Efficient Preparation of Racemic Isomers of *ansa*-Zirconocene Complexes with a Vinyl Substituted Silylene Bridge

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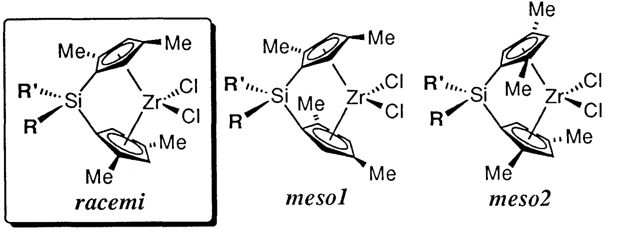
The reaction of dilithiated silylene-bridged Cp-ligands, whose silylene had one or two vinyl substituents, with $ZrCl_4$ gave *racemo*-rich mixtures of the complex $RR'Si(C_5H_2\text{-}2,4\text{-}Me_2)_2ZrCl_2$ (**1**: R = vinyl, R' = Me, *rac*/*meso* = 77/23, **4**: R = R' = vinyl, *rac*/*meso* = 77/23). The pure racemic complex **1-*rac*** was isolated after several recrystallization processes in a satisfactory yield (31%, *rac*/*meso* >99/1) and was structurally characterized. Polymerization of propylene with **1-*rac***/MAO gave highly isotactic polypropylene.

Since the discovery of the stereoregular α-olefin polymerization catalysts which consist of group 4 metallocenes,[1] various types of *ansa*-metallocene complexes have been reported.[2] In particular, C_2-symmetric *ansa*-zirconocene complexes have attracted interest as precursors of isospecific polymerization catalysts for propylene. Unfortunately synthetic reactions of these complexes usually give initially an almost 1:1 mixture of *racemo*- and *meso*-isomers, which require subsequent tedious separation procedures to obtain pure *rac*-isomers (C_2-symmetric) often in very low yields. In order to minimize this problem, some reaction systems have been developed which produce *racemo*-rich mixtures.[3] Their strategies have been the utilization of (i) direct interactions between two Cp rings by introducing bulky substituents on them,[4] (ii) steric repulsion between Cp-substituents and the metal-bound amide which later is converted to chloride,[5] (iii) chirality of the bridging moiety,[6] (iv) a double bridge.[7] These methodologies, however, require complicated synthetic procedures and/or the resulting metallocenes are often not active or isospecific enough for propylene polymerization. We became interested if steric interaction between a substituent on the silylene bridge and that on Cp rings could enhance the *racemo*-selectivity. An example related to this line has been reported by Rausch et al. on the synthesis of *rac*-bis(indenyl)zirconium dichloride with a bulky spiro-germylene bridge.[8]

As a parent *ansa*-zirconocene dichloride to be modified, we herein chose previously reported $Me_2Si(C_5H_2\text{-}2,4\text{-}Me_2)ZrCl_2$ (**6**).[9] The preparative reaction of **6** has been known to give a ca. 1:1 mixture of *rac*/*meso* isomers, and a *racemo*-rich fraction (*rac*/*meso* = 94/6) was obtained only in 3% yield after repeated recrystallization. Selective synthesis of *rac*-isomers in *ansa*-zirconocene complexes bearing only smallest alkyl substituents such as methyl groups on their Cp-rings appeared challenging.

Substitution of the methyl groups on the silicon in **6** for vinyl groups was conveniently attained by simply using commercially available $SiCl_2Me(CH{=}CH_2)$ or $SiCl_2(CH{=}CH_2)_2$ in place of $SiCl_2Me_2$ as a starting material. A typical procedure for the final step, i.e. the zirconocene complex forming reaction was as follows. To a solution of methylvinylbis(2,4-dimethylcyclopentadien-1-yl)silane (4.88 g, 19 mmol) in dimethoxyethane (DME) was added *n*-butyllithium (1.69 M hexane solution, 38 mmol) dropwise at -78 °C. The mixture was stirred at r.t. for 24h. This mixture was added dropwise to a DME solution of zirconium tetrachloride (4.4 g, 19 mmol) at r.t. and then heated at 70 °C for 40h. The solvent was removed in vacuo, and the residue was dissolved in toluene. Filtration to remove Li salts and cooling the filtrate at -30 °C gave the first crystals of $Me(CH_2{=}CH)Si(C_5H_2\text{-}2,4\text{-}Me_2)_2ZrCl_2$ (**1**). More crops of crystals were obtained from the mother liquid. Combined crystals were repeatedly (5-6 times) recrystallized from hexane yielding finally a total of 2.46 g (31% yield) of the pure *rac*-isomer (**1-*rac***).[10]

