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# Binuclear Heteroligated Titanium Catalyst Based on Phenoxyimine Ligands: Synthesis, Characterization, and Ethylene (Co)polymerization

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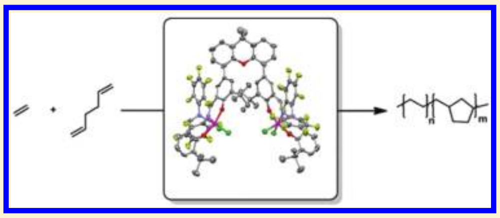
*Supporting Information*



**ABSTRACT:** A binuclear heteroligated titanium(IV) catalyst based on phenoxyimine ligands (**FI$^2$-Ti$_2$**) with its crystal structure elucidated has been developed for the first time for olefin (co)polymerization. In ethylene polymerization, the activity of the binuclear catalyst **FI$^2$-Ti$_2$** can reach $3.0 \times 10^6$ g mol$^{-1}$ h$^{-1}$, and the polydispersity of the resulting polymers is narrow. In copolymerization of ethylene and other olefins, similar incorporation ratios for monoenes are obtained for **FI$^2$-Ti$_2$** and **FI-Ti$_1$**. However, the incorporation ratio of 1,5-hexadiene increases from 3.2% using **FI-Ti$_1$** to 8.8% with **FI$^2$-Ti$_2$**. In comparison, the binuclear monophenoxyimine catalyst, [**FI$^2$-Ti$_2$(THF)$_2$**], exhibits higher catalytic activity and incorporates more $\alpha$-olefins than its mononuclear analogue [**FI-Ti$_1$(THF)**] in the copolymerization. These results are interpreted as consequences of two effects. First, the cooperativity between the two metal centers facilitates the coordination of olefin. Second, the substitutions near the active sites exert a steric effect by blocking and suppressing the binding of comonomers.

## INTRODUCTION

In order to gain control over the properties of polymers by devising and adjusting the structures of organometallic catalysts, non-metallocene catalysts with diamide, $\beta$-diketiminates, iminopyrrolides, amidinates, diimine, alkoxide, and aryl oxide[1a−c] as ligands have been developed since the mid-1990s. Among these candidates, phenoxyimine catalysts demonstrate high performance in both catalytic activity and stereoregularity control in olefin polymerization.[1d,e,2] In particular, the *ortho*-fluorinated *N*-arylbis(phenoxyimine)titanium derivatives catalyze the polymerization of ethylene and/or propylene in a "living" manner,[3] leading to the synthesis of a series of block copolymers with controlled structures.[3b,4] However, very few successful phenoxyimine catalysts have been reported that effectively catalyze random copolymerization of ethylene and other olefins due to the low comonomer incorporation ratio. Polymers with high comonomer incorporation ratio are nonetheless highly desirable, since they can be used as polyolefin elastmers,[5] which have superior properties when compared to common thermoplastic elastomers.

Recently, several examples have been reported suggesting the importance of cooperativity among multiple metallic sites in the development of new catalysts.[6] Coates et al. employed a binuclear cobalt catalyst in the polymerization of racemic terminal epoxides, yielding isotactic polyethers.[7] Guan's group introduced a pyridine group to an $\alpha$-diimine ligand at the axial position. In combination with AlMe$_2$Cl, this catalyst can produce high molecular weight polyethylenes, most likely due to the formation of bimetallic Ni−Al or Pd−Al complexes via a chloride bridge.[8] Marks' group systematically studied a series of binuclear catalysts and found that the binuclear catalysts were more efficient than their mononuclear analogues in olefin polymerization.[9] It was proposed that when the olefinic unit of an alkene comonomer was bound to one of the metal centers, the second highly electrophilic d$^0$ metal center could stabilize the associated alkene, possibly by the agostic effect, thereby modifying relative enchainment and chain transfer rates. It was therefore revealed that the nuclearity and cooperative effects between the two active centers were important. On the basis of these facts, we are particularly interested in bringing two bis(phenoxyimine)titanium catalysts to a close distance by covalently linking them into one molecular framework. This strategy may help develop catalysts that not only possess high catalytic activity but also enchain more comonomers. In this contribution, we report a new binuclear heteroligated titanium catalyst possessing phenoxyimine ligands thus designed and its catalytic properties in the olefin (co)polymerization.

