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Polymerization of Olefins by Rare Earth Metal Complex with Bulky Substituents

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Abstract: Sterically bulky substituents, t-$BuMe_2Si$ groups, and Me_3Si groups were introduced into Me_2Si bridged Cp rings and the compound, $Me_2Si(Me_3Si$-t-$BuC_5H_3)_2$, was used as a ligand for rare earth metal complex. As a result of the complexation, new yttrium complexes, $Me_2Si(2$-Me_3Si-4-t-$BuMe_2SiC_5H_2)_2YCl_2Li(THF)_2$ and $Me_2Si(2$-Me_3Si-4-t-$BuMe_2SiC_5H_2)_2YCH(SiMe_3)_2$, were synthesized. Hydride derivative of these complexes, $[Me_2Si(2$-Me_3Si-4-t-$BuMe_2SiC_5H_2)_2YH]_2$, showed high activity for olefin polymerization. α-Olefins such as 1-hexene and 1-pentene were transformed into their polymers in high yield (>75%). The polymerization proceeded in a stereoselective manner, giving highly isotactic poly(α-olefin)s (selectivity>95%). The hydride complex can polymerize 1,5-hexadiene, affording high molecular weight poly(methylene-1,3-cyclopentane) ($Mn > 10x10^4$).

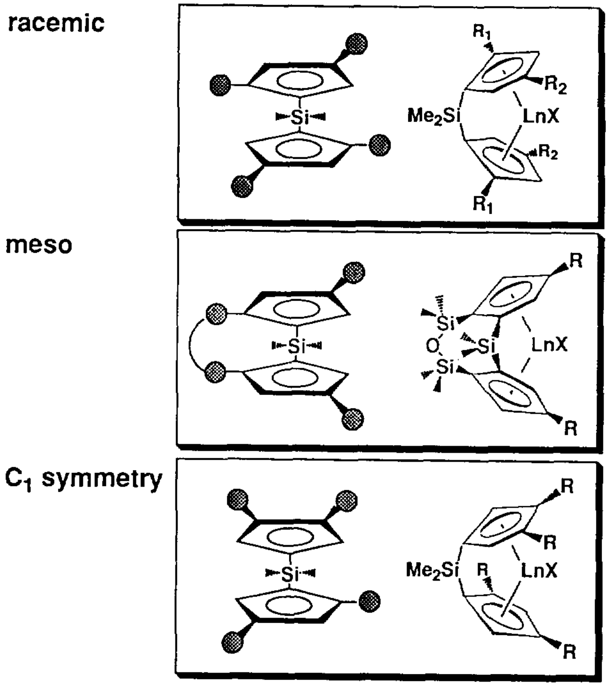
INTRODUCTION

Rare earth element including lanthanide metals has attracted much attention in various scientific fields. Recently, we have been trying to use lanthanide complexes as polymerization initiators. We have found that organolanthanide complexes with pentamethylcyclopentadienyl rings (Cp*), such as $Cp^*{}_2SmH$ and $Cp^*{}_2SmMe(THF)$ initiate living polymerization of methyl methacrylate (MMA).[1] High molecular weight ($Mn > 500x10^3$) poly(methyl methacrylate) (PMMA) with extremely narrow molecular weight distribution ($Mw/Mn < 1.05$) was obtained in high yield. The polymerization proceeded in a stereoselective manner giving highly syndiotactic PMMA at low temperature (selectivity = 95.3% at -95°C). Organolanthanide initiated polymerization of alkyl acrylate and lactone also proceeded in a living manner affording high molecular weight monodisperse polymers.[2]

On the other hand, it is widely known that organolanthanide complex can polymerize olefins without any cocatalysts or inorganic supports. Being a single component system is the greatest advantage of lanthanide catalyst compared to Ziegler type catalyst based on group IV metals (Ti, Zr and Hf). Lanthanide complexes with Cp* ligand such as Cp^*_2LaH,[3] $Cp^*_2YbMe(OEt_2)$,[4] and $Cp^*_2Sm(THF)_2$[5] were shown to have ethylene polymerization activity.

