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Highly diastereoselective reduction of ferrocene bis-imines with methyllithium and the formation of C_2 -symmetric Zr complexes[†]

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Alkylation of ferrocene bis-imines $Fc[N=C(H)Ar]_2$ (Ar = Ph, *p*-Tol) with MeLi was found to proceed in a highly diastereoselective fashion producing the C_2 -symmetric ferrocene diamines $Fc[NC(H)(Me)Ar]_2-H_2$ with 90% diastereomeric excess. This process allowed for the synthesis of C_2 -symmetric zirconium complexes $Fc[NC(Me)Ar]_2rBn_2$.

The most widely investigated aspects of olefin polymerization chemistry relate to factors controlling stereochemistry of the resulting polymer. In a site-control mechanism of Ziegler-Natta olefin polymerization, the initiator geometry and symmetry dictate the stereochemical outcome of each successive olefin insertion.1 Based on the studies of metallocene complexes of Group 4 metals, relationships have been established between the symmetry of the initiator and the tacticity of the resulting polymer. In particular, production of an isotactic polymer can often be rationalized on the basis of the C_2 -symmetric structure of the initiator.² A large number of C_2 -symmetric metallocene initiators have been reported. Their synthesis is often complicated by the formation of a C_s -symmetric *meso* byproduct. Separation of the isomers can be tedious and it is desirable to generate the C_2 -symmetric rac isomer selectively. Since the complex need not be enantiopure, the term "racemo-selective" has been used to describe the diastereoselectivity of this method.3 Although several highly diastereoselective methods of producing C2-symmetric Group 4 metallocenes have been developed, the process is not readily generalized.

Transition to non-metallocene initiators creates the possibility of using inherently chiral racemic C_2 -symmetric ligands for the synthesis of C_2 -symmetric Group 4 metal complexes. A number of non-metallocene systems of this type have already been investigated as potential olefin polymerization catalysts.⁴ In particular, several C_2 -symmetric diamide Ti and Zr complexes incorporating a chiral backbone were reported.^{5–8} A recent report by Long and coworkers concerning the reduction of a ferrocene bis-imine Fc[N=C(H)Ph] to the corresponding diamine Fc(NCH₂Ph)₂–H₂ using LiAlH₄⁹ raised the possibility of using the related reaction with MeLi to produce a C_2 symmetric diamine. This report describes the highly diastereoselective formation of racemic ferrocene diamines and the subsequent conversion of these diamines to C_2 -symmetric Zr complexes.

Several Schiff-base complexes of 1,1'-diaminoferrocene were reported recently,^{9,10} including the preparation of a simple bis-benzaldimine $Fc[N=C(H)Ph]_2$ (1) through Schiff base condensation of 1,1'-diaminoferrocene with benzaldehyde in toluene.⁹ We found that conducting the condensation reaction in EtOH resulted in the isolation of the analytically pure burgundy-colored bis-imine 1[‡] in 93% yield (Scheme 1). The ¹H NMR spectrum of the product contained a set of two ferrocene resonances (virtual triplets) at 4.59 and 4.10 ppm, a pattern characteristic of C_{2v} -symmetric ferrocene derivatives. In an analogous fashion, the reaction of 1,1'-diaminoferrocene

† Electronic supplementary information (ESI) available: experimental procedures and characterization data for all new compounds. See http:// www.rsc.org/suppdata/cc/b3/b308360h/



with p-MeC₆H₄CHO produced the corresponding bis-imine **2** in 95% yield.

Addition of MeLi to a THF suspension of 1 at -60 °C led to the formation of a dark-blue mixture, which, upon warming to above approx. -8 °C, afforded a red solution. Hydrolysis of the mixture led to a yellow solution from which diamine 3 was obtained as an orange air-sensitive solid in 92% yield (Scheme 2). The reduction of the bis-imine 2 proceeded in a similar fashion and afforded, upon hydrolysis, the corresponding diamine 4 in 78% yield.



Although in principle the diamine **3** is expected to form as a mixture of the *trans* and the *cis* isomers (Fig. 1), only one major product was observed by ¹H NMR spectroscopy.

The product displayed four ferrocene ABCD multiplets, consistent with the formation of a ferrocene derivative with two chiral substituents in the 1,1'-positions. The resonances of the newly incorporated methyl group show coupling to the methine hydrogen and appear as doublets. A closer analysis of the spectrum revealed the presence of the minor isomer. The two diastereomers are found in a 90 : 10 ratio, which corresponds to a diastereomeric excess (de) of 80%. The ¹H NMR spectrum of diamine **4** showed the same ratio of two diastereomers.



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It is important to note that in the case of diamines **3** and **4** the assignment of diastereoisomers as *trans* or *cis* is not straightforward. In each isomer the two (η^5 -C₅H₄)NCH(Me)(Ar) groups are related by a symmetry element: a mirror plane in the *cis* isomer and a two-fold rotation axis in the *trans* isomer. The ¹H NMR patterns exhibited by the two diastereomers are, therefore, indistinguishable.¹¹ The question of the assignment of the major diastereomer was addressed by the synthesis of zirconium dibenzyl complexes (Scheme 3). Reaction of diamine **3** with ZrBn₄ afforded the desired zirconium dibenzyl complex {Fc[NCH(Me)(Ph)]₂}ZrBn₂ (**5**) (Scheme 3). As expected, the ¹H NMR analysis of the product shows the presence of two diastereomers in a 90 : 10 ratio. This ratio mirrors the isomer distribution in diamine **3**.

