

Available online at www.sciencedirect.com



POLYHEDRON www.elsevier.com/locate/poly

Polyhedron 26 (2007) 3063-3068

Synthesis, structures and catalytic properties of stable oxo-bridged half-sandwich titanium complexes

Qiao-Lin Wu^a, Guang-Hua Li^b, Ling Ye^a, Wei Gao^a, Ying Mu^{a,*}

^a Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, School of Chemistry, Jilin University,

2699 Qianjin Street, Changchun 130012, People's Republic of China

^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, School of Chemistry, Jilin University, 2699 Qianjin Street,

Changchun 130012, People's Republic of China

Received 29 October 2006; accepted 7 February 2007 Available online 20 February 2007

Abstract

Hydrolysis of 1,2-diphenyl-4-R-cyclopentadienyl titanium trichloride (R = Me (1), *n*-Bu (2)) affords the corresponding oxo-bridged monocyclopentadienyl titanium compounds $(1,2-Ph_2-4-R-CpTiCl_2)_2(\mu-O)$ (R = Me (3), *n*-Bu (4)), new dinuclear species. The molecular structures of complexes 3 and 4 have been confirmed by single-crystal X-ray diffraction. Both complexes have been characterized by elemental analysis, ¹H and ¹³C NMR spectroscopy. When activated with Al(ⁱBu)₃ and Ph₃C⁺B(C₆F₅)₄⁻, complexes 3 and 4 show reasonable catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weights, and upon activation with methylaluminoxane (MAO), complexes 3 and 4 exhibit high catalytic activity and syndiospecificity for the polymerization of styrene. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Metallocene; Olefin polymerization; Polyethylene; Syndiotactic polystyrene; Titanium

1. Introduction

Group 4 metallocene catalysts have attracted extensive interest due to their applications in the fields of organometallic chemistry, catalysis and polymer science [1–3]. In particular titanium catalysts based on the cyclopentadienyl ligand have been widely studied as active catalysts employed in industry and academic institutions [4–15]. It is well known that even minor modification of the ligands can result in remarkable changes in catalytic activity, as well as polymer properties, such as molecular weight, comonomer incorporation and stereoregularity [16–20]. Thus, it is of great significance to develop new homogeneous catalysts producing a number of high performance polyolefins. Recently we have reported a series of diphenyl substituted cyclopentadienyl titanium trichloride complexes as precatalysts for styrene polymerization [21]. Further study on these titanium systems found that these complexes could be readily hydrolyzed to produce corresponding dimeric compounds in solution. In previous instances, dinuclear complexes bearing a cyclopentadienyl ligand play a significant role in some catalytic processes, because a cooperative effect of two close reactive metal centers is generated to accomplish unusual coordination modes [22]. Herein we report the synthesis and structural characterization of the oxo-bridged binuclear complexes, as well as their catalytic performance in ethylene and styrene polymerization.

2. Experimental

2.1. General comments

All manipulations involving air and moisture sensitive compounds were carried out under a nitrogen atmosphere (ultra-high purity) using either standard Schlenk techniques or glovebox techniques. Et_2O and toluene were

^{*} Corresponding author. Tel.: +86 431 5168472; fax: +86 431 5193421. *E-mail address:* YMu@jlu.edu.cn (Y. Mu).

^{0277-5387/\$ -} see front matter @ 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2007.02.007

dried over sodium/benzophenone under nitrogen and were freshly distilled prior to use. CH₂Cl₂ and *n*-hexane were refluxed under nitrogen over calcium hydride and distilled before use. Methylaluminoxane (MAO, 10 wt.% solution in toluene, $M = 800 \text{ g mol}^{-1}$, Al = 5.3 wt.%) was purchased from Wtico. Al(${}^{i}Bu$)₃, methyl lithium, *n*-butyl lithium and titanium tetrachloride were purchased from Aldrich. 1,2-Diphenyl-4-methyl-cyclopentadienyl titanium trichloride (1), 1,2-diphenyl-4-*n*-butyl-cyclopentadienyl titanium trichloride (2) [21] and $Ph_3C^+B(C_6F_5)^-$ [23–25] were prepared according to the literature procedures. The crystal structure was determined with a CCD diffraction apparatus. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240c element analyzer. Viscosity-average molecular weights of the polyethylenes were determined in decahydronaphthalene at 135 °C using a Schott Gerate Mod. AVS/T2 Ubbelohde viscosimeter. Viscosity-average molecular weights of the polystyrenes were determined in o-dichlorobenzene at 135 °C using a Schott Gerate Mod. AVS/T2 Ubbelohde viscosimeter. Melting transition temperatures (T_m) of the polyethylenes and polystyrenes were determined by DSC (Du Pont 910 differential scanning calorimeter) at a heating rate of $10 \,^{\circ}\text{C min}^{-1}$.

