Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 457–467
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

o-Phenylene-bridged Cp/amido titanium and zirconium complexes and their polymerization reactivity

Sang Hoon Lee [a], Chun Ji Wu [a], Jina Yoo [a], Jung-eun Kwak [b], Hoseop Yun [b], Bun Yeoul Lee [a,*]

[a] *Department of Molecular Science and Technology Ajou University, Suwon 443-749, Republic of Korea*
[b] *Energy System Division, Ajou University, Suwon 443-749, Republic of Korea*

Received 27 September 2007; received in revised form 13 November 2007; accepted 14 November 2007
Available online 21 November 2007

Abstract

o-Phenylene-bridged trimethylcyclopentadienyl/amido titanium complexes [(η^5-2,3,5-Me_3C_5H)C_6H_4NR-κ*N*]$TiCl_2$ (**18**, R = CH_3; **19**, R = CH_2CH_3; **20**, R = $CH_2C(CH_3)_3$; **21**, R = $CH_2(C_6H_{11})$) and zirconium complexes {[(η^5-2,3,5-Me_3C_5H)C_6H_4NR-κ*N*]ZrCl-μCl}$_2$ (**22**, R = CH_3; **23**, R = CH_2CH_3; **24**, R = $CH_2C(CH_3)_3$; **25**, R = $CH_2(C_6H_{11})$; **26**, R = C_6H_{11}; **27**, R = $CH(CH_2CH_3)_2$) are prepared via a key step of the Suzuki-coupling reaction between 2-dihydroxyboryl-3-methyl-2-cyclopenten-1-one (**2**) and the corresponding bromoaniline compounds. The molecular structures of titanium complexes **18** and **19** and dinuclear zirconium complexes **24** and **26** were confirmed by X-ray crystallography. The Cp(centroid)–Ti–N and Cp(centroid)–Zr–N angles are smaller, respectively, than those observed for the Me_2Si-bridged complex [Me_2Si(η^5-Me_4C_5)(N^{t}Bu)]$TiCl_2$ and its Zr-analogue, indicating that the *o*-phenylene-bridged complexes are more constrained than the Me_2Si-bridged complex. Titanium complex **19** exhibits comparable activity and comonomer incorporation to the CGC ([Me_2Si(η^5-Me_4C_5)(N^{t}Bu)]$TiCl_2$) in ethylene/1-octene copolymerization. Complex **19** produces a higher molecular-weight polymer than CGC.

Keywords: Constrained geometry catalyst; Titanium complexes; Cyclopentadienyl; Polymerization

1. Introduction

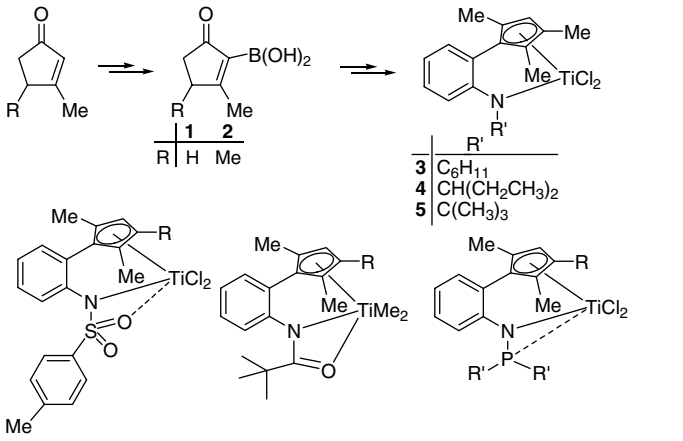
The Constrained-Geometry Catalyst (CGC), [Me_2Si(η^5-Me_4C_5)(N^{t}Bu)]$TiCl_2$ [1] is a typical representative among the homogeneous Ziegler–Natta catalysts [2,3]. Its activated complex is thermally stable and provides a high molecular-weight polymer with a high content of α-olefin in ethylene/α-olefin copolymerizations, thereby enabling its use in commercial processes. This catalyst is based on a ligand design first introduced by Bercaw for scandium complex [4]. The ligand is prepared by successive attacks of tetramethylcyclopentadienyl-anion and *tert*-BuNH-anion onto Me_2SiCl_2. A number of its derivatives have been prepared through the replacement of the Me_4C_5-unit with other π-donor ligands such as substituted cyclopentadienyls, indenyls, or fluorenyls [5]. Derivatization through the replacement of the *tert*-BuN-unit with other amides or phosphides has been also commonly reported [6]. However, the modification on the bridge-unit by replacing the Me_2Si-bridge to hydrocarbyl-based ones has been rare and relatively unsuccessful because it requires a different synthetic route. Erker reported preparation of alkylidene (R^1R^2C) bridged complexes, but their activities for ethylene polymerization are significantly lower than those of the standard CGC [7,8]. Ethylene-bridged complex, [(η^5-Me_4Cp)CH_2CH_2(N^{t}Bu)]$TiCl_2$ was prepared, but it exhibited a much lower α-olefin incorporation [9].

Recently, we disclosed a synthetic route for *o*-phenylene-bridged complexes Eq. (1). A key step in this novel route is the Suzuki-coupling reaction between 2-bromoaniline derivatives and the boronic acids of cyclopentenones

* Corresponding author. Tel.: +82 31 219 1844; fax: +82 31 219 2394.
E-mail address: bunyeoul@ajou.ac.kr (B.Y. Lee).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.11.021

(**1**–**2**), which can be prepared in a 30 g scale without column chromatography [10]. The route allows for a number of complexes, especially through derivatization on the amide-unit. Among the prepared amido [10], sulfonamido [11], carboxamido [12], and phosphinoamido complexes [13], the amido complexes exhibited the best catalytic performance. Contrary to the observation on the Me_2Si-bridged CGC complexes, *tert*-butyl amido complex **5** exhibited not only a low activity but also a low α-olefin incorporation, while the secondary hydrocarbyl-based amido complexes **3** and **4** showed a good activity and good α-olefin incorporation [10a]. These polymerization results prompt us to prepare sterically less bulky primary hydrocarbyl-based amido complexes. The preparation of the zirconium complexes using the same *o*-phenylene-bridged Cp/amide ligand system and their reactivity are another concern.



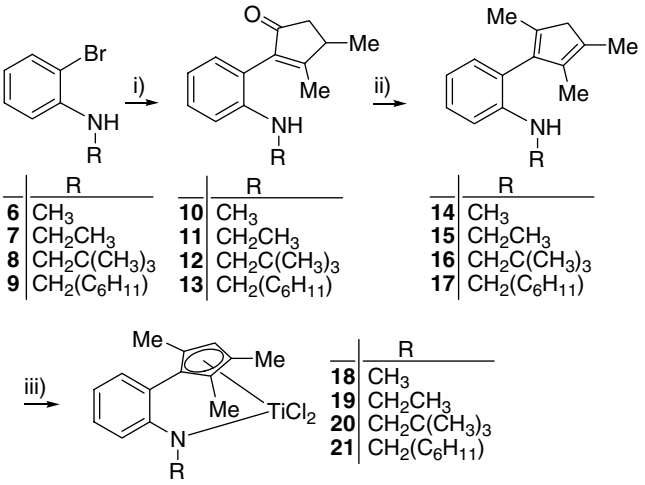
(1)

2. Results and discussion

2.1. Synthesis and characterization

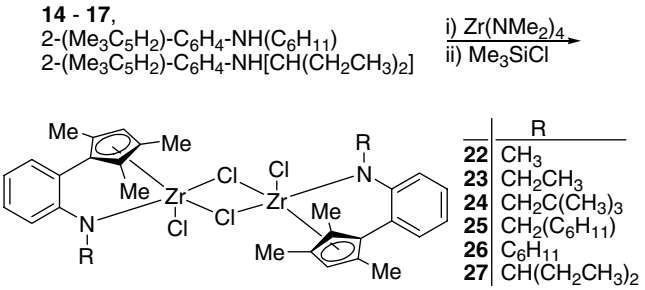
Various *N*-alkylated anilines containing trimethylcyclopentadienyl-unit at 2-position are prepared (Scheme 1). *N*-(primary alkyl)-*o*-bromoanilines (**8**–**9**) are prepared by reductive amination reaction between *o*-bromoaniline and the corresponding aldehydes [14]. The Suzuki-coupling reaction of **6**–**9** with 2-dihydroxyboryl-3,4-dimethyl-2-cyclopenten-1-one (**2**) affords the corresponding cyclopentenones **10**–**13** in excellent yields (89–92%). The yields for the transformation of cyclopentenone compounds **10**–**13** to trimethylcyclopentadiene compounds **14**–**17** are significantly improved by employing recently reported THF-soluble $CeCl_3$/2LiCl reagent [15]. Thus, the addition of two equivalents of MeLi in the presence of two equivalents of THF-soluble $CeCl_3$/2LiCl provides the desired ligands **14**–**17** in high yields (87–91%). Elimination reaction of the resulting tertiary alcohol is accomplished during the aqueous HCl work-up.

