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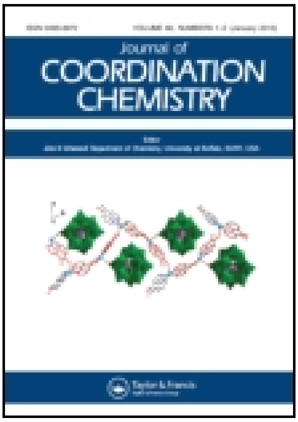

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Synthesis, structure and catalytic properties of new half-titanocene complexes bearing substituted cyclopentadienyl and aryloxide ligands

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Synthesis, structure and catalytic properties of new half-titanocene complexes bearing substituted cyclopentadienyl and aryloxide ligands

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New cyclopentadienyltitanium aryloxide complexes, 1-phenyl-2,3,4,5-$Me_4CpTi(O-2,6-{}^iPr_2-4-{}^nBu-C_6H_2)Cl_2$ (**1**) and [4,4′-biphenyl-(2,3,4,5-$Me_4Cp)_2][Ti(O-2,6-{}^iPr_2-4-{}^nBu-C_6H_2)Cl_2]_2$ (**2**), have been prepared by treatment of cyclopentadienyltitanium trichloride complexes [$PhMe_4CpTiCl_3$ and 4,4′-biphenyl-$(Me_4CpTiCl_3)_2$] with 1 or 2 equiv of lithium salt of 2,6-di-*iso*propyl-4-butylphenol. Complexes **1** and **2** have been characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy. The molecular structure of **1** has been determined by single-crystal X-ray diffraction. Upon activation with $^iBu_3Al$ and $Ph_3CB(C_6F_5)_4$, **1** and **2** both exhibit good catalytic activity for ethylene polymerization, producing polyethylene with moderate molecular weight and melting point.

Keywords: Ethylene polymerization; Half-titanocene; Metallocene catalysts; Olefin polymerization; Polyethylene

1. Introduction

Group 4 metallocene complexes have applications as homogeneous catalyst precursors for a variety of high performance poly-olefins with tailored structures and properties [1–5]. Many studies have been devoted to the development of more effective catalysts improving catalytic activities and polymer properties with precise control over molecular weight, polydispersity, comonomer enchainment level and pattern, as well as the tacticity of poly-olefins [6–8]. Bridged half-metallocene pre-catalysts such as constrained geometry complexes (CGCs) are the most important family of active homogeneous polymerization catalysts, exhibiting high activity and good incorporation of comonomers [9, 10]. As extension of half-metallocene pre-catalysts, non-bridged half-titanocene complexes have been developed by Nomura as high performance catalysts for copolymerization of ethylene with α-olefins, styrene, and norbornene [11]. Non-bridged half-metallocenes, $CpM(OAr)Cl_2$, exhibit unique characteristics for the produced polymers in comparison with ordinary metallocene and/or CGCs. This type of catalyst can be easily synthesized and effectively modified by

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*Corresponding authors. Emails: suqing@jlu.edu.cn (Q. Su); wuql@jlu.edu.cn (Q. Wu) replacement of both the cyclopentadienyl fragment and anionic ancillary ligands to change steric and/or electronic factors [12]. We recently reported that analogous titanium and zirconium complexes bearing aryloxy or anilides show good catalytic performance for ethylene-hexene copolymerization and propylene-hexene copolymerization [13]. Generally, ligand modification has the most profound effect on catalyst performance including catalytic activities and the properties of the obtained polymers. To improve catalytic performance, we have introduced the n-butyl chain into this type of non-bridged half-titanocene complexes to increase solubility, stability, and increase steric bulk. Structural modification of cyclopentadienyl and/or aryloxide ligands should allow us to design well-defined binuclear and polynuclear catalysts with flexible or rigid bridging groups. Recently, dinuclear half-titanocene complexes have been explored for catalytic properties in olefin polymerization with comparison to those of defined mononuclear systems [6b, 14]. Multinuclear metallocene catalysts linked by different bridging units have exhibited cooperative catalytic properties in olefin polymerization [15]. These results encouraged us to develop well-defined binuclear and polynuclear half-titanocene catalysts with similar active sites to investigate both their structural features and catalytic properties. Herein, we report the synthesis and structural characterization of two new half-titanocene complexes, as well as their application for homogeneous ethylene polymerization.

