

# Titanium and zirconium complexes with novel phenoxy-phosphinimine ligands

Chang-He Qi<sup>a,b</sup>, Suo-Bo Zhang<sup>a,\*</sup>, Jing-Hui Sun<sup>a,b</sup>

<sup>a</sup> State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China

<sup>b</sup> Graduate School of the Chinese Academy of Sciences, China

Received 8 April 2005; received in revised form 8 May 2005; accepted 19 May 2005

Available online 5 July 2005

## Abstract

A series of novel phenoxy-phosphinimine ligands (L): L = 2-(Ph<sub>2</sub>P=NR), **4**, 6-(CMe<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>OH [**2**, R = SiMe<sub>3</sub>; **3**, R = Ph] have been prepared in the yield of 65–71%. And bis(phenoxy-phosphinimide) group 4 complexes of the type L<sub>2</sub>MCl<sub>2</sub> [**4**, M = Ti, R = SiMe<sub>3</sub>; **5**, M = Zr, R = SiMe<sub>3</sub>; **6**, M = Ti, R = Ph; **7**, M = Zr, R = Ph] have been synthesized by the reaction of the ligands with TiCl<sub>4</sub> and ZrCl<sub>4</sub>. The structure of complex **7** has been determined by X-ray crystallography. The complexes **4–7** showed inactive to ethylene polymerization 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>. These results should be caused by overdoing the steric congestion around central metal.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Phenoxy; Phosphinimine; Titanium; Zirconium; Complex

## 1. Introduction

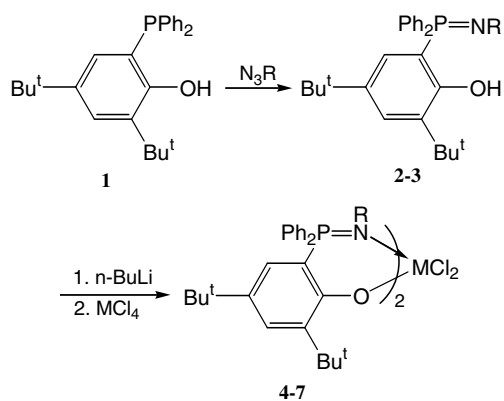
The search for non-metallocene transition complexes to catalyze olefin polymerization has resulted in a wide range of new catalysts base on new or known ancillary ligands [1]. And in recent years, there has been considerable and growing interest in the coordination chemistry to steric hindered phosphinimine and phosphinimato complexes [2]. Among them, titanium complexes bearing phosphinimide ligands have been shown by Stephan and co-workers [3] to give highly active ethylene polymerization catalysts. At the same time, Fujita and co-workers [4] developed a series of group 4 transition metal complexes containing bis(phenoxy-imine) (PHI) ligands, and these complexes showed to be excellent precatalysts for olefin polymerization. Subsequently, Coates et al. [5] also reported living ethylene polymerization by titanium

catalysts with phenoxy-ketimine ligands. However, to the best of our knowledge, there is no report of complex based on the ligand of phenoxy-phosphinimine (PHPI) (most recently, Piers et al. and Stephan et al. [6] reported independently mono(anilido-phosphinimide) group 13 complexes). Compared to PHI ligands, PHPI ligands should be more resistant to nucleophilic attack while improving its ability as donor, and the replacement of an imine-carbon with a PPh<sub>2</sub> fragment will significantly increase the steric environment around central metal. Herein, we would like to report the synthesis and characterization of a series of novel bis(phenoxy-phosphinimide) (PHPI) group 4 complexes.

## 2. Results and discussion

The synthesis of the ligands and complexes is outlined in Scheme 1, and the (2-diphenylphosphanyl, 4, 6-di-*tert*-butyl) phenol **1** is obtained according to the

\* Corresponding author. Tel./fax: +86 431 5262347.  
E-mail address: [sbzhang@ciac.jl.cn](mailto:sbzhang@ciac.jl.cn) (S.-B. Zhang).



