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Synthesis and characterization of new bis(2-R-indenyl) zirconium dichloride complexes for the olefin polymerization

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Abstract

A series of 2-alkylindene(2-RInd; R = Me, i-Pr, n-Bu, Bzl, Cy, t-Bu) were prepared by nucleophilic addition of the corresponding alkyl anions to 2-indanone in the presence (or absence) of $LaCl_3$. With these 2-alkylindenes, bis(2-alkylindenyl)zirconium dichloride complexes were synthesized to investigate the effects of alkyl substituents at 2-position of indene on the rotational conversion rate between rotamers (racemic and meso) and the catalytic activities toward olefin polymerization. Analysis of NMR spectra could line up the electron donating abilities and steric bulkiness of alkyl substituents in order and variable temperature NMR analysis (from 298 to 193 K) proved that these alkyls could not freeze free rotation of indenyl ligands. These complexes showed catalytic activities toward ethylene and propylene polymerization and the variation of catalytic activities(PE, Me > Cy > i-Pr > Bzl > n-Bu; PP, Me > n-Bu > i-Pr > Cy > Bzl), molecular weights(PE, n-Bu > Cy > i-Pr > Me > Bzl; PP, n-Bu > Me > Cy > i-Pr > Bzl), and polydispersities(PE, 2.80–5.05; PP, 2.23–3.30) were rationalized with steric, electronic, and structural factors. Steric bulkiness of substituents played an important role in the propylene polymerization but relative importance of these factors were different in the ethylene polymerization. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: 2-Alkylindene; Nucleophilic addition; Alkyl substituents

1. Introduction

Synthetic rubber has been obtained through the polymerization of diene units followed by vulcanization. Due to the lack of thermoplastic properties chemically crosslinked rubber cannot be recycled but only burned away for the waste treatment. This treatment inevitably causes environmental pollution and the development of recyclable thermoplastic rubber was extensively sought. Up to date, thermoplastic rubber was mainly synthesized by ABA-type triblock copolymerization with styrene and butadiene but this process requires strict control of reaction conditions; instant mixing when monomers are added during the reaction, high purity of monomers, and difficult control of reaction composition. These characteristics lead to high cost of production and products are of limited special use. Recent development of the new process for the thermoplastic elastomers employing propylene and bent metallocene catalysts has been drawing considerable interests due to prospects of much improved economics, resulted from lower cost of monomer and adoption of continuous processes of polymerization. In a recent overview on the future rubber and plastics markets [1], it is expected that thermoplastic elastomers will grow more rapidly than other synthetic and natural rubber and enjoy the much improved market share. Thermoplastic elastomeric properties can be obtained by alternating ordered and disordered stereogenic blocks. Polymers with

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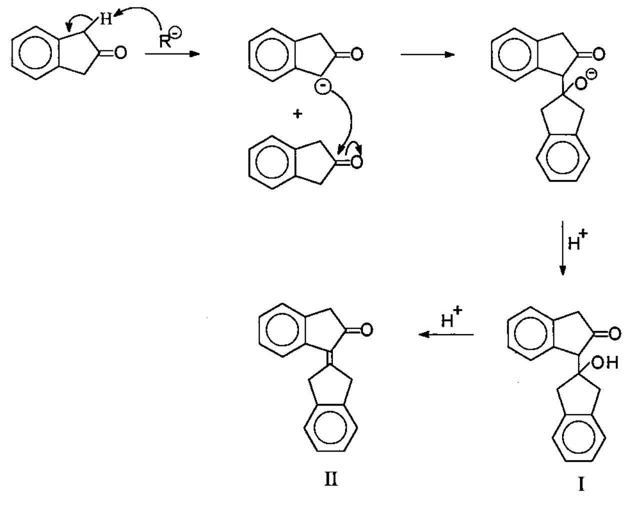


Scheme 1.

