

Titanium complexes with novel triaryl-substituted phosphinimide ligands: Synthesis, structure and ethylene polymerization behavior

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Abstract

A series of titanium phosphinimide complexes $[\text{Ph}_2\text{P}(2\text{-RO-C}_6\text{H}_4)_2\text{TiCl}_2$ (**7**, R = CH₃; **8**, R = CHMe₂) and $[\text{PhP}(2\text{-Me}_2\text{CHO-C}_6\text{H}_4)]\text{[THF]TiCl}_3$ (**9**) have been prepared by reaction of TiCl₄ with the corresponding phosphinimines under dehalosilylation. The structure of complex **9** has been determined by X-ray crystallography, and a solvent molecule THF was found to be coordinated with the central metal and the Ti–O bond was consistent with the normal Ti–O (donor) bond length. The complexes **7** and **8** displayed inactive to ethylene polymerization, and the complex **9** displayed moderate activity in the presence of modified methylaluminoxane (MMAO) or *i*-Bu₃Al/Ph₃CB(C₆F₅)₄, and this should be partly attributed to coordination of THF with titanium and the steric effect of two *iso*-propoxyl. And catalytic activity up to 32.2 kg-PE/(mol-Ti h bar) was observed.

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1. Introduction

The search for non-metallocene olefin polymerization catalysts has been the subject of a number of research groups around the world for many years [1]. There were many reports for early and late transition metal complexes based on new or known ligands, such as bidentate diamides [2], phenoxy-imines [3], pyrrolide-imines [4], phenoxyethers [5], and tridentate [6] [N⁻, N, N⁻], [N⁻, O, N⁻], [O⁻, N, P] chelate ligands.

More recently, Stephan and coworkers have reported a series of titanium and zirconium phosphinimide complexes and most of them showed to be excellent olefin polymerization catalysts under both laboratory screening (1 atm. and

25 °C) and commercially relevant (103 bar and 160 °C) polymerization conditions [7]. They thought that bulky phosphinimide ligands could provide the metal environments that sterically and electronically mimic metallocenes. Importantly, the phosphinimines were easily prepared by simple azide oxidation of phosphine ligands, and the high oxidate-state P-based ligands were expected to be thermally stable. Most of phosphinimines they used were based on alkylphosphines [8].

There were many reports of titanium complexes based on triphenylphosphinimine ligands [9], however, few of them were used as olefin polymerization catalysts. Herein, we would like to report the synthesis, structure, and ethylene polymerization of titanium phosphinimide complexes bearing alkyloxy substituted triphenylphosphines. We hope that these ligands could also function well as analogy of cyclopentadienyl ligands and *o*-alkoxy substituents could protect the phosphinimide-N atom from the attack of Lewis acid activators by steric effect effectively.

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2. Results and discussion

2.1. Synthesis and characterization of complexes

The synthesis of the ligands and complexes was outlined in Scheme 1. The substituted triphenylphosphines **1–3** were readily prepared according to literature [10]. Oxidation of the **1–3** with Me_3SiN_3 resulted in the evolution of N_2 . The pure phosphinimines **4–6** could be obtained after distillation in yield 57–79%. Treatment of **4–6** with TiCl_4 (at the molar ratio 2:1 (**4, 5**) or 1:1 (**6**)) in THF under dehalosilylation generated titanium phosphinimide complexes **7–9** in yield 86–92% (the attempt to prepare the dichloride titanium complex based on ligand **6** was failed at the ratio 2:1 and only little **9** could be obtained).

All the new compounds **4–9** were characterized by NMR, element analysis and mass analysis. The single crystals of complex **9** suitable for X-ray diffraction study were grown from THF/hexane under argon atmosphere at -20°C . The ORTEP diagram was shown in Fig. 1. The crystal data was summarized in Table 1 and selected bond lengths and angles were summarized in Table 2.

The Ti–N bond distance of complex **9** was found to be $1.716(6)\text{ \AA}$ and showed the double bond characters. It was found that there was a solvent THF coordinating with the central metal and it was consistent with NMR data. Ti–O distance ($2.156(5)\text{ \AA}$) was consistent with the normal Ti–O (donor) bond length ($\sim 2.15\text{--}2.20\text{ \AA}$) [6b]. Therefore, the coordination of the oxygen in THF with titanium appeared to be capable of stabilizing the incipient electrophilic titanium cation to a significant degree. The P–N–Ti angle ($175.3(4)^\circ$) was essentially linear and consistent with similar complexes in the literature.

