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Ethylene-bridged *ansa*-zirconocene dichlorides for syndiospecific propene polymerization

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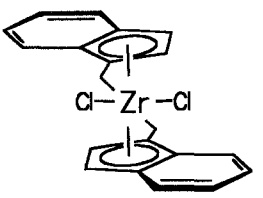
Summary

Three ethylene-bridged unsymmetric zirconocene dichlorides bearing a cyclopentadienyl unit together with either a tetraphenylcyclopentadienyl- (**8**), a 7,9-diphenylcyclopent[a]-acenaphtha-dienyl- (**9**) or a fluorenyl group (**10**) were used for propene polymerization after activation with methylalumoxane (MAO) at 30, 50, 70 and 80°C. Whereas **8** is inactive at all, **9** produces atactic polypropene waxes with high activity. The polypropene products of **10** are syndiotactic with stereoregularities depending on the polymerization temperature as well as on monomer and on MAO concentration.

Introduction

The discovery of chiral *ansa*-zirconocene dichlorides as a new generation of homogeneous catalysts for stereoselective propene polymerization has stimulated intensive research activities in academia as well as in industry. For the production of isotactic polypropene the C_2-symmetric ethylene-bridged bisindenyl zirconocene dichloride **1**, first prepared by Brintzinger et. al., can be regarded as a key structure[1].



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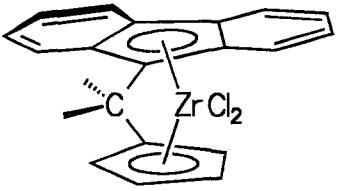

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A practicable synthetic route to syndiotactic polypropene was first opened by Ewen et. al. by the preparation of the C_S-symmetric zirconocene **2**[2].

We have established a construction kit, based on chiral epoxides, for the synthesis of ethylene bridged *ansa*-metallocene dichlorides bearing two different cyclopentadienyl fragments and a stereogenic carbon center in the bridge[3]. The intention of the present work was to use our synthetic approach for the preparation of unsymmetric ethylene bridged zirconocene dichloride complexes and to study the influence of symmetry variations on the properties of the catalysts and the microstructure of polypropene products.

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Experimental

All preparative reactions were carried out under an atmosphere of dry argon using standard Schlenk tube techniques. The hydrocarbon and ether solvents were purified by destillation from $LiAlH_4$. CH_2Cl_2 was distilled from CaH_2. NaCp(dioxane)[4], **4**,**5**,**6**,**7a**,**c**[3a,c], **8**,**10**[3a] and 7,9-Diphenylcyclopent[a]acenaphthadiene[5] were prepared by literature procedures. The polymerization experiments were carried out as described before[3b].

2-(7,9-Diphenylcyclopent[a]acenaphthadienyl)-2-phenylethanol (4b): A solution of 7,9-Diphenylcyclopent[a]acenaphthadiene (14.0 g, 41 mmol) in 200 ml of diethyl ether was first treated with *n*-butyllithium in hexane (1.6 M, 25.6 ml, 41 mmol) at 0°C and subsequently with a solution of epoxystyrene (5.4 ml, 45 mmol) in 50 ml of diethyl ether. The suspension was stirred overnight and then neutralized with 200 ml of a saturated aqueous solution of NH_4Cl. The organic layer was separated and the water phase washed twice with diethyl ether. The combined and dried (Na_2SO_4) organic phases were concentrated in vacuo. The crude orange to yellow product was purified by column chromatography over silica (eluent: toluene) (16.9 g, 37 mmol, 89.0%), mp.: 169°C. ^1H NMR ($CDCl_3$): δ 3.42 (ddd, J = 3.13, 7.85 Hz, 1H, CH_{bridge}), 3.67 - 3.80 (m, 2H, $CH_{2,bridge}$), 5.19 (d, J = 3.14 Hz, 1H, CH_{cp}), 6.57 - 7.97 (m, 21H, arom. H) ppm. FDMS: 462 (M^+), 444 (M^+ - H_2O). Anal. Calcd for $C_{35}H_{26}O$: C, 90.88; H, 5.67. Found: C, 91.53; H, 5.91.