extremely short block of this structure was hemiisotactic polypropylene (hit-PP). The first example of hit-PP was reported by Farina [2]. It was obtained by two-step synthesis with substituted butadienes. A new route to hit-PP employing metallocene catalysts was found by Ewen [3]. The production of hit-PP was exploited to rationalize the polymerization mechanism with metallocene catalysts [4]. Recently, Erker [5] published an interesting variation of stereocontrol with temperature in propylene polymerization with an unbridged metallocene catalyst and visualized the possibility to produce thermoplastic elastomers with a single metallocene catalyst. Along with this newly adopted strategy employing metallocene catalysts, Collins [6,7] and Chien [8–11] produced elastomeric polypropylenes, yet properties were far beyond satisfaction. On the other hand, Waymouth [12,13] reported much improved synthesis of thermoplastic elastomers with several bis(2-R-indenyl)zirconium dichlorides (R = phenyl, 3,5-dimethylphenyl, and 3,5-ditrifluoromethylphenyl). He explained the formation of thermoplastic elastomers by introducing the equilibrium between meso and racemic complexes where free rotation of indenyl ligands occurs on the basis of isolated both forms in the solid state. Elastomeric properties can be observed with the coexistence of isotactic and atactic blocks caused by racemic and meso catalysts, respectively. However, change of free rotational speed could not be monitored even though bulky substituents were introduced to the phenyl group in the 2-position of indene. This is not unexpected because Erker [14] reported that bent metallocene complexes of the early transition metals usually displayed very low torsional activation barriers for the Cp-M moieties and torisional isomersim exhibited only in the solid state. Recently, we also reported the production of elastomeric polypropylene by using bis(2-methylindenyl)zirconium dichloride as a catalyst [15]. In this paper, direct change of substitients on the 2 position of an indenyl ligand to examine the steric effects on the properties of the products was tried with a hope to slow down the exchange rate to be able to be monitored by the NMR spectroscopy. Also reaction pathways were proposed based on the side products observed in the preparation of ligands. Combined electronic and steric factors and reaction conditions would change the free rotational speed of the indenyl ligands in metallocene catalysts and properties of the thermoplastic polypropylene and these effects were investigated and detailed results will be reported elsewhere.

2. Experiment

All manipulation were performed under a nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. Solvents were reagent grade and were distilled under nitrogen over appropriate drying agents prior to use. Reagent grade chemicals were purchased from Aldrich and used without further purification unless stated otherwise. 2-Indanone [16], 2-methylindene [17] and $ZrCI_4$-2THF [18] were prepared by the procedures of the literature. ^1H- and ^{13}C-NMR spectra were recorded by using 5 mm tube on a Bruker AC-250 FT-NMR spectrometer operating at 250.133 and 62.896 MHz, respectively and were referenced to tetramethylsilane (TMS). Variable temperature NMR spectra were obtained using toluene-d_8 or CD_2Cl_2 as a solvent in the range of 193–298 K. Elemental analyses were performed in the Korea Institute of Science and Technology. Mass spectral analyses were carried out employing a HP5890A GC/HP 5917A MS detector equipped with 30-m long capillary column packed with liquid methyl silicon.

Table 1
^1H-NMR Spectroscopic parameters of ligands

Ligand	Aromatic (ppm)	C_1 (ppm)	C_3(ppm)	R (ppm)
2-methylindene	7.02–7.26 (m, 4H)	6.36 (s, 1H)	3.10(s, 2H)	2.01 (s 3H)
2-isopropylindene	7.51–7.22 (m, 4H)	6.62 (s, 1H)	3.44(s, 2H)	2.88 (h, 1H), 1.35 (d, 6H)
2-*n*-butylindene	7.29–6.97 (m, 4H)	6.41 (s, 1H)	3.21 (s, 2H)	2.39 (t, 2H), 1.54 (m, 2H), 1.31 (m, 2H), 0.85 (t, 3H)
2-benzylindene	7.27–6.95 (m, 9H)	6.40 (s, 1H)	3.69(s, 2H)	3.16(s, 2H)
2-cyclohexylindene	728–6.96 (m, 4H)	6.38 (s, 1H)	3.21 (s, 2H)	2.31 (br t, 1H), 1.87--1.09 (m, 10H)

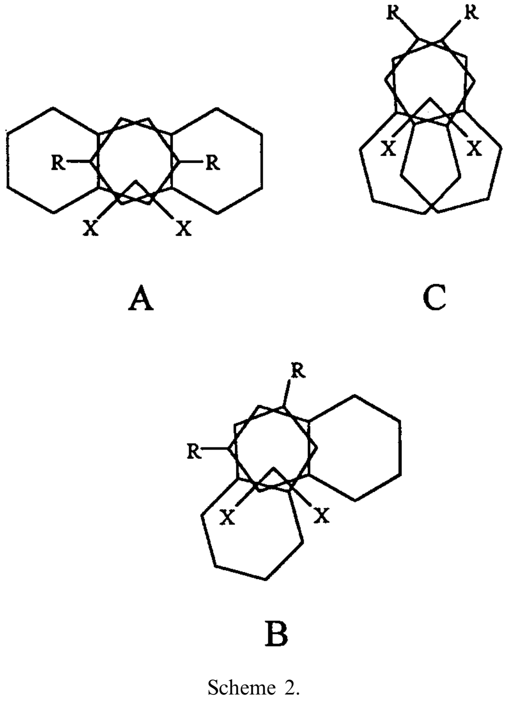
Table 2
^{1}H-NMR spectroscopic parameters of metal complexes