Treatment $Ti(NMe_2)_4$ to **14**–**17** at 80 °C for 1 day provides cleanly the corresponding bis(dimethylamido)titanium complexes which are directly transformed to the desired dichlorotitanium complexes **18**–**21** in excellent yields (overall 72–94%) through the treatment of Me_2SiCl_2 at room temperature for 6 hours. The ^1H NMR spectra indicate that both Me_2N-ligands are replaced with the chloride-ligands, and a Cp–H signal is observed at 6.0 ppm (C_6D_6). A doublet *o*-phenylene-H signal is markedly up-filed shifted by the chlorination, and it is observed at 5.96, 6.03, 6.37, and 6.30 ppm for **18**, **19**, **20**, and **21**, respectively. The corresponding *o*-phenylene-H signal is observed at 6.44, 6.45, 6.64, and 6.55 ppm, respectively, in the ^1H NMR spectra of the corresponding bis(dimethylamido)titanium complexes. The two methylene protons on N–CH_2CH$_3$ unit in **19** are diastereotopic to each other, and hence two signals are separately observed at 4.32 and 4.39 ppm as a doublet quartet ($^2J_{HH} = 15.2$, $^3J_{HH} = 6.8$ Hz). The N–CH_2 methylene protons in **21** are also separately observed at 4.35 and 4.46 ppm as a doublet ($^2J_{HH} = 15.6$, $^3J_{HH} = 7.6$ Hz). Three Cp–CH$_3$ signals are observed in the range of 1.6–2.2 ppm as a sharp singlet. In the ^1H NMR spectrum of **20**, the N–CH_2 signal and the two Cp–CH_3 signals among the three Cp–CH_3 signals are significantly broadened, which might be attributed to a slow rotation around the N–CH$_2$ axis in the NMR time scale.



Scheme 1. [a]Legend: (i) **2**, Na_2CO_3, $Pd(PPh_3)_4$ (1 mol%); (ii) MeLi/($CeCl_3$–2LiCl), then HCl (2 N); and (iii) $Ti(NMe_2)_4$ then Me_2SiCl_2.

The zirconium dichloride complexes are prepared in good yields (63–89%) using the same strategy applied for the preparation of the titanium complexes with $Zr(NMe_2)_4$ instead of $Ti(NMe_2)_4$ (Scheme 2). Contrary to the observation in the titanium complexes, a doublet *o*-phenylene-*H* signal is not up-filed shifted by the chlorination, and a single N–CH_2 signal is observed, not separated. In the ^1H NMR spectra of **23**, **24**, and **25**, the N–CH_2 signal is observed at 3.95 ppm as a quartet, at 3.78 ppm as a singlet, and at 3.78 ppm as a doublet. The *ortho*-C_6H_4 signal and the N–C*H* signal are very broad at 6.4–6.6 ppm and 3.3–3.5 ppm, respectively, in the ^1H NMR spectrum of **26**.



Scheme 2.

2.2. X-ray crystallographic studies

Single crystals of titanium complexes **18** and **19** are obtained from benzene solution at room temperature through the slow evaporation of the solvent. The X-ray crystallographic studies confirm the structures, which are shown in Figs. 1 and 2, and the selected bond distances and angles are summarized in Table 1. The Cp(centroid)–Ti–N angles (105.11° and 104.90° for **18** and **19**, respectively) are smaller than that observed for the standard CGC, $[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$ (107.6°) [16]. All the *o*-phenylene-bridged complexes characterized by the X-ray crystallography have exhibited smaller Cp(centroid)–Ti–N angles than the CGC (104.7° for $[2\text{-}(\eta^5\text{–}Me_3C_5H)\text{–}C_6H_4\text{–}NC_6H_{11}\text{-}\kappa N]TiCl_2$ [10]; 100.91° for $[2\text{-}(\eta^5\text{–}Me_3C_5H)\text{–}C_6H_4\text{–}NSO_2C_6H_4CH_3\text{-}\kappa^2N, O]TiCl_2$ [11]; 101.36° for $[2\text{-}(\eta^5\text{-}Me_3C_5H)\text{–}C_6H_4\text{–}NC(O)tBu\text{-}\kappa^2N, O]\text{-}TiCl_2$ [12]; 103.19° for $[2\text{-}(\eta^5\text{-}Me_3C_5H)\text{–}C_6H_4\text{–}N\text{–}PPh_2\text{-}\kappa^2N, P]TiCl_2$) [13]. The Cp(centroid)–Ti–N angle has been used as a qualitative measure for "constrained geometry". The smaller the angle, the more pronounced the "constrained geometry" feature should be. The smaller angles observed for the *o*-phenylene-bridged complexes imply that the *o*-phenylene-bridge framework provides a more constrained feature in the complexes than the Me_2Si-bridge framework. The bridge atoms in the *o*-phenylene-bridged complexes are not situated in a severely strained position. The *ipso*-carbon (C(9)) is placed almost on the cyclopentadienyl plane (C(centroid)–C(bridgehead)–C(*ipso*) angle, 170.07° and 170.08° for **18** and **19**, respectively). The

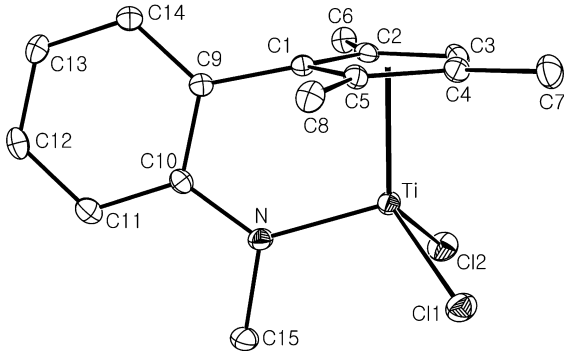


Fig. 1. Thermal ellipsoid plot (30% probability level) of **18**.

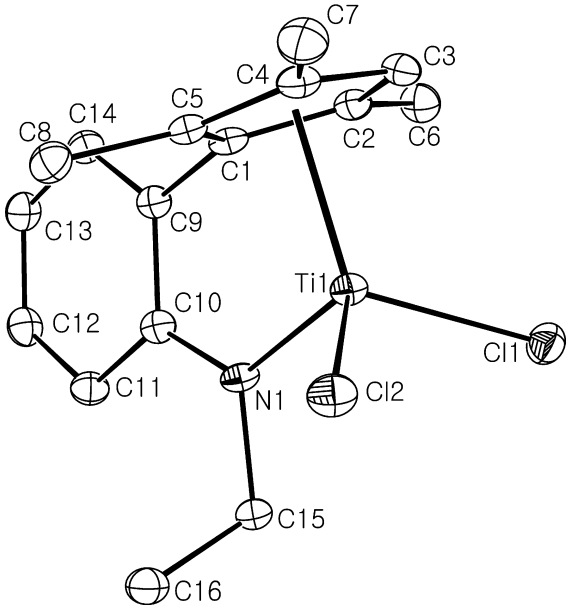


Fig. 2. Thermal ellipsoid plot (30% probability level) of **19**.

Ti–Cp(centroid) vector is situated almost perpendicularly to the cyclopentadienyl plane (Ti–Cp(centroid)–C(bridgehead) angle, 89.11° and 88.83° for **18** and **19**, respectively). On the contrary, the bridging silicon atom in the CGC and the bridge carbon atom in the C1-bridged Cp/amido complexes are situated severely deviated from the cyclopentadienyl plane. The Cp(centroid)–C(bridgehead)–Si angles for $C_5R_4SiMe_2$(N-*t*-Bu) titanium complexes [16] are 150–154°, and the corresponding Cp(centroid)–C(bridgehead)–C(bridge) angles for C1-bridged Cp/amido titanium complexes are 152–156° [8].

The Cp(centroid)–Ti distances are slightly smaller in **18** and **19** (2.001 and 2.002 Å, respectively) than that observed for the standard CGC (2.030 Å), while the Ti–N distances (1.911(3) and 1.919(3) Å for **18** and **19**, respectively) are slightly longer than that in CGC (1.907(4) Å). The Ti–Cl distances are also slightly longer than those in CGC. The Cl–Ti–Cl angles are wider in **18** and **19** (105.16(4)° and 103.97(5)°, respectively) than that observed for the CGC (102.97(7)°).

