Preparation of isospecific metallocene catalysts for olefin polymerization that are covalently tethered on solid surface

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^a *TRMGP* *Vj g *Kpukwq qhRj f ukecncpf Ej go kecnTgugctej + Ycnq. Uekco c 573/23; . Lcrp*

^b *Fgrctwo gpvqhCrrrkf Ej go kat f. Hkewnf qhGpi kpggtkpi. Uekco c Kpukwq qhVgej pqrqi f. Qnwdg. Uekco c 58;/24; 5. Lcrp*

^c *EcvrfukuTgugctej Egpvt. J qmckf q Wpkxgtulof. Urrrtq 282/2; 33. Lcrp*

Abstract

Novel methodology was developed for preparation of isospecific metallocene catalysts for olefin polymerization that are tethered on silica surfaces with covalent bonds. A racemic *cpuc*-zirconocene complex that has a Si-Cl moiety on its bridge was immobilized on SiO₂ by the reaction of the Si-Cl anchor with Si-OH on the solid surface. The prepared solid catalyst was found to be effective for isospecific propene polymerization (catalyst **C**). Pretreatment of silica surfaces with Me₃SiCl improved the catalyst performance (catalyst **D**). An *cpuc*-zirconocene complex with a BH group reacted with "vinyl-coated" silica gel to afford another immobilized catalysts (catalyst **E**). This catalyst achieved satisfactorily high catalytic activity and high isotacticity in its produced polypropene. © 2002 Elsevier Science B.V. All rights reserved.

Key words: Olefin polymerization catalyst; Metallocene; Silica support; Covalent bond

1. Introduction

The group 4 metallocene catalysts for olefin polymerization have been extensively investigated over the last few decades [1–3]. Heterogenization of the metallocene catalysts is of much interest recently, since it is desired for industrial application [4,5]. Adsorption of the metallocene catalysts on the methylaluminoxane(MAO)-treated surface of solid supports is the commonly adopted method. In this method, however, leaching out during polymerization

was pointed out [6], and since the adsorption method seems to highly depend on supports and metallocene complexes, it often suffers poor reproducibility. On the other hand, some examples for immobilization of metallocene complexes with covalent bonds on supports, such as polystyrene [7,8], silica gel [9–11] and polysiloxane [12,13], have been reported. In most of such examples, ligands were tethered on supports first, and then ZrCl₄ was reacted to form immobilized metallocene complexes (method (a) in Fig. 1), and a few of them could even catalyze syndiospecific olefin polymerization [8,13]. However, this is not suitable for preparation of *luqurgethk* polymerization catalysts because this method cannot avoid formation of *o guq*-isomers of metallocene complexes and their purification to obtain pure-racemic ones seems difficult.

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Fig. 1. Preparative methods for covalently tethered metallocenes on a support.

Hong et al. reported preparation of *tcgo q*-rich zirconocene catalysts from purely ‘racemic’ ligands that were tethered on polysiloxanes, although their reaction with metal chlorides gave a considerable amount of *o guq*-isomers [7]. Therefore, the catalysts immobilized by method (a) must produce a mixture of atactic and isotactic polymers, and extraction of atactic portion is needed in order to obtain isotactic polymers.

For preparation of covalently immobilized isospecific catalysts, to tether well-defined racemic metallocene complexes onto the support with anchors appears to be the only route (method (b) in Fig. 1). Tethering non-bridged *curgekk* zirconocene compounds with a cyclopentadienyl [14] or siloxy [15] anchor on SiO_2 has been reported. Alt and coworkers reported metallocenes with vinyl groups which are incorporated in the polyethylene chain by copolymerization [16–18]. To the best of our knowledge, however, isospecific metallocene complexes chemically anchored on solid supports have not appeared in the literature [19].² A major barrier to achieve

this aim seems to be the difficulty of preparation of racemic complexes with an anchor moiety.