Recently, Bercaw et al. have reported yttrium hydride complex $[Me_2Si(2\text{-}Me_3Si\text{-}4\text{-}t\text{-}BuC_5H_2)_2H]_2$ polymerized α-olefins, polymerization of which has been difficult by rare earth metal complexes so far.[6] Their result indicates that the reactivity of rare earth metal complex can be controlled by modification of ligand environment. We started investigation into the relation between the structures of rare earth metal complexes and their reactivity toward olefins by preparing various bridged Cp based complexes. By using bridged Cp rings with bulky substituents (Me_3Si and/or t-Bu) as ligands, we prepared three types of lanthanide complexes (racemic, meso, C_1 symmetry)[7] (Scheme 1). Each complex exhibited characteristic reactivity to olefins. Among the three types of trivalent complexes [$X=CH(SiMe_3)_2$], only C_1 symmetric complex (**3**) showed activity for ethylene polymerization while the other two complexes (**1**, **2**) did not show it at all. All the three kinds of divalent Sm complexes [$X=(THF)_2$] polymerized ethylene effectively. Meso complex (**5**) showed the highest activity giving rather low molecular weight polyethylene ($Mn<5\times10^4$). C_1 type complex (**6**) with modest reactivity gave the highest molecular weight polyethylene ($Mn>100\times10^4$). Only racemic complex (**4**) exhibited activity for α-olefin polymerization.

Scheme 1



1: R_1, $R_2=SiMe_3$, Ln=Sm, $X=CH(SiMe_3)_2$

4: $R_1=SiMe_3$, R_2=t-Bu, Ln=Sm, $X=(THF)_2$

2: $R=SiMe_3$, Ln=Y, $X=CH(SiMe_3)_2$

5: $R=SiMe_3$, Ln=Sm, $X=(THF)_2$

3: $R=SiMe_3$, Ln=Sm, $X=CH(SiMe_3)_2$

6: $R=SiMe_3$, Ln=Sm, $X=(THF)_2$

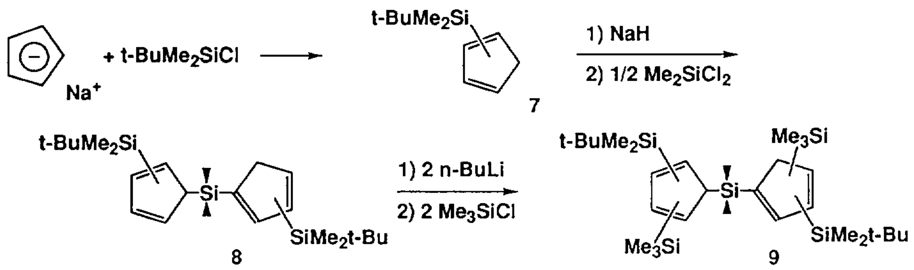
As an extension of the ligand modification for lanthanide complexes, we attempted to introduce more sterically bulky substituent than Me_3Si or t-Bu. t-$BuMe_2Si$ group was chosen for the purpose. Herein, we describe the syntheses of lanthanide complexes with that bulky substituent and their reaction with various olefin monomers.

RESULTS AND DISCUSSION

Synthesis of ligand

Ligand synthesis was carried out as shown in Scheme 2. t-BuMe$_2$Si group was introduced into Cp ring by the reaction of t-BuMe$_2$SiCl with sodium cyclopentadienyl anion. The resulting **7** was bridged with Me$_2$Si group by the reaction of the anion of **7** and Me$_2$SiCl$_2$. Reaction of dilithium salt of **8** and Me$_3$SiCl resulted in the formation of **9**. Since there may exist some isomers of **9** in terms of the positions of substituents and carbon-carbon double bonds in the Cp rings, we could not characterize the correct structure of **7**, **8**, and **9**. Therefore, assuming the distillated viscous liquid as the desired ligand **9**, we used it for complexation with rare earth metal.