[2-(7,9-Diphenylcyclopent[a]acenaphthadienyl)-2-phenylethyl] Methanesulfonate (5b): A solution of **4b** (9.7 g, 21 mmol) and triethyl amine (3.2 ml, 23 mmol) in 100 ml CH_2Cl_2 was treated dropwise with methanesulfonyl chloride (1.8 ml, 23 mmol) in 20 ml CH_2Cl_2 at 0°C. The reaction mixture was stirred overnight at ambient temperature and then extracted three times with water. The CH_2Cl_2 layer was dried (Na_2SO_4) and the solvent destilled off, leaving crude **5b** as yellow oil. Crystallization of the yellow product was performed by stirring a suspension of the oil in ethanol overnight. Yellow **5b** was isolated by filtration (10.4 g, 19 mmol, 92%), mp.: 164°C (decomp.). ^1H NMR ($CDCl_3$): δ 2.64 (s, 3H, CH_3), 3.62 (ddd, J = 3.06, 7.6 Hz, 1H, CH_{bridge}), 4.23 (dd, J = 2.12, 7.8 Hz, 1H, $CH_{2,bridge}$), 4.33 (dd, J = 2.09, 7.9 Hz, 1H, $CH_{2,bridge}$), 5.14 (d, J = 3.07 Hz, 1H, CH_{cp}), 6.6 - 7.8 (m, 21H, arom. H) ppm. FDMS: 540 (M^+). Anal. Calcd. for $C_{36}H_{28}O_3S$: C, 79.97; H, 5.22, S 5.93. Found: C, 79.36; H, 5.17; S 5.97.

Spiro[(2-phenylcyclopropane)-1,1′-(7,9-diphenylcyclopent[a]acenaphthadiene)] (6b): To a suspension of diisopropyl amine (2.9 ml, 20 mmol) and *n*-butyllithium (1.6 M, 12.7 ml, 20 mmol) in 125 ml diethyl ether at 0°C **5b** (10.5 g, 19 mmol) was added. After stirring overnight at ambient temperature the solution was neutralized by the addition of a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with diethyl ether (6 x 100 ml). The organic phase was dried (Na_2SO_4) and concentrated in vacuo. **6b** was crystallized from toluene (5.24 g, 12 mmol, 61%). mp.: 184°C. ^1H NMR ($CDCl_3$): δ 2.29 (dd, J = 5.6, 9.1 Hz, 1H, CH), 2.69 (dd, J = 5.65, 8.46 Hz, 1H, CH_2), 2.94 (dd, J = 8.77 Hz, 1H, CH_2), 6.66 - 7.56 (m, 21H, arom. H) ppm. FDMS: 444 (M^+). Anal. Calcd. $C_{35}H_{24}$: C, 94.56; H, 5.44. Found: C, 94.70; H, 5.36.

[1-Cyclopentadienyl-2-(7,9-diphenylcyclopent[a]acenaphthadienyl)-1-phenyl]ethane (7b): **6b** (5.2 g, 11.7 mmol) was dissolved in DMF (100 ml) and treated with NaCp(dioxane) (3.5 g, 20 mmol) at 0°C. The red solution was stirred at room temperature overnight and then heated for 2h at 80°C. DMF was evaporated off in vaccuo. The dark oily residue was suspended in diethyl ether (200 ml). A saturated aqueous solution of NH_4Cl was added (200 ml). The ether phase was separated and the water layer was

washed with diethyl ether (3 x 200 ml). The combined organic phases were dried (Na_2SO_4) and the solvent was destilled off. The dark solid residue was purified by column chromatography (eluent: toluene) leaving **7b** as pale yellow glassy solid (2.8 g, 5.4 mmol, 46%). Due to double bond tautomerism of the Cp-unit the ligand was characterized by means of NMR spectroscopy in form of its Zr(IV)-complex. FD-MS: 510 (M^+). Anal. Calcd. $C_{40}H_{30}$: C, 94.08; H, 5.92. Found: C, 95.03; H, 4.14.