We recently reported preparation of the *cpuc*-zirconocene complex with a vinyl group on its silylene-bridge **3** that serves as an isospecific olefin polymerization catalyst [20]. The advantage of this complex is ease of purification of its racemic form. This compound led us to design racemic *cpuc*-zirconocenes functionalized on that vinyl group. Herein we wish to report the synthesis of isospecific silylene-bridged metallocene complexes that have Si–Cl or B–H functionality as anchoring moieties and their immobilization on silica surfaces (Fig. 2). This is the first example of isospecific olefin polymerization using racemic metallocene catalysts that are covalently immobilized on solid supports. A part of this work was previously communicated [21].

40 Tgumncpf f kxwukqp

4080 Kō o qdkk/cvkqp qhvjg /keqpqegpg eqo rrgz y kj
c UóEncpej qt qp c uktec umt hceg *ecwrfuwA+

4080 O qf gntgcxvkqp kp j qo qi gpgqwu xgtukqp

The racemic silylene-bridged zirconocene complex with a vinyl group **3** (*tcgo q/o guq* > 99/1) reacted with chlorodimethylsilane (Me_2SiHCl) in the presence of H_2PtCl_6 to afford the hydrosilated product **4** with excellent regioselectivity (Scheme 1). Compound **4** was fully characterized by ^1H , ^{13}C and ^{29}Si NMR spectroscopy. A possible regioisomer was not observed by NMR. Since a chlorodimethylsilyl group is known to be reactive enough, complex **4** can be expected to serve as a racemic zirconocene with a functional anchor moiety.

Scheme 1. Hydrosilylation of *cpuc*-zirconocene with a vinyl group.

² Immobilization of isospecific *cpuc*-metallocenes with a Si–Cl anchor on SiO_2 was reported in a patent but without an experimental description of isospecific olefin polymerization.

Fig. 2. Covalently immobilized isospecific metallocene catalysts.

We first examined the formation of Si–O–Si bonds in a homogeneous reaction of **4** with a silyl alcohol. When **4** was treated with 1 eq. of *n*-BuMe₂SiOH in the presence of imidazole in THF at RT, the formation of **5** was observed in an excellent yield after 3 h. ²⁹Si NMR spectroscopy showed disappearance of the Si–Cl bond (32.65 ppm) of **4** and formation of new Si–O–Si bonds (7.94, 11.18 ppm), indicating that Si–OH reacted predominantly with Si–Cl instead of Zr–Cl (Fig. 3).

Thus, we next investigated the immobilization of **4** on silica by its reaction with surface Si–OH groups (Scheme 2). Compound **4** was treated with calcined silica gel in toluene or tetrahydrofuran (THF) in the presence of bases. Two kinds of silica were used (I and II, in Table 1). CP/MAS high-resolution solid-state ²⁹Si NMR spectra of the obtained solid catalyst is shown in Fig. 3. A broad signal at 14–17 ppm and a sharp one at –10.6 ppm are assignable to O–SiMe₂CH₂– of the backside

anchor and the metallocene-bridging silicon, respectively, and the signal for Si–Cl of **4** at 32.7 ppm disappeared. IR spectroscopy showed a decrease of Si–OH on SiO₂ (3750 cm^{–1}) due to the immobilization of **4** on the silica. These results supported the expected immobilization of complex **4** on SiO₂. The Zr content in the prepared catalysts was determined by ICP analysis (Table 1). Catalysts prepared with toluene/triethylamine (runs 2–5) contained more Zr than that from THF/imidazole (run 1). For comparison, **3** was adsorbed on the silica surface similarly without a base and studied as a reference (runs 6 and 7).

Polymerization of propene was carried out by suspending the immobilized catalysts in a toluene solution of propene and methylaluminoxane (MAO). Table 1 summarizes the results of polymerization. The catalysts based on **4** (catalyst C) produced isotactic polypropene in moderate catalytic activity (runs 1–5), although the catalytic activities were much lower compared to the corresponding homogeneous catalyst **3** (run 8). It should be noted that the catalyst prepared with **3** as a reference showed much less catalytic activity than catalyst C, in spite of its similar Zr content (runs 6 and 7). This is probably because the Zr–Cl bonds of **3** reacted with Si–OH on the silica surfaces. When the amount of MAO was reduced from 2500 to 120 eq. of Al/Zr, the catalytic activity was 82 kg PP/mol Zr h atm (run 4), which is still

Scheme 2. Immobilization of the racemic zirconocene **4**.