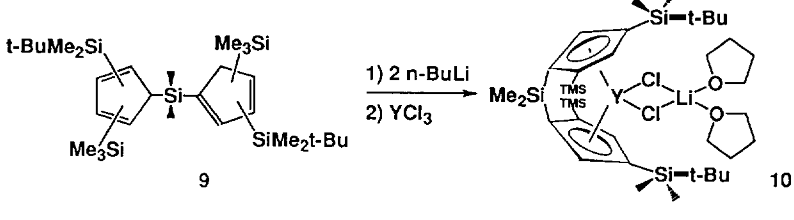
Scheme 2



Syntheses of yttrium complexes

Complexation of anhydrous YCl$_3$ with dilithium salt of **9** was carried out in THF under reflux for 12 hrs (Scheme 3). Yttrium complex **10** was obtained as single crystals after recrystallization from hexane. ^{1}H-NMR spectrum of this complex is shown in Figure 1. The intensity ratio of THF protons to ligand substituents protons indicates that the structure of **10** is ate complex as shown in Scheme 3. Each peak of protons for t-Bu and Me$_3$Si group appears as a singlet. Three singlet peaks for Me$_2$Si groups can be assigned to one bridging Me$_2$Si and two diastereotopic Me groups of t-BuMe$_2$Si group. Two proton signals appear as doublets for Cp-H. These results indicate that two Cp rings of **10** are equivalent. Therefore we characterized the structure of **10** to be C$_2$ symmetric racemic type as shown in Scheme 3. We did not observe the existence of C$_1$ symmetric complex in contrast to the case of all the substituents were Me$_3$Si group (**1** and **3**). This would be ascribed to the steric repulsion of bulky t-BuMe$_2$Si and Me$_3$Si groups when they were located in the 3 and 4 positions in the same Cp ring.

Scheme 3



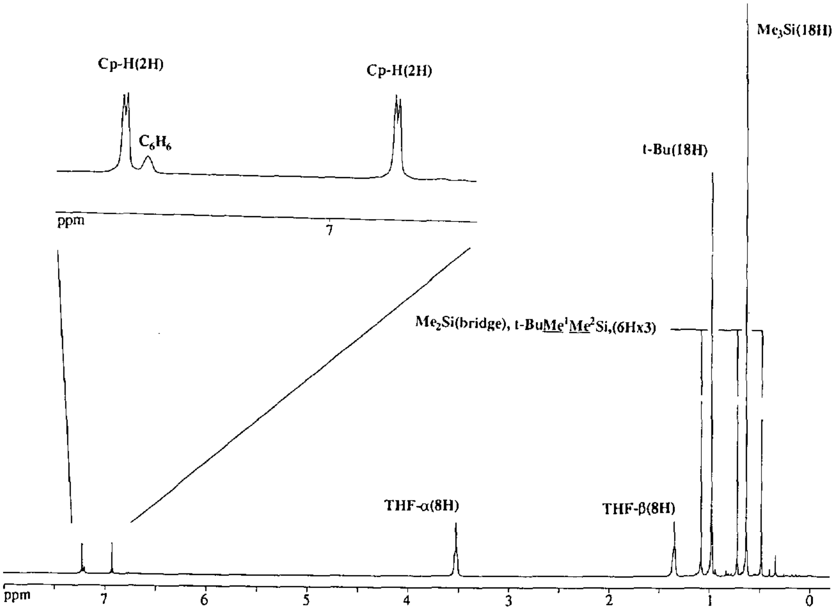
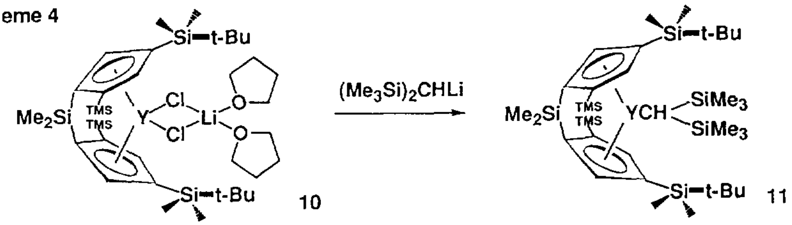


Figure 1. ^{1}H-NMR spectrum of **10**.