{[1-η^5-Cyclopentadienyl-2-(η^5-7,9-diphenylcyclopent[a]acenaphthadienyl)-2-phenyl]-ethane}zirconium Dichloride (9): **7b** (3.6 g, 7.0 mmol) was dissolved in diethyl ether (75 ml) and treated dropwise with *n*-butyllithium (1.6 M, 8.8 ml, 14.0 mmol) at 0°C. The solvent was removed in vaccuo and the dilithio salt was dissolved in THF (100 ml). $ZrCl_4(THF)_2$ (1.8 g, 7.7 mmol) was added and the mixture was heated under reflux for 4h. An orange suspension formed which was filtered over a 1-inch pad of Celite. The solvent was removed in vaccuo and the solid residue was extracted with hot toluene. To the clear toluene solution hexane was added and the solid impurities which formed were filtered off over Celite. From the bright yellow solution **9** (0.89 g, 1.3 mmol, 18.8%) crystallized as microcrystalline yellow solid at -30°C. ^1H NMR ($CDCl_3$): δ 3.71 (dd, J = 13.25, 14.55 Hz, 1H, CH_{bridge}), 3.87 (dd, J = 5.54, 14.62 Hz, 1H, $CH_{2,bridge}$), 4.3 (dd, J = 5.43, 13.2 Hz, 1H, $CH_{2,bridge}$), 5.8 (dd, J = 2.67, 5.3 Hz, 1H, CH_{cp}), 5.87 (dd, J = 2.5, 5.06 Hz, 1H, CH_{cp}), 6.49 (dd, J = 3.06, 5.47 Hz, 1H, CH_{cp}), 6.91 - 8.07 (m, 22H, arom. H) ppm. FAB-MS: 670 [M^+], 635 [M^+-Cl]; Anal. Calcd. $C_{40}H_{28}Cl_2Zr$: C, 71.62; H, 4.21. Found: C, 70.89; H, 4.53.

Synthesis of *ansa*-zirconocene dichlorides with different cyclopentadienyl fragments

In a series of papers[3] we have demonstrated that chiral epoxides like **3** can be converted to a variety of the ligand precursor compounds **7** (Fig. 1). Treatment of the dilithio salts of **7a,b,c** with $ZrCl_4$ affords the formation of the zirconocene dichlorides **8 - 10** (Fig. 2). Crystals, suitable for an X-ray structure analyses could be obtained from **8**[3a]. The results confirm the structure which is depicted below.

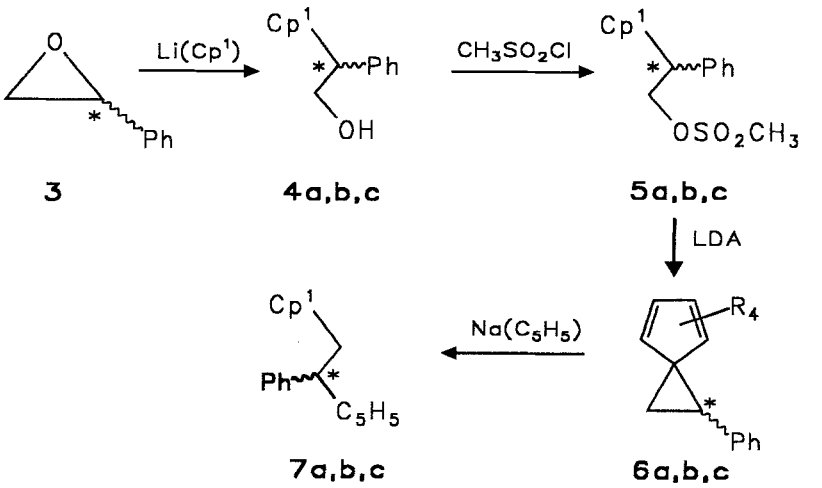

Figure 1. Ligand formation (Cp^1: a: Tetraphenylcyclopentadienyl; b: 7,9-Diphenylcyclopent[a]acenaphthadienyl; c: Fluorenyl).

