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Highly active self-assembled group-IV-metal multinuclear catalysts for ethylene polymerization

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ABSTRACT

Group-IV metals play an important role in the production of practical catalysts for polyethylene industry. To develop new highly active catalysts, we designed a new self-assembly strategy that leads to a new family of group-IV-metal multinuclear catalysts with bis-phenoxy-imine ligands. These multinuclear catalysts are formed *via* three bridging strategies, by linking the imine-N, the 4-position of phenolate, or the mixed linking strategy. The coordination environment of the catalysts was investigated with far-IR and Raman. The multiple imine-H shift found in ¹H NMR revealed that the multinuclear catalysts were more active and stable, and produced polyethylene of higher MW than the corresponding mononuclear catalysts. The bridging spacer has an evident effect on catalytic activity, stability, polymer MW and incorporation rate of propylene into the polyethylene backbone.

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1. Introduction

The development of high performance catalysts for olefin polymerization is of great importance to the chemical industry. Among the various catalysts studied so far [1–7], phenoxy-iminebased Group 4 metal catalysts [8–17] (see Scheme 1 and model-1 in Scheme 2) have received much attention because they are a class of non-metallocene catalysts with high initial activity that may potentially compete with the commercial metallocene or halfsandwich Group 4 metal catalysts. However, these phenoxy-imine catalysts have been reported to have poor stability resulting in limited lifetime which was attributed to the transfer of the supporting ligand to the aluminum in co-catalyst [18-21], especially at elevated temperatures used in commercial processes. As a consequence these catalysts were usually studied at low temperature and/or short reaction time [8-17]. Therefore there is substantial incentive to develop robust phenoxy-imine catalysts with high activity and minimal catalyst decay.

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As bidentate phenoxy-imine catalysts (see FI-Ti/Zr in Scheme 1) have limited lifetime, much effort has been made to improve their stability by using tetradentate ligands, which were expected to form more stable mono-nuclear catalysts of coordination model-2 (see Scheme 2). Ishii et al. [17] reported that tetradentate ligands of C_n -chain-bridged phenoxy-imine units (see II, n = 2-6, in Scheme 3) formed mono-nuclear catalysts with zirconium. The results showed that the complexes with ligands of longer bridge (n = 5 or 6) displayed high activity for five minutes run, while the complexes with ligands of shorter bridge (n = 2-4) displayed low activity, and the issue of catalyst rapid deactivation was not addressed. Scott and co-workers [18-21] also believed that the tetradentate ligands incorporating titanium and zirconium may form more stable catalysts bearing the coordination model-2 with two imine-N linked. However, experimental results demonstrated that the tetradentate ligands III and XII (see Scheme 3) did not afford olefin polymerization catalysts, principally because of a destructive 1,2-migratory insertion of a metal-bound alkyl/polymeryl chain into the imine C=N unit [18-20]. Subsequently, Knight et al. [19,20] found that introducing an alkyl group at the position R^4 (see ligand XI in Scheme 3) of a zirconium salicylaldiminato complex leads to a long-lived catalyst (1 h test) for ethylene polymerization because of steric blocking of an intramolecular 1,2migratory insertion. However, this steric blocking promotes a

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Scheme 1. Synthesis of mono-nuclear Ti/Zr catalysts and five possible isomers.



Scheme 2. Comparison of catalyst models: multinuclear vs mononuclear.

new radical catalyst decomposition mechanism in certain instances, thus resulting in far lower activities compared to the corresponding catalyst based on the FI ligand. In addition, all the zirconium complexes of ligands IV ~ X have no activity probably due to the lack of steric bulk in the phenolate 2-position [20]. In their further studies, Clarkson et al. [21] investigated more tetradentate ligands (see XIII-XVII in Scheme 3). For titanium complexes, [(XIII)TiCl₂] had no activity for ethylene polymerization when treated with MAO because the two chloride ligands are in *trans*-arrangement. The *cis*-complex [(XIV)TiCl₂] however was also unproductive, perhaps due to enhanced imine reactivity brought on by ring-strain in the diamine backbone. Complex [(XV)TiCl₂] produced only a trace of polymer. Although complexes [(XVI)TiCl₂] and [(XVII)TiCl₂] demonstrated significantly improved activity at 25 °C (in excess of 2×10^3 Kg_{PE} mol_{cat}⁻¹ h⁻¹ bar⁻¹ for a one hour test), the overall productivities are much lower at 50 °C resulting from more rapid catalyst decomposition. For zirconium complexes, complex [(XV)ZrCl₂] produced only a trace of polymer. The complexes [(XVI) ZrCl₂] and [(XVII)ZrCl₂] demonstrated only low activities. Similarly, introducing a methyl group at the phenolate 5-position of the simple phenoxy-imine ligand may block the intramolecular 1,2migratory insertion, however this steric blocking failed to improve the catalytic lifetime [20]. Therefore, after many investigations of various tetradentate ligands, the development of long-lived and highly efficient phenoxy-imine-based Group 4 metal catalysts is still a challenge.

The coordination of metal with multi-dentate ligands form a material known as MOF (Metal-Organic Frameworks) or coordination polymer where the ligand acts as a bridging spacer among the metals [22,23]. Although the published catalytic applications using MOF or coordination polymer generally suffer from a lack of characterization with respect to sample homogeneity and purity [22], this kind of materials have been receiving more and more

attention in developing new catalysts. So far, some of the materials have been demonstrated to be efficient catalysts with better selectivity and/or stability relative to corresponding mono-nuclear catalysts. In order to develop highly active Ti(IV) and Zr(IV) catalysts of phenoxy-imine with improved stability, here we use selfassembly strategy between metals and bisphenoxy-imine ligands to form multinuclear catalysts. The key of this strategy is the use of bis-phenoxy-imine ligand that has a bridging spacer to separate the two phenoxy-imine coordination units so that they have to coordinate with different metals, thus leading to the formation of multinuclear catalysts over mono-nuclear catalysts. One-step selfassembly (see Fig. 1) using one ligand and two-step programmed self-assembly (see Fig. 2) using two different ligands were investigated. The ethylene polymerization studies reveal that these multinuclear catalysts are much more active, decay at a significantly slower rate, and produce higher MW polymers compared to the corresponding mono-nuclear catalysts. The multinuclear Ti-catalyst with short bridging spacer ($-C_6H_5$ -) displayed improved propylene incorporation compared to the mono-nuclear FI catalyst. Here we report that, besides using polymeric ligand [24,25], self-assembly is an alternative approach to synthesize highly active multinuclear catalysts for ethylene polymerization.