2.2. Ethylene polymerization

Preliminary evaluation of compounds **7–9** as ethylene polymerization catalysts was performed in the presence of

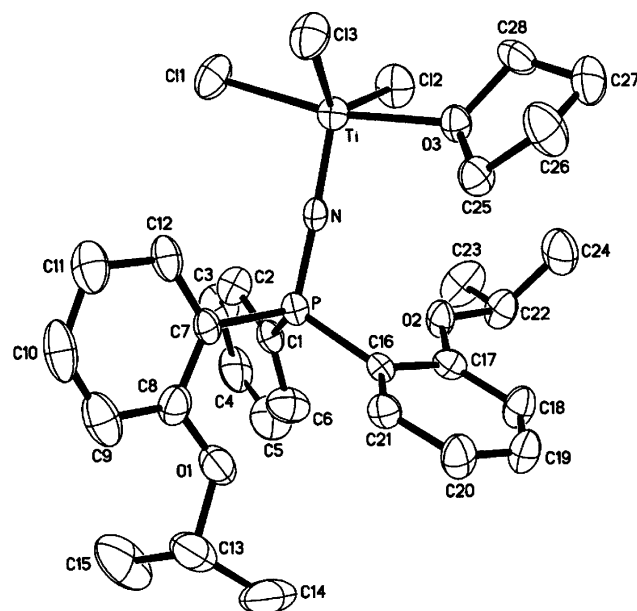
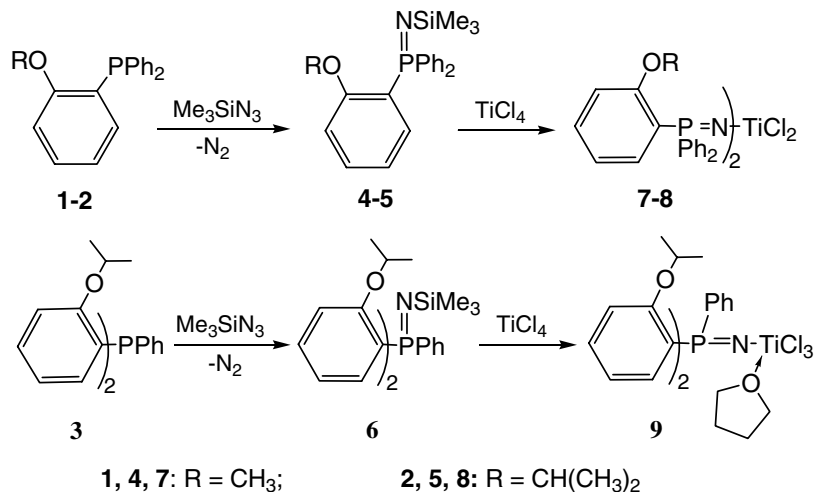


Fig. 1. ORTEP drawings of complex **9**. Thermal ellipsoids at the 30% level are shown. The hydrogen atoms are omitted for clarity.

MMAO, and only trace of polymers was obtained for complexes **7** and **8**. While, the complex **9** displayed moderate activity ($23.2\text{ kg-PE}/(\text{mol-Ti h bar})$, $\text{Al/Ti} = 2000/1$, $7.6\text{ }\mu\text{mol}$, 15 min) under atmospheric pressure at room temperature.

It was the electron-withdrawing of phenyl on phosphinimines that resulted in the inactivity of complexes **7** and **8** (the complex $(t\text{-Bu}_3\text{PN})_2\text{TiCl}_2$ also showed poor activity in the presence of MAO at atmospheric pressure but no exact data was reported [7a]), and it was consistent with the computational results of Stephan and coworkers [11], which indicated that the use of electron-donating substituents would result in significantly smaller ion pair separation energy, thus enhancing catalytic activity. So, the use of electron-withdrawing substituents should correspondingly



Scheme 1. The synthesis of ligands and complexes.

Table 1
Crystallographic data structure refinements of **9**

Empirical formula	C ₂₈ H ₃₅ Cl ₃ NO ₃ PTi
Formula mass	618.79
Crystal size (mm)	0.30 × 0.23 × 0.10
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.8910(16)
<i>b</i> (Å)	10.0026(16)
<i>c</i> (Å)	16.189(16)
α (°)	79.108(4)
β (°)	86.353(4)
γ (°)	82.694
<i>V</i> (Å ³)	1558.8(4)
<i>Z</i>	2
Density (calcd.) (Mg cm ⁻³)	1.318
Absorption coefficient (mm ⁻¹)	0.611
<i>F</i> (000)	644
θ Range for data collected (°)	2.08–25.04
Reflection collected	8146
Data/restraints/parameters	5386/0/338
Independent reflections	5386 (<i>R</i> _{int} = 0.0764)
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0825, <i>wR</i> ₂ = 0.1456
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2196, <i>wR</i> ₂ = 0.1957
Absorption correction	Semi-empirical from equivalents
Goodness-of-fit on <i>F</i> ²	0.961
Largest difference peak and hole (e Å ⁻³)	0.475 and -0.323