Metal complex	Aromatic (ppm)	C-5 membering (ppm)	R (ppm)
Bis(2-methylInd) $ZrCl_2$	7.27 (m, 4H)	5.84 (s, 4H)	2.05 (s, 3H)
Bis(2-isopropylInd) $ZrCl_2$	7.74 (m, 4H), 7.27(m, 4H)	5.74(s, 4H)	2.85(h, 2H), 0.86 (d, 12H)
Bis(2-*n*-butylInd) $ZrCl_2$	7.56 (m, 4H)	5.77 (s 4H)	2.29 (t, 4H), 1.21 (m, 8H), 0.77 (t, 6H)
Bis(2-benzylInd) $ZrCl_2$	7.60 (m, 4H), 7.21–7.08 (m, 10H), 6.95 (m, 4H)	5.79 (s, 4H)	3.64 (s, 4H)
Bis(2-cyclohexylInd)$ZrCl_2$	7.73–7.66 (m, 4H), 7.27–7.19 (m, 4H)	5.72 (s, 4H)	2.58–2.53 (br t, 2H), 1.67--1.63 (br d, 4H), 1.36--1.19(m, 8H), 1.12--0.87 (m, 8H)

3. Ligand synthesis

3.1. 2-Isopropylindene

Anhydrous $LaCl_3$ (3.19 g, 13 mmol) was placed in a 100 ml schlenk flask and heated in vacuo at 140°C for 1 h while stirring. Nitrogen was introduced and the flask was cooled in an ice bath. Then 50 ml of THF was introduced while stirring vigorously. The resulting white suspension was stirred overnight under nitrogen at room temperature. The suspension was cooled to 0°C again and the i-PrMgBr (13 mmol) prepared in situ by the reaction between isopropyl bromide and magnesium turning was added dropwise. After stirring for 1 h at 0°C, 2-indanone (1.32 g, 10 mmol) in 20 ml of THF was added dropwise and the suspension was stirred for 2 h. The color of the solution slowly turned from white to brown as the reaction proceeded. The reaction was quenched with 10% aqueous acetic acid (100 ml). The product was extracted by ether and washed with brine, $NaHCO_3$ aqueous solution, and brine consecutively and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the residue was purified to produce the yellow solid by the silica gel chromatography and the mixed solvent of ether and *n*-hexane (1:4) as an eluting solvent. The yellow solid (2-hydroxy-2-isopropylindane) and p-TsOH · H_2O (50 mg, 0.24 mmol) in 30 ml of toluene was refluxed for 2 h. The solution was washed with saturated aqueous solution of $NaHCO_3$ and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The brown oily residue was purified to a colorless liquid on a silica gel column by using *n*-hexane as an eluting solvent. Yield: 0.36 g (23%) ^{1}H-NMR ($CDCl_3$) 7.51–7.22 (m, 4H), 6.62 (s, 1H), 3.44 (s, 2H), 2.88 (h, 1H), 1.35 (d, 6H), ^{13}C-NMR ($CDCl_3$) 156.95, 145.51, 142.94, 126. 19, 124.57, 124.07, 123.54, 119.99, 39.09, 30.03, 22.55, GC-MS (EI) 158.2 (M +), 143.2 (M–Me), 128.2 (M–2Me),



Scheme 2.

Table 3
Effect of substituents on the catalytic activities of bis(2alkylindenyl)zirconium dichloride complexes toward olefin polymerization

Substituent	PE (10^6 g Zr mol^{-1} h^{-1} atm^{-1})	PP (10^5 g Zr mol^{-1} h^{-1} atm^{-1})
Me[a]	3.1	44.5
i-Pr	2.1	3.4
n-Bu	0.6	6.6
Cy	2.5	2.8
Bzl	1.9	0.17

Polymerization temperature: 0°C, Al/Zr = 3500, polymerization pressure = 1 atm.
Polymerization time = 1.5 h, [Zr] = 5.9×10^{-5} M.
[a] Polymerization time = 0.5 h.