Table 1
Catalysts with immobilized zirconocene complexes (catalyst **A**) and polymerization of propene^a

Run	Catalyst	Complex (base)	Silica gel	Solvent ^b	Zr-atom (wt.%)	MAO Al/Zr	PP yield (g)	Catalytic activity ^c	M_w	M_w/M_n	[<i>mmmm</i>] (%)	mp (°C)
1	A	2 /imidazole	I ^d	THF	0.47	3900	0.525	113	106000	2.59	91.1	151.0
2	A	2 /Et ₃ N	I	Toluene	0.75	2400	0.796	108	94000	2.45	87.7	150.8
3	A					600	0.755	101	91900	2.33	87.5	149.7
4	A					120	0.605	81	106000	2.24	–	152.3
5	A	2 /Et ₃ N	II ^e	Toluene	0.78	2300	0.641	83	74500	2.87	86.9	146.1
6	Ref.	1 /none	I	Toluene	0.79	2300	0.073	9.4	65100	1.85	92.4	156.0
7	Ref.	1 /none	II	Toluene	0.76	2400	0.137	18	106000	2.06	93.2	159.0
8	Ref.	1		Homogeneous ^f		5000	2.35	7840	76500	1.99	95.7	157.1

^a Reaction conditions: in a 100 ml autoclave, toluene 30 ml, catalyst 30 mg, propene 3 atm, 30 °C, 1 h.

^b Solvents for immobilization reactions.

^c kg PP/mol Zr h atm.

^d I: Degussa corporation “Aerosil 300”: 300 m²/g.

^e II: Fuji Silysia Chemical Ltd. “CARiACT P-10”: 281 m²/g.

^f Zr = 0.1 μmol.

Fig. 3. ^{29}Si NMR spectra for **4**, **5** and immobilized catalyst C.

comparable to that of run 2. It was reported that supported catalysts require less amount of MAO to achieve high activity [22,23]. Isotacticity of the polymers was determined using the obtained polymers without extraction of an atactic portion. The percentage of *o guq*-pentad ($[o o o o]$), which is an index of isotacticity of the polymer, was satisfactory. However, both $[o o o o]$ and melting point were slightly lower than those observed in the homogeneous reaction. Similar results were obtained with two kinds of silica

supports (I and II), indicating the reproducibility of this method.

These results revealed that immobilization of racemic *cpuc*-metallocene with a Si-Cl anchor is effective. Their catalytic activities, however, were not satisfactory when compared to homogeneous reactions. A possible reason could be the presence of excess hydroxy groups on the silica surface, compared to the amount of zirconium used. It was reported that, in general, silica treated under vacuum at 500 °C

Scheme 3. Masking excess OH groups.

Table 2

Pretreatment of SiO₂ with Me₃SiCl: polymerization of propene with catalyst **D**^a

Run	Me ₃ SiCl ^b (mmol (g SiO ₂) ⁻¹)	Zr-atom (wt.%)	Catalyst (mg)	PP yield (g)	Catalytic activity ^c	<i>O_w</i>	<i>O_w/O_n</i>	[<i>o o o o</i>]
5	0	0.78	30	0.64	83	74500	2.87	86.9
9	0.3	0.74	30	0.88	121	71000	2.34	84.1
10	0.9	0.47	15	2.03	876	98600	2.60	86.8
11	1.8	0.13	30	0.46	359	91900	2.42	83.4

^a Reaction conditions: silica gel = II, MMAO: Al = 2 mmol/10 mg of catalyst, toluene = 30 ml, propene = 3 atm, 30 °C, 1 h.^b mmol of Me₃SiCl/1 g of SiO₂.^c kg PP/mol Zr h atm.

contains about two OH groups on 1 nm² of its surface [24]. This corresponds to ca. 1 mmol of OH groups in 1 g of the silica used here, while 0.1 mmol of Zr was used for tethering on 1 g of SiO₂. These excess hydroxy groups might damage the active species.