Alkylation of **10** with bistrimethylsilylmethyl lithium [$(Me_3Si)_2CHLi$] was carried out in toluene at 0°C~r.t. (Scheme 4). Hydrocarbyl complex **11** was obtained as single crystals after recrystallization from hexane. In ^{1}H-NMR spectrum of **11**, introduction of $(Me_3Si)_2CH$ group was confirmed by the disappearance of THF signals and appearance of additional two Me_3Si peaks compared to the spectrum of **10**. Interestingly, signals of substituents on each two Cp rings appeared independently (two Me_3Si, two t-Bu, six Me_3Si, and four Cp-H signals were observed for substituents of ligand), which indicated that the two Cp rings were not equivalent in this complex. Since Marks et al. have reported this phenomenon in the case of $Cp^*{}_2LnCl_2Li(OEt_2)$ to $Cp^*{}_2LnCH(SiMe_3)_2$[3] and migration of substituent may not be feasible here, we can assume the structure of **11** to be racemic as shown in Scheme 4.

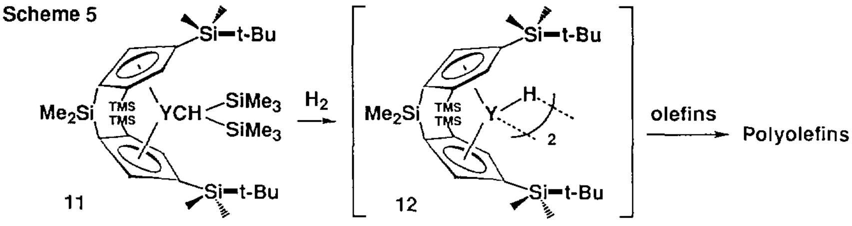
Scheme 4



Alkyl complex **11** did not exhibit polymerization activity of olefins in accordance with the result of the racemic complex with four Me_3Si group, $Me_2Si[2,4\text{-}(Me_3Si)_2C_5H_2]_2SmCH(SiMe_3)_2$ (**3**).

Bercaw et al. have reported that racemic hydride complex $Me_2Si[2\text{-}Me_3Si\text{-}4\text{-}t\text{-}BuC_5H_2]_2YH$ showed polymerization activity for α–olefins.[6] To examine the effect of the bulky substituent on the reactivity to olefins, we attempted to synthesize hydride derivative of **11** (Scheme 5). The reaction of **11** with H_2 was performed in degassed toluene under the 1 atm pressure of H_2 at r.t.. In ^{1}H-NMR spectrum of the reaction mixture, we observed Y-H signals at 4.46 ppm as triplet (J = 29.9 Hz) which indicated the formation of dimer complex **12**. However, we did not succeed in isolation and characterization of **12** due to its unstability. Therefore, we examined the reactivity of **12** with olefins by in situ reaction.

Scheme 5



Polymerization of olefins by 12

In spite of in situ reaction, yttrium hydride complex **12** exhibited high activity for olefin polymerization. The results are summarized in Table 1. Ethylene can be polymerized effectively giving polyethylenes with Mn=~10^5. Noteworthy is the high reactivity of **12** to α-olefins (Scheme 6). 1-Hexene and 1-pentene were polymerized into polymers of Mn=1~5x10^4 in high yield. The lower reaction temperature gave higher molecular weight polymers, which suggested that the termination or chain transfer reaction might occur at high temperature.