2. Results and discussion

2.1. *Synthesis of 1 and 2*

The new half-titanocene complexes **1** and **2** were readily synthesized by treatment of cyclopentadienyltitanium trichloride complexes [$PhMe_4CpTiCl_3$ and 4,4′-biphenyl-(Me_4Cp-$TiCl_3)_2$], respectively, with the lithium salt of 2,6-$^iPr_2$-4-^{n}Buphenol in toluene according to modified literature procedure [13a, 16]. The ligand precursor 2,6-diisopropyl-4-butylphenol was unexpectedly prepared by lithiation of 1-bromo-3,5-diisopropyl-4-methoxybenzene with *n*-butyllithium, followed by addition of tetrachlorosilane and tribromoborane. The procedure was expected to synthesize tetrakis(3,5-diisopropyl-4-hydroxyphenyl)-silane, similar to the procedure used to prepare tetrakisphenylsilane [17].

Analytically pure **1** and **2** could be obtained by recrystallization from methylene chloride/hexane mixed solvent as red crystalline solids. Both complexes are soluble in methylene chloride, diethyl ether, tetrahydrofuran, and toluene, while slightly soluble in *n*-hexane and *n*-pentane. Both **1** and **2** are air- and moisture-stable in the solid state, similar to the analogous aryloxide titanium complexes [11c, 13a]. The two new half-titanocene complexes are somewhat sensitive to moisture in solution by hydrolysis with H_2O and should be stored and handled under an inert atmosphere. These titanium complexes were characterized by ^1H and ^{13}C NMR spectroscopy along with elemental analysis. The ^1H NMR spectra of **1** and **2** show two characteristic singlets for the $CpCH_3$ protons from 2.25 to 2.40 ppm, similar to those of tetramethyl(phenyl)cylopentadienyltitanium trichloride. In ^{13}C NMR spectra, both **1** and **2** show similar resonances in the aliphatic region with the signals from 13.4 to13.5 ppm assigned to $CpCH_3$. The ^{13}C NMR spectra of **1** and **2** display a downfield resonance from 158.4 to 158.6 ppm, assigned to the carbon adjacent to oxygen in the aryloxy ligand.

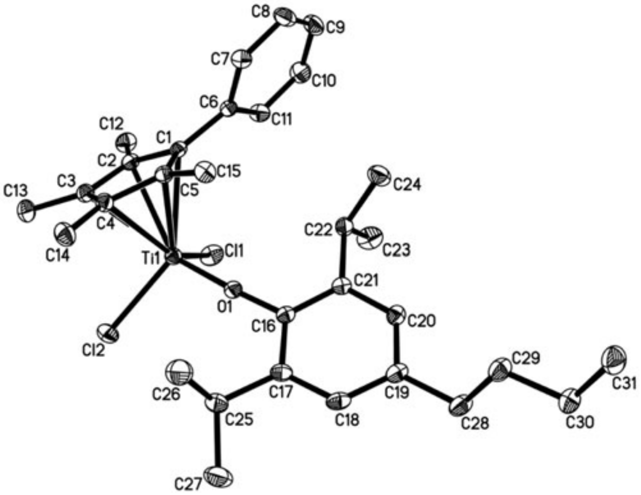

Figure 1. Molecular structure of **1** (thermal ellipsoids are drawn at the 30% probability level). Hydrogens are omitted for clarity.

2.2. *Crystal structure of 1*

The molecular structure of **1** was determined by single-crystal X-ray diffraction. The ORTEP of the molecule is shown in figure 1. Important bond lengths and angles are summarized in table 1. The coordination geometry around titanium can be described as pseudo-octahedral, consisting of a substituted cyclopentadienyl ring, two chlorides, and a phenolate oxygen. The Ti–C distances in **1** from 2.3440(17) to 2.4204(18) Å are similar to those previously reported for similar complexes [18, 19]. The average Ti–Cl distance of 2.2661(6) Å is also in the range of observed values (2.250–2.305 Å) for titanium complexes [20, 21]. The Ti–O bond length (1.7729(13) Å) of 1.772–1.820 Å is reported for the same kind of titanium complexes [20]. The Cp(cent)–Ti–O angle in **1** of 121.9(1)° is larger than the one in (TCP)Ti(CH_2Ph)$_2$ (107.7°) [22] and Cp–Ti–N angle in $Me_2Si(Me_4C_5)(^tBuN)TiCl_2$ (107.6°) [23], which are related to the sterically open degree in front of the central titanium for these complexes as catalyst precursors. The Ti–O–C angle of 172.96(12)° together with the corresponding Ti–O distance suggest that the Ti–O bond may be stabilized by partial π-donation from the oxygen of phenolate. The dihedral angle between the Cp ring and the adjacent phenyl plane in **1** (49.2(1)°) is comparable to those of half-titanocene

Table 1. Selected bond lengths (Å) and angles (°) for **1**.

