Synthesis of Ethylene Bridged Biscyclopentadiene Ligand Precursor Compounds and Some of their *ansa*-Zirconocene Derivatives *via* Chiral Epoxides:

A Synthetic Strategy of High Variability

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Chiral Epoxides. Fluorenyl Alcohols, Spirocyclopropanes, Biscyclopentadienes, Chiral *ansa*-Zirconocene Dichlorides

The chiral ligand precursor systems \(1-\text{Cp}^1-1^-\text{R}^1^-2^-\text{R}^2^-2^-\text{Cp}^2\)ethane 5a–d bearing two different cyclopentadienyl fragments (\(\text{Cp}^1, \text{Cp}^2 = \text{Cp}, \text{Ind}, \text{Flu}\)) and a variable bridge substitution pattern (\(\text{R}^1, \text{R}^2 = \text{H}, \text{Ph}, \text{cyclopentyl}, \text{cyclohexyl}\)) were prepared starting from the corresponding epoxides. The solid state structures of six organic intermediates are reported in order to prove the stereochemistry of the ligand forming reactions. Treatment of the dilithio salts of 5a–d with \(\text{ZrCl}_4\) in \(\text{CH}_2\text{Cl}_2\) afforded chiral *ansa*-zirconocene dichlorides (6a–d).

Introduction

In recent years chiral *ansa*-metallocene compounds have attracted considerable interest as polymerization catalysts [1] for catalytic hydrogenation [2] and metal-assisted Diels-Alder reactions [3]. These wide-spread applications make it necessary to look for a synthetic approach which allows easy tailoring of the catalyst structures. In a first report we have shown recently that epoxystyrene can serve as cheap starting material for the preparation of ethylene bridged zirconocene dichlorides [4]. We report here on the use of differently substituted epoxides in the preparation of a variety of new, stereorigid biscyclopentadiene ligand precursor systems with variable backbone substitution and some of their *ansa*-zirconocene dichloride complexes. In order to prove the stereocentric course of the ligand forming reactions the solid state structures of six significant organic intermediates are reported.

Results and Discussion

**Ligand preparation**

The epoxides (1a–c) allow the preparation of ethylene bridged biscyclopentadiene ligand precursor systems (5a–d) with two different cyclopentadienyl units according to the reaction procedures shown in Schema 1A and 1B.

In a first clean ring opening reaction the fluorenyl group is introduced leading to the corresponding alcohols 2a–c, as reported by us recently [4, 5]. From the cyclic epoxides (1a,b) the crystalline alcohols (2a,b) are formed nearly quantitatively. The X-ray structure determination of 2b shows that the fluorenyl group and the OH function are in an *trans*-arrangement, as expected (Fig. 1). The primary alcohol product 2c can be isolated after ring opening of epoxystyrene in 75% yield. For both alcohols bond lengths and angles are in the range of expectation.

Substitution of the OH function can now be accomplished according to two different routes. Reaction of 2c with trifluoromethanesulfonic anhydride gives the trifluoromethanesulfonate derivative 6. Subsequent treatment with one equivalent of indenyllithium results in the formation of the ethylene bridged biscyclopentadiene 5d by direct substitution of the leaving group [6]. The phenyl backbone substituent does not change its position over the entire reaction sequence (2c–5d).

The methanesulfonate derivatives 3a–c behave differently. Reaction with an equivalent of a strong sterically hindered base like \(\text{CpNa}\) or \(\text{LDA}\) affords the formation of the spiro-cyclopropanes 4a–c by intramolecular substitution of the leaving group in high yield. Exemplarily the solid state...
Scheme 1A:

1a: n = 1

1b: n = 2

2a, b

3a, b

4a, b

5a (Cp²; Cp, n: 1)

5b (Cp²; Ind, n: 2)

1B:

1c

2c

3c

6

4c

5c

5d

I

II

III

IV

V

VI

VII

1. [Flu]Li (1 equiv), (i-prop)₂O, 0 °C, 75–86%; II CH₅SO₂Cl (1 equiv), NET₃ (1 equiv), CH₂Cl₂, 0 °C, ~95%; III LDA (1.2 equiv), THF, ~90%; IV [Cp]Na (1.3 equiv), DMF, 80 °C, 3d, 60%; V [Ind]Li (1.3 equiv), DMF, 80 °C, 3d, 60%; VI (CF₃SO₂)₂O (1 equiv), pyridine (1 equiv), CH₂Cl₂, 0 °C, ~90%; VII [Ind]Li (1.2 equiv), dioxane, ~70%.