2. Experimental

2.1. General considerations

All manipulations involving air-sensitive materials were carried out by using standard Schlenk line techniques or in a glove box under an atmosphere of argon. 4,4'-methylenedianiline, benzidine, 1,4-diaminobenzene, 3-tert-butyl-2-hydroxy-benzaldehyde and anhydrous hexane were purchased from Sigma-Aldrich and used without pre-treatment. 5,5-Methylene-di-3-tert-butyl salicylaldehyde was prepared according to literature methods [26–28]. Methanol was dried over 4 Å molecular sieves. DCM and THF were purified using an MBRAUN-SPS solvent purification system. ¹H NMR and ¹³C NMR were recorded in CDCl₃ on a BRUKER 400 MHz spectrometer. HRMS(EI) was performed on a Thermo Finnigan MAT 95. HRMS(ESI) was performed on an Agilent LC-MS TOF. Elemental analysis was performed on a EuroEA3000 Series Elemental Analyzer. Metal content was tested with ICP. Methyl aluminoxane solution (Al%: ~5.2%) in toluene was purchased from Chemtura Organometallics GmbH and used directly without any pretreatment. The known ligand (FI) and known FI-Ti/Zr catalysts were prepared following the reported methods [8-17]. The multinuclear catalysts (MNTi-1~5 and MNZr-1~5) were synthesized via the same procedure. High temperature GPC analyses of polyethylene were performed on a Polymer Labs GPC-220 with a refractive index detector. Typical operating conditions for analyzing polyethylene are: two PLgel 10 μm Mixed B columns (300 \times 7.5 mm) and one PLGel 10 μ m guard column (50 \times 7.5 mm) at 160 °C using 1,2,4-trichlorobenzene stabilized with 0.0125 wt. % BHT as the eluent. Polymer samples were prepared at a concentration of 1 mg/mL using a Polymer Labs SP260 sample preparation system at 150 °C until dissolved (typically about 4–6 h), followed by filtration where necessary. X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALAB 250 spectrometer and Al K α radiation was used as the X-ray source. The C1 peak at 284.5 eV was used as a reference for the calibration of the binding energy (BE) scale. FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer. Laser Raman spectra were recorded on an InVia Reflex instrument (Renishaw) equipped with a near infrared enhanced deep-depleted thermoelectrically Peltier cooled CCD array detector (576 \times 384 pixels) and a high grade Leica microscope. The methyl branching of the copolymers was measured with

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Scheme 3. Tetradentate ligands forming mononuclear catalysts [17-21].

FT-IR by comparison against standard samples.

2.2. General procedure for ethylene homo-polymerization in 300 mL reactor

The polymerization was carried out in a 300 mL stainless steel autoclave equipped with a mechanical stirrer with adjustable stirring rate. The autoclave was heated by a heating mantle. Before reaction, the autoclave was dried under vacuum at 100 °C for 2 h during which period the autoclave was swept with dry argon at least three times. Then the temperature was lowered to the reaction temperature (60 °C) and the reactor was evacuated and refilled with ethylene. Hexane (100 mL), MAO (2.0 mmol) and catalyst solution in DCM were added consecutively via syringe under ethylene atmosphere (~10 PSI) at a stirring rate of 300 RPM. Then the autoclave was quickly pressurized to 80 PSI (5.5 bar) with ethylene and the stirring rate was adjusted to 500 RPM. After the polymerization was run for the required time, the ethylene pressure was vented quickly and the reaction was quenched with 2 mL ethanol. The produced polyethylene was collected by filtration, washed with ethanol and hexane and dried in vacuo at 50 °C. The obtained white polymer was weighed and analyzed with GPC. The activity was calculated in unit of $Kg_{PE} \operatorname{mol}_{M}^{-1} h^{-1} \operatorname{bar}^{-1}$.

2.3. General procedure for copolymerization of Ethylene and propylene in 1 L reactor

The copolymerization of ethylene and propylene was carried out

in a 1 L stainless steel autoclave, which was heated by recycling hot oil. Before reaction, the autoclave was dried under vacuum at 100 °C for 2 h during which period the autoclave was swept with dry argon at least three times. After the temperature was lowered to the reaction temperature (60 °C), hexane (600 mL) and MAO (12.0 mmol) were introduced, followed by the addition of catalyst (6 µmol) solution in DCM (3 mL) at a stirring rate of 300 RPM. Then the autoclave was quickly pressurized to 3.0 bar with propylene, followed by ethylene being added to 7.0 bar total pressure. During the polymerization process, when the pressure dropped to 5.0 bar, 1 bar propylene and 1 bar ethylene were pressurized in up to 7.0 bar. After the copolymerization was run for 0.5 h, the pressure was vented quickly and the reaction was quenched with 12 mL ethanol. The produced copolymer was collected by filtration, washed with ethanol and hexane and dried in vacuo at 50 °C. The obtained white polymer was weighed and analyzed with GPC. The activity was calculated against the total pressure in unit of KgPE $mol_{M}^{-1}h^{-1}bar^{-1}$.

2.4. Bis-phenoxy-imine ligand (BFI-1, see Scheme 4)

4,4'-methylenedianiline (1.34 g, 6.76 mmol) was dissolved into anhydrous methanol (25 mL). After being stirred for several minutes, 3-*tert*-butyl-2-hydroxy-benzaldehyde (2.65 g, 14.87 mmol) was added, followed by several drops of formic acid. The resulting mixture was stirred for one hour at room temperature and then refluxed for one day under argon atmosphere. After cooling to room temperature, the product was isolated by filtration, washed

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Fig. 1. Self-assembly to design multinuclear catalysts.

with methanol (12 mL) and dried in vacuo affording 3.45 g of a yellow powder, yield 98%. ¹H NMR (CDCl₃, 400 MHz, δ): 1.50 (s, 18H, C(CH₃)₃), 4.04 (s, 2H, CH₂), 6.89 (t, 2H, Ph-H, *J* = 7.60 Hz), 7.26 (s, 10H, Ph-H), 7.41 (d, 2H, Ph-H, *J* = 7.20 Hz), 8.63 (s, 2H, CH=N), 13.96 (s, 2H, OH). ¹³C NMR (CDCl₃, 100 MHz, δ): 29.38, 34.93, 41.04, 118.34, 119.13, 121.37, 129.89, 130.30, 130.62, 137.67, 139.64, 146.66, 160.55, 162.90. Elemental analysis C₃₅H₃₈N₂O₂ (518.71): Calc.: C 81.05%, H 7.38%, N 5.40%; Found: C 80.89%, H 7.41%, N 5.46%. HRMS (EI, m/z): Calculated 518.2933; Found 518.2903 (M⁺).

2.5. Bis-phenoxy-imine ligand (BFI-2, see Scheme 4)

The ligand BFI-2 was synthesized via the same procedure as ligand BFI-1 using benzidine (1.06 g, 5.74 mmol) and 3-*tert*-butyl-2-hydroxy-benzaldehyde (2.09 g, 11.49 mmol) in anhydrous methanol (30 mL). The product was obtained as a yellow powder in 99% yield (2.80 g). ¹H NMR (CDCl₃, 400 MHz, δ): 1.51 (s, 18H, C(CH₃)₃), 6.92 (t, 2H, Ph-H, *J* = 7.60 Hz), 7.30 (dd, 2H, Ph-H, *J* = 7.60 Hz, *J* = 1.6 Hz), 7.40–7.45 (m, 6H, Ph-H), 7.70 (d, 4H, Ph-H, *J* = 8.40 Hz), 8.71 (s, 2H, CH=N), 13.96 (s, 2H, OH). ¹³C NMR (CDCl₃, 100 MHz, δ): 29.36, 34.94, 118.41, 119.12, 121.74, 127.87, 130.48, 130.71, 137.72, 138.80, 147.64, 160.61, 163.11. Elemental analysis C₃₄H₃₆N₂O₂ (504.68): Calc. C 80.92%, H 7.19%, N 5.55%; Found C 80.98%, H 7.12%, N 5.62%. HRMS(EI, m/z): Calculated 504.2777; Found 504.2823 (M⁺). Single crystal was crystallized from toluene solution (for the crystal details, see the supporting information).