Single crystals of zirconium complexes **24** and **26** are obtained through layer diffusion of pentane onto a benzene solution at room temperature. The X-ray crystallographic studies reveal μ-chloro dimeric structures, which are shown in Figs. 3 and 4. The selected bond distances and angles are tabulated compared with those observed for the titanium complexes and the zirconium analogue of the standard CGC, $[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]ZrCl_2$ (Table 1). One Zi–Cl bond distance is normal (2.4414(13) and 2.4314(11) Å for **24** and **26**, respectively), while the other Zr–Cl(μ) bond distance is long (2.7449(10) and 2.7239(11) for **24** and **26**, respectively). The Cl–Zr–Cl angles are also deviated from the one observed for the monomeric Cp/amido zirconium or titanium dichloride complexes. The formation of μ-chloro dinuclear zirconium complexes

Table 1
Selected bond distances (Å) and angles (°) in **18**, **19**, **24**, **26**, [(η^5-Me_4Cp)CH_2CH_2(N^tBu)]$TiCl_2$, and [(η^5-Me_4Cp)CH_2CH_2(N^tBu)]$ZrCl_2$

	18	**19**	CGC–Ti[a]	**24**	**26**	CGC–Zr[b]
M–Cp(cent)	2.001	2.002	2.030	2.168	2.165	2.163
M–C(1) (bridgehead-C)	2.320(3)	2.313(4)		2.450(4)	2.455(4)	
M–C(2)	2.344(3)	2.335(4)		2.454(4)	2.486(4)	
M–C(5)	2.330(3)	2.348(4)		2.507(4)	2.478(4)	
M–C(3)H (peripheral-C)	2.331(3)	2.329(4)		2.474(5)	2.483(4)	
M–C(4)CH_3 (peripheral-C)	2.359(3)	2.368(4)		2.517(4)	2.490(4)	
M–N	1.911(3)	1.919(3)	1.907(4)	2.072(3)	2.058(3)	2.052(2)
M–Cl(1)	2.2760(9)	2.2809(13)	2.2635(11)	2.4414(13)	2.7449(10)	2.4065(10)
M–Cl(2)	2.2764(10)	2.2816(11)		2.7239(11)	2.4314(11)	2.4082(10)
Cp(cent)–M–N	105.11	104.90	107.6	99.79	99.13	102.0
Cl(1)–M–Cl(2)	105.16(4)	103.97(5)	102.97(7)	80.28(4)	79.40(4) (4)	104.92(4)
				73.30	74.43	
				131.22(4)	130.69	
Cp(cent)–C(1)–C(9)	170.07	170.08		172.88	173.40	
C(1)–Cp(cent)–M	89.11	88.83		88.49	88.95	
M–N–C(10)	127.67(19)	127.7(2)		127.8(3)	129.4(3)	
M–N–C(15)	115.2(2)	113.7(2)		113.9(3)	107.4(2)	
C(10)–N–C(15)	117.1(3)	118.7(3)		117.5(4)	123.1(3)	
C(1)–C(9)–C(10)	112.9(3)	113.1(3)		114.8(3)	114.7(3)	
C(9)–C(10)–N	114.4(3)	114.0(3)		114.7(4)	114.4(4)	

[a] [(η^5-Me_4Cp)CH_2CH_2(N^tBu)]$TiCl_2$, data from Ref. [16].
[b] [(η^5-Me_4Cp)CH_2CH_2(N^tBu)]$ZrCl_2$, data from Ref. [16].

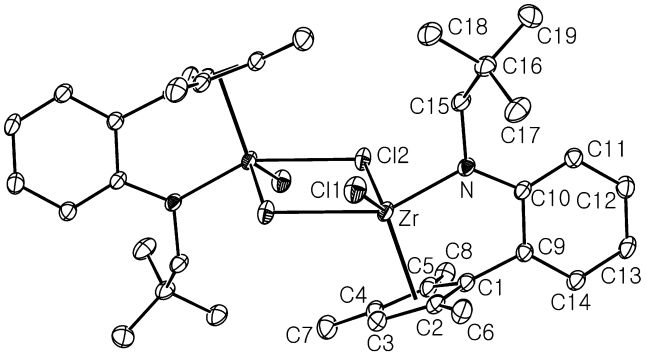


Fig. 3. Thermal ellipsoid plot (30% probability level) of **24**.

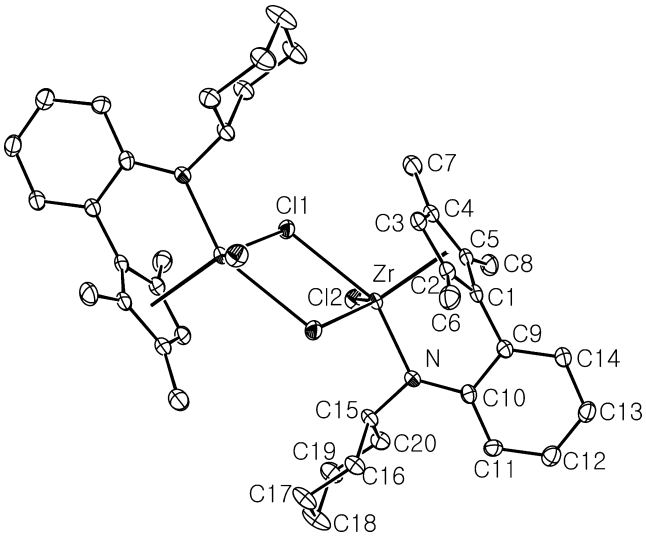


Fig. 4. Thermal ellipsoid plot (30% probability level) of **26**.

is in contrast with the monomeric structure observed for the [Me_2Si(η^5-Me_4C_5)(N^tBu)]$ZrCl_2$. That is, in the monomeric structure of [Me_2Si(η^5-Me_4C_5)(N^tBu)]$ZrCl_2$, the Cl–Zr–Cl angle (104.92(4)°) is normal, and the two Zr–Cl distances (2.4065(10) and 2.4082(10) Å) are almost the same [16].

The Cp(centroid)–Zr–N angles (99.79° and 99.13° for **24** and **26**, respectively) are smaller than that observed for the zirconium analogue of the CGC, [Me_2Si(η^5-Me_4C_5)-(N^tBu)]$ZrCl_2$ (102.0°) still indicating the more constrained feature in the *o*-phenylene bridged complexes than in the Me_2Si-bridged complex. The more opened nature around the zirconium center in the *o*-phenylene bridged Cp/amido complexes, which is inferred from the smaller Cp(centroid)–Zr–N angles, might result in the formation of μ-chloro dinuclear complexes. Similar μ-chloro dinuclear structures were observed for the more constrained C1-bridged zirconium dichloride complexes [8]. The elements constituting the chelation are not also situated in a severely strained position as is observed for the titanium complexes (Cp(centroid)–C(bridgehead)–C(*ipso*) angle, 172.88° and 173.40° for **24** and **26**, respectively). The sum of bond angles around the N atoms for both titanium and zirconium complexes, namely, **18**, **19**, **24**, and **26**, is very close to 360°, which is consistent with the sp^2-hybridization of the N atom.

2.3. Polymerization studies

The newly prepared complexes and **3**–**4** are tested for ethylene/1-octene copolymerization after activation with (Ph_3C)[$B(C_6F_5)_4$] and *i*Bu_3Al. The triisobutylaluminum is added both as a scavenger of the polar impurities and as

Table 2
Ethylene/1-octene copolymerization results[a]

Entry	Complex	Yield (g)	Activity[b]	[Oct][c]	M_w	M_w/M_n
1	**18**	0.29	12	14	433000	2.6
2	**19**	0.75	30	16	415000	2.2
3	**20**	0.99	40	9	226000	2.2
4	**21**	0.27	11	15	525000	2.4
5	**3**	0.57	23	11	315000	2.2
6	**4**	0.56	22	13	514000	2.5
7	**22–27**	negligible				
8	**CGC**[d]	0.97	39	18	192000	2.6

[a] Polymerization conditions: 30 mL toluene solution of 1-octene (0.3 M, 1.0 g), 0.50 μmol Ti, 2.0 μmol $[Ph_3C][B(C_6F_5)_4]$, 0.20 mmol $Al(iBu)_3$, 60 psig ethylene, 3 min, initial temperature 70 °C.
[b] Averaged activity in 2 or 3 runs in unit of 10^6 g/molTi h.
[c] *c*1-Octene content in the copolymer determined by the ^1H NMR.
[d] $[Me_2Si(\eta^5\text{-}Me_4Cp)(N^tBu)]TiCl_2$.

an alkylating agent. The polymerization conditions and the results are summarized in Table 2. Ethylamido titanium complex **19** and neopentylamido titanium complex **20** exhibit higher activities than secondary-hydrocarbyl amido titanium complexes **3** and **4**, and the activities of **19** and **20** (30 and 40 × 10^6 g/molTi h, respectively) are comparable to that of the standard CGC (39 g/molTi h). The activities of the methylamido complex **18** and cyclohexylmethylamido complex **21** are inferior, and the zirconium complexes **22–27** show a negligible activity under the same conditions.