The C_s and the C_2 symmetrical zirconium dibenzyl complexes can be easily distinguished by the ¹H NMR pattern of the benzylic methylene protons. In a C_2 -symmetric compound, the two benzyl groups are equivalent, but the protons on the same benzyl group are diastereotopic and appear as two doublets. Conversely, the two benzyl groups in a \hat{C}_s -symmetric complex are distinct, but each group contains a pair of equivalent benzylic protons (Fig. 2). In this case, the spectrum would consist of two singlets. The major diastereomer of 5 contains two doublets at 2.69 and 2.65 ppm ($^{2}J = 10.4$ Hz) corresponding to the benzylic hydrogen atoms. This pattern identifies this isomer as the C_2 -symmetric *trans* diastereomer. Therefore, the remaining 10% of the product is the C_s -symmetric cis diastereomer. The zirconium dibenzyl complex Fc[NCH(Me)(p-MeC₆H₄)]₂ZrBn₂ (6) formed from ZrBn₄ and 4 again was shown by ¹H NMR to contain mainly the trans diastereomer

The results obtained from these experiments indicate that the reduction of ferrocene bis-imines **1** and **2** with methyllithium is highly racemoselective. It is well established that high diastereoselectivities are often achieved in the formation of vicinal diamines through alkylation of glyoxal-derived bis-imines.^{11,12} With other bis-imines, the outcome of the alkylation varies from the selective formation of the *meso* diamines¹³ to the selective generation of the racemic diamines.¹⁴ However, the favorable sense of the selectivity (*rac*) coupled with the proven ability of diaminoferrocene-based complexes to polymerize ethylene render the alkylation of ferrocene an attractive route to C_2 -symmetric olefin polymerization catalysts.

In order to further optimize the selectivity of the alkylation step, solvent and temperature effects on the product distribution were investigated. Conducting the reaction at room temperature reduced the diastereomeric excess from 80% to 72%. The best





H_c and H_d: two singlets



selectivity was achieved in toluene. Reaction of **1** with methyllithium in toluene at -60 °C produced a 95 : 5 mixture of the *trans* and *cis* isomers (90% de). This result allowed for a highly selective synthesis of C_2 -symmetric Group 4 metal complexes. The sequence is summarized in Scheme 4 showing the formation of a chiral racemic zirconium complex **5** with a 90% diastereometric excess.

In summary, a method for the highly diastereoselective formation of C_2 -symmetric racemic diaminoferrocenes is described. The compounds are obtained through a reaction of methyllithium with ferrocene bis-imines. Under the optimized reaction conditions the formation of the *trans*-diastereomer proceeded with a 90% diastereomeric excess. The diaminoferrocenes thus obtained were subsequently used to generate C_2 -symmetric zirconium diamide complexes, whose chemistry is presently under investigation. Additional work is in progress to establish the origin of the selectivity of the reduction of bisimines with MeLi.

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Notes and references

[‡] Characterization details for 1, 3, and 5. Compound 1: Mp. 126–128 °C. ¹H NMR (C₆D₆), δ8.38 (s, 2H, N=CH), 7.68 (m, 4H, o-Ph), 7.10-7.02 (m, 6H, *m*-Ph and *p*-Ph), 4.59 (virt t, 4H, Fc), 4.10 (virt t, 4H, Fc). ¹³C NMR (C₆D₆), δ 157.9, 137.4, 130.2, 128.7, 128.3, 106.1 (Fc_{ipso}), 68.8 (Fc), 64.8 (Fc). Anal. Calcd for C₂₄H₂₀FeN₂: C, 73.48; H, 5.14; N, 7.14. Found: C, 73.39; H, 5.16; N, 7.15%. 3: Major product (3-trans): ¹H NMR (C₆D₆), δ7.34 (m, 4H, o-Ph), 7.20 (m, 4H, m-Ph), 7.10 (m, 2, p-Ph), 4.09 (qd, $J_{H-H(Me)} = 6.7$ Hz, $J_{H-H(NH)} = 2.5$ Hz, 2H, MeCH), 3.80 (m, 2H, Fc), 3.78 (m, 2H, Fc), 3.66 (m, 2H, Fc), 3.54 (m, 2H, Fc), 2.35 (d, J = 2.5 Hz, 2H, NH), 1.19 (d, J = 2.5 Hz, 2H, 100 Hz, 2H, 100 Hz), 1.19 (d, J = 2.5 Hz, 2Hz, 100 Hz), 1.19 (d, J = 2.5 Hz, 2Hz), 1.19 (d, J = 2.5 Hz, 2Hz), 1.19 (d, J = 2.5 Hz, 2Hz), 1.19 (d, J = 2.5 Hz), 1.19 (d, JJ = 6.7 Hz) ppm. ¹³C{¹H} NMR (C₆D₆), δ 146.5, 128.4, 128.2, 126.1, 109.4 (Fcispo), 63.4 (Fc), 63.3 (Fc), 57.6 (Fc), 57.4 (MeCH), 57.10 (Fc), 25.2 (MeCH) ppm. Anal. Calcd for C₂₆H₂₈FeN₂: C, 73.59; H, 6.65; N, 6.60. Found: C, 73.32; H, 6.45; N, 6.78. 5: ¹H NMR (only the major trans diastereomer is described) (C₆D₆), δ 7.25–6.90 (m, 20H, Ar), 4.89 (q, ³J = 6.7 Hz, 2H, NCH), 3.77 (m, 2H, Fc), 3.75 (m, 2H, Fc), 2.90 (m, 2H, Fc), 2.81 (m, 2H, Fc), 2.66 (d, ${}^{2}J = 10.4$ Hz, 2H, ZrCH₂), 2.62 (d, ${}^{2}J = 10.4$ Hz, 2H, ZrCH₂), 1.67 (d, ${}^{3}J = 6.7$ Hz, 6H, Me) ppm. Anal. Calcd for C40H40FeN2Zr: C, 69.04; H, 5.79; N, 4.03. Found: C, 68.70; H, 5.60; N,

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