Ti(1)−C(1)	2.3838(18)	Ti(1)−Cl(1)	2.2637(6)
Ti(1)−C(2)	2.4204(18)	Ti(1)−Cl(2)	2.2686(6)
Ti(1)−C(3)	2.4073(19)	Ti(1)−O(1)	1.7729(13)
Ti(1)−C(4)	2.3491(18)	Ti(1)−Cp(cent)	2.050(2)
Ti(1)−C(5)	2.3440(17)		
O(1)−Ti(1)−Cl(1)	101.32(4)	Ti(1)−O(1)−C(16)	172.96(12)
O(1)−Ti(1)−Cl(2)	101.92(4)	O(1)−Ti(1)−C(1)	107.45(6)
Cl(1)−Ti(1)−Cl(2)	101.79(2)	O(1)−Ti(1)−C(2)	142.18(6)
Cp(cent)−Ti(1)−O(1)	121.9(1)	O(1)−Ti(1)−C(3)	144.62(6)
Cp(cent)−Ti(1)−Cl(1)	114.7(2)	O(1)−Ti(1)−C(4)	109.84(6)
Cp(cent)−Ti(1)−Cl(2)	112.6(1)	O(1)−Ti(1)−C(5)	90.70(6)

Table 2. Summary of ethylene polymerization catalyzed by **1** and **2** activated with Al(^{i}Bu)$_3$ and Ph$_3$CB(C$_6$F$_5$)$_4$.[a]

Run	Catalyst	Al:Ti	T (°C)	Yield (g)	Activity[b]	M_w[c] × 10^{-4}	M_w /M_n[c]	T_m (°C)[d]
1	**1**	150	60	0.439	878	9.12	3.10	139.4
2	**1**	200	60	0.448	896	8.56	2.91	137.6
3	**1**	300	60	0.253	506	7.82	3.36	135.7
4	**1**	200	80	0.333	666	8.83	3.41	138.3
5	**2**	150	60	0.226	452	9.85	4.32	140.1
6	**2**	200	60	0.240	480	8.71	2.09	138.4

[a] Polymerization conditions: solvent 60 mL of toluene, catalyst 2 μmol (1 μmol for **2**), B/Ti ratio 1.1, time 5 min, ethylene pressure 3 bar.
[b] Polymerization activity: 10^3 kg PE (M Ti)$^{-1}$ bar^{-1} h^{-1}.
[c] Determined by GPC in trichlorobenzene at 140 °C *vs.* polystyrene standards.
[d] Determined by DSC at a heating rate of 10 °C min^{-1}.

complexes reported by our groups (43.7–58.7°) [13a], which should be due to steric interactions among the two bulky aryl groups and the Me$_4$Cp ring in these complexes.

2.3. *Ethylene polymerization studies*

Ethylene polymerizations were carried out using **1** and **2** as pre-catalysts under different conditions, and the results are summarized in table 2. Upon activation with Al(^{i}Bu)$_3$ and Ph$_3$CB(C$_6$F$_5$)$_4$, **1** and **2** exhibit catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weight and melting point. Under the same conditions, the **1**/Ph$_3$CB(C$_6$F$_5$)$_4$ system displays slightly higher catalytic activities than that

Table 3. Crystal data and structural refinement details for **1**.