The 1-octene content in the copolymer is dependent on the size of the substituent on the nitrogen atom. Primary-hydrocarbyl amido titanium complexes **18**, **19**, and **21** are able to incorporate more 1-octene (14, 16, 15 mol%, respectively) than secondary-hydrocarbyl amido titanium complexes **3** and **4** (11 and 13 mol%, respectively). The 1-octene incorporation ability of neopentylamido titanium complex **20** is inferior (9 mol%) even though it is a primary-hydrocarbyl amido titanium complex. This low 1-octene incorporation might be attributed to the bulkiness of the neopentyl group. Ethylamido complex **19**, which shows fairly good activity, can incorporate the highest amount of 1-octene, but the incorporated amount (16 mol%) is slightly less than that observed for the polymer obtained with the standard CGC (18 mol%). The molecular weights of the polymers obtained with the *o*-phenylene-bridged complexes are higher than that of the polymer obtained with CGC. The molecular weight of the polymer obtained with **19** (M_w, 415000) is almost two times higher than that of the polymer obtained with CGC (M_w, 192000). The molecular weight distributions are narrow in all cases (M_w/M_n, 2.2–2.6), indicating a single active site.

3. Experimental

3.1. General remarks

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene, pentane, THF, and C_6D_6 were distilled from benzophenone ketyl. Me_2SiCl_2 and Me_3SiCl were dried over CaH_2 and transferred under the vacuum to reservoirs. The NMR spectra were recorded on a Varian Mercury plus 400. Elemental analyses were carried out at the Analytical Center, Kyunghee University. Mass spectra were obtained on a Micromass VG Autospec. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using Waters Model 150-C+GPC and the data were analyzed using a polystyrene analyzing curve. Compound **2** was prepared according to the procedure and conditions reported in the literature [10a].

3.2. Compound 8

2-Bromoaniline (4.25 g, 24.71 mmol) and trimethylacetadehyde (3.19 g, 37.1 mmol) were dissolved in toluene (60 mL) and molecular sieves (4.0 g) were added. The flask was sealed with a screw-cap and heated at 100 °C for 2 days. After the molecular sieves were filtered off, all volatiles were removed under vacuum at 60 °C to give a crude imine compound. The imine compound was dissolved in degassed methanol (75 mL). After sodium borohydride (2.80 g, 74.13 mmol) was added slowly under a weak stream of nitrogen gas, the mixture was stirred at room temperature for 2 h. Aqueous 1 N KOH (75 mL) was added, and the product was extracted with methylene chloride (100 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$ and then the solvent was removed with a rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 10:1). Yellow oil was obtained (3.65 g, 65%). IR (neat): 3423 (N–H) cm^{-1}. ^1H NMR (C_6D_6): δ 0.82 (s, 9H, CH_3), 2.61 (d, $J = 6.0$ Hz, 2H, N–CH_2), 4.38 (br s, 1H, NH), 6.40 (t, $J = 8.0$ Hz, 1H, C_6H_4), 6.44 (d, $J = 8.0$ Hz, 1H, C_6H_4), 7.01 (t, $J = 8.0$ Hz, 1H, C_6H_4), 7.37 (dd, $J = 7.6$, 1.2 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 27.71, 31.97, 55.54, 110.22, 111.63, 117.64, 128.71, 132.60, 145.82 ppm. HRMS (EI): *m*/*z* calcd ($[M]^+$ $C_{11}H_{16}BrN$) 241.0466. Found: 241.0470%.

3.3. Compound 9

The compound was synthesized using the same conditions and procedure as those for **8** with cyclohexanecarboxaldehyde. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 10:1). Light yellow oil was obtained in 63% yield. IR (neat): 3408 (N–H) cm^{-1}. ^1H NMR (C_6D_6): δ 0.72–0.80 (m, 2H, Cy), 1.02–1.12 (m, 4H, Cy), 1.28–1.33 (m, 1H, Cy), 1.58–1.65 (m, 4H, Cy), 2.66 (t, $J = 6.4$ Hz, 2H, N–CH_2), 4.34 (br s, 1H, NH), 6.40 (t, $J = 8.0$ Hz, 1H, C_6H_4), 6.44 (d, $J = 8.0$ Hz, 1H, C_6H_4), 7.01 (t, $J = 8.0$ Hz, 1H, C_6H_4), 7.38 (dd, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 26.43, 27.04, 31.55, 37.65, 50.57, 110.01, 111.58, 117.60, 128.73, 132.66, 145.56 ppm. HRMS (EI): *m*/*z* calcd ($[M]^+$ $C_{13}H_{13}BrN$) 267.0623. Found: 267.0620%.

3.4. Compound **10**

Compound **2** (0.63 g, 4.09 mmol), Na_2CO_3 (0.65 g, 6.14 mmol), $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol), and compound **6** (0.73 g, 3.90 mmol) were added into a Schlenk flask inside a glovebox. The flask was brought out from the glove box and degassed DME (23 mL) and degassed water (7.5 mL) were successively added with a syringe. The mixture was stirred at 95 °C overnight. After the solution was cooled to room temperature, it was transferred to a separatory funnel containing ethyl acetate (25 mL). Water (25 mL) was added and then the organic phase was collected. The water phase was extracted with additional ethyl acetate (10 mL × 2). The combined organic phase was dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 3:1). A light yellow solid was obtained (0.76 g, 91%). M.p. 88 °C. IR (neat): 3394 (N–H) cm^{-1}, 1690 (C=O) cm^{-1}. ^1H NMR (C_6D_6): δ 0.73 (d, $J = 7.2$ Hz, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.82 (dd, $J = 18.0$, 2.0 Hz, 1H, CH_2), 2.15–2.22 (m, 2H, CH), 2.40 (dd, $J = 18.4$, 6.4 Hz, 1H, CH_2), 2.47 (s, 3H, N–CH_3), 4.11 (br s, 1H, NH), 6.64 (d, $J = 8.4$ Hz, 1H, C_6H_4), 6.83 (t, $J = 8.0$ Hz, 1H, C_6H_4), 6.99 (dd, $J = 7.6$, 1.6 Hz, 1H, C_6H_4), 7.26 (td, $J = 8.8$, 1.6 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 16.02, 19.19, 30.84, 37.75, 43.63, 111.04, 117.07, 119.10, 131.03, 140.02, 148.26, 177.19, 205.65 ppm. Anal. Calc. ($C_{14}H_{17}NO$): C, 78.10; H, 7.96; N, 6.51. Found: C, 77.83; H, 8.26; N, 6.45%.

3.5. Compound **11**

The compound was synthesized using the same conditions and procedure as those for **10** with **7**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 3:1). A light yellow solid was obtained (89%). M.p. 84 °C. IR (neat): 3401 (N–H) cm^{-1}, 1682 (C=O) cm^{-1}. ^1H NMR (C_6D_6): δ 0.73 (d, $J = 6.8$ Hz, 3H, CH_3), 1.02 (t, $J = 6.8$ Hz, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.82 (dd, $J = 18.4$, 2.4 Hz, 1H, CH_2), 2.16–2.22 (m, 1H, CH), 2.40 (dd, $J = 18.4$, 7.2 Hz, 1H, CH_2), 2.88 (q, $J = 6.4$ Hz, 2H, N–CH_2), 4.11 (br s, 1H, NH), 6.68 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.82 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.00 (d, $J = 6.4$ Hz, 1H, C_6H_4), 7.25 (td, $J = 7.2$, 1.6 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 15.07, 16.13, 19.25, 37.75, 38.84, 43.63, 111.67, 117.06, 119.05, 129.52, 131.23, 135.14, 147.49, 177.05, 205.60 ppm. Anal. Calc. ($C_{15}H_{19}NO$): C, 78.56; H, 8.35; N, 6.11. Found: C, 78.89; H, 8.34; N, 6.37%.

3.6. Compound **12**

The compound was synthesized using the same conditions and procedure as those for **10** with **8**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 3:1). A light yellow solid was obtained (93%). M.p. 73 °C. IR (neat): 3422 (N–H) cm^{-1}, 1691 (C=O) cm^{-1}. ^1H NMR (C_6D_6): δ 0.79 (d, $J = 7.2$ Hz, 3H, CH_3), 0.91 (s, 9H, CH_3), 1.61 (s, 3H, CH_3), 1.84 (dd, $J = 18.4$, 2.0 Hz, 1H, CH_2), 2.20–2.24 (m, 1H, CH), 2.43 (dd, $J = 18.0$, 6.4 Hz, 1H, CH_2), 2.70–2.79 (m, 2H, N–CH_2), 4.16 (br s, 1H, NH), 6.71 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.81 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 6.99 (dd, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.24 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 16.14, 19.63, 28.03, 31.84, 37.75, 43.71, 56.10, 111.65, 116.94, 119.07, 129.47, 131.11, 135.24, 139.98, 147.77, 177.18, 205.40 ppm. Anal. Calc. ($C_{13}H_{25}NO$): C, 79.66; H, 9.28; N, 5.16. Found: C, 79.62; H, 8.94; N, 5.02%.

