

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 $\text{RR}'\text{Si}(\text{C}_5\text{H}_2-2,4\text{-Me}_2)_2\text{ZrCl}_2$ (**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.

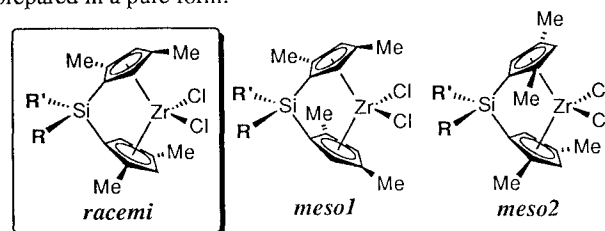
Since the discovery of the stereoregular α -olefin polymerization catalysts which consist of group 4 metallocenes,¹ various types of *ansa*-metallocene complexes have been reported.² In particular, C_2 -symmetric *ansa*-zirconocene complexes have attracted interest as precursors of isospecific polymerization 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 $\text{Me}_2\text{Si}(\text{C}_5\text{H}_2-2,4\text{-Me}_2)_2\text{ZrCl}_2$ (**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 $\text{SiCl}_2\text{Me}(\text{CH}=\text{CH}_2)$ or $\text{SiCl}_2(\text{CH}=\text{CH}_2)_2$ 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 $\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\text{C}_5\text{H}_2-2,4\text{-Me}_2)_2\text{ZrCl}_2$ (**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.



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**, $\text{RR}'\text{Si}(\text{C}_5\text{H}_2-2,4\text{-Me}_2)_2\text{ZrCl}_2$, 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'	<i>rac</i> : <i>meso1</i> : <i>meso2</i> ^a (<i>rac</i> : <i>meso</i>)			yield ^b /%
1	vinyl	Me	77	15	8	44 ^c
2	Et	Me	65	25	10	67 ^d
3	<i>i</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

^aDetermined by ^1H NMR of the reaction mixtures. ^bCombined yield of all the isomers. ^cIsolated yield. ^dDetermined by ^1H NMR. ^eCited from ref. 9.

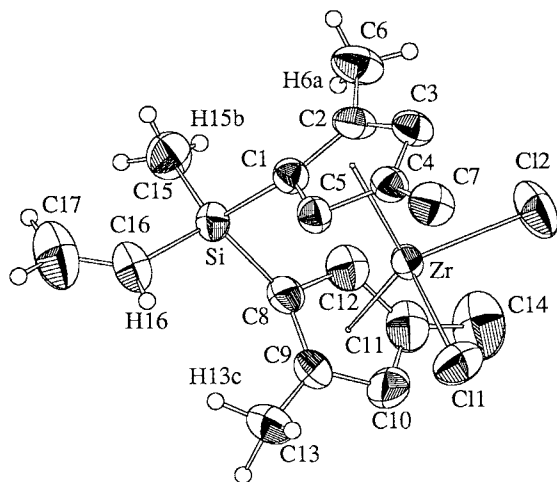


Figure 1. Crystal structure of **1-rac**.

Selected bond lengths (Å) and angles (deg): Zr–C11 = 2.434(2), Zr–C12 = 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); C11–Zr–C12 = 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), \angle 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 *meso*-isomer was favored. The synthesis of $\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\text{C}_5\text{H}_2-2,3,5\text{-Me}_3)_2\text{ZrCl}_2$, 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*:*meso*:*meso*2 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 (C₆D₆, Me₄Si): 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). ¹³C NMR (C₆D₆): 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 C₁₇H₂₂Cl₂ZrSi: C: 49.02, H: 5.32, Cl: 17.02; found C: 49.00, H: 5.39, Cl: 17.00. **1-meso**: ¹H NMR (C₆D₆, Me₄Si): 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-meso**2: ¹H NMR (C₆D₆, Me₄Si): 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 *meso*-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: C₁₇H₂₂Cl₂ZrSi, 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) Å³, Z = 2, D_{calc} = 1.516 g/cm³, R = 0.0499, R_w = 0.0540 (w = 1). Data were collected on Enraf-Nonius CAD4 diffractometer at 295 K with a graphite monochromator using Mo $K\alpha$ radiation. A total of 4429 reflections was measured in the ω scan mode ($4^\circ \leq 2\theta \leq 55^\circ$). The structure was solved by direct method using MULTAN. The final cycle of least-squares refinement was based on 3192 observed reflections ($F_o \geq 3\sigma(F_o)$) with 279 variable parameters.
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- 13 The polymerization reactions using **1-rac** and **6-rac** were carried out in the same conditions. At 25 °C for 1 h under 3 atm of propylene; in a 100 cm³ autoclave, 0.2 μ mol of zirconocenes and MAO (2.0 mmol of Al) was dissolved in toluene (30 cm³).