



Supported bis(peralkylindenyl)metallocene catalysts for slurry phase ethylene polymerisation



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ARTICLE INFO

Article history:

Received 7 April 2016

Accepted 29 April 2016

Available online 6 May 2016

Dedicated to Professor M.L.H. Green FRS on the occasion of his 80th birthday.

Keywords:

Metallocenes

Zirconium

Indenyl

Polymerisation and ethylene

ABSTRACT

A series of bis(peralkylindenyl)zirconocene and hafnocene complexes were synthesised and characterised by NMR spectroscopy, mass spectrometry and elemental analyses. 3-ethyl-2,4,5,6,7-pentamethylindanone, $(^{3-Et}Ind^{\#})=O$; 3-ethyl-2,4,5,6,7-pentamethylindene, $(^{3-Et}Ind^{\#})H$, and *rac*-3-ethyl-2,4,5,6,7-pentamethylindenylhafnium dichloride, *rac*- $(^{3-Et}Ind^{\#})_2HfCl_2$, were also characterised by X-ray crystallography. *rac*- and *meso*- $(^{3-Et}Ind^{\#})_2MCl_2$ ($M = Zr$ or Hf) were obtained from the reaction of $(^{3-Et}Ind^{\#})Li$ with $ZrCl_4$ or $HfCl_4$. The group 4 metallocenes were then reacted with methylaluminoxane-functionalised silica (SSMAO) to afford silica supported catalysts. A mixture of *rac*- and *meso*- $(^{3-Et}Ind^{\#})_2ZrCl_2$ supported on SSMAO demonstrated an initial polymerisation activity of 250 $kg_{PE}/mol_M/h/bar$. At 70 °C, using *rac*- $(^{3-Et}Ind^{\#})_2ZrCl_2$, solution phase polymerisation activities were twenty times faster than slurry phase polymerisation using SSMAO-*rac*- $(^{3-Et}Ind^{\#})_2ZrCl_2$ (1243 and 75 $kg_{PE}/mol_{Zr}/h/bar$ respectively).

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1. Introduction

The cyclopentadienyl ligand ($C_5H_5^-$; Cp) was first used in ferrocene in 1951 [1], with the connectivity determined in 1952 by Wilkinson and Fischer [2,3]. Ever since, the Cp ligand has been at the forefront of organometallic chemistry with complexes featuring elements from the s, p, d and f blocks [2,4–9]. Group 4 metallocenes were discovered by Wilkinson in the synthesis of Cp_2TiCl_2 in 1954 [2]. This result launched the platform for research into its uses; most relevantly as a catalyst in ethylene polymerisation [10].

The first synthesis of permethylated indene (Ind^*H) was reported by Miyamoto *et al.* [11]. O'Hare and co-workers later reported an improved Ind^*H preparation and the synthesis of $(Ind^*)_2M$ ($M = Fe, Co$) [12]. The synthesis and use of the *ansa*-bridged analogue, ethylenebis(hexamethylindenyl)lithium (EBI^*Li_2), was then developed [13]. O'Hare and co-workers very recently reported an optimised synthesis, removing the use of toxic chemicals such as $BrCN$, improving reaction time and yield, and reducing the number of reaction steps required to furnish the final EBI^*Li_2 ligand [14,15].

Polyethylene, with a production capacity of 70 M tonnes per year is still at the forefront of the academic and industrial research

[16a,b]. Partially dehydroxylated silica (SiO_2) is the most commonly used support material for heterogeneous metallocene catalysts due to its versatility and adaptability [16a,c]. Contacting a solution of methylaluminoxane (MAO) with carefully calcined silica, results in the formation of silica-supported MAO (SSMAO), which can also be utilised for immobilising metallocene catalysts [17,18].

Herein, we report the synthesis of new peralkylated bis(indenyl) group 4 metallocenes, their immobilisation on SSMAO and their use in slurry phase ethylene polymerisation.

2. Experimental

2.1. General

Air- and moisture-sensitive compounds were manipulated under an inert atmosphere of nitrogen, using standard Schlenk line techniques on a dual manifold vacuum/nitrogen line or a MBraun UNILab glove box. Protio solvents (pentane, hexane, toluene, DCM, benzene) were dried using an MBraun SPS 800 solvent purification system and stored over potassium mirrors or pre-activated 3 Å molecular sieves (DCM) in oven-dried ampoules under an atmosphere of nitrogen, sealed with either Rotaflo or Young's taps. Diethylether and THF were distilled from Na/K and Na/benzophenone respectively, and stored over pre-activated 3 Å molecular sieves. C_6D_6 (99.6%, Sigma Aldrich) and $C_6D_5CD_3$

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(99.5%, Goss Scientific) were dried over potassium. CDCl_3 (99.8%, Sigma Aldrich) and $\text{C}_5\text{D}_5\text{N}$ (99.5%, Goss Scientific) were dried over calcium hydride. All deuterated solvents were vacuum transferred and freeze–pump–thaw degassed three times prior to use.