2: R = SiMe<sub>3</sub>; 3: R = Ph; 4: M=Ti, R = SiMe<sub>3</sub>;  
5: M = Zr, R = SiMe<sub>3</sub>; 6: M= Ti, R = Ph; 7: M= Zr, R = Ph.

Scheme 1. The synthesis of ligands and complexes.

literature [7]. Oxidation of **1** with phenyl azide or trimethylsilyl azide resulted in the evolution of N<sub>2</sub>, and the ligands **2–3** could be obtained by recrystallizing from CH<sub>3</sub>CN in yield 65–71%. After deprotonation by *n*-BuLi at –78 °C in THF, ligands **2–3** could react with TiCl<sub>4</sub> or ZrCl<sub>4</sub> to give the desired bis(phenoxy-phosphinimide) complexes **4–7** in good yields (**4**: 93%; **5**: 88%; **6**: 86%; **7**: 81%). All of the new compounds were characterized by NMR, element analysis, and mass analysis. NMR data indicated that these octahedral complexes are predominantly C<sub>2</sub>-symmetric in solution, as they are in the solid state. Single crystals of the complex **7** suited for X-ray diffraction study were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexane at –20 °C under argon. The ORTEP is shown in Fig. 1. The crystal data are summarized

in Table 1, and selected bond lengths and angles (similar data of complex (PHI)<sub>2</sub>ZrCl<sub>2</sub> [8] are also listed for comparison) are collected in Table 2.

The structure of complex **7** is similar to that of (PHI)<sub>2</sub>ZrCl<sub>2</sub>, with *trans*-O, *cis*-N, and *cis*-Cl arrangement. About the bond lengths, the Zr–N (2.251(2) Å), of complex **7** is shorter than that of (PHI)<sub>2</sub>ZrCl<sub>2</sub> (2.355(2) Å), which may be resulted by the lower electronegative of phosphinimide-phosphorus compared with imine-carbon. And the bond lengths of Zr–Cl (2.4932(7) Å) is somewhat longer than that of (PHI)<sub>2</sub>ZrCl<sub>2</sub> (2.4234(9) Å). The significant differences can be found to the bond angles. The N–Zr–N (96.65(10)°) increases by 22° comparing with (PHI)<sub>2</sub>ZrCl<sub>2</sub> (74.0(1)°) and the Cl–Zr–Cl (89.36(3)°) decreases by 11° comparing with (PHI)<sub>2</sub>ZrCl<sub>2</sub> (100.38(5)°). These important differences should be caused by the introducing of PPh<sub>2</sub>, which make the environment of central metal more congestion as expected.

Preliminary evaluation of complexes **4–7** as ethylene polymerization catalysts was performed (20 °C and 1 atm) and several activation conditions were attempted. But only traces of polymer can be obtained while using either MMAO (Al/M = 2000/1) or *i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB-(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (Al/M/B<sub>4</sub> = 100/1/2) as cocatalysts. These results showed remarkable difference to those reported for the species of bis(phenoxy-imine) group **4** complexes, although they displayed the structure similarity each other. These findings clearly suggested that such phenoxy-phosphinimide complexes are not simple analogs of phenoxy-imine complexes, albeit the ligands (PHPI) provide the sheltered metal environment which is thought to be the very effective factor for the active