3.7. Compound **13**

The compound was synthesized using the same conditions and procedure as those for **10** with **9**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 3:1). A light yellow solid was obtained (92%). M.p. 70 °C. IR (neat): 3409 (N–H) cm^{-1}, 1682 (C=O) cm^{-1}. ^1H NMR (C_6D_6): δ 0.76 (d, $J = 7.2$ Hz, 3H, CH_3), 0.85–0.93 (m, 2H, Cy), 1.03–1.20 (m, 3H, Cy), 1.46–1.66 (m, 4H, Cy), 1.62 (s, 3H, CH_3), 1.77–1.81 (m, 2H, Cy), 1.83 (dd, $J = 18.4$, 2.0 Hz, 1H, CH_2), 2.17–2.23 (m, 1H, CH), 2.41 (dd, $J = 18.4$, 6.8 Hz, 1H, CH_2), 2.83 (t, $J = 6.4$ Hz, 2H, N–CH_2), 4.26 (br s, 1H, NH), 6.73 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.81 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 6.99 (dd, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.26 (td, $J = 7.2$, 1.6 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 16.14, 19.39, 26.53, 27.13, 31.79, 37.77, 38.07, 43.67, 51.18, 111.67, 116.88, 119.02, 129.50, 131.22, 140.16, 147.63, 177.14, 205.52 ppm. Anal. Calc. ($C_{20}H_{27}NO$): C, 80.76; H, 9.15; N, 4.71. Found: C, 80.98; H, 8.99; N, 4.82%.

3.8. Compound **14**

The $CeCl_3$/2LiCl solution in THF (0.33 M; 17 mL, 5.45 mmol), which was prepared according to the literature method [15], was added into a Schlenk flask. After the solution was cooled to −78 °C, MeLi (3.5 mL, 1.6 M in diethyl ether, 5.45 mmol) was added with a syringe. The solution was stirred for 1 h at −78 °C. Compound **10** (0.59 g, 2.73 mmol) dissolved in THF (1.0 mL) was added with a syringe. After the mixture was stirred for 2 h at −78 °C, it was transferred to a separatory funnel containing ethyl acetate (10 mL) and water (5 mL). The organic phase was collected and the water phase was further extracted with additional ethyl acetate (5 mL × 2). The combined organic phase was washed with water (10 mL) and it was shaken vigorously with aqueous HCl solution (2 N, 5 mL) for 2 min. Aqueous saturated $NaHCO_3$ (10 mL) was added carefully to neutralize the water phase. The organic phase was collected and dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give a residue which was purified by column chromatography on

silica gel eluting with hexane and ethyl acetate (v/v, 30:1). A light yellow solid was obtained (0.53 g, 91%). M.p. 39 °C. ^{1}H NMR (C_6D_6): δ 1.75 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 2.40 (d, 3H, N–CH_3), 2.67 (AB, $J = 22.8$ Hz, 1H, CH_2), 2.75 (AB, $J = 22.8$ Hz, 1H, CH_2), 3.65 (br d, $J = 4.4$ Hz, 1H, NH), 6.60 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.84 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.11 (dd, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.27 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm, ^{13}C{^{1}H} NMR (C_6D_6): δ 12.00, 13.85, 14.55, 30.55, 49.06, 109.66, 116.82, 122.86, 128.71, 130.14, 133.15, 136.43, 136.97, 140.78, 147.47 ppm. Anal. Calc. ($C_{15}H_{19}N$): C, 84.46; H, 8.98; N, 6.57. Found: C, 84.60; H, 8.74; N, 6.38%.

3.9. Compound **15**

The compound was synthesized using the same conditions and procedure as those for **14** with **11**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). Light yellow oil was obtained in 87% yield. ^{1}H NMR (C_6D_6): δ 0.87 (t, $J = 7.2$ Hz, 3H, CH_3), 1.78 (s, 3 H, CH_3), 1.87 (s, 6H, CH_3), 2.67 (AB, $J = 22.8$ Hz, 1H, CH_2), 2.76 (AB, $J = 22.4$ Hz, 1H, CH_2), 3.71 (br s, 1H, NH), 6.66 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.84 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.12 (dd, $J = 7.6$, 1.6 Hz, 1H, C_6H_4), 7.26 (td, $J = 8.0$, 1.2 Hz, 1H, C_6H_4) ppm, ^{13}C{^{1}H} NMR (C_6D_6): δ 12.05, 13.85, 14.62, 15.04, 38.47, 49.04, 110.27, 116.79, 122.88, 128.67, 130.36, 133.31, 136.32, 136.87, 140.82, 146.48 ppm. HRMS (EI): *m/z* calcd ([M]$^+$ $C_{16}H_{21}N$) 227.1674. Found: 227.1674%.

3.10. Compound **16**

The compound was synthesized using the same conditions and procedure as those for **14** with **12**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). Yellow oil was obtained in 91% yield. ^{1}H NMR (C_6D_6): δ 0.82 (s, 9H, CH_3), 1.78 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 2.68 (AB, $J = 22.8$ Hz, 1H, CH_2), 2.75 (AB, $J = 22.8$ Hz, 1H, CH_2), 2.73–2.81 (m, 2H, N–CH_2), 3.93 (br t, $J = 4.8$ Hz, 1H, NH), 6.72 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.85 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.14 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.28 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm, ^{13}C{^{1}H} NMR (C_6D_6): δ 12.07, 13.82, 14.67, 27.80, 32.12, 49.05, 55.91, 110.28, 116.65, 122.90, 128.65, 130.18, 133.37, 136.26, 137.07, 140.82, 147.12 ppm. HRMS (EI): *m/z* calcd ([M]$^+$ $C_{19}H_{27}N$) 269.2143. Found: 269.2144%.

3.11. Compound **17**

The compound was synthesized using the same conditions and procedure as those for **14** with **13**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). Light yellow oil was obtained in 87% yield. ^{1}H NMR (C_6D_6): δ 0.75–0.81 (m, 2H, Cy), 1.03–1.12 (m, 2H, Cy), 1.32–1.37 (m, 2H, Cy) 1.56–1.65 (m, 6H, Cy), 1.80 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.67 (AB, $J = 22.8$ Hz, 1H, CH_2), 2.77 (AB, $J = 22.8$ Hz, 1H, CH_2), 2.77–2.85 (m, 2H, N–CH_2), 3.94 (br s, 1H, NH), 6.73 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.85 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.14 (d, $J = 7.2$ Hz, 1H, C_6H_4), 7.28 (t, $J = 7.2$ Hz, 1H, C_6H_4) ppm, ^{13}C{^{1}H} NMR (C_6D_6): δ 12.09, 13.85, 14.67, 26.43, 27.09, 31.64, 38.01, 49.09, 51.00, 110.44, 116.69, 122.96, 128.68, 130.34, 133.34, 136.41, 136.41, 137.03, 140.92, 146.85 ppm. HRMS (EI): *m/z* calcd ([M]$^+$ $C_{21}H_{29}N$) 295.2300. Found: 295.2300%.

3.12. Complex **18**

Compound **14** (0.238 g, 1.12 mmol), $Ti(NMe_2)_4$ (0.250 g, 1.12 mmol), and toluene (5 mL) were added into a Schlenk flask. The solution was stirred for 1 day at 80 °C. Removal of the solvent gave red oil. The ^{1}H NMR datum for the intermediate bis(dimethylamido)titanium complex (C_6D_6): δ 1.78 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 2.89 (s, 6H, N–CH_3), 3.23 (s, 6H, N–CH_3), 3.45 (s, 3H, N–CH_3), 5.76 (s, 1H, Cp–H), 6.44 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.94 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.22 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.32 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. The resulting bis(dimethylamido)titanium complex was dissolved in toluene (5 mL) and Me_2SiCl_2 (0.432 g, 3.35 mmol) was added. After the solution was stirred 6 h at room temperature, all volatiles were removed under vacuum to give a dark red solid which was triturated in pentane (0.35 g, 94%). The analytical data for **18**: ^{1}H NMR (C_6D_6): δ 1.64 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 3.66 (s, 3H, N–CH_3), 5.96 (d, $J = 8.0$ Hz, 1H, C_6H_4), 5.99 (s, 1H, Cp–H), 6.95 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.03 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.12 (t, $J = 8.0$ Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 12.66, 14.87, 14.99, 40.11, 108.63, 117.96, 123.50, 128.29, 129.28, 130.85, 131.63, 143.20, 143.68, 144.16, 167.06 ppm. Anal. Calc. ($C_{15}H_{17}Cl_2NTi$): C: 54.58; H, 5.19; N, 4.24. Found: C, 54.42; H, 5.32; N, 4.05%.