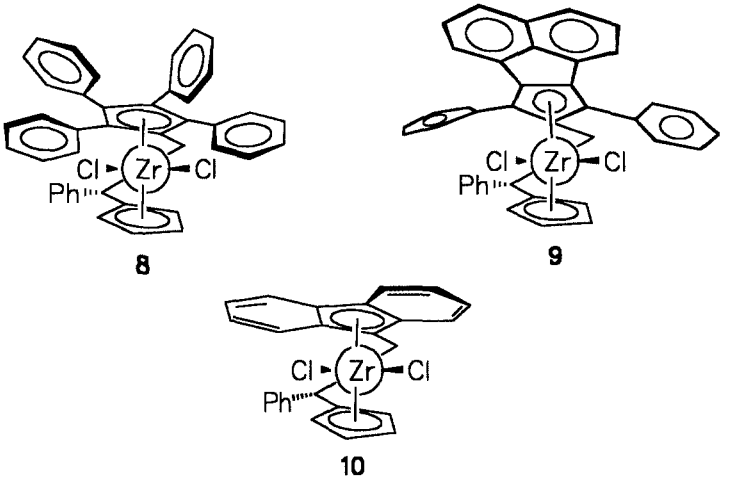

Figure 2. Three unsymmetric complexes prepared from epoxystyrene.

Propene polymerization: Temperature dependence of the activity

Propene polymerization was performed using the complexes **8** - **10** at polymerization temperatures (T_p) of 30, 50, 70 and 80°C and constant monomer concentration (0.71 mol/l) after activation with methylalumoxane (MAO, Al/Zr=2000, Tab. 1).

Table 1. Polymerization results at different temperatures.

Cat.	T_p, °C	[Zr], 10^{-5} mol/l	Yield, g	Activity[a]	[rrrr], %	M_W, 10^3 g/mol	M_W/M_N
8	70	7.0	0	0	---	---	---
	80	7.0	2.8	60	atactic	0.6	---
9	30	1.7	11.2	1150	atactic	31.0	1.8
	50	3.3	18.8	1440	atactic	26.0	1.7
	70	1.7	12.2	5320	atactic	n.d.[b]	---
	80	1.7	8.2	11100	atactic	n.d.	---
10	30	0.8	7.9	3320	67.5	50.0	1.8
	50	0.8	9.1	4380	36.7	28.0	1.9
	70	0.8	9.8	12300	31.7	16.7	2.2
	80	0.8	11.2	14200	20.3	8.3	2.0

[a] Activity in 10^3g pp([mol C_3][mol Zr]·h)$^{-1}$; [b] n.d.: not determined.

Variable temperature NMR experiments, performed on **8**, have demonstrated that the phenyl-Cp substituents rotate almost unhindered above 0°C[3a]. Thus the phenyl groups block the Cl-Zr-Cl-plane. **8** shows no polymerization activity at low temperatures. At 80°C a small fraction of regio- and stereoirregular propene oligomers could be isolated. The hypothesis of blocked polymerization sites is supported by complex **9** which bears a 7,9-

diphenylcyclopent[a]acenaphthadienyl (Ace) fragment and hence resembles the structure of **8** with two annellated phenyl groups. In **9** the inner phenyl substituents should not hinder chain growth. Indeed, polymerization experiments show an essential activity increase for **9**. However, the highest polymerization activity was found for complex **10**. Surprisingly **9** produces only atactic polypropene oils and waxes. We attribute this behaviour to the steric influence of the bulky Ace group which hinders an effective orientation of the incoming propene monomer[6]. The use of **10** results in the formation of syndiotactic polypropene at lower polymerization temperatures. The stereoselectivity of this catalyst resembles that of the C_S-symmetric iPr[CpFlu]$ZrCl_2$[6a,7].

Influence of monomer concentration on the stereoselectivity

Complexes **9** and **10** were used for polymerization experiments at constant temperature (T_p=50°C) and variable monomer concentration (Tab. 2).

Table 2. Polymerization results at variable monomer concentrations.

