11988 J. Am. Chem. Soc. **1996,** *118,* 11988−11989

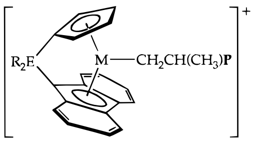
# A New Class of Zirconocene Catalysts for the Syndiospecific Polymerization of Propylene and Its Modification for Varying Polypropylene from Isotactic to Syndiotactic

Timothy A. Herzog, Deanna L. Zubris, and John E. Bercaw*

*Arnold and Mabel Beckman Laboratories*
*of Chemical Synthesis*
*California Institute of Technology*
*Pasadena, California 91125*

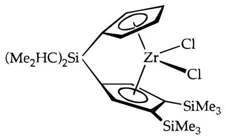
*Received July 15, 1996*

Metallocene catalysts for the polymerization of ethylene, propylene and other α-olefins are the focus of intense current interest.[1] A wide variety of metallocene catalysts from groups 3 and 4 have now been prepared. The tacticity of polypropylene varies predictably with the structure of the metallocene catalyst: $C_{2v}$ symmetric metallocenes generally afford atactic polypropylene; $C_2$ symmetric metallocenes produce highly isotactic polypropylene; $C_1$ metallocenes also produce isotactic polypropylene, but generally with less stereospecificity. Whereas the types of isospecific metallocene catalysts are structurally highly variable, syndiotactic polypropylene has been produced using essentially a single type of $C_s$ symmetric *ansa*-metallocene catalyst **1**, or minor variants thereof.[2] According to the original proposals from Ewen and Razavi,[2a] the syndiospecificity arises from propylene insertions occurring from alternating (enantiotopic) sides of the metallocene wedge with the propylene methyl group directed away from the larger fluorenyl ligand. Our interests in preparing single-component, syndiospecific group 3 metallocene catalysts led us to the ligand system of the $C_s$ symmetric zirconocene **2**,[3] seemingly closely related to that of **1**. We anticipated that the bulky [$SiMe_3$] substituents on the lower cyclopentadienyl ligand would function as does the fluorenyl ligand of **1**, directing the methyl group toward the less sterically hindered (upper) cyclopentadienyl ligand. Surprisingly, **2** in combination with $10^3$ equiv of methylaluminoxane (MAO) in liquid propylene at 0 °C produces essentially *atactic* polypropylene (55% *r* diads).



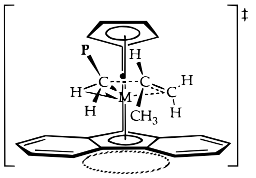
**1**

(M = Zr, Hf; E = C, Si; R = $CH_3$, $C_6H_5$).



**2**

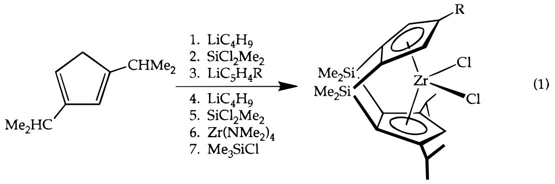
Re-evaluation of the relative importance of the various steric interactions operating for propylene polymerizations with metallocene catalysts,[4] as well as experiments supporting α C−H agostic assistance in the transition state for chain propagation,[5] led us to conclude that the transition structure for propylene polymerization with the Ewen/Razavi catalyst system is likely **3**.[6] The preference for the polymer chain extending from the α methylene group (**P**) and the methyl group of the propylene monomer to assume a trans relationship dominates, forcing the methyl group down toward the fluorenyl ligand. The relatively flat fluorenyl ligand with its open region between the benzo substituents nicely accommodates this orientation. In contrast, the ligand system for **2** lacks this feature.



**3**

(• = $ER_2$)

A new ligand has been designed with 1,2-[$SiMe_2$]$_2$ linking of cyclopentadienyl and 3,5-diisopropylcyclopentadienyl groups. Zirconocene **4** (eq 1)[7] thus incorporates all three features of **1**: (a) $C_s$ symmetry, (b) cyclopentadienyls of differing size, and (c) steric bulk flanking the metallocene wedge with an open region in center. Furthermore, this ligand design allows systematic variation of the cyclopentadienyl substituent (R) contained in the mirror plane, permitting steric changes for the catalyst while maintaining $C_s$ symmetry (*e.g.*, **4a−d**) or lowering the overall symmetry to $C_1$ (*e.g.*, **5a,b**).



**4a-d** ($C_s$ symmetry)
(**a**, R = H; **b**, R = $CHMe_2$; **c**, R = $SiMe_3$; **d**, R = $CMe_3$)
**5a-b** ($C_1$ symmetry)
(**a**, R = CHMeEt; **b**, R = $CHMeCMe_3$).

When activated with MAO, **4a−d** and **5a,b** are active catalysts for the polymerization of propylene (Table 1). Indeed, the $C_s$ symmetric zirconocenes **4a−d** are highly syndiospecific.