3.13. Complex **19**

It was synthesized using the same conditions and procedure as those for **18** with **15**. It was purified by trituration in pentane. Overall yield from **15** was 90%. The ^{1}H NMR datum for the intermediate bis(dimethylamido)titanium complex (C_6D_6): δ 1.02 (t, $J = 7.2$ Hz, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 2.88 (s, 6H, N–CH_3), 3.12 (s, 6H, N–CH_3), 3.85 (dq, $J = 13.6$, 6.8 Hz, 1H, N–CH_2), 4.08 (dq, $J = 13.6$, 6.8 Hz 1H, N–CH_2), 5.72 (s, 1H, Cp–H), 6.46 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.91 (t, $J = 8.0$ Hz, 1H, C_6H_4), 7.24 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.28 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. The analytical data for **19**: ^{1}H NMR (C_6D_6): δ 1.10

(t, $J = 6.8$ Hz, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 4.32 (dq, $J = 15.2$, 6.8 Hz, 1H, N–CH_2), 4.39 (dq, $J = 15.2$, 16.8 Hz, 1H, N–CH_2), 6.01 (s, 1H, Cp–H), 6.03 (d, $J = 8.8$ Hz, 1H, C_6H_4), 6.94 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.04 (dd, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.10 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 11.56, 12.65, 14.91, 15.03, 45.45, 109.11, 118.00, 123.28, 128.61, 129.16, 131.35, 131.63, 143.05, 143.52, 143.96, 165.28 ppm. Anal. Calc. ($C_{16}H_{19}Cl_2NTi$): C, 55.85; H, 5.57; N, 4.07. Found: C, 55.98; H, 5.69; N, 3.82%.

3.14. Complex **20**

It was synthesized using the same conditions and procedure as those for **18** with **16**. It was purified by recrystallization in pentane at −30 °C. Overall yield from **16** was 72%. The ^1H NMR datum for the intermediate bis(dimethylamido)titanium complex (C_6D_6): δ 0.97 (s, 9H, CH_3), 1.64 (br s, 3H, CH_3), 1.93 (s, 3H, CH_3), 2.03 (br s, 3H, CH_3), 3.13 (s, 12H, N–CH_3), 3.81 (d, $J = 14.4$ Hz, 1H, CH_2), 3.96 (d, $J = 14.4$ Hz, 1H, CH_2), 5.74 (s, 1H, Cp–H), 6.64 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.83 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.21 (d, $J = 7.2$ Hz, 1H, C_6H_4), 7.22 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. The analytical data for **20**: ^1H NMR (C_6D_6): δ 1.08 (s, 9H, CH_3), 1.75 (br s, 6H, CH_3), 2.07 (s, 3H, CH_3), 3.65 (s, 1H, N–CH_2), 5.32 (s, 1H, N–CH_2), 6.03 (s, 1H, Cp–H), 6.37 (d, $J = 8.8$ Hz, 1H, C_6H_4), 6.92 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.03 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.11 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.90, 15.00, 31.43, 36.67, 61.24, 110.65, 119.08, 123.16, 128.55, 130.15, 141.92, 166.64 ppm. Anal. Calc. ($C_{19}H_{25}Cl_2NTi$): C, 59.09; H, 6.53; N, 3.63. Found: C, 58.97; H, 6.59; N, 3.75%.

3.15. Complex **21**

It was synthesized using the same conditions and procedure as those for **18** with **17**. It was purified by trituration in pentane. Overall yield from **17** was 84%. The ^1H NMR datum for the intermediate bis(dimethylamido)titanium complex (C_6D_6): δ 0.85–1.02 (m, 2H, Cy), 1.12–1.21 (m, 4H, Cy), 1.61–1.73 (m, 5H, Cy), 1.70 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 3.13 (s, 6H, N–CH_3), 3.16 (s, 6H, N–CH_3), 3.76 (dd, $J = 14.0$, 7.6 Hz, 1H, N–CH_2), 3.95 (dd, $J = 14.0$, 7.6 Hz, 1H, N–CH_2), 5.74 (s, 1H, Cp–H), 6.55 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.92 (t, $J = 8.0$ Hz, 1H, C_6H_4), 7.24 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.29 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4) ppm. The analytical data for **21**: ^1H NMR (C_6D_6): δ 1.02–1.07 (m, 2H, Cy), 1.22–1.30 (m, 4H, Cy), 1.50–1.53 (m, 1H, Cy), 1.61 (br d, $J = 6.0$ Hz, 4H, Cy), 1.69 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 4.35 (dd, $J = 15.6$, 7.6 Hz, 1H, N–CH_2), 4.46 (dd, $J = 15.6$, 7.6 Hz, 1H, N–CH_2), 6.01 (s, 1H, Cp–H), 6.30 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.93 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.04 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.12 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.76, 14.97, 15.14, 26.79, 32.06, 32.11, 39.12, 57.74, 110.10, 118.57, 123.18, 128.63, 129.92, 130.78, 132.04, 142.49, 143.40, 143.81, 166.11 ppm. Anal. Calc. ($C_{21}H_{27}Cl_2NTi$): C, 61.19; H, 6.60; N, 3.40. Found: C, 61.35; H, 6.76; N, 3.28%.

3.16. Complex **22**

Compound **14** (0.097 g, 0.46 mmol), $Zr(NMe_2)_4$ (0.134 g, 0.50 mmol) and toluene (2.5 mL) were added into a Schlenk flask. The solution was stirred for 1 day at 80 °C. Removal of the solvent gave red oil. The ^1H NMR datum for the intermediate bis(dimethylamido)titanium complex (C_6D_6): δ 1.82 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.79 (s, 6H, N–CH_3), 3.02 (s, 6H, N–CH_3), 3.18 (s, 3H, N–CH_3), 5.73 (s, 1H, Cp–H), 6.45 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.90 (td, $J = 7.2$, 0.8 Hz, 1H, C_6H_4), 7.21 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.32 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. The resulting bis(dimethylamido)titanium complex was dissolved in toluene (2.5 mL) and Me_3SiCl (0.300 g, 2.76 mmol) was added. After the solution was stirred 6 hours at room temperature, all volatiles were removed under vacuum to give a yellow solid which was triturated in benzene (0.13 g, 77%). The analytical data for **22**: ^1H NMR ($CDCl_3$): δ 1.91 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.42 (s, 3H, N–CH_3), 6.19 (s, 1H, Cp–H), 6.54 (t, $J = 8.0$ Hz, 1H, C_6H_4), 7.03 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.25 (dd, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.32(t, $J = 8.0$ Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.32, 14.17, 14.26, 34.79, 109.92, 114.06, 120.55, 127.77, 127.35, 127.51, 128.34, 128.99, 129.94, 136.69, 136.98, 139.74, 165.13 ppm. Anal. Calc. ($C_{15}H_{17}Cl_2NZr$): C: 48.24; H, 4.59; N, 3.75. Found: C, 48.03; H, 4.70; N, 3.84%.

3.17. Complex **23**

It was synthesized using the same conditions and procedure as those for **22** with **15**. It was purified by recrystallization in $CHCl_3$. Overall yield from **15** was 64%. The ^1H NMR datum for the intermediate bis(dimethylamido)titanium complex (C_6D_6): δ 1.12 (t, $J = 7.2$ Hz, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 2.78 (s, 6H, N–CH_3), 3.00 (s, 6H, N–CH_3), 3.61–3.75 (m, 2H, N–CH_2), 5.71 (s, 1H, Cp–H), 6.49 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.87 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.22 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.28 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. The analytical data for **23**: ^1H NMR ($CDCl_3$): δ 1.35 (t, $J = 6.8$ Hz, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.95 (q, $J = 6.4$ Hz, 2H, N–CH_2), 6.21 (s, 1H, Cp–H), 6.54 (d, $J = 8.0$ Hz, 1H, C_6H_4), 7.00 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.25 (dd, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.34 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.94, 12.21, 13.99, 14.34, 40.89, 110.63, 113.57, 119.86, 125.19, 127.51, 127.87, 128.03, 128.63, 136.43, 138.69, 163.62 ppm. Anal. Calc. ($C_{16}H_{19}Cl_2NZr$): C, 49.60; H, 4.94; N, 3.62. Found: C, 49.57; H, 4.73; N, 3.75%.

