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Polyhedral oligomeric silsesquioxane-conjugated bis(diphenylphosphino) amine ligand for chromium(III) catalyzed ethylene trimerization and tetramerization

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ABSTRACT

Polyhedral oligomeric silsesquioxanes (POSSs) were attached to conventional bis(diphenylphosphino)amine (PNP) ligand as solubility-enhancing materials for catalytic ethylene trimerization and tetramerization. Differently functionalized arylphosphine ligands of the type $(Ph)_2PN(POSS)P(Ph)(Ar^R)$ (R = functional groups) were systematically developed, and their corresponding chromium(III) complexes were formed. The developed precatalysts exhibited excellent tolerance in solvents, including even low-carbon-number hydrocarbons such as *n*-pentane, *n*-hexane, or cyclohexane. In particular, the *ortho*-fluorophenyl-substituted complex showed higher stability even at higher temperatures above 120 °C. The *ortho*-OCF_3–phenyl-substituted complex showed outstanding catalytic activity, which reached 2287 kg/g Cr/h at 30 bar.

1. Introduction

Selective oligomerization of ethylene for linear α-olefins (LAOs), such as 1-hexene and 1-octene, is a highly challenging subject in catalysis and has been researched extensively [1]. LAOs, which are valuable co-monomers in the production of linear low-density polyethylene (LLDPE), are produced industrially via a generally less-selective oligomerization of ethylene. The conventional oligomerization process produces not only 1-hexene and 1-octene, but also higher-molecular-weight oligomers according to the Schulz-Flory or Poisson distribution [2–4]. To address the selectivity issue, various catalytic systems that utilize chromium complexes have been developed [5–12]. Generally, an active chromium catalyst can be generated in situ using a ligand and Cr $(acetylacetonate)_3$ or $Cr(ethylhexanoate)_3$ or $CrCl_3(THF)_3$ [13–18]. The generated precatalyst, however, has poor solubility in many non-polar solvents, which often causes lower catalytic activities, so that several attempts have been reported to overcome the low solubility. For instance, K. Blann et al. demonstrated significant improvement on catalytic activity by increasing carbon number and solubility with results of methyl-(26 kg/g Cr/h), *n*-pentyl-(43 kg/g Cr/h), and *n*-decyl-(50 kg/g Cr/h)PNP precatalysts [19]. Meanwhile, hydrocarbon solvents with fewer carbon atoms have not been evaluated adequately, and most selective oligomerization reactions have conventionally been carried out in toluene or methylcyclohexane (MCH). The use of light hydrocarbon solvents, however, has a potential advantage since they dissolve ethylene well [20–22]. The solubility of ethylene in some hydrocarbon solvents has been calculated by Aspen Plus (Table S1). It is higher in light hydrocarbon solvents at lower temperatures, and also in a linear aliphatic solvent than in a cyclic one with the same number of carbon atoms. Furthermore, the processing temperature for the oligomerization is still restrictive, although numerous modifications and developments have been made to improve the catalytic systems. Because of the intrinsic activity of conventional catalytic systems, operation at 45–60 °C is encouraged; otherwise, at elevated temperatures, the performance drops significantly, resulting in a drastic decrease in the productivity [23]. The advantage of operating at higher temperatures is that viscous byproduct polymers can be dissolved, preventing post-process plugging. In order to enable operation at high temperatures, more innovative catalytic systems are required.

Polyhedral oligomeric silsesquioxanes (POSSs) have been highlighted as advanced materials with excellent solubility and thermal stability [24–29]. Guenthner et al. showed that POSSs have excellent solubility in non-polar solvents such as *n*-hexane by measuring the Hansen solubility parameters [30]. Fina et al. reported that POSSs have high thermal stability; for instance, isobutyl-substituted POSS has a pyrolysis temperature above 260 °C [31]. Owing to such advantageous properties, POSSs have been widely used as scaffolds for organic/inorganic hybrid catalysts [32], microfluidic formats [33], monolithic

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structures [34–36], tailored internal chemistries of porous materials [37], conjugates to nanoparticles [38–40] as well as stiffeners for transparent electronic devices with inherent thermal stability [41]. Duchateau et al. reported the use of titanium- and zirconium-tethered POSSs as catalysts for ethylene polymerization [42]. However, the use of chromium-tethered POSSs for ethylene oligomerization has not been investigated thus far. In this study, versatile chromium complexes based on POSS-conjugated ligands were developed as catalysts with excellent solubility and thermal stability for selective ethylene oligomerization.

