Notiz / Note

A Convenient Synthesis of Enantiomerically Pure Ethylene-Bridged Metallocene Complexes Bearing Fluorenyl- and Octahydrofluorenyl Ligands[1]

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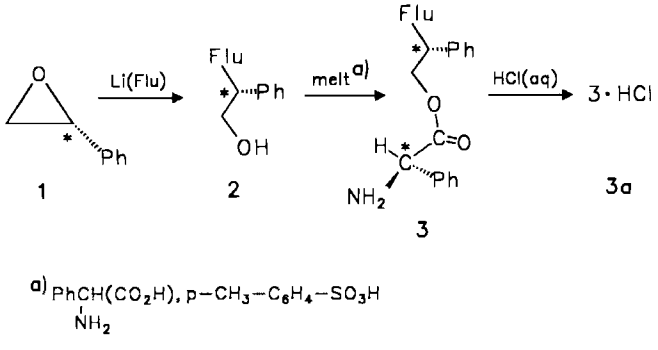
Ring opening of (*R*)-(−)-epoxystyrene (**1**) with fluorenyllithium leads to the optically active alcohol **2** in high yield. Derivatization of **2** to the trifluoromethanesulfonate **4** and subsequent reaction with one equivalent of fluorenyllithium gives the ligand precursor (1*S*)-1,2-bis(9-fluorenyl)-1-phenylethane (**5**), which is used for the synthesis of [(1*R*)-1,2-bis(η^5-9-fluorenyl)-1-phenylethane]$ZrCl_2$ (**6**).

Besides the use of racemic *ansa*-metallocene dichlorides as catalysts for olefin polymerization the enantiomerically pure complexes[2] have found application in enantioselective cyclopolymerization[3] and in the enantioselective hydrogenation of imines[4]. Most of the optically pure catalysts used for these reactions must be isolated from their racemic mixtures after diastereomeric derivatization[5]. We report here that enantiomerically pure *ansa*-metallocene dichlorides can be prepared directly from optically pure epoxides.

Results and Discussion

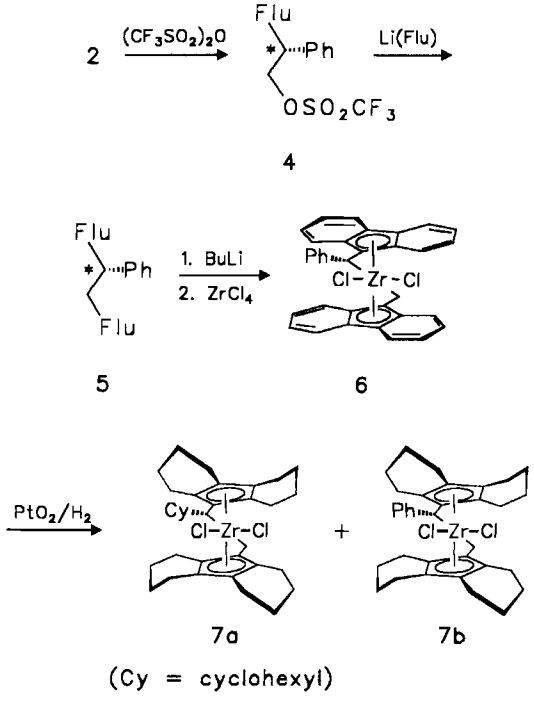
In a series of papers we have recently reported on the ring opening reaction of racemic epoxides with fluorenyllithium (Li[Flu]) as an efficient method for the preparation of ethylene-bridged *ansa*-zirconocene dichlorides[6]. If the same reaction is performed with (*R*)-(−)-epoxystyrene (**1**) the optically pure alcohol **2** is isolated (Scheme 1). In order to determine the enantiospecificity of the ring opening reaction by means of NMR spectroscopy **2** was converted into the ester **3** in a melt (≈200°C) consisting of **2**, (*R*)-α-aminophenylacetic acid and *p*-toluenesulfonic acid within a few minutes. Acidic workup afforded the crystalline hydrochloride **3a**. In the ^{1}H-NMR spectrum of **3a** only one set of resonances could be detected, indicating the presence of a single enantiomer of **2**[7]. Within the error limit of the NMR experiment the ring opening of (*R*)-(−)-epoxystyrene with fluorenyllithium is enantiospecific and results in the formation of (2*S*)-2-(9-fluorenyl)-2-phenylethanol (**2**)[8].