3.18. Complex **24**

It was synthesized using the same conditions and procedure as those for **22** with **16**. It was purified by trituration in pentane. Overall yield from **16** was 88%. The ^{1}H NMR datum for the intermediate bis(dimethylamido)titanium complex (C_6D_6): δ 0.98 (s, 9H, CH_3), 1.74 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.69 (s, 6H, N–CH_3), 2.93 (s, 6H, N–CH_3), 3.50 (d, $J = 15.2$ Hz, 1H, N–CH_2), 3.69 (d, $J = 14.4$ Hz, 1H, N–CH_2), 5.73 (s, 1 H, Cp–H), 6.70 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.81 (td, $J = 7.2$, 0.8 Hz, 1H, C_6H_4), 7.21 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.23 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. The analytical data for **24**: ^{1}H NMR ($CDCl_3$): δ 1.01 (s, 9H, CH_3), 1.80 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.78 (s, 2H, N–CH_2), 6.21 (s, 1H, Cp–H), 6.50 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.87 (td, $J = 7.2$, 0.8 Hz, 1H, C_6H_4), 7.12 (dd, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.18 (td, $J = 7.2$, 1.2 Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.65, 13.76, 13.78, 30.72, 36.02, 38.44, 38.44, 48.54, 56.43, 112.26, 113.67, 120.46, 126.40, 126.46, 128.23, 128.87, 136.51, 137.09, 163.83 ppm. Anal. Calc. ($C_{19}H_{25}Cl_2NZr$): C, 53.13; H, 5.87; N, 3.26. Found: C, 53.24; H, 5.60; N, 3.45%.

3.19. Complex **25**

It was synthesized using the same conditions and procedure as those for **22** with **17**. It was purified by trituration in pentane. Overall yield from **17** was 84%. The ^{1}H NMR datum for the intermediate bis(dimethylamido)titanium complex (C_6D_6): δ 0.77–0.96 (m, 2H, Cy), 1.06–1.22 (m, 3H, Cy), 1.61–1.74 (m, 6H, Cy), 1.78 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.75 (s, 6H, N–CH_3), 2.99 (s, 6H, N–CH_3), 3.51 (dd, $J = 14.4$, 8.0 Hz, 1H, N–CH_2), 3.62 (dd, $J = 14.4$, 5.6 Hz, 1H, N–CH_2), 5.73 (s, 1H, Cp–H), 6.59 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.87 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.24 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.30 (td, $J = 8.0$, 1.6 Hz, 1H, C_6H_4) ppm. The analytical data for **25**: ^{1}H NMR (C_6D_6): δ 1.01–1.18 (m, 4H, Cy), 1.51–1.68 (m, 6H, Cy), 1.72 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.99–2.04 (m, 1H, Cy), 2.04 (s, 3H, CH_3), 3.78 (d, $J = 6.8$ Hz, 2H, N–CH_2), 5.84 (s, 1H, Cp–H), 6.41 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.91 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.07 (dd, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.18 (td, $J = 8.0$, 1.2 Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 11.61, 13.69, 13.78, 26.64, 26.80, 32.04, 32.10, 38.05, 53.17, 111.99, 113.57, 120.99, 126.15, 127.58, 128.53, 129.16, 129.24, 136.68, 136.72, 138.20, 164.16 ppm. Anal. Calc. ($C_{21}H_{27}Cl_2NZr$): C, 55.36; H, 5.97; N, 3.07. Found: C, 55.27; H, 5.89; N, 3.19%.

3.20. Complex **26**

It was synthesized using the same conditions and procedure as those for **22** with 2-($Me_3C_5H_2$)–C_6H_4– NH(C_6H_{11}). It was purified by trituration in pentane. Overall yield from 2-($Me_3C_5H_2$)–C_6H_4– NH(C_6H_{11}) was 89%. The ^{1}H NMR datum for the intermediate bis(dimethylamido)titanium complex (C_6D_6): δ 1.16–1.22 (m, 2H, Cy), 1.32–1.14 (m, 4H, Cy), 1.66–1.69 (m, 2H, Cy), 1.79–1.83 (m, 2H, Cy), 1.84 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 2.78 (s, 6H, N–CH_3), 2.88 (s, 6H, N–CH_3), 3.66 (br s, 1H, N–CH_2), 5.68 (s, 1H, Cp–H), 6.77 (br d, $J = 8.0$ Hz, 1H, C_6H_4), 6.87 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.21 (dd, $J = 7.2$, 1.6 Hz, 1H, C_6H_4), 7.28 (t, $J = 8.0$ Hz, 1H, C_6H_4) ppm. The analytical data for **26**: ^{1}H NMR (C_6D_6): δ 1.14 (br s, 4H, Cy), 1.45 (br s, 2H, Cy), 1.66–1.69 (m, 2H, Cy), 1.72 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 2.22–2.04 (m, 2H, Cy), 2.07 (s, 3H, CH_3), 5.90 (s, 1H, Cp–H), 6.51 (br s, 1H, C_6H_4), 6.92 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.06 (dd, $J = 7.2$, 1.2 Hz, 1H, C_6H_4), 7.18 (t, $J = 8.0$ Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 11.54, 13.78, 13.85, 25.87, 26.47, 32.15, 57.33, 111.88, 114.56, 120.77, 129.11, 129.29, 136.23, 136.34, 137.99, 162.08 ppm. Anal. Calc. ($C_{15}H_{17}Cl_2NZr$): C, 54.40; H, 5.71; N, 3.17. Found: C, 54.67; H, 5.76; N, 3.22%.

3.21. Complex **27**

It was synthesized using the same conditions and procedure as those for **22** with 2-($Me_3C_5H_2$)–C_6H_4–NH[$CH(CH_2CH_3)_2$]. It was purified by trituration in pentane. Overall yield from 2-($Me_3C_5H_2$)–C_6H_4–NH-[$CH(CH_2CH_3)_2$] was 63%. The ^{1}H NMR datum for the intermediate bis(dimethylamido)titanium complex (C_6D_6): δ 0.82–1.02 (m, 6H, pentyl-CH_3), 1.81 (s, 3H, CH_3), 1.92 (s, 6H, CH_3), 1.95 (br s, 3H, CH_3), 2.78 (br s, 4H, pentyl-CH_3), 2.98 (s, 12H, N–CH_3), 3.57 (br s, 1H, N–CH_2), 5.75 (s, 1H, Cp–H), 6.68 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.82 (t, $J = 7.6$ Hz, 1H, C_6H_4), 7.17 (br s, 2H, C_6H_4) ppm. The analytical data for **27**: ^{1}H NMR (C_6D_6): δ 0.94 (t, $J = 7.6$ Hz, 3H, pentyl-CH_3), 0.96 (t, $J = 7.6$ Hz, 3H, pentyl-CH_3), 1.69 (s, 3H, CH_3), 1.81 (s, 6H, CH_3), 1.80–1.86 (m, 4H, pentyl-CH_2), 2.03 (s, 3H, CH_3), 4.25 (quin, $J = 7.2$ Hz, 1H, N–CH), 5.86 (s, 1H, Cp–H), 6.50 (d, $J = 8.0$ Hz, 1H, C_6H_4), 6.88 (t, $J = 7.2$ Hz, 1H, C_6H_4), 7.06 (d, $J = 7.2$ Hz, 1H, C_6H_4), 7.08 (t, $J = 8.0$ Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 11.39, 12.38, 12.41, 13.51, 13.60, 27.25, 27.30, 59.83, 113.08, 113.51, 120.95, 126.08, 128.84, 129.59, 136.21, 136.19, 137.93, 162.04 ppm. Anal. Calc. ($C_{19}H_{25}Cl_2NZr$): C, 53.13; H, 5.87; N, 3.26. Found: C, 52.92; H, 5.93; N, 3.50%.

