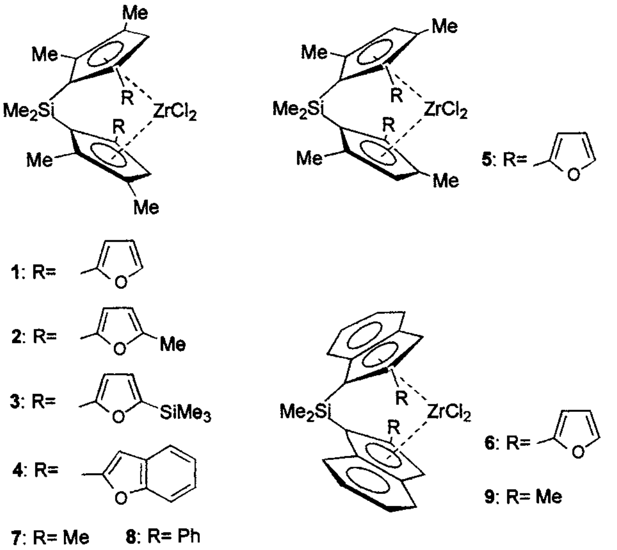
Novel High Performance *ansa*-Zirconocene Catalysts for Isospecific Polymerization of Propylene

Hiroshi Yamazaki,* Keisuke Kimura, Masato Nakano,† and Tsutomu Ushioda†
Department of Applied Chemistry, Faculty of Science and Industry, Chuo University, Kasuga, Bunkyo-ku, Tokyo 112-8551
†*Chisso Petrochemical Corporation, Polymer Research Center, Ichihara, Chiba 290-0058*

(Received September 10, 1999; CL-990779)

The introduction of furyl groups to the position next to the silylene bridge of an *ansa*-zirconocene catalyst was found to remarkably enhance the catalytic activity and the molecular weight of PP during the isospecific polymerization of propylene.

The effect of varying the steric and electronic characteristics of substituents of the *ansa*-metallocene catalyst on the degree of activity and stereoselectivity of the propylene polymerization has been the subject of a recent intense investigation.[1] One of the important developments in this field was made by Spaleck who found a considerable increase in the catalytic activity and the molecular weight by the introduction of a bulky substituent at the 4-position of the Me_2Si-bridged indenyl zirconocene catalyst.[2] It is also well established that the polymer properties are much improved by the introduction of methyl groups next to the silylene bridge. Previously, we reported that the $Me_2Si(2,3,5\text{-}Me_3C_5H)_2ZrCl_2/MAO$ catalyst provides highly isotactic but relatively low molecular weight polypropylene(PP) which is not satisfactory for industrial application.[3] During the course of our experiments to improve this catalyst, we found that the introduction of a furyl group to the position next to the Me_2Si-bridge resulted in a remarkable increase in the catalytic activity and the molecular weight. Here, we report the synthesis of 2-furyl substituted *ansa*-zirconocenes **1-6** and the related 2-phenyl substituted one **8**, and their use in the polymerization of propylene.



Furyl-3,4- or 2,4-dimethylcyclopentadienes, 1,2-dimethyl-4-phenylcyclopentadiene, and 2-furylindene were prepared by the reaction of 3,4-dimethyl-2-cyclopentenone, 2,4-dimethyl-2-cyclopentenone and 2-indanone with the corresponding lithium compounds. After the treatment with BuLi, they were reacted with Me_2SiCl_2 to afford the corresponding bis(cyclopentadienyl)- and bis(indenyl)-dimethylsilanes as a mixture of *rac* and *meso* diastereomers.[4] It is noteworthy that the formation of bis(2-furyl-3,5-dimethy-1-cyclopentadienyl)dimethylsilane from 1-furyl-2,4-dimethyl-cyclopentadienyllithium and Me_2SiCl_2 proceeds regioselectively. This may suggest the involvement of the furyl oxygen in the product determination step, because a similar reaction of 1,4-dimethyl-2-phenylcyclopentadienyllithium with Me_2SiCl_2 produces only bis(2,5-dimethyl-3-phenylcyclopentadienyl)-dimethylsilane. Zirconocenes obtained from these silanes consisted of a mixture of *rac* and *meso* diastereomers of varying ratios; **1**(58:42), **2**(55:45), **3**(75;25), **4**(40:60), **5**(80:20) **6**(75:25), **7**(50:50), and **8**(60:40). The *rac*-complexes were isolated from hexane, free of their *meso* isomers and employed as catalysts for the polymerization of propylene in combination with MAO.