Scheme 1. Ring opening of (*R*)-(−)-epoxystyrene (**1**)



2 is used for the preparation of the ligand precursor compound (1*S*)-1,2-bis(9-fluorenyl)-1-phenylethane (**5**)[8,9], as depicted in Scheme 2. Derivative **5** gives, after deprotonation with two equivalents of *n*-butyllithium and subsequent reaction with $ZrCl_4$, the enantiomerically pure complex [(1*R*)-1,2-bis(9-η^5-fluorenyl)-1-phenylethane]$ZrCl_2$ (**6**)[8,10] (13% isolated yield).

Scheme 2. Preparation of the enantiomerically pure zirconocene dichloride **6** and the ethylene-bridged bis(octahydrofluorenyl)$ZrCl_2$ complexes **7**



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In some preliminary experiments we found in addition that bis-fluorenyl complexes like **6** can be catalytically hydrogenated to form their 1,2,3,4,5,6,7,8-octahydrofluorenyl derivatives (Scheme 2). In our case both fluorenyl groups as well as the phenyl-backbone substituent of a racemic mixture of **6** were converted to [(1*R*,*S*)-1-cyclohexyl-1,2-bis(η^5-1,2,3,4,5,6,7,8-octahydro-9-fluorenyl)ethane]$ZrCl_2$ (**7a**) by using platinum as a catalyst (PtO_2/H_2). Depending on the hydrogen pressure and the reaction time [(1*R*,*S*)-1,2-bis(9-η^5-1,2,3,4,5,6,7,8-octahydrofluorenyl)-1-phenylethane]-$ZrCl_2$ (**7b**) is found as a byproduct in variable quantities. The yield of **7a** and **7b** is almost quantitative.

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Experimental

All reactions were carried out under dry Ar using standard Schlenk-tube techniques. The hydrocarbon and ether solvents were purified by distillation from $LiAlH_4$. CH_2Cl_2 was distilled from CaH_2. **2** [m.p. 89–90°C; $[\alpha]_D^{20}$ = +26.6 (*c* = 1.95, toluene)] was prepared from (*R*)-(−)-epoxystyrene (**1**) according to the procedure already described for its racemic analogue[6a]. **1** ($[\alpha]_D^{20}$ = −24, neat) was a gift from BASF AG, Ludwigshafen.

NMR: Bruker AC 250/AMX 400, internal TMS. – MS: Finnigan MAT-711A, modified by AMD Intectra (FD, FAB). – Elemental analyses: Microanalytical laboratory of the Institute (Carlo Erba, Model 1106). – Optical rotations: Knauer chiral detektor A 1000, Na_D line (589 nm).

(2S)-2-(9-Fluorenyl)-2-phenylethyl (R)-α-Aminophenylacetate (**3**) *and Its Hydrochloride* (**3a**): A mixture of **2** (0.55 g, 1.92 mmol), (*R*)-α-aminophenylacetic acid (0.41 g, 2.69 mmol), and *p*-toluenesulfonic acid (0.65 g, 3.46 mmol) was heated at 200°C in vacuo. After the evaluation of water had ceased (ca. 5–10 min) CH_2Cl_2 (100 ml) was added, and the organic phase was washed twice with an aqueous solution of Na_2CO_3. The organic layer was separated and treated several times with an aqueous solution of HCl (10%). The organic phase was dried with Na_2SO_4. Evaporation of the solvent and subsequent recrystallization from hot toluene/cyclohexane (1:6) gave **3a** as colorless microcrystalline material (0.74 g, 1.6 mmol, 85%), m.p. 96–97°C. – ^{1}H NMR (CD_3OD): δ = 3.70 (ddd, *J* = 5.9/7.9 Hz, 1H, CH_{bridge}), 4.14 (d, *J* = 4.79 Hz, 1H, CH_{Flu}), 4.40–4.67 (m, 2H, $CH_{2,bridge}$), 5.1 (s, 1H, $CH_{amino\ acid}$), 6.76–7.71 (m, 18H, aromatic H). – MS (FD), *m/z* (%): 419.5 (92) [M^+ − HCl]. – $C_{29}H_{26}ClNO_2$ (456.0): calcd. C 76.39, H 5.75, Cl 7.77, N 3.07; found C 75.65, H 6.54, Cl 6.55, N 2.71.