3.22. Polymerization

In a glove box, 30 mL of toluene solution of 1-octene (1.0 g, 0.30 M) was added to a dried 60 mL glass reactor. The reactor was assembled and brought out from the glovebox. The reactor was then heated to 70 °C by a mantle. After an activated catalyst, which was prepared by mixing the complex (0.50 μmol), $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ (2.0 μmol), and (iBu)$_3$Al (0.20 mmol) for 5 min, was added with a syringe, the ethylene gas (60 psig) was fed immediately. After polymerization was conducted for 3 min, the

Table 3
Crystallographic parameters of **18**, **19**, **24**, and **26**

	18	**19**	**24**	**26**
Formula	$C_{15}H_{17}Cl_2NTi$	$C_{16}H_{19}Cl_2NTi$	$C_{19}H_{25}Cl_2NZr$	$C_{20}H_{24}Cl_2NZr$
F_w	330.08	344.11	429.54	440.56
Size (mm^3)	$0.5 \times 0.4 \times 0.3$	$0.4 \times 0.3 \times 0.3$	$0.5 \times 0.4 \times 0.4$	$0.4 \times 0.3 \times 0.3$
a (Å)	7.3913(10)	7.7969(6)	16.4245(8)	9.9199(8)
b (Å)	25.769(3)	16.1013(10)	7.4451(5)	10.8132(8)
c (Å)	7.8466(9)	25.1753(16)	17.6997(9)	10.8662(8)
α (°)	90	90	90	105.185(2)
β (°)	98.092(4)	90	117.9866(12)	100.255(2)
γ (°)	90	90	90	113.116(2)
V ($Å^3$)	1479.7(3)	3160.5(4)	1911.26(18)	981.40(13)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/a$	$Pbca$	$P2_1/n$	$P\bar{1}$
D_{calc} (g cm^{-1})	1.482	1.446	1.493	1.491
Z	4	8	4	2
μ (mm^{-1})	0.924	0.869	0.854	0.834
No. of data collected	14372	26253	17206	4429
No. of unique data [R(int)]	3359 [0.0591]	3597 [0.1163]	4331 [0.0628]	4429 [0.0474]
No. of variables	172	187	214	247
R (%)	0.0423	0.0700	0.0598	0.0552
R_w (%)	0.0977	0.1649	0.1418	0.1469
Goodness-of-fit	1.090	1.055	1.113	1.078

[a] Data collected at 150(2) K with Mo Kα radiation (λ(Kα) = 0.7107 Å), $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$.

ethylene gas was vented. Acetone was added to the reactor to give white precipitates which were collected by filtration, and then they were dried under vacuum at 60 °C. The 1-octene contents were calculated by the analysis of the ^{1}H NMR spectra of the copolymers. In the ^{1}H NMR spectra, the methyl (CH_3) signal (0.93–1.02 ppm) is well isolated from the methine (CH) and methylene (CH_2) signals (1.30–1.50 ppm), and the 1-octene content can be calculated from the integration values of the two regions by the equation of [1-octene] (mol%) = $[(B/3)]/\{(B/3) + [A - (B/3) \times 13]/4\}$, where A is the integration value of 1.6–1.2 ppm region and B is the integration value of 1.0–0.85 ppm region. The integration values were rather sensitively changeable depending on the conditions of the instrument shimming, signal phase, or integration phase. However, cutting with seizers and weighing the two signals after printing the spectrum on a paper in the 0.5–2.0 ppm region gave consistently invariable values. The copolymer (5 mg) was dissolved in C_6D_6, and the ^{1}H NMR spectra were recorded at 80 °C.

3.23. X-ray crystallography

Crystals of **18**, **19**, **24**, and **26** coated with grease (Apiezon N) were mounted onto a thin glass fiber with epoxy glue and placed in a cold nitrogen stream at 150(2) K on Rigaku single crystal X-ray diffractometer. The structures were solved by direct methods (SHELXL-97) and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results are summarized in Table 3.

Acknowledgement

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2007-314-C00190).

Appendix A. Supplementary material

CCDC 661641, 661642, 661643, 661644 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.11.021.

References

[1] (a) A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587;
(b) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283;
(c) A. Motta, I.L. Fragala, T.J. Marks, J. Am. Chem. Soc. 129 (2007) 7327.
[2] Review: (a) R. Kempe, Chem. Eur. J. 13 (2007) 2764;
(b) H.G. Alt, Dalton Trans. (2005) 3271;
(c) K. Nomura, J. Liu, S. Padmanabhan, B. Kitiyanan, J. Mol. Catal. A: Chem. 267 (2007) 1;
(d) Z. Hou, Y. Luo, X. Li, J. Organomet. Chem. 691 (2006) 3114.
[3] Recent progress: (a) D.J. Arriola, E.M. Carnahan, P.D. Hustad, R.L. Kuhlman, T.T. Wenzell, Science 312 (2006) 714;
(b) C. Alonso-Moreno, S.J. Lancaster, C. Zuccaccia, A. Macchioni, M. Bochmann, J. Am. Chem. Soc. 129 (2007) 9282;
(c) S.B. Amin, T.J. Marks, J. Am. Chem. Soc. 129 (2007) 2938;
(d) T.A. Manz, K. Phomphrai, G. Medvedev, B.B. Krishnamurthy, S. Sharma, J. Haq, K.A. Novstrup, K.T. Thomson, W.N. Delgass, J.M. Caruthers, M.M. Abu-Omar, J. Am. Chem. Soc. 127 (2005) 3776;

(e) J. Zhang, Y.-J. Lin, G.-X. Jin, Organometallics 26 (2007) 4042;
(f) P.M. Gurubasavaraj, H.W. Roesky, P.M.V. Sharma, R.B. Oswald, V. Dolle, R. Herbst-Irmer, A. Pal, Organometallics 26 (2007) 3346.
[4] P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867.
[5] (a) D.J. Arriola, M. Bokota, R.E. Campbell Jr., J. Klosin, R.E. LaPointe, O.D. Redwine, R.B. Shankar, F.J. Timmers, K.A. Abboud, J. Am. Chem. Soc. 129 (2007) 7065;
(b) C. Ramos, P. Royo, M. Lanfranchi, M.A. Pellinghelli, A. Tiripicchio, Organometallics 26 (2007) 445;
(c) K. Nishii, H. Hagihara, T. Ikeda, M. Akita, T. Shiono, J. Organomet. Chem. 691 (2006) 193;
(d) L.J. Irwin, S.A. Miller, J. Am. Chem. Soc. 127 (2005) 9972;
(e) C. Grandini, I. Camurati, S. Guidotti, N. Mascellani, L. Resconi, I.E. Nifant'ev, I.A. Kashulin, P.V. Ivchenko, P. Mercandelli, A. Ironi, Organometallics 23 (2004) 344;
(f) C. De Rosa, F. Auriemma, O. Ruiz de Ballesteros, L. Resconi, A. Fait, E. Ciaccia, I. Camurati, J. Am. Chem. Soc. 125 (2003) 10913;
(g) J. Klosin, W.J. Kruper Jr., P.N. Nickias, G.R. Roof, P. De Waele, K.A. Abboud, Organometallics 20 (2001) 2663;
(h) F.G. Sernetz, R. Mülhaupt, F. Amor, J. Polym. Sci., Part A: Polym. Chem. 35 (1997) 1571.
[6] (a) G. Altenhoff, S. Bredeau, G. Erker, G. Kehr, O. Kataeva, R. Frohlich, Organometallics 21 (2002) 4084;
(b) J.A.M. Canich (Exxon), U.S. Patent 5026798 (1991);
(c) J.A.M. Canich (Exxon), U.S. Patent 5504169 (1996).
[7] (a) C. Wang, G. Erker, G. Kehr, K. Wedeking, R. Frohlich, Organometallics 24 (2005) 4760;
(b) K. Kunz, G. Erker, S. Doring, R. Frohlich, G. Kehr, J. Am. Chem. Soc. 123 (2001) 6181;
(c) K. Kunz, G. Erker, S. Doring, S. Bredeau, G. Kehr, R. Frohlich, Organometallics 21 (2002) 1031.
[8] T.H. Kim, Y.C. Won, B.Y. Lee, D.M. Shin, Y.K. Chung, Eur. J. Inorg. Chem. (2004) 1522.
[9] D. van Leusen, D.J. Beetstra, B. Hessen, J.H. Teuben, Organometallics 19 (2000) 4084, and references therein.
[10] (a) D.J. Cho, C.J. Wu, S. S, W.-S. Han, S.O. Kang, B.Y. Lee, Organometallics 25 (2006) 2133;
(b) S.H. Lee, C.J. Wu, U.G. Joung, B.Y. Lee, J. Park, Dalton Trans. (2007) 4608.
[11] D.J. Cho, C.J. Wu, T. Bok, E.J. Lee, C.H. Lee, W.-S. Han, S.O. Kang, B.Y. Lee, Dalton Trans. (2006) 4056.
[12] U.G. Joung, C.J. Wu, S.H. Lee, C.H. Lee, E.J. Lee, W.-S. Han, S.O. Kang, B.Y. Lee, Organometallics 25 (2006) 5122.
[13] C.J. Wu, S.H. Lee, H. Yun, B.Y. Lee, J. Organomet. Chem. 691 (2006) 5626.
[14] (a) A. Kessler, C.M. Coleman, P. Charoenying, D.F. O'Shea, J. Org. Chem. 69 (2004) 7836;
(b) A.F. Abdel-Magid, K.G. Carson, B.D. Harris, C.A. Maryanoff, R. Shah, J. Org. Chem. 61 (1996) 3849.
[15] A. Krasovskiy, F. Kopp, P. Knochel, Angew. Chem., Int. Ed. 45 (2006) 497.
[16] D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, Organometallics 15 (1996) 1572.