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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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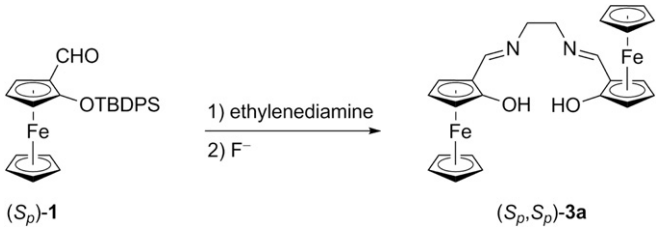


Scheme 1. Synthesis of the "ferro-salen" ligand (S_p,S_p)-**3a** starting from the hydroxyferrocene-derivative (S_p)-**1**.

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.

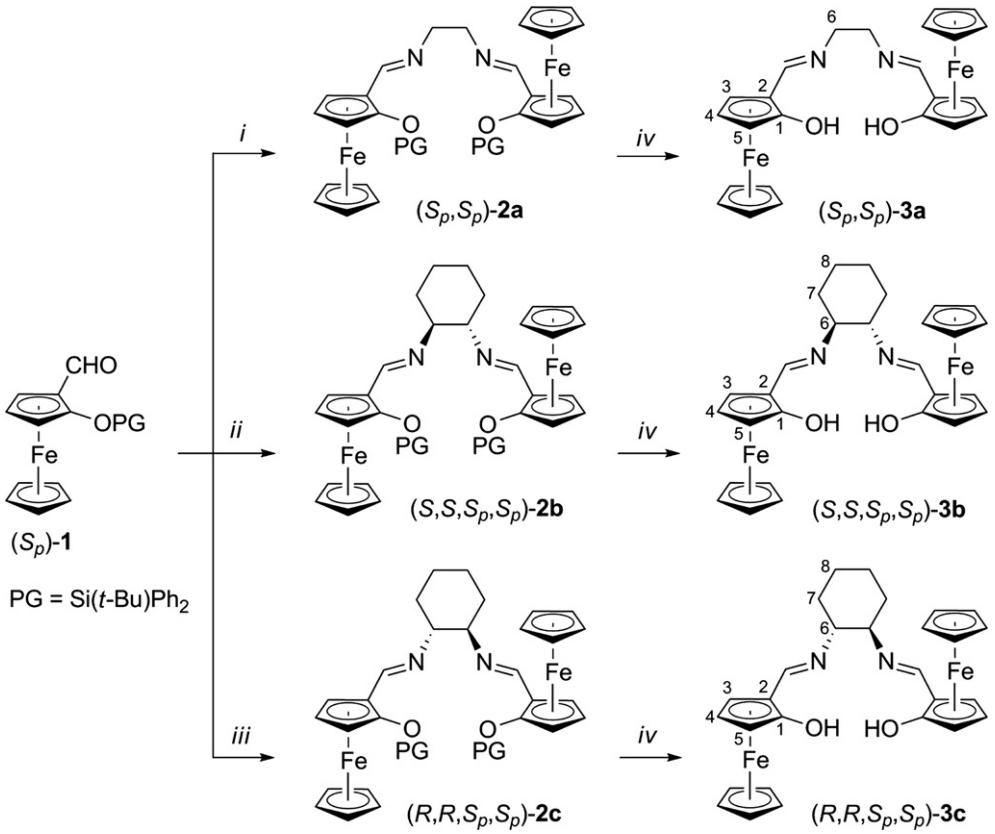
2. Results and discussion

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

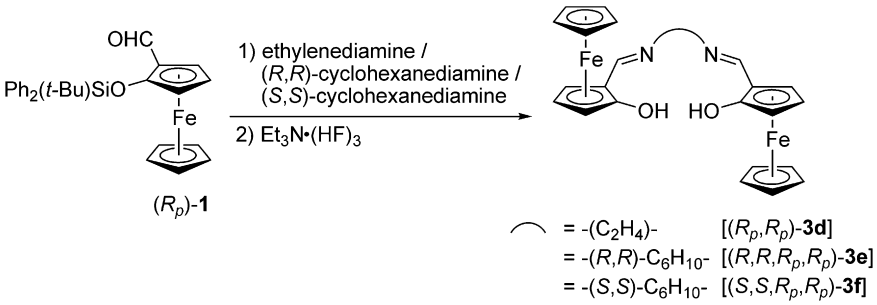
The synthesis of the "ferro-salen" ligands in the (S_p)-series started from the enantiomerically pure 2-siloxyferrocene carbaldehyde derivate (S_p)-**1**, which is available in a four-step synthesis [14] starting from the chiral ferrocenyl acetal that had been developed by Kagan et al. [15]. The synthesis 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%).



Scheme 3. Synthesis of the (R_p)-ligands series.

optical rotations determined for all compounds clearly indicate the successful formation of the six pairs of optical antipodes (e.g. $[\alpha]_D^{20}$ ((S_p,S_p)-**3a**) = −2120°, $[\alpha]_D^{20}$ ((R_p,R_p)-**3d**) = +2180°, for details see the Experimental section).

As can be seen from the corresponding NMR-spectra, all ligands exhibit a C_2-symmetric structure in solution, resulting in the observation of a single set of resonances for the ferrocene-subunits. For example, the ethylene-bridged ligands **3a/d** display a set of three resonances for the disubstituted C_5H_3-subunits in the ^{1}H NMR (δ 4.40 (H-3), 3.63 (H-4), 3.74 (H-5), in [D_6]-benzene, for the numbering Scheme see Scheme 2), in addition the unsubstituted Cp-units give rise to a singlet at δ 4.07. In the ^{13}C NMR spectrum, the resonances for the cyclopentadienyl units appear in the typical area (δ 64.0 (C-2), 58.3 (C-3), 62.8 (C-4), 62.2 (C-5), 70.1 (Cp)), with exception of the resonance for the carbon atoms bearing the hydroxy-groups (C-1), which is significantly shifted to lower field (δ 127.3). The corresponding OH-protons show a broad low field resonance at δ 9.41, the signal of the CHN-group can be found at δ 7.87 (^{1}H) and 167.7 (^{13}C), respectively. The ethylene-linker gives rise to two signals resulting from the diastereotopic geminal methylene protons, which can be found at δ 3.28 (H-6) and δ 3.15 (H-6′, corresponding ^{13}C NMR resonance: δ 60.7).

The cyclohexylene-bridged ligands (**3b**/**c**/**e**/**f**) show similar overall NMR-patterns. Yet, the pairwise diastereotopic ligands show distinct chemical shift differences, allowing a differentiation between the like- [(*S*,*S*,S_p,S_p)-**3b**/(*R*,*R*,R_p,R_p)-**3e**] and unlike- [(*R*,*R*,S_p, S_p)-**3c**/(*S*,*S*,R_p,R_p)-**3f**] diastereomers. The CHN-protons (in [D_2]-dichloromethane) can be found at δ 8.49 (like) and δ 8.26 (unlike) in the ^{1}H NMR. The unsubstituted Cp-rings give resonances at δ 4.14 (like) and δ 4.07 (unlike), with the signals for the protons of the substituted C_5H_3-unit being in the same area (δ 4.35/3.89/4.08 (like) and δ 4.31/3.81/3.98 (unlike)). The methylene units of the respective (*S*,*S*)- or (*R*,*R*)-cyclohexylene fragments give rise to partly separated signals at high field (δ 1.93–1.49 (H-7/8)), while the methine protons (H-6) can be found at δ 3.40 (like) and δ 3.14 (unlike).

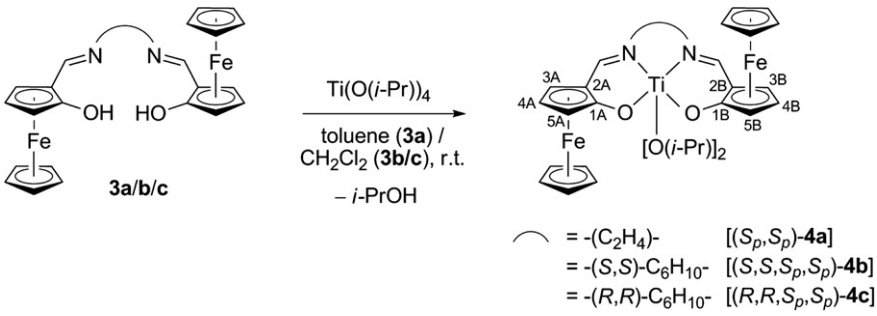
2.2. Synthesis and characterization of the (ferro-salen) Ti and Al metal complexes

In order to study the coordination chemistry of the newly developed ferro-salen ligands, we have used all three isomers of the (S_p)-series for the construction of corresponding mononuclear (ferro-salen) metal complexes. For this purpose, both the ethylene-bridged ligand (S_p,S_p)-**3a** and the diastereomeric cyclohexylene-bridged ligands (*S*,*S*,S_p,S_p)-**3b** and (*R*,*R*,S_p,S_p)-**3c** were reacted with suitable titanium- and aluminum metal precursors, with the aim of generating chiral ferro-salen metal complexes suitable for asymmetric *Lewis*-acid catalysis.