## EXPERIMENTAL SECTION

**Materials and Methods.** All manipulations with air and/or moisture-sensitive compounds were performed under dry nitrogen using standard Schlenk techniques or in a *m*Braun Labstar nitrogen glovebox with a high capacity recirculator (<1 ppm O$_2$). $^1$H and $^{13}$C NMR spectra for small molecules were recorded on a Varian-300 (300 MHz) and a Bruker 400 (400 MHz) spectrometer and referenced versus internal tetramethylsilane. $^{19}$F NMR was recorded on a Varian Inova (289 MHz) and referenced versus external CF$_3$COOH. Elemental analyses were performed using a German Vario EL III

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elemental analyzer. Electron spray ionization (ESI) mass spectra were obtained on a Bruker APEX IV mass spectrometer. X-ray crystallographic data were collected using an MM007-HF CCD (Saturn 724+) detector system (Mo K$\alpha$, $\lambda$ = 0.710 73 Å), and structures were solved and refined using software contained in SHELXS-97 programs.

All solvents ($CH_2Cl_2$, diethyl ether, THF, *n*-hexane, and toluene) for ligand and metal complex synthesis were purified by passing through the *m*Braun solvent purification system and stored over activated 4 Å molecular sieves in resealable flasks. Methylaluminoxane (MAO, 10 wt % Al in toluene) was concentrated in vacuo to dryness (30 Pa) at 30 °C for 24 h. Commercial ethylene was used directly for polymerization without further purification. 1-Hexene, 1-octene, 1,5-hexadiene, and isoprene for polymerization were purchased from the Alfa Aesar Co. and distilled from $CaH_2$ before use. All other reagents and solvents were purchased and used as received.

**General Procedure for Ethylene Homopolymerization by Ti Complexes.** Ethylene polymerizations were carried out in 250 mL three-neck flasks equipped with a large magnetic stirring bar. For this experiment, a preassembled, degassed reactor containing toluene (50 mL) and MAO (250 equiv relative to Ti) was presaturated under ethylene (1.0 atm) and equilibrated at the desired reaction temperature using an external bath. The required amount of the titanium catalyst was dissolved in toluene (2 mL) at room temperature under nitrogen, and the solution was added to the reactor via a gastight syringe to initiate the polymerization. The temperature of the toluene solution was monitored using a thermocouple probe. The temperature rise observed for the exotherm reaction was invariably less than 2 °C during the polymerizations. After a given period of time, the polymerization was quenched by the addition of 2% acidified methanol (15 mL). The polymer was collected by filtration, washed with methanol, and dried in the vacuum line overnight until a constant weight was reached.

**General Procedure for Copolymerization of Ethylene and $\alpha$-Olefins by Ti Complexes.** Copolymerizations were carried out in 250 mL three-neck flasks equipped with a large magnetic stirring bar. In a typical experiment, the comonomer was injected into a preassembled, degassed reactor containing toluene (50 mL) and MAO (250 equiv relative to Ti). The solution was presaturated with ethylene (1.0 atm) and equilibrated to the desired reaction temperature using an external bath. The required amount of the titanium catalyst was dissolved in toluene (2 mL) at room temperature under a nitrogen atmosphere, and the solution was then injected into the reactor via a gastight syringe to initiate the polymerization. The temperature of the toluene solution was monitored by a thermocouple probe. The temperature rise observed for the exotherm reaction was invariably less than 2 °C during the polymerizations. After a given period of time, the polymerization was quenched by the addition of 2% acidified methanol.The polymer was collected by filtration, washed with methanol, and dried in the vacuum line overnight until a constant weight was reached.