The structures of **1**, **5** and **8** were determined by X-ray crystallography. They have an approximate C_2 symmetry. The molecular structure of **5** is depicted in Figure 1, showing unambiguously that the furyl group occupies the position next to the Me_2Si bridge. Angles between the planes of the furyl and

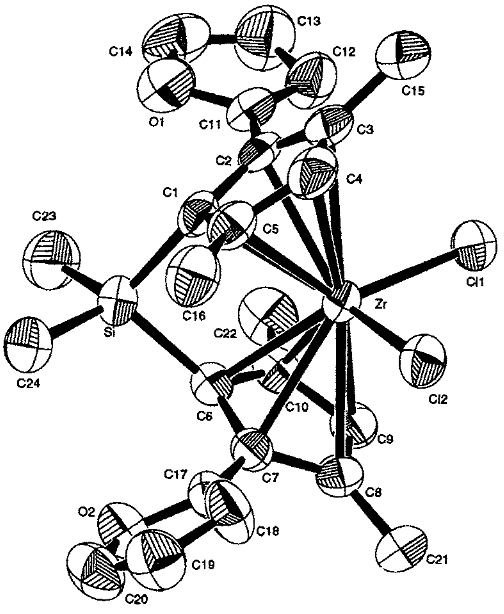


Figure 1. Molecular structure of complex **5** with 50% probability thermal ellipsoids depicted. All hydrogen atoms are omitted for clarity. Important bond distances (Å) and angles (°): Zr-Cl(1), 2.438(2); Zr-Cl(2), 2.432(2); Zr-Cp(centroid), 2.23, 2.22; ∠Cl(1)ZrCl(2), 98.63(8); ∠C(1)SiC(6), 94.6(3); ∠Cp(centroid)ZrC(centroid), 128.1.

phenyl substituents and the planes defined by the Cp rings are 34.58° and 37.37° in **1**, 39.03° and 52.50° in **5**, and 45.14° and 48.41° in **8**, respectively. The large shift from coplanarity may be due to the steric interactions with the Me$_2$Si-bridge. The furyl oxygens in **1** and **5** are located outside the molecules, being apart from the zirconium centers. The overall geometries of these complexes are similar to each other. However, distinct differences between the furyl derivatives (**1** and **5**) and the phenyl derivative (**8**) are observed in the values of $\angle$ClZrCl which may reflect the degree of steric hindrance.[5] The $\angle$ClZrCl of **8** (94.55(6)°) is in the same range as those of the strained *meso*-Me$_2$Si(2-PhInd)$_2$ZrCl$_2$ (94.41°)[5] and *rac*-Me$_2$Si(2-(Me$_2$N)Ind)$_2$ ZrCl$_2$ (94.9°).[6] In contrast, the corresponding angles of **1** (97.4(1)°) and **5** (98.63(8)°) are in the usual range of the Me$_2$Si bridged *ansa*-zirconocenes (97-100°).

The polymerization data obtained using complexes **1-6** are compared with the structural analogues **7-9** having methyl and phenyl groups in the place of the furyl groups (Table 1). Furyl substituted complexes (**1**, **5** and **6**) show higher activity and produce an i-PP of higher molecular weight than those by the methyl substituted ones (**7** and **9**). Unexpectedly, **8** exhibited a low activity and stereoselectivity which might be due to the higher steric congestion around the Zr center. Substituents on a furyl group also influence the catalytic performance. The introductions of Me and Me$_3$Si groups at the 5-position of the furyl substituent (**2** and **3**) resulted in a further increase in the catalytic activity and the molecular weight, although complex **4** having a benzofuryl group in the place of a furyl group showed a rather low activity. It is not clear why the furyl groups have a strong effect on enhancing the catalytic activity and the molecular weight of PP. In addition to the smaller steric bulkiness of the furyl group than a phenyl group, the electron withdrawing nature enhanced by the coordination of the furyl oxygen to MAO may play an important role. It should be noted that the X-ray crystallography of the thienyl analogue of **1** revealed the structure in which the thienyl sulfurs located near from the zirconium center in contrast to those of **1** and **5** and showed a poor catalytic performance similar to **8**.