Table 4
Effects of substituents of bis(2-alkylindenyl)zirconium dichloride complexes on the molecular weights and polydispersities in the polyolefins

Substituent	Molecular weights (PP)		PD (PP)	Molecular weights (PE)		PD (PE)
	M_w	M_n		M_w	M_n	
Me	136 500	41 400	3.30	1 292 100	461 100	2.80
i-Pr	58 900	22 700	2.59	1 368 800	415 200	3.30
n-Bu	220 900	72 200	3.06	1 557 700	548 900	2.84
Cy	112 000	46 900	2.39	1 494 800	295 800	5.05
Bzl	46 200	20 700	2.23	811 100	215 200	3.77

115.1 (M−i-Pr) Anal. Calcd. for $C_{12}H_{14}$, C: 91.14, H: 8.86, Found C: 87.00, H: 8.59.

3.2. 2-*n*-Butylindene

The same procedure described above in the case of 2-isopropylindene was followed except n-butyllithium (5.2 ml, 13 mmol, 2.5 M in hexane) was employed instead of i-PrMgBr. The red-brown sticky liquid was obtained before dehydration and after dehydration the brown oily residue was purified to a colorless liquid on a silica gel column by using *n*-hexane as an eluting solvent. Yield: 0.90 g (52%) ^{1}H-NMR (CDCl$_3$) 7.29–6.97 (m, 4H), 6.41 (s, 1H), 3.21 (s, 2H), 2.39 (t, 2H), 1.54 (m, 2H), 1.31 (m, 2H), 0.85 (t, 3H), ^{13}C-NMR (CDCl$_3$) 150.86, 145.60, 142.98, 126.06, 123.59, 119.67, 40.88, 31.06, 30.78, 22.39, 13.82, GC-MS(EI) 172.2 (M +), 143.1 (M−Et), 129.2 (M−Pr), 115.1 (M−n-Bu) Anal. Calcd. for $C_{13}H_{16}$, C; 90.70, H: 9.30, Found C: 89.70, H: 9.31.

3.3. 2-Benzylindene

Magnesium turning (0.80 g, 33 mmol) was placed in 10 ml of ether and the solution was refluxed while benzylbromide (3.6 ml, 30 mmol) was slowly added through a pressure-equalized dropping funnel. After the reaction was completed, 2-indanone (4.0 g, 30 mmol) in 50 ml of ether was introduced for a period of about 12 h to the well stirred solution. After the addition was completed, the solution was refluxed for 2 h. After cooling, the reaction was quenched with 200 g of ice and 16 ml of concentrated sulfuric acid. Then 80 ml of 25% ammonium chloride aqueous solution was added and the product was extracted by ether and dried over anhydrous MgSO$_4$. After filtration, the solvent was removed under reduced pressure to produce white solid. 30 ml of toluene and 0.5 g of p-TsOH · H$_2$O was added to this solid and the solution was refluxed for 2 h. After cooling, the solution was washed with saturated NaHCO$_3$ aqueous solution and the product was extracted with ether and dried over anhydrous MgSO$_4$. After filtration, the solvent was removed under reduced pressure. The residue was purified to produce white solid by silica gel column and *n*-hexane as an eluting solvent. Yield: 4.6 g (75%) m.p.: 32–34°C ^{1}H-NMR (CDCl$_3$) 7.27–6.95 (m, 9H), 6.40 (s, 1H), 3.69 (s, 2H), 3.16 (s, 2H), ^{13}C-NMR (CDCl$_3$) 149.29, 145.33, 143.44, 140.03, 128.90, 128.50, 127.82, 126.30, 123.90, 123.50, 120.23, 40.83, 37.97, GC-MS(EI) 206 (M +), 128 (M−Ph-1), 115 (M−Bzl), 91 (Bzl) Anal. Calcd. for $C_{16}H_{14}$, C: 93.20, H: 6.80, Found C; 93.00, H; 6.97

3.4. 2-*t*-Butylindene

The same procedure described above in the case of 2-isopropylindene was followed except in situ formed t-BuMgBr was employed instead of i-PrMgBr. The yellow white solid was obtained before dehydration and after dehydration the white solid was purified on a silica gel column by using *n*-hexane as an eluting solvent. Yield: 50 mg (0.97%) ^{1}H-NMR (CDCl$_3$) 7.45–7.13 (m, 5H), 6.58 (s, 1H), 3.45 (s, 2H), 1.31 (s, 9H), ^{13}C-NMR (CDCl$_3$) 158.58, 143.94, 141.55, 124.67, 122.05, 121.93, 121.84, 118.51, 36.16, 31.77, 28.77 GC-MS(EI) 172.1 (M +), 157.2 (M−Me), 142.1 (M−2Me), 127 (M−3Me), 1 1 5.0 (M−t-Bu), 57.2 (t-Bu).