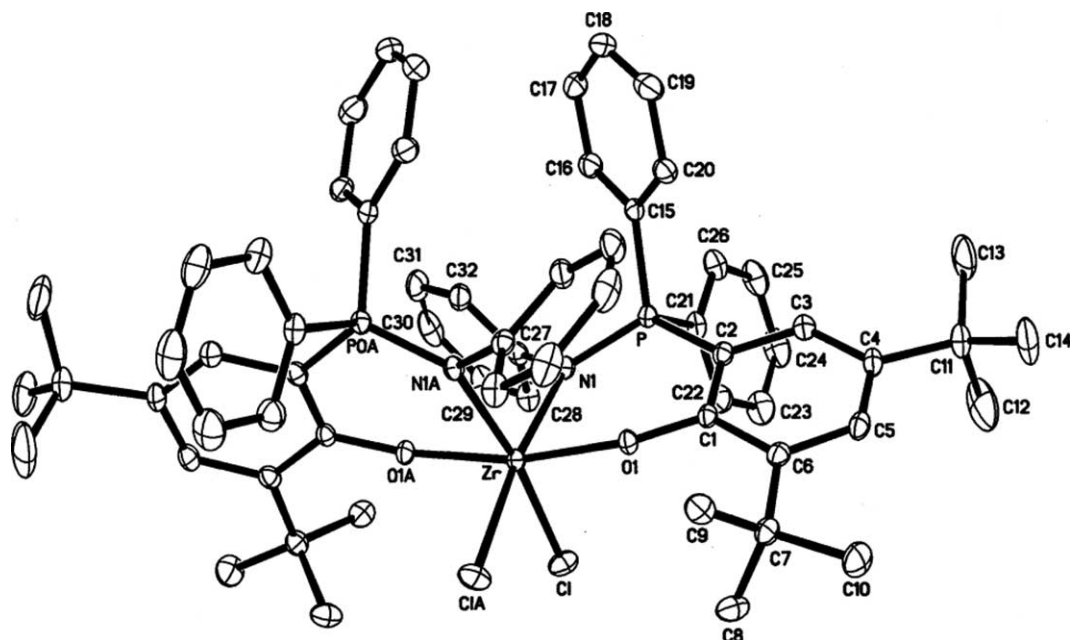


Fig. 1. ORTEP drawings of complex **7**. Thermal ellipsoids at the 30% level are shown. The hydrogen atoms are omitted for clarity.

Table 1  
Crystal data and structure refinement for complex 7

Empirical formula	C <sub>64</sub> H <sub>70</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Zr
Formula weight	1123.28
Temperature (K)	187 (2)
Crystal size (mm)	0.44 × 0.15 × 0.07
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	26.698(2)
<i>b</i> (Å)	11.8002(10)
<i>c</i> (Å)	20.9438 (18)
$\alpha$ (°)	90
$\beta$ (°)	118.2360(10)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	5813.0(9)
<i>Z</i>	4
Density(calc.) (Mg cm <sup>-3</sup> )	1.284
Absorption coefficient (mm <sup>-1</sup> )	0.381
<i>F</i> (0 0 0)	2352
Wavelength (Å)	0.71073
$\theta$ Range for data collection (°)	1.73–25.03
Reflection collected	14,719
Data/restraints/parameters	5130/0/336
Independent reflections	5130 ( <i>R</i> <sub>int</sub> = 0.0383)
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0425, <i>wR</i> <sub>2</sub> = 0.1062
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0500, <i>wR</i> <sup>2</sup> = 0.1111
Absorption correction	Semi-empirical from equivalents
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.054
Maximum and minimum transmission	0.9735 and 0.8504
Largest difference peak and hole	1.100 and -0.404

Table 2  
Selected bond lengths (Å) and angles (°) for complex 7

	Complex 7	(PHI) <sub>2</sub> ZrCl <sub>2</sub>
<i>Bond lengths</i>		
Zr–O(1)	2.0012(16)	1.985(2)
Zr–N(1)	2.251(2)	2.355(2)
Zr–Cl(1)	2.4932(7)	2.4234(9)
P–N(1)	1.629(2)	
<i>Bond angles</i>		
O(1)–Zr–O(2)	168.35(10)	165.5(1)
N(1)–Zr–N(2)	96.65(10)	74.0(1)
Cl(1)–Zr–Cl(2)	89.36(3)	100.38(5)
P(1)–N(1)–Zr	130.40(11)	
C(1)–O(1)–Zr	148.87(16)	

olefin polymerization catalysts. Similar bis(phenoxy-imine)-based group 4 complex (containing [N,O,P] tridentate ligand) with more steric congestion but inactive for olefin polymerization was also reported by Tang and co-workers [9]. Thus, to the bis(phenoxy-imine)-based group 4 complexes, overdoing the steric effects will probably suppress the active species (which was produced from the reaction of complex and cocatalyst), because the strong steric congestion around central metal will hinder the effective coordination of the olefin monomers with the active species. Efforts to adjust the steric environment of these complexes and apply in olefin polymerization are underway.

