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# Salen-ligands based on a planar-chiral hydroxyferrocene moiety: Synthesis, coordination chemistry and use in asymmetric silylcyanation

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ABSTRACT

Condensation of the O-protected hydroxyferrocene carbaldehyde ($S_p$)-**1** with suitable diamines, followed by liberation of the hydroxyferrocene moiety leads to a new type of ferrocene-based salen ligands (**3**). While the use of ethylenediamine in the condensation reaction yields the planar-chiral ethylene-bridged ligand [($S_p$,$S_p$)-**3a**], reaction with the enantiomers of *trans*-1,2-cyclohexylendiamine gives rise to the corresponding diastereomeric cyclohexylene-bridged systems [(*S*,*S*,$S_p$,$S_p$)-**3b** and (*R*,*R*,$S_p$,$S_p$)-**3c**], which feature a combination of a planar-chiral ferrocene unit with a centrochiral diamine backbone. Starting with the ferrocene-aldehyde derivative ($R_p$)-**1**, the enantiomeric ligand series (**3d**/**e**/**f**) is accessible via the same synthetic route.

The ($S_p$)-series of these newly developed $N_2O_2$-type ligands was used for the construction of the corresponding mononuclear bis(isopropoxy)titanium (**4a**/**b**/**c**), methylaluminum (**5a**/**b**/**c**) and chloro-aluminum-complexes (**6a**/**b**/**c**), which were isolated in good yields and identified by X-ray diffraction in several cases. The aluminum complexes (**5**/**6**) were successfully used in the *Lewis*-acid catalyzed addition of trimethylsilylcyanide to benzaldehyde, yielding the corresponding cyanohydrins in 45–62% enantiomeric excess.



## 1. Introduction

Ferrocene-derived ligands have found widespread application in almost all fields of coordination chemistry and catalysis [1]. This was made possible by the development of synthetic methodologies for the selective attachment of a variety of functional groups to the ferrocene backbone, which has allowed the directed synthesis of a huge number of functionalized ferrocene derivatives. This was mostly used for the generation of ferrocene derivatives featuring pairs of functional groups, including both 1,1′-disubstituted ferrocenes (e.g. dppf and derivatives) [2], but more importantly homoannularly disubstituted ferrocene derivatives, mostly bearing two functional groups in a 1,2-fashion [3]. The 1,2-substitution pattern is of high interest for the synthesis of ligands applicable in asymmetric catalysis, since it allows the generation of ferrocene-ligands possessing an inherent planar-chirality [4]. Some planar-chiral ferrocene-derivatives have paved their way to being used as chiral ligands in large-scale industrial applications (e.g. the well-known Josiphos ligand family) [5]. While most of these ligands feature a planar-chiral ferrocene-backbone in combination with an additional element of chirality, it has been shown that 1,2-disubstituted ferrocenes possessing an element of planar chirality as the sole source of chiral information can also be used for a variety of asymmetric transformations, both as ligands in metal-catalyzed reactions [6] and as nucleophilic organocatalysts [7].

A few reports have demonstrated the successful use of ferrocene-derivatives as building blocks for the construction of salen-like tetradentate ligand frameworks [8]. Thus, 1,1′-diaminoferrocene has been used as an achiral bridging unit for $O_2N_2$-type salen-ligands [9], while planar-chiral 2-phosphanyl-substituted ferrocene carbaldehydes have been used for the construction of $P_2N_2$-type salen ligands, which have found application in asymmetric catalysis [10]. In contrast to this, hydroxyferrocene-derivatives have mostly been used for the synthesis of bidentate ligands [11], while their use as building blocks for the generation of $O_2N_2$-type salen ligands has only found little attention so far [12]. To the best of our knowledge, the only example of a hydroxyferrocene-derived salen-type ligand has been described by Ito et al., who made use of a resolution process in order to obtain the necessary hydroxyferrocene carbaldehyde species in optically pure form [12a].

