

# Synthesis, structure and ethylene polymerization behavior of titanium phosphinoamide complexes

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## Abstract

(Phosphinoamide)(cyclopentadienyl)titanium(IV) complexes of the type  $\text{Cp}^*\text{TiCl}_2(\eta^2\text{-Ph}_2\text{PNR})$  [ $\text{Cp}^*=\text{C}_5\text{Me}_5$ ;  $\text{R} = t\text{-Bu}$  (**2a**),  $\text{R} = n\text{-Bu}$  (**2b**),  $\text{R} = \text{Ph}$  (**2c**)] have been prepared by the reaction of  $\text{Cp}^*\text{TiCl}_3$  with the corresponding lithium phosphinoamides. The structure of  $\text{Cp}^*\text{TiCl}_2(\eta^2\text{-Ph}_2\text{PN}^t\text{Bu})$  (**2a**) and  $\text{Cp}^*\text{TiCl}_2(\eta^2\text{-Ph}_2\text{PNPh})$  (**2c**) have been determined by X-ray crystallography. These complexes exhibited moderate catalytic activities for ethylene polymerization in the presence of modified methylaluminoxane (MMAO). Catalytic activity of up to  $2.5 \times 10^6$  g/(mol Ti h) was observed when activated by  $i\text{-Bu}_3\text{Al/Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ . © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Phosphinoamide; Titanium catalysts; Cocatalyst; Ethylene polymerization

## 1. Introduction

Development of new “single-site” group 4 catalyst precursors for optimizing polymerization catalysis is one of the most attractive subjects in the field of organometallic chemistry [1–4]. Within this area, mono(cyclopentadienyl) complexes of group 4 with an additional monoanionic p-donor ancillary ligand are currently receiving increasing attention. In comparison to conventional metallocene initiators  $\text{Cp}_2\text{MX}_2$ , monocyclopentadienyl complexes  $\text{CpM}(\text{L})\text{X}_2$  offer the advantage of catalyst modification by changing the nature of the spectator ligand, L. Typical p-donor ancillary ligands L that have been used in these catalysts are substituted phenoxides [5,6], amido [7–9], amidinate [10–12], ketimides [13–15], phosphinimides [16], and iminoimidazolide [17].

These mono-Cp Ti or Zr complexes incorporating with cocatalyst have been shown to exhibit appreciable catalytic activities for olefin polymerization. About the ligand of phosphinoamide, Roesky et al. [18] reported homoleptic phosphinoamide complexes of lanthanide. Recently, Kotov et al. [19] reported the phosphorus-bridged Cp-amide Ti complex, which produced linear, high-molecular-weight PE with an activity of  $10^5$  g/(mol Ti h bar). We have also prepared a series of non-bridged phosphinoamide cyclopentadienyl complexes of titanium. We expected that the phosphorus atom in the phosphinoamide can coordinate with the central titanium atom and form a three-membered complex. The  $\eta^2$ -coordination of the phosphinoamide ligand can satisfy to some extent the electron requirement of the electron-deficient metal center by donating the lone-pair electron of phosphorus into vacant titanium orbital, and the three-membered structure will make the complex more electronically flexible [20], which is very important according to Fujita's FI catalysts [21]. Herein, we report

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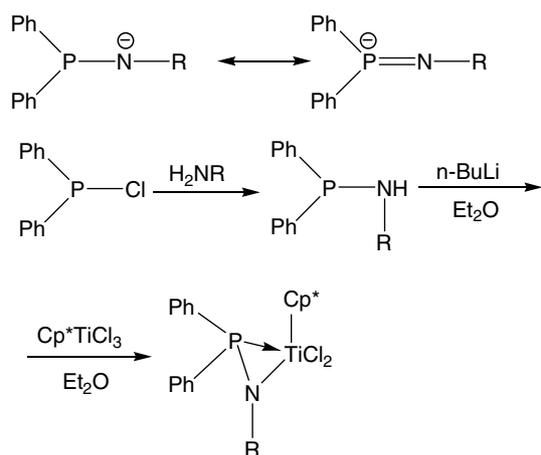
E-mail address: [sbzhang@ciac.jl.cn](mailto:sbzhang@ciac.jl.cn) (S. Zhang).

the synthesis and characterization of several titanium phosphinoamide half-sandwich complexes and the catalytic behavior of these complexes for polymerization of ethylene in the presence of modified methylaluminoxane (MMAO) and *i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>.