4040 Kō rtqxo gpv qhecrfve rgtlqto cpeg d{
o cunkpi j {ftqz{ i tqwru qp vjg uktec umtceg
*ecrfuwB+

We reasoned that masking a part of surface-OH groups with trimethylsilyl groups would improve the activity of the catalyst (Scheme 3) [25].³ A silica support was pretreated with chlorotrimethylsilane, Me₃SiCl, in order to convert –OH groups on the surface into –OSiMe₃ groups. Assuming that 1 g of silica has about 1.0 mmol of hydroxy groups, the amount of the masking agent was made to vary from 0.3 to 1.8 mmol per 1 g of silica gel. Pretreated silica was washed and dried, and then compound **4** was immobilized similarly to catalyst **C**. Zr-contents of the obtained solid (catalyst **D**) were smaller than catalyst **C** when more than 0.9 mmol/g SiO₂ of Me₃SiCl

was used. Table 2 summarizes the results of propene polymerization using catalyst **D**. Catalyst **D** showed remarkably improved catalytic activity in propene polymerization. The yield of the polymer increased even though the amount of Zr-atom was smaller. Pretreatment with 0.9 mmol/g SiO₂ of Me₃SiCl gave the highest activity (run 10). Treatment with excess Me₃SiCl resulted in a decrease of Zr on the surface and a polymer yield as expected (run 11). Isotacticity of the polymer, however, remains lower, while the catalytic activity was improved by this masking method. Although the reason for the low isotacticity in the present system is not clear yet, it may be because the active species stay too close to the solid surface. Thus, we designed further study on tethering the complex with a longer spacer to improve this method (Section 2.3).

4050 Kō o qdkt/cvqp qh o gwmegpgu d{
j {ftqdtcvqp qp xlp/wvgf umtcegu *ecrfuwC+

4050 J {ftqdtcvqp qhego rnz 1 kp j qo qi gpgquw
uqnwkp

Hydroboration of alkenes is one of the most versatile reactions in organic synthesis. We considered that this reaction could be applied for immobilization

³ Pretreatment of SiO₂ with Me₃SiCl for silica-supported zirconocene was reported.

Fig. 4. ^{13}C NMR for zirconocene complexes and immobilized catalyst **E**, (a) complex **3**, (b) complex **6**, (c) catalyst **E**, (d) vinyl-coated SiO_2 .

Scheme 4. Immobilization of metallocenes by hydroboration.

of metallocene complexes [26].⁴ We first tested the hydroboration reaction of **3** (Eq. (1)) with 9-borabicyclo[3.3.1]nonane (9-BBN), a common hydroborating reagent. When **3** reacted with 1.5 eq. of 9-BBN, hydroboration cleanly proceeded in 15 h at 50 °C to give **6** in a good yield. ¹³C NMR spectra of **3** and **6** are shown in Fig. 4. The vinyl groups of **3** at 133.73 and 135.98 ppm disappeared and new methylene signals for –BCH₂CH₂Si– were observed at 18.89 and 6.53 ppm accompanied with three signals assignable to the borabicyclo moiety (spectrum **d**, Fig. 4). ¹H NMR also supported the structure of **6** and signals for a regioisomer were not detected. The combination of **6** with MAO catalyzed propene polymerization to give highly isotactic polypropene, indicating that the zirconocene moiety survived the hydroboration reaction.

ethanol or toluene in order to cover the surface with –OSiMe₂(CH=CH₂) groups. The signals of vinyl groups on the silica surface were observed at 131 and 138 ppm by CP/MAS high-resolution solid-state ¹³C NMR (Fig. 4d). Ethoxy groups were also observed (17 and 60 ppm) when ethanol was used as a solvent. All hydroxy groups on the surface must be masked by this procedure. Complex **3** was treated with a large excess of borane-tetrahydrofuran complex (BH₃·THF) in THF, and the volatile material was removed in vacuo. The vinyl group of **3** disappeared judging from NMR, although the hydroborated product **7** could not be identified by NMR. ¹H NMR spectroscopy of the hydroboration products showed a mixture of some species probably because of the dimerization of primary boranes (RBH₂) and the formation of by-products such as regioisomers and doubly hydroborated products.