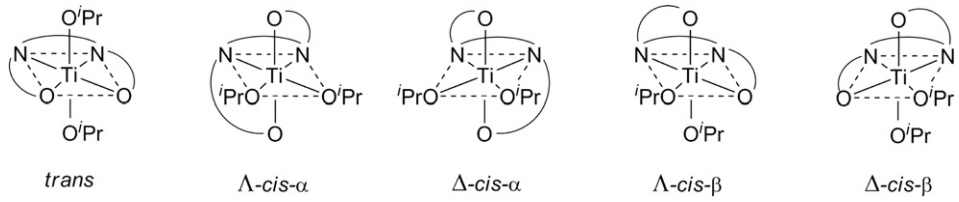
Reaction of the ligands **3a**/**b**/**c** with an equimolar amount of titanium tetraisopropoxide led to the formation of the corresponding (ferro-salen)-bisisopropoxytitanium complexes by liberation of two equivalents of isopropanol (see Scheme 4). Simple removal of all volatiles from the reaction mixtures gave the titanium complexes (**4a**/**b**/**c**) as highly air-sensitive, deep-red solids in good yields (81–86%).

The coordination of the tetradentate ferro-salen ligands to the bisisopropytitanium fragment allows the formation of several pseudo-octahedral coordination isomers, namely the formation of *trans*-, *cis*-α and *cis*-β structures [17]. The latter two of these isomers possess an octahedrally chiral metal atom, which can result in the formation of the corresponding Λ- and Δ-isomers, which in this case would produce diastereoisomers due to the chiral nature of the ferro-salen ligand framework. This gives rise to a total of five different diastereomeric coordination isomers, which are depicted in Scheme 5.

The NMR-analysis of the three Ti-complexes **4a**/**b**/**c** revealed the formation of selected isomers in all cases. As for the ethylene-bridged Ti-complex (S_p,S_p)-**4a**, two different isomers could be observed, which were found in an approximate ratio of 1.2:1 in [D_6]-benzene solution. The minor isomer exhibits a C_2-symmetric structure, thus indicating a *trans*- or a *cis*-α complex geometry. Only a single set of resonances can be found for the ferrocene-subunits,



Scheme 4. Synthesis of the bisisopropoxy–titanium complexes **4a**/**b**/**c**.



Scheme 5. Schematic representation of the possible octahedral isomers of complexes **4a**/**b**/**c**.

giving rise to the typical signals for the ferrocene units in the ^{1}H NMR (δ 7.69 (CHN), 4.34 (H-3), 3.93 (H-4), 3.99 (H-5), 4.19 (Cp)). Accordingly, three signals can be found for the Ti-bound isopropoxy ligands, originating from the methine (δ 4.39, 2 H) and the diastereotopic geminal methyl groups (δ 1.06, 1.03, each 6 H), respectively.

In contrast to this, the major isomer in solution has a lower symmetry (C_1), which results in the appearance of clearly separated signals for the both ferrocenyl-subunits (δ 7.81/7.71 (CHN$^{A/B}$), 4.22/4.32 (H-3$^{A/B}$), 3.86/3.80 (H-4$^{A/B}$), 4.02/3.89 (H-5$^{A/B}$)) and the isopropoxy-ligands (δ 5.17/4.93 (CH), 1.51, 1.40, 1.31, 1.03 (CH_3)). The C_1-symmetry observed for this isomer in solution would be in agreement with a *cis*-β type structure in either Λ- or Δ-configuration. This hypothesis is supported by an X-ray crystal structure analysis of a partial hydrolysis product of (S_p,S_p)-**4a**, which features a Ti_2O_2-core ligated by two intact ferro-salen units in a (*cis*-β)-(S_p,S_p,Δ)-configuration (as depicted in an earlier communication [13] and not shown again within this account). The hydrolysis product is thus presumably formed by partial hydrolysis of the C_1-symmetric major isomer in solution, which in turn can tentatively be assigned as the (*cis*-β)-(S_p,S_p,Δ)-isomer of **4a**.

In contrast to the observed formation of two different isomers for the ethylene-bridged complex **4a**, the cyclohexylene-substituted derivatives **4b**/**c** each show the selective formation of only one isomer in solution. As observed by NMR ([D$_2$]-dichloromethane), the like-complex (*S*,*S*,S_p,S_p)-**4b** displays a C_2-symmetric structure in solution, once again giving rise to only one set of resonances for both the ferrocene-subunits and the isopropoxy-ligands (for details see the Supporting Information). The methine-protons of the cyclohexylene backbone (H-6) can be found at δ 3.20 in the ^{1}H NMR, while the respective methylene protons (H-7, H-8) give rise to partly separated resonances in the area of δ 2.52–1.43 (respective ^{13}C-resonances: δ 67.0 (C-6), 29.6 (C-7), 24.9 (C-8)). The unlike-complex (*R*,*R*,S_p,S_p)-**4c** is also generated as a single isomer, albeit displaying a C_1-symmetry in solution ([D$_2$]-dichloromethane). Most strikingly, this leads to the observation of two resonances for the protons H-6$^{A/B}$, which are separated by nearly 2 ppm in the ^{1}H NMR (δ 4.59 (H-6^A), 2.67 (H-6^B). Accordingly, the ferrocenylimino-groups also show separated sets of signals (e.g. δ 8.34/8.32 (CHN$^{A/B}$)), as do the Ti-(O-^{i}Pr) ligands (e.g. δ 4.90/4.50 ($CH(CH_3)_2$)$^{1/2}$), for details see the Supporting Information).

These findings indicate that the octahedral geometry around the central Ti-atoms is strongly influenced by the configuration of the linking unit in the ferro-salen ligands. While the conformational flexibility of the ethylene-linker in complex (S_p,S_p)-**4a** allows for the formation of two different isomers, the rigidity of the cyclohexylene-units in **4b**/**c** results in the selective generation of only one isomer in each case. While the complex (*S*,*S*,S_p,S_p)-**4b** adopts a C_2-symmetric structure, thus having either a *trans*- or a *cis*-α-configuration, the C_1-symmetric diastereomeric system (*R*,*R*,S_p,S_p)-**4c** seems to possess a *cis*-β-structure. This assumption was confirmed by an X-ray single crystal structure analysis of (*R*,*R*,S_p,S_p)-**4c**, which shows a distorted *cis*-β-type configuration of the octahedrally coordinated Ti-center (see Fig. 1, for selected bond lengths see the Supporting Information). The complex features a Δ-configuration of the central Ti-atom, giving compound **4c** as a single diastereoisomer (as analogously observed in solution) in an overall (*cis*-β)-(*R*,*R*,S_p,S_p, Δ)-configuration [18,19].

The isopropoxy-ligands can be found in a *cis*-arrangement (angle O2A–Ti–O2B 91.8(1)°), with one ligand being *trans* to an imino-nitrogen (angle O2A-Ti-N1B 171.1(1)°) and the other isopropoxy-group *trans* to an oxygen of a hydroxyferrocene subunit (angle O2B-Ti-O1A 169.2(1)°). Only one of the six-membered chelate rings formed by the hydroxyferrocene carbaldimine units adopts a nearly planar conformation (dihedral angles C1B–C2B–O1B–Ti = −2.9(4)°, C2B–O1B–Ti–N1B = −6.7(2)°), while the other chelate ring is strongly distorted from planarity (dihedral angles C1A–C2A–O1A–Ti = 30.8(3), C2A–O1A–Ti–N1A = −44.5(2)°).

The ferro-salen ligands **3a**/**b**/**c** were furthermore used for the construction of pentacoordinate methylaluminum complexes. Reaction with a stoichiometric amount of trimethylaluminum gave the corresponding (ferro-salen)-methylaluminum complexes **5a**/**b**/**c** (see Scheme 6), which were isolated as pink solids in good yields (73–96%).

In the ^{1}H NMR spectrum, the successful generation of the monomethyl–aluminum complexes can be deduced from the distinct resonances for the corresponding methyl groups, which can be found as singlets at δ −0.46 (**5a**, in [D$_6$]-benzene), −0.92 (**5b**) and −1.01 (**5c**, both in [D$_2$]-dichloromethane). The AlMe-fragment additionally leads to breaking the C_2-symmetry of the free ligand set, rendering C_1-symmetric (ferro-salen)AlMe complexes in all cases. For example, clearly separated signals for the CHN-protons (δ 7.62/7.60 (**5a**), 8.55/8.36 (**5b**), 8.63/8.22 (**5c**), each 1H) or the Cp-protons ((δ 4.18/3.96 (**5a**), 4.28/4.21 (**5b**), 4.14/3.96 (**5c**), each 5 H) can be found in the corresponding ^{1}H NMR spectra. This is also true for the respective C_5H_3-units and for the bridging alkylen-fragments, as seen for example for the ethylene-unit in **5a**, which gives rise to four separated signals for the two inequivalent pairs of diastereotopic

