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# Excellent Stereoregular Isotactic Polymerizations of Propylene with $C_2$-Symmetric Silylene-Bridged Metallocene Catalysts

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New $C_2$-symmetric silylene-bridged metallocene compounds, $[Me_2Si(\eta^5\text{-}R_nC_5H_{4-n})(\eta^5\text{-}R'_nC_5H_{4-n})]MCl_2$(M=Zr,Hf; $R_n$,$R'_n$=Me,t-Bu,2,4-$Me_2$, 2,3,5-$Me_3$), were synthesized together with $C_1$-symmetric ones (M=Zr, Hf; $R_n$= 2,3,5-$Me_3$, 2,4-$Me_2$, 3,4-$Me_2$, t-Bu, Me; $R'_n$= Me, H) for comparison and employed as the catalysts for isotactic polymerization of propylene in combination with methylaluminoxane. The $C_2$-symmetric metallocenes bearing methyl groups at 2- or 5-positions gave polymers of the highest melting point (160-163 °C) and stereospecificity ([mmmm]: 97-99%).

Recently homogeneous olefin polymerization catalysts consisting of combinations of titanium, zirconium, or hafnium metallocenes with methylaluminoxanes have drawn much attention because these metallocene-aluminoxane systems exhibit extraordinary activities and produce polymers with very narrow molecular weight distributions and in addition they provide good models for studying the relation between the ligand structure and the catalytic activity and specificity.1) Previously we reported the preparation of all members of zirconium compounds$(\eta^5\text{-}Me_nC_5H_{5-n})_2ZrCl_2$ and their use to atactic polymerization of propylene.2) It was found that the catalytic activity and the molecular weight thus obtained were markedly influenced by changing the numbers and the positions of the methyl groups on the cyclopentadienyl (Cp) rings suggesting that electronic and steric effects are both important.

Ethylene-bridged indenyl or tetrahydroindenyl moiety is a well known ligand of chiral metallocene catalysts to generate isotactic polypropylene.1) We thought that the use of a silylene-bridged Cp ligand bearing various substituents instead of the ethylene-bridged ones could provide a new chiral metallocene-aluminoxane system for isotactic polymerizations of α-olefins. One of the foremost advantages is the easy accessibility of the ligand owing to higher reactivity of $Me_2SiCl_2$ to metal cyclopentadienide than $XCH_2CH_2X$. We report here the successful synthesis of new chiral dimethylsilylenebis(substituted-cyclopentadienyl)metal dichlorides3,4) which are highly active as the isotactic propylene polymerization catalysts.3)

$C_2$-symmetric dimethylsilylenebis($\eta^5$-2,4-dimethylcyclopentadienyl)zirconium dichloride (**1b**) was prepared in the following way. A suspension of the dilithium salt of dimethylbis(2,4-dimethylcyclopentadienyl)silane (3.67 g, 15 mmol) in THF

(50 ml) was added dropwise to the THF solution (200 ml) of $ZrCl_4$ (3.5 g, 15 mmol) at -78 °C. The mixture was allowed to warm to room temperature and the resulting solution was refluxed for 24 h. After the solvent was removed in vacuo, the solid residue was extracted with $CH_2Cl_2$ (200 ml). The filtered solution contained the racemic(dl) and meso isomers of **1b** in a 53/47 ratio, as indicated by the $^1H$ NMR spectrum in $CDCl_3$ of the sample obtained by evaporation of an aliquot of the solution ($\delta$(ppm) at 100 MHz, dl: 0.77(s, 6H, $SiMe_2$), 2.05(s, 6H, Me), 2.28(s, 6H, Me), 5.27(d, 2H, $C_5H_2$, J=2.2 Hz), 6.44(d, 2H, $C_5H_2$, J=2.2 Hz), meso: 0.65(s, 3H, $SiMe_2$), 0.91(s, 3H, $SiMe_2$), 2.19(s, 6H, Me), 2.23(s, 6H, Me), 5.26(d, 2H, $C_5H_2$, J=2.2 Hz), 6.25(d, 2H, $C_5H_2$, J=2.2 Hz)). The solution was evaporated to dryness in vacuo to give solid. Recrystallization from heptane (200 ml) afforded colorless crystals of **1b** (1.83 g, 30%, dl/meso=57/43). Fractional crystallization from toluene-hexane gave 0.23 g of colorless crystals of **1b** (dl/meso=94/6). Similarly, other $C_2$-symmetric metallocenes were synthesized as the racemic and meso mixtures (dl/meso=1/1 except **1l**(3/2) and **1m**(2/1)). $C_1$-symmetric ones were also prepared according to the equations (1)-(4). All these compounds gave satisfactory elemental analysis and identified by $^1H$ NMR spectra. In the preparation of **1c-1g**, **1j-1k**, **1n-1p**, only the isomer having a 1,3-disubstituted cyclopentadienyl ligand was isolated

