Synthesis of Cylindrically Chiral Ferrocenedicarboxylic Acids

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Enantiomerically pure dicarboxylic acids with well-defined chirality may be useful as a bidentate Brønsted acid catalyst in double activation of functional groups,1 and as a chirality-bearing anionic part of metallic carboxylate, which may be used as an asymmetric catalyst such as the rhodium dimers of chiral carboxylic acid.2 The latter has been particularly useful in catalytic asymmetric cyclopropanation by transfer of the carbene fragments from diazoalkanes to alkenes.3

In designing such systems, the two carboxy groups must be situated in such a way that the mutual distance between them is appropriate enough for double coordination onto a functional group such as 1 (a carbonyl group in the present case). Herein are reported new cylindrically chiral4 dicarboxylic acids with ferrocene backbone and a brief survey of the compounds as the catalysts for the catalytic asymmetric cyclopropanation.

The modular preparation of the ferrocene dicarboxylic acid derivatives is summarized in Schemes 1. The diastereomerically pure diamines 2 were treated with n-BuLi in THF (two-fold introduction of planar chirality) and the resulting doubly ortho-lithiated species were quenched with dibromoteterachloroethane to give ca. 80% yields of diastereomerically pure bromides 3. Subsequently, the diamine moieties were converted to the corresponding hydrocarbon by the reaction with Ac2O, followed by reductive alkylation of the acetates with AlEt3 or PhZnBr-BF3·OEt2.

The subsequent preparation of ferrocenedicarboxylic acid derivatives 4 (hereafter abbreviated as Ferroacid) was accomplished by double lithium-bromine exchange with n-BuLi in THF at −78 °C followed by bubbling of CO2 gas into the flask containing the di-lithiated species via cannula, which furnished the dicarboxylic acids in acceptable yields after acidic work-up and recrystallization (81% (4a: ethyl acetate) and 80% (4b: CH2Cl2 and n-hexane)) or chromatography (4c).6 (Scheme 1)

With the new chiral dicarboxylic acids in hands, preparation of the rhodium dimers for catalytic asymmetric cyclopropanation was carried out to quickly test the chiral environment of the dicarboxylic acids. The preparation of the rhodium(II) salt dimers of Ferroacid 4 was accomplished by the ligand exchange reaction7: A mixture of the dicarboxylic acid 4 (3.0 equiv) and dirhodium tetraacetate was refluxed in chlorobenzene under an argon atmosphere for 6 days through a Soxhlet extractor filled with CaCO3. During the reaction, the liberated acetic acid was trapped by CaCO3, which would accelerate the ligand exchange process. Even with this well-established procedure, the preparations were not universally successful; Increase in steric size of the CHR2 group in 4 resulted in formation of polymers. In line with the assertion, the pure rhodium(II) dimer of 3-pentylferrocene, 5a, could be obtained after recrystallization with THF and n-hexane in ca. 50% yields, while the preparation of the corresponding diphenylmethyl derivative, 5b, was erratic, giving polymeric materials in some cases.7 On the other hand, the corresponding dimer from the sterically more demanding DTM-Ferroacid, 8c, could not be obtained clean-
only moderate, it was the first catalytic asymmetric cyclopropanation using the cylindrical chirality. A thorough study of the catalyst dimers is guaranteed in other reactions.

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References


6. Selected spectroscopic data. 3-Pt Ferroacid ([(pS,pS)-1,1'-di(3-pentyl)-2,2'-ferrocenedicarboxylic acid] 4a: [α]D +152 (c 0.5, CHCl3); MS (TOF) m/z (relative intensity): 413.4441 (100, M+); 414.4666 (25.8), 415.4713 (5.2); δ 12.101 (bs, 2H), 4.474-4.471 (m, 2H), 4.253-4.247 (m, 4H), 3.006-2.992 (m, 2H), 1.955-1.908 (m, 2H), 1.516-1.419 (m, 4H), 1.369-1.315 (m, 2H), 1.008-0.978 (t, JHH = 7.5 Hz, 6H), 0.480-0.451 (t, JHH = 7.5 Hz, 6H); 13C NMR (CDCl3, 125.7 MHz): δ 171.687, 97.557, 73.058, 71.615, 70.561, 70.309, 36.328, 25.749, 23.972, 12.470, 8.385. DPM-Ferroacid ([(pS,pS)-1,1'-bis(diphenylmethyl)-2,2'-ferrocene dicarboxylic acid] 4b: [α]D +394 (c 0.5, CHCl3); MS (TOF) m/z (relative intensity): 629.1393 (100, M+Na), 630.1290 (45.8), 631.1313 (9.7), 632.1815 (3,2); 1H NMR (DMSO, 500 MHz): δ 4.070 (s, 2H), 3.809 (s, 2H), 2.828 (s, 6H), 2.195 (s, 6H). In conclusion, we have succeeded in the synthesis of new cylindrically chiral ferrocenyldicarboxylic acid. Although the ee value of catalytic asymmetric cyclopropanation was not highly reproducible.

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