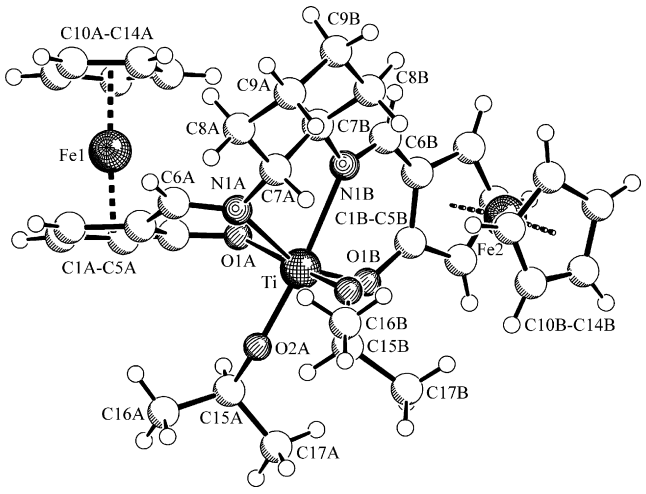
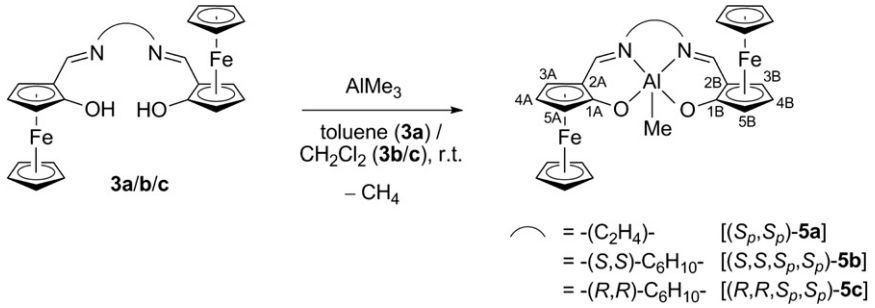


Fig. 1. A view of the molecular structure of the Ti-complex (*R*,*R*,S_p,S_p)-**4c** in the crystal.



Scheme 6. Synthesis of the methylaluminum complexes **5a**/**b**/**c**.

geminal methylene protons (δ 3.21, 2.47 (H-6^{A}), 2.75, 2.53 (H-6^{B}), respective ^{13}C NMR resonances: δ 54.7 (C-6^{A}), 54.8 (C-6^{B})), for more details concerning all complexes see the Supporting Information).

The solid state structures of the cyclohexylene-bridged complexes (*S*,*S*,S_p,S_p)-**5b** and (*R*,*R*,S_p,S_p)-**5c** were analyzed by X-ray crystal structure analyses using small crystalline material of just sufficient quality (obtained by slow diffusion of pentane into solutions of **5b**/**c** in tetrahydrofuran). Due to the poor quality of the crystals of the Al-complexes investigated by X-ray diffraction in this study (both **5b**/**c** and **6b**/**c**), we will not discuss the bonding parameters in detail. However, a table of tentative bond lengths and angles is provided within the Supporting Information.

In the crystal both **5b** and **5c** feature pentacoordinate central Al-atoms. In both cases, the identical (S_p)-configuration of the planar-chiral ferrocene-subunits leads to anti-orientations of the pairs of Fe(C_5H_5)-fragments with respect to the central (N_2O_2)Al-unit, with the Al-methyl groups being in the apical position of the central distorted square-pyramidal coordination polyeders. Complex **5b**, featuring the ferro-salen ligand framework in an (*S*,*S*,S_p,S_p)-configuration, only shows a slight distortion from an ideal square-pyramidal geometry, the O1A–O1B–N1B–N1A unit is nearly planar and the Al-atom is found slightly above this plane (see Fig. 2 left). The overall coordination geometry around the central Al-atom can also be expressed by means of the τ-value, which has been developed for the description of the geometry of pentacoordinate species [20]. For complex (*S*,*S*,S_p,S_p)-**5b**, the resulting τ-value of 0.10 also indicates only a slight distortion of the complex geometry from a perfect square-pyramidal arrangement.

In contrast to this, the (*R*,*R*,S_p,S_p)-configuration of the ligand framework in complex **5c** leads to a considerably stronger distortion of the complex geometry. The angle O1A–Al–N1B is significantly enlarged while the angle O1B–Al–N1A has decreased, which also leads to a strong tilting of one of the ferrocene-subunits (subunit B, see Fig. 2). This can be described as a distortion of the coordination geometry towards a trigonal-bipyramidal arrangement, which is also expressed by the larger τ-value of 0.45 for complex (*R*,*R*,S_p,S_p)-**5c**.

In order to generate the related (ferro-salen)-chloroaluminum complexes, the ligands **3a**/**b**/**c** were reacted with diethylaluminumchloride, which gave the corresponding mononuclear chloroaluminum-complexes by elimination of two equivalents of ethane (see Scheme 7). Simple removal of all volatiles from the reaction mixtures gave complexes **6a**/**b**/**c** as pink solids in good yields (80–86%).

The structures of the diastereomeric chloroaluminum complexes (*S*,*S*,S_p,S_p)-**6b** and (*R*,*R*,S_p,S_p)-**6c** could be verified by X-ray crystal structure analyses (see Fig. 3). The central Al-atoms are found to be pentacoordinate, with the chloro-ligands occupying the apical positions of the distorted square-pyramidal coordination environment (for details see the Supporting Information).

The complex geometries are very similar to those of the corresponding methylaluminum complexes (**5b**/**c**), indicating that the conformation of the rigid ferro-salen ligand backbones is only slightly altered upon variation of the apical Al-ligand. The (*S*,*S*,S_p,S_p)-configuration of the ferro-salen ligand in complex (*S*,*S*,S_p,S_p)-**6b** leads to a square-pyramidal complex structure which is only slightly distorted ($\tau = 0.14$), while the diastereomeric system (*R*,*R*,S_p,S_p)-**6b** shows a significantly larger extent of distortion towards a trigonal-bipyramidal coordination geometry. This is also expressed by the corresponding τ-value of 0.50, so that the solid state structure of **6c** may be described as an intermediate between a square–pyramidal and a trigonal-bipyramidal geometry.

According to the solid state structures of complexes **6b** and **6c**, a C_1-symmetric structure would also be expected in solution. Yet,

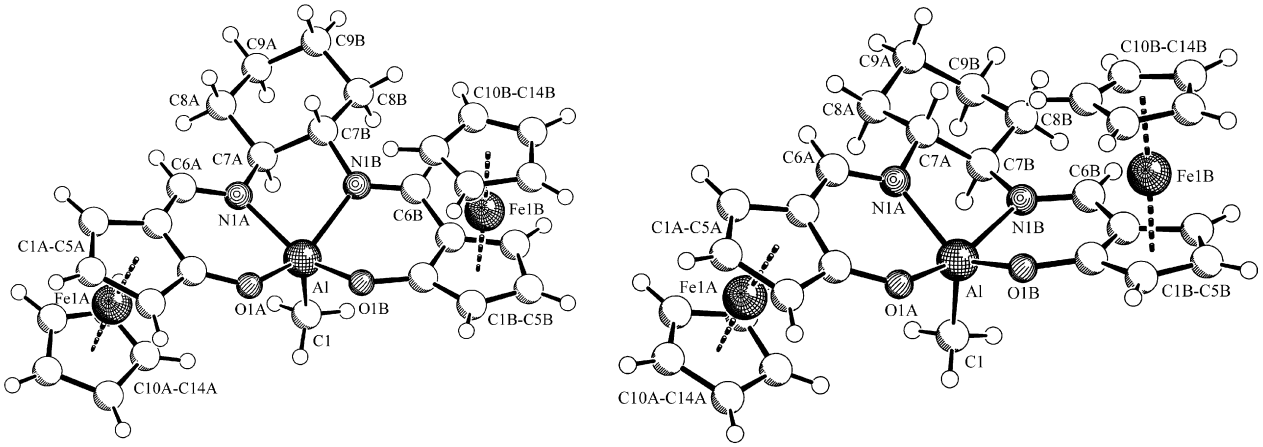
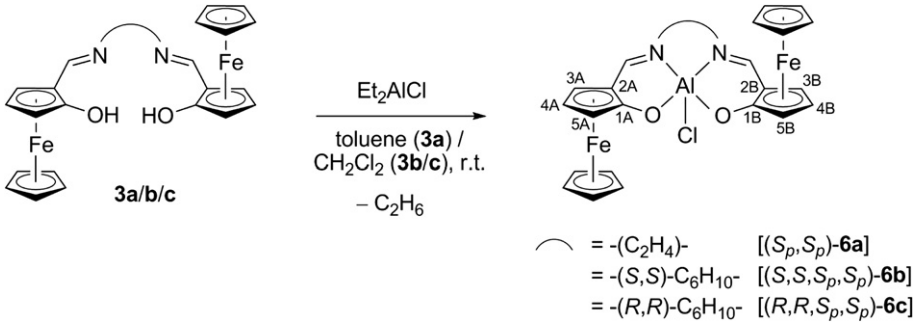


Fig. 2. Molecular structures of the methylaluminum complexes (*S*,*S*,S_p,S_p)-**5b** (left) and (*R*,*R*,S_p,S_p)-**5c** (right).



Scheme 7. Synthesis of the chloroaluminum-complexes **6a**/**b**/**c**.

the NMR analysis of all chloroaluminum-complexes (**6a**/**b**/**c**) reveals the existence of a dynamic equilibrium process, which results in the coalescence of the expected two signal sets into a single signal set (in [D_2]-dichloromethane), indicating pseudo C_2-symmetric structures in solution at temperatures around room temperature.