2. Experimental

2.1. General conditions

All reactions were performed under an inert atmosphere using standard Schlenk techniques. All solvents and gases were dried and degassed using standard procedures. Chemicals were purchased from Sigma Aldrich or Strem and used without further purification unless otherwise stated. mMAO-3A was obtained from Akzo Nobel Corporation as a 7% w/w solution in heptane. The IR spectra were recorded with a Nicolet 6700 FT-IR Spectrometer from Thermo Scientific. ^{1}H, ^{19}F, ^{29}Si and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III HD 500 MHz spectrometer in $CDCl_3$ or C_6D_6. Chemical shifts are reported in ppm with reference to tetramethylsilane. ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD 600 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with reference to internal chloroform. Bruker Daltonics (Billerica, MA, USA) APPI 7T FT-ICR MS was used for (+) mode atmospheric pressure photoionization analysis. Quantitative chromatographic analysis of the oligomerization products was performed using an Agilent 7890 A GC-FID with an HP-PONA column (50 m × 0.20 mm). The reaction solvent was used as an internal standard.

2.2. Ethylene oligomerization

All runs were carried out in a 50-mL stainless steel Parr autoclave with a magnetic stirrer. In a glovebox, a glass vial was charged with the ligand (0.5 μmol) and $CrCl_3(THF)_3$ (0.5 μmol) followed by 1 mL of dichloromethane, and then the solution was stirred for 10 min. After this, the solvent was removed under reduced pressure and the resultant solid was suspended in 20 mL of the reaction solvent. The solution was placed in the autoclave and mMAO (0.14 mL, 0.25 mmol, 500 equivalents) was added; then, the solution was pressurized with ethylene and stirred at 600 rpm. Ethylene was fed on demand to keep the reactor pressure constant, and the uptake was monitored using a flow meter. After 15 min, the autoclave was cooled to 0 °C and depressurized slowly to atmospheric pressure. The product was quenched by adding 2-ethylhexanol (1 mL). The crude products were filtered and analyzed using GC-FID. The polymeric products were recovered by filtration and dried overnight in an oven at 100 °C.

2.3. Ligand preparation

2.3.1. Preparation of POSS-NH_2

3-Aminopropyl-substituted heptaisobutyl-POSS (POSS-NH_2) was synthesized as described in the literature [43–46]. Isobutyltrisilanol-POSS (5.57 g, 7.0 mmol) was dissolved in THF (47 mL) and then (3-aminopropyl)trimethoxysilane (1.64 g, 9.1 mmol) was added. The reaction mixture was vigorously stirred for 24 h at 25 °C and then the solvent was removed in vacuo. The crude product which was further dissolved with 30 mL of *n*-hexane was filtered out to remove some of insoluble residue. The obtained clear solution was added to the same amount of acetonitrile to precipitate the desired product, filtered, washed with acetonitrile (2 × 20 mL), and dried over in vacuo. The product was further purified by recrystallization in *n*-hexane/acetonitrile to yield 4.32 g (70.2%) of the colorless solid.; *m/z* (APPI) $[M + H]^+$ calcd for $C_{31}H_{72}NO_{12}Si_8^+$: 874.3203; found: 874.3178. ν ($CHCl_3$)/cm^{-1}: 2953s, 2926 w, 2902 w, 2868 w, 1463s, 1398 w, 1388 w, 1366 w, 1332 w, 1229s, 1096s, 907 s, 852 s, 732 s. δ_H($CDCl_3$): 2.65 (t, 2 H, -CH_2N), 1.84 (m, 7 H, CH), 1.51 (m, 2 H, -CH_2-), 1.14 (b, 2 H, NH_2), 0.94 (m, 42 H, CH_3), 0.58 (m, 16 H, Si-CH_2). δ_C($CDCl_3$): 44.7, 27.1, 25.7, 23.9, 22.5, 9.2.