2.2. X-ray crystallography

Crystals were mounted on MiTeGen MicroMounts using perfluoropolyether oil, then transferred to a goniometer head on the diffractometer and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems Cryostream unit [19]. Data collections were carried out at 150 K either with an Oxford Diffraction Supernova diffractometer using mirror-monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and data processed using CrysAlisPro [20], or using a Nonius Kappa CCD diffractometer utilising graphite-monochromated $\text{Mo K}\alpha$ X-ray radiation ($\lambda = 0.71073 \text{ \AA}$), reduced using DENZO-SMN [21] and corrected for absorption using SORTAV [22]. The structures were solved using direct methods (SIR-92) [23] or a charge-flipping algorithm (SuperFlip) [24] and refined using full matrix least-squares procedures using CRYSTALS [25a,b] or the Win-GX software suite [25c]. Illustrations of the solid-state molecular structures were created using ORTEP [26].

2.3. Ethylene polymerisation

The supported metallocene catalysts were tested for their ethylene polymerisation activity under slurry conditions in the presence of 150 mg tri(isobutyl)aluminium (TIBA), used as scavenger. The reactions were performed under 2 bar of ethylene in a 150 mL ampoule, with 10 mg of the supported complex suspended in 50 mL of hexanes. The reactions were carried out for between 5 and 60 min at varying temperatures controlled by heating in an oil bath. The resulting polyethylene was immediately filtered off, washed with pentane ($2 \times 25 \text{ mL}$) and then dried for at least 30 min. A typical homogeneous polymerisation was prepared by adding 500 equivalents MAO to a 150 mL ampoule containing 0.5 mg of the complex, followed by addition of 50 mL of hexanes. The run was then continued as above and the resulting polyethylene was dried in a vacuum oven overnight. The tests were carried out at least twice for each individual set of polymerisation conditions. The activities were reported as an average with ± 1 SD error.

2.4. Synthesis of 3-ethyl-2,4,5,6,7-pentamethylindanone (($^{3\text{-Et}}\text{Ind}^\#$)=O)

One equivalent of oxalyl chloride (26.5 g, 208 mmol) was added to a 2 L reaction vessel containing one equivalent of (*E*)-2-methylpent-2-enoic acid (23.9 g, 208 mmol) in DCM (500 mL) under a flow of N_2 . While stirring, five drops of dry DMF were added into the mixture resulting in effervescence. The reaction mixture was left stirring for 2 h. Then, the reaction was cooled to $8 \text{ }^\circ\text{C}$ and allowed to equilibrate. 1.1 equivalents of aluminium trichloride (30.6 g, 230 mmol) was added, under a flow of N_2 , to the reactor. The reaction mixture changed in colour from a pale yellow to a deep orange almost instantly. 0.9 equivalents of 1,2,3,4-tetramethylbenzene (25.0 g, 176 mmol) was diluted in DCM (100 mL) and transferred to an addition funnel. This mixture was added to the reaction vessel dropwise over 15 min where a colour change from deep orange to blood red was observed. The solution was then left to stir for 4 h, after which a 1:1 mixture of conc. HCl and ice (200 mL) was added slowly to quench the reaction. The reaction mixture changed colour from blood red to a light orange during this work-up. The product was extracted with DCM ($3 \times 100 \text{ mL}$) and the combined organic layers were washed with deionised water ($3 \times 100 \text{ mL}$) before being dried using anhydrous MgSO_4 . This was filtered and the DCM solvent was removed *in*

vacuo to afford ($^{3\text{-Et}}\text{Ind}^\#$)=O as a beige solid in 100% yield (41.8 g, 214 mmol). Colourless crystals suitable for a single crystal X-ray diffraction study were grown from a hexanes solution at $5 \text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3 , $25 \text{ }^\circ\text{C}$): δ (ppm) 0.56 (t, 3H, $^3J_{\text{HH}} = 7.5 \text{ Hz}$, Me), 1.27 (d, 3H, $^3J_{\text{HH}} = 7.2 \text{ Hz}$, Me), 1.763 (m, 2H, CH_2), 2.23 (s, 3H, Ar-Me), 2.28 (s, 3H, Ar-Me), 2.28 (s, 3H, Ar-Me), 2.62 (s, 3H, Ar-Me), 2.74 (dq, 1H, $^3J_{\text{HH}} = 7.2 \text{ Hz}$, CH), 3.45 (m, 1H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , $25 \text{ }^\circ\text{C}$): δ (ppm) 9.9 (Me), 11.0 (Me), 13.8 (Ar-Me), 15.2 (Ar-Me), 15.4 (Ar-Me), 16.8 (Ar-Me), 23.9 (CH_2), 41.4 (CH), 48.1 (CH), 130.1 (Ar), 131.1 (Ar), 133.4 (Ar), 134.9 (Ar), 141.4 (Ar), 152.7 (Ar), 209.7 (C=O). MS (ESI): Calculated 231.17434; Found: 231.17446. CHN Anal. (%): Expected: C 83.43, H 9.63; Found: C 83.53, H 9.75. IR (cm^{-1}): 1691.52 (C=O stretching). X-ray parameters: $\text{C}_{16}\text{H}_{22}\text{O}$, $M = 230.33 \text{ g/mol}$, Triclinic, $P1$, $a = 5.2601(2) \text{ \AA}$, $b = 8.7982(3) \text{ \AA}$, $c = 15.0482(6) \text{ \AA}$, $\alpha = 74.690(1)^\circ$, $\beta = 85.558(2)^\circ$, $\gamma = 78.454(2)^\circ$, $V = 657.89(4) \text{ \AA}^3$, $Z = 2$, $\mu = 0.07 \text{ mm}^{-1}$, $R = 0.056$ and CCDC number: 1472636.