## 2. Results and discussion

### 2.1. Synthesis and characterization complexes

The phosphinoamines (**1a–c**) were obtained from the reaction of chlorodiphenyl phosphine with two equivalents of the corresponding amines in good yields accord-



a. R=t-Bu; b. R=n-Bu; c. R=Ph

Scheme 1. The synthesis of complexes **2a–c**.

ing to the literature [22–24]. These ligands are readily deprotonated by *n*-BuLi, and there existed two mesomeric structures in the produced anions in which the negative charge is localized at the N (phosphinoamide) or P (iminophosphide). The phosphinoamide structure is dominant according to the theoretical calculations [25]. The synthesis of complexes **2a–c** is outlined in Scheme 1. When R<sub>2</sub>PN<sup>−</sup>R is reacted with one equivalent of Ti(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Cl<sub>3</sub> in ethereal solution, the phosphinoamide pentamethylcyclopentadienyl titanium complexes can be isolated as red crystals (**2a** and **2c**) or powder (**2b**), respectively.

The red single crystals of complex **2a** and **2c** · CH<sub>2</sub>Cl<sub>2</sub> suited for the X-ray analysis can be grown from ether/hexane or dichloromethane/hexane at −20 °C under argon atmosphere. Crystals were manipulated and mounted in capillaries and a dry argon environment for each crystal when X-ray analysis was performed. Both **2a** and **2c** have two independent molecules in the asymmetric unit, and only one of the two enantiomers in the asymmetric unit is shown, respectively. The ORTEP diagrams of **2a** and **2c** are shown in Fig. 1, and selected bond distances and bond angles are listed in Tables 1 and 2, and crystal data of **2a** and **2c** are summarized in Table 3.

The Ti–N bond lengths of the complex **2a** (2.004(2) and 2.000(2) Å) are longer than that of constrained geometry catalyst (CGC) complexes such as [(C<sub>5</sub>Me<sub>5</sub>)SiMe<sub>2</sub>(N<sup>t</sup>Bu)]TiCl<sub>2</sub> (1.907(4) Å) [26], and non-bridged Ti(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)[N(Me)Cy] (1.870(3) Å) [7] [27], and (<sup>t</sup>Bu<sub>3</sub>P=N)TiCl<sub>3</sub> (1.709(6) Å) [28], but closer to the estimated value (2.02 Å) for Ti–N single bond according to Pauling's covalent radii [29]. The bond lengths Ti–P are