Upon lowering of the temperature to −85 °C, the equilibration processes can be slowed down, leading to the observation of the expected C_1-symmetric complex geometries in solution. For all complexes (**6a**/**b**/**c**), this gives separated signals for the two ferrocenylimino-subunits, most clearly seen from the corresponding CHN-signals (δ 8.60/8.54 (**6a**), 8.53/8.40 (**6b**), 8.71/8.33 (**6c**)) and the resonances arising from the unsubstituted C_5H_5-fragments (δ 4.20/4.08 (**6a**), 4.19/4.06 (**6b**), 4.21/3.96 (**6c**)).

We tentatively assign the observed equilibration process to a dissociation/reassociation process of the chloride-ligands, deduced from the fact that the nearly isostructural methylaluminum complexes show no such equilibration process in the same temperature range. The ionic character of the Al–Cl bond might favour a ligand dissociation, a process which has also been observed for related (salen)AlCl-complexes upon addition of additional *Lewis*-basic ligands [21]. A fast dissociation/reassociation process would lead to an equilibration between two identical C_1-symmetric structures, thus giving an averaged C_2-symmetric structure, as observed for complexes **6a**/**b**/**c** at room temperature. The activation barrier for the equilibrium process is almost identical for the ethylene-bridged complex (S_p,S_p)-**6a** and the cyclohexylene-bridged system (S,S,S_p,S_p)-**6b** ($\Delta G^{\ddagger} = 11.0 \pm 0.3$ kcal/mol (**6a**), 10.8 ± 0.2 kcal/mol (**6b**), as determined by variable-temperature NMR-studies). The corresponding activation barrier for complex (R,R,S_p,S_p)-**6c** is significantly larger ($\Delta G^{\ddagger} = 14.1 \pm 0.1$ kcal/mol), which is in agreement with the higher coalescence temperature observed for complex **6c** in the ^{1}H NMR (see Table 1, for details see the Supporting Information).

2.3. Asymmetric trimethylsilylcyanation reactions

In order to evaluate the potential use of the new (ferro-salen)-metal complexes in asymmetric *Lewis*-acid catalyzed reactions, we decided for the investigation of their applicability in the asymmetric trimethylsilylcyanation of benzaldehyde. Due to the high synthetic value of the resulting cyanohydrins [22] as chiral building blocks in asymmetric synthesis, the development of chiral catalysts for the asymmetric addition of cyanide to carbonyl derivatives has been in the focus of numerous catalytic surveys [23], which amongst others has led to the identification of salen–titanium [24] and salen–aluminum [25] complexes as highly potent catalysts for this reaction type.

The use of the (ferro-salen)-titanium complexes **4** for the asymmetric cyanation of benzaldehyde only led to the desired cyanohydrin **7** (see Scheme 8) in poor enantiomeric excesses, even with high catalysts loadings (20%), independent of the catalyst system (**4a**/**b**/**c**) used in the reaction. Thus, only the methylaluminum (**5a**/**b**/**c**) and chloroaluminum-complexes (**6a**/**b**/**c**) were used for the further investigations, with a special focus on the influence of the different sources of chirality present in the (ferro-salen)-based catalysts on the outcome of addition reaction.

The catalytic reactions were performed by reacting benzaldehyde with an excess of trimethylsilylcyanide (2.5 equivalents) in dichloromethane solution, yielding the corresponding O-protected cyanohydrin **7** after workup. We found that the best results were obtained by carrying out the reactions at low temperature (−20 °C) with catalyst loadings of 5% (for **5a**/**b**/**c**) or 1% (for **6a**/**b**/**c**), respectively. In addition, the use of additives, such as phosphine

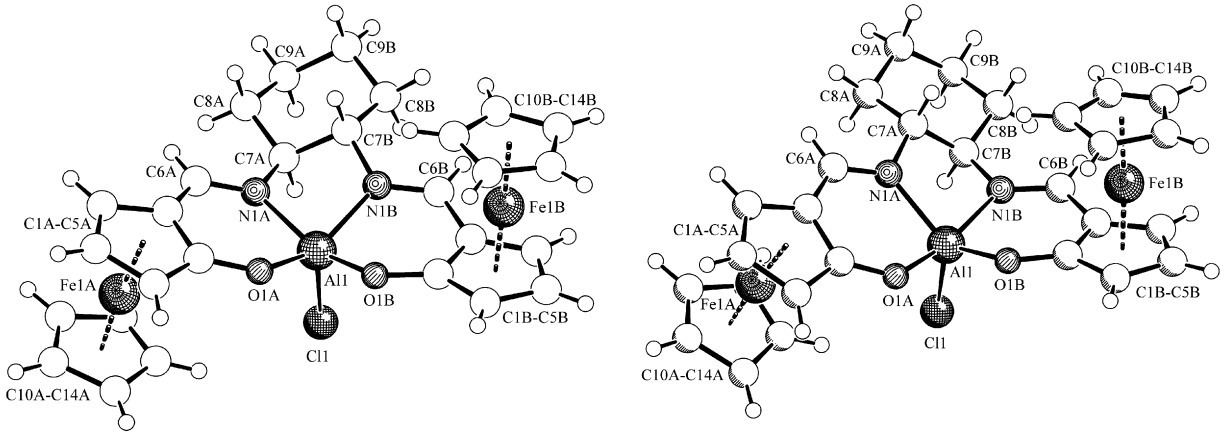


Fig. 3. Molecular structures of the chloroaluminum-complexes (S,S,S_p,S_p)-**6b** (left) and (R,R,S_p,S_p)-**6c** (right).

Table 1
Calculation of the activation barriers for the dynamic equilibrium process of complexes **6a**/**b**/**c** in solution.

Complex	Coalescence temperature T_c[a]	$\Delta G^{\ddagger}$ (kcal/mol)
(S_p,S_p)-**6a**	238 K	11.0 ± 0.3
(*S*,*S*,S_p,S_p)-**6b**	228 K	10.8 ± 0.2
(*R*,*R*,S_p,S_p)-**6c**	298 K	14.1 ± 0.1

[a] Cp-resonance, ^{1}H NMR, CD_2Cl_2.

oxides, led to a significant increase of the observed enantioselectivities, as found earlier by other groups [25]. The best selectivities were obtained when using trioctylphosphine oxide, with the ideal amount of additive depending on the type of catalyst used in the addition reaction (100% for complexes **5a**/**b**/**c**, 5% for complexes **6a**/**b**/**c**).

These optimized conditions were subsequently applied for all isomers of the respective complexes. It was found that the overall reactivity of the methylaluminum-complexes **5** was lower compared to that of the chloroaluminum-complexes **6**, as indicated by the longer reaction times needed for full consumption of benzaldehyde (followed by TLC analysis). Yet, the desired protected cyanohydrin **7** could be isolated in >90% yield in almost all cases; only for complex (*R*,*R*,S_p,S_p)-**6c** no full conversion could be achieved, leading to a lower isolated yield (65%).

The enantioselectivity of the addition reaction was found to be nearly independent of the nature of the Al-bound ligand (Me/Cl), as very similar results were obtained for the pairs of complexes bearing the same ferro-salen ligand set (**5**/**6a**, **5**/**6b** and **5**/**6c**, respectively). Using the ethylene-bridged (ferro-salen)-aluminum complexes, both featuring the planar-chiral ferrocene units as the sole source of chirality, the cyanohydrin **7** could be isolated in good optical purity (53% *ee* for **5a**, 62% *ee* for **6a**, see Table 2), in both cases giving the (*R*)-isomer of the product as the major isomer. This indicates a significant chiral induction of the planar-chiral ferrocene units and might suggest that the enantioselectivity of the addition reaction might be further improved by replacing the achiral ethylene-bridge by a chiral cyclohexylene-unit, as present in complexes **5**/**6b** and **5**/**6c**. Unfortunately, the introduction of this additional element of chirality into the ferro-salen ligand backbone did not lead to a significant increase in enantioselectivity under the conditions used within this investigation. Interestingly, the use of complexes (*S*,*S*,S_p,S_p)-**5**/**6b** led to very similar enantioselectivities compared to those observed for catalysts **5**/**6a** (59% *ee* for **5b**, 54% *ee* for **6b**), once again giving (*R*)-**7** as the main product. In contrast to this, the use of the diastereomeric complexes (*R*,*R*,S_p,S_p)-**5**/**6c** led to an inversion of the selectivity, now favouring the formation of the (*S*)-isomer of **7** (45% *ee* for **5c**, 56% *ee* for **6c**). While the similar selectivities for the pairs of complexes featuring the ferro-salen ligand in an identical configuration (**5**/**6b** and **5**/**6c**) are not surprising keeping in mind their very similar solid state structures, it is rather surprising that no significant *matched*/*mismatched* behaviour was observed for the diastereomeric pairs of complexes (**5b**/**c** and **6b**/**c**). Although the planar-chiral ferrocene units seem to possess a considerable chiral induction when combined with an achiral linking unit (as found for complexes **5**/**6a**), the enantioselectivity of the cyanation reaction when catalyzed by the cyclohexylene-bridged complexes seems to be mainly determined by the configuration of the diamine-backbone. This might be indicative of different complex geometries of the ethylene-bridged systems as compared to the cyclohexylene-bridged analogues, leading to a different influence of the planar-chiral ferrocene units on the overall enantioselectivity of the cyanide addition.

Table 2
Results of the asymmetric addition of TMSCN[a] to benzaldehyde catalyzed by complexes **5**/**6**.