2.2. Synthesis of $(1,2-Ph_2-4-Me-CpTiCl_2)_2(\mu-O)$ (3)

A mixture of Et₂O (20 mL) and distilled H₂O (9.0 µL, 0.50 mmol) was slowly added at -15 °C to solid complex 1 (385.5 mg, 1.00 mmol), and the obtained solution was warmed to room temperature and stirred for 48 h (Scheme 1). The solvent was removed in vacuo, and the resulting residue was extracted with a mixed solvent of CH₂Cl₂/n-hexane (1:3, 15×2 mL). The solution was concentrated to give a red solid (317.3 mg, 88.6%). Red crystals of the complex suitable for X-ray diffraction were obtained by recrystallization from a mixture of CH_2Cl_2/n -hexane (1:5) at room temperature. Anal. Calc. for $C_{36}H_{30}Cl_4OTi_2$ (716.20): C, 60.37; H, 4.22. Found: C, 60.31; H, 4.18%. ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 2.40 (s, 6H, CH₃), 6.87 (s, 4H, C₅H₂), 7.28–7.50 (m, 20H, C₆H₅). ¹³C NMR (CDCl₃, 75 MHz, 298 K): δ 17.2 (CH₃), 128.9, 133.4, 137.9 (C₅H₂), 123.2, 128.4, 129.7, 136.3 (C₆H₅).





2.3. Synthesis of $(1,2-Ph_2-4-n-Bu-CpTiCl_2)_2(\mu-O)$ (4)

Compound **4** was prepared in the same manner as described above for the synthesis of **3** (Scheme 1), and isolated in 89.2% as a red crystalline solid. *Anal.* Calc. for $C_{42}H_{42}Cl_4OTi_2$ (800.36): C, 63.03; H, 5.29. Found: C, 63.05; H, 5.21%. ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 0.91 (t, ³*J*_{HH} = 7.7 Hz, 6H, CH₃), 1.35 (m, ³*J*_{HH} = 7.5 Hz, 4H, CH₂), 1.60 (m, ³*J*_{HH} = 7.6 Hz, 4H, CH₂), 2.73 (t, ³*J*_{HH} = 7.8 Hz, 4H, CH₂), 6.88 (s, 4H, C₅H₂), 7.27–7.50 (m, 20H, C₆H₅). ¹³C NMR (CDCl₃, 75 MHz, 298 K): δ 14.1, 22.6, 31.4, 32.7 (C₄H₉), 128.9, 133.4, 143.3 (C₅H₂), 122.3, 128.4, 129.8, 136.1 (C₆H₅).

2.4. X-ray structure determination of 3 and 4

Crystals of **3** and **4** 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. Diffraction data were collected at 293 K on a Bruker SMART-CCD diffractometer using Mo K α radiation. The structures were solved using direct methods and refined by full-matrix leastsquares procedures [26]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in ideal positions. All calculations were performed using the SHELXTL crystallographic software packages [27]. Relevant crystallographic data are summarized in Table 1.

2.5. Polymerization of ethylene

The ethylene polymerizations (runs 1-8) were carried out according to the following procedure: A dry 250 mL steel autoclave with a magnetic stirrer was charged with 70 mL of toluene, thermostated at the desired temperature and saturated with ethylene (1.5 bar). The polymerization reaction was initiated by addition of a mixture solution of precatalyst and Al('Bu)₃ in toluene (5 mL) and a solution of $Ph_3C^+B(C_6F_5)_4^-$ in toluene (5 mL) at the same time. The gaseous ethylene was then admitted into the reactor vessel through a gas purification column. The gas pressure was maintained at 6 bar throughout the polymerization period by means of a pressure manometer. After 15 min, the polymerization was quenched by addition of 120 mL of 1:1 (v/v) methanol and HCl solution. The white polymer was collected by filtration, washed several times with water, methanol, and dried to a constant weight under vacuum.