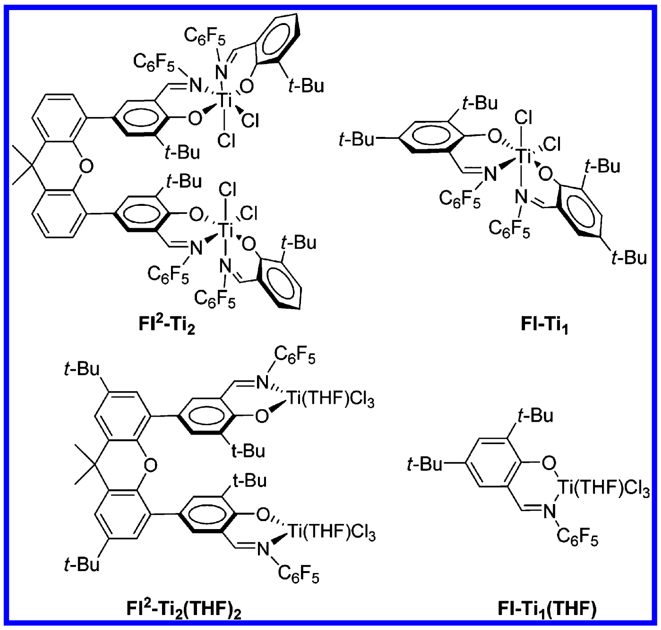
**Polymer Characterization.** $^{13}C$ NMR spectra of the polymers were recorded on a Bruker VXR-400 (100 MHz) spectrometer, and resonance assignments were made according to the literature for copolymers of ethylene–$\alpha$-olefin and ethylene–diene.[11] Gel permeation chromatography (GPC) was carried out at 150 °C for the polymers, with 1,2,4-trichlorobenzene as the eluent at a flow rate of 1.0 mL/min. The experiments were performed on a Waters GPC2000CV instrument coupled with a Waters RI detector and a Waters viscometer detector equipped with four 5 $\mu$m PL gel columns (Polymer Laboratories). Chromatograms were processed with Waters Empower software (version 2002); number-average molecular weight ($M_n$) and polydispersity index ($M_w/M_n$) of the polymers were given relative to PS standards. Melting temperatures of the polymers were measured by DSC (DSC 822$^e$, METTLER TOLEDO) from the second scan with a heating rate of 10 °C/min, unless otherwise noted.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Binuclear Heteroligated Catalysts.

The chemical structures of catalysts **FI$^2$-Ti$_2$**, **FI-Ti$_1$**,[3b] **FI$^2$-Ti$_2$(THF)$_2$**, and **FI-Ti$_1$(THF)** are shown in Chart 1. The xanthene was used as a rigid linker to connect two phenoxyimine catalysts in order to maintain a constant distance between the two active metal centers during the catalytic process.

**Chart 1**

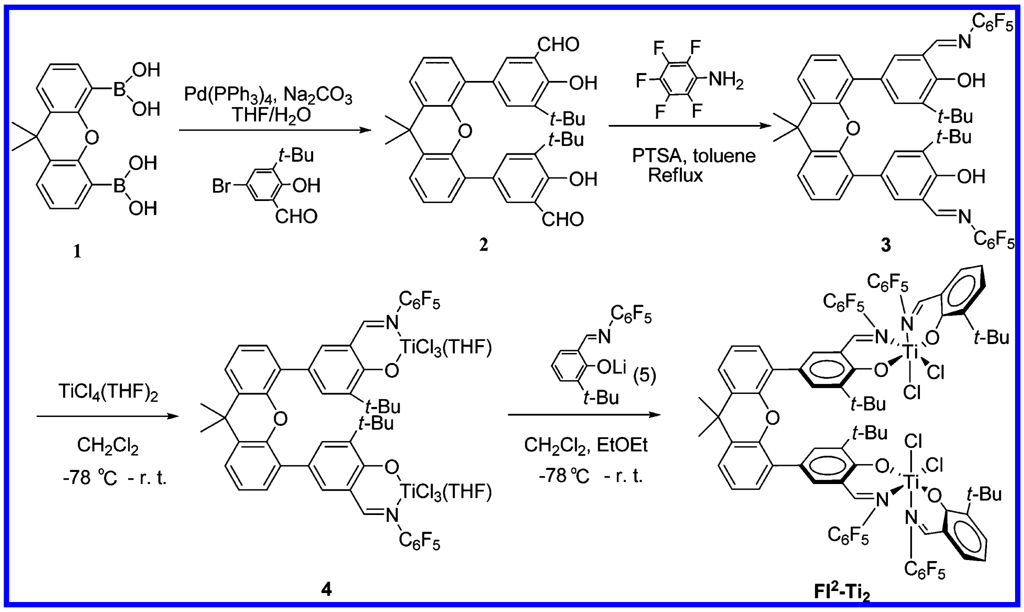


Initially, **FI$^2$-Ti$_2$(THF)$_2$** was synthesized (see Supporting Information) as precursor to react with the lithium salt of phenoxyimine ligand **5** for generating the binuclear heteroligated catalyst. However, the presence of multiple *tert*-butyl groups in the structure made the final heteroligated metal complex difficult to crystallize and separate from the solution, hindering further purification and characterizations. In subsequent studies, xanthene scaffold without *tert*-butyl substitution was used instead, and catalyst **FI$^2$-Ti$_2$** was synthesized successfully (Scheme 1).