3.5. 2-Cyclohexylindene

The same procedure described above in the case of 2-isopropylindene was followed except in situ formed CyMgBr was employed instead of i-PrMgBr. The yellow white solid was obtained before dehydration and after dehydration the white solid was purified on a silica gel column by using *n*-hexane as an eluting solvent. Yield: 2.10 g (43.8%) ^{1}H-NMR (CDCl$_3$) 7.28–6.96 (m, 4H), 6.38 (s, IH), 3.21 (s, 2H), 2.31 (br t, IH), 1.87–1.09 (m, IOH), ^{13}C-NMR (CDCl$_3$) 156.11, 145.58, 142.83, 126.17, 124.14, 123.47, 123.40, 119.96, 39.90, 39.23, 33.14, 26.44, 26.28, GC-MS(EI) 198 (M +), 155 (M−Pr), 141 (M−Bu), 127 (M−Pen), 115 (M−Cy), 83 (Cy) Anal. Calcd. for $C_{15}H_{18}$, C: 90.91, H: 9.09, Found C: 90.90, H: 9.22.

Table 5
Methyl pentad distributions of polypropylenes

Substituents	mmmm	mmmr	rmmr	mmrr	mmrmrmrr	mrmr	rrrr	mrrr	mrrrn	mm (%)
Me	11.59	14.09	7.37	12.68	21.23	12.48	4.42	8.75	7.39	33.1
i-Pr	5.46	11.01	12.34	10.84	15.79	18.63	11.58	6.66	7.69	28.8
n-Bu	16.36	16.41	7.40	11.86	20.30	12.41	2.20	6.13	6.93	40.2
Cy	13.41	15.16	8.67	12.28	19.29	13.53	3.44	6.80	7.43	37.3
Bzl	20.86	16.48	7.92	9.53	19.16	9.86	3.46	4.86	7.87	45.3

[mm] = [mmm] + 0.5[mmr], [mmm] = [mmmm] + 0.5[mmmr], [mmr] = [mmmr] + 2[rmmr].

4. Synthesis of bis(2-alkylindenyl)zirconium dichloride

4.1. *Bis(2-methylindenyl)zirconium dichloride*

2-Methylindene (650 mg, 5.0 mmol) was dissolved in 20 ml of THF and the solution was cooled to − 78°C. 2.1 ml of n-butyllithium solution (2.5 M hexane solution, 5.3 mmol) was slowly added to this solution through a syringe over a period of 30 min. The solution was warmed up to room temperature and stirred for another 30 min. This yellow solution was cannulated into a suspension of $ZrCl_4$-2THF(950 mg, 2.5 mmol) in 20 ml of toluene precooled at 0°C over 2 h and the mixture was warmed up to room temperature and stirred for 2 h. The yellow powder was obtained by filtration and washed with THF/toluene(1:2) and dried under vacuum overnight. Yield: 480 mg (45%) ^{1}H-NMR ($CDCl_3$) 7.65 (dd, 4H), 7.24 (dd, 4H), 5.83 (s, 4H), 2.04 (s, 6H) ^{13}C-NMR ($CDCl_3$) 136.49, 124.57, 123.57, 123.52, 104.55, 15.14 GC-MS(EI) 420 (M +), 289 (M−L-1), 253 (M−L−Cl-1), 128 (L-2), 115 (indene) Anal. Calcd. for $C_{20}H_{20}Cl_2Zr$, C: 56.86, H: 4.77, Found C: 56.63, H: 4.85.

4.2. *Bis(2-isopropylindenyl)zirconium dichloride*

2-Isopropylindene (400 mg, 2.5 mmol) was dissolved in 7 ml of ether and the solution was cooled to − 78°C. 2.1 ml of *n*-butyllithium solution (2.5 M hexane solution, 2.5 mmol) was slowly added to this solution through a syringe over a period of 30 min. The solution was warmed up to room temperature and stirred for another 30 min. This yellow slurry was cannulated into a suspension of $ZrCl_4 \cdot 2THF$ (470 mg, 1.25 mmol) in 20 ml of toluene precooled at 0°C over 30 min and the mixture was warmed up to room temperature and stirred for 2 h. The solution was filtered and the solvent was removed under reduced pressure. Yellow precipitate was obtained by adding CH_2Cl_2/*n*-hexane to the resulting residue. The yellow powder was obtained by filtration and washed with n-hexane and dried under vacuum overnight. Yield: 200 mg (33%) ^{1}H-NMR ($CDCl_3$) 7.74 (dd, 4H), 7.27 (dd, 4H), 5.74 (s, 4H), 2.85 (h, 2H), 0.86 (d, 12H) ^{13}C-NMR ($CDCl_3$) 150.44, 125.04, 124.97, 124.04, 102.51, 28.36, 21.82 GC-MS(EI) 475.9 (M +), 316.9 (M−L-1), 158.1 (L), 141.0 (L−Me-2), 128.0 (L-2Me), 115 (indene) Anal. Calcd. for $C_{24}H_{26}Cl_2Zr$, C: 60.50, H: 5.46, Found C: 60.40, H: 5.50.