No	Catalyst	Catalyst loading	Oct_3PO	React. time	Yield (isol.)	*ee*[b] (conf.)[c]
1	(S_p,S_p)-**5a**	5%	100%	3 d	90%	53% (*R*)
2	(*S*,*S*,S_p,S_p)-**5b**	5%	100%	3 d	90%	59% (*R*)
3	(*R*,*R*,S_p,S_p)-**5c**	5%	100%	6 d	97%	45% (S)
4	(S_p,S_p)-**6a**	1%	5%	1 d	99%	62% (*R*)
5	(*S*,*S*,S_p,S_p)-**6b**	1%	5%	1 d	99%	54% (*R*)
6	(*R*,*R*,S_p,S_p)-**6c**	1%	5%	3 d	65%	56% (*S*)

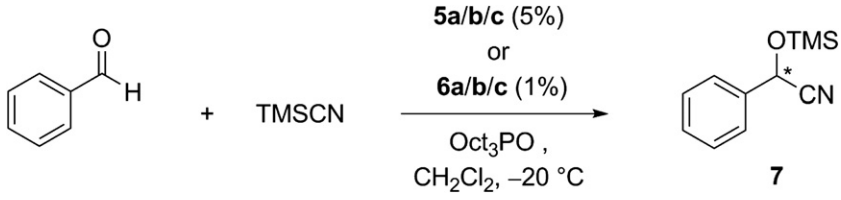
[a] 2.5 equivalents of TMSCN were used.
[b] Enantiomeric excesses were determined by GC-analysis using a chiral β-cyclodextrin stationary phase.
[c] The absolute configuration was determined after hydrolysis with 2N HCl by comparison of the optical rotation with literature values for mandelonitrile [25a].

3. Some conclusions

In summary, we have demonstrated a viable synthetic route for a series of new ferrocene-based salen ligands, which are the first examples of salen-ligands based on a planar-chiral hydroxyferrocene moiety. The modular synthetic approach allows the introduction of different diamines as the linking unit, in this case giving rise to both ethylene- and cyclohexylene-bridged ligands, the latter of which possess a combination of planar and central chirality. In addition, the availability of both enantiomers of the starting hydroxyferrocene carbaldehyde derivative **1** further broadens the scope of chiral ligands which are accessible by this route, making both enantiomeric series (**3a**/**b**/**c** and **3d**/**e**/**f**) of the ferro-salen ligands available.

The three ligands **3a**/**b**/**c** have shown to be ideal precursors for the construction of a series of chiral metal complexes (**4**–**6**), which are easily accessible in high yields upon reaction of the free ligands with corresponding metal precursors. The analysis of the resulting metal complexes has shown that especially the conformationally rigid cyclohexylene-bridged ligands show high selectivities for the formation of homoisomeric metal complexes, which is one prerequisite for the use of these metal complexes as catalysts for highly enantioselective asymmetric transformations.

In addition, it has been shown that the generated metal complexes can serve as moderately selective catalysts for the asymmetric addition of trimethylsilylcyanide to benzaldehyde. Interestingly, the ethylene-bridged complexes **5**/**6a** allow a similar degree of chiral induction as compared to the more rigid cyclohexylene-bridged isomers, which indicates that the introduction of an element of planar chirality in salen-type ligands may in principle



Scheme 8. Asymmetric trimethylsilylcyanation of benzaldehyde using complexes **5**/**6**.

be of high value for asymmetric catalysis. The future development of these "ferro-salen" ligands will include modifications of the ferrocene-subunits (e.g. the introduction of controlling substituents in vicinity to the donor functionalities), but may also be accomplishable by the use of different linking diamine-units (both chiral and achiral). We hope that this strategy will allow us to further improve this new generation of salen-type metal catalysts, extending the scope of transformations catalyzed by these complexes while allowing higher levels of asymmetric induction.

4. Experimental section

4.1. General information

All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas atmosphere (Argon) by using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Compounds (S_p)-**1** [14], (R_p)-**1** [14], (S_p,S_p)-**2a** [13], (S_p,S_p)-**3a** [13], (S_p,S_p)-**4a** [13], (S_p,S_p)-**5a** [13] and (S_p,S_p)-**6a** [13] were prepared according to literature procedures. For the analytical data of (S_p,S_p)-**2a** and (S_p,S_p)-**3a** see the Supporting Information.

The following instruments were used for physical characterization of the compounds: melting points: TA-instruments DSC Q-20; elemental analyses: Foss–Heraeus CHNO-Rapid; GC: Agilent 6890N gas chromatograph, Supelco Beta-Dex 120 column; IR: Varian 1300 FT-IR; NMR: Varian UNITY plus NMR spectrometer; Varian INOVA 500; Polarimetric measurements: Perkin–Elmer Polarimeter.

X-ray crystal structure determinations: Data sets were collected with Nonius KappaCCD diffractometers, in case of Mo-radiation equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, Methods in Enzymology 276 (1997) 307–326), absorption correction SORTAV (R.H. Blessing, Acta Cryst. A51 (1995) 33–37; R.H. Blessing, J. Appl. Cryst. 30 (1997) 421–426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, Acta Cryst. A59 (2003) 228–234), structure solution SHELXS-97 (G.M. Sheldrick, Acta Cryst. A46 (1990) 467–473), structure refinement SHELXL-97 (G.M. Sheldrick, Acta Cryst. A64 (2008) 112–122), graphics SCHAKAL (E. Keller, Uni. Freiburg (1997)).

4.2. Synthesis of the ferro-salen ligands in the (S_p)-series

4.2.1. Preparation of (S,S,S_p,S_p)-**2b**

The aldehyde (S_p)-**1** (3.94 g, 8.41 mmol, 2 eq), (S,S)-1,2-cyclohexanediamine (480 mg, 4.21 mmol, 1 eq) and *p*-toluenesulfonic acid (80.1 mg, 0.421 mmol, 0.1 eq) were dissolved in toluene (40 ml). Activated molecular sieves (4 Å, ca. 10 g) were added and the mixture was heated to 60 °C for 4 h. The solvent was removed and pentane (100 ml) was added. The mixture was heated to reflux and the hot solution was isolated by cannula filtration. Removal of the solvent gave the bisimine (S,S,S_p,S_p)-**2b** as an orange solid (3.53 g, 3.48 mmol, 82.6%). M.p.: 168 °C (DSC); $[\alpha]_D^{20} = +489$ ($c = 0.995$, CH_2Cl_2); ^{1}H NMR (500 MHz, C_6D_6, 298 K, TMS): $\delta = 8.87$ (s, 2H, C*H*N), 8.00 (m, 4H, *o*-Ph), 7.65 (m, 4H, *o*-Ph′), 7.29–7.23 (m, 6H, *m*-Ph, *p*-Ph), 7.10 (m, 2H, *p*-Ph′), 7.05 (m, 4H, *m*-Ph′), 4.64 (dd, $^3J = 2.7$ Hz, $^4J = 1.5$ Hz, 2H, H-3), 4.07 (s, 10H, Cp), 3.68 (dd, $^3J = 2.7$ Hz, $^4J = 1.5$ Hz, 2H, H-5), 3.62 (m, 2H, H-6), 3.46 (t, $^3J = 2.7$ Hz, 2H, H-4), 1.97 (m, 2H, H-7), 1.94 (m, 2H, H-7′), 1.74 (m, 2H, H-8), 1.43 (m, 2H, H-8′), 1.16 (s, 18H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K, TMS): $\delta = 157.3$ (*C*HN), 136.2 (*o*-Ph), 135.9 (*o*-Ph′), 134.1 ($^1J_{SiC} = 75.1$ Hz, *i*-Ph), 132.6 ($^1J_{SiC} = 73.6$ Hz, *i*-Ph′), 130.4 (*p*-Ph), 130.0 (*p*-Ph′), 128.2 (*m*-Ph′), 128.1 (*m*-Ph), 122.7 (C-1), 76.0 (C-6), 71.0 (C-2), 70.5 (Cp), 62.9 (C-4), 61.7 (C-3), 61.3 (C-5), 34.3 (C-7), 27.1 (C(*C*H$_3$)$_3$), 25.0 (C-8), 19.7 ($^1J_{SiC} = 68.9$ Hz, *C*(CH$_3$)$_3$); IR (KBr): ν bar = 1639 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{60}H_{66}Fe_2N_2O_2Si_2$ (1015.04 g/mol): C, 71.00; H, 6.55; N, 2.76; found: C, 70.70; H, 6.77; N, 2.60.