### 3. Experimental

#### 3.1. General

All preparations involving air and moisture sensitive compounds were carried out under an atmosphere of argon using standard Schlenk or cannula 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. NMR data of ligands and complexes were obtained on a Varian Unity 300 MHz spectrometer at ambient temperature, C<sub>6</sub>D<sub>6</sub> or CDCl<sub>3</sub> as solvent. Mass spectra were obtained using electron impact (EI-MS) and LDI-1700 (Linear Scientific Inc.). Elemental analyses were recorded on an elemental Vario EL spectrometer. The compound **1** was synthesized according to the literature [7].

#### 3.2. Synthesis of ligands

##### 3.2.1. Synthesis of ligand 2

Trimethylsilyl azide (4.6 g, 40 mmol) was injected into (2-diphenylphosphanyl, 4,6-di-*tert*-butyl)phenol **1** (15.6 g, 40 mmol) and stirred for 5 h at 110 °C. The pure product was obtained after recrystallization from CH<sub>3</sub>CN and dried in vacuo. Yield: 12.4 g (65%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.72–7.65 (m, 4H, Ar-H); 7.57–7.45 (m, 6H, Ar-H); 6.84 (m, 1H, Ar-H); 1.45 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.17 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); -0.06 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calc. for C<sub>29</sub>H<sub>40</sub>NOPSi: C, 73.00; H, 8.39; N, 2.94. Found: C, 72.91; H, 8.37; N, 2.98%. EI-MS: *m/z* = 477 [M<sup>+</sup>].

##### 3.2.2. Synthesis of ligand 3

A solution of phenyl azide (5.5 g, 46.2 mmol) in THF (10 ml) was added dropwise to a solution of (2-diphenylphosphanyl, 4,6-di-*tert*-butyl)phenol **1** (12.8 g, 46 mmol) in THF (40 ml) at 0 °C and stirred for 10 h at room temperature. The solvents were evaporated and yield a crude product. The pure white crystals were obtained after recrystallization from CH<sub>3</sub>CN and dried in vacuo. Yield: 7.63 g (71%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.77–7.74 (m, 3H, Ar-H); 7.71–7.63 (m, 3H, Ar-H); 7.49–7.38 (m, 5H, Ar-H); 7.01–6.95 (m, 2H, Ar-H); 6.84–6.79 (m, 1H, Ar-H); 6.65–6.63 (m, 3H, Ar-H); 1.42 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.09 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calc. for C<sub>32</sub>H<sub>36</sub>NOP: C, 79.83; H, 7.48; N, 2.91. Found: C, 79.50; H, 7.51; N, 2.85%. EI-MS: *m/z* = 481 [M<sup>+</sup>].

#### 3.3. Synthesis of complexes

##### 3.3.1. Synthesis of complex 4

A 1.6 M solution of *n*-BuLi (2.56 ml, 4.1 mmol) was added dropwise to a solution of ligand **2** (1.51 g, 4.1 mmol) in THF at -78 °C, then the mixture was warmed to room temperature and stirred for 3 h. The