(1)

40040 Rtgrctcvkqp qhko o qdtkk gf ecwrw dw df j fftqdqtcvkqp

These results encouraged us to investigate the immobilization of **3** by hydroboration reactions (Scheme 4). Silica gel was treated with excess chlorodimethylvinylsilane, ClSiMe₂(CH=CH₂), in

Anyhow, this reaction mixture was treated with the “vinyl-coated” silica in a toluene suspension at RT and then stirred overnight. The solid was rinsed with toluene and dried in vacuo to give the immobilized catalyst (catalyst **E**). CP/MAS solid-state ¹³C NMR spectroscopy of the catalyst exhibited a broad signal at 9 ppm assignable to sp³-methylene carbons adjacent to the silicon atoms and other signals which are due to the zirconocene complex, suggesting that the complex

⁴ Hydroboration of vinylated silica surface has been reported recently.

Scheme 5. An alternative method for immobilization of metallocenes.

was successfully immobilized (Fig. 4c). ICP analysis showed that the zirconium-contents of the catalysts were 0.34–0.36 wt.%, indicating that about 30% of the complexes was loaded. The low efficiency of loading may be due to isomeric by-products in the first hydroboration.

We also prepared another catalyst by an alternative approach. The “vinyl-coated” silica surface was treated with BH₃ first, then with the vinyl complex **3** (catalyst **E'**, Scheme 5). Catalyst **E'** contained only 0.15 wt.% of Zr, and it was even smaller than catalyst **E**. This might be due to deficiency of BH moieties because BH₃ immediately reacted with three vinyl groups to afford trialkylboranes on the surface.

4050 Rqr o gk/cvkqp qhrtqrgpg wukpi ecvrfwC

Table 3 summarizes the results of propene polymerization using catalyst **E** and gives a comparison

with the results for catalysts **C** and **D**. It should be emphasized that the novel catalyst **E** exhibited significantly higher catalytic activity than **C** or **D**. When the ratio Al/Zr was 2000 (runs 12 and 15), the activity of **E** (946 kg PP/mol Zr h atm) was twice as high as that of **D** (504 kg PP/mol Zr h atm). Catalytic activity amounted to 3500 kg PP/mol Zr h atm when Al/Zr was 5100 (run 14). Furthermore, isotacticity of the obtained polypropene with **E** was much higher than those with **C** or **D**. Observed *o gmq*-pentad probability was more than 94% and it was comparable to the homogeneous catalyst, although catalytic activity was somewhat lower than the homogeneous one. High isotacticity of the polymers was also confirmed by their melting points. Catalyst **E** was prepared twice in the same manner (runs 13 and 14). These two catalysts showed the same Zr-contents and exhibited similar results in polymerization, indicating the reproducibility

Table 3
Comparison of catalysts **C–E**: polymerization of propene^a

Run	Catalyst	Zr-atom (wt.%)	Catalyst (mg)	Al/Zr	PP yield (g)	Catalytic activity ^b	<i>O_w</i>	<i>O_w/O_n</i>	[<i>o o o o</i>]	mp
5	C	0.78	30	2300	0.64	83	74500	2.87	86.9	146.1
10	D	0.47	15	3900	2.03	879	98600	2.60	86.8	152.5
12	D	0.47	10	2000	0.78	504	106000	2.61	86.3	153.5
13	E	0.34	10	5400	2.64	2380	98900	1.49	94.1	156.2
14	E	0.36	10	5100	4.18	3570	80900	1.46	94.7	154.5
15	E	0.36	10	2000	1.12	946	112000	2.02	95.3	156.2
16	E'	0.15	30	12000	1.38	917	99200	1.62	93.3	157.6

^a Reaction conditions: silica gel = II, toluene = 30 ml, propene = 3 atm, 30 °C, 1 h.

^b kg PP/mol Zr h atm.

of this method. These results showed that the present methodology for tethering isospecific polymerization catalysts is extremely effective.

Catalyst **E'** exhibited lower activity than **E** despite a higher Al/Zr ratio (run 16). There would be an excess alkylboranes around Zr in this catalyst. Since BR_3 groups have strong Lewis acidity, it may interact with a cationic active species to disturb the polymerization.