Table 1. Polymerization of Olefins by **12**.[a]

entry	monomer	temp(°C)	time	activity(g/mol h)	Mn(x10^{-4})	Mw/Mn
1	Ethylene	r.t.	0.5m	5.84x10^5	8.23	4.18
2	Ethylene	r.t.	2m	4.87x10^5	9.08	4.12
				Yield(%)		
3	1-Hexene	0°C	12h	94	5.30	2.46
4	1-Hexene	r.t.	12h	99	1.29	2.30
5	1-Pentene	0°C	18h	77	2.86	1.50
6	1,5-Hexadiene	0°C	12h	62	13.7	2.44
7	1,5-Hexadiene	r.t.	12h	99	1.76	2.50

[a] All reactions were carried out in toluene.

Scheme 6

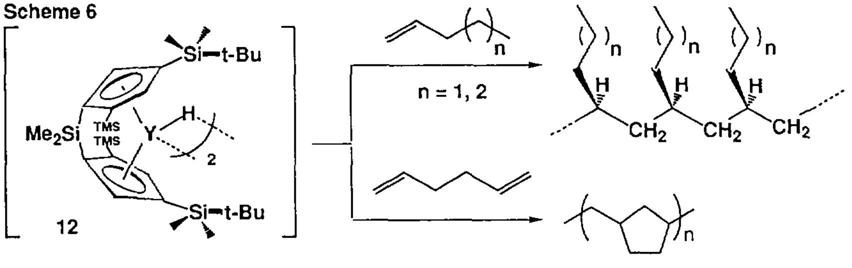


Figure 2 and 3 show ^{13}C-NMR spectra of the poly(1-hexene) and poly(1-pentene) thus obtained respectively. In both spectra, only one peak indicating mmmm pentad appears in the C3 carbon region (34.91 ppm in Figure 2, 38.01 ppm in Figure 3).[8] Accordingly the polymerization proceeded stereoselectively giving highly isotactic poly(α-olefin)s. Judging from the peak intensity ratio, the selectivity is higher than 95%. It is widely accepted that Kaminsky catalyst of racemic structure affords isotactic poly(α-olefin)s.[9] Thus, high isotacticity of the resulting polymer is in good accord with the racemic structure of **12**.

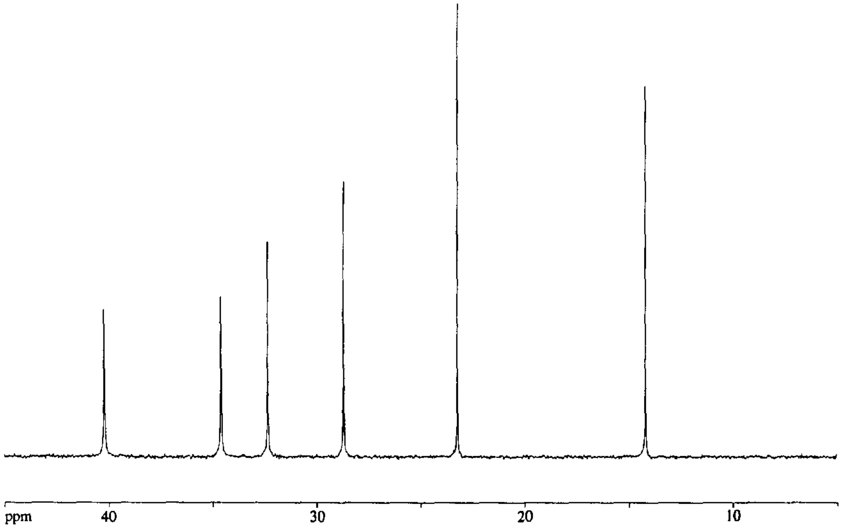


Figure 2. ^{13}C-NMR spectrum of poly(1-hexene) obtained by **12**.