4.2.2. Preparation of (R,R,S_p,S_p)-**2c**

The aldehyde (S_p)-**1** (4.04 g, 8.62 mmol, 2 eq), (R,R)-1,2-cyclohexanediamine (492 mg, 4.31 mmol, 1 eq) and *p*-toluenesulfonic acid (82.0 mg, 0.431 mmol, 0.1 eq) were dissolved in toluene (40 ml). Activated molecular sieves (4 Å, ca. 10 g) were added and the mixture was heated to 60 °C for 4 h. The solvent was removed and pentane (100 ml) was added. The mixture was heated to reflux and the hot solution was isolated by cannula filtration. Removal of the solvent gave the bisimine (R,R,S_p,S_p)-**2c** as an orange solid (4.07 g, 4.01 mmol, 93.0%). M.p.: 65 °C (DSC); $[\alpha]_D^{20} = +268$ ($c = 1.02$, CH_2Cl_2); ^{1}H NMR (600 MHz, C_6D_6, 298 K, TMS): $\delta = 8.74$ (s, 2H, C*H*N), 8.01 (m, 4H, *o*-Ph), 7.78 (m, 4H, *o*-Ph′), 7.28–7.23 (m, 6H, *m*-Ph, *p*-Ph), 7.18–7.14 (m, 6H, *m*-Ph′, *p*-Ph′), 4.49 (dd, $^3J = 2.7$ Hz, $^4J = 1.5$ Hz, 2H, H-3), 4.07 (s, 10H, Cp), 3.73 (dd, $^3J = 2.7$ Hz, $^4J = 1.5$ Hz, 2H, H-5), 3.66 (m, 2H, H-6), 3.49 (t, $^3J = 2.7$ Hz, 2H, H-4), 1.99 (m, 2H, H-7), 1.96 (m, 2H, H-7′), 1.78 (m, 2H, H-8), 1.45 (m, 2H, H-8′), 1.26 (s, 18H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K, TMS): $\delta = 157.6$ (*C*HN), 136.3 (*o*-Ph), 136.2 (*o*-Ph′), 134.1 (*i*-Ph), 133.0 (*i*-Ph′), 130.4 (*p*-Ph), 130.2 (*p*-Ph′), 128.07, 128.05 (*m*-Ph, *m*-Ph′), 122.2 (C-1), 75.7 (C-6), 71.2 (C-2), 70.4 (Cp), 62.8 (C-4), 62.6 (C-3), 61.7 (C-5), 34.5 (C-7), 27.1 (C(*C*H$_3$)$_3$), 25.0 (C-8), 19.9 (*C*(CH$_3$)$_3$); IR (KBr): ν bar = 1642 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{60}H_{66}Fe_2N_2O_2Si_2$ (1015.04 g/mol): C, 71.00; H, 6.55; N, 2.76; found: C, 70.57; H, 6.68; N, 2.50.

4.2.3. Preparation of (S,S,S_p,S_p)-**3b**

The protected bisimine (S,S,S_p,S_p)-**2b** (3.53 g, 3.48 mmol, 1 eq) was dissolved in toluene (100 ml). Triethylamine trihydrofluoride (374 mg, 2.32 mmol, 2/3 eq) was added and the mixture was stirred for 3 h, giving a yellow precipitate. This was isolated by removal of the mother liquor and then suspended in pentane (60 ml). Filtration and washing with pentane (2 × 10 ml) gave the diol (S,S,S_p,S_p)-**3b** as a yellow solid (1.21 g, 2.25 mmol, 64.6%). M.p.: 209 °C (DSC); $[\alpha]_D^{20} = -1650$ ($c = 0.202$, CH_2Cl_2); ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K, TMS): $\delta = 9.09$ (bs, 2H, O*H*), 8.49 (s, 2H, C*H*N), 4.35 (dd, $^3J = 2.7$ Hz, $^4J = 1.3$ Hz, 2H, H-3), 4.14 (s, 10H, Cp), 4.08 (dd, $^3J = 2.7$ Hz, $^4J = 1.3$ Hz, 2H, H-5), 3.89 (t, $^3J = 2.7$ Hz, 2H, H-4), 3.40 (m, 2H, H-6), 1.92 (m, 2H, H-7), 1.82 (m, 2H, H-8), 1.51 (m, 2H, H-7′), 1.49 (m, 2H, H-8′); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K, TMS): $\delta = 165.5$ (*C*HN), 126.7 (C-1), 70.3 (C-6), 70.0 (Cp), 64.7 (C-2), 62.7 (C-4), 62.3 (C-5), 57.8 (C-3), 32.7 (C-7), 24.1 (C-8); IR (KBr): ν bar = 1634 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{28}H_{30}Fe_2N_2O_2$ (538.24 g/mol): C, 62.48; H, 5.62; N, 5.20; found: C, 61.77; H, 5.51; N, 5.01.

4.2.4. Preparation of (R,R,S_p,S_p)-**3c**

The protected bisimine (R,R,S_p,S_p)-**2c** (4.07 g, 4.01 mmol, 1 eq) was dissolved in toluene (40 ml). Triethylamine trihydrofluoride (431 mg, 2.67 mmol, 2/3 eq) was added and the mixture was stirred for 3 h. Addition of pentane (60 ml) yielded a red precipitate, which was isolated by filtration and washed with pentane (20 ml). This gave the diol (R,R,S_p,S_p)-**3c** as a red solid (1.30 g, 2.42 mmol, 60.2%). M.p.: 199 °C (DSC); $[\alpha]_D^{20} = -2090$ ($c = 0.202$, CH_2Cl_2); ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K, TMS): $\delta = 9.23$ (bs, 2H, O*H*), 8.26 (s, 2H, C*H*N), 4.31 (m, 2H, H-3), 4.07 (s, 10H, Cp), 3.98 (m, 2H, H-5), 3.81 (t, $^3J = 2.5$ Hz, 2H, H-4), 3.14 (m, 2H, H-6), 1.93–1.84 (m, 4H, H-7, H-8), 1.68 (m, 2H, H-7′), 1.50 (m, 2H, H-8′); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K, TMS): $\delta = 165.5$ (*C*HN), 126.8 (C-1), 73.2 (C-6), 70.0 (Cp), 64.0 (C-2), 62.6 (C-4), 62.5 (C-5), 57.9 (C-3), 33.9 (C-7), 24.7

(C-8); IR (KBr): ν bar = 1626 cm^{-1} (C═N); elemental analysis calcd (%) for $C_{28}H_{30}Fe_2N_2O_2$ (538.24 g/mol): C, 62.48; H, 5.62; N, 5.20; found: C, 62.49; H, 5.76; N, 4.97.

4.3. Synthesis of the ferro-salen ligands in the (R_p)-series

4.3.1. Preparation (R_p,R_p)-**2d**

The aldehyde (R_p)-**1** (1.32 g, 2.82 mmol, 2 eq) was dissolved in dry ethanol (15 ml) and the mixture was heated to reflux until complete dissolution was achieved. Ethylenediamine (93.9 μl, 1.41 mmol, 1 eq) was added and the mixture was heated to reflux for another 30 min. The solvent was removed and pentane (10 ml) was added. Removal of the solvent *in vacuo* gave the bisimine (R_p, R_p)-**2d** as an orange solid (1.34 g, 1.39 mmol, 98.9%). M.p.: 48 °C (DSC); $[\alpha]_D^{20} = -451$ (c = 1.02, CH_2Cl_2); NMR: All NMR-data are in agreement with those for the enantiomer (S_p,S_p)-**2a**; elemental analysis calcd (%) for $C_{56}H_{60}Fe_2N_2O_2Si_2$ (960.95 g/mol): C, 69.99; H, 6.29; N, 2.92; found: C, 70.81; H, 6.68; N, 2.59.

4.3.2. Preparation (R,R,R_p,R_p)-**2e**

The aldehyde (R_p)-**1** (2.69 g, 5.74 mmol, 2 eq), (R,R)-1,2-cyclohexanediamine (328 mg, 2.87 mmol, 1 eq) and *p*-toluenesulfonic acid (54.6 mg, 0.287 mmol, 0.1 eq) were dissolved in toluene (20 ml). Activated molecular sieves (4 Å, ca. 5 g) were added and the mixture was heated to 60 °C for 4 h. The solvent was removed and pentane (80 ml) was added. The mixture was heated to reflux and the hot solution was isolated by cannula filtration. The volume of the solution was reduced to 40 ml, which resulted in precipitation of a first fraction of product (373 mg), which was isolated by filtration. The remaining mother liquor was stored at −30 °C for another two days, resulting in precipitation of a second fraction of (R,R,R_p,R_p)-**2e**, which was isolated by filtration (1.31 g, total yield 1.68 g, 1.66 mmol, 57.8%). M.p.: 162 °C (DSC); $[\alpha]_D^{20} = -488$ (c = 0.995, CH_2Cl_2); NMR: All NMR-data are in agreement with those for the enantiomer (S,S,S_p,S_p)-**2b**; elemental analysis calcd (%) for $C_{60}H_{66}Fe_2N_2O_2Si_2$ (1015.04 g/mol): C, 71.00; H, 6.55; N, 2.76; found: C, 70.96; H, 6.33; N, 2.66.

4.3.3. Preparation (S,S,R_p,R_p)-**2f**

The aldehyde (R_p)-**1** (2.50 g, 5.34 mmol, 2 eq), (S,S)-1,2-cyclohexanediamine (305 mg, 2.67 mmol, 1 eq) and *p*-toluenesulfonic acid (50.8 mg, 0.267 mmol, 0.1 eq) were dissolved in toluene (20 ml). Activated molecular sieves (4 Å, ca. 5 g) were added and the mixture was heated to 60 °C for 4 h. The solvent was removed and pentane (80 ml) was added. The mixture was heated to reflux and the hot solution was isolated by cannula filtration. Storage at −30 °C overnight resulted in precipitation of a first fraction of product (656 mg), which was isolated by filtration. The volume of the remaining mother liquor was reduced to 40 ml and the solution was stored at −30 °C for another 2 h, resulting in precipitation of a second fraction of (S,S,R_p,R_p)-**2f**, which was isolated by filtration (640 mg, total yield 1.30 g, 1.28 mmol, 48.0%). M.p.: 59 °C (DSC); $[\alpha]_D^{20} = -247$ (c = 1.01, CH_2Cl_2); NMR: All NMR-data are in agreement with those for the enantiomer (R,R,S_p,S_p)-**2c**; elemental analysis calcd (%) for $C_{60}H_{66}Fe_2N_2O_2Si_2$ (1015.04 g/mol): C, 71.00; H, 6.55; N, 2.76; found: C, 71.34; H, 6.79; N, 2.53.