(1S)-1,2-Bis(9-fluorenyl)-1-phenylethane (**5**) *via (2S)-2-(9-Fluorenyl)-2-phenylethyl Trifluoromethanesulfonate* (**4**): Trifluoromethanesulfonic anhydride (3.44 ml, 21.0 mmol) was slowly dropped to a solution of alcohol **2** (6.0 g, 21.0 mmol) and pyridine (1.7 ml, 21.0 mmol) in CH_2Cl_2 (150 ml) at 0°C. The reaction mixture was stirred for 30 min. The organic layer was washed with icecold water and dried (Na_2SO_4, 0°C). Evaporation of the solvent at 0°C gave **4** as a colorless solid which was dissolved in 100 ml of dioxane. The solution was added to an orange suspension of fluorenyllithium in dioxane (200 ml), which was prepared by the reaction of fluorene (3.48 g, 21.0 mmol) with *n*-butyllithium (13.1 ml, 1.6 M in hexane). After stirring overnight at room temp. the reaction mixture was heated for 30 min at 60°C. The solvent was destilled off, and the solid residue was suspended in 200 ml of a saturated aqueous solution of NH_4Cl. The mixture was extracted thoroughly with diethyl ether, and the combined organic phases were dried (Na_2SO_4). After evaporation of the solvent and column chromatography over silica (eluent: toluene/hexane, 2:3) 7.8 g of **5** (17.9 mmol, 85%) were isolated, m.p. 165.8°C. $[\alpha]_D^{20}$ = +35.4 (*c* = 1.51, toluene). – ^{1}H NMR ($CDCl_3$): δ = 1.81 (ddd, *J* = 14.25/9.5/4.2 Hz, 1H, $CH_{2,bridge}$), 2.57 (ddd, *J* = 14.5/10.8/4.2 Hz, 1H, $CH_{2,bridge}$), 3.70 (dd, *J* = 9.5/4.2 Hz, 1H, CH_{Flu}), 3.89 (ddd, *J* = 11.2/4.2/4.3 Hz, 1H, CH_{bridge}), 4.13 (d, *J* = 4.3 Hz, 1H, CH_{Flu}), 7.0–7.6 (m, 21H, aromatic H). – MS (FD), *m/z* (%): 434.3 (100) [M^+]. – $C_{34}H_{26}$ (434.6): calcd. C 93.97, H 6.03; found C 94.08, H 6.24.

[(1R)-1,2-Bis(η^5-9-fluorenyl)-1-phenylethane]zirconium Dichloride (**6**): To a solution of **5** (3.7 g, 8.5 mmol) in 100 ml diethyl ether *n*-butyllithium (10.6 ml, 1.6 M in hexane) was added slowly at 0°C. The solvent was removed and the dry dilithio salt was mixed with $ZrCl_4$ (1.98 g, 8.5 mmol) and cooled to −78°C. CH_2Cl_2 (100 ml, precooled to −80°C) was added, and the suspension was stirred overnight at ambient temp. The mixture was filtered through a 1-in pad of Celite, and the solvent was evaporized leaving deep-red microcrystalline **6** which was recrystallized from toluene at −30°C to give a first fraction of pure **6** (190 mg, 0.32 mmol, 3.7%, $[\alpha]_D^{20}$ = +569, *c* = 0.1, toluene). Concentration of the solution resulted in a second fraction (472 mg, 0.79 mmol, 9.3%). – ^{1}H NMR ($CDCl_3$): δ = 4.65 (dd, *J* = 14.4/7.7 Hz, 1H, $CH_{2,bridge}$), 5.09 (dd, *J* = 14.7/12.8 Hz, 1H, $CH_{2,bridge}$), 6.53 (dd, *J* = 7.8/13.3 Hz, 1H, CH_{bridge}), 6.97–8.09 (m, 21H, aromatic H). – MS (FAB), *m/z* (%): 594.1 (100) [M^+], 558.7 (94) [M^+ − Cl].