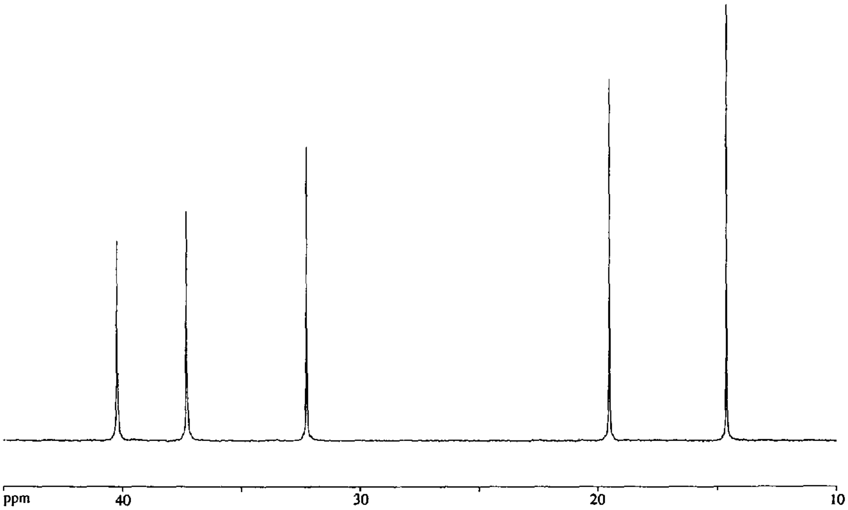


Figure 3. ^{13}C-NMR spectrum of poly(1-pentene) obtained by **12**.

Kaminsky type catalyst conducts cyclopolymerization of 1,5-hexadiene affording poly(methylene-1,3-cyclopentane). *Mn* of the polymer obtained there is lower than 4×10^4. We applied **12** for the polymerization and found that much higher *Mn* polymer was obtained than that by Kaminsky catalyst.[10] However, stereoselectivity of this polymer regarding the cis/trans of cyclopentane ring structure is quite low (cis/trans=45/55).[11]

In conclusion, we found that use of t-BuMe$_2$Si group was effective to prepare racemic complex exclusively while a mixture of racemic and C$_1$ symmetric complex was always obtained in the case of four Me$_3$Si groups. In addition bulkiness of this group plays an significant role in α-olefin polymerization.

EXPERIMENTAL SECTION

General. All operations were performed under argon with rigorous exclusion of oxygen and moisture with the use of Schlenk techniques. All solvents and liquid monomers were distilled from Na/K alloy under argon. NMR spectra were measured with a JEOL EX-270 or a Bruker AM-X400wb. *Mn* and *Mw/Mn* of poly(1-hexene) and poly(1-pentene) were determined by gel permeation chromatography (GPC) on a Tosoh SC-8010 using columns, TSKgel G2000, G3000, G4000 and G5000 in chloroform at 40°C. *Mn* and *Mw/Mn* of polyethylene and poly(methylene-1,3-cyclopentane) were determined by GPC on a Waters 150C using Shodex AT806MS column in 1,2,4-trichlorobenzene at 140°C. *Mn* and *Mw/Mn* were calibrated from standard polystyrene.

t-BuMe$_2$SiC$_5$H$_5$ (7): To a stirred solution of CpNa (0.74mol) in THF 200ml was added t-BuMe$_2$SiCl (106g, 0.70mol) at r.t.. After stirred for 18 hrs at r.t., the reaction mixture was poured into ice water. After extractive work up with hexane and water, distillation of resulting liquid (100°C/0.01mmHg) afforded **7** in 60% yield.

Me$_2$Si(t-BuMe$_2$SiC$_5$H$_4$)$_2$ (8): To a stirred solution of **7** (80g, 0.44mol) in 400ml of THF was added n-BuLi (240ml of 1.61M solution in n-hexane, 0.39mol) dropwise at 0°C. The solution was stirred for 21 hrs at 0°C~r.t., then, Me$_2$SiCl$_2$ (23.5ml, 0.19mol) was added at r.t.. After stirred for 13 hrs at r.t., the reaction mixture was poured into water. After extractive work up with hexane and water, bulb-to-bulb distillation of resulting liquid (170°C/0.01mmHg) afforded **8** in 85% yield (based on the amount of n-BuLi).