2.3.2. Preparation of $(Ph)_2$PN(POSS)P$(Ph)_2$ (L1)

POSS-NH_2 (0.6 g, 0.68 mmol) and triethylamine (1.0 mL, 7.20 mmol) were dissolved in dichloromethane (10 mL), and then chlorodiphenylphosphine (0.317 g, 1.44 mmol) was added. The solution was stirred at ambient temperature for 1 h. The volatile solvent was evaporated and the product was washed with methanol (2 × 3 mL). Further purification was performed by recrystallization in *n*-hexane/methanol, recovered, and dried to yield 0.71 g (83%) of $(Ph)_2$PN(POSS)P$(Ph)_2$ as a white solid.; *m/z* (APPI) $[M + H]^+$ calcd for $C_{55}H_{90}NO_{12}P_2Si_8^+$: 1242.4087; found: 1242.4033. ν ($CHCl_3$)/cm^{-1}: 2952s, 2915 w, 2868 w, 2848 w, 1464s, 1434s, 1401 w, 1382 w, 1365 w, 1331 w, 1229s, 1096s, 866 s, 837 s, 741 s, 725 s. δ_H($CDCl_3$): 7.35 (b, 8 H, aromatics), 7.26 (b, 12 H, aromatics), 3.17 (m, 2 H, -CH_2N), 1.80 (m, 7 H, -CH-), 1.24 (b, 2 H, -CH_2-), 0.92 (m, 42 H, CH_3), 0.56 (m, 14 H, Si-CH_2), 0.15 (t, 6 H, Si-CH_2). δ_C($CDCl_3$): 139.8, 132.7, 128.6, 127.9, 55.5, 45.7, 25.6, 23.8, 22.5, 9.2. δ_P(C_6D_6): 61.8. δ_{Si}(C_6D_6): -67.9.

2.3.3. Preparation of $(Ph)_2$PN(*n*-Bu)P$(Ph)_2$ (L2)

$(Ph)_2$PN(*n*-Bu)P$(Ph)_2$ was prepared according to a modified literature method [12]. *N*-Butylamine (0.1 g, 1.37 mmol) and triethylamine (1.72 mL, 8.4 mmol) were dissolved in dichloromethane (5 mL), and then chlorodiphenylphosphine (0.618 g, 2.8 mmol) was added. The solution was stirred at ambient temperature for 1 h. The volatile solvent was evaporated and the product was washed with methanol (2 × 3 mL), recovered, and dried to yield 0.5 g (83%) of $(Ph)_2$PN(*n*-Bu)P$(Ph)_2$ as a white solid.; *m/z* (APPI) $[M + H]^+$ calcd for $C_{28}H_{30}NP_2^+$: 442.1848; found: 442.1843. δ_H($CDCl_3$): 7.39 (b, 8 H, aromatics), 7.29 (b, 12 H, aromatics), 3.23 (t, 2 H, -CH_2N), 1.07 (b, 2 H, -CH_2-), 0.92 (m, 2 H, -CH_2-), 0.60 (t, 3 H, CH_3). δ_C($CDCl_3$): 139.7, 132.7, 128.6, 128.0, 52.8, 33.4, 19.9, 13.6. δ_P(C_6D_6): 62.2.

2.3.4. Preparation of *N,N*-diethylaminochlorophenylphosphine

N,N-Diethylaminochlorophenylphosphine was prepared according to a literature method [47]. Pyridine (13.05 g, 165 mmol) was added dropwise to a solution of dichlorophenylphosphine (14.77 g, 82.5 mmol) in *n*-hexane (80 mL) at −78 °C, and this was followed by the dropwise addition of diethylamine (12.07 g, 165 mmol). The reaction mixture was warmed to room temperature, stirred for 3 h, and then filtered to remove the precipitated diethylammonium chloride salt. Removal of the solvent under reduced pressure gave a pale yellow oil (17.75 g, 99.75%), which was distilled to yield 13.53 g (76.05%) of pure *N,N*-diethylaminochlorophenylphosphine as colorless oil. b.p. 110 °C/150 mbar.

2.3.5. Typical procedure for ClPPh(Ar^R) for L3–L8, L10, L11, L13, and L14

Magnesium turnings (30 mmol) were activated in anhydrous THF (40 mL), and then functionalized aryl bromide (20 mmol) was added dropwise. The reaction mixture was stirred overnight at 45 °C. After it had cooled to room temperature, the reaction mixture was separated from excess magnesium via decantation to obtain a Grignard reagent (0.5 M). A portion of the reagent (8 mL, 4 mmol) was added to a dilute solution of *N,N*-diethylaminochlorophenylphosphine (3.2 mmol), and the reaction mixture was refluxed for 3 h. After it had cooled to room temperature, the volatile solvent was removed in vacuo, and then the crude mixture was slurried in *n*-hexane (20 mL). The slurry was filtered using an activated alumina pad, and the filter cake was washed with *n*-