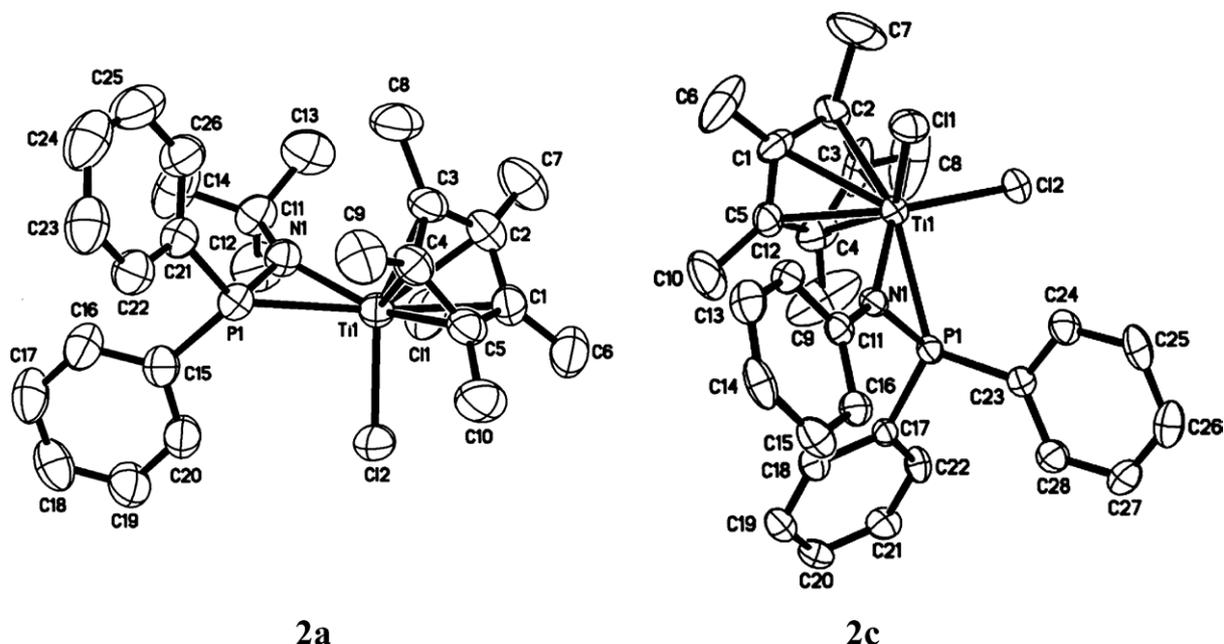


Fig. 1. ORTEP drawings of **2a** and **2c**. Thermal ellipsoids at the 30% level are shown. The hydrogen atoms and CH<sub>2</sub>Cl<sub>2</sub> in **2c** are omitted for clarity.

Table 1  
Selected bond distances (Å) and bond angles (°) for complex **2a**

Bond distances (Å)	
Ti(1)–N(1)	2.004(2)
Ti(1)–P(1)	2.4928(9)
N(1)–P(1)	1.638(2)
Ti(1)–Cl(1)	2.3296(9)
Ti(1)–Cl(2)	2.3287(9)
Bond angles (°)	
N(1)–Ti(1)–P(1)	40.96(6)
N(1)–P(1)–Ti(1)	53.28(8)
P(1)–N(1)–Ti(1)	85.76(9)
Cl(1)–Ti(1)–Cl(2)	92.05(4)

Table 2  
Selected bond distances (Å) and bond angles (°) for complex **2c**

Bond distances (Å)	
Ti(1)–N(1)	1.983(5)
Ti(1)–P(1)	2.477(2)
N(1)–P(1)	1.652(5)
Ti(1)–Cl(1)	2.288(2)
Ti(1)–Cl(2)	2.312(2)
Bond angles (°)	
N(1)–Ti(1)–P(1)	41.66(14)
N(1)–P(1)–Ti(1)	52.93(17)
P(1)–N(1)–Ti(1)	85.4(2)
Cl(1)–Ti(1)–Cl(2)	93.40(8)

Table 3  
Crystal data structure refinements of **2a** and **2c**

Complex	<b>2a</b>	<b>2c</b>
Empirical formula	C <sub>26</sub> H <sub>34</sub> Cl <sub>2</sub> NPTi	C <sub>29</sub> H <sub>32</sub> Cl <sub>4</sub> NPTi
Formula weight	510.31	615.23
Crystal size (mm)	0.25 × 0.18 × 0.10	0.31 × 0.27 × 0.09
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	20.9743(19)	17.473(9)
<i>b</i> (Å)	16.1666(15)	14.950(7)
<i>c</i> (Å)	16.4196(15)	23.084(10)
α (°)	90	90
β (°)	110.900(2)	96.211(12)
γ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	5201.3(8)	5994(5)
<i>Z</i>	8	8
<i>D</i> <sub>calc</sub> (Mg cm <sup>-3</sup> )	1.303	1.363
Absorption coefficient (mm <sup>-1</sup> )	0.610	0.715
<i>F</i> (000)	2144	2544
θ Range for data collected (°)	1.63–25.05	1.77–25.12
Reflection collected	26 749	31 001
Data/restraints/parameters	9158/0/575	10 635/0/658
Independent reflections ( <i>R</i> <sub>int</sub> )	9158 (0.0540)	10 635 (0.1220)
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0445, <i>wR</i> <sub>2</sub> = 0.0960	<i>R</i> <sub>1</sub> = 0.0744, <i>wR</i> <sub>2</sub> = 0.1447
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0717, <i>wR</i> <sub>2</sub> = 0.1057	<i>R</i> <sub>1</sub> = 0.2023, <i>wR</i> <sub>2</sub> = 0.1885
Absorption correction	none	semi-empirical from equivalents
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.973	0.979
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.406 and –0.210	0.619 and –0.516