The excellent catalytic performance of this catalyst **E** could be ascribed to the following two points. First, pretreatment of each silica surface with excess chlorodimethylvinylsilane not only afforded 'vinyl'-surface for hydroboration, but also masked hydroxy groups effectively. Second, a spacer moiety is longer compared to catalysts **C** and **D**. When a spacer is shorter, polymerization would occur near solid surfaces. It is possible that the solid surface disturbs the insertion reaction so as to decrease its activity and/or stereoselectivity. In catalyst **E**, zirconocene complexes would catalyze the polymerization in locations distant from the solid surface because of the longer spacer. These complexes might behave in a nearly homogeneous fashion. Indeed, polymers produced by **E** have smaller molecular weight distribution ($O_w/M_n \leq 2.0$), while the values were larger than 2.0 in **C** and **D**. This implies that the zirconocene complex in catalyst **E** behaved like a single site catalyst.

The possibility of leaching out of loaded complexes was investigated according to the reported method [6]. Catalyst **E** was suspended in a toluene solution of MAO and filtered. When the filtrate was exposed to propene (3 atm), a trace of polymer was obtained. However, the yield was very low and the result suggested that only a few percent of the polymer was due to metallocene complexes that were leached out. The siloxane spacer might react with MAO, because the filtrate did not polymerize propene at all when catalyst **E** was suspended in toluene *y kj qww* MAO.

50 Eqpenukqp

In conclusion, we developed a novel methodology for preparation of covalently immobilized isospecific metallocene catalysts. Metallocene complexes

were tethered on the support surface by siloxane formation (catalyst **C**). The catalyst performance was improved by masking excess hydroxy groups on each solid surface (catalyst **D**). Tethering complexes by hydroboration gave the most active catalysts (catalyst **E**) and they produced highly isotactic polypropene.

60 Gzrgtkb gpvcn

6080 I gpgtcn

All manipulation was carried out under argon or nitrogen. Solvents were distilled over sodium benzophenoneketyl prior to use. Chlorodimethylsilane, *γ*-butyldimethylsilanol, 9-borabicyclo[3.3.1]nonane (9-BBN, 0.4 M hexane solution) and $\text{BH}_3 \cdot \text{THF}$ (1.0 M THF solution) were purchased from Aldrich Chemical Co. Inc., and used without further purification. Complex **3** was prepared according to the reported method [20]. Silica gel ("Aerosil 300": $300 \text{ m}^2/\text{g}$ and "CARIACT P-10": $281 \text{ m}^2/\text{g}$) was provided from Degussa Corporation and Fuji Silysia Chemical Ltd., respectively, and was dried under vacuum (10^{-3} Torr, 1 Torr = 133 Pa) at 500°C for 16 h. Solution NMR was recorded on a JEOL AL300 spectrometer. All ^{13}C CP/MAS spectra were acquired at 100.3 MHz with a Chemagnetics Infinity 400 MHz solid-state NMR spectrometer and were internally referenced to tetramethylsilane and the methine peak of adamantane (29.5 ppm). The spectra were measured with 4.5 ms pulse width (90° pulse), 3 ms contact time, 5 s pulse delay and 40,000 accumulations. The spinning was carried out at 5.0 kHz spinning rate. All ^{29}Si CP/MAS spectra were obtained at 79.3 MHz with a JEOL α -400 NMR spectrometer with solid-state NMR attachments and were externally referenced to tetramethylsilane. The ^{29}Si spectra were measured with 6.0 μs pulse width (90° pulse), 3 ms contact time, 5 s pulse delay and 3000 accumulations. The spinning was carried out at 6.0 kHz spinning rate. Gel permeation chromatography (GPC) was recorded on SSC-7100 high temperature GPC (Senshu Scientific Co. Ltd.) at 135°C using 1,2-dichlorobenzene as an eluent and monodispersed polystyrene as standards. The melting point of polypropene was determined by Rigaku DSC 8230.