2.6. Polymerization of styrene

The styrene polymerizations (runs 1-10) with complexes 3 and 4 were carried out according to the following procedure: A 250 mL Schlenk flask with a magnetic stirrer was attached to high vacuum line and then sealed under a nitrogen atmosphere. Fifty milliliters of toluene, 5 mL of freshly distilled styrene and an appropriate amount of MAO were added to the flask which was placed in an oil bath at the

Table 1 Crystal data and structural refinements details for **3** and **4**

	3	4
Empirical formula	C ₃₆ H ₃₀ Cl ₄ OTi ₂	C ₄₂ H ₄₂ Cl ₄ OTi ₂
Formula weight	716.20	800.36
Crystal system	monoclinic	monoclinic
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Space group	C2/c	<i>C</i> 2/c
a (Å)	25.099(2)	26.3294(10)
b (Å)	10.5871(8)	9.7594(4)
c (Å)	17.1279(11)	16.8576(8)
β (°)	132.224(3)	116.657(2)
Volume ($Å^3$)	3370.4(4)	3871.3(3)
Ζ	4	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.411	1.373
F(000)	1464	1656
Absorption coefficient (mm ⁻¹)	0.819	0.721
Scan type	ω –2 $ heta$	ω –2 θ
2θ Range (°)	$4.38 \leqslant 2 heta \leqslant 50.00$	$3.46 \leqslant 2\theta \leqslant 46.62$
Reflections collected	9058	9136
Reflections unique $[R_{int}]$	2960 [0.0570]	2800 [0.0328]
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	2960/0/204	2800/0/222
Goodness-of-fit on F^2	0.921	1.028
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0403,$	$R_1 = 0.0319,$
	$wR_2 = 0.0889$	$wR_2 = 0.0861$
<i>R</i> indices (all data)	$R_1 = 0.0807,$	$R_1 = 0.0449,$
	$wR_2 = 0.1046$	$wR_2 = 0.0921$
Largest difference peak and hole (e $Å^{-3}$)	0.349 and -0.271	0.322 and -0.323

desired temperature, and the mixture was stirred for 10 min. The titanium catalyst $(2.5 \,\mu\text{mol})$ in toluene was injected into the flask and the polymerization was performed at 25 °C, 50 °C or 75 °C for the desired reaction times. The polymerization was terminated by addition of 10% HCl in methanol. The precipitated polymer was washed three times with methanol and dried at 80 °C *in vacuo* to a constant weight. The polymer was extracted with refluxing 2-butanone for 24 h in a Soxhlet extractor to remove any atactic polymer and dried again at 80 °C for 24 h.

3. Results and discussion

3.1. Synthesis and analysis of complexes 3 and 4

Complexes 3 and 4 were synthesized readily via the hydrolysis reaction of complexes 1 and 2 in solution, and obtained after recrystallization in good yields as red crystalline solids. These titanium complexes are quite soluble in most organic solvents, such as Et_2O , CH_2Cl_2 and toluene. Both complexes can be stored at room temperature, under an inert nitrogen atmosphere, without obvious change, either in the solid state or solution. It is noteworthy that they also exhibit good thermostability and can be heated to about 90 °C in toluene without decomposition. The stability of titanium complexes to water-induced metathesis has been reported previously [28–30]. Com-

plexes **3** and **4** have been confirmed by X-ray diffraction, elemental analysis, ¹H and ¹³C NMR spectroscopy.

The ¹H and ¹³C NMR spectra indicate higher symmetry in solution than in the solid state, and complexes **3** and **4** have similar resonance signals, with just slight shifts to higher field, compared to those of **1** and **2**. The ¹H NMR spectra show only one single signal for the protons of the Cp groups (6.87 ppm for **3**, 6.88 ppm for **4**), since they are equivalent in solution for C_{2c} symmetric complexes, and the ¹³C NMR signals for the Cp groups of complexes **3** and **4** shift 0.5–2.6 ppm to higher field compared to the signals of the Cp groups of complexes **1** and **2** [21].