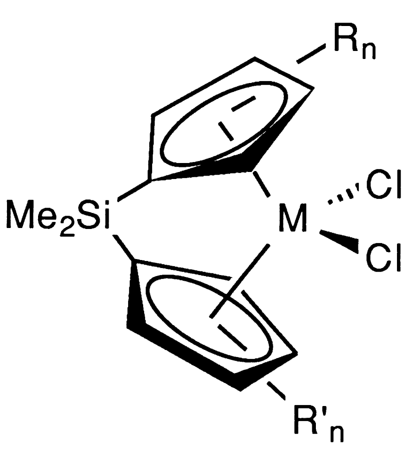
$$Y^1(R_nC_5H_{5-n}) + Me_2SiCl_2 \longrightarrow Me_2Si(R_nC_5H_{5-n})Cl + Y^1Cl \qquad (1)$$

$$Y^2(R'_nC_5H_{5-n}) + Me_2Si(R_nC_5H_{5-n})Cl \rightarrow Me_2Si(R_nC_5H_{5-n})(R'_nC_5H_{5-n}) + Y^2Cl \qquad (2)$$

$Y^1, Y^2$=Li,Na

$$Me_2Si(R_nC_5H_{5-n})(R'_nC_5H_{5-n}) + 2RLi \rightarrow Li_2[Me_2Si(R_nC_5H_{4-n})(R'_nC_5H_{4-n})] \qquad (3)$$

$$Li_2[Me_2Si(R_nC_5H_{4-n})(R'_nC_5H_{4-n})] + MCl_4 \rightarrow [Me_2Si(\eta^5\text{-}R_nC_5H_{4-n})(\eta^5\text{-}R'_nC_5H_{4-n})]MCl_2 \qquad (4)$$



| | | | | |
|---|---|---|---|---|
| M=Zr | **1a** | (36%) | $R_n$=2,3,5-$Me_3$ | $R'_n$=2',4',5'-$Me_3$ |
| | **1b** | (30%) | 2,4-$Me_2$ | 3',5'-$Me_2$ |
| | **1c** | (33%) | 3-t-Bu | 4'-t-Bu |
| | **1d** | (36%) | 3-Me | 4'-Me |
| | **1e** | (17%) | 2,4-$Me_2$ | 3'- or 4'-Me |
| | **1f** | (19%) | 3,4-$Me_2$ | 3'-Me |
| | **1g** | ( 6%) | 3-t-Bu | 3'- or 4'-Me |
| | **1h** | (13%) | 2,3,5-$Me_3$ | H |
| | **1i** | (16%) | 2,4-$Me_2$ | H |
| | **1j** | (10%) | 3-t-Bu | H |
| | **1k** | (19%) | 3-Me | H |
| M=Hf | **1l** | (35%) | 2,3,5-$Me_3$ | 2',4',5'-$Me_3$ |
| | **1m** | (34%) | 2,4-$Me_2$ | 3',5'-$Me_2$ |
| | **1n** | (17%) | 3-t-Bu | 4'-t-Bu |
| | **1o** | (28%) | 3-Me | 4'-Me |
| | **1p** | (14%) | 3-Me | H |

among several expected positional isomers, probably because of the steric hindrance between substituents on the Cp ring and on the silicon atom.

Polymerization by chiral complexes **1a**-**1p** were carried out in the following way. After sufficiently purged with nitrogen gas, toluene (500 ml), methylaluminoxane (Tosoh Akzo Corp., molecular weight: 930, 1.25 mmol, Al/M=10000 ) and **1** (0.002 mmol) were placed in a 1.5 L capacity stainless-steel autoclave equipped with a stirrer. The temperature was kept at 30 °C, continuously introducing propylene so as to keep the total pressure at 3 kg/cm$^2$. After 2 h, the reaction mixture was treated with methanol (200 ml) and the resulting powdery polypropylene was collected by filtration and vacuum dried at 70 °C for 10 h. The molecular weight and melting point were measured by GPC and by DSC. The tacticity (mmmm) was determined by $^{13}$C-NMR spectroscopy.

The yields and physical properties of the polypropylene obtained by these catalysts are listed in Table 1 together with those of the ones obtained by indenocene catalyst for comparison purpose.