9,9-Dimethyl-9*H*-xanthene-4,5-diyldiboronic acid was synthesized following the literature procedures (see Supporting Information). The product then underwent a $Pd(PPh_3)_4$-catalyzed Suzuki coupling with 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde, generating a dialdehyde derivative which was subsequently condensed with pentafluoroanilines to produce ligand **3**. Complex **4** was obtained by the metalation of **3** with tetrachlorobis(tetrahydrofuran)titanium(IV) in dichloromethane, which then reacted with the lithium salt of another phenoxyimine ligand **5** to give the binuclear heteroligated catalyst **FI$^2$-Ti$_2$**.

$^1H$ NMR spectroscopy and elemental analysis both confirmed the structures of **FI$^2$-Ti$_2$(THF)$_2$** and **FI$^2$-Ti$_2$**. Moreover, single crystals of **FI$^2$-Ti$_2$** suitable for X-ray analysis were successfully obtained via a slow diffusion of hexane into a solution of mixed solvents of dichloromethane and ethyl ether. The structure determined by X-ray diffraction crystallography is shown in Figure 1. To the best of our knowledge, this is the first single crystal structure reported for a binuclear heteroligated catalyst based on phenoxyimine ligands. The bimetallic molecule shows a tweezer-like structure of $C_2$ symmetry; four molecules were packed in one unit cell. The distance between the two titanium atoms is 7.88 Å, while the

**Scheme 1. Synthetic Route to the Binuclear Complex $FI^2$-$Ti_2$ (PTSA = *p*-Toluenesulfonic Acid)**



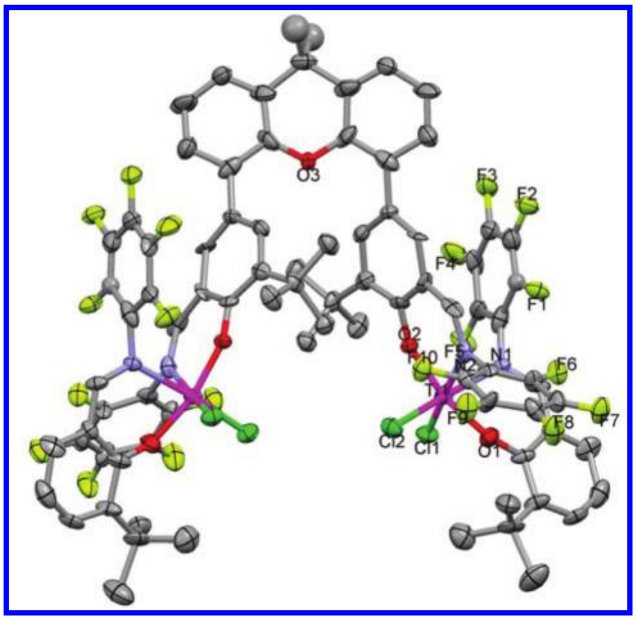


**Figure 1.** Molecular structure of complex **$FI^2$-$Ti_2$** with thermal ellipsoids at 30% probability level.

oxygen−oxygen distance between two phenoxyimine connected by xanthene (O2 in Figure 1) is only 6.35 Å. The elongated distance between Ti atoms suggests significant repulsive interaction between the two catalytic sites. The length of the Ti1−O2 bond is 1.87 Å, which is longer than the Ti−O bond length in catalyst **FI−$Ti_1$**.[3b] The oxygen atoms are still situated in the *trans* configuration in both of the phenoxyimine catalysts. Meanwhile, the chlorine atoms are oriented in the *cis* positions, near the other Ti center, which indicates the two catalytic sites would possibly face each other in the olefin polymerization after removing chloride atoms in the activation process. This arrangement may facilitate the cooperative effect of the two catalytic sites (*vide infra*).

