Journal of Organometallic Chemistry, 420 (1991) C17–C20
Elsevier Sequoia S.A., Lausanne
JOM 22303PC

Preliminary communication

Preparation and some properties of chiral *ansa*-mono(η^5-fluorenyl)zirconium(IV) complexes

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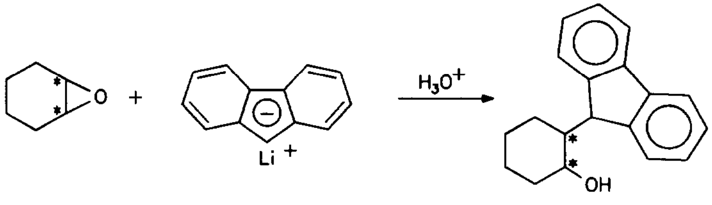
(Received August 5th, 1991)

Abstract

Symmetrically-substituted epoxides react with fluorenyllithium to give the corresponding alcohols in high yields. These were used to prepare *ansa*-bridged mono(η^5-fluorenyl)-zirconium complexes of the general formula $[(C_{13}H_8\text{-CHR-CHR-O}]ZrCl_2(thf)_2$ (CHR–CHR = cyclohexyl, cyclopentyl, 1,2-diphenylethyl). With $Al(CH_3)_3$ as cocatalyst these complexes catalyze the polymerization of ethene.

There is much current interest in the development of new mono(η^5-cyclopentadienyl)zirconium(IV) compounds for the catalytic formation of C–C bonds. This includes Diels–Alder reactions [1] and the polymerization of ethene and styrene to homo- and co-polymers [2]. Up to now either unbridged cyclopentadienyl derivatives with chiral substituents [3] or Me_2Si-bridged achiral compounds [4] have been used for those reactions. We report below a facile route to chiral bridged mono(η^5-fluorenyl)zirconium(IV) complexes. The compounds could possibly be useful as chiral Lewis acids or as polymerization catalysts.

The reaction of epoxycyclohexane with fluorenyllithium gives a racemic mixture of *trans*-2-fluorenyl-cyclohexanol-1, $(C_{13}H_9)C_6H_{10}OH$ (**1a**), in 90% yield after hydrolysis [5*].



1a

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* Reference number with asterisk indicates a note in the list of references.

Table 1

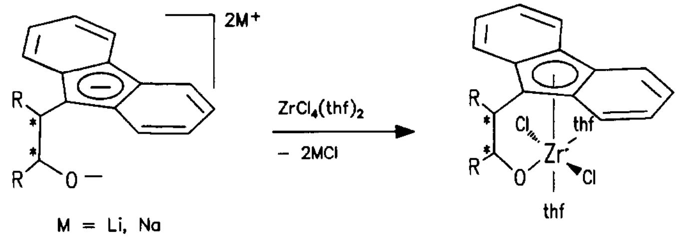
^{1}H NMR data [a], melting points and MS data for **1a–d**

Alcohol	$\delta(C_{13}H_9)$ [J(H,H) in Hz]	δ(bridge)	M.p. (°C)	MS (m/e)
1a	7.2–7.9 (m,8H) 4.55 (d,1H) [3.0]	3.85–3.95 (m,1H) 0.5–2.2 (m,10H)	124–125	264
1b	7.2–8.0 (m,8H) 4.25 (d,1H) [4.0]	4.02–4.10 (m,1H) 2.56–2.65 (m,1H) 1.1–1.8 (m,7H)	87– 88	250
1c	6.2–8.1 (m,8H) 5.01 (d,1H) [4.5]	5.44 (dd,1H) [10.6,2.2] 3.86 (dd,1H) [10.6,4.5] 2.29 (d,1H) [2.2]	156–157	362
1d	6.8–7.6 (m,8H) 4.14 (d,1H) [5.6]	5.5 (dd,1H) [8.1,2.7] 3.41 (dd,1H) [8.1,5.6] 1.92 (d,1H) [2.7]	168–169	344 [b]

[a] $CDCl_3$, 20 °C, 250 MHz, δ (ppm) rel. TMS (0 ppm). [b] The M^+-peak was not detected; 344 results after dehydration; the same peak is observable for **1c**.

The same reaction is applicable to epoxycyclopentane, yielding *trans*-2-fluorenylcyclopentanol-1 (**1b**) and to *cis*- and *trans*-epoxystilbene, yielding racemic- (**1c**) and *meso*- (**1d**) 2-fluorenyl(1,2-diphenyl)ethanol, respectively [6]. The ^{1}H NMR- and MS data for these colourless crystalline products are summarized in Table 1.

The dianions **2a–d** were prepared by the addition of either two equivalents of n-butyllithium or an excess of sodium hydride in THF. The deep red compounds react with $ZrCl_4(thf)_2$ to give the corresponding *ansa*-mono(η^5-fluorenyl)zirconium alkoxide · thf adducts **4a–d** [7*,8].