Fig. 1. Molecular structures of the chiral alcohols 2b and 2c in the solid state with displacement ellipsoids at the 20% probability level (only the structure of one of the independent molecules is depicted for 2b and 2c, respectively). Selected distances (pm): 2b, C13–C14: 156.4(5); C14–C19: 144.4(6). 2c, C1–C2: 139.6(9); C2–C3: 160.9(12); O1–C1: 156(8); C2–C21: 156.3(8).
structures of 4a and 4c are shown in Fig. 2. Both compounds encompass two highly constrained cyclopropyl ring systems. The cyclopentyl group in 4a is nearly planar. The two least-square planes defined by the atoms C1, C2, C3, C4 and C3, C4, C5 have a common angle of 14.5°.

The tension of the cyclopropyl rings of 4a–c together with the ability of the fluorenyl groups to stabilize a negative charge is used to introduce a second Cp or indenyl fragment. All three spiro compounds undergo a clean opening reaction of the cyclopropyl ring systems with one equivalent of CpNa or Indenyllithium in dimethylformamid (DMF) at 80 °C [7]. The reaction of the cycloalkyl substituted species 4a,b is expected to happen via nucleophilic attack of the Cp" or Ind~ groups at C1 or C2 (e.g. 4a, Fig. 2) of the spiro-compounds, since the trans ligand precursors 5a,b were isolated exclusively.

The reaction is fully regiospecific for 4c and leads in good yield to 5c were the phenyl group is located in an α-position to the incoming indenyl fragment. Both reaction paths, i.e. direct substitution (6→5d) and introduction of the indenyl group via ring opening of the spirocyclopropanes (4c→5c) allow efficient control of the backbone substitution pattern. The synthesis of the cycloalkyl-bridged systems 5a,b also benefits from the spiro-compounds, since the trans ligand precursors with two different cyclopentadienyl units can be prepared from the trans alcohols 2a,b.

The solid state structures of the sterically extremely crowded ethanes 5b and 5d are depicted in Fig. 3. The 1H NMR spectrum of 5b shows significant line broadening for the protons at C1, C2, and C16 (Fig. 3) at ambient temperature, indicating hindered rotation of the fluorenyl- and the indenyl moieties even at room temperature. At −20 °C these rotations are frozen in and two new sets of resonances appear for each of the above mentioned nuclei.
Complex formation

The biscyclopentadienes 5a–d were transformed into their dilithio salts by reaction with two equivalents of n-butyllithium in diethyl ether at 0 °C. Subsequent reaction with ZrCl$_4$ in CH$_2$Cl$_2$ at −80 °C afforded the ansa-zirconocene dichlorides 6a–d (Scheme 2). All fluorenyl containing lithio salts gave no products if the reaction was performed in THF or diethyl ether. The complexes 6b–d were isolated as a mixture of two diastereomeric compounds [8]. Separation and structural characterization of the isomers of 6d was described by us previously [6]. Efforts to separate the diastereomers of 6b and 6c remained unsuccessful.

Experimental

All reactions were carried out under dry argon by using standard Schlenk tube techniques. The hydrocarbon and ether solvents were purified by distillation over LiAlH$_4$. CH$_2$Cl$_2$ was distilled from CaH$_2$. DMF was purified by distillation of the azeotrop with toluene and water, followed by stirring for 12 h over CaO and distillation at reduced
Preparation of the methanesulfonates (3a–c)

To a solution of one of the alcohols 2a–c (75 mmol) and triethyl amine (10.4 ml, 75 mmol) in CH₂Cl₂ (150 ml) was added methanesulfonyl chloride (5.8 ml, 75 mmol) at 0 °C. After 30 min stirring at this temperature the organic phase was washed with a saturated aqueous solution of NH₄Cl (5.8 ml, 75 mmol) and triethyl amine (10.4 ml, 75 mmol) in THF over a period of 15 min. After stirring overnight at room temperature the solvents were evaporated and the dark oily residue was suspended in a saturated aqueous solution of NH₄Cl. The mixture was extracted thoroughly with diethyl ether (5 times, 100 ml each). The organic phase was dried (Na₂SO₄) and concentrated in vacuo, leaving a brown oily residue. Chromatography over silica (eluent: toluene/hexane, 2:7) gave 4a–c as colorless to pale yellow crystals.