4.3. *Bis(2-n-butylindenyl)zirconium dichloride*

2.0 ml of *n*-buthyllithium (2.5 M hexane solution, 5 mmol) was added to a solution of 2-*n*-butylindene (860 mg, 5 mmol) in 50 ml of diethylether at − 78°C over a period of 15 min. After warming to room temperature and stirring for 20 min at room temperature, this yellow solution of the indenyllithium compound was cannulated into a white suspension of $ZrCl_4$-2THF(950 mg, 2.5 mmol) in 50 ml of toluene at 0°C over a period of 4 h. The mixture was then warmed up to room temperature and stirred for 30 h. The solvent was removed under reduced pressure and then 20 ml of *n*-hexane was added to precipitate the yellow solid. The yellow solid was collected by filtration and washed with 5 ml of *n*-hexane three times. The yellow compound was extracted by hot toluene (ca. 150 ml) until the color of the precipitate changed to white completely. The yellow compound was obtained by removing the solvent under reduced pressure and recrystallized by adding toluene/*n*-hexane. Yield: 140 mg (11%) ^{1}H-NMR ($CDCl_3$) 7.56 (m, 4H), 7.16 (m, 4H), 5.77 (s, 4H), 2.29 (t, 4H), 1.21 (m, 8H), 0.77 (t, 6H) ^{13}C-NMR ($CDCl_3$) 142.33, 125.32, 124.47, 124.23, 104.39, 31.89, 30.13, 21.36, 12.80 GC-MS(EI) 504.0 (M +), 331.0 (M−L-1), 172.1 (L), 129.1 (L−n-Pr), 115.0 (L−n-Bu) Anal. Calcd. for $C_{26}H_{30}Cl_2Zr$, C: 61.90, H: 5.95, Found C: 61.50, H: 6.07.

4.4. *Bis(2-benzylindenyl)zirconium dichloride*

2-Benzylindene (0.53 g, 2.6 mmol) was dissolved in 30ml of ether and the solution was cooled down to − 78°C. 1.2 ml of n-BuLi (2.86 mmol, 2.5 M in hexane) was added to this solution dropwise. After addition was completed, the solution was warmed up to room temperature and stirred for 30 min. This solution was transferred to the solution of $ZrCl_4$-2THF(0.54 g, 1.43 mmol) in 50 ml of toluene dropwise by a cannula and the resulting solution was stirred overnight. The light yellow suspension was filtered and the solvent was removed under reduced pressure. The product was recrystallized to produce light yellow solid with THF and *n*-hexane. Yield: 0.70 g (47%) ^{1}H-NMR ($CDCl_3$) 7.60(m, 4H), 7.21–7.08 (m, 1 OH), 6.95 (d, 4H), 5.79 (s, 4H), 3.64 (s, 4H) ^{13}C-NMR ($CDCl_3$) 141.29, 139.81, 128.60, 128.43, 126. 33, 125.49, 125.35, 105.72, 37.42, GC-MS(EI) 572 (M+), 535 (M–Cl-2), 442 (M–Cl–Bzl-3), 410 (M–2Cl–Bzl), 365(M–L-2), 294 (M–2Cl–L-2), 206 (L+1), 115 (L–Bzl), 91 (Bzl) Anal. Calcd. for $C_{32}H_{26}Cl_2Zr$, C: 67.13, H: 4.54, Found C: 67.30, H: 4.53.