3.2. Crystal structures of 3 and 4

The molecular structures of complexes **3** and **4** were confirmed by single-crystal X-ray diffraction analysis. The ORTEP drawing of the molecular structure is shown in Fig. 1 and Fig. 2. Selected bond lengths and angles are summarized in Table 2. The molecular structure shows a dimetallic moiety with two $(1,2-Ph_2-4-R-CpTiCl_2)_2(\mu-O)$ (R = Me (**3**), *n*-Bu (**4**)) units linked by Ti–O bonding. The coordination geometry around the titanium atom can be described as pseudo-tetrahedral, formed by a substituted cyclopentadienyl ring, two chloride atoms and an oxygen atom (oxo-bridge). The Ti1–C distances for **3** and **4** are in the range of 2.336(3)–2.430(2) Å, which are similar to the corresponding values of **1** and **2** [21]. The average

Table 2



Fig. 1. Structure of complex **3** (thermal ellipsoids are drawn at the 30% probability level).



Selected bond lengths	and angles fo	or complexes 3 and 4	
Complex 3			
Ti(1) - O(1)	1.786(1)	Ti(1)-C(5)	2.339(3)
Ti(1)-C(1)	2.386(3)	Ti(1)-Cl(1)	2.197(2)
Ti(1)-C(2)	2.417(3)	Ti(1)-Cl(2)	2.242(1)
Ti(1)-C(3)	2.369(3)	Ti(1)-Cp(cent)	2.041(3)
Ti(1)-C(4)	2.345(3)		
O(1)-Ti(1)-Cl(1)	108.2(3)	O(1)-Ti(1)-C(4)	107.3(1)
O(1)-Ti(1)-Cl(2)	103.7(1)	O(1)-Ti(1)-C(5)	84.4(1)
Cl(1)-Ti(1)-Cl(2)	95.4(3)	Cp(cent)-Ti(1)-O(1)	114.5(2)
O(1)-Ti(1)-C(1)	97.5(1)	Cp(cent)-Ti(1)-Cl(1)	114.6(3)
O(1)-Ti(1)-C(2)	132.2(1)	Cp(cent)-Ti(1)-Cl(2)	118.3(3)
O(1)-Ti(1)-C(3)	140.7(1)	Ti(1)-O(1)-Ti(2)	157.0(2)
Complex 4			
Ti(1) - O(1)	1.800(1)	Ti(1)-C(5)	2.378(2)
Ti(1)-C(1)	2.430(2)	Ti(1)-Cl(1)	2.251(1)
Ti(1)-C(2)	2.370(3)	Ti(1)-Cl(2)	2.242(1)
Ti(1)-C(3)	2.336(3)	Ti(1)-Cp(cent)	2.048(2)
Ti(1)-C(4)	2.363(3)		
O(1)-Ti(1)-Cl(1)	102.2(1)	O(1)-Ti(1)-C(4)	109.4(1)
O(1)-Ti(1)-Cl(2)	104.6(4)	O(1)-Ti(1)-C(5)	142.2(1)
Cl(1)-Ti(1)-Cl(2)	101.1(4)	Cp(cent)-Ti(1)-O(1)	115.7(3)
O(1)-Ti(1)-C(1)	132.1(1)	Cp(cent)-Ti(1)-Cl(1)	115.3(5)
O(1) - Ti(1) - C(2)	97.6(1)	Cp(cent)-Ti(1)-Cl(2)	115.9(1)
O(1)-Ti(1)-C(3)	85.9(1)	Ti(1)-O(1)-Ti(2)	159.6(2)

stability of **3** and **4**. The Ti–O–Ti angles of complexes **3** and **4** (157.0(2)°, 159.6 (2)° respectively) fall within the range of observed values (154–180°) in similar structures, which indicates that there exists different π back-bonding affected by intramolecular steric effects [35,36] (Fig. 2).