6040 Rtgrctcvkqp qhecwrwA cpf tgrvvgf tgcevkpu

6040 J {ftqukvkqp qh1 y kj ej rqtqf ko gj {nukcp g

To a solution of **3** (34.2 mg, 0.082 mmol) in diethyl ether (1 ml) was added dimethylchlorosilane (0.1 ml), and then a drop of THF solution of H_2PtCl_6 (1 M) was added at RT. After the reaction mixture was stirred for 1 h, the volatiles were removed in vacuo. ^1H NMR observation showed quantitative formation of the hydrosilation product **4**. ^1H NMR (C_6D_6 , Me_4Si): δ = 0.24 (s, 6H), 0.36 (s, 3H), 0.66–0.74 (m, 2H), 0.96–1.07 (m, 2H), 1.88 (s, 3H), 1.89 (s, 3H), 2.27 (s, 3H), 2.34 (s, 3H), 5.06 (s, 1H), 5.10 (s, 1H), 6.32 (s, 1H), 6.34 (s, 1H). ^{13}C NMR (C_6D_6 , Me_4Si): δ = –5.00 (Si– EH_3), 0.85, 0.90 ($\text{ClSi}(\text{EH}_3)_2$ –), 5.58 (Si EH_2), 10.30 (Si EH_2), 15.74, 15.82, 16.91, 16.97 (CpOg), 102.81, 103.31, 112.41, 113.41, 127.52, 128.93, 129.44, 130.29, 137.56, 138.28. ^{29}Si NMR (C_6D_6 , Me_4Si): δ = –10.84, 32.65.

6040 Rtgrctcvkqp qh3

Complex **4** was prepared as described above and the volatiles were removed in vacuo. The residual solid was used for the reaction. Imidazole (34 mg, 0.5 mmol) and dimethyl- γ -butylsilanol (78.8 ml, 0.5 mmol) was dissolved in 5 ml of THF. A portion (0.7 ml) of this solution was added to **4** (0.07 mmol) at RT. A white solid immediately precipitated from the reaction mixture and it was stirred for overnight. The formation of **5** was detected in ^{29}Si NMR and no other signals were observed. ^1H NMR (C_6D_6 , Me_4Si): δ = 0.06 (s, 6H), 0.13 (s, 6H), 0.44 (s, 3H), 0.55–0.67 (m, 2H), 0.93 (s, 9H), 1.04–1.11 (m, 2H), 1.88 (s, 3H), 1.96 (s, 3H), 2.25 (s, 3H), 2.27 (s, 3H), 5.09 (s, 1H), 5.19 (s, 1H), 7.16 (m, 2H). ^{13}C NMR (C_6D_6 , Me_4Si): δ = –4.90, –2.85, 1.34, 5.91, 9.42, 15.73 (2C), 16.94 (2C), 18.22, 25.83, 103.09, 103.66, 112.31, 113.26, 129.30, 129.91, 133.53, 135.76, 137.38, 137.84. ^{29}Si NMR (C_6D_6 , Me_4Si): δ = –10.87, 7.94, 11.18.

6040 Rtgrctcvkqp qhecwrwA <ko o qdhrk/cvkqp qh2 qp uktec wmtkegu

The typical procedure for the preparation of catalyst **C** was as follows. Dry silica gel (0.5 g) was suspended in dry tetrahydrofuran (THF, 10 ml) under argon, and to the suspension was added a THF solu-

tion of **4** (0.05 mmol) at RT. Then imidazole (3.4 mg, 0.05 mmol) was added, and the mixture was stirred at RT overnight. Toluene/triethylamine was also used as a solvent/base. After the solid was washed with toluene twice, it was dried up in vacuo. The catalyst was analyzed by high-resolution solid-state CP/MAS ^{29}Si NMR spectroscopy. The Zr content in the prepared catalysts was determined by ICP analysis. Reference catalysts were prepared similarly using complex **3** without base.

6050 Rtgrctcvkqp qhecwrwB <rtqgevkqp qhgzeguu j {ftqz{ i tqwru qp uktec wmtkegu

Typically, to a suspension of silica gel (0.5 g) in toluene (10 ml) was added a toluene solution of Me_3SiCl (0.45 mmol) and triethylamine (0.45 mol), and the mixture was stirred at RT overnight. The solid was washed twice with toluene and dried in vacuo, and then used for the immobilization of **4**. The immobilization process was similarly conducted to that described for catalyst **C**.