**Polymerization Properties of $FI^2$-$Ti_2$ Complex Activated by MAO.** The ethylene (co)polymerization at ambient pressure was examined using catalysts **$FI^2$-$Ti_2$** and **FI-$Ti_1$** in the presence of methylaluminoxane (MAO) in toluene at 40 °C. The results are summarized in Table 1. The activity of catalyst **$FI^2$-$Ti_2$** in homopolymerization reached 2946 kg $mol^{-1}$ $h^{-1}$, which is similar to that of the mononuclear analogue at the same concentration of the active titanium site. The molecular weight of the produced polymer is $1.7 \times 10^5$ g/mol and the polydispersity index is 1.71, both of which are comparable to those obtained from catalyst **FI-$Ti_1$** (Table 1, entry 1 vs entry 2). The melting point of the product was determined by DSC to be 139 °C, indicating that the polyethylene has a linear structure. The $^1$H and $^{13}$C NMR spectra recorded at a high temperature show no signals of branching points or vinylic end groups were detected, suggesting that a chain transfer to Al is the main termination pathway.[10] These data indicate that catalyst **$FI^2$-$Ti_2$** retains the general polymerization features of phenoxyimine-type catalysts. Additional results of ethylene homopolymerization are summarized in the Supporting Information (Table S6).

In the copolymerization of ethylene and monoenes, **$FI^2$-$Ti_2$** and **FI-$Ti_1$** show similar catalytic activities, and the molecular weights of corresponding copolymers exhibit little difference. Nevertheless, the melting points are much lower than those of ethylene homopolymers. The $^{13}$C NMR spectroscopy confirmed the occurrence of a branched structure and provided the incorporation ratio of the comonomer in the polymer chain.[11] Catalysts **$FI^2$-$Ti_2$** and **FI-$Ti_1$** manifested similar efficiency at incorporating 1-hexene or 1-octene into the copolymer chain (Table 1, entry 3 vs entry 4; entry 5 vs 6). The incorporation ratio of the comonomer is 2.3% for 1-hexene and 2.2% for 1-octene. These data are comparable to those reported by Fujita's group, using the analogous type of catalysts.[13a] However, catalyst **$FI^2$-$Ti_2$** shows much better catalytic properties than the mononuclear catalyst in the copolymerization of ethylene and dienes. When 1,5-hexadiene was employed as the comonomer at a concentration of 1.0 M, catalyst **$FI^2$-$Ti_2$** introduced 8.8% diene comonomer in the polymer chains, which is more than twice the value obtained from **FI-$Ti_1$** (Table 1, entry 7 vs 8). The percentages of *cis*- and *trans*-1,3-cyclopentyl fragments in the polymer chains generated by **$FI^2$-$Ti_2$** were 48% and 52%, respectively, while the corresponding numbers are 30% and

Table 1. Ethylene (Co)polymerization Results for $FI^2$-$Ti_2$ and FI-$Ti_1$ Complexes[a]

| entry | catalyst [μmol] | comonomer | yield [g] | activity [kg/(mol h)] | $M_w$[b] [$\times 10^5$] | $M_w/M_n$[b] | $T_m$[c] [°C] | incorporation (%)[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | **FI-$Ti_1$(2)** | n/a | 0.520 | 3120 | 1.9 | 1.66 | 140 | n/a |
| 2 | **$FI^2$-$Ti_2$(1)** | n/a | 0.491 | 2946 | 1.7 | 1.71 | 139 | n/a |
| 3 | **FI-$Ti_1$(2)** | 1-hexene | 0.156 | 936 | 1.0 | 1.27 | 106 | 3.2 |
| 4 | **$FI^2$-$Ti_2$(1)** | 1-hexene | 0.147 | 882 | 1.8 | 2.65 | 120 | 2.3 |
| 5 | **FI-$Ti_1$(2)** | 1-octene | 0.207 | 1242 | 1.4 | 1.44 | 112 | 2.4 |
| 6 | **$FI^2$-$Ti_2$(1)** | 1-octene | 0.189 | 1134 | 1.5 | 1.73 | 118 | 2.2 |
| 7 | **FI-$Ti_1$(2)** | 1,5-HD | 0.187 | 1122 | 2.0 | 1.64 | 108 | 3.2 |
| 8 | **$FI^2$-$Ti_2$(1)** | 1,5-HD | 0.212 | 1272 | 2.2 | 1.93 | 100 | 8.8 |
| 9 | **FI-$Ti_1$(2)** | 1,5-HD[e] | 0.178 | 1068 | 0.9 | 1.81 | 108 | 1.1 |
| 10 | **$FI^2$-$Ti_2$(1)** | 1,5-HD[e] | 0.194 | 1164 | 1.4 | 1.79 | 106 | 2.6 |
| 11 | **FI-$Ti_1$(2)** | isoprene | trace | n/a | n/a | n/a | n/a | n/a |
| 12 | **$FI^2$-$Ti_2$(1)** | isoprene | 0.101 | 606 | 1.9 | 2.04 | 136 | 2.3[f] |