Cat.	T_p, °C	$[C_3]^a$, mol/l	[Zr], 10^{-6} mol/l	Yield, g	Activity^b	[rrrr], %	M_W, 10^3 g/mol	M_W/M_N
9	50	0.71	3.3	18.8	1440	atactic	26	1.7
		1.16	5	5.3	1720	atactic	31	1.7
		1.76	10	11.0	3650	atactic	46	1.9
		3.38	5	17.2	5700	atactic	74	1.8
10	50	0.71	8	9.1	4380	36.7	28	1.9
		1.16	8	7.0	5340	43.1	48	1.6
		1.76	8	14.3	6520	46.7	79	2.1
		3.38	8	36.3	7290	53.5	110	1.8
	30	5.4	5	28.1	6380	78.1	160	2.0

^{a} $[C_3]$: propene concentration; ^{b} Activity in 10^3g pp([mol C_3][mol Zr]·h)$^{-1}$.

The syndiotacticity (rrrr) of the products of **10** increases with monomer concentration. The pentad distribution of the polymers prepared at 50°C show a decrease of the rmrr pentad by raising the propene pressure (Tab. 3). A similar result was observed for iPr[CpFlu]$ZrCl_2$[6a,8]. Since this pentad is characteristic for chain migration without insertion ("skipped insertions") it reflects a reduced probability of skipped insertions at increased monomer concentrations. The rmmr pentad can be regarded as a characteristic probe for the particular stereoselectivity of a given catalyst structure[6a]. This pentad shows only a slight change with monomer concentration, as expected (Tab. 3). The polymers of **10** with [rrrr] = 53.5 and 78.1% have elastomeric properties.

Table 3. Pentad distributions (%) of polymer samples obtained with **10**/MAO at different monomer concentrations (T_p=50°C).

$[C_3]^a$	mmmm	mmmr	rmmr	mmrr	rmrr	mrmr	rrrr	mrrr	mrrm
0.71	2.1	3.8	3.8	9.2	14.7	4.8	36.7	17.5	7.4
1.16	1.6	3.2	3.7	8.8	12.7	4.2	43.1	15.7	7.0
1.76	1.5	3.1	3.4	8.5	11.3	3.8	46.7	15.4	6.3
3.38	0.8	2.9	3.1	7.7	10.7	2.2	53.5	13.3	5.8

[a] $[C_3]$: propene concentration.

Stereoselectivity and Al/Zr-ratio

10 was used to investigate the influence of different Al/Zr-ratios on the stereoselectivity of the syndiospecific polymerization reaction, keeping T_p (30°C), the monomer concentration (0.71 mol/l) and the Zr-concentration ($2.5 \cdot 10^{-6}$ mol/l) constant. An increase of the Al/Zr-ratio from 250 to 2000 is paralleled by an increase of the rrrr-pentad content from 55.5 to 67.5%. An further increase of Al/Zr = 4000 and 8000 is only of a marginal effect on the syndiotacticity of the polymer products (Fig. 3).

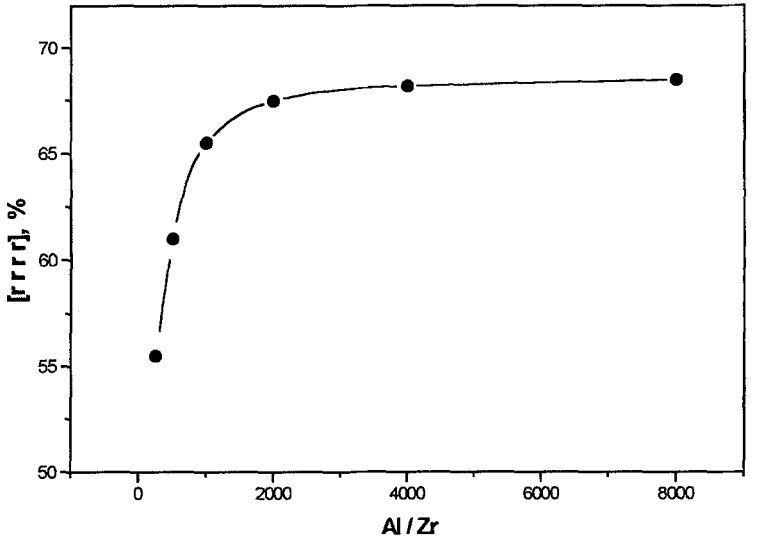

Figure 3. Syndiotacticity and Al/Zr-ratio for catalyst **10**.

