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# Stereoselective Synthesis of a Germanium-Bridged Zirconocene for Temperature-Invariant Propylene Polymerizations

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*Summary: Synthesis of rac-[((1,2,3,4-tetraphenyl-1,3-butadiene-1,4-diyl)germylene)bis(1-$\eta^5$-indenyl)]dichlorozirconium (1) was achieved with substantial suppression of the undesired meso diastereomer as predicted by MM2 force field calculations. The corresponding zirconocenium ion of 1 polymerizes propylene with high catalytic activity and stereospecificity to very high molecular weight. The characteristics of this catalysis are essentially independent of polymerization temperature over a broad temperature range.*

Much of the research on metallocene catalysis has been directed toward the synthesis of group 4 *ansa*-metallocenes[1] as precursors to stereospecific olefin polymerization catalysts.[2] We have synthesized a new spirogermylene precursor (Figure 1), *rac*-[((1,2,3,4-tetraphenyl-1,3-butadiene-1,4-diyl)germylene)bis(1-$\eta^5$-indenyl)]-dichlorozirconium (1). The cation of 1 polymerizes propylene with high activity ($A$) and stereospecificity (IY) over a broad temperature range ($T_p$).

The chief challenge in homogeneous Ziegler–Natta catalysis is to design a molecular structure which strongly directs the regio- and stereochemical pathways for monomer incorporation. Isotactic propagation requires $C_2$-symmetric *ansa*-zirconocene precursors, the synthesis of which usually produces both racemic and meso diastereomers. The meso isomer lacks profacial selectivity; several methods have been reported to suppress its formation.[3–7] Our approach was to design a ligand, calculate the racemic/meso ratio of its metallocene complexes by a molecular mechanics (MM2) calculation,[8] and proceed with synthesis only when the prognosis is favorable for the racemic diastereomer. The steric energies for the two diastereomers of 1 are $E_{rac} = 11.5$ kcal/mol and $E_{meso} = 13.4$ kcal/mol. This result indicates that the formation of the desired *rac* isomer will dominate the diastereomeric mixture in the synthesis of 1.[9]

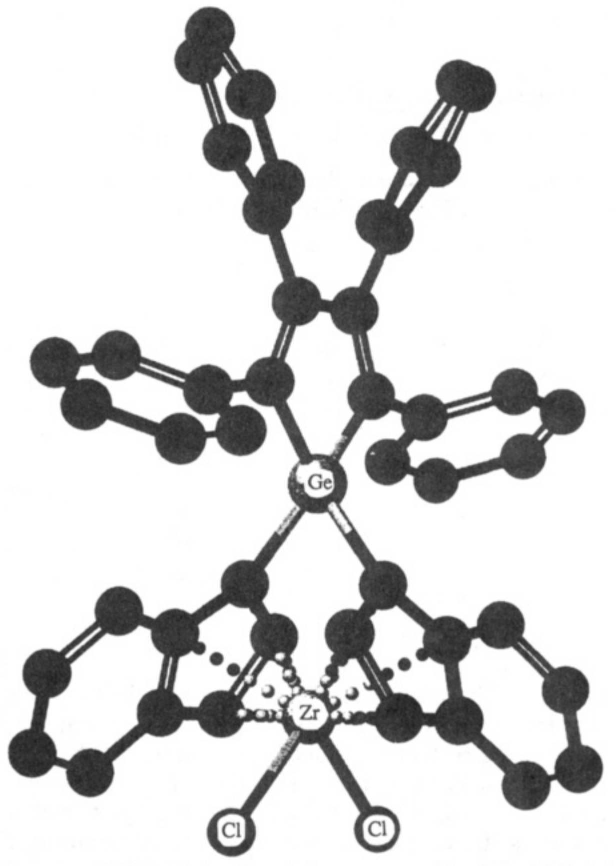

**Figure 1.** MM2-derived model structure of 1. All unlabeled atoms are carbon.

All reactions were carried out using Schlenk or glovebox techniques under an argon atmosphere. 1,4-Dilithio-1,2,3,4-tetraphenylbutadiene[10] and 1,1-dichlorotetraphenyl-1-germacyclopentadiene (**2**)[11] were obtained by literature methods. 1,1-Bis(indenyl)tetraphenyl-1-germ-

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(1) (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982,** *232,* 233. (b) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985,** *288,* 63.

(2) (a) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 507. (b) Ewen, J. A. *J. Am. Chem. Soc.* **1984,** *106,* 6355.