Empirical formula	$C_{31}H_{42}Cl_2OTi$
Formula mass	549.45
Crystal system	Triclinic
Space group	*P-1*
a/Å	10.7309(5)
b/Å	11.4544(5)
c/Å	12.8551(6)
α/°	110.3210(10)
β/°	92.3750(10)
γ/°	100.0150(10)
V/Å^3	1450.28(11)
Z	2
D_c/g cm^{-3}	1.258
F(000)	584
Abs. coeff./mm^{-1}	0.501
Collect range/°	$1.70 \leq \theta \leq 26.02$
Limiting indices	$-13 \leq h \leq 12$ $-14 \leq k \leq 13$ $-15 \leq l \leq 14$
Reflections collected/unique	7658/5561
R_{int}	0.0122
Data/restraints/parameters	5561/0/325
Final R indices [I>2σ(I)] (R_1[a]/wR_2[b])	$R_1 = 0.0380$, $wR_2 = 0.0943$
R indices (all data)	$R_1 = 0.0433$ $wR_2 = 0.0985$
Goodness of fit	1.035
Largest diff. peak and hole/e Å^{-3}	0.284 and −0.250

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

observed for the **2**/$Ph_3CB(C_6F_5)_4$ system, while the molecular weight of the polyethylenes produced by **2**/$Ph_3CB(C_6F_5)_4$ system is slightly higher than that obtained with **1**/$Ph_3CB(C_6F_5)_4$ system under identical conditions. The results also indicate that the catalytic performance is influenced by the nature of the substituents on the ligands. GPC and DSC analysis on the obtained polyethylenes suggest that the catalytically active species formed in binuclear catalyst systems might be identical and behave as independent single active sites [24]. The resultant polyethylenes possessed essentially unimodal molecular weight distributions, similar to those found in other titanium catalyst systems [25].

The effects of the Al/Ti molar ratio and polymerization temperature on the catalytic activity of **1** and **2** were investigated. The highest catalytic activity is reached at Al/Ti molar ratio of 200 for both catalyst systems. Further increase in the Al/Ti molar ratio would result in a decrease in the catalytic activity. These results are in agreement with those observed for other half-titanocene catalyst systems [13a]. The results demonstrate that the catalytic performance of these catalysts also depends on polymerization temperature; catalytic activities of **1** and **2** increase with increase in polymerization temperature, and reach the highest value around 60 °C.

3. Conclusions

New half-titanocene complexes **1** and **2** were synthesized from the reaction of the lithium salt of 2,6-diisopropyl-4-butylphenol with the corresponding cyclopentadienyl titanium trichloride. The molecular structure of **1** was determined by X-ray crystallography. When activated with $Al(^{i}Bu)_3$ and $Ph_3CB(C_6F_5)_4$, both **1** and **2** exhibit reasonable catalytic activity for ethylene polymerization, producing polyethylene with moderate molecular weight, and melting point.

4. Experimental

4.1. *General comments*

All manipulations involving air and moisture sensitive compounds were carried out under argon (ultra-high purity) using either standard Schlenk techniques or glovebox techniques. Solvents were dried and distilled prior to use [26]. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO. 4-Bromo-2,6-diisopropyl-phenol [27], $PhMe_4CpTiCl_3$ [18, 28], 4,4′-biphenyl-$(Me_4CpTiCl_3)_2$, [29] and $Ph_3CB(C_6F_5)_4$ [30] were prepared according to literature procedures. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. Elemental analyzes were performed on a Perkin-Elmer 240c element analyzer. Melting transition temperatures (T_m) of the polyethylenes were determined by DSC (Du Pont 910 differential scanning calorimeter) at a heating rate of 10 °C min^{-1}. Molecular weight of the polyethylenes were determined by PL-GPC 220 at 140 °C with 1,2,4-trichlorobenzene as the eluent.

4.2. *Synthesis of 2,6-diisopropyl-4-butylphenol*

To a stirred solution of 4-bromo-2,6-diisopropyl-phenol (5.14 g, 20.0 mM) in THF (50 mL) was added NaH (0.528 g, 22.0 mM) at 0 °C. The resulting mixture was stirred for 1 h. Then, MeI (3.12 g, 22.0 mM) was added over 10 min and stirring was continued for another 2 h.

The reaction was quenched by addition of H_2O (50 mL), stirred for 10 min, and extracted with Et_2O (3 × 30 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated to give a crude product, which was further purified by silica gel column chromatography (petroleum ether) to afford 1-bromo-3,5-diisopropyl-4-methoxybenzene (4.96 g, 91.6%) as a yellowish oil. Anal. Calcd for $C_{13}H_{19}BrO$ (271.19): C, 57.57; H, 7.06. Found: C, 57.53; H, 7.16%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): 1.21 (d, 12H, J = 7.5 Hz, $CH(CH_3)_2$), 3.21–3.34 (m, 2H, $CH(CH_3)_2$), 3.71 (s, 3H, OCH_3), 7.18 (s, 2H, C_6H_2).