[a] Copolymerizations carried out for 5 min at 40 °C on a high-vacuum line with 2 μmol of Ti and MAO as cocatalysts (Al:Ti = 250:1) in 50 mL of toluene under an ethylene pressure of 1.0 atm. Comonomer concentration is 1.0 M. [b] From GPC calibrated with polystyrene standards. [c] Data determined by DSC. [d] Comonomer incorporation based on $^{13}C$ NMR spectra.[11a,b] [e] Comonomer concentration is 0.5 M. [f] Comonomer incorporation based on $^1H$ NMR spectra (n/a: not applicable).[11c]

Table 2. Ethylene (Co)polymerization Results for $FI^2$-$Ti_2$(THF)$_2$ and FI−$Ti_1$(THF) Catalysts[a]

| entry | catalyst [μmol] | comonomer | yield [g] | activity [$10^4$ g/(mol h)] | $M_w$[b] [$\times 10^5$] | $M_w/M_n$[b] | $T_m$[c] [°C] | comonomer incorporation (%)[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | **FI-$Ti_1$(THF) (10)** | n/a | 0.057 | 0.6 | 5.1 | 49.3 | 133 | |
| 2 | **$FI^2$-$Ti_2$(THF)$_2$ (5)** | n/a | 0.161 | 1.6 | 6.4 | 3.26 | 138 | |
| 3 | **FI−$Ti_1$(THF) (10)** | 1-hexene (0.5 M) | 0.053 | 0.5 | 3.5 | 18.1 | 113 | 3.0 |
| 4 | **$FI^2$-$Ti_2$(THF)$_2$ (5)** | 1-hexene (0.5 M) | 0.126 | 1.3 | 3.8 | 10.8 | 114 | 6.1 |
| 5 | **FI-$Ti_1$(THF) (10)** | 1-octene (0.7 M) | 0.031 | 0.3 | 4.0 | 27.4 | 116 | 3.7 |
| 6 | **$FI^2$-$Ti_2$(THF)$_2$ (5)** | 1-octene (0.7 M) | 0.068 | 0.9 | 6.4 | 16.1 | 112 | 13.7 |
| 7 | **FI-$Ti_1$(THF) (10)** | 1,5-HD (0.7 M) | trace | n/a | n/a | n/a | n/a | n/a |
| 8 | **$FI^2$-$Ti_2$(THF)$_2$ (5)** | 1,5-HD (0.7 M) | 0.134 | 1.3 | 11 | 4.95 | 108 | 5.6 |

[a] (Co)polymerizations carried out for 1 h at 40 °C in a high-vacuum line with 10 μmol of Ti and MAO as the cocatalysts (Al:Ti = 1000: 1) in 50 mL of toluene under an ethylene pressure of 1.0 atm. [b] From GPC calibrated by polystyrene standards. [c] Data were determined by DSC. [d] Comonomer incorporations based on $^{13}C$ NMR spectra (n/a: not applicable).[11a,b]

70% for **FI-$Ti_1$** produced polymers. When the concentration of 1,5-hexadiene is lowered to 0.5 M, catalyst **$FI^2$-$Ti_2$** still incorporates more 1,5-hexadiene into the polymer chain than **FI-$Ti_1$**. The incorporation ratio is 2.6%, which is more than doubled compared to that in the polymer obtained from **FI-$Ti_1$** (Table 1, entry 9 vs 10). When the comonomer was isoprene, only a trace amount of polymer was observed within the monitored reaction time using catalyst **FI-$Ti_1$**. In contrast, **$FI^2$-$Ti_2$** exhibits an activity of 606 kg $mol^{-1}$ $h^{-1}$ and an incorporation ratio of 2.3% for 1,4-isoprene units under similar conditions (Table 1, entry 11 vs 12).

**Polymerization Properties of $FI^2$-$Ti_2$(THF)$_2$ Complexes Activated by MAO.** Overall, the binuclear catalyst exhibits superior catalytic properties to its mononuclear analogue, especially in the copolymerization of ethylene with dienes. In order to investigate the correlation between the catalyst's structure and properties, we used the **$FI^2$-$Ti_2$(THF)$_2$** as the initiator, which features a less steric environment around the active center.[9f] The polymerization results are compared with those of its mononuclear analogue.