We have recently described an improved synthesis of this "ferro-salen" ligand [($S_p$,$S_p$)-**3a**, see Scheme 1], plus some first examples of its coordination chemistry and use in catalysis [13]. Our synthesis was based on an enantiomerically pure ($S_p$)-isomer of

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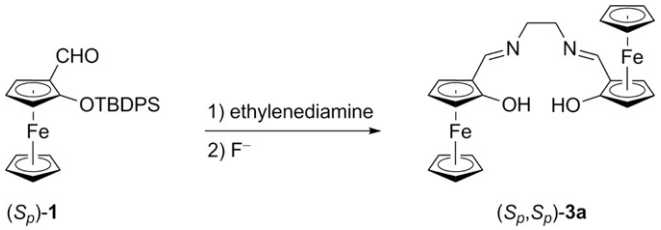



**Scheme 1.** Synthesis of the "ferro-salen" ligand ($S_p$,$S_p$)-**3a** starting from the hydroxyferrocene-derivative ($S_p$)-**1**.

the O-protected 2-hydroxyferrocene carbaldehyde derivative ($S_p$)-**1**. An efficient synthetic route to ($S_p$)-**1** had recently been developed in our group [14].

In this account, we would now like to present the synthesis of the related cyclohexylene-bridged ligands [(*S*,*S*,$S_p$,$S_p$)-**3b**, (*R*,*R*,$S_p$,$S_p$)-**3c**], together with the ligands of the corresponding enantiomeric series [($R_p$,$R_p$)-**3d**, (*R*,*R*,$R_p$,$R_p$)-**3e**, (*S*,*S*,$R_p$,$R_p$)-**3f**], which were generated starting from the ($R_p$)-isomer of the ferrocene carbaldehyde derivative **1**. In addition, a series of metal complexes (**4**,**5**,**6**) based on the ($S_p$)-series of these new ligands will be described, together with a first application of some of these complexes in the asymmetric silylcyanation of benzaldehyde.