A solution of *n*-BuLi (18.3 mM) was added dropwise to a solution of the 1-bromo-3,5-diisopropyl-4-methoxybenzene (4.96 g, 18.3 mM) in THF (50 mL) at –15 °C. The resulting mixture was kept at –15 °C for 30 min, and then $SiCl_4$ (0.778 g, 4.58 mM) was added dropwise. The mixture was stirred at –15 °C for 30 min and then allowed to warm to room temperature and stirred for an additional 2 h. The reaction was quenched by addition of 1 M aqueous HCl, stirred for 10 min, and then extracted with Et_2O (3 × 30 mL). The combined extracts were washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated. The residue was dissolved in CH_2Cl_2 (20 mL) and then BBr_3 (26.0 mM) was added dropwise to the solution. The mixture was stirred for 12 h at room temperature. The reaction was quenched by addition of concentrated hydrochloric acid, stirred for 30 min, and then extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were washed with $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford 2,6-diisopropyl-4-butylphenol (1.84 g, 42.9%) as an oil. Anal. Calcd for $C_{16}H_{26}O$ (234.38): C, 81.99; H, 11.18. Found: C, 81.92; H, 11.23%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): 0.93 (t, 3H, J = 7.5 Hz, CH_3), 1.26 (d, 12H, J = 7.5 Hz, $CH(CH_3)_2$), 1.32–1.43 (m, 2H, CH_2), 1.52–1.62 (m, 2H, CH_2), 2.53 (t, 2H, J = 7.8 Hz, CH_2), 3.06–3.20 (m, 2H, $CH(CH_3)_2$), 6.86 (s, 2H, C_6H_2).

4.3. *Synthesis of 1*

A solution of *n*-BuLi (2.0 mM) was added dropwise to a solution of 2,6diisopropyl-4-butylphenol (0.468 g, 2.0 mM) in Et_2O (20 mL) at –20 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed *in vacuo* and the residue was washed with hexane. The obtained white powder was dissolved in toluene (10 mL), and then a solution of 1,1-phenyl-2,3,4,5-tetramethylcyclopentadienyltitanium trichloride (0.669 g, 1.90 mM) in toluene (10 mL) was added at room temperature. The reaction mixture was heated to 80 °C and stirred for 12 h. The mixture was filtered and the precipitate was washed with toluene (2 × 5 mL). The filtrate was concentrated to leave a black-red residue. Recrystallization from CH_2Cl_2–*n*-hexane (1 : 3) gave pure **1** as red crystals (0.820 g, 78.5%). Melting point: 96–97 °C. Anal. Calcd for $C_{31}H_{42}Cl_2OTi$ (549.44): C, 67.77; H, 7.70. Found: C, 67.70; H, 7.62%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): 0.93 (t, 3H, J = 7.2 Hz, CH_3), 1.04 (d, 12H, J = 6.9 Hz, $CH(CH_3)_2$), 1.31–1.41 (m, 2H, CH_2), 1.50–1.60 (m, 2H, CH_2), 2.26 (s, 6H, Cp-CH_3), 2.29 (s, 6H, Cp-CH_3), 2.53 (t, 2H, J = 7.5 Hz, CH_2), 2.95–3.09 (m, 2H, $CH(CH_3)_2$), 6.79 (s, 2H, C_6H_2), 7.31–7.50 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): 13.46, 14.21, 22.78, 23.02, 24.07, 26.94, 34.02, 35.93, 123.2, 126.9, 130.9, 131.3, 132.6, 133.5, 136.1, 138.4, 139.5, 140.2, 158.6.