**Compound 3a:** 23.8 g, 72.5 mmol, 97%; m.p. 100–101 °C (decomp. > 120 °C); ¹H NMR (CDCl₃): δ = 1.38–1.97 (m, 6H, cyclopentyl), 2.42 (s, 3H, O₂S–CH₃), 4.2 (d, J = 3.3 Hz, 1H, CH₃Flu), 4.4–4.5 (m, 1H, CH₂bridge), 7.2–7.8 (m, 8H, CH₂arom).

**Analysis for C₁₈H₁₆O₃S**
- Calcd C 68.64 H 5.82 S 10.05%, Found C 69.48 H 6.14 S 9.77%.

**Compound 3b:** 25.3 g, 73.9 mmol, 98%; m.p. 121–122 °C (decomp. > 130 °C); ¹H NMR (CDCl₃): δ = 0.6–1.7 (m, 7H, cyclohexyl), 2.3–2.5 (m, 2H, cyclohexyl + CH₂bridge), 3.06 (s, 3H, O₂S–CH₃), 4.33 (d, J = 2.1 Hz, 1H, CH₃Flu), 5.1–5.2 (m, 1H, CH₂bridge), 7.3–7.8 (m, 8H, CH₂arom).

**Analysis for C₁₉H₁₆O₃S**
- Calcd C 70.15 H 6.48 S 9.37%, Found C 70.49 H 7.02 S 8.98%.

**Compound 3c:** 26.0 g, 71.3 mmol, 97.7%; m.p. 93–94 °C; ¹H NMR (CDCl₃): δ = 2.76 (s, 3H, CH₃), 3.87 (m, 1H, CH₂Ph), 4.3–4.6 (m, 3H, CH₂bridge + CH₃Flu), 7.0–7.8 (m, 13H, CH₂arom).

**Analysis for C₂₁H₂₃O₃S**
- Calcd C 72.51 H 5.53 S 8.80%, Found C 72.42 H 5.54 S 8.70%.

Preparation of the spiro compounds (4a–c)

A solution of diisopropylamine (8.0 ml, 56.9 mmol) and n-butyllithium (1.6 M, 35.6 ml, 56.9 mmol) in 150 ml THF at 0 °C was treated with a solution of one of the methanesulfonates 3a–c (54.9 mmol) in 100 ml THF over a period of 15 min. After stirring overnight at room temperature the solvents were evaporated and the dark oily residue was suspended in a saturated aqueous solution of NH₄Cl. The mixture was extracted thoroughly with diethyl ether (5 times, 100 ml each). The organic phase was dried (Na₂SO₄) and concentrated in vacuo, leaving a brown oily residue. Chromatography over silica (eluent: toluene/hexane, 2:7) gave 4a–c as colorless to pale yellow crystals.

**Compound 4a:** 11.8 g, 50.8 mmol, 92.5%; m.p. 86–87 °C; ¹H NMR (CDCl₃): δ = 1.78–2.02 (m, 6H, cyclopentyl), 2.15–2.16 (m, 2H, CH₂cyclopropyl), 6.7–7.8 (m, 8H, CH₂arom).

**Analysis for C₁₃H₁₈**
- Calcd C 93.06 H 6.94%, Found C 93.08 H 7.02%.

**Compound 4b:** 12.0 g, 48.7 mmol, 89.7%; m.p. 933–94 °C; ¹H NMR (CDCl₃): δ = 0.84–1.87 (m, 10H, cyclohexyl), 6.69–7.85 (m, 8H, CH₂arom).

**Analysis for C₁₄H₂₄**
- Calcd C 92.63 H 7.37%, Found C 92.75 H 7.42%.

**Compound 4c:** 26.0 g, 71.3 mmol, 97.7%; m.p. 133–134 °C; ¹H NMR (CDCl₃): δ = 2.22 (d, J = 8.4 Hz, 2H, CH₂), 3.38 (s, J = 8.4 Hz, 1H, CH₂Ph), 6.1–7.7 (m, 13H, CH₂arom).

**Analysis for C₂₁H₂₈**
- Calcd C 93.99 H 6.01%, Found C 93.91 H 6.17%.

trans-/[1-Cyclopentadienyl-2-(9-fluorenyl)]-cyclopentane (5a)

NaCp(dioxane) (10.0 g, 57 mmol) was added to a solution of 4a (10.4 g, 42.6 mmol) in DMF (200 ml) at −15 °C. The dark red mixture was heated to 80 °C and stirred at this temperature for three days. The solvent was distilled off at reduced pressure and the dark brown residue was suspended in a saturated aqueous solution of NH₄Cl (250 ml). The mixture was extracted thoroughly with diethyl ether (5 times, 100 ml each). The combined organic phases were dried (Na₂SO₄) and the solvent was distilled off leaving a dark brown oil. Column
chromatography over silica (elucent: hexane/toluene = 7:2) gave 5a (5.8 g, 19.4 mmol, 46%) as colorless oil. The $^1$H NMR spectrum of 5a provides no reasonable structural information due to double bond tautomerism of the Cp unit. The ligand was characterized by NMR after preparation of the corresponding zirconium complex. FDMS: 289 (M+, 100).