2.4928(9) and 2.4912(9) Å, which are somewhat shorter than those Ti–P bond distances shown in the literature (ca. 2.63 Å) [30,31]. The longer Ti–N distances than those in typical titanium amide complexes and shorter Ti–P distances than those in typical titanium phosphine complexes can simply be explained by the partial contribution of iminophosphide canonical form. The N–P bond lengths (1.638(2) and 1.640(2) Å, respectively) are longer than the N=P double bond but shorter than N–P single bond, indicate that these bonds have somewhat double bond characters. All of the Ti–Cl bond lengths of 2.3296(9), 2.3287(9), 2.3270(9), and 2.3307(9) Å are in good agreement with those of Cp<sub>2</sub>TiCl<sub>2</sub> [32]. The Cl–Ti–Cl angles are 92.05(4)° and 91.05(3)°, respectively, however, are smaller than that of Cp<sub>2</sub>TiCl<sub>2</sub> which is 94.4°. The small angles of N–Ti–P (40.96(6)° and 41.05(6)°, respectively) maybe result from the double bond character of P–N bonds. About the complex **2c**, it is some similar to the complex **2a**. The Ti–N bonds (1.983(5) and 1.996(5) Å), which are somewhat shorter than that of **2a**, display the single bond character of Ti–N. The Ti–P bonds (2.477(2) and 2.484(2) Å), which also shorter than that of **2a**, show the stronger interaction between Ti and P. The P–N bonds (1.652(5) and 1.644(5) Å) are longer than that of **2a**, and also show the double bond character.

About the P–N bond lengths, there is no significant difference can be found between the coordination of [Ph<sub>2</sub>PNR]<sup>−</sup> and neutral ligands. For example, the P–N bond lengths of **2a** (1.638(2), 1.640(2) Å), **2c** (1.652(5), 1.644(5) Å) and Ph<sub>2</sub>PNHPh (1.696(3) Å) all lie in a narrow range. The <sup>31</sup>P NMR spectra show only one signal. This may be the result of a rapid isomerization of the phosphorus atom in solution. Therefore the Ti–P interaction should only be weak compared to Ti–N interaction (although the Ti–P interaction is somewhat stronger than the Ti–P interaction in the literatures [30,31]), and the negative charge mainly locates on the N center, and the anion [Ph<sub>2</sub>PNR]<sup>−</sup> should be treated as phosphinoamide anion.

## 2.2. Polymerization

With MMAO as cocatalysts, the several titanium complexes **2a–2c** have been investigated as catalysts for ethylene polymerization under atmospheric pressure. The polymerization results were collected in Table 4. It was revealed that complexes **2a–2c** exhibited moderate catalytic activity for ethylene polymerization when employing MMAO as cocatalyst, and the activity in the sequence of *n*-Bu < Ph < *t*-Bu from 23 to 64 kg-PE/(mol-Ti h bar). The activity further decreased significantly at 50 and 70 °C, and only trace polymer was obtained.

Using *i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> as cocatalyst, **2a** showed high activity for ethylene polymerization and

Table 4  
Polymerization of ethylene by the complexes **2a–2c**/MMAO<sup>a</sup>

Run	Catalyst	<i>T</i> (°C)	Yield (mg)	Activity <sup>b</sup>	<i>M<sub>v</sub></i>
1	<b>2a</b>	20	80	64	78000
2	<b>2b</b>	20	29	23	89000
3	<b>2c</b>	20	36	29	80000
4	<b>2a</b>	50	Trace		
5	<b>2a</b>	70	Trace		

<sup>a</sup> Polymerization condition: 1 atm pressure of ethylene; toluene 50 ml; 15 min; complex 5 μmol; Al/Ti = 2000; Al = MMAO.

<sup>b</sup> Activity in kg-PE/(mol-Ti h bar).

the results were summarized in Table 5. Large effects were observed for changes in the Al/Ti ratio (see runs 1, 3, 4, 5 and 10 in Table 5). The increase of Al/Ti ratio resulted in a distinct increase in catalytic activity, from 20/1 (trace polymer) to 200/1 (2516 kg/(mol-Ti h bar)). The ratio of B/Ti also influenced the catalytic activity obviously (see runs 5, 6 and 7 in Table 5). The activity of B/Ti ratio 2/1 (1702 kg/(mol-Ti h bar)) was over two times as much as the B/Ti ratio 1.5/1 (756 kg/(mol-Ti h bar)) and 1/1 (671 kg/(mol-Ti h bar)). Most worthy of note was the fact that the activity of **2a** still higher than 900 kg/(mol-Ti h bar) even when the temperature raised from 20 to 70 °C (see runs 5, 8 and 9 in Table 5). The highest activity (2516 kg-PE/(mol-Ti h bar)) was observed with the ratio of Al/Ti/TB (200/1/2). This was comparable with that of complexes (1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)TiCl<sub>2</sub>(Ncy<sub>2</sub>) (2000 kg-PE/(mol-Ti h bar)) [27], but higher than that of complexes C<sub>5</sub>Me<sub>5</sub>TiCl<sub>2</sub>[N-(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(SiMe<sub>3</sub>)] (180 kg-PE/(mol-Ti h bar)) [9].