4.4. *Synthesis of 2*

Complex **2** was synthesized from 4,4′-biphenyl-($Me_4CpTiCl_3)_2$ by the same procedure as described for **1**. Complex **2** was obtained in 75.3% yield as a red crystalline solid. Melting point: 185–186 °C. Anal. Calcd for $C_{62}H_{82}Cl_4O_2Ti_2$ (1096.86): C, 67.89; H, 7.54. Found: C, 67.80; H, 7.65%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): 0.92 (t, 6H, J = 7.2 Hz, CH_3), 1.05 (d, 24H, J = 6.6 Hz, $CH(CH_3)_2$), 1.31–1.40 (m, 2H, CH_2), 1.51–1.60 (m, 2H, CH_2), 2.29 (s, 12H, Cp-CH_3), 2.34 (s, 12H, Cp-CH_3), 2.53 (t, 4H, J = 7.5 Hz, CH_2), 2.98–3.09 (m, 4H, $CH(CH_3)_2$), 6.80 (s, 4H, C_6H_2), 7.59–7.67 (m, 8H, C_6H_4). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): 13.39, 14.11, 22.77, 23.03, 24.06, 26.92, 34.01, 35.92, 123.1, 128.1, 128.4, 130.8, 131.0, 133.2, 133.3, 136.8, 138.1, 139.5, 158.5.

4.5. *X-ray structure determinations of 1*

Crystals of **1** suitable for X-ray structure determination were obtained from a saturated solution of CH_2Cl_2/*n*-hexane (1:5, v/v) at room temperature. The data were collected at 293 K on a Rigaku RAXIS-RAPID diffractometer using Mo-Kα radiation. The structures were solved by direct methods [31] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogens were included in idealized positions. All calculations were performed using the SHELXTL crystallographic software package [32]. Details of the crystal data, data collections, and structure refinements are summarized in table 3.

4.6. *Polymerization reactions*

Ethylene polymerizations were carried out according to the following procedure: A dry 250 mL steel autoclave was charged with 50 mL of toluene, thermostated at the desired temperature and saturated with 1.0 bar of ethylene. The polymerization reaction was started by addition of a mixture of catalyst and $Al(^iBu)_3$ in toluene (5 mL) and a solution of $Ph_3CB(C_6F_5)_4$ in toluene (5 mL) at the same time. The reaction mixture was stirred for 5 min under 3 bar of ethylene. The polymerization was then quenched by injecting 120 mL of acidified methanol [HCl (3 M)/methanol = 1 : 1], and the polymer was collected by filtration, washed with water, methanol, and dried at 60 °C in vacuum to a constant weight.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number: 931,680 (**1**). Copy of this information may be obtained free of the 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 http://www.ccd.cam.ac.uk).

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References

[1] (a) A.L. McKnight, R.M. Waymouth. *Chem. Rev.*, **98**, 2587 (1998); (b) H.G. Alt, A. Köppl. *Chem. Rev.*, **100**, 1205 (2000).

[2] G.W. Coates, R.M. Waymouth. *Science*, **267**, 217 (1995).

[3] A. Motta, I.L. Fragala, T.J. Marks. *J. Am. Chem. Soc.*, **129**, 7327 (2007).

[4] H. Sinn, W. Kaminsky. *Adv. Organomet. Chem.*, **18**, 99 (1980).

[5] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth. *Angew, Chem., Int. Ed. Engl.*, **34**, 1143 (1995).

[6] G.W. Coates. Chem. Rev., **100**, 1223 (2000); (b) M. Delferro, T.J. Marks. *Chem. Rev.*, **111**, 2450 (2011).

[7] W. Kaminsky, M. Arndt. *Adv. Polym. Sci.*, **127**, 143 (1997).

[8] R.J. Keaton, K.C. Jayaratne, D.A. Henningsen, L.A. Koterwas, L.R. Sita. *J. Am. Chem. Soc.*, **123**, 619 (2001).

[9] J.A.M. Canich (Exxon), U.S. Patent, 5026798 (1991).

[10] (a) P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw. *J. Am. Chem. Soc.*, **116**, 4623 (1994). (b) P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw. *Organometallics*, **9**, 867 (1990). (c) Y. Zhang, Y. Mu, C. Lü, G. Li, J. Xu, Y. Zhang, D. Zhu, S. Feng. *Organometallics*, **23**, 540 (2004).

[11] (a) K. Nomura, K. Itagaki, M. Fujiki. *Macromolecules*, **38**, 2053 (2005); (b) K. Nomura, K. Oya, T. Komatsu, Y. Imanishi. *Macromolecules*, **33**, 3187 (2000); (c) K. Nomura, N. Naga, M. Miki, K. Yanagi, A. Imai. *Organometallics*, **17**, 2152 (1998). (d) H. Zhang, K. Nomura. *J. Am. Chem. Soc.*, **127**, 9364 (2005).