**Analysis for C$_{30}$H$_{22}$Cl$_2$Zr**
Calcd C 66.16 H 4.07%,
Found C 66.41 H 4.21%.

**trans-$$\{1-(9-$$Fluorenyl)-2-(1-Indenyl)\}/cyclohexane (5b)**

Indene (7.5 ml, 63.8 mmol) in 100 ml diethyl ether was treated with n-butyllithium (1.6 M in hexane, 39.8 ml) at 0 °C. When the addition was finished the solvent was evaporated leaving pale yellow solid indenyllithium which was cooled to −80 °C and dissolved in DMF (200 ml, precooled to −50 °C). To the solution 4b (12.1 g, 49.0 mmol) was added. The brown to yellow solution was warmed to 80 °C and stirred at this temperature for three days. The work up was performed similar to that of 5a leaving crude 5b (14.5 g) as yellow to red oil after column chromatography. Crystallization from pentane at room temperature yielded 5b (10.3 g, 28.4 mmol, 58%). $^1$H NMR (CDCl$_3$): δ = 0.67−0.75 (m, 1H, CH$_2$-cyclohexyl), 0.88−1.00 (m, 1H, CH$_2$-cyclohexyl), 1.18−1.34 (m, 3H, CH$_2$-cyclohexyl), 1.54−1.58 (m, 1H, CH$_2$-cyclohexyl), 1.74 (m, broad signals, 1H, CH$_2$-cyclohexyl), 1.9−2.3 (m, broad signals, 1H, CH$_2$-cyclohexyl), 2.5−3.0 (m, broad signals, 1H, CH$_2$-cyclohexyl), 3.2−3.3 (m, 1H, CH$_2$-cyclohexyl), 3.43 (m, broad signal, 2H, CH$_2$-indenyl), 4.0−4.5 (m, broad signal, 1H, CH$_2$-indenyl), 6.5 (s, 1H, CH$_2$-indenyl), 6.9−8.0 (m, 12H, CH$_{arom}$); FDMS: 362 (M+, 100).

**Analysis for C$_{28}$H$_{18}$Cl$_2$Zr**
Calcd C 64.35 H 4.02%,
Found C 64.72 H 4.84%.

**[1-(9-Fluorenyl)-2-(indenyl)-2-phenyl]ethane (5c)**

4c (8.0 g, 29.8 mmol) was treated with indenyllithium in a manner similar to that of 4b to yield 5c (7.0 g, 18.2 mmol, 61%) as pale yellow oil. $^1$H NMR (CDCl$_3$): δ = 2.31−2.65 (m, 2H, CH$_2$-bridge), 3.32 (m, 2H, CH$_2$-indenyl), 3.91 (m, 1H, CH$_2$-indenyl), 4.4 (m, 1H, CH$_2$-indenyl), 6.4 (m, 1H, CH$_2$-indenyl), 7.0−7.7 (m, 17H). FDMS: 384 (M+, 100).

**Analysis for C$_{36}$H$_{34}$**
Calcd C 92.77 H 7.23%,
Found C 92.54 H 7.38%.

**Preparation of the zirconocene dichlorides (6a−c)**

To a solution of one of the ligand precursors 5a−c (22 mmol) in 50 ml diethyl ether n-butyllithium (1.6 M in hexane, 27.5 ml, 44 mmol) was added at room temperature. The solvent was evaporated off and the dry dilithio salt was mixed with ZrCl$_4$ (5.12 g, 22 mmol) followed by the addition of 100 ml CH$_2$Cl$_2$ which was precooled to −80 °C. The suspension was warmed up to room temperature and stirred overnight. The mixture was passed through a 1-in. pad of Celite, washing with CH$_2$Cl$_2$. Removal of the solvent gave yellow to orange powders from which the zirconocene dichlorides 6a−c were obtained by recrystallization from toluene solution at −30 °C. The isolated molar ratio was 3:2 for the diastereomers 6b1:6b2 and 6c1:6c2, respectively [8].