4.3.4. Preparation of (R_p,R_p)-**3d**

The protected bisimine (R_p,R_p)-**2d** (1.00 g, 1.04 mmol, 1 eq) was dissolved in toluene (10 ml). Triethylamine trihydrofluoride (112 mg, 0.694 mmol, 2/3 eq) was added and the mixture was stirred for 3 h. After cannula filtration the volume of the solution was reduced to 2 ml and pentane (30 ml) was added, resulting in precipitation of the product. This was isolated by filtration and washed with pentane (2 × 5 ml). Recrystallisation from a mixture of toluene (5 ml) and pentane (50 ml) at −30 °C gave the diol (R_p,R_p)-**3d** as an orange solid (283 mg, 0.585 mmol, 56.2%). M.p.: 161 °C (DSC); $[\alpha]_D^{20} = +2180$ (c = 0.204, CH_2Cl_2); NMR: All NMR-data are in agreement with those for the enantiomer (S_p,S_p)-**3a**; elemental analysis calcd (%) for $C_{24}H_{24}Fe_2N_2O_2$ (484.15 g/mol): C, 59.54; H, 5.00; N, 5.79; found: C, 59.78; H, 5.03; N, 5.76.

4.3.5. Preparation of (R,R,R_p,R_p)-**3e**

The protected bisimine (R,R,R_p,R_p)-**2e** (1.38 g, 1.36 mmol, 1 eq) was dissolved in toluene (50 ml). Triethylamine trihydrofluoride (146 mg, 0.906 mmol, 2/3 eq) was added and the mixture was stirred for 3 h, giving a yellow precipitate. This was isolated by removal of the mother liquor and then suspended in pentane (30 ml). Filtration and washing with pentane (2 × 5 ml) gave the diol (R,R,R_p,R_p)-**3e** as a yellow solid (540 mg, 1.00 mmol, 73.8%). M.p.: 208 °C (DSC); $[\alpha]_D^{20} = +1700$ (c = 0.202, CH_2Cl_2); NMR: All NMR-data are in agreement with those for the enantiomer (S,S,S_p,S_p)-**3b**; elemental analysis calcd (%) for $C_{28}H_{30}Fe_2N_2O_2$ (538.24 g/mol): C, 62.48; H, 5.62; N, 5.20; found: C, 62.53; H, 5.44; N, 5.35.

4.3.6. Preparation of (S,S,R_p,R_p)-**3f**

The protected bisimine (S,S,R_p,R_p)-**2f** (1.01 g, 0.995 mmol, 1 eq) was dissolved in toluene (10 ml). Triethylamine trihydrofluoride (107 mg, 0.663 mmol, 2/3 eq) was added and the mixture was stirred for 3 h. Addition of pentane (30 ml) yielded a red precipitate, which was isolated by filtration and washed with pentane (10 ml). This gave the diol (S,S,R_p,R_p)-**3f** as a red solid (234 mg, 0.438 mmol, 43.7%). M.p.: 191 °C (DSC); $[\alpha]_D^{20} = +1950$ (c = 0.200, CH_2Cl_2); NMR: All NMR-data are in agreement with those for the enantiomer (R,R, S_p,S_p)-**3c**; elemental analysis calcd (%) for $C_{28}H_{30}Fe_2N_2O_2$ (538.24 g/mol): C, 62.48; H, 5.62; N, 5.20; found: C, 62.08; H, 5.46; N, 5.31.

4.4. Synthesis and characterization of the (ferro-salen)-titanium and -aluminum metal complexes

4.4.1. Preparation of (S,S,S_p,S_p)-**4b**

The diol (S,S,S_p,S_p)-**3b** (103 mg, 0.191 mmol, 1 eq) and titanium tetraisopropoxide (54.4 mg, 0.191 mmol, 1 eq) were dissolved in dichloromethane (4 ml) and the mixture was stirred overnight. The solution was filtered and the solvent was removed, giving complex (S,S,S_p,S_p)-**4b** as a red solid (110 mg, 0.157 mmol, 82.0%). M.p.: 224 °C (DSC); $[\alpha]_D^{20} = -1760$ (c = 0.051, CH_2Cl_2); ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K, TMS): δ = 8.22 (s, 2H, C*H*N), 4.28 (ddd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, ^4J = 0.6 Hz, 2H, H-3), 4.25 (dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 2H, H-5), 4.15 (s, 10H, Cp), 4.10 (t, ^3J = 2.7 Hz, 2H, H-4), 3.98 (sept, ^3J = 6.0 Hz, 2H, C*H*), 3.20 (m, 2H, H-6), 2.52 (m, 2H, H-7), 2.08 (m, 2H, H-8), 1.50−1.43 (m, 4H, H-7′, H-8′), 0.85 (d, ^3J = 6.0 Hz, 6H, CH_3), 0.64 (d, ^3J = 6.0 Hz, 6H, CH_3′), [position 4 and 5 are tentatively assigned]; ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K, TMS): δ = 159.7 (*C*HN), 131.4 (C-1), 73.2 (*C*H), 69.6 (Cp), 68.8 (C-2), 67.0 (C-6), 65.5 (C-4), 64.1 (C-5), 57.9 (C-3), 29.6 (C-7), 26.6 (*C*H_3), 26.4 (*C*H_3′), 24.9 (C-8); IR (KBr): ν bar = 1609 cm^{-1} (C═N); elemental analysis calcd (%) for $C_{34}H_{42}Fe_2N_2O_4Ti$ (702.27 g/mol): C, 58.15; H, 6.03; N, 3.99; found: C, 58.60; H, 5.98; N, 3.93.

4.4.2. Preparation of (R,R,S_p,S_p)-**4c**

The diol (R,R,S_p,S_p)-**3c** (103 mg, 0.191 mmol, 1 eq) and titanium tetraisopropoxide (54.4 mg, 0.191 mmol, 1 eq) were dissolved in dichloromethane (4 ml) and the mixture was stirred overnight. The solution was filtered and the solvent was removed, giving complex (R,R,S_p,S_p)-**4c** as a red solid (115 mg, 0.164 mmol, 85.7%). X-ray quality crystals could be obtained by diffusion of pentane into a solution of (R,R,S_p,S_p)-**4c** in tetrahydrofurane at –30 °C. M.p.: 197 °C (DSC); $[\alpha]_D^{20} = -2030$ (c = 0.050, CH_2Cl_2); ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K, TMS): δ = 8.34 (m, 1H, C*H*N^A), 8.32 (m, 1H, C*H*N^B),

4.90 (sept, ^3J = 6.1 Hz, 1H, CH^1), 4.59 (m, 1H, H-6^A), 4.50 (sept, ^3J = 6.1Hz, 1H, CH^2), 4.31 (ddd, ^3J = 2.6 Hz, ^4J = 1.4 Hz, ^4J = 0.7 Hz, 1H, H-3^B), 4.29 (dd, ^3J = 2.8 Hz, ^4J = 1.3 Hz, 1H, H-5^A), 4.24 (ddd, ^3J = 2.6 Hz, ^4J = 1.3 Hz, ^4J = 0.6 Hz, 1H, H-3^A), 4.22 (s, 5H, Cp^1), 4.20 (dd, ^3J = 2.8 Hz, ^4J = 1.4 Hz, 1H, H-5^B), 4.08 (dd, ^3J = 2.8 Hz, ^3J = 2.6 Hz, 1H, H-4^B), 4.07 (dd, ^3J = 2.8 Hz, ^3J = 2.6 Hz, 1H, H-4^A), 3.95 (s, 5H, Cp^2), 2.67 (m, 1H, H-6^B), 2.49 (m, 1H, H-7^A), 2.25 (m, 1H, H-7^B), 2.09 (m, 1H, H-8^A), 2.05 (m, 2H, H-8^B), 1.71 (m, 1H, H-7$^{A'}$), 1.71 (m, 1H, H-7$^{B'}$), 1.56 (m, 1H, H-8$^{A'}$), 1.53 (m, 2H, H-8$^{B'}$), 1.27 (d, ^3J = 6.1 Hz, 3H, CH_3^1), 1.22 (d, ^3J = 6.1 Hz, 3H, C$H_3^{1'}$), 0.97 (d, ^3J = 6.1 Hz, 3H, CH_3^2), 0.79 (d, ^3J = 6.1 Hz, 3H, C$H_3^{2'}$); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K, TMS): δ = 165.1 (*C*HN^B), 158.3 (*C*HN^A), 134.2 (C-1^A), 130.2 (C-1^B), 77.4 (*C*H^2), 76.9 (*C*H^1), 71.7 (C-6^B), 71.1 (C-2^A), 70.1 (Cp^1), 69.6 (Cp^2), 69.0 (C-6^A), 66.3 (C-2^B), 66.1 (C-4^A), 64.9 (C-4^B), 64.0 (C-5^B), 62.6 (C-5^A), 58.5 (C-3^B), 57.2 (C-3^A), 32.5 (C-7^A), 28.8 (C-7^B), 26.41, 26.38 (*C*H$_3^1$, *C*H$_3^{1'}$), 25.9 (*C*H$_3^{2'}$), 25.61 (C-8^B), 25.58 (*C*H$_3^2$), 25.1 (C-8^A); IR (KBr): ν bar = 1610 cm^{-1} (C═N); elemental analysis calcd (%) for $C_{34}H_{42}Fe_2N_2O_4Ti$ (702.27 g/mol): C, 58.15; H, 6.03; N, 3.99; found: C, 58.29; H, 6.08; N, 3.91.