Unfortunately, all of the obtained polyethylene did not dissolve at 150 °C under the GPC measurement conditions. Molecular weight was measured by Ubbelohde viscometer on ~0.08% (w/v) polymer solution in decalin at 135 °C. The following equation was used to estimate the molecular weight:  $\eta = 6.2 \times 10^{-4} M_{\eta}^{0.7}$  [33]. The use of cocatalyst *i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> resulted in large increase of *M<sub>v</sub>* relative to MMAO. In the case of *i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, the *M<sub>v</sub>* has a distinct increase with the

Table 5  
Polymerization of ethylene by the complex **2a**/*i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>a</sup>

Run	<i>T</i> (°C)	Al/Ti/TB	Yield (mg)	Activity <sup>b</sup>	<i>M<sub>v</sub></i>
1	20	40/1/2	143	636	283000
2	20	40/1/1	Trace		
3	20	20/1/2	Trace		
4	20	80/1/2	352	1564	601000
5	20	150/1/2	383	1702	766000
6	20	150/1/1.5	170	756	416000
7	20	150/1/1	151	671	331000
8	50	150/1/2	257	1142	489000
9	70	150/1/2	213	947	330000
10	20	200/1/2	566	2516	811000

<sup>a</sup> Polymerization condition: 1 atm pressure of ethylene; toluene 50 ml; 5 min; complex 2.7 μmol; Al = *i*-Bu<sub>3</sub>Al; TB = trityl tetrakis(pentafluorophenyl)borate.

<sup>b</sup> Activity in kg-PE/(mol-Ti h bar).

increase on the ratio of both Al/Ti and B/Ti, and with the raising of temperature, *M<sub>v</sub>* has some decrease (see runs 5, 8 and 9 in Table 5).

In conclusion, we have prepared monocyclopentadienyl titanium complexes having phosphinoamide ligands, and the choice of cocatalyst system has a distinct effect on the catalytic performance. The highest activity (2516 kg-PE/(mol-Ti h bar)) was obtained with **2a**/*i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>. Moreover, **2a** also showed high activity even at 50 and 70 °C.

### 3. Experimental

#### 3.1. General procedures and materials

All work involving air and moisture sensitive compounds were carried out using standard Schlenk techniques. Solvents were dried over Na/benzophenone (THF, ether, toluene, and hexane) or CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>) and distilled prior to use. <sup>1</sup>H NMR data of complexes were obtained on a Varian Unity 400 MHz spectrometer at ambient temperature, C<sub>6</sub>D<sub>6</sub> or CDCl<sub>3</sub> as solvent. The <sup>31</sup>P NMR spectra were recorded on a Varian Unity 400 MHz spectrometer with δ referenced to external phosphoric acid. Mass spectra were obtained using electron impact (EIMS) and LDI-1700 (Linear Scientific Inc.). Elemental analyses were recorded on an elemental Vario EL spectrometer. *n*-BuLi (1.6 M in hexane), Ph<sub>2</sub>PCL, *t*-BuNH<sub>2</sub>, Cp\*TiCl<sub>3</sub> were obtained from Aldrich and used without purification. Modified methylaluminumoxane (MMAO, 7% aluminum in heptane solution) was purchased from AkzoNobel Chemical Inc. The ligands **1a–1c** were synthesized according to the literature [22–24].