Table 2
Selected bond distances (Å) and angles (°) for complex **9**

<i>Bond lengths</i> (Å)	
Ti–N	1.716(6)
P–N	1.617(6)
Ti–Cl(1)	2.307(3)
Ti–Cl(2)	2.284(2)
Ti–Cl(3)	2.302(2)
Ti–O(3)	2.156(5)
<i>Bond angles</i> (°)	
P–N–Ti	175.3(4)
N–Ti–O(3)	91.8(2)
Cl(1)–Ti–Cl(2)	92.35(10)
Cl(1)–Ti–Cl(3)	92.23(9)
Cl(2)–Ti–Cl(3)	132.88(11)

decrease catalytic activity. Compared with complexes **7–8**, there were two *iso*-propoxyl at the *ortho*-position of phosphorus in one ligand as electron-donor in complex **9**. Mainly, they could protect the phosphinimide-N atom from the attack of Lewis acid activators by steric effect. And the coordination of THF with titanium will also satisfy to a certain extent the electron requirement of titanium.

Activated by *i*-Bu₃Al/Ph₃CB(C₆F₅)₄, the complex **9** was further investigated for ethylene polymerization, and the results were collected in Table 3. Moderate activities, but slightly higher than that in the case of MMAO, were observed at different ratio of Al/Ti and B/Ti. 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: $\eta = 6.2 \times 10^{-4} M_w^{0.7}$ [12].

Table 3
Polymerization of ethylene by the complex **9**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄^a

Run	Al/Ti/TB	Yield (mg)	Activity ^b	<i>M</i> _v
1	100/1/1	15.3	19.3	–
2	100/1/2	25.5	32.2	131.5
3	100/1/3	24.6	31.1	172.3
4	200/1/2	19.5	24.6	–
5	400/1/2	17.6	22.2	–

^a Polymerization condition: 1 atm pressure of ethylene; toluene 50 ml; 10 min; complex 4.75 μmol; Al, *i*-Bu₃Al; TB, trityl tetrakis(pentafluorophenyl)borate.

^b Activity in kg-PE/(mol-Ti h bar).

The attempts to prepare other similar bulky and electron-donating *ortho*-substituted phosphinimines and their complexes are underway.

3. Experimental

3.1. General

All manipulations were done under an atmosphere of dry argon employing standard Schlenk and cannula technique. Solvents were distilled under argon over sodium-benzophenone (THF, ether, toluene, *n*-hexane). NMR data of complexes were obtained on a Varian Unity 300 MHz spectrometer at ambient temperature, C₆D₆ or *d*₆-DMSO as solvent. Mass spectra were obtained using electron impact (EIMS) and LDI-1700 (Linear Scientific Inc.). Elemental analyses were recorded on an elemental Vario EL spectrometer. The substituted triphenylphosphines **1–3** were synthesized according to literatures [9].

3.2. Synthesis of ligands

3.2.1. Synthesis of ligand **4**

Me₃SiN₃ (2.17 g, 18.9 mmol) was injected into the compound (2-methoxyphenyl)diphenylphosphine **1** and stirred 10 h at 100 °C. Fractional distillation of the residue gave the product as a viscous liquid; yield 4.6 g, 71%, b.p. ca. 195 °C (0.3 mmHg). Anal. Calcd. for C₂₂H₂₆NOPSi: C, 69.65; H, 6.86; N, 3.69; Found: C, 69.73; H, 6.81; N, 3.66%. ¹H NMR (300 MHz, DMSO): δ : 7.56–7.45 (m, 6H, Ar-H); 7.42–7.34 (m, 6H, Ar-H); 7.01–6.99 (m, 6H, Ar-H); 3.99 (s, 3H, OCH₃); -0.25 (s, 9H, -Si(CH₃)₃). MS: *m/z* = 379 (M⁺).

3.2.2. Synthesis of ligand **5**

The synthesis of **5** was carried out by the same procedure as that for ligand **4** except that compound (2-*iso*-propoxyphenyl)diphenylphosphine **2** was used in place of compound **1**. Yield: 79%. b.p. ca. 203 °C (0.3 mmHg). Anal. Calcd. for C₂₄H₃₀NOPSi: C, 70.76; H, 7.37; N, 3.44; Found: C, 70.84; H, 7.29; N, 3.24%. ¹H NMR (300 MHz, DMSO): δ : 7.67–7.62 (m, 1H, Ar-H); 7.60–7.57 (m, 2H, Ar-H); 7.56–7.53 (m, 2H, Ar-H); 7.44–7.33 (m, 7H, Ar-H); 6.98–6.90 (m, 2H, Ar-H); 4.45 (m, 1H,

OCH₃); 0.72 (d, 6H, C(CH₃)₂); -0.23 (s, 9H, -Si(CH₃)₃). MS: *m/z* = 407 (M⁺).