3.3. Ethylene polymerization studies

Ethylene polymerizations were carried out in toluene using complexes **3** and **4** as precatalysts under different conditions, and the results of the polymerization catalyzed by complexes **3** and **4** are summarized in Table 3. When activated with $Al({}^{i}Bu)_{3}$ and $Ph_{3}C^{+}B(C_{6}F_{5})_{4}^{-}$, complexes **3** and **4** both show good catalytic activity for ethylene polymerization, producing moderate molecular weight polyethylene

Fig. 2. Structure of complex 4 (thermal ellipsoids are drawn at the 30% probability level).

Ti-Cl distance of 2.219 (1) Å in **3** is shorter than that of 2.247(1) Å in **4**, which could be attributed to the difference in the crowded environment on the titanium atoms. The Ti-O bond lengths (1.786(1) Å for 3 and 1.800(1) Å for 4) are slightly shorter than the average Ti-O distance in other known complexes [31-34]. For this reason, we suggest that there is relatively higher electron density at the metal atoms of **3** and **4**, which is responsible for the high

Table 3	
Summary of ethylene polymerization catalyzed by complexes 3 and 4 activated with $Al(^{i}Bu)_{3}$ and $Ph_{3}C^{+}[B(C_{6}F_{5})_{4}]^{-a}$	

Run	Catalyst	Al:Ti	$T_{\rm p}$ (°C)	Yield (g)	$A^{\rm b}$ (×10 ⁻⁵)	M_{η}^{c} (×10 ⁻⁴)	$T_{\rm m}^{\rm d}$ (°C)
1	3	50	80	0.47	1.56	5.3	124.3
2	3	100	80	1.08	3.60	4.6	135.0
3	3	200	80	1.59	5.31	4.2	126.4
4	3	300	80	1.12	3.73	3.5	124.0
5	4	50	80	0.66	2.20	5.0	126.7
6	4	100	80	1.25	4.17.	4.7	130.1
7	4	200	80	1.87	6.23	3.9	127.2
8	4	300	80	1.02	3.40	3.6	123.6

^a Polymerization conditions: [Ti] 2 μ M, B/Ti ratio 1.2, reaction time 15 min, polymerization temperature 80 °C, ethylene pressure 6 bar. ^b Activity = g PE (mol Ti)⁻¹ bar⁻¹ h⁻¹.

^c Measured in decahydronaphthalene at 135 °C.

^d Determined by DSC at a heating rate of 10 °C min⁻¹.

with melting temperatures in the range 123-135°. As seen in Table 3, the catalytic activity increases in the order 3 < 4, which indicates that the activity is influenced by the nature of the substituents on the cyclopentadiene ring. It is well known that the electron-donating effect and steric effect of the *n*-Bu group would stabilize the active species and hence increase the catalytic activity of complex 4. For both 3 and 4, the catalytic activity is affected by the Al/Ti molar ratio and the highest catalytic activity is reached at an Al/Ti ratio of about 200. A further increase in the Al/Ti ratio results in a decrease in the catalytic activity. During the polymerization, the molecular weight of the polymer gradually decreases with an increase in the Al/Ti molar ratio, which points out that a high Al/Ti molar ratio results in premature chain termination of the polymer, influenced by the relative rates of the two competing processes: β -hydride elimination and chain propagation.

3.4. Styrene polymerization studies

Styrene polymerizations were carried out in toluene using complexes 3 and 4 as precatalysts under different conditions, and the results of the styrene polymerization with complexes 3 and 4 are summarized in Table 4. The 3 or 4/MAO systems show good catalytic performance for styrene polymerization in terms of catalytic activity and polymer properties, such as syndiotacticity, melting temperature and molecular weight of the produced polystyrene. In comparison with the 1 or 2/MAO systems [21], the title catalyst systems were found to be active for syndiotactic polymerization of styrene at a low Al/Ti ratio of 2000, thus reducing the costs of the catalysts. The findings could be attributed to the important factor of the cooperative effect caused by the two adjacent metal centers in this type of catalyst. One catalytically active site can construct a crowded environment around the other site in the catalyst systems, which effectively protects the active species, resulting in a reduction in the amount of MAO in regard to the reactivation of the dormant catalyst species.