2a–d

4a–d

The ^{1}H NMR spectra of the compounds **4a–d** show two sets of signals, one for the aromatic and one for the aliphatic region. All the aromatic protons are inequivalent due to the asymmetry of the bridging backbone [9]. The coupling patterns for the CHR–CHR protons become simpler after complex formation, as expected (Table 2). Compounds **4a,b** show a doublet of triplets for each proton, whereas **4c,d** exhibit only two doublets due to the phenyl substituents.

There is one set of resonances for each thf fragment coordinated either *cis* or *trans* to the fluorenyl unit in the pseudo octahedral complexes **4a–d**. All the thf signals are broadened. This confirms the fluxional behaviour of the thf ligands previously found for $CpZrCl_3(thf)_2$ by Erker et al. [10].

The activities of **4a–d** for ethene polymerization were tested in some exploratory experiments. All four compounds are active when used along with

Table 2

^{1}H NMR [a] and MS data for **4a–d**

Complex	$\delta(C_{13}H_9)$ [J(H,H) in Hz]	δ(bridge)	δ(THF)	MS (m/e)
4a	7.1–8.0 (m,8H)	4.74 (dt,1H) [4.3,10.4] 2.69 (dt, 1H) [4.3,10.8] 0.3–2.1 (m,8H)	4.18, 1.45, 3.94, 1.25[b]	425[c]
4b	7.2–8.0 (m,8H)	4.92 (dt,1H) [4.1,9.3] 2.80 (dt,1H) [4.1,9.6] 1.0–1.8 (m,6H)	4.26, 1.40, 3.84, 1.23[b]	411
4c	6.3–8.1 (m,8H)	7.32 (d,1H) [8.1] 6.01 (d,1H) [8.1]	3.93, 1.45, 3.71, 1.28[b]	523
4d	6.8–7.6 (m,8H)	7.71 (d,1H) [7.6] 6.38 (d,1H) [7.6]	3.67, 1.43, 3.56, 1.30[b]	523

[a] C_6D_6, 20 °C, 250 MHz, δ (ppm) rel. TMS (0 ppm). [b] m, 4H each signal, two THF ligands *cis* and *trans* to the fluorenyl unit. [c] The THF ligands could not be detected.

methylalumoxane (MAO). The catalysts show even higher activity with $Al(CH_3)_3$ as cocatalyst. The potential of these new polymerization catalysts will be the subject of intensive further investigation.

Acknowledgements. Generous financial support from Professor Dr. E. Lindner, the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the BASF Aktiengesellschaft is gratefully acknowledged.

References and notes

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5 Preparation of **1a**: Butyllithium (75.2 ml, 120.3 mmol in hexane) was transferred by cannula to a solution of fluorene (20 g, 120.3 mmol) in 200 ml of diethyl ether at 0 °C. Epoxycyclohexane (11.4 g, 116.2 mmol in 30 ml of diethyl ether) was then added during 1 h at the same temperature. After overnight stirring the mixture was hydrolyzed with saturated aqueous ammonium chloride (50 ml). The ether layer was separated and dried (Na_2SO_4). Evaporation of the solvent yielded 30 g of a slightly yellow oil. Recrystallization from boiling hexane/toluene gave **1a** (27.6 g, 90% yield). Anal. Found: C, 86.33; H, 7.49. $C_{19}H_{20}O$ (264.3) calcd.: C, 86.34; H, 7.63%. Compounds **1b,c** were prepared analogously.

6 In all compounds **a** refers to a *trans*-1,2-cyclohexyl, **b** to a *trans*-1,2-cyclopentyl, **c** to the racemic mixture of 1,2-diphenyl-ethyl and **d** to a *meso*-1,2-diphenyl-ethyl backbone.

7 Preparation of **4a**: Butyllithium (17.0 ml, 27.2 mmol in hexane) was added to a solution of **1a** (3.58 g, 13.6 mmol) in 50 ml of THF at 0 °C. $ZrCl_4(thf)_2$ (5.13 g, 13.6 mmol) was added at −70 °C. The solution was refluxed for 4 h and the solvent evaporated off. A suspension of the residual powder in 50 ml CH_2Cl_2 was filtered through Celite. Evaporation of the solvent and extraction of the residue with boiling heptane (five times) yielded 5.86 g of **4a** (10.3 mmol, 75.7% yield) as bright yellow powder. Anal. Found: C, 56.82; H, 6.08. $C_{27}H_{34}Cl_2O_3Zr$ (568.7) calcd.: C, 57.02; H, 6.03 g. **4b–d** were prepared analogously and gave similarly acceptable analytical data.

8 The reaction of compounds **2a–d** with $ZrCl_4$ in CH_2Cl_2 results in the formation of the THF free complexes. These compounds contain one equivalent of LiCl or NaCl, depending on the nature of

the dianion counter ions. According to osmometric molecular weight determination the complexes are monomeric in solution (cf. W.E. Piers, E.E. Bunel and J.E. Bercaw, J. Organomet. Chem., 407 (1991) 51).

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