4.5. *Bis(2-cyclohexylindenyl)zirconium dichloride*

2-Cyclohexylindene (0.50 g, 2.53 mmol) was dissolved in 20 ml of ether and the solution was cooled down to −20°C. 1.1 ml of n-BuLi (2.75 mmol, 2.5 M in hexane) was added to this solution dropwise (color of the solution turned to yellow, red, and yellow successively). After addition was completed, the solution was warmed up to room temperature and stirred for 1 h to obtain a yellow slurry solution. This solution was transferred to the solution of $ZrCl_4 \cdot 2THF$(0.52 g, 1.40 mmol) in 40 ml of toluene dropwise by a cannula for 4 h at 0°C and the resulting solution was stirred overnight (ca. 12 h). The light yellow suspension was filtered and the solvent was removed under reduced pressure. The product was recrystallized to produce bright yellow solid with methylenechloride and *n*-hexane. Yield: 0.21 g (30%) ^{1}H-NMR ($CDCl_3$) 7.73–7.66 (m, 4H), 7.27–7.19 (m, 4H), 5.72 (s, 4H), 5.79 (s, 4H), 2.58–2.53 (br t, 2H), 1.67–1.63 (br d, 4H), 1.36–1.19 (m, 8H), 1.12–0.87 (m, 8H) ^{13}C-NMR ($CDCl_3$) 150.04, 125.78, 124.86, 123. 47, 103.31, 38.78, 33.37, 26.44, 26.16 GC-MS(EI) 556.0(M+), 357.0 (M–L-1), 198.0 (L), 115.0 (L–Cy) Anal. Calcd. for $C_{30}H_{34}Cl_2Zr$, C: 64.72, H: 6.11, Found C: 65.10, H: 6.20.

5. Results and discussion

Initially, synthesis of 2-alkyl substituted indene was tried by simple addition of Grignard reagents (alkyl magnesium halide) to 2-indanone as reported by Waymouth. Unfortunately, 2-alkyl substituted indene could not be obtained. Instead, dimerization of 2-indanone (compound **1**) and dehydration of dimer product (compound **2**) were induced and as shown in Scheme 1. In these reactions Grignard reagents did not act as nucleophiles but as bases and induced aldol condensation. Compound **1** and **2** were analyzed by ^{1}H, ^{13}C-NMR (including C–H COSY) and GC-Mass spectroscopies [19]. GC-MS spectra show that the fragmentation patterns of compound I and 2 are almost identical even though relative intensities of fragmentations are slightly different. This may reflect the easy removal of a water molecule from compound **1** and these two compounds are closely related with each other. After many trials, it was finally found that formation of these compounds was favored with rapid addition of Grignard reagents. By much slower addition, 2-benzylindene was successfully prepared but other 2-substituted indene could not be obtained even by this modification. It has been reported that the use of MCl_3 (M = Ce, La) greatly improved the nucleophilic addition of ketones [20] and this improved method was adopted to synthesize the other ligands. In our experiments, $LaCl_3$ was more efficient than $CeCl_3$ even though these compounds should be exploited with stoichiometric amounts. However, the yield of t-butylindene is very low possibly due to partial conversion to a Grignard reagent and retardation of nucleophilic addition resulted from steric bulkiness of t-butyl group. Therefore, complexation of this ligand could not be achieved and investigations for the more efficient synthetic pathway are still underway. Also, solvent and molar ratio of reactants were found to be important. Reactions in THF produced more products than in any other solvents such as diethylether. Optimal molar ratio of reactants was found to be 1:1.5:1.5(ketone: Grignard reagent: $LaCl_3$) and optimal reaction temperature was 0°C in case of Grignard reagents and −78°C in case of organolithium reagents. However, reasons for these behaviors cannot be explained. In cases of n-butyl and i-propyl indene, elemental analyses were not satisfactory partially due to their instabilities. It was found that these compounds slowly decomposed during storage even in a refrigerator. However, complexation with a transition metal stabilized the ligand and satisfactory elemental analysis data could be obtained. Electron donating abilities of the alkyl groups at the 2-position can be differentiate from the C3 proton chemical shifts in Table 1. The order of electron donating abilities of alkyl groups was as follows; Me > Cy, n-Bu > i-Pr > Bzl. As shown in Table 2, the effect of the substituents on the properties of the metallocene complexes appears to be originated not from electronic but steric factor. This conclusion resulted from the fact that the chemical shifts of 5-member ring protons are very similar (5.72–5.84 ppm). Generally, upfield shifts of Cp protons in ^{1}H-NMR spectra has been observed with increase of η^3 (ring slipped) structure contribution, which can be expected from the destruction of the aromaticity [21]. Therefore, deviation from the plane (η^5) structure due to steric bulkiness of alkyl group at 2-position can be represented by the relative chemical shifts of protons in the 5-member ring even though the differences are very small. By these references, steric bulkiness of alkyl groups can be ordered as follows; Me < Bzl < n-Bu < i-Pr < Cy. This order is not quite different from the instinctive sense. For the benzyl case, if a phenyl ring located in the same plane of the indene ring above order can be acceptable. Waymouth also reported the structures of bis(2-phenylindenyl)zirconiumdichloride or analogues where the conformations of the phenyl ring are similar to those described above [12,13]. The combination of these electronic and steric effects of substituents at the 2 position in