2.5. Synthesis of 3-ethyl-2,4,5,6,7-pentamethylindene (($^{3\text{-Et}}\text{Ind}^\#$)H)

One equivalent of 3-ethyl-2,4,5,6,7-pentamethylindanone (22.4 g, 97 mmol) was added to dry, degassed THF (50 mL) in a Schlenk tube. 0.5 equivalents of LiAlH_4 (2.0 M in THF, 24.2 mL, 48 mmol) were added dropwise over 30 min and the resultant mixture left to stir for 2 h under a N_2 atmosphere. The reaction mixture was cooled to $0 \text{ }^\circ\text{C}$ and was quenched by adding one equivalent of deionised water (1.74 mL, 97 mmol) dropwise. The resultant solution was transferred to a 2 L reaction vessel and stirred for 30 min under a flow of N_2 . Upon addition of five equivalents of conc. H_2SO_4 (26.1 mL, 483 mmol) dropwise over 20 min, the reaction mixture turned dark brown in colour. Subsequently, the reaction was quenched with deionised water (250 mL) and extracted with DCM ($3 \times 500 \text{ mL}$). The combined organic layers were washed with deionised water ($3 \times 100 \text{ mL}$), dried over anhydrous MgSO_4 , filtered, and the solvent was removed *in vacuo* to afford ($^{3\text{-Et}}\text{Ind}^\#$)H as a light brown solid (16.8 g, 78 mmol) in 81% yield. Colourless crystals suitable for a single crystal X-ray diffraction study were grown from a toluene solution at $5 \text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3 , $25 \text{ }^\circ\text{C}$): δ (ppm) 0.44 (t, 3H, $^3J_{\text{HH}} = 7.4 \text{ Hz}$, Me), 1.95 (m, 1H, CH_2), 2.07 (s, 3H, Me), 2.19 (m, CH_2), 2.26 (s, 6H, Ar-Me), 2.34 (s, 3H, Ar-Me), 2.35 (s, 3H, Ar-Me), 3.43 (t, 1H, $^3J_{\text{HH}} = 4.5 \text{ Hz}$, CH), 6.59 (s, 1H, vinylic-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , $25 \text{ }^\circ\text{C}$): δ (ppm) 7.6 (Me), 15.4 (Ar-Me), 16.1 (Me), 16.2 (Ar-Me), 16.3 (Ar-Me), 16.6 (Ar-Me), 21.1 (CH_2 -Me), 52.9 (CH), 124.8 (Ar), 126.1 (vinylic-CH), 128.9 (Ar), 130.7 (Ar), 133.0 (Ar), 141.9 (Ar), 142.1 (Ar), 146.7 (Ar). MS (ESI): Expected 215.17943; Found: 215.17966. CHN Anal. (%): Expected: C 89.65, H 10.35; Found: C 89.62, H 10.47. X-ray parameters: $\text{C}_{16}\text{H}_{22}$, $M = 214.33 \text{ g/mol}$, Monoclinic, C2/c , $a = 21.5383(7) \text{ \AA}$, $b = 5.1578(1) \text{ \AA}$, $c = 23.8471(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 101.441(3)^\circ$, $\gamma = 90^\circ$, $V = 2596.54(12) \text{ \AA}^3$, $Z = 8$, $\mu = 0.45 \text{ mm}^{-1}$, $R = 0.052$ and CCDC number: 1472637.

2.6. Synthesis of 3-ethyl-2,4,5,6,7-pentamethylindenyl lithium (($^{3\text{-Et}}\text{Ind}^\#$)Li)

To 3-ethyl-2,4,5,6,7-pentamethylindene (16.8 g, 78 mmol) was added pentane (100 mL), followed by dropwise addition of 1.1 equivalents of $^n\text{BuLi}$ (2.5 M in hexanes, 34.5 mL, 86 mmol) at $0 \text{ }^\circ\text{C}$. The solution was allowed to warm to room temperature and left stirring for 16 h. The resulting yellow suspension was filtered and the solids were washed with pentane ($2 \times 50 \text{ mL}$) and then dried under *in vacuo* to yield ($^{3\text{-Et}}\text{Ind}^\#$)Li as a white solid in 52% yield (9.05 g, 41 mmol). ^1H NMR (400 MHz, $\text{C}_5\text{D}_5\text{N}$, $25 \text{ }^\circ\text{C}$): δ (ppm) 1.47 (t, 3H, $^3J_{\text{HH}} = 7.3 \text{ Hz}$, Me), 2.45 (s, 3H, Ar-Me), 2.46 (s, 3H, Ar-Me), 2.65 (s, 3H, Ar-Me), 2.66 (s, 3H, Ar-Me), 2.89 (s, 3H,

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