(3) Several methods have been described. Halterman and co-workers[4] introduced chirality in the bridging group in order to convert the previously enantiotopic faces of the indenyl ligands into diastereotopic faces so as to favor a single diastereomer in the synthesis of *ansa*-bis(indenyl)metal complexes by means of diastereofacial selection. Brintzinger, Katz, and co-workers[5] created structures such as biphenyl-bridged metallocenes which cannot possibly give meso forms. Coughlin and Bercaw[6] designed a specific ligand for selective metalation to produce only the racemic isomer in the synthesis of the chloride precursor. Marks et al.[7] generated a chiral, non-$C_2$-symmetric zirconocene system for the efficient isospecific polymerization of propylene.

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(6) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992,** *114,* 7606.

(7) Giardello, M. A.; Eisen, M. S.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1993,** *115,* 3326.

(8) Molecular mechanics calculations have been found to be exceedingly useful in geometrical, conformational, and configurational analysis: Boyd, D. B.; Lipkowitz, K. B. *J. Chem. Educ.* **1982,** *59,* 269.

(9) Molecular mechanics calculations were carried out using the CAChe modeling software system (2.7 version, 1991) and the MM2 force fields of: Allinger, N. L. *J. Am. Chem. Soc.* **1977,** *99,* 8127. Steric energies of the meso ($E_{meso}$) and racemic ($E_{rac}$) diastereomers in 37 zirconocene complexes have been calculated. The experimental isomeric ratios were found to scale with $E_{meso} - E_{rac}$.

(10) Leavitt, F. C.; Manuel, T. A.; Johnson, F.; Matternas, L.; Lehman, D. S. *J. Am. Chem. Soc.* **1960,** *82,* 5099.

(11) Curtis, M. D. *J. Am. Chem. Soc.* **1969,** *91,* 6011.

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**Table 1. Propylene Polymerizations Catalyzed with $1^{+}$ [a]**

| run no. | $T_p$ (°C) | [Zr] (μM) | [TIBA] (mM) | time (min) | yield (g) | $A^b$ | $T_m$ (°C) | IY[c] (%) | $10^{-5}M_w$[d] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 25 | 10 | 2.0 | 25 | 0.96 | $9.18 \times 10^6$ | 150.71 | 81.1 | 5.92 |
| 2 | 0 | 10 | 2.4 | 23 | 2.10 | $1.46 \times 10^7$ | 157.23 | 93.8 | 8.39 |
| 3 | −20 | 10 | 3.0 | 10 | 1.05 | $1.34 \times 10^7$ | 157.30 | 94.3 | 8.54 |
| 4 | −40 | 10 | 3.5 | 10 | 1.20 | $1.27 \times 10^7$ | 157.82 | 94.0 | 8.04 |
| 5 | −60 | 10 | 4.0 | 10 | 0.83 | $7.53 \times 10^6$ | 157.57 | 92.5 | 7.54 |

[a] Conditions: toluene 50 mL; $P_{C_3H_6}$ = 10 psig. [b] $A$ in units of g of PP/[(mol of Zr)·[$C_3H_6$]·h]. [c] Weight percentage of PP insoluble in refluxing *n*-heptane. [d] $M_w$ by viscosity.

acyclopentadiene (**3**) was prepared by the reaction of 2 equiv of indenyllithium and **2** in refluxing THF for 48 h in 63.0% yield. Anal. Calcd for $C_{46}H_{34}Ge$: C, 83.79; H, 5.20. Found: C, 83.50; H, 5.10.

The ligand **3** (5.16 g, 7.67 mmol) in 100 mL of THF was reacted with *n*-BuLi (9.59 mL of 1.6 M solution in hexane) for 4 h at room temperature to form, after washing and drying, the dilithiated derivative of **3** in quantitative yield. The product was added to a suspension of $ZrCl_4$ (1.79 g, 7.67 mmol) in $CH_2Cl_2$ at −78 °C, and the reaction mixture was then warmed to room temperature with stirring for an additional 12 h. The product, obtained by filtering through a Celite plug, removing solvent in vacuo, and washing with hexane, was found by $^1$H NMR to be a mixture of *rac* and *meso* (*rac*/*meso* ≈ 7/1) isomers of **1** with some polymeric material. Purification[12] afforded 1.42 g (22.6% yield) of **1**. Anal. Calcd for $C_{46}H_{32}Cl_2GeZr$ (819.48): C, 67.42; H, 3.94. Found: C, 67.00; H, 4.52. $^1$H NMR ($C_6D_6$) as measured on a Bruker/IBM 200 AC spectrometer: $\delta$ 7.70–6.50 (m, 28H), 6.10 (d, $J$ = 3.23 Hz, 2H), 5.79 (d, $J$ = 3.23 Hz, 2H).