this series of indenyl complexes might induce the largest downfield change of C3 proton chemical shift by deprotonation and coordination to a metal atom in the case of methyl substituent and the lowest one in benzyl case. It is expected that bulky substituents on a ring might slow down the free rotation rate of the indenyl ligand as reported in the literature [22]. and these behavior could be monitored by NMR. However, even at the temperature down to − 80°C these behaviors cannot be freezed as reported by Waymouth. This indicates that exchange rates among rotamers are very fast or slow on the NMR time scale. Meanwhile, it is worth mentioning the directions of chemical shifts of alkyl protons with lowering the temperature. In i-Pr and Cy complexes, alkyl protons shifted downfield, especially protons of carbons bonded directly to indene (Cα protons); chemical shift changes (from 297 to 243 K) were 0.09 (i-Pr), and 0.13 (Cy), respectively. In Bzl case, Cα proton went upfield (−0.10, from 297 to 213 K) and no appreciable shift was monitored in Me and n-Bu ones. It is known that aromatic ring current of the benzo group induces high-field shifts in the protons of other groups that spend a substantial amount of their time directly above the benzo ring [23]. Therefore, it is concluded that structures with bulky substituents might prefer racemic conformers (A) but complexes with less bulky ones prefer meso ones (C) at the room temperature (Scheme 2). In the high temperature limit spectra, sharp peaks, especially singlets of 5-member ring can effectively exclude the possibility of intermediate (B) structure where two singlets are expected. In the cyclopentadienyl analogues, Me and i-Pr complexes were found to have meso-like structures but t-Bu induced racemic-like one [24]. Catalytic activities toward ethylene and propylene polymerization were found as follows; PE, Me > Cy > i-Pr > Bzl > n-Bu, PP, Me > n-Bu > i-Pr > Cy > Bzl (Table 3). For the propylene polymerization above order coincides with the order of steric bulkiness except benzyl case. However, the fact that phenyl in the benzyl group is an electron withdrawing group would rationalize the order on the basis of known effect of electron withdrawing substituents on the catalytic activities of metallocene complexes [25] As reported elsewhere [15], produced PP, especially one produced at lower temperature with bis(2-methylindenyl)zirconium dichloride complex indeed possessed thermoplastic properties. In the ethylene polymerization, combined electronic, steric and structural effects appear to play a certain role even though difference in catalytic activity was not great. Racemic isomers were known to show more catalytic activities than meso ones and isopropyl and cyclohexyl complexes were found to have racemic-rich conformer. In the methyl ones, electronic and steric factors dominates over structural ones and electron withdrawing nature of benzyl group decreased the catalytic activity. Meso-rich conformers in the n-butyl complexes could be attributed to the lower activities. Substituent effects on the molecular weights (M_w) and polydispersity (PD) were summarized in Table 4. Molecular weights were generally pretty high from the view point of low reaction temperature (0°C) and relatively wide PDs were rationalized by the nonrigid structures of catalysts. PDs in the polypropylene followed the reverse order of steric bulkiness except benzyl case (Me > n-Bu > i-Pr > Cy > Bzl). However, PDs in the polyethylene showed reverse trend probably due to smaller bulkiness of ethylene. Tacticities of PP produced in the presence of various catalysts were summarized in Table 5, but this could not be clearly rationalized yet. Nonrigidity of the catalysts used in this paper induced lower stereoregularity than ansa type catalysts [7,10]. Analysis of the microstructures of PP is under investigation. More detailed properties of polypropylenes, especially thermoplastic ones and effects of other reaction parameters on the catalytic activities will be discussed elsewhere.

6. Conclusions

A series of 2-alkylindene(2-RInd; R = i-Pr, n-Bu, Bzl, Cy, t-Bu) were prepared by the modification of the nucleophilic addition of corresponding alkyl anions to 2-indanone with moderate yields. Simple addition of anions to 2-indanone induced aldol condensation to form dimer of 2-indanone and dehydration product of the dimer. With these 2-alkylindenes, bis(2-alkylindenyl)zirconium dichloride complexes were synthesized to investigate the effects of alkyl substituents at 2-position of indene on the rotational conversion rate between rotamers (racemic and meso) and the catalytic activities toward olefin polymerization. Analysis of NMR spectra could differentiate the electron donating abilities and steric bulkiness of alkyl substituents and deduce the structures of metallocene complexes. However, variable temperature NMR analysis proved that these alkyls were not able to freeze free rotation of indenyl ligands and resolve low temperature limit structures of metallocenes. These complexes showed catalytic activities toward olefin polymerization and the variations of catalytic activities, molecular weights, and polydispersities were rationalized with steric, electronic and structural factors. Relative importance of these factors were found to be different in each complex.

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