surface. $\text{SSMAO-Me}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ (**1_{SSMAO}**) and $\text{LDHMAO-Et}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ (**2_{LDHMAO}**) demonstrated good activities (around 600 kgPE/molZr/h/bar), indicating the benefits of the new unsymmetrical C_1 complexes. However, $\text{sMAO-Me}_2\text{SB}(\text{tBu}_2\text{Flu},\text{I}^*)\text{ZrCl}_2$ (**1_{sMAO}**) demonstrated the highest activity overall (around 7000–9000 kgPE/molZr/h/bar).

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