The catalytic activity of the title type catalyst is dependent on the polymerization temperature. The catalytic activity of complexes 3 and 4 increases with an increase in polymerization temperature, and the highest activity observed is about 1.35×10^7 g PS (mol Ti)⁻¹ (mol styrene)⁻¹ h⁻¹ at 50 °C. The catalytic activity then decreases at higher polymerization temperatures. These findings are similar to the polymerization behavior of the mother titanium catalyst [21]. The catalytic performance of the title type catalyst is dependent on the polymerization time too. For complexes 3 and 4, better catalytic behavior was observed for 10 min polymerization experiments, which indicates the partial decomposition of the syndiospecific active species and/or increased viscosity during the polymerization. Furthermore, the results in Table 4 are also consistent with the fact that the catalytic activity and polymer properties depend greatly on the electronic and steric effects of the substituted cyclopentadiene ligands in halfsandwich titanocenes as homogeneous catalysts. The catalytic activity is in the order 3 < 4, which indicates that both the electronic and steric factors of the substituted cyclopentadiene group play a remarkable role in the styrene polymerizing process.

4. Conclusion

Two new oxo-bridged dinuclear titanium complexes 3 and 4 have been synthesized by hydrolysis of the corresponding monocyclopentadienyl titanium compounds 1 and 2. The structures of 3 and 4 have been confirmed by ¹H and ¹³C NMR spectra and X-ray crystallography. Upon activation with $Al({}^{i}Bu)_{3}$ and $Ph_{3}C^{+}B(C_{6}F_{5})_{4}^{-}$, complexes 3 and 4 exhibit reasonable catalytic activity for ethylene polymerization, producing moderate molecular weight polyethylene with melting temperatures in the range 123–135°. The 3 or 4/MAO systems show good catalytic performance for styrene polymerization in terms of catalytic activity, syndiotacticity, melting temperature and molecular weight of the produced polystyrene.

summary of styrene polymenzation catalyzed by complexes 5 and 4 activated with MAO								
Run	Catalyst	Time (min)	$T_{\rm p}~(^{\circ}{\rm C})$	$A^{\rm b}$ (×10 ⁻⁷)	SY ^c (%)	$T_{\rm m}^{\rm d}$ (°C)	$M_{\eta}^{e} (\times 10^{-5})$	
1	3	10	25	0.78	92.7	272.3	1.26	
2	3	10	50	1.21	95.2	269.8	0.94	
3	3	10	75	0.93	94.0	270.6	1.13	
4	3	15	50	1.12	92.6	271.5	0.92	
5	3	30	50	0.90	91.8	271.2	1.17	
6	4	10	25	0.82	92.6	272.8	1.19	
7	4	10	50	1.35	95.7	270.4	0.92	
8	4	10	75	0.91	95.1	272.3	1.06	
9	4	15	50	1.16	94.3	271.9	0.95	
10	4	30	50	1.03	93.5	271.0	1.10	

Table 4					
Summary of styrene	e polymerization	catalyzed b	v complexes	3 and 4 acti	vated with MAO ^a

^a Polymerization conditions: [Ti] 50 μM; [Al]/[Ti] 2000; reaction time 10 min, 15 min, or 30 min; [styrene] 0.87 M.

^b A (activity) = (g bulk polymer)/(mol Ti)(mol monomer)(h).

^c Percentage s-PS = $[(g \text{ of } 2\text{-butanone insoluble polymer})/(g \text{ of butanone polymer})] \times 100.$

^d $T_{\rm m}$, melting temperature of s-PS, determined with DSC at a heating rate of 10 °C min⁻¹.

^e $M_{\rm n}$, Measured in *o*-dichlorobenzene at 135 °C.

5. Supplementary material

CCDC 601715 and 601716 contain the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam. ac.uk.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 20374023).