Table 1. Propylene polymerization results[a]

Catalyst	Activity/ kg mmol^{-1} cat^{-1}.h^{-1}	MW/ g mol^{-1} x10^4	Tm/℃	mmmm/ %[b]
1	38	47.8	154.0	94.3
2	25	63.5	154.8	95.4
3	40	63.3	151.5	94.1
4	9.2	37.6	151.7	93.5
5	70	48.3	156.9	95.6
6	16	128	148.0	94.3
7	26	17.6	160.2	95.9
8	2.0	8.1	nd	20.0
9	46	34.8	153.1	94.5

[a]Polymerization conditions: [Al]/[Zr]=10^4, T=30 ℃, t=60 min., P=3 Kg/cm^{2}G. [b]Determined by ^{13}CNMR.

References and Notes

1 P. C. Möhring and N. J. Coville, *J. Organomet. Chem.*, **479**, 1, (1994); H.-H. Brinzinger, D. Fischer, R. Mülhaupt, B. Rieger, and R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.*, **34**, 1143 (1996).

2 W. Spaleck, F. Küber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, and E. F. Paulus, *Organometallics*, **13**, 954 (1994).

3 T. Mise, S. Miya, and H. Yamazaki, *Chem. Lett.*, **1989**, 1853.

4 For a smooth reaction, it is recommended to use a small amount of CuSCN or CuCN as the catalyst; Y. Kiso, K. Kawaai, and M. Nitabara, *Eur. Pat. Appl.*, EP617,044 (1994) (Mitsui Petro. Chem. Ind.).

5 J. L. Maciejewski Petoff, T. Agoston, T. K. Lal, and M. Waymouth, *J. Am. Chem. Soc.*, **120**, 11316 (1998).

6 E. Barsties, S. Schaible, M.-H. Prosenc, U. Rief, W. Röll, O. Weyand, B. Dorer, and H.-H. Brinzinger, *J. Organomet. Chem.*, **520**, 63 (1996).

7 Crystallographic data for **1**: $C_{24}H_{26}O_2Cl_2SiZr$, Fw = 536.68, monoclinic, space group $P2_1/a$ (# 14), a = 9.129(6) Å, b = 13.974(6) Å, c = 18.463(5) Å, β = 96.49(4)°, V = 2340(1) Å^3, Z = 4, D_{calc} = 1.523 g cm^{-3}, R = 0.069, Rw = 0.065 for 2032 reflections with $I > 3\sigma(I)$. Crystallographic data for **5**: $C_{24}H_{26}O_2Cl_2SiZr$, Fw = 536.68, monoclinic, space group $P2_1/a$ (# 14), a = 11.975(3) Å, b = 16.580(4) Å, c = 12.278(2) Å, β = 99.69(2)°, V = 2403.0(9) Å^3, Z = 4, D_{calc} = 1.483 g cm^{-3}, R = 0.052, Rw = 0.049 for 2394 reflections with $I > 3\sigma(I)$. Crystallographic data for **8**: $C_{28}H_{32}Cl_2SiZr$, Fw = 558.77, monoclinic, space group $P2_1/a$ (# 14), a = 15.03(2) Å, b = 9.359(5) Å, c = 18.803(5) Å, β = 99.59(6)°, V = 2607(3) Å^3, Z = 4, D_{calc} = 1.423 g cm^{-3}, R = 0.044, Rw = 0.038 for 3070 reflections with $I > 3\sigma(I)$