[(1R,S)-1-Cyclohexyl-1,2-bis(η^5-1,2,3,4,5,6,7,8-octahydro-9-fluorenyl)ethane]zirconium Dichloride (**7a**) *and (1R,S)-1,2-Bis(η^5-1,2,3,4,5,6,7,8-octahydro-9-fluorenyl)-1-phenylethane]zirconium Dichloride* (**7b**): In a 250-ml high-pressure autoclave the racemic complex **6** (0.40 g, 0.67 mmol) and $PtO_2 \cdot xH_2O$ (80 mg) were suspended in CH_2Cl_2 (100 ml). The autoclave was filled with H_2 (200 bar), and the suspension was stirred for 2 d. The resulting slightly green slurry was filtered through a 1-in pad of Celite, and the solvent was evaporized. Recrystallisation from hexane at 0°C results in a 1:1 mixture of pale yellow micro crystalline **7a** and **7b** (320 mg, 0.52 mmol, 78%). – ^{1}H NMR ($CDCl_3$) **7a**: δ = 3.43 (dd, *J* = 7.3/13.9 Hz, 1H, $CH_{2,bridge}$), 3.59 (dd, *J* = 7.6/14.0 Hz, 1H, $CH_{2,bridge}$), 3.64 (dd, *J* = 13.5/13.0 Hz, 1H, $CH_{cyclohex}$). **7b**: δ = 3.96 (dd, *J* = 13.7/13.3 Hz, 1H, CH_{bridge}), 4.99 (dd, *J* = 7.4/12.7 Hz, 1H, $CH_{2,bridge}$), 5.25 (dd, *J* = 7.5/12.8 Hz, 1H, $CH_{2,bridge}$), 6.87–7.45 (m, 5H, aromatic H). – MS (FD) **7a**, *m/z* (%): 616.7 (100) [M^+]; **7b**: 610.4 (100) [M^+]. – $C_{34}H_{40}Cl_2Zr$ (610.8)/$C_{34}H_{46}Cl_2Zr$ (616.9) (1:1 mixture): calcd. C 66.53, H 7.06, Cl 11.55; found C 66.67, H 6.44, Cl 11.09.

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[1] Dedicated to Professor Dr. *Ekkehard Lindner* on the occasion of his 60th birthday.

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[7] By the use of racemic **2** two sets of resonance signals appear in the ^{1}H-NMR spectrum. All peaks could be assigned to the corresponding protons by ^{1}H/^{1}H-COSY NMR experiments.

[8] The absolute configuration of the stereogenic backbone center of **2**, **5**, and **6** was deduced from an X-ray structure analysis which was performed on the fluorenyl-indenyl analog [(1*R*,2*S*)-1-(η^5-9-fluorenyl)-2-(η^5-1-indenyl)-1-phenylethane]$ZrCl_2$ of **6**. This complex was prepared according to the same reaction procedure as described in the present report using indenyl instead of fluorenyllithium in the ligand synthesis (cf. ref.[6b]). Details of this X-ray structure analysis will be published elsewhere.

[9] Several recrystallizations did not change the optical rotation of ligand **5** and complex **6**.

[10] The change from absolute (*S*) to (*R*) configuration of the stereogenic backbone center during the conversion of ligand **5** to complex **6** is due to a change in the priority of the carbon substituents according to the CIP rules. It is not caused by an chemically induced inversion of the handedness of this carbon atom.

[250/94]