**Compound 6a**: 0.8 g, 1.7 mmol, 8%; $^1$H NMR (CDCl$_3$): δ = 0.7−2.1 (m, 6H, CH$_2$-cyclohexyl), 2.4−2.6 (m, 1H, CH$_2$-bridge), 3.3−3.4 (m, 1H, CH$_2$-bridge), 6.02, 6.10, 6.28, 6.36 (m, 1H, each, CH$_{arom}$), 7.0−7.7 (m, 8H, CH$_{arom}$); FABMS: 459 (M+, 30), 424 (M$^+$−Cl, 100).

**Analysis for C$_{32}$H$_{21}$Cl$_2$Zr**
Calcd C 66.05 H 4.40%,
Found C 66.25 H 4.02%.

**Compound 6b1,2**: 1.3 g, 2.5 mmol, 11%; $^1$H NMR (CDCl$_3$): δ = 6b1,2: 0.7−2.3 (m, 10H, CH$_2$-cyclohexyl), 6.8−8.0 (m, 12H, CH$_{arom}$); 6b1: 3.84 (m, 1H, CH$_2$-bridge), 4.21 (m, 1H, CH$_2$-bridge), 6.30 (d, J = 3.5 Hz, 1H, CH$_2$-indenyl), 6.46 (d, J = 3.5 Hz, 1H, CH$_2$-indenyl); 6b2: 4.05 (m, 1H, CH$_2$-bridge), 4.50 (m, 1H, CH$_2$-bridge), 5.85 (d, J = 3.2 Hz, 1H, CH$_2$-indenyl), 6.14 (d, J = 3.2 Hz, 1H, CH$_2$-indenyl); FABMS: 523 (M$, 85), 487 (M$^+$−Cl, 70).

**Analysis for C$_{32}$H$_{21}$Cl$_2$Zr**
Calcd C 64.35 H 4.63%,
Found C 64.72 H 4.84%.

**Compound 6c1,2**: 1.0 g, 1.8 mmol, 8%; $^1$H NMR (CDCl$_3$): δ = 6c1,2: 6.8−8.0 (m, 17H, CH$_{arom}$); 6c1: 4.15−4.14 (m, 2H, CH$_2$-bridge), 5.85−5.95 (m, 1H, CH$_2$-bridge), 6.51 (d, J = 3.5 Hz, 1H, CH$_2$-indenyl), 6.60 (d, J = 3.5 Hz, 1H, CH$_2$-indenyl); 6c2: 4.35−4.30 (m, 2H, CH$_2$-bridge), 5.75−5.85 (m, 1H, CH$_2$-bridge), 6.08 (d, J = 3.2 Hz, 1H, CH$_2$-indenyl), 6.23 (d, J = 3.2 Hz, 1H, CH$_2$-indenyl); FABMS: 545 (M$, 60), 510 (M$^+$−Cl, 80).

**Analysis for C$_{36}$H$_{34}$Cl$_2$Zr**
Calcd C 66.16 H 4.07%,
Found C 66.41 H 4.21%.
X-ray structure determinations [10]

All samples were mounted on glass fibers. Graphite-monochromated Mo-Kα radiation was used. Two check reflections were monitored after every 58 intensity measurements. The structures were solved by Direct Methods (Program: SHELXTL-PC). Hydrogen atoms are placed in calculated positions (riding model) and phenyls were treated as rigid groups. All attempts to solve the structure of 2c in space group Pī failed. The final cell parameters and specific data collection parameters are summarized in Table I. The final atomic positional parameters can be found in the supplementary material.

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Table I. Crystallographic data for the compounds 2b, c, 4a, c, and 5b, d.

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[8] 6a contains two stereogenic carbon centers in the backbone. Due to the trans-substitution only the enantiomeric (R,R)- or (S,S)-combinations are possible. 6b encompasses the chirality of the complexed 1-(R,S)-indenyl fragment in addition to the two stereogenic backbone centers. For the bridge only (R,R)- or (S,S) are possible again. The two diastereomeric combinations (R)-indenyl-(R,R)-backbone and (S)-indenyl-(R,R)-backbone, as well as their enantiomeric counterparts are allowed, giving rise to two sets of NMR-resonances. The same number of NMR-signals appears for 6c,d [(R)-indenyl-(R)-backbone and (S)-indenyl-(R)-backbone plus enantiomers].


[10] Further details on the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57778, the names of the authors, and the journal citation.