[12] (a) K. Nomura, J. Liu, S. Padmanabhan, B. Kitiyanan. *J. Mol. Catal. A*, **267**, 1 (2007); (b) K. Nomura, M. Tsubota, M. Fujiki. *Macromolecules*, **36**, 3797 (2003); (c) H. Zhang, K. Nomura. *Macromolecules*, **39**, 5266 (2006).

[13] (a) Q. Wu, Q. Su, L. Ye, G. Li, Y. Mu. *Dalton Trans.*, 2525 (2010); (b) K. Liu, Q. Wu, W. Gao, Y. Mu, L. Ye. *Eur. J. Inorg. Chem.*, **12**, 1901 (2011); (c) K. Liu, Q. Wu W. Gao, Y. Mu. *Dalton Trans.*, 4715 (2011).

[14] (a) S.W. Yoon, Y. Kim, S.K. Kim, S.Y. Kim, Y. Do, S. Park. *Macromol. Chem. Phys.*, **212**, 785 (2011); (b) M. Horáček, R. Gyepes, J. Merna, J. Kubišta, K. Mach, J. Pinkas. *J. Organomet. Chem.*, **695**, 1425 (2010); (c) L. Postigo, A.B. Vázquez, J. Sánchez-Nieves, P. Royo, E. Herdtweck. *Organometallics*, **27**, 5588 (2008).

[15] (a) J.C. Flores, T.E. Ready, J.C.W. Chien, M.D. Rausch. *J. Organomet. Chem.*, **562**, 11 (1998); (b) S.K. Noh, W. Jung, H. Oh, Y.R. Lee, W.S. Lyoo. *J. Organomet. Chem.*, **691**, 5000 (2006); (c) J. Cacciola, K.P. Reddy, J.L. Petersen. *Organometallics*, **11**, 665 (1992).

[16] K. Nomura, T. Komatsu, Y. Imanishi. *J. Mol. Catal. A: Chem.*, **152**, 249 (2000).

[17] (a) H. Yu, C. Shen, M. Tian, J. Qu, Z. Wang. *Macromolecules*, **45**, 5140 (2012); (b) J.-H. Fournier, X. Wang, J.D. Wuest. *Can. J. Chem.*, **81**, 376 (2003).

[18] M. Björgvinsssson, S. Halldorsssson, I. Amason, J. Magull, D. Fenske. *J. Organomet. Chem.*, **544**, 207 (1997).

[19] J.L. Pearson. *Inorg. Chem.*, **19**, 181 (1980).

[20] K. Nomura, A. Tanaka, S. Katao. *J. Mol. Catal. A*, **254**, 197 (2006).

[21] M.G. Thorn, J.S. Vilardo, J. Lee, B. Hanna, P.E. Fanwick, I.P. Rothwell. *Organometallics*, **19**, 5636 (2000).

[22] Y.X. Chen, T.J. Marks. *Organometallics*, **16**, 5958 (1997).

[23] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickas, R.K. Rosen, G.W. Knight, S.Y. Lai, Eur. Pat. Appl. EP 416 815 A2, 1991 (Dow).

[24] S.H. Kim, S. Yoon, S.-d. Mun, H.-H. Lee, J. Lee, Y. Kim. *Polyhedron*, **31**, 665 (2012).

[25] T. Xu. *Polyhedron*, **64**, 3652 (2011).

[26] D.D. Perrin, W.L.F. Armarego, D.R. Perrin. *The Purification of Laboratory Chemicals.*, Pergamon, New York (1980).

[27] M.L. Brown, H.A. Eidam, M. Paige, P.J. Jones, M.K. Patel. *Bioorg. Med. Chem.*, **17**, 7056 (2009).

[28] Y. Kim, Y. Han, J.-W. Hwang, M.W. Kim, Y. Do. *Organometallics*, **21**, 1127 (2002).

[29] M.H. Lee, S.K. Kim, Y. Do. *Organometallics*, **24**, 3618 (2005).

[30] (a) A.G. Massey, A.J. Park. *J. Organomet. Chem.*, **5**, 218 (1966); (b) J.C.W. Chien, W.M. Tsai, M.D. Rausch. *J. Am. Chem. Soc.*, **113**, 8570 (1991).

[31] Siemens, *SMART* and *SAINT* Software Packages; Siemens Analytical X-ray Instruments, Madison, WI (1996).

[32] G.M. Sheldrick, *SHELXL (Version 5.1)*, Siemens Industrial Automation Inc., Madison, WI (1997).