3.2.3. Synthesis of ligand 6

The synthesis of **6** was carried out by the same procedure as that for ligand **4** except that compound (2-di-*iso*-propoxyphenyl)phenylphosphine **3** was used in place of compound **1**. Yield: 57%. b.p. ca. 211 °C (0.3 mmHg). Anal. Calcd. for C₂₇H₃₆NO₂PSi: C, 69.68; H, 7.74; N, 3.01; Found: C, 70.05; H, 7.66; N, 3.12%. ¹H NMR (300 MHz, DMSO): δ: 7.90–7.83 (m, 1H, Ar-H); 7.80–7.74 (m, 1H, Ar-H); 7.40–7.31 (m, 7H, Ar-H); 6.92–6.83 (m, 4H, Ar-H); 4.46–4.37 (m, 2H, OCH₃); 0.75–0.69 (d, 12H, C(CH₃)₂); -0.23 (s, 9H, -Si(CH₃)₃). MS: *m/z* = 465 (M⁺).

3.3. Synthesis of complexes

3.3.1. Synthesis of complex 7

Twenty milliliter of THF solution of ligand **4** (2.2 g, 5.8 mmol) was added via a cannula to a 20 ml Et₂O solution of TiCl₄ (0.55 g, 2.9 mmol) at 0 °C. The solution was allowed to warm to room temperature and stirred for 16 h. Then, the solvent was removed in vacuo to give a yellow solid. THF (15 ml) and *n*-hexane (40 ml) were added one by one. The product was crystallized at -20 °C as yellow solid. Yield: 1.82 g, 86%. ¹H NMR (300 MHz, C₆D₆): δ: 7.82–7.81 (m, 10H, Ar-H); 7.27–7.07 (m, 18H, Ar-H); 3.11 (s, 6H, OCH₃). Anal. Calcd. for C₃₈H₃₄Cl₂N₂O₂P₂Ti: C, 62.38; H, 4.65; N, 3.83; Found: C, 63.19; H, 4.62; N, 3.80%. MS: *m/z* = 731 (M⁺).

3.3.2. Synthesis of complex 8

The synthesis of **8** was carried out by the same procedure as that for ligand **7** except that ligand **5** was used in place of ligand **4**. Yield: 89%. ¹H NMR (300 MHz, C₆D₆): δ: 7.44–7.43 (m, 10H, Ar-H); 6.86–6.68 (m, 14H, Ar-H); 6.35–6.33 (m, 2H, Ar-H); 5.99–5.97 (m, 2H, Ar-H); 3.58 (m, 2H, OCH₃); 0.37–0.36 (d, 12H, CMe₂). Anal. Calcd. for C₄₂H₄₂Cl₂N₂O₂P₂Ti: C, 64.12; H, 5.34; N, 3.56; Found: C, 64.50; H, 5.29; N, 3.59%. MS: *m/z* = 786 (M⁺).

3.3.3. Synthesis of complex 9

The synthesis of **9** was carried out by the same procedure as that for ligand **7** except that ligand **6** was used in place of ligand **4**. Yield: 92%. ¹H NMR (300 MHz, C₆D₆): δ: 7.96 (m, 2H, Ar-H); 7.73–7.65 (m, 5H, Ar-H); 7.43 (m, 1H, Ar-H); 7.25 (m, 1H, Ar-H); 7.18 (m, 2H, Ar-H); 7.00–6.95 (m, 2H, Ar-H); 4.60–4.56 (m, 2H, OCH₃); 3.84 (b, 4H, O-CH₂THF); 1.91 (b, 4H, C-CH₂THF); 1.03–0.97 (d, 12H, CMe₂). Anal. Calcd. for C₂₈H₃₅Cl₃NO₃PTi: C, 54.37; H, 5.66; N, 2.26; Found: C, 54.62; H, 5.57; N, 2.29%. MS: *m/z* = 618 (M⁺).

3.4. Typical polymerization procedure

Ethylene polymerization was carried out in a 250 ml glass reactor equipped with a mechanical stirrer. Toluene

(50 ml) was added after the reactor was flammable dried. Then, MMAO (2 mol/L) was injected, the toluene solution of catalysts was added to initiate the polymerization. In the case of *i*-Bu₃Al/Ph₃CB(C₆F₅)₄, toluene solution of *i*-Bu₃Al was added first, toluene solution of Ph₃CB(C₆F₅)₄ was added to initiate polymerization after the addition of catalysts solution. After the desired 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.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 254442 for **9**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://ccdc.cam.ac.uk>).

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