It should be emphasized that *racemo*-isomer was formed in preference to *meso*- in the synthetic reaction of **1** and **4** (Table 1). In addition, we found that **1-*rac*** readily crystallize: the first crop of recrystallization already has 94% *racemo*-purity and the yield was also satisfactory (19%). As a result, **1-*rac*** was efficiently prepared in a pure form.



racemi *meso1* *meso2*

Crystal structure of **1-*rac*** is shown in Figure 1.[11] It is noteworthy that one Cp ring (C8-C12) is twisted at the Si-C8 bond by 5.7° from the normal position perpendicular to the C1-Si-C8 plane. This may be the result of steric repulsion between the α-methyl group (C13) and the vinyl group on the silicon bridge. Actually, the distance of H13c-H16 is 2.2(1) Å while H6a-H15b is 2.6(1) Å. Most of other structural features are similar to those observed in other *ansa*-2,4-dialkylcyclopentadienyl zirconocenes.[4b,12]

Hoping to get insight into the steric effect which might control the *rac*/*meso* ratio, we prepared several analogs of **1**, $RR'Si(C_5H_2\text{-}2,4\text{-}Me_2)_2ZrCl_2$, and examined by NMR the crude reaction mixtures right after the final reaction step (Table 1). Besides **1** and **4** (R = vinyl), the formation of **2** and **5** (R = Et)

Table 1. The formation ratio of *rac*- and *meso*-isomers

product	R	R'	*rac* : *meso1* : *meso2*[a] (*rac* : *meso*)			yield[b] /%
1	vinyl	Me	77	15	8	44[c]
2	Et	Me	65	25	10	67[d]
3	*i*-Pr	Me	48	44	8	84[d]
4	vinyl	vinyl	77	23		50[c]
5	Et	Et	62	38		54[d]
6[e]	Me	Me	57	43		30[c]

[a]Determined by ^1H NMR of the reaction mixtures. [b]Combined yield of all the isomers. [c]Isolated yield. [d]Determined by ^1H NMR. [e]Cited from ref. 9.

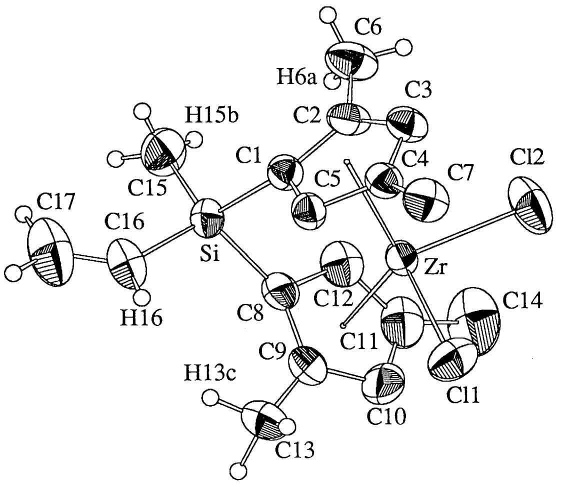


Figure 1. Crystal structure of **1-*rac***.
Selected bond lengths (Å) and angles (deg): Zr–Cl1 = 2.434(2), Zr–Cl2 = 2.431(2), Zr–Cp1(c) = 2.214, Zr–Cp2(c) = 2.208, Si–C1 = 1.876(5), Si–C8 = 1.866(5), Si–C15 = 1.844(7), Si–C16 = 1.861(7), C16–C17 = 1.291(10); Cl1–Zr–Cl2 = 99.5(1), Cp1(c)–Zr–Cp2(c) = 126.6, C1–Si–C8 = 94.0(2), C15–Si–C16 = 111.0(3), Si–C16–C17 = 122.6(7), ∠Cp1–Cp2 = 60.8. (Cp1: C1-C5, Cp2: C8-C12, Cp(c): Cp centroids) Hydrogens are omitted in part for clarity.

was also *rac*-selective in spite of low selectivity. These results imply that the steric repulsion between the backside substituents on Si and the α-methyl groups on the Cp rings may cause the predominant formation of *rac*-isomers.[12] Isopropyl groups, however, appeared to be so bulky that even the formation of the *rac*-isomer would be suppressed and that the less crowded *meso1*-isomer was favored. The synthesis of $Me(CH_2{=}CH)Si(C_5H\text{-}2,3,5\text{-}Me_3)_2ZrCl_2$, in which both α-positions of the Cp rings are occupied by a methyl group and hence sterically even, ended up low *rac*/*meso* ratio (*rac*:*meso1*:*meso2* in 59:25:16), indicating the lack of the advantage of the steric effect of α-methyl groups. Contribution of an additional factor, i.e. coordination of the vinyl group to Zr during the stereo-determining step of **1** and **4**, cannot be ruled out.