The polymerization of ethylene using **$FI^2$-$Ti_2$(THF)$_2$** and **FI-$Ti_1$(THF)** as catalysts is also performed at an atmosphere pressure in the presence of methylaluminoxanue (MAO) in toluene at 40 °C. The activity of the binuclear catalyst in homopolymerization is found to be $1.6 \times 10^4$ g $mol^{-1}$ $h^{-1}$, also more than twice that of the mononuclear analogue under similar conditions (Table 2, entry 2 vs entry 1). Molecular weight of the polymer obtained from the bimetallic catalyst is $6.4 \times 10^5$ g/mol, higher than that derived from mononuclear catalyst under the same conditions. Similar results are observed in a previous report.[9f] The large value of the polydispersity index (3.26) suggests there are multiple active sites present in the polymerization process.[9f,12] DSC and $^{13}C$ NMR measurements indicate that the polyethylenes had linear structures.

In the copolymerization of ethylene with other olefins, the activity of **$FI^2$-$Ti_2$(THF)$_2$** and the incorporation ratio of comonomers are both found to be higher than those of **FI-$Ti_1$(THF)**. Specifically, in the copolymerization of ethylene with monoenes (Table 2, entry 4 vs entry 3, entry 6 vs entry 5), the activity of the bimetallic catalyst is more than twice the value of the monometallic catalyst. The comonomer incorporation ratios of **$FI^2$-$Ti_2$(THF)$_2$** are 6.1% and 13.7% for 1-hexene and 1-octene, respectively, which are roughly double the values of corresponding monometallic catalyst. The melting points of the resulting copolymers are less than 120 °C, indicating the presence of alkyl branches on the linear chains. The molecular weights of the two copolymers from **$FI^2$-$Ti_2$(THF)$_2$** are both higher than those generated by **FI-$Ti_1$(THF)**, with narrower polydispersity than the former. The improvement is more pronounced in the copolymerization of ethylene with 1,5-hexadiene. The bimetallic catalyst produces a copolymer of the diene at an activity of $1.3 \times 10^4$ g $mol^{-1}$ $h^{-1}$ and incorporates 5.6% of the comonomers in the polymer chain. The $M_w$ is $1.1 \times 10^6$ g/mol and PDI is 4.95. In contrast, the monometallic catalyst produces only a trace amount of polymer, unsuitable for characterizations.

In conclusion, the results from the present investigation indicate that a binuclear catalyst is more efficient in

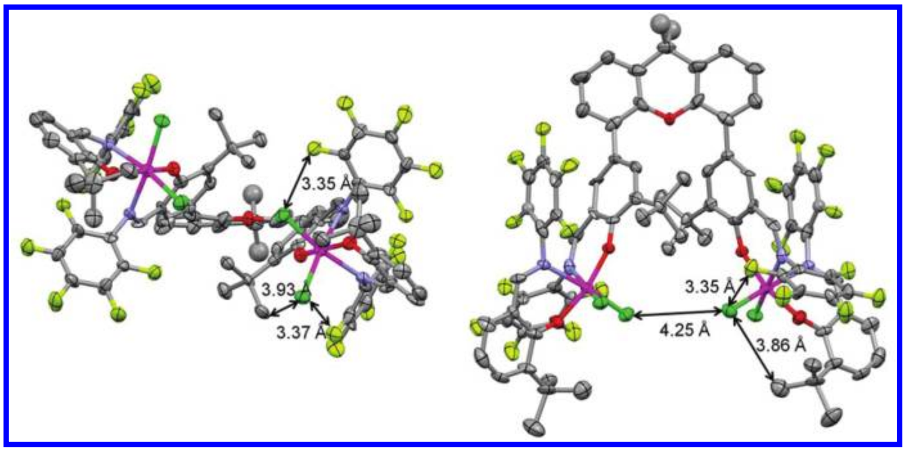


**Figure 2.** Side view (left) and top view (right) of molecular structure of **FI$^2$-Ti$_2$**.

(co)polymerization than its mononuclear analogue, which is probably due to the cooperative effect of the two metal centers.[9f]

**Comparison of FI$^2$-Ti$_2$(THF)$_2$ and FI$^2$-Ti$_2$ and Discussion of Cooperative and Steric Effect.** Comparing the properties of catalysts **FI$^2$-Ti$_2$(THF)$_2$** to **FI$^2$-Ti$_2$**, the activity of ethylene polymerization increased dramatically from $10^4$ to $10^6$ g mol$^{-1}$ h$^{-1}$ upon the introduction of the second phenoxyimine ligand. The smaller molecular weights and the narrower polydispersity of the polymers suggests that **FI$^2$-Ti$_2$** are unlikely to possess multiple catalytic sites, which is exhibited by **FI$^2$-Ti$_2$(THF)$_2$**.