2.6. Bis-phenoxy-imine ligand (BFI-3, see Scheme 4)

The ligand BFI-3 was synthesized via the same procedure as ligand BFI-1 using 1,4-diaminobenzene (0.61 g, 5.61 mmol) and 3-tert-butyl-2-hydroxy-benzaldehyde (2.00 g, 11.22 mmol) in anhydrous methanol (45 mL). The product was obtained as a yellow powder in 94% yield (2.25 g). ¹H NMR (CDCl₃, 400 MHz, δ): 1.50 (s, 18H, C(CH₃)₃), 6.91 (t, 2H, Ph-H, *J* = 7.80 Hz), 7.29 (dd, 2H, Ph-H, *J* = 7.60 Hz, *J* = 1.4 Hz), 7.39 (s, 4H, Ph-H), 7.43 (dd, 2H, Ph-H, *J* = 7.80 Hz, *J* = 1.4 Hz), 8.69 (s, 2H, CH=N), 13.90 (s, 2H, OH). ¹³C NMR (CDCl₃, 100 MHz, δ): 29.35, 34.93, 118.44, 119.08, 122.25, 130.51, 130.71, 137.72, 146.93, 160.58, 162.95. Elemental analysis C₂₈H₃₂N₂O₂ (428.58): Calcd. C 78.47%, H 7.53%, N 6.54%; Found C 78.31%, H 7.50%, N 6.55%. HRMS(EI, m/z): Calculated 428.2464; Found 428.2485 (M⁺). Single crystal was crystallized from toluene solution (for the crystal details, see the supporting information).

2.7. Bis-phenoxy-imine ligand (BFI-4, see Scheme 5)

The ligand BFI-4 was synthesized via the same procedure as ligand BFI-1 using aniline (1.01 g, 10.86 mmol) and 5,5-methylenedi-3-tert-butyl salicylaldehyde (2.00 g, 5.43 mmol) in anhydrous



Fig. 2. Two-step programmed self-assembly to design multinuclear catalysts.

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Scheme 4. Synthesis of multinuclear catalysts by bridging the imine-N.

methanol (80 mL). After reaction, the yellow slurry was concentrated to about 10 mL. The product was filtered, washed with methanol (2×5 mL) and dried in vacuo affording 2.56 g of a yellow powder (91% yield). ¹H NMR (CDCl₃, 400 MHz, δ): 1.46 (s, 18H, C(CH₃)₃), 3.92 (s, 2H, CH₂), 7.01 (d, 2H, Ph-H, *J* = 2.04 Hz), 7.23–7.27 (m, 8H, Ph-H), 7.39 (t, 4H, Ph-H, *J* = 7.80 Hz), 8.57 (s, 2H, CH=N), 13.79 (s, 2H, OH). ¹³C NMR (CDCl₃, 100 MHz, δ): 29.41, 34.93, 40.41, 118.93, 121.18, 126.68, 129.36, 130.28, 130.70, 131.32, 137.76, 148.53, 158.94, 163.38. Elemental analysis C₃₅H₃₈N₂O₂ (518.71): Calculated: C 81.05%, H 7.38%, N 5.40%; Found: C 81.09%, H 7.46%, N 5.47%. HRMS (ESI): Calculated for [M + H]⁺: 519.3006; Found 519.3004.

2.8. Multinuclear catalyst MNTi-1 (see Scheme 4)

To a stirred solution of BFI-1 (1.00 g, 1.93 mmol) in THF (20 mL), a solution of *n*-butyllithium (1.6 M, 2.4 mL, 3.86 mmol) in hexane

was added dropwise over a period of 10 min at -78 °C. Then the mixture was allowed to warm to room temperature and stirred for two hours. The resulting solution was added dropwise to a stirred solution of TiCl₄ (0.366 g, 1.93 mmol) in THF (15 mL) at -78 °C via a cannula over a period of 20 min. The resulting mixture was again warmed to room temperature and stirred overnight for 18 h. After removal of THF, the residual solid was extracted with 30 mL DCM and filtered to give a clear solution. Removal of DCM gave a deep reddish-brown solid which was ground to a fine powder with a spatula. The obtained catalyst was dried in vacuo at room temperature for several hours until its weight was equal to the theoretical yield calculated with C35H36Cl2N2O2Ti•THF. The catalyst has a general repeating unit of C₃₅H₃₆Cl₂N₂O₂Ti•xTHF. Elemental analysis and ¹H NMR showed that x was close to 1. The catalyst yield was 1.35 g (99%). FT-IR (cm⁻¹): 1608 (M), 1595 (S), 1587 (SH), 1554 (S), 1503 (M), 1481 (W), 1425 (M), 1393 (SH), 1384 (M), 1362



M = Tr, cat = MNZr-4M = Zr, cat = MNZr-4

Scheme 5. Synthesis of multinuclear catalysts by bridging the phenolate-4 position.

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(W), 658 (W), 600 (W), 564 (W), 498 (W), 460 (W), 360 (W). Raman (cm⁻¹): 1590 (M), 1553 (W), 1424 (S), 1296 (S), 1175 (W), 889 (W), 552 (W), 439 (W), 362 (W), 325 (W). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.25-1.61$ (m, 18H, *t*-Bu), 3.55-3.59 (m-broad, 2H, CH₂), 6.44-7.66 (m-broad, 14H, Ar-H), 7.83(s), 7.87-8.07 (m-broad), 8.13 (s), 8.14 (s), 8.18 (s) (2H, CH=N). Calculated for C₃₅H₃₆Cl₂N₂O₂-Ti•THF (FW 707.55): C 66.20%, H 6.27%, N 3.96%, Ti 6.77%; Found: C 66.05%, H 6.38%, N 3.81%, Ti 6.52%.

2.9. Multinuclear catalyst MNTi-2 (see Scheme 4)

The title catalyst MNTi-2 was synthesized via the same procedure as MNTi-1 using ligand BFI-2 (1.00 g, 1.98 mmol) in 30 mL THF and equimolar TiCl₄ (0.376 g, 1.98 mmol) in 30 mL THF. The multinuclear catalyst MNTi-2 was obtained as a deep reddishbrown solid with a general repeating unit of $C_{34}H_{34}Cl_2N_2O_2$. Ti•xTHF. Elemental analysis and ¹H NMR showed that x was close to 1. The catalyst yield was 1.37 g (100%). FT-IR (cm⁻¹): 1606 (SH), 1595 (S), 1586 (M), 1554 (S), 1490 (S), 1466 (W), 1425 (M), 1393 (SH), 1384 (M), 1362 (W), 659 (W), 612 (W), 601 (W), 565 (W), 552 (SH), 460 (W), 360 (W,BR). Raman (cm⁻¹): 1593 (S), 1553 (M), 1424 (S), 1297 (S), 1177 (S), 889 (W), 560 (W), 447 (W), 364 (W), 334 (W). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.24$ –1.66 (m, 18H, *t*-Bu), 6.65–7.66 (mbroad, 14H, Ar–H), 7.90–8.21 (m-broad) (2H, CH=N). Calculated for $C_{34}H_{34}Cl_2N_2O_2$ Ti•THF (FW 693.52): C 65.81%, H 6.10%, N 4.04%, Ti 6.90%; Found: C 65.67%, H 6.01%, N 4.09%, Ti 6.75%.

2.10. Multinuclear catalyst MNTi-3 (see Scheme 4)

The title catalyst MNTi-3 was synthesized via the same procedure as MNTi-1 using ligand BFI-3 (1.00 g, 2.33 mmol) in 30 mL THF and equimolar TiCl₄ (0.442 g, 2.33 mmol) in 30 mL THF. The multinuclear catalyst MNTi-3 was obtained as a deep reddishbrown solid with a general repeating unit of C₂₈H₃₀Cl₂N₂O₂₋ Ti·xTHF. Elemental analysis and ¹H NMR showed that x was close to 1. The catalyst yield was 1.43 g (99%). FT-IR (cm⁻¹): 1608 (M,SH), 1601 (S), 1586 (M), 1554 (S), 1506 (M,SH), 1497 (M), 1482 (W), 1427 (M), 1386 (M,BR), 1362 (W), 670 (W), 625 (W), 612 (W), 595 (W), 565 (W), 542 (W), 497 (W), 462 (W), 455 (W,SH), 402 (W), 363 (W,BR). Raman (cm⁻¹): 1587 (S), 1554 (W), 1427 (S), 1294 (S), 1171 (W) 893 (W), 564 (W), 458 (W), 367 (W), 323 (W). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.24-1.68$ (m, 18H, t-Bu), 6.46-7.62 (mbroad, 10H, Ar-H), 7.88-8.18 (m-broad) (2H, CH=N). Calculated for C28H30Cl2N2O2Ti THF (FW 617.43): C 62.25%, H 6.20%, N 4.54%, Ti 7.75%; Found: C 62.41%, H 6.19%, N 4.70%, Ti 7.73%.