Me$_2$Si(Me$_3$Si-t-BuMe$_2$SiC$_5$H$_3$)$_2$ (9): To a stirred solution of **8** (25g, 0.06mol) in 180ml of THF was added n-BuLi (90ml of 1.61M solution in n-hexane, 0.145mol) dropwise at 0°C. The solution was stirred for 16 hrs at r.t., then, Me$_3$SiCl (35ml, 0.27mol) was added at r.t.. After stirred for 24hrs at r.t., the reaction mixture was poured into saturated NaHCO$_3$ aqueous solution. After extractive work up with hexane and water, bulb-to-bulb distillation of resulting liquid (250°C/0.01mmHg) afforded **9** in 52% yield.

Me$_2$Si(2-Me$_3$Si-4-t-BuMe$_2$SiC$_5$H$_2$)$_2$YCl$_2$Li(THF)$_2$ (10): To a stirred solution of **9** (2.6g, 4.6mmol) in 25ml of THF was added n-BuLi (6ml of 1.61M solution in n-hexane, 9.7mmol) dropwise at 0°C. The solution was stirred for 5 hrs at 0°C~r.t.. The solution was added to the stirred suspension of anhydrous YCl$_3$ (1.23g, 6.3mmol) in 20ml of THF at r.t.. The reaction mixture was stirred under reflux for 24 hrs. After the solvent was removed in vacuo, 90ml of n-hexane was added and the suspension was stirred for 24 hrs. Insoluble solid was removed by centrifugation. Recrystallization of the remaining solution afforded **10** in 36% yield. ^{1}H-NMR (C_6D_6) δ 0.48, 0.72, 1.08 (s, 6Hx3, Me_2Si), 0.63 (s, 18H, Me_3Si), 0.98 (s, 18H, t-Bu), 1.35 (m, 8H, THF-β), 3.52 (m, 8H, THF-α), 6.93 (d, J = 1.7 Hz, 2H, Cp-H), 7.23 (d, 1.7 Hz, 2H, Cp-H)

$Me_2Si(2\text{-}Me_3Si\text{-}4\text{-}t\text{-}BuMe_2SiC_5H_2)_2YCH(SiMe_3)_2$ (11): To a stirred solution of **10** (2g, 2.3mmol) in 60ml of toluene was added $(Me_3Si)_2CHLi$ (4.5ml of 0.79M solution in Et_2O, 3.5mmol) at 0°C. The mixture was stirred for 13 hrs at 0°C~r.t., then the solvent was removed in vacuo. Hexane (80ml) was added to the residue and the suspension was stirred for 24 hrs. Insoluble solid was removed by centrifugation and recrystallization of the hexane solution afforded **11** in 36% yield. ^{1}H-NMR (C_6D_6) δ 0.20, 0.33, 0.39, 0.46 (s, 9Hx4, Me_3Si), 0.76, 0.78 (s, 9Hx2, t-Bu), 0.26, 0.42, 0.48, 0.53, 0.94, 0.96 (s, 3Hx6, MeSi), 6.62 (d, J = 1.9 Hz, 1H, Cp-H), 6.77 (d, J = 1.9 Hz, 1H, Cp-H), 6.96 (d, J = 1.9 Hz, 1H, Cp-H), 7.64 (m, 1H, Cp-H)

Polymerization of olefins by 12 (General procedure): A solution of **12** (4mg) in 10ml of toluene was degassed 3 times. To the solution H_2 (1atm) was introduced from balloon for 1hr at r.t.. After the H_2 was removed by degassing 3 times, monomer was added to the solution.

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11. The stereoselectivity was determined from ^{13}C-NMR spectrum of the polymers according to the data in reference 10.

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