References

- H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. Engl. 34 (1995) 1143.
- [2] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.
- [3] M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255.
- [4] J.A.M. Canich, U.S. Patent 5,079,205, 1992.
- [5] Dow Chemical Co. Eur. Pat. Appl. 0416815.
- [6] Exxon Chemical Co. U.S. Patent 5,026,798, 1991. U.S. Patent 5,055,438, 1991.
- [7] J.C. Flores, J.C.W. Chien, M.D. Rausch, Organometallics 13 (1994) 4140.
- [8] M. Enders, R. Rudolph, H. Pritzkow, Chem. Ber. 129 (1996) 459.
- [9] A.A.H. van der Zeijden, C. Mattheis, R. Fröhlich, Organometallics 16 (1997) 2651.
- [10] A.M. Cardoso, R.J.H. Clark, S. Moorhouse, J. Chem. Soc., Dalton Trans. (1980) 1156.
- [11] Y. Qian, G. Li, W. Chen, B. Li, X. Jin, J. Organomet. Chem. 373 (1989) 185.
- [12] H. Sinn, W. Kaminsky, Adv. Org. Chem 18 (1990) 99.
- [13] P. Foster, J.C.W. Chien, M.D. Rausch, Organometallics 15 (1996) 2404.
- [14] R. Fandos, A. Meetsma, J.H. Teuben, Organometallics 10 (1991) 59.
- [15] J. Okuda, K.E. du Plooy, P.J. Toscanno, J. Organomet. Chem. 495 (1995) 195.

- [16] P. Jutzi, M.D. Kristen, J. Dahlhaus, B. Newmann, H.-G. Stammler, Organometallics 12 (1993) 2906.
- [17] F.G. Sernetz, R. Mülhaupt, S. Fokken, J. Okuda, Macromolecules 30 (1997) 1562.
- [18] W. Kaminsky, F. Freidanck, Macromol. Symp. 183 (2002) 89.
- [19] D. Ruchatz, G. Fink, Macromolecules 31 (1998) 4669.
- [20] W. Spaleck, M. Antberg, J. Rohrmann, A. Winter, B. Bachmann, P. Kiprof, J. Behm, W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 31 (1992) 1347.
- [21] Q.-L. Wu, Q. Su, G.-H. Li, W. Gao, Y. Mu, S.-H. Feng, Polyhedron 25 (2006) 2565.
- [22] (a) E. Royo, P. Royo, T. Cuenca, M. Galakhov, Organometallics 19 (2000) 5559;
 (b) T. Cuenca, M. Galakhov, G. Jimézez, E. Royo, P. Royo, M. Bochmann, J. Organomet. Chem. 543 (1997) 209;
 (c) G. Jimézez, P. Royo, T. Cuenca, M. Galakhov, Organometallics 20 (2001) 5237.
- [23] J.C.W. Chien, W.M. Tsai, M.D. Rasch, J. Am. Chem. Soc. 113 (1991) 8570.
- [24] A.G. Massey, A.J. Park, J. Organomet. Chem. 5 (1966) 218.
- [25] A.G. Massey, A.J. Park, J. Org. Chem. 2 (1962) 245.
- [26] SHELXTL, PC Siemens Analytical X-ray Instruments, Madison WI, 1993.
- [27] G.M. Sheldrick, SHELXTL Structure Determination Programs, Version 5.0; PC Siemens Analytical Systems, Madison, WI, 1994.
- [28] J.C. Flores, J.S. Wood, J.C.W. Chien, M.D. Rausch, Organometallics 15 (1996) 4944.
- [29] L.M. Bobcock, V.W. Day, W.G. Klemperer, J. Chem. Soc., Chem. Commun. (1987) 858.
- [30] M. Björgvinssson, S. Halldorssson, I. Amason, J. Magull, D. Fenske, J. Organomet. Chem. 544 (1997) 207.
- [31] S.P. Varkey, M. Schormann, T. Pape, H.W. Roesky, et al., Inorg. Chem. 40 (2001) 2427.
- [32] J.L. Pearson, Inorg. Chem. 19 (1980) 181.
- [33] S.G. Blanco, M.P. Gómez-Sal, S.M. Carreras, M. Mena, et al., J. Chem. Soc., Chem. Commun. (1986) 1572.
- [34] S.L. Troyanov, V.B. Rybakov, V. Varga, P. Sedmera, K. Max, Metalloorg. Khim. 4 (1991) 1004.
- [35] U. Thewalt, D. Schomburg, J. Organomet. Chem. 127 (1977) 169.
- [36] P. Gowik, T. Klapötke, J. Pickardt, J. Organomet. Chem. 393 (1990) 343.