2.11. Multinuclear catalyst MNTi-4 (see Scheme 5)

The title catalyst MNTi-4 was synthesized via the same procedure as MNTi-1 using ligand BFI-4 (0.60 g, 1.16 mmol) in 20 mL THF and equimolar TiCl₄ (0.220 g, 1.16 mmol) in 15 mL THF. The multinuclear catalyst MNTi-4 was obtained as a deep reddishbrown solid with a general repeating unit of $C_{35}H_{36}Cl_2N_2O_2$. Ti·xTHF. Elemental analysis and ¹H NMR showed that x was close to 1. The catalyst yield was 0.81 g (99%). FT-IR (cm⁻¹): 1606 (M), 1591 (M), 1551 (S), 1487 (M), 1451 (W), 1433 (M), 1422 (M), 1384 (M,SH), 1362 (W), 596 (W), 564 (W), 498 (W), 471 (W), 443 (W), 362 (W,BR). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.21-1.60$ (m, 18H, *t*-Bu), 3.78–3.94 (m-broad, 2H, CH₂), 6.71–7.43 (m-broad, 14H, Ar–H), 7.83–8.10 (m-broad, 2H, CH=N). Calculated for $C_{35}H_{36}Cl_2N_2O_2$. Ti•THF (FW 707.55): C 66.20%, H 6.27%, N 3.96%, Ti 6.77%; Found: C 66.34%, H 6.37%, N 4.02%, Ti 6.58%.

2.12. Multinuclear catalyst MNTi-5 (see Scheme 6)

2.12.1. Synthesis of BFI-1-(TiCl₃)₂ solution in THF

To a stirred solution of BFI-1 (0.50 g, 0.96 mmol) in THF (15 mL), a solution of *n*-butyllithium (1.6 M, 1.2 mL, 1.92 mmol) in hexane was added dropwise over a period of 10 min at -78 °C. Then the mixture was allowed to warm to room temperature and stirred for two hours. The resulting solution was added dropwise to a stirred solution of TiCl₄ (0.364 g, 1.92 mmol) in THF (15 mL) at -78 °C via a cannula over a period of 20 min. The resulting mixture was again warmed to room temperature and stirred for 18 h affording a solution of BFI-1-(TiCl₃)₂ in THF.

2.12.2. Synthesis of catalyst MNTi-5

To a stirred solution of BFI-4 (0.50 g, 0.96 mmol) in THF (15 mL), a solution of *n*-butyllithium (1.6 M, 1.2 mL, 1.92 mmol) in hexane was added dropwise over a period of 10 min at -78 °C. Then the mixture was allowed to warm to room temperature and stirred for two hours. The resulting solution was added dropwise to the solution of BFI-1-(TiCl₃)₂ via a cannula over a period of 20 min at -78 °C. The resulting mixture was warmed to room temperature and stirred for 18 h. After removal of THF, the residue was extracted with DCM (40 mL) and filtered to give a clear solution. Removal of DCM gave a deep reddish-brown solid which was ground to a fine powder. The multinuclear catalyst was dried in vacuo at room temperature for several hours until its weight was equal to the theoretical yield calculated with C35H36Cl2N2O2TioTHF. The catalyst has a general repeating unit of C₃₅H₃₆Cl₂N₂O₂Ti•xTHF. Elemental analysis and ¹H NMR showed that x was close to 1. The catalyst yield was 1.36 g (100%). FT-IR (cm⁻¹): 1606 (M,SH), 1590 (M), 1554 (S), 1502 (W), 1486 (W), 1430 (M,BR), 1392 (M,SH), 1362 (W), 650 (W,BR), 600 (W), 592 (W,SH), 564 (W), 498 (W,BR), 458 (W), 362 (W). Raman (cm⁻¹): 1584 (S), 1541 (S), 1427 (S), 1378 (M), 1302 (S), 1244 (W), 884 (M, SH), 866(M), 549 (M), 425 (W), 369 (W), 327 (W). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.20 - 1.65$ (m, 18H, *t*-Bu), 3.55 - 3.59 (m-broad), 3.83–3.91 (m-broad) (2H, CH₂), 6.50–7.66 (m-broad, 14H, Ar-H), 7.81(s), 7.83 (s), 7.92-8.09 (m-broad), 8.13 (s), 8.15 (s), 8.17 (s), 8.18 (s), 8.22 (s) (2H, CH=N). Calculated for C35H36Cl2N2O2Ti•THF (FW 707.55): C 66.20%, H 6.27%, N 3.96%, Ti 6.77%; Found: C 66.34%, H 6.35%, N 3.96%, Ti 6.55%.

2.13. Multinuclear catalyst MNZr-1 (see Scheme 4)

The title catalyst MNZr-1 was synthesized via the same procedure as MNTi-1 using ligand BFI-1 (1.00 g, 1.93 mmol) and equimolar ZrCl₄ (0.450 g, 1.93 mmol). The multinuclear Zr catalyst was obtained as pale yellow solid with a general repeating unit of $C_{35}H_{36}Cl_2N_2O_2Zr \cdot xTHF$. Elemental analysis and ¹H NMR showed that x was close to 1. The catalyst yield was 1.42 g (98%). FT-IR (cm⁻¹): 1610 (M), 1590 (S), 1553 (S), 1513 (M,SH), 1503 (M), 1482 (W), 1428 (M), 1389 (M,BR), 1360 (W), 650 (W,BR), 635 (W), 601 (W), 574 (W), 548 (W), 526 (W), 500 (W,BR), 480 (W), 445 (W), 426 (W), 370 (W), 330 (W). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.26-1.58$ (m, 18H, *t*-Bu), 3.65 (broad, 2H, CH₂), 6.68–7.65 (m-broad, 14H, Ar–H), 7.97–8.10 (m-broad), 8.15 (s), 8.16 (s), 8.21 (s) (2H, CH=N). Calculated for $C_{35}H_{36}Cl_2N_2O_2Zr\bulletTHF$ (FW 750.91): C 62.38%, H 5.91%, N 3.73%, Zr 12.15%; Found: C 62.50%, H 6.10%, N 3.71%, Zr 12.15%.

2.14. Multinuclear catalyst MNZr-2 (see Scheme 4)

The title catalyst MNZr-2 was synthesized via the same procedure as MNTi-1 using ligand BFI-2 (1.00 g, 1.98 mmol) in 30 mL THF and equimolar ZrCl₄ (0.461 g, 1.98 mmol) in 30 mL THF. The multinuclear catalyst MNZr-2 was obtained as a pale yellow solid

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Scheme 6. Synthesis of multinuclear catalysts with two different bis-phenoxy-imine ligands.

with a general repeating unit of $C_{34}H_{34}Cl_2N_2O_2Zr \cdot xTHF$. Elemental analysis and ¹H NMR showed that x was close to 1. The catalyst yield was 1.43 g (98%). FT-IR (cm⁻¹): 1607 (M,SH), 1590 (S), 1553 (S), 1488 (M), 1428 (M), 1391 (M), 1361 (W), 654 (W), 602 (W), 558 (W), 445 (W), 370 (W), 330 (W). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.24-1.63$ (m, 18H, *t*-Bu), 6.79–7.70 (m-broad, 14H, Ar–H), 7.88–8.30 (m-broad) (2H, CH=N). Calculated for C₃₄H₃₄Cl₂N₂O₂Zr•THF (FW 736.88): C 61.94%, H 5.74%, N 3.80%, Zr 12.38%; Found: C 61.83%, H 5.71%, N 3.94%, Zr 11.30%.