---

[1] For recent reviews and leading references, see: (a) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Intl. Ed. Engl.* **1995**, *34,* 1143. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255.

[2] (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (b) Patsidis, K.; Alt, H. G.; Milius, W.; Palackal, S. J. *J. Organomet. Chem.* **1996**, *509*, 63. (c) Shiomura, T.; Kohno, M.; Inoue, N.; Yokote, Y.; Akiyama, M.; Asanuma, T.; Sugimoto, R.; Kimura, S.; Abe, M. *Stud. Surf. Sci. Catal.* **1994**, *89*, 326. (d) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1993**, *459*, 117. (e) Winter, J.; Rohrmann, M.; Dolle, V.; Spaleck, W. *Eur. Pat. Appl.* 0,387,690 and 0,387,691, 1991. (f) Spaleck, W.; Aulbach, M.; Bachmann, B.; Küber, F.; Winter, A. *Macromol. Symp.* **1995**, *89*, 237−247. (g) Ewen, J. A. *Macromol. Symp.* **1995**, *89*, 181−196.

[3] Henling L. M.; Herzog, T. A.; Bercaw, J. E. *Acta Crystallogr.* Submitted.

[4] (a) Longo, P.; Grassi, A.; Pellechi, C.; Zambelli, A. *Macromolecules* **1987**, *20*, 1015. (b) Pino, P.; Galimberti, M. *J. Organomet. Chem.* **1989**, *370*, 1. (c) Gilchrist, J. C.; Bercaw, J. E. *J. Am. Chem. Soc.* In press.

[5] (a) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406−9407. (b) Brintzinger, H. H.; Krauledat, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412. (c) Brintzinger, H. H.; Leclerc, M. *J. Am. Chem. Soc.*, **1995**, *117*, 1651. (d) Burger, B. J.; Cotter, W. D.; Coughlin, E. B.; Chacon, S. T.; Hajela, S.; Herzog, T. A.; Köhn, R. O.; Mitchell, J. P.; Piers, W. E.; Shapiro, P. J.; Bercaw, J. E. In *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer: Berlin, 1995. (e) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85.

[6] Calculations are in agreement with this overall transition structure: Cavallo, L.; Guerra, G.; Vacatello, M.; Corradini, P. *Macromolecules* **1991**, *24*, 1784.

[7] (a) Clark, T. J.; Killian, C. M.; Luthra, S.; Nile, T. A. *J. Organomet. Chem.* **1993**, *462*, 247. (b) Cano, A.; Cuenca, T.; Gomez-Sal, P.; Royo, B.; Royo, P. *Organometallics* **1994**, *13*, 1688−1694. (c) Lang, H.; Blau, S.; Muth, A.; Weiss, K.; Neugenauer, U. *J. Organomet. Chem.* **1995**, *490*, C32. (d) Mengele, W.; Diebold, J.; Troll, C.; Roll, W.; Brintzinger, H. H. *Organometallics* **1993**, *12*, 1931−1935. (e) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5. (f) Christopher, J. N.; Diamond, G. M.; Jordan, R. F. *Abstracts of Papers* 210th National Meeting of the American Chemical Society, Chicago, Illinois, Fall 1995; American Chemical Society: Washington, DC, 1995; INOR310.