Propylene was polymerized by the zirconocenium intermediate of the title complex ($1^+$), which was formed *in situ* by the reaction of **1**, triisobutylaluminum (TIBA), and triphenylcarbenium tetrakis(pentafluorophenyl)borate.[13] The polymerization procedures have been given in detail elsewhere.[14] The polymerization behaviors of $1^+$ are much more insensitive to $T_p$ than those of *rac*-[((1,4-butanediyl)silylene)bis(1-$\eta^5$-indenyl)]alkylzirconocenium ion ($4^+$)[15] and *rac*-[(dimethylsilylene)bis(1-$\eta^5$-indenyl)]-alkylzirconocenium ion ($5^+$),[13] which are compared below.

The key performance parameters for the catalyst $1^+$, activity and stereospecificity, are invariant of $T_p$ between −60 and 0 °C. The $T_m$ and $\bar{M}_w$ data for the isotactic poly(propylene)[16] it produced are shown in Table 1. The average values with standard deviations for $T_p$ from −60 to 0 °C are $A = (1.25 \pm 0.23) \times 10^7$ g of PP/[(mol of Zr)·[$C_3H_6$]·h], $T_m$ = 157.5 ± 0.5 °C, IY = 93.7 ± 0.8%, and $\bar{M}_w = (8.1 \pm 0.4) \times 10^5$. In comparison, both the activities and the stereospecificities of $4^+$ and $5^+$ decrease with increasing $T_p$, as do $T_m$ and $\bar{M}_w$ of the poly(propylene) formed by them.[13,15] At $T_p$ = 25 °C, the performance of $1^+$ suffers some decline: IY = 81.1%, $\bar{M}_w = 5.9 \times 10^5$, $T_m$ = 150.7 °C, and $A = 9.2 \times 10^6$ g of PP/[(mol of Zr)·[$C_3H_6$]·h). However, these results are still superior to those for other catalysts such as $4^+$, which at 25 °C has IY = 52.2%, $\bar{M}_w = 8.4 \times 10^4$, and $T_m$ = 143.5 °C.

The *ansa*-zirconocene catalysts discussed above all have unperturbed structures of very high stereospecificity, as indicated by the high IY, $T_m$, and $\bar{M}_w$ of the isotactic poly(propylene) they produce at $T_p$ = −55 °C. The reason these attributes decline with the increase of $T_p$ is not fully understood. One can envisualize a thermally activated distortion of the catalytic structures to lower the stereoselectivity. This perturbation may also promote $\beta$-H elimination to lower the polymer molecular weight. The other contributory process is the exchange of the propagating chains in the two opposite antipods of the catalytic species.[17] The excessively bulky germanium bridging moiety probably enhances the stereorigidity of the zirconocenium structure against conformation change or bimolecular exchange of its polymer ligands. The occurrence of $\beta$-H elimination is also appreciably suppressed so that a very high $\bar{M}_w$ of 800 000 was maintained over a broad $T_p$ range of −60 to 0 °C. Unexpectedly, this steric effect does not cause a significant reduction of polymerization activity, since catalysts $1^+$ and $4^+$ have very similar propylene polymerization activities. Whether the Ge atom exerts a more positive influence than the Si atom in olefin $\pi$-complexation or migratory insertion, or both, merits further investigation. Unfortunately, $1^+$ is unstable above 50 °C and its performance as a catalyst under manufacturing conditions cannot be assessed.

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(12) The crude mixture of **1** was crystallized from toluene/hexane, affording an orange powder. It was redissolved in toluene, passed through a Bio-Beads column (S-X 8, 200–400 mesh), and eluted with toluene. Pure **1** was obtained by fractional recrystallization of the eluent from toluene/hexane. It decomposes slowly above 208 °C without melting.

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(14) Polymerization of propylene (10 psig) in toluene (50 mL) was catalyzed by **1** (10 μM), TIBA (2–4 mM), and $Ph_3CB(C_6F_5)_4$ (10 μM). The procedures were described previously.[13]

(15) Tsai, W.-M.; Chien, J. C. W. *J. Polym. Sci., Part A* **1994**, *32*, 149.

(16) Isotactic poly(propylene) is characterized by high melting temperature ($T_m$) and $^{13}$C NMR isotacticity, which are related by

$$1/T_m - 1/T^\circ_m = -(R/\Delta H_u) \ln([mmmm])$$

where the properties for the ideally *i*-PP are $T^\circ_m$ = 184 °C and $\Delta H_u$ = 2.7 kcal/mol: Rieger, B.; Mu, X.; Mallin, D. T.; Rausch, M. D.; Chien, J. C. W. *Macromolecules* **1990**, *23*, 3559.

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