2.15. Multinuclear catalyst MNZr-3 (see Scheme 4)

The title catalyst MNZr-3 was synthesized via the same procedure as MNTi-1 using ligand BFI-3 (0.50 g, 1.17 mmol) in 20 mL THF and equimolar ZrCl₄ (0.273 g, 1.17 mmol) in 15 mL THF. The multinuclear catalyst MNZr-3 was obtained as a pale yellow solid with a repeating unit of $C_{28}H_{30}Cl_2N_2O_2Zr \cdot xTHF$. Elemental analysis and ¹H NMR showed that x was close to 1. The catalyst yield was 0.77 g (100%). FT-IR (cm⁻¹): 1611 (M,SH), 1597 (S), 1589 (S), 1553 (S), 1506 (M), 1495 (M), 1482 (W), 1460 (W), 1426 (M,BR), 1390 (M), 1361 (W), 662 (W), 618 (W), 445 (W,BR), 370 (W,BR), 330 (W,BR). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.26-1.62$ (m, 18H, *t*-Bu), 6.44–7.58 (m-broad, 10H, Ar–H), 7.92–8.22 (m-broad) (2H, CH=N). Calculated for $C_{28}H_{30}Cl_2N_2O_2Zr \cdot THF$ (FW 660.79): C 58.16%, H 5.80%, N 4.24%, Zr 13.81%; Found: C 58.31%, H 5.92%, N 4.28%, 13.78%.

2.16. Multinuclear catalyst MNZr-4 (see Scheme 5)

The title catalyst MNZr-4 was synthesized via the same procedure as MNTi-1 using ligand BFI-4 (0.60 g, 1.16 mmol) in 20 mL THF and equimolar ZrCl₄ (0.270 g, 1.16 mmol) in 15 mL THF. The multinuclear catalyst MNZr-4 was obtained as a pale yellow solid with a general repeating unit of $C_{35}H_{36}Cl_2N_2O_2Zr \cdot xTHF$. Elemental analysis and ¹H NMR showed that x was close to 1. The catalyst yield was 0.87 g (100%). FT-IR (cm⁻¹): 1607 (M), 1589 (S), 1551 (S), 1482 (M), 1451 (W), 1432 (M), 1390 (M), 1361 (W), 665 (W), 616 (W), 584 (W), 556 (W), 500 (W), 460 (W), 330 (W). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.21-1.46$ (m, 18H, *t*-Bu), 3.81–3.92 (mbroad, 2H, CH₂), 6.71–7.43 (m-broad, 14H, Ar–H), 8.04 (s-broad, 2H, CH=N). Calculated for C₃₅H₃₆Cl₂N₂O₂Zr•THF (FW 750.91): C 62.38%, H 5.91%, N 3.73%, Zr 12.15%; Found: C 62.56%, H 6.27%, N 3.90%, Zr 12.13%.

2.17. Multinuclear catalyst MNZr-5 (see Scheme 6)

The title catalyst MNZr-5 was synthesized via the same procedure as MNTi-5 using BFI-1 (0.50 g, 0.96 mmol), BFI-4 (0.50 g, 0.96 mmol) and ZrCl₄ (0.447 g, 1.92 mmol). The catalyst MNZr-5 was obtained as a pale yellow solid with a general repeating unit of $C_{35}H_{36}Cl_2N_2O_2Zr \cdot xTHF$. Elemental analysis and ¹H NMR showed that x was close to 1. The catalyst yield was 1.41 g (98%). FT-IR (cm⁻¹): 1608 (M), 1589 (S), 1553 (S), 1485 (M), 1432 (M,BR), 1390 (M), 1361 (W), 665 (W), 650 (W), 601 (W), 585 (W), 558 (W), 500 (W), 445 (W,BR), 370 (W, BR), 330 (W,BR). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.19-1.61$ (m, 18H, *t*-Bu), 3.65 (broad), 3.82–3.98 (mbroad) (2H, CH₂), 6.70–7.40 (mbroad, 14H, Ar–H), 7.75(s), 7.78 (s), 8.01–8.12 (mbroad), 8.15 (s), 8.17 (s), 8.20 (s), 8.21 (s), 8.25 (s) (2H, CH=N). Calculated for $C_{35}H_{36}Cl_2N_2O_2Zr \bullet THF$ (FW 750.91): C 62.38%, H 5.91%, N 3.73%, Zr 12.15%; Found: C 62.51%, H 6.12%, N 3.81%, Zr 12.09%.

3. Results and discussions

3.1. Three strategies to form Methylene-linked multinuclear catalysts

Containing two phenoxy-imine ligands is one of the key features of the mono-nuclear FI catalyst (see Scheme 1). Hence, here we use

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three strategies to bridge the mono-nuclear catalyst to form methylene-linked multinuclear catalysts: (I) Link the aniline fragment to make the catalysts MNTi-1 and MNZr-1 (see Scheme 4), (II) Link the phenolate fragment to make the catalysts MNTi-4 and MNZr-4 (see Scheme 5) and (III) Use a combination of the above two linking strategies to make the catalysts MNTi-5 and MNZr-5 (see Scheme 6).

3.2. Catalytic activity and stability of methylene-linked multinuclear catalysts

The multinuclear catalysts were evaluated for ethylene polymerization for different reaction times using MAO as co-catalyst (see Tables 1 and 2). The results showed that all the methylenelinked multinuclear catalysts displayed higher activity and better stability than the corresponding mono-nuclear catalysts (see Figs. 3 and 4, also see Fig. S1-S9 in supporting information). For multinuclear Ti-based catalysts, the catalyst MNTi-1 showed much higher activity and much slower catalyst decay compared to its mono-nuclear counterpart FI-Ti at 60 °C in hexane. Its cumulative average activities after 30, 60 and 120 min were 1.4, 2.0 and 2.4 times higher than those of FI-Ti (see entries 1-3 and 16-18 in Table 1). The average activities over the three reaction periods of 0-30 min, 30-60 min and 60-120 min, can be obtained by comparing the productivity of three reaction times (30, 60 and 120 min). The average activities of the multinuclear MNTi-1 over the above three reaction periods were 1.4, 4.5, and 5.8 times higher than those of FI-Ti. The other two multinuclear catalysts MNTi-4 and MNTi-5 with different linking strategies also showed improvements in catalytic activity and stability (see entries 10-15). Both MNTi-4 and MNTi-5 were 1.7 times more active than FI-Ti over a 120 min period (see entries 12, 15 and 18 in Table 1). When comparing the linking strategies, MNTi-1 with the anilines linked is more active than MNT-4 with the phenolates linked.

The three methylene-linked multinuclear Zr-based catalysts also displayed much improved activity and stability compared to the mono-nuclear FI-Zr catalyst (see Fig. 4). The cumulative average activities of MNZr-1 after 5, 15, 30, 60 and 120 min were 1.9, 2.4, 2.7, 3.3 and 4.3 times higher, respectively, than those of mono-nuclear FI-Zr (see entries 1–5 and 26–30 in Table 2). During the second hour of polymerization, MNZr-1 still attains a high activity of

Table 1			
Ethylene polymerization	with	MNTi and FI-Ti ^a .	