As is obvious from the crystal structure, **1-*rac*** is pseudo-C_2-symmetric with respect to the coordination sphere of the Zr center. In fact, polymerization of propylene using **1-*rac*** (*racemi*- >99%) with MAO as the catalyst gave highly isotactic polypropylene ([mmmm] = 98.0%, M_w = 169,000; M_w/M_n = 2.61), and the catalytic activity was 16.0 ton-PP/mol-Zr•h. To our surprise, the catalytic activity of **1-*rac*** was higher than that of the Me_2Si- bridged complex **6-*rac*** (*rac*/*meso* = 96/4; 6.28 ton-PP/mol-Zr•h, M_w = 155,000, M_w/M_n = 2.81).[13]

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10 A combined yield of *rac*- and *meso*-isomers of **1** was 44%. **1-*rac***: ^1H NMR (C_6D_6, Me_4Si): δ 0.29 (s, 3H), 1.82 (s, 3H), 1.87 (s, 3H), 2.24 (s, 3H), 2.26 (s, 3H), 5.02 (d, *J* = 2 Hz, 1H), 5.16 (d, *J* = 2 Hz, 1H), 5.87 (dd, *J* = 21, 3 Hz, 1H), 5.96 (dd, *J* = 16, 3 Hz, 1H), 6.24 (dd, *J* = 21, 16 Hz, 1H), 6.32 (d, *J* = 2 Hz, 1H), 6.36 (d, *J* = 2 Hz, 1H). ^{13}C NMR (C_6D_6): δ -3.38, 15.71, 15.82, 16.88, 16.99, 101.59, 102.77, 112.91, 113.07, 128.20, 128.95, 129.26, 130.32, 133.73, 135.98, 137.31, 138.30. Calcd. for $C_{17}H_{22}Cl_2SiZr$, C: 49.02, H: 5.32, Cl: 17.02; found C: 49.00, H: 5.39, Cl: 17.00. **1-*meso1***: ^1H NMR (C_6D_6, Me_4Si): δ 0.25 (s, 3H), 2.01 (s, 6H), 2.15 (s, 6H), 5.05 (d, *J* = 2 Hz, 2H), 5.87 (dd, *J* = 19, 3 Hz, 1H), 6.02 (dd, *J* = 15, 3 Hz, 1H), 6.07 (d, *J* = 2 Hz, 2H), 6.17 (dd, *J* = 19, 15 Hz, 1H). **1-*meso2***: ^1H NMR (C_6D_6, Me_4Si): δ 0.31 (s, 3H), 2.05 (s, 6H), 2.18 (s, 6H), 4.83 (d, *J* = 2 Hz, 2H), 5.86 (dd, *J* = 20, 3 Hz, 1H), 5.99 (dd, *J* = 15, 3 Hz, 1H), 6.13 (d, *J* = 2 Hz, 2H), 6.41 (dd, *J* = 20, 15 Hz, 1H). *meso*-Isomers were identified judging from NOE observed between MeSi- and α-Me groups on the Cp rings (3% in *meso1*-isomer).

11 To the best of our knowledge, this is the first X-ray analysis of an *ansa*-metallocene bearing 2,4-dimethylated Cp rings. Crystal data: $C_{17}H_{22}Cl_2SiZr$, FW = 416.57, triclinic, space group = $P\bar{1}$, a = 8.701(2), b = 8.990(2), c = 12.401(2) Å, α = 87.23(1), β = 88.25(2), γ = 70.30(2) °, V = 912.2(3) Å^3, Z = 2, D_{calc} = 1.516 g/cm^3, R = 0.0499, R_w = 0.0540 (w = 1). Data were collected on Enraf-Nonius CAD4 diffractometer at 295 K with a graphite monochromater using Mo $K\alpha$ radiation. A total of 4429 reflections was measured in the ω scan mode ($4° \le 2\theta \le 55°$). The structure was solved by direct method using MULTAN. The final cycle of least-squares refinement was based on 3192 observed reflections ($F_o \ge 3\sigma(F_o)$) with 279 variable parameters.

12 The steric repulsion between the Si-bridge and the α-methyl groups in *ansa*-zirconocenes was previously proposed. P. Burger, K. Hortmann, J. Diebold, and H.-H. Brintzinger, *J. Organomet. Chem.*, **417**, 9 (1991).

13 The polymerization reactions using **1-*rac*** and **6-*rac*** were carried out in the same conditions. At 25 °C for 1h under 3 atm of propylene; in a 100 cm^3 autoclave, 0.2 μmol of zirconocenes and MAO (2.0 mmol of Al) was dissolved in toluene (30 cm^3).