An empirical explanation of this behaviour can be discussed on the bases of the coordination equilibrium between the uncoordinated cation **A** and the MAO-coordinated species **B**.

$$\underset{\mathbf{A}}{Cp_2Zr\text{-}P^{1+}} + MAO \rightleftarrows \underset{\mathbf{B}}{[Cp_2Zr\text{-}P\cdot MAO]^{1+}}$$

A is expected to be the favoured state of the zirconocenium cation at low Al/Zr-ratios (Cp_2 = Flu-Cp ligand). An increase of the Al/Zr-ratio forces the coordination equilibrium to **B**. In this case the propene monomers and MAO are in a competition for coordination which results in a reduced frequency for skipped insertions and hence in an increase of the polymer stereoregularity. Similar results were reported by Fink et. al. for iPr[CpFlu]$ZrCl_2$[8].

Table 4. Pentad distributions of polymers obtained at different Al/Zr-ratios.

Al/Zr	mmmm	mmmr	rmmr	mmrr	rmrr	mrmr	rrrr	mrrr	mrrm
250	0	5.1	5.1	10.2	12.0	1.9	55.5	5.6	4.6
500	0	3.3	5.0	9.1	11.5	0.7	61.0	5.9	3.5
1000	0	3.3	4.9	7.1	10.8	0	65.5	9.3	2.2
2000	0	2.6	4.8	7.3	10.0	0	67.5	5.7	2.1
4000	0	2.9	4.8	7.1	9.3	0	68.5	5.3	2.1
8000	0	2.9	4.8	6.8	8.7	0	68.2	5.3	2.1

A ^{13}C-NMR analysis of the products pentad distributions supports our hypothesis (Tab. 4). The rmmr-pentad is hardly touched by an increase of Al/Zr, indicating the stereoselectivity which is defined by the structure of **10**. However, the rmrr-pentad as a probe for stereoerrors arising from skipped insertions decreases rapidly with an increase of Al/Zr (Fig. 4).

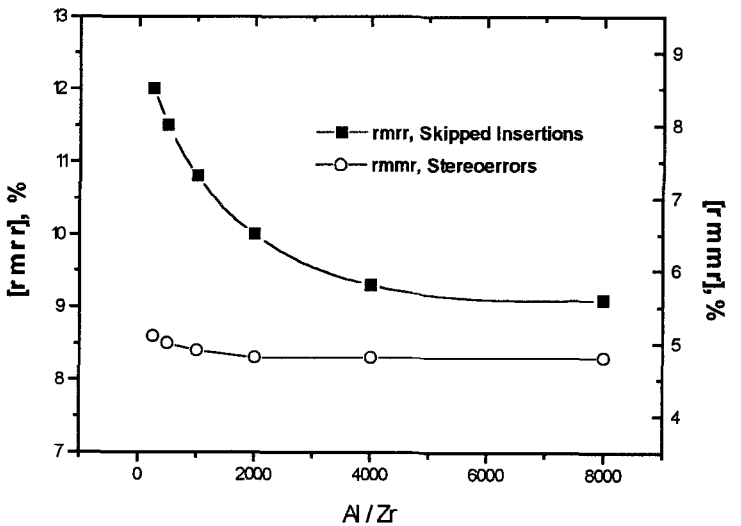

Figure 4. Characteristic pentads and Al/Zr-ratio.

Currently we are investigating the syndiotactic homopolypropene elastomers. Their mechanical properties seem to be a function of both stereoregularity and molecular weight. We hope that we can find catalyst structures which allow the introduction of controlled error sequences.

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