#### 3.2. Synthesis of pentamethylcyclopentadienyl titanium(IV) complexes (**2a–c**)

##### 3.2.1. (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)TiCl<sub>2</sub>(Ph<sub>2</sub>PN<sup>*t*</sup>Bu) (**2a**)

A solution of *n*-butyllithium (1.45 ml, 1.60 M in hexane) was added dropwise to a stirred solution of ligand **1a** (0.58 g, 2.25 mmol) in diethyl ether (25 ml) at –78 °C over 10 min period, and the mixture was allowed to stir for 3 h. The resulting solution was added via a cannula to a solution of Cp\*TiCl<sub>3</sub> (0.65 g, 2.25 mmol) in diethyl ether (25 ml) at –78 °C over a period of 10 min. The red solution was stirred overnight, and the solvent was removed in vacuo to give a red solid, and dichloromethane (40 ml) was added to this crude product and stirred for 15 min, and then filtered. The filtrate was evaporated to afford a solid residue. Diethyl ether (10 ml) and *n*-hexane (40 ml) were added one after another. Slow cooling of the solution to –20 °C afforded red crystals which were isolated by decanting the supernatant and washing with hexane. Removal of the residual solvents in vacuo

afforded 0.86 g (75% yield) of the desired complex.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm): 7.85–7.06 (m, 10H, Ar–H); 2.10 (s, 15H,  $\text{C}_5\text{Me}_5$ ); 1.23 (s, 9H, *t*-Bu).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  (ppm): 6.70. EI-MS:  $m/z = 510$  [ $\text{M}^+$ ]. *Anal. Calc.* for  $\text{C}_{26}\text{H}_{34}\text{Cl}_2\text{NPTi}$ : C, 61.18; H, 6.67; N, 2.74. Found: C, 61.05; H, 6.72; N, 2.68%.

### 3.2.2. $(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_2(\text{Ph}_2\text{PNBu}^n)$ (**2b**)

Complex **2b** was prepared via a procedure similar to that for complex **2a** as red powder in the yield of 67%.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm): 7.58–6.96 (m, 10H, Ar–H); 2.04 (s, 15H,  $\text{C}_5\text{Me}_5$ ); 1.69 (t, 2H, N– $\text{CH}_2$ –), 1.20–1.13 (m, 4H, N–C– $\text{CH}_2\text{CH}_2$ –); 0.79 (t, 3H, N–C–C– $\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  (ppm): 10.21. EI-MS:  $m/z = 510$  [ $\text{M}^+$ ]. *Anal. Calc.* for  $\text{C}_{26}\text{H}_{34}\text{Cl}_2\text{NPTi}$ : C, 61.18; H, 6.67; N, 2.74. Found: C, 61.32; H, 6.77; N, 2.61%.

### 3.2.3. $(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_2(\text{Ph}_2\text{PNPh})$ (**2c**)

Complex **2c** was prepared via a procedure similar to that for complex **2a** as red crystals in the yield of 77%.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm): 7.57–7.05 (m, 10H, P–Ar–H), 6.93–6.82 (m, 5H, N–Ar–H), 2.05 (s, 15H,  $\text{C}_5\text{Me}_5$ );  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  (ppm): –16.92. EI-MS:  $m/z = 530$  [ $\text{M}^+$ ]. *Anal. Calc.* for  $\text{C}_{28}\text{H}_{30}\text{Cl}_2\text{NPTi}$ : C, 63.39; H, 5.66; N, 2.64. Found: C, 63.43; H, 5.60; N, 2.70%.

## 3.3. Typical polymerization procedure

Polymerization of ethylene was performed in a glass reactor equipped with a mechanical stirrer. The solvent (toluene, 50 ml) was thermostated to the required polymerization temperature, and then saturated with ethylene gas (**2a** as example).

(1) *Catalyzed by 2a–2c–MMAO systems.* A 2 M solution of MMAO in heptane (5 ml) was added into the reactor. Polymerization was initiated by injecting the solution of complex in toluene into the reactor with stirring.

(2) *Catalyzed by 2a *i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> systems.* A 10  $\mu\text{M}$  solution of *i*-Bu<sub>3</sub>Al in toluene (2.7 ml) was added into the reactor. In a Schlenk flask, a 0.9  $\mu\text{M}$  solution of complex in toluene (3 ml) a 10  $\mu\text{M}$  solution of *i*-Bu<sub>3</sub>Al in toluene (8.1 ml) were mixed and stirred for 10 min at room temperature. The resulted solution was added into the reactor. A 5  $\mu\text{M}$  solution of Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> in toluene (1.08 ml) was added to initiate the polymerization.

After the described period of time, the polymerization was stopped by quenching with 200 ml of aqueous HCl/ethanol. The polymer was collected by filtration, washed subsequently with HCl solution, ethanol, water, and dried at 50 °C to a constant weight.

All polymerization experiments were repeated at least twice, whereby no large deviations have been observed.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 254258 for **2a** and 254259 for **2c**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://ccdc.cam.ac.uk>).

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