S0002-7863(96)02413-4 CCC: $12.00

**Table 1.** Propylene Polymerizations with Catalyst Derived from **4a**−**d** and **5a**−**b**[a]

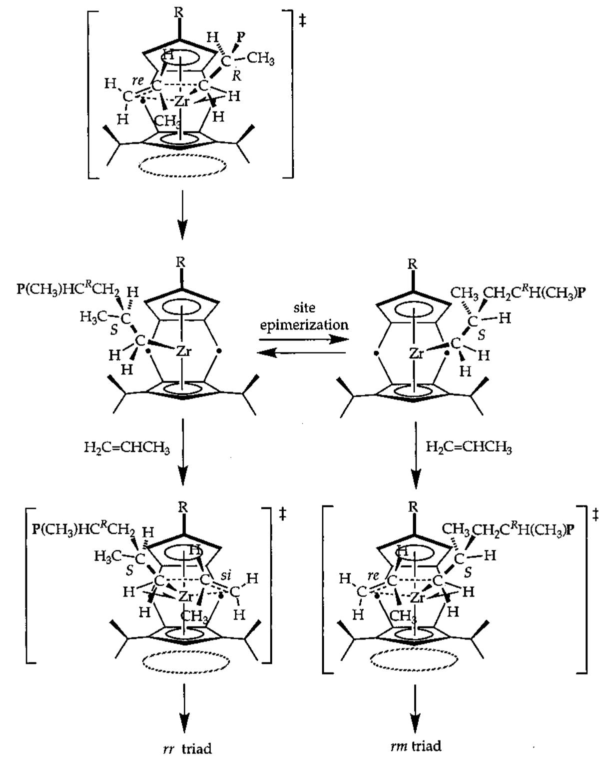
| entry | catalyst | activity[f] | [*rrrr*][g] | [*mmmm*][g] | [*r*][h] | [*m*][i] |
|---|---|---|---|---|---|---|
| 1 | **4a**[b] | 2160 | 83.7 | 0.0 | 94.0 | 6.0 |
| 2 | **4a**[c] | 300 | 27.3 | 0.0 | 74.1 | 25.9 |
| 3 | **4a**[d] | 74200 | 76.0 | 0.1 | 92.6 | 7.4 |
| 4 | **4b**[b] | 1750 | 98.9 | 0.0 | 99.6 | 0.4 |
| 5 | **4b**[c] | 230 | 38.8 | 0.0 | 75.6 | 24.3 |
| 6 | **4c**[b] | 1730 | 95.9 | 0.0 | 99.0 | 1.0 |
| 7 | **4c**[c] | 230 | 33.9 | 0.0 | 75.2 | 24.8 |
| 8 | **4d**[b] | 722 | 90.5 | 0.0 | 96.9 | 3.1 |
| 9 | **4d**[c] | 200 | 29.6 | 0.0 | 76.2 | 23.8 |
| 10 | **5a**[b] | 1500 | 83.1 | 0.0 | 94.4 | 5.6 |
| 11 | **5a**[c] | 200 | 20.0 | 4.8 | 62.0 | 38.0 |
| 12 | **5b**[b] | 930 | 41.8 | 5.6 | 73.5 | 26.5 |
| 13 | **5b**[c] | 156 | 0.0 | 61.2 | 14.6 | 85.4 |
| 14 | **5b**[e] | 110 | 0.0 | 58.5 | 17.6 | 82.4 |

[a] See Supporting Information for full experimental details. [b] Liquid propylene at 0 °C; 2 mg of catalyst and 2000 equiv of MAO. [c] Propylene (40 psig) in 35 mL toluene at 25 °C; 10 mg of catalyst and 430 equiv of MAO. [d] Liquid propylene at 60 °C; 300 equiv of MAO. [e] Propylene (10 psig) in toluene at 25 °C; 10 mg of catalyst and 430 equiv of MAO. [f] Polymer isolated (g)/catalyst (g)/hour. [g] Percentage of [*rrrr*] or [*mmmm*] pentad by $^{13}$C NMR analysis. [h] [*r*] = [*rr*] + 0.5[*mr*]. [i] [*m*] = [*mm*] + 0.5[*mr*].

Zirconocene **4a** produces polypropylene of syndiotacticity comparable to $\{(Et_2C)(fluorenyl)(cyclopentadienyl)\}ZrCl_2$.[8] Zirconocene **4b**[3] exhibits the highest syndiospecificity: at 0°C in liquid propylene good yields of polypropylene are obtained having 98.9% *rrrr*.

$C_1$ zirconocene **5a** performs similarly to $C_s$ symmetric and closely related **4b**. On the other hand, chiral **5b** produces moderately syndiotactic polypropylene at 0 °C in liquid propylene (entry 12), but switches to moderately *isospecific* at lower propylene concentrations and higher temperatures (entries 13 and 14). A likely explanation for the behavior of these catalysts is that site epimerization by "chain swinging" may compete with insertion of propylene at lower propylene concentrations and higher temperatures, thus lowering syndiospecificity (Scheme 1). For catalyst **5b**, insertions from the same enantioface of propylene occur mostly from only one side of the zirconocene wedge under conditions where site epimerization is faster than chain propagation. Hence, isotactic polypropylene is produced.

**Scheme 1**



The mechanisms for these processes are presently under further investigation.

**Acknowledgment.** The work has been supported by the USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER13431) and by Exxon Chemicals Americas. We thank Professor Terry Nile at the University of North Carolina, Greensboro, for providing advice on the preparation of 1,3-diisopropylcyclopentadiene and Drs. Terry Burkhardt and Charles Ruff of Exxon Chemicals Americas for assistance with polymerizations and $^{13}$C NMR characterization of some of the polypropylene samples.

**Supporting Information Available:** Experimental details describing the syntheses and characterization (including NMR data) for **2**, **4a**−**d**, and **5a**−**b**, as well as experimental details of the polymerizations of propylene and characterization of the polypropylenes (28 pages). See any current masthead page for ordering and Internet access instructions.

JA962413Z

---

(8) In a parallel run (*cf.* entry 3 of Table 1) in liquid propylene at 60 °C, $\{(Et_2C)(fluorenyl)(cyclopentadienyl)\}ZrCl_2$ with 300 equiv of MAO yielded 30 300 g of PP/g of catalyst/h with [*r*] content of 92.6%.