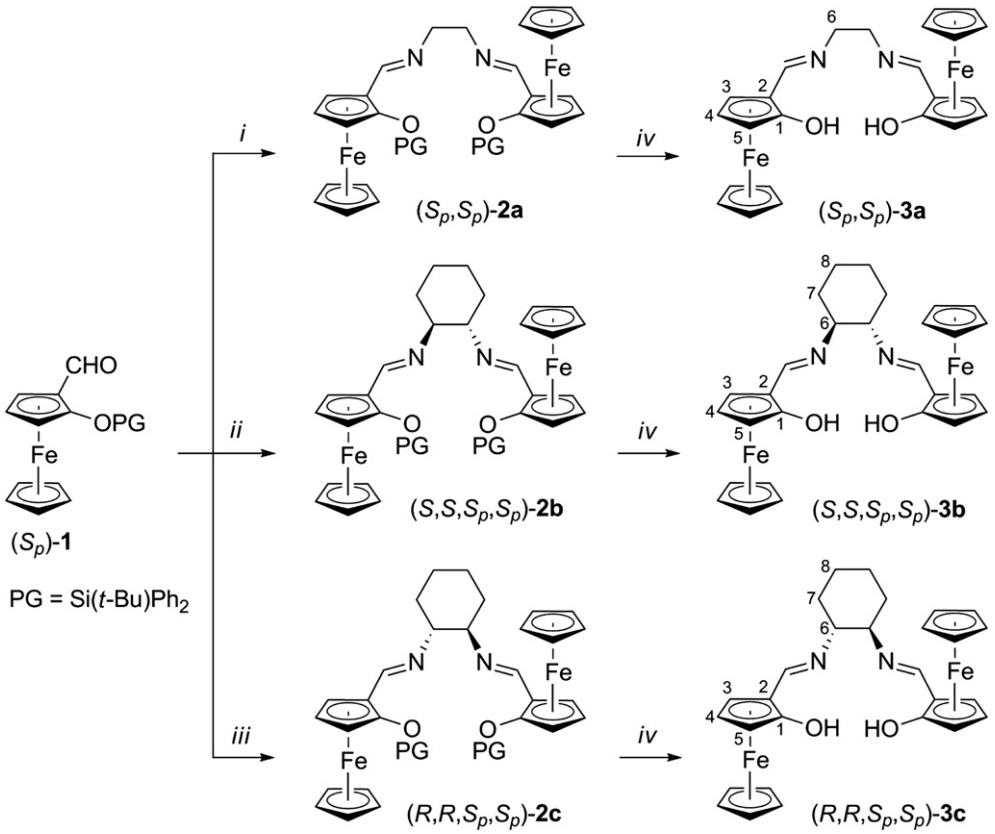
## 2. Results and discussion

### 2.1. Synthesis of the ferro-salen ligands in the ($S_p$)- and ($R_p$)-series

The synthesis of the "ferro-salen" ligands in the ($S_p$)-series started from the enantiomerically pure 2-siloxyferrocene carbaldehyde derivate ($S_p$)-**1**, which is available in a four-step synthesis [14] starting from the chiral ferrocenyl acetal that had been developed by Kagan et al. [15]. The synthesis of the ethylene-bridged ferro-salen ligand ($S_p$,$S_p$)-**3a** was carried out as previously described by us, namely by condensation of ($S_p$)-**1** with ethylenediamine and subsequent fluoride-induced deprotection of the O-silyl proctected hydroxyferrocene units [13]. In analogous fashion, the acid-catalyzed condensation of ($S_p$)-**1** with 0.5 equivalents of the respective enantiomers of *trans*-1,2-cyclohexanediamine [16] in toluene solution gave the corresponding O-protected bisimines (*S*,*S*,$S_p$,$S_p$)-**2b** and (*R*,*R*,$S_p$,$S_p$)-**2c**, respectively (see Scheme 2). Treatment of these ligand precursors with triethylamine trihydrofluoride (as for **2a**) resulted in a clean deprotection of the hydroxyferrocene-units, which led to precipitation of the diols (*S*,*S*,$S_p$,$S_p$)-**3b** and (*R*,*R*,$S_p$,$S_p$)-**3c** from the reaction mixtures. Subsequent filtration led to the isolation of the diastereomeric ferro-salen ligands in moderate yields (53–56% over two steps, see Scheme 2).

In order to synthesize the enantiomeric ligand series, exhibiting the hydroxyferrocene carbaldimine-units in an ($R_p$)-configuration, we made use of the same synthetic route, albeit starting from the ($R_p$)-isomer of the ferrocene-aldehyde derivative **1** (which in turn is accessible from the chiral *Kagan* ferrocene-acetal in six steps, as described by us earlier [14]). Thus we were able to generate the three enantiomeric ferro-salen ligands ($R_p$,$R_p$)-**3d**, (*R*,*R*,$R_p$,$R_p$)-**3e** and (*S*,*S*,$R_p$,$R_p$)-**3f**, each in a two-step condensation/deprotection sequence starting from ($R_p$)-**1** (see Scheme 3, for details see the Supporting Information).

Both the ligand precursors (**2a**-**f**) and the deprotected ferro-salen ligands (**3a**-**f**) were fully characterized by NMR, IR and elemental analyses. As expected, the IR and NMR-data obtained for the respective enantiomers is in good agreement, in addition the




**Scheme 2.** Synthesis of the ($S_p$)-ligands series. *i*) ethylenediamine, EtOH, 78 °C (99%); *ii*) (*S*,*S*)-1,2-cyclohexanediamine, PTSA, toluene, 60 °C (83%); *iii*) (*R*,*R*)-1,2-cyclohexanediamine, PTSA, toluene, 60 °C (93%); *iv*) $Et_3N{\cdot}(HF)_3$, thf, r.t. (60–67%).