6060 Rtgrctcvkqp qhecwrwC cpf tgrvvgf tgcevkpu

6060 J {ftqdqtkvqp qh1by9/BBN(compound4+

To a solution of 83.5 mg (0.20 mmol) of **3** in 5 ml of toluene was added a hexane solution of 9-borabicyclo[3.3.1]nonane (9-BBN, 0.5 M, 0.30 mmol) and this mixture was stirred at 50 °C overnight. After removal of the volatiles in vacuo, compound **6** remained as a colorless oil in nearly quantitative yield. ^1H NMR (C_6D_6 = 7.16 ppm): δ = 0.45 (s, 3H), 1.1 (m, 2H), 1.16–1.26 (m, 2H), 1.37–1.51 (m, 2H, B–CJ₂), 1.58–1.91 (m, 12H), 1.90, 1.92, 2.25, 2.29, 5.10 (d, J = 2 Hz, 1H), 5.15 (d, J = 2 Hz, 1H), 6.33–6.40 (m, 2H). ^{13}C NMR (C_6D_6 = 128.0 ppm): δ = –4.65 (EH_3 –Si), 6.53 (EH_2Si), 15.78, 15.82, 16.90, 16.99 (CpOg $\times 4$), 18.89 (br, EH_2 –B), 23.55, 31.52 (br, B–EH), 33.57, 103.44, 103.81, 112.60, 113.46, 127.86, 128.88, 129.56, 130.16, 137.63, 138.06.

Polymerization of propene using **6** was conducted in an autoclave. To a solution of **6** (10 μmol) in toluene (30 ml) was added methylaluminoxane (20 mmol of Al) at RT and the mixture was stirred for 20 min. The solution was then exposed to propene (3 atm) and was stirred at RT for 15 min. An exothermic reaction was

quenched with acidic methanol. Polymer was collected as white powder and dried in vacuo. Yield 7.55 g (activity 1010 kg PP/mol Zr h atm).

6640 *Rtgrctvkap qhecwrwC*

Calcined silica gel (0.4 g) was suspended in an ethanol solution of chlorodimethylvinylsilane (0.11 ml, 0.8 mmol) at RT and the mixture was stirred overnight. The solid was washed twice with ethanol and the volatiles were removed in vacuo thoroughly to afford the vinyl-coated silica gel. Meanwhile, to a THF solution (1 ml) of **3** (16.7 mg, 0.04 mmol) was added a large excess of borane-THF adduct (1 M THF solution, 0.4 mmol), and the mixture was stirred at RT overnight. The volatiles were removed in vacuo and the residue was dissolved in toluene (6 ml). This solution was added to the vinyl-coated silica gel. The suspension was stirred for 3 days at RT, washed twice with toluene, and dried in vacuo. ICP analysis showed that Zr content was 0.34–0.37 wt.%.

6650 *Rtgrctvkap qhecwrwC'*

The “vinyl-coated” silica (0.43 g) prepared similarly to the described above was suspended in THF, and borane-THF adduct (1 M THF solution, 2.0 mmol) was added at RT. The mixture was stirred overnight. The solid was washed twice with THF, and the volatiles were removed in vacuo. To the suspension of the solid in toluene was added complex **3** (17.7 mg, 0.043 mmol) and the mixture was stirred overnight at RT. The solid was then rinsed twice with toluene and the solvent was removed in vacuo. ICP analysis showed that Zr content was 0.15 wt.%.

6670 *Rqrfo gtlcvkap qhrtqrgps*

A typical procedure of polymerization of propene using the prepared catalysts is as follows. In a 100 ml glass autoclave, the catalyst (10 mg) was treated with MMAO (1.9 M toluene solution, 3.0 ml). After 10 min, toluene (27 ml) was added and the mixture was immersed in a water bath at 30 °C. Then propene was introduced, the mixture was stirred for 1 h and the pressure was kept at 3 kg/cm² during the reaction. The mixture was poured into acidic methanol to quench the reaction, the white powder was filtered and

dried in vacuo at 70 °C overnight. Molecular weight of the polymer and its distribution were measured by GPC analysis and the isotacticity was determined by ¹³C NMR spectroscopy at 120 °C in 1,2-dichlorobenzene-*d*₄.

Cenpqy rgi go gpw

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Tghgt gpegu

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