In the copolymerization of ethylene and $\alpha$-olefins, in comparison with their mononuclear analogue, the results are rather different between **FI$^2$-Ti$_2$** and **FI$^2$-Ti$_2$(THF)$_2$**. The catalyst **FI$^2$-Ti$_2$(THF)$_2$** shows a higher activity and incorporates a greater percentage of comonomer into the polymer chains than **FI-Ti$_1$(THF)** in all polymerization experiments. According to the previous report,[9a,f] the *agostic* interaction between the comonomer and metal center can stabilize the coordinated bimetallic olefin complex and enchains olefin comonomers more easily than mononuclear analogues. In addition, in polymerization of the bifunctional comonomer 1,5-hexadiene, the activity is even similar to that of ethylene homopolymerization. We thus reasonably propose that the coordination effect between the two double bonds and two metal centers has a positive impact on this phenomenon.

The heteroligated catalyst **FI$^2$-Ti$_2$** incorporated a similar percentage of monoenes but a greater amount of dienes into copolymers compared to **FI-Ti$_1$**. The unexpected difference of the polymerization capability prompts us to investigate the catalyst's structure in greater detail (Figure 2). The chlorine atoms that become active sites in polymerization are close to each other in **FI$^2$-Ti$_2$**, surrounded by *tert*-butyl groups and pentafluorophenyl groups. The distance between the methyl carbon atom in *tert*-butyl groups and the chlorine atom in the titanium center is only 3.93 Å (Figure 2, side view), while the nearest fluorine atom to the chlorine atom is 3.35 Å (Figure 2, top view). Meanwhile, the chlorine atoms in different titanium centers are close to each other, with a distance of 4.25 Å (Figure 2, top view). Therefore, the steric hindrance in active sites in **FI$^2$-Ti$_2$** is more pronounced than that of **FI-Ti$_1$**, which is unfavorable to the access of the $\alpha$-olefin monomer to the active sites.[9a,13] As a result, there are fewer monoene comonomers incorporated into the polymer chains. As for 1,5-hexandiene, the two double bonds can coordinate with the two metal sites properly, which enhances the binding capability of 1,5-hexadiene, stabilizes the coordination complexes, and therefore facilitates the diene insertion. Consequently, the binuclear catalyst introduced more dienes in the polymer chains. The copolymerization of ethylene and isoprene also shows that the binuclear catalyst is more efficient than its mononuclear analogue. But the methyl group in C2 position of isoprene causes greater steric hindrance and thus lowers the catalytic activity and comonomer incorporation.

## ■ CONCLUSION

We have synthesized and characterized a new heteroligated titanium catalyst, **FI$^2$-Ti$_2$**. To our best knowledge, it is the first reported binuclear heteroligated catalyst based on phenoxyimine ligands with its crystal structure elucidated. For comparison, a monophenoxyimine catalyst **FI$^2$-Ti$_2$(THF)$_2$** was also synthesized. Their performances in ethylene polymerization and copolymerization of ethylene with monoenes or dienes were investigated. **FI$^2$-Ti$_2$(THF)$_2$** exhibits a higher catalytic activity and generally enchains more comonomers than **FI-Ti$_1$(THF)**. However, the overall activity of **FI$^2$-Ti$_2$(THF)$_2$** is relatively low, and the polydispersity of the generated polymer is relatively broad. In contrast, **FI$^2$-Ti$_2$** exhibits a much higher activity and produces polymers with a narrower polydispersity than **FI$^2$-Ti$_2$(THF)$_2$**. In addition, although catalyst **FI$^2$-Ti$_2$** generates similar polymerization results to **FI-Ti$_1$** possibly due to the steric effect, it can enchain dienes more efficiently than its mononuclear analogue. Therefore, the **FI$^2$-Ti$_2$** catalyst has the potential to be applied in the (co)-polymerization of bifunctional monomers, offering new polymer materials.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Synthesis and characterization of ligands and catalysts, tables of crystal structure data, ethylene polymerization results of **FI$^2$-Ti$_2$**, and polymer analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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