Entry	Cat.	Time (min)	PE (g)	Activity ^b ($\times 10^3$)	$M_{\rm n}$ (×10 ³)	$M_{\rm w}/M_{\rm n}$
1	MNTi-1	30	6.55	2.65	651	2.5
2	MNTi-1	60	11.19	2.26	662	2.9
3	MNTi-1	120	15.61	1.58	740	3.2
4	MNTi-2	30	7.14	2.88	642	4.5
5	MNTi-2	60	12.92	2.61	716	4.1
6	MNTi-2	120	20.02	2.02	828	3.7
7	MNTi-3	30	7.34	2.97	445	7.2
8	MNTi-3	60	11.93	2.41	357	9.6
9	MNTi-3	120	16.10	1.63	693	5.7
10	MNTi-4	30	6.01	2.43	285	8.5
11	MNTi-4	60	8.42	1.70	664	3.6
12	MNTi-4	120	10.82	1.09	887	6.0
13	MNTi-5	30	4.85	1.96	492	4.7
14	MNTi-5	60	7.92	1.60	903	3.0
15	MNTi-5	120	10.87	1.10	984	3.9
16	FI-Ti	30	4.69	1.89	329	2.0
17	FI-Ti	60	5.73	1.16	385	2.0
18	FI-Ti	120	6.49	0.66	493	3.2

 $^a~300$ mL stainless steel autoclave, 100 mL of hexane, 5.5 bar of ethylene pressure, 60 °C, 2.0 mmol of MAO, catalyst loading: 0.9 μ mol metal.

 b kg_{PE} mol_M⁻¹ h⁻¹ bar⁻¹.

Table 2

Entry	Cat.	Time (min)	PE (g)	Activity ^b ($\times 10^3$)	$M_{\rm n}(imes 10^3)$	M_w/M_n
1	MNZr-1	5	2.74	66.4	6.8	35.2
2	MNZr-1	15	4.27	34.5	10.3	41.0
3	MNZr-1	30	4.94	20.0	12.0	47.3
4	MNZr-1	60	6.20	12.5	14.2	56.0
5	MNZr-1	120	8.46	8.55	23.4	38.6
6	MNZr-2	5	2.78	67.4	38.0	6.8
7	MNZr-2	15	4.11	33.2	15.5	11.9
8	MNZr-2	30	6.68	27.0	16.8	14.7
9	MNZr-2	60	8.91	18.0	34.0	42.2
10	MNZr-2	120	9.73	9.83	40.2	7.6
11	MNZr-3	5	1.93	46.8	9.4	46.5
12	MNZr-3	15	3.97	32.1	11.5	75.9
13	MNZr-3	30	6.29	25.4	11.3	118
14	MNZr-3	60	8.16	16.5	10.8	135
15	MNZr-3	120	9.73	9.83	18.8	111
16	MNZr-4	5	2.11	51.2	17.2	56.4
17	MNZr-4	15	3.69	29.8	41.4	45.3
18	MNZr-4	30	4.74	19.2	31.6	54.0
19	MNZr-4	60	6.33	12.8	32.3	70.5
20	MNZr-4	120	7.38	7.45	29.1	83.9
21	MNZr-5	5	3.11	75.4	11.0	43.0
22	MNZr-5	15	5.78	46.7	22.6	52.5
23	MNZr-5	30	8.00	32.3	16.7	69.7
24	MNZr-5	60	10.23	20.7	35.6	44.4
25	MNZr-5	120	12.45	12.6	35.3	59.1
26	FI-Zr	5	1.44	34.9	3.43	6.1
27	FI-Zr	15	1.76	14.2	3.63	10.2
28	FI-Zr	30	1.81	7.31	4.29	19.1
29	FI-Zr	60	1.89	3.82	4.56	67.8
30	FI-Zr	120	1.96	1.98	5.10	36.0

 a 300 mL stainless steel autoclave, 100 mL of hexane, 5.5 bar of ethylene pressure, 60 °C, 2.0 mmol of MAO, catalyst loading: 0.09 μ mol metal.

^b kg_{PE} mol_M⁻¹ h^{-1} bar⁻¹.

 $4.57 \times 10^3 \text{ kg}_{\text{PE}} \text{ mol}_{\text{M}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$, but FI-Zr dropped to a very low activity after 1 h. The other two new catalysts MNZr-4 and MNZr-5 showed similar improvements in activity and stability. Compared to the activities of FI-Zr after 5, 15, 30, 60 and 120 min, the cumulative average activities of MNZr-4 were 1.5, 2.1, 2.6, 3.3 and 3.8 times higher (see entries 16–20, Table 2), while the cumulative average activities of MNZr-5 were 2.2, 3.3, 4.4, 5.4 and 6.4 times higher (see entries 21–25, Table 2).



Fig. 3. Productivity comparison of MNTi-1, 4 and 5 with FI-Ti.

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Fig. 4. Productivity comparison of MNZr-1, 4 and 5 with FI-Zr.

3.3. Molecular weight (MW) and polydispersity (M_w/M_n)

Besides being more active and stable, the methylene-linked multinuclear catalysts also produced polyethylene of higher MW compared to the corresponding mono-nuclear catalysts (see Tables 1 and 2). For example, the M_n of the polyethylene produced during 2 h of polymerisation was much higher for MNTi-1, MNTi-4 and MNTi-5 (M_n = 740 × 10³, 887 × 10³ and 984 × 10³) than that of FI-Ti (M_n = 493 × 10³). Similarly, the M_n of the polyethylene produced by MNZr-1, MNZr-4 and MNZr-5 (M_n = 23.4 × 10³; 29.1 × 10³ and 35.3 × 10³) was much higher than that of FI-Zr (M_n = 5.10 × 10³).

On the other hand, the multinuclear catalysts afforded broader molecular weight distributions (MWD) compared to the corresponding mono-nuclear catalysts. For example, after 60 min, the M_w/M_n was 2.9, 3.6 and 3.0 for MNTi-1, MNTi-4 and MNTi-5, respectively, while for FI-Ti the M_w/M_n was only 2.0. For the Zrbased catalysts, both the MNZr catalysts and FI-Zr afforded very broad MWDs after long reaction times (60 min and 120 min). Contrastingly, after only 5 min reaction time, the MWD was much broader for MNZr-1, MNZr-4 and MNZr-5 ($M_w/M_n = 35.2$, 56.4 and 43.0) than that of FI-Zr ($M_w/M_n = 6.1$). When comparing the multinuclear Ti vs Zr catalysts, the MNTi were found to produce polyethylene of higher MW and narrower MWD than MNZr (for 2-h run time, MNTi-1: $M_n = 740 \times 10^3$, $M_w/M_n = 3.2$ vs MNZr-1: $M_n = 23.4 \times 10^3$, $M_w/M_n = 38.6$, see entry 3 in Table 1, entry 5 in Table 2). The broader MWD of polyethylene produced by the multinuclear catalysts is consistent with them behaving more like multi-site Ziegler-Natta catalysts than single-site homogeneous catalysts.

3.4. The impact of bridging spacer in ethylene homopolymerization

For methylene-linked multinuclear catalysts MNTi-1 and MNZr-1, the bridging spacer between the two imine-N is $-C_6H_5CH_2C_6H_5-$ (see Scheme 4). Because the bridging spacer controls the distance between the metal centres, it is expected to have an impact on the catalytic capabilities. Hence it is essential to study the effect of bridging spacer.

