Planar-chiral Ferrocenes in Asymmetric Catalysis: The Impact of Stereochemically Inhomogeneous Ligands

Carsten Bolm,* Kilian Muñiz and Jens P. Hildebrand

Supporting Information

I Experimental and analytical details for dimethylzinc additions

All ferrocenes were synthesized as previously described.[1]
Dimethylzinc was purchased from Aldrich as 2.0 M-solution in toluene and used as received. Toluene was freshly distilled under argon from benzophenone ketyl radical. All catalyses were carried out under an atmosphere of argon employing common Schlenk techniques.

General procedure for the dimethylzinc addition to benzaldehyde:

A well-dried Schlenk flask under argon is charged with 5 mol% of the ferrocene. The Schlenk flask is evacuated twice and flushed with argon. Then, 5 mL of freshly distilled toluene are added and the solution is cooled to 0°C followed by addition of 1.5 eq. of dimethylzinc (2.0 M-solution in toluene). The resulting solution is stirred for 30 min and 1.0 eq. of benzaldehyde are added directly via syringe. The reaction flask is sealed and the proceeding of the reaction is monitored by tlc.
The reaction is worked-up by careful addition of 10 mL of 2 M HCl and the resulting mixture is extracted four times with 25 mL of dichloromethane. The combined organic phases are washed with brine, dried over $MgSO_4$ and the solvent is removed on a rotary evaporator. The crude product is purified by column chromatography (silica gel, hexanes/MTBE = 9/1) which yields 1-phenylethanol as a colorless oil.
The enantiomeric excess of the product was determined by analytical HPLC.
Column: Daicel Chiralcel OD, eluent: *n*-hexane/isopranol 98.5/1.5, flow rate: 1.0 mLmin^{-1}.
Retention times: 21.9 min (*R*-enantiomer), 29.4 min (*S*-enantiomer).

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[1] (a) C. Bolm, K. Muñiz-Fernández, A. Seger, G. Raabe, *Synlett* **1997**, 1051. (b) C. Bolm, K. Muñiz-Fernández, A. Seger, G. Raabe, K. Günther, *J. Org. Chem.* **1998**, *63*, 7860.

II Results of catalysis with scalemic ferrocene ((R_p))-4

Table. Data for the asymmetric dimethylzinc addition to benzaldehyde (**5**) to give (*R*)-**6** in the presence of 5 mol% of scalemic **4**.

Entry	Ee of of **4** [%] [a]	Reaction Time [h]	Yield of **6** [%][b]	Ee of **6** [%][a]
1	100	12	87	78
2	71	16	78	56.5
3	52	14	84	40
4	32	17	91	22

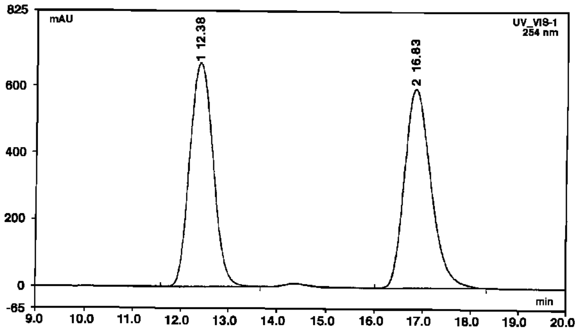
[a] Determined by HPLC as described above.

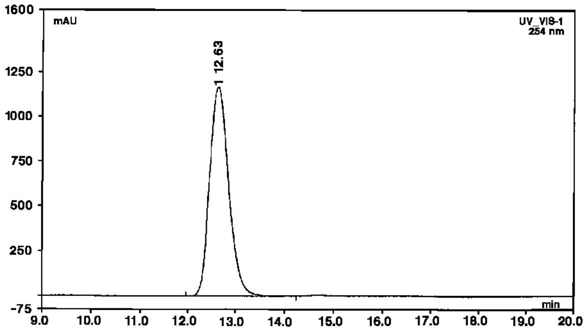
[b] After column chromatography.

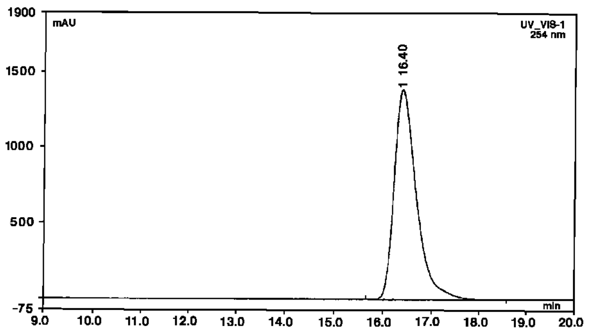
III Preparation and HPLC separation conditions for ferrocene 4

Ferrocene **4** was synthesized as described previously.[1b]

The enantiomeric excess for ferrocene **4** was determined by analytical HPLC prior to catalysis. Column: Daicel Chiralpak AD, eluent: *n*-hexane/isopropanol 97/3, flow rate: 0.4 mLmin^{-1}. Retention times: 12.4 min (*R*-enantiomer), 16.8 min (*S*-enantiomer).







IV Spectral reproduction of a 1:1-mixture of ferrocenes 1 and 3

The diastereomeric excess for ferrocenes **1** and **3** was determined prior to catalysis by comparison of the signals for the two *t*-butyl groups in the ^{1}H nmr spectra of the respective mixtures: δ = 0.42 [$C(CH_3)_3$ (**3**)], 0.96 [$C(CH_3)_3$ (**1**)].