resulting solution was transferred by cannula to a solution of  $\text{TiCl}_4$  (0.38 g, 2 mmol) in  $\text{Et}_2\text{O}$  at 78 °C. After stirring for 15 h at room temperature, the solvent was removed under vacuum to give the crude product, then 40 ml of  $\text{CH}_2\text{Cl}_2$  was added and stirred for 30 min and filtered. The filtrate was concentrated under vacuum to ca. 10 ml, and 60 ml hexane was added and cooled slowly to  $-20$  °C. The pure product was obtained as pale yellow crystals. Yield 1.92 g (93%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89–7.74 (m, 10H, Ar-H); 7.35–7.29 (m, 8H, Ar-H); 7.11–7.09 (m, 4H, Ar-H); 6.97 (m, 2H, Ar-H); 1.53 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ); 1.27 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ); 0.53 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ). Anal. Calc. for  $\text{C}_{58}\text{H}_{78}\text{Cl}_2\text{N}_2\text{O}_2\text{P}_2\text{Si}_2\text{Ti}$ : C, 64.99; H, 7.28; N, 2.61. Found: C, 65.08; H, 7.21; N, 2.55%. EI-MS:  $m/z = 1036$  [ $\text{M}^+ - \text{Cl}$ ].

### 3.3.2. Synthesis of complex 5

Complex **5** was prepared via a procedure similar to that for **4** as white solid in the yield of 88%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.11–7.94 (m, 8H, Ar-H); 7.86–7.43 (b, 8H, Ar-H); 7.37–7.14 (m, 6H, Ar-H); 7.03 (m, 2H, Ar-H); 1.67 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ); 1.31 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ); 0.49 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ). Anal. Calc. for  $\text{C}_{58}\text{H}_{78}\text{Cl}_2\text{N}_2\text{O}_2\text{P}_2\text{Si}_2\text{Zr}$ : C, 62.48; H, 7.00; N, 2.51. Found: C, 63.02; H, 6.97; N, 2.49%. EI-MS:  $m/z = 1079$  [ $\text{M}^+ - \text{Cl}$ ].

### 3.3.3. Synthesis of complex 6

Complex **6** was prepared via a procedure similar to that for **4** as orange solid in the yield of 86%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.54 (b, 2H, Ar-H); 7.91–7.69 (b, 10H, Ar-H); 7.06–6.93 (b, 18H, Ar-H); 6.83–6.78 (b, 4H, Ar-H); 1.94 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ); 1.05 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ). Anal. Calc. for  $\text{C}_{64}\text{H}_{70}\text{Cl}_2\text{N}_2\text{O}_2\text{P}_2\text{Ti}$ : C, 71.18; H, 6.49; N, 2.59. Found: C, 70.75; H, 6.51; N, 2.63. EI-MS:  $m/z = 1044$  [ $\text{M}^+ - \text{Cl}$ ].

### 3.3.4. Synthesis of complex 7

Complex **7** was prepared via a procedure similar to that for **4** as white crystals in the yield of 81%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.37 (b, 2H, Ar-H); 7.75–7.71 (b, 4H, Ar-H); 7.08–6.94 (b, 24H, Ar-H); 1.82 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ); 1.08 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ). Anal. Calc. for  $\text{C}_{64}\text{H}_{70}\text{Cl}_2\text{N}_2\text{O}_2\text{P}_2\text{Zr}$ : C, 68.45; H, 6.24; N, 2.50. Found: C, 68.53; H, 6.18; N, 2.44%. EI-MS:  $m/z = 1052$  [ $\text{M}^+ - 2\text{Cl}$ ].

## 3.4. Typical polymerization procedure

A 250 ml flask was equipped with an ethylene inlet, a mechanical stirrer, and a vacuum line. The typical reaction procedure was as follows. Toluene (50 ml) and MMAO (2 M in heptane) were added into the dried flask. The toluene solution containing catalyst precursor

was then injected into the flask to initiate the polymerization under atmospheric condition.

In the case of  $i\text{-Bu}_3\text{Al}/\text{Ph}_3\text{BC}(\text{C}_6\text{F}_5)_4$  as cocatalyst, toluene (50 ml) and  $i\text{-Bu}_3\text{Al}$  (1/4 of the desired content) were added into the dried flask. In a Schlenk flask, the toluene solution of catalyst was mixed with  $i\text{-Bu}_3\text{Al}$  (the other 3/4 of the desired content) and stirred for 10 min at room temperature. The resulted solution was added into the reactor. The borate in toluene solution was added to initiate the polymerization under atmospheric condition.