Here we selected two more different bridging spacers $(-C_6H_5C_6H_5-$ and $-C_6H_5-)$ and prepared the corresponding

ligands BFI-2 and 3 and multinuclear catalysts MNTi-2 and 3. The crystal structures of BFI-2 and BFI-3 clearly showed that the two phenoxy-imine unites cannot coordinate to a single metal atom, therefore it is impossible to form mononuclear catalyst (see Fig. S12 and S13 in supporting information). The ethylene polymerization results showed that MNTi-2 with -C₆H₅C₆H₅- as the bridging spacer displayed the highest activity and slowest decay with an activity of 2.88 \times 10³ Kg_{PE} mol_M⁻¹ h⁻¹ bar⁻¹ for a 30 min run (see entry 4, Table 1). Its cumulative average activities after 30, 60 and 120 min run times were 1.5, 2.3, and 3.1 times higher (see entries 4-6, Table 1) compared to those of FI-Ti (see entries 16-18, Table 1). When measured over the three reaction periods of 0-30, 30-60, and 60-120 min, its average activities were 1.5, 5.6, and 9.3 times higher relative to FI-Ti. When the bridging spacer was further shortened to one phenyl $(-C_6H_5-)$, the corresponding catalyst MNTi-3 was still more active and stable than FI-Ti. However, MNTi-3 produced polyethylene with the broadest MWD among the catalysts MNTi-1~3 because the shortest bridging spacer results in the most crowded metal centres. For example, after 60 min, the Mw/Mn was 9.6 for MNTi-3, which is broader than in the case of MNTi-1 and MNTi-2 ($M_w/M_n = 2.9$ and 4.1). Compared to the flexible bridging spacer -C₆H₅CH₂C₆H₅-, the two spacers -C₆H₅C₆H₅and $-C_6H_5-$ are more rigid and hence the distance between the metal centres may be better controlled. This could be the reason why both MNTi-2 and MNTi-3 afforded higher activity and better stability than MNTi-1 with a flexible spacer $(-C_6H_5CH_2C_6H_5-)$.

On the other hand, the multinuclear catalysts MNZr-2 and 3 containing two different bridging spacers ($-C_6H_5C_6H_5-$ and $-C_6H_5-$) were also prepared and investigated together with MNZr-1. The results showed that all the catalysts displayed improvements in catalytic activity and stability relative to their mono-nuclear analogue (see entries 1–15, Table 2). After 120 min of run time, the activities of MNZr-1~3 were 4.3, 5.0 and 5.0 times higher than that of FI-Zr. The MNZr-3 with shortest bridging spacer ($-C_6H_5-$) afforded the broadest MWD. For example, its M_w/M_n after 60 min of polymerisation was 135, which is broader than those obtained with MNZr-1~2 ($M_w/M_n = 56.0$ and 42.2, respectively).

The bridging spacer can also affect the reactor fouling. MNTi-1 and MNTi-3 showed reduced levels of fouling compared to the mono-nuclear catalyst FI-Ti which caused severe reactor fouling (see Fig. S11 in supporting information). Interestingly, MNTi-2 can significantly reduce reactor fouling besides displaying the highest activity and the best stability. The reactor is still quite clean after 2 h polymerization (see Fig. S10 in supporting information). In conclusion, multinuclear catalysts with suitable bridging spacers (such as $-C_6H_5C_6H_5-$) resemble heterogeneous catalysts with respect to reactor fouling. This is important for achieving continuous production in industrial applications.

3.5. The impact of bridging spacer in copolymerization of ethylene and propylene

The multinuclear MNTi-1~3 catalysts were investigated for the copolymerization of ethylene and propylene (see Table 3). The levels of methyl branching obtained with MNTi-1~3 were 12.4%, 14.0% and 18.4% for the three different bridging spacers $(-C_6H_5CH_2C_6H_5-, -C_6H_5C_6H_5- \text{ and } -C_6H_5-)$, indicating that the shortest bridging spacer afforded the highest propylene incorporation. Compared to the mono-nuclear FI-Ti, the MNTi-3 with short bridging spacer $(-C_6H_5-)$ demonstrated improved propylene incorporation (methyl branching: 18.4% vs 13.5%) while also displaying a higher activity (729 vs 419 Kg_{PE} mol_M⁻¹ h⁻¹ bar⁻¹). This result is consistent with that of bi-metallic catalysts which was reported to display a cooperative effect to improve their copolymerization capability [29–31].

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Table 3

Copolymerization of ethylene and propylene with MNTi-1~3 and FI-Ti^a.

Entry	Cat.	Bridging spacer	PE (g)	Activity ^b	Branch (wt%)	$M_{\rm n}(imes 10^3)$	M_w/M_n
1	MNTi-1	-C ₆ H ₅ CH ₂ C ₆ H ₅ -	12.0	571	12.4	191	3.0
2	MNTi-2	$-C_{6}H_{5}C_{6}H_{5}-$	16.7	795	14.0	190	3.6
3	MNTi-3	-C ₆ H ₅ -	15.3	729	18.4	94	5.5
4	FI-Ti	N.A.	8.8	419	13.5	206	2.5

^a 1L stainless steel autoclave, 600 mL of hexane, 4.0 bar of ethylene pressure, 3.0 bar of propylene pressure, 12.0 mmol of MAO, catalyst loading: 6.0 μmol metal, 60 °C. ^b $kg_{PE} mol_{M}^{-1} h^{-1} bar^{-1}$.

3.6. Catalyst analysis with FT-IR, Raman, ¹H NMR and XPS

For practical applications, we want to use all the obtained catalysts without further purification after they were isolated from LiCl because washing with solvents or re-crystallization or reprecipitation from solvents usually loses much catalyst resulting in much lower yield. The solvent residue THF can be removed from the catalyst by Al(III) in excess MAO since Al (III) is a stronger Lewis acid [32]. Hence the catalyst can be completely activated by MAO and display its catalytic capability.

To understand the formation of multinuclear catalysts, their metal coordination environments were studied with FT-IR and Laser Raman spectroscopy. In the mid-IR spectra of Ti-based catalysts (see left spectra in Fig. 5), the C=N vibrations ($v_{C}=_{N}$) of ligands BFI-1, BFI-2, BFI-3, BFI-4 and FI were observed at 1616, 1611, 1605, 1618 and 1615 cm⁻¹. After coordination to titanium, all the C= N vibrations displayed a similar blue-shift. In MNTi-1~3, MNTi-5 and FI-Ti, all the C=N vibrations shifted to the same position at 1554 cm⁻¹, while the C=N vibration of MNTi-4 shifted to 1551 cm⁻¹. This may be due to MNTi-4's linker (methylene) which make the conjugated system ($C_6H_5-C=N$) more electro-rich. In the far-IR spectra of Ti-based catalysts (see right spectra in Fig. 5), the Ti-O bond vibrations (v_{Ti-O}) of MNTi-1–5 and FI-Ti were observed at 498, 500, 497, 498, 498 and 500 cm⁻¹. The Ti–Cl bond vibrations (v_{Ti-Cl}) of MNTi-1-5 and FI-Ti were observed at 460, 460, 462, 472, 458 and 458 cm⁻¹. The Ti–N bond vibrations (v_{Ti-N}) of MNTi-1–5 and FI-Ti were observed at 360, 360, 363, 362, 362 and 365 cm⁻¹. In the mid-IR spectra of Zr-based catalysts (see left spectra in Fig. 6), it can be found that MNZr-1~5 and FI-Zr also displayed a similar blueshift relative to corresponding ligands. The C=N vibrations (ν_{C} =N) of MNZr-1–3, MNZr-5 and FI-Zr were all observed at the same position of 1553 cm⁻¹, while the C=N vibration of MNZr-4 was observed at 1551 cm⁻¹ due to a different linking strategy as well. In the far-IR spectra of MNZr-1–3, MNZr-5 and FI-Zr (see right spectra in Fig. 6), the Zr–O, Zr–Cl and Zr–N bonds were observed at 445, 370 and 330 cm⁻¹, respectively. The Zr–N bond of MNZr-4 was also observed at 330 cm⁻¹, but the Zr–O and Zr–Cl bonds could not be identified.