Table 1. Polymerization of propylene with chiral Zr and Hf metallocenes

| Chiral metallocene | Isomer ratio[a)] [dl/meso] | Activity[b)] ($10^6$gPP/molM·h) | Mw | Mw/Mn | Mp $\theta_m$/°C | [mmmm] % |
|---|---|---|---|---|---|---|
| **1a** | 85/15 | 1.59 | 133900 | 1.99 | 162.0 | 97.7 |
| **1b** | 94/6 | 11.1 | 86500 | 1.93 | 160.4 | 97.1 |
| **1c** | 73/27 | 0.31 | 9560 | 2.32 | 149.4 | 93.4 |
| **1d** | 88/12 | 16.3 | 13700 | 2.25 | 147.8 | 92.5 |
| **1e** | 90/10[c)] | 2.54 | 18700 | 2.06 | 154.5 | -[d)] |
| **1f** | | 1.94 | 5050 | 2.38 | 133.0 | -[d)] |
| **1g** | | 5.91 | 6370 | 2.61 | 146.0 | 89.4 |
| **1h** | | 7.35[e)] | 15500 | 2.27 | 85.1 | 49.9 |
| **1i** | | 5.23[e)] | 10600 | 2.33 | 68.9 | 41.0 |
| **1j** | | 7.94 | 4260 | 2.13 | 125.7 | 77.9 |
| **1k** | | 6.69[e)] | 6610 | 2.19 | 79.5 | 52.4 |
| [$C_2H_4$(indenyl)$_2$]$ZrCl_2$ | 100/0 | 21.0 | 35900 | 2.40 | 142.3 | 85.2 |
| **1l** | 93/7 | 0.30 | 256100 | 2.38 | 162.8 | 98.7 |
| **1m** | 100/0 | 0.14 | 139200 | 1.84 | 162.4 | 98.5 |
| **1n** | 26/74 | 0.03 | 17190 | 2.87 | 157.4 | -[d)] |
| **1o** | 52/48 | 1.61 | 66800 | 3.53 | 148.2 | -[d)] |
| **1p** | | 0.06 | 52800 | 2.59 | 103.8 | -[d)] |
| [$C_2H_4$(indenyl)$_2$]$HfCl_2$ | 100/0 | 2.13 | 354000 | 2.56 | 137.0 | 81.3 |

a) dl-Enriched metallocenes obtained by recrystallization (except **1n** and **1o**) were used. meso-Metallocenes gave toluene-soluble atactic polymers. b)Fraction of polymer insoluble in toluene. c) Isomer ratio of 3'-Me and 4'-Me isomers. d) Not determined. e) Fraction of polymer soluble in toluene (no fraction of polymer insoluble in toluene).

The $C_2$-symmetric metallocenes, contrary to the $C_1$-symmetric ones, produced polymers of higher molecular weights, melting points, and tacticities (**1a** vs. **1h**, **1b** vs. **1i**, **1c** vs. **1j**, **1d** vs. **1k**, **1o** vs. **1p**). This is the first example which show the efficiency of $C_2$-symmetric ligands over $C_1$-symmetric ones for isotactic polymerization reactions. In the $C_2$-symmetric catalysts, metallocenes bearing methyl groups at 2- or 5-positions (**1a**, **1b**, **1l**, and **1m**) gave polymers of the highest molecular weights (86500-256100), melting points (160-163 °C), and tacticities ([mmmm]: 97-99%). This stereospecificity may be ascribed as the stabilization of an intermediate conformation which leads isotactic-propagation by the restriction of the mobility of two Cp rings in the presence of methyl groups at 2- or 5-positions. When bulky substituents were introduced at 3-positions in the $C_2$-symmetric catalysts, considerable decrease of activity was observed (**1c** vs. **1d**, **1n** vs. **1o**). With hafnocene catalysts, higher molecular weight and slightly more stereoregular polymers were produced compared to those with zirconocene catalysts, although the yields were very low. Same trend is observed in ethylene-bridged indenyl and tetrahydroindenyl metallocene catalysts.$^{1)}$ Under comparable conditions, **1a** and **1b** gave polymers of higher molecular weight and stereospecificity (higher melting point and [mmmm]) than Et(indenyl)$_2$ZrCl$_2$ and also **1l** and **1m** gave more stereospecific polymers than Et(indenyl)$_2$HfCl$_2$. This superiority of metallocenes bearing dimethylsilylene-bridged ligands over those of ethylene-bridged ones may arise from a higher stereorigidity of the former connecting two Cp rings with only one atom.

## References

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