After 15 min, the polymerization was terminated with the addition of  $\text{HCl}/\text{EtOH}$ .

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 267151 for complex **7**. 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>).

## Acknowledgments

The authors are grateful for the financial support by the National Natural Science Foundation of China and SINOPEC (No. 20334030).

## References

- [1] G.G. Hlatky, *Coord. Chem. Rev.* 199 (2000) 235; G.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed.* 38 (1999) 428; V.C. Gibson, S.K. Spitzmesser, *Chem. Rev.* 103 (2003) 283.
- [2] K. Dehnicke, M. Krieger, W. Massa, *Coord. Chem. Rev.* 182 (1999) 19; K. Dehnicke, F. Weller, *Coord. Chem. Rev.* 158 (1997) 103; R. Vollmerhaus, P. Shao, N.J. Taylor, S. Collins, *Organometallics* 18 (1999) 2731; J.D. Masuda, P. Wei, D.W. Stephan, *J. Chem. Soc., Dalton Trans.* (2003) 3500; M. Said, M. Thornton-Pett, M. Bochmann, *J. Chem. Soc., Dalton Trans.* (2001) 2844; H.J. Cristau, M. Taillefer, N. Rahier, *J. Organomet. Chem.* 646 (2002) 94.
- [3] C. Carraz, D.W. Stephan, *Organometallics* 19 (2000) 3791; D.W. Stephan, J.C. Stewart, F. Guérin, S. Courtenay, J. Kickham, E. Hollink, C. Beddie, A. Hoskin, T. Graham, P. Wei, R.E.v.H. Spence, W. Xu, L. Koch, X. Gao, D.G. Harrison, *Organometallics* 22 (2003) 1937; F. Guérin, J.C. Stewart, C. Beddie, D.W. Stephan, *Organometallics* 19 (2000) 2994.
- [4] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, H. Tanaka, T. Fujita, *Chem. Lett.* (1999) 1263–1264;

- J. Saito, M. Mitani, J. Mohri, Y. Yoshida, S. Matsui, S. Ishii, S. Kojoh, N. Kashiwa, T. Fujita, *Angew. Chem. Int. Ed.* 40 (2001) 2918;
- M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* 124 (2002) 7888;
- M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, T. Nakano, H. Tanaka, T. Fujita, *J. Am. Chem. Soc.* 125 (2003) 4293;
- R. Furuyama, M. Mitani, J. Mohri, R. Mori, H. Tanaka, T. Fujita, *Macromolecules* 38 (2005) 1546.
- [5] S. Reinartz, A.F. Mason, E.B. Lobkovsky, G.W. Coates, *Organometallics* 22 (2003) 2542.
- [6] G.C. Welch, W.E. Piers, M. Parvez, R. McDonald, *Organometallics* 23 (2004) 1811;
- J.D. Masuda, D.M. Walsh, P.R. Wei, D.W. Stephan, *Organometallics* 23 (2004) 1819.
- [7] J. Heinicke, R. Kadyrov, M.K. Kindermann, M. Koesling, P.G. Jones, *Chem. Ber.* 129 (1996) 1547.
- [8] M. Mitani, J. Saito, S. Ishii, Y. Nakayama, H. Makio, N. Matsukawa, S. Matsui, J. Mohri, R. Furuyama, H. Terao, H. Bando, H. Tanaka, T. Fujita, *Chem. Rec.* 4 (2004) 137.
- [9] W.-Q. Hu, X.-L. Sun, C. Wang, Y. Gao, Y. Tang, L.-P. Shi, W. Xia, J. Sun, H.-L. Dai, X.-Q. Li, X.-L. Yao, X.-R. Wang, *Organometallics* 23 (2004) 1684.