The C=N vibrations (ν_{C} =_N) and the titanium coordination environment comprising of Ti–O, Ti–Cl and Ti–N bonds were also observed in the Laser Raman spectra (see Fig. 7). In general, the MNTi-1~3, MNTi-5 and FI-Ti gave similar spectra. Their C=N vibrations were observed at 1590/1553 cm⁻¹, 1593/1553 cm⁻¹, 1587/ 1554 cm⁻¹, 1584/1541 cm⁻¹ and 1586/1555 cm⁻¹, respectively. Their Ti–O bond vibrations were observed at 889/552/439 cm⁻¹, 889/ 560/447 cm⁻¹, 893/564/458 cm⁻¹, 884/866/549/425 cm⁻¹ and 890/ 558/446 cm⁻¹, respectively. Their Ti–Cl bond vibrations were observed at 362, 364, 367, 369 and 363 cm⁻¹, respectively. Their Ti–N bond vibrations were observed at 325, 334, 323, 327 and 336 cm⁻¹, respectively.

In general, the coordination bonds and coordination geometry are the key factors of an active catalyst. The FT-IR and Raman studies revealed that the multinuclear catalysts have the same coordination bonds relative to the corresponding mono-nuclear catalysts. However, all the multinuclear catalysts were improved in catalytic activity and stability. This may indicate that the multinuclear catalysts have different coordination geometries. Because the imine-H is close to N that is coordinated to metal, the change in



Fig. 5. FT-IR of Ti-based multinuclear catalysts and FI-Ti. (Left: mid-IR. Right: far-IR).

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Fig. 6. FT-IR of Zr-based multinuclear catalyst and FI-Zr. (Left: mid-IR. Right: far-IR).



Fig. 7. Raman spectra of MNTi-1~3, 5 and FI-Ti.

coordination geometry should result in imine-H shift in ¹H NMR. It is reported that the mono-nuclear FI catalyst have five possible isomers and it is believed that the most possible active isomer is *cis*-I (see Scheme 1) [14,16]. In CDCl₃ at RT, we observed one main isomer and two small isomers of FI-Ti (see Fig. 8), the main isomer is most possible to be *cis*-I. For FI-Zr, we observed only one isomer

cis-I in CDCl₃ (see Fig. 8). After the mono-nuclear catalyst was bridged with different strategies or spacers to form multinuclear catalysts, the bridging spacer between the two N–O coordination units may change the N–O coordination behavior with metals in different ways affording a large number of coordination geometries. Accordingly, the imine-H shift in ¹H NMR displayed multiple

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Fig. 8. Comparison of ¹H NMR shifts of imine-H of multinuclear catalysts and FI catalyst.

nature (see Fig. 8). When bridging the imin-N with three different spacers, the imine-H shift became more and more broad with the increasing of the rigidity of the spacer (rigidity order: $-C_6H_5CH_2C_6H_5- < -C_6H_5C_6H_5- < -C_6H_5-$) (see Fig. 8). The multiple imine-H shift of MNTi is similar to that of MNZr with the same ligand, indicating that the bis-phenoxy-imine ligand is crucial in determining the coordination geometries. Especially, MNTi-5 and MNZr-5 using combined linking strategy afforded very complicated imin-H shifts, hence there are more coordination geometries formed in this two catalysts.

Mono-nuclear FI catalyst is a typical fluxional catalyst, isomer cis-I may transfer to other isomers that are less active. In insertiontype polymerization systems, the active catalyst forms a close-ion pair with the MAO-derived counter-anion, which is typically used in large excess (e.g.1000 equiv). Hence transfer of the supporting ligand to the aluminum in MAO is easy and results in fast catalyst deactivation for the mono-nuclear catalysts. Bridging the mononuclear catalyst may have two effects on catalyst structure. One is restricting in the mobility of coordination unit N-O on metal, hence reducing the transformation of *cis*-I to the other isomeric structures. Another effect is limiting in the catalyst mobility to decrease the transfer of ligand from Ti/Zr to Al contained in MAO, this may result in a different interaction of the cationic catalyst and the anionic MAO counteranion. Both of these two effects can stabilize the catalyst to achieve higher activity and longer lifetime. In addition, XPS analysis showed that the metal centers of MNTi-1 and MNZr-1 have a slightly higher binding energy than the mononuclear FI-Ti/Zr catalysts (Ti2p of MNTi-1: 465.0 eV and 458.8 eV *vs* FI-Ti: 464.7 eV and 458.5 eV, $\Delta = +0.3$ ev and +0.3 ev; Zr3d of MNZr-1: 185.2 eV and 182.7 eV vs FI-Zr: 184.6 eV and 182.2 eV, $\Delta = +0.6$ eV and +0.5 eV). In principle, an atom in higher positive oxidation state displays a higher binding energy due to the extra coulombic interaction between the ion core and the photoemitted electron. The higher binding energy of Ti or Zr in multinuclear catalysts may imply that the metal contributes a little more *d* electron cloud to form a stronger (*d-p*) π bond with O and N, hence the multinuclear catalyst is more stable. On the other hand, the higher oxidation state means the metal is more electronphilic, hence it is easier to accept electrons from olefins to form a weak bond for chain initiation and subsequent chain growth in catalytic olefin polymerizations.

The multiple imine-H shifts in ¹H NMR (see Fig. 8) may also indicate that a multinuclear catalyst is a mixture of different structures. Hence the multinuclear catalysts are typical multi-site catalysts behaving like the classical multi-site Ziegler–Natta catalyst used in industry. This is consistent with the GPC results that polyethylene produced with multinuclear catalysts have broader MWD compared to corresponding mono-nuclear catalyst. In addition the multinuclear catalysts with different bis-phenoxy-imine ligands have different structures. At this stage the bridging effect has been clearly demonstrated that it can improve the catalytic activity and stability to produce polymers of higher molecular weight, albeit the

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detailed catalyst structures are still difficult to be made clearer.

4. Conclusion

We developed a new family of multinuclear Group-IV-metal catalysts with self-assembly between metals and bis-phenoxyimine ligands. The bridging spacer between the two phenoxyimine units was selected such that tetradentate coordination of the ligand to a single metal is impossible, and instead the ligand has to coordinate to two metal atoms to form multinuclear catalysts. These multinuclear catalysts can be formed via three bridging strategies, by linking the imine-N, the 4-position of phenolate, or the mixed linking strategy. FT-IR and Laser Raman studies show that the multinuclear catalysts have similar metal coordination environment relative to the corresponding mono-nuclear catalysts. The multiple ¹H NMR shifts of the imine-H are evidence for the formation of multi-site catalysts comprising of different coordination geometries. All of these new catalysts displayed much higher activity, better stability and produced polyethylene of higher MW than the corresponding mono-nuclear phenoxy-imine catalysts. The bridging spacer has an evident effect on the catalytic activity, stability, polyethylene molecular weight and incorporation rate of propylene into the polyethylene backbone. The multinuclear catalyst with shorter bridging spacer, such as phenyl, afforded higher propylene incorporation. In addition, multinuclear catalysts with a biphenyl spacer can reduce reactor fouling in ethylene polymerizations. We hope this study could inspire the development of highly active multinuclear catalysts with self-assembly coordination strategy for olefin polymerizations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.05.036.

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