X-ray crystal structure analysis of (*R*,*R*,*S*$_p$,*S*$_p$)-**4c**: formula $C_{34}H_{42}Fe_2N_2O_4Ti$, M = 702.30, red crystal 0.40 × 0.20 × 0.10 mm, a = 11.5364(1), b = 11.9713(1), c = 23.0457(3) Å, V = 3182.74(6) Å^3, ρ_{calc} = 1.466 g cm^{-3}, μ = 1.185 mm^{-1}, empirical absorption correction (0.649 ≤ T ≤ 0.891), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 21 508 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.66 Å^{-1}, 7345 independent (R_{int} = 0.040) and 6307 observed reflections [$I \geq 2\sigma(I)$], 392 refined parameters, R = 0.033, wR^2 = 0.079, Flack parameter −0.018(13), max. (min.) residual electron density 0.58 (−0.32) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. CCDC 762152.

4.4.3. Preparation of (*S*,*S*,*S*$_p$,*S*$_p$)-*5b*

Trimethylaluminium (12.9 mg, 0.179 mmol, 1 eq) was dissolved in dichloromethane (1 ml) and a solution of the diol (*S*,*S*,*S*$_p$,*S*$_p$)-**3b** (96.3 mg, 0.179 mmol, 1 eq) in dichloromethane (4 ml) was added. The mixture was stirred for 1 h, the solvent was removed and pentane (2 ml) was added. Removal of the solvent *in vacuo* gave complex (*S*,*S*,*S*$_p$,*S*$_p$)-**5b** as a pink solid (75.1 mg, 0.130 mmol, 72.6%). X-ray quality crystals could be obtained by diffusion of pentane into a solution of (*S*,*S*,*S*$_p$,*S*$_p$)-**5b** in tetrahydrofurane at −30 °C. M.p.: 277 °C (DSC); $[\alpha]_D^{20}$ = −3410 (578 nm), +1450 (436 nm) (c = 0.021, CH_2Cl_2); ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K, TMS): δ = 8.55 (d, ^4J = 1.9 Hz, 1H, C*H*N^A), 8.36 (d, ^4J = 1.9 Hz, 1H, C*H*N^B), 4.63 (m, 1H, H-3^A), 4.59 (m, 1H, H-3^B), 4.28 (s, 5H, Cp^1), 4.21 (m, 1H, H-5^B), 4.21 (m, 2H, H-5^B), 4.21 (s, 5H, Cp^2), 4.20 (t, ^3J = 2.7 Hz, 1H, H-4^A), 4.17 (t, ^3J = 2.7 Hz, 1H, H-4^B), 3.38 (m, 1H, H-6^B), 2.79 (m, 1H, H-6^A), 2.49 (m, 1H, H-7^B), 2.35 (m, 1H, H-7^A), 2.09 (m, 1H, H-8^B), 2.07 (m, 1H, H-8^A), 1.52 (m, 1H, H-8$^{B'}$), 1.45 (m, 1H, H-8$^{A'}$), 1.41 (m, 1H, H-7$^{B'}$), 1.39 (m, 1H, H-7$^{A'}$), −0.92 (s, 3H, AlCH_3); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K, TMS): δ = 170.4 (*C*HN^A), 166.6 (*C*HN^B), 133.8 (C-1^A), 131.5 (C-1^B), 69.84, 69.81 (Cp^1, Cp^2), 66.5 (C-4^A), 66.1 (C-6^A), 65.2 (C-4^B), 62.8 (C-6^B), 62.5 (C-5^A), 62.4 (C-2^A), 61.8 (C-2^B), 61.7 (C-5^B), 60.6 (C-3^B), 60.3 (C-3^A), 29.9 (C-7^B), 27.8 (C-7^A), 24.7 (C-8^A), 24.3 (C-8^B), −6.8 (br, AlCH_3); IR (KBr): ν bar = 1631 cm^{-1} (C═N); elemental analysis calcd (%) for $C_{29}H_{31}AlFe_2N_2O_2$ (578.24 g/mol): C, 60.24; H, 5.40; N, 4.84; found: C, 59.63; H, 5.33; N, 4.73.

X-ray crystal structure analysis of (*S*,*S*,*S*$_p$,*S*$_p$)-**5b**: formula $C_{29}H_{31}AlFe_2O_2N_2\cdot 2C_4H_8O$, M = 722.45, red crystal 0.30 × 0.04 × 0.03 mm, a = 12.6911(6), c = 21.7816(9) Å, V = 3508.2 (3) Å^3, ρ_{calc} = 1.368 g cm^{-3}, μ = 7.199 mm^{-1}, empirical absorption correction (0.221 ≤ T ≤ 0.813), Z = 4, tetragonal, space group $P4_3$ (No. 78), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 14 408 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 4347 independent (R_{int} = 0.093) and 2882 observed reflections [$I \geq 2\sigma(I)$], 358 refined parameters, R = 0.089, wR^2 = 0.260, Flack parameter −0.010(13), max. (min.) residual electron density 0.57 (−0.37) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, due to crystal shape and disordered solvent molecules the quality of the analysis is poor. CCDC 762154.

4.4.4. Preparation of (*R*,*R*,*S*$_p$,*S*$_p$)-*5c*

Trimethylaluminum (24.0 mg, 0.333 mmol, 1 eq) was dissolved in dichloromethane (1 ml) and a solution of the diol (*R*,*R*,*S*$_p$,*S*$_p$)-**3c** (179 mg, 0.333 mmol, 1 eq) in dichloromethane (4 ml) was added. The mixture was stirred for 1 h, the solvent was removed and pentane (4 ml) was added. Removal of the solvent *in vacuo* gave complex (*R*,*R*,*S*$_p$,*S*$_p$)-**5c** as a pink solid (150 mg, 0.259 mmol, 77.9%). X-ray quality crystals could be obtained by diffusion of pentane into a solution of (*R*,*R*,*S*$_p$,*S*$_p$)-**5c** in tetrahydrofurane at −30 °C. M.p.: 273 °C (DSC); $[\alpha]_D^{20}$ = −3100 (578 nm), +596 (436 nm) (c = 0.021, CH_2Cl_2); ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K, TMS): δ = 8.63 (d, ^4J = 1.4 Hz, 1H, C*H*N^A), 8.22 (d, ^4J = 1.8 Hz, 1H, C*H*N^B), 4.46 (m, 2H, H-3^A, H-3^B), 4.18 (t, ^3J = 2.8 Hz, 1H, H-4^A), 4.14 (s, 5H, Cp^1), 4.13 (dd, ^3J = 2.8 Hz, ^4J = 1.3 Hz, 1H, H-5^A), 4.12 (dd, ^3J = 2.8 Hz, ^4J = 1.3 Hz, 1H, H-5^B), 3.99 (t, ^3J = 2.8 Hz, 1H, H-4^B), 3.96 (s, 5H, Cp^2), 3.39 (m, 1H, H-6^B), 2.70 (m, 1H, H-6^A), 2.59 (m, 1H, H-7^A), 2.29 (m, 1H, H-7^B), 2.12−2.03 (m, 2H, H-8^A, H-8^B), 1.52 (m, 1H, H-7$^{A'}$), 1.49 (m, 4H, H-7$^{B'}$), 1.53, 1.50 (m, 2H, H-8$^{A'}$, H-8$^{B'}$), −1.01 (s, 3H, AlCH_3); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K, TMS): δ = 174.7 (*C*HN^A), 162.6 (*C*HN^B), 133.3 (C-1^A), 131.9 (C-1^B), 69.99, 69.95 (Cp^1, Cp^2), 67.4 (C-6^A), 66.8 (C-4^A), 64.9 (C-4^B), 62.7 (C-2^B), 62.4 (C-5^B), 61.90, 61.88 (C-5^A, C-6^B), 60.9 (C-3^B), 60.4 (C-2^A), 60.0 (C-3^A), 30.6 (C-7^A), 27.6 (C-7^B), 24.8 (C-8^B), 24.3 (C-8^A), −6.1 (br, AlCH_3); IR (KBr): ν bar = 1630 cm^{-1} (C═N); elemental analysis calcd (%) for $C_{29}H_{31}AlFe_2N_2O_2$ (578.24 g/mol): C, 60.24; H, 5.40; N, 4.84; found: C, 59.47; H, 5.26; N, 4.94.

X-ray crystal structure analysis of (*R*,*R*,*S*$_p$,*S*$_p$)-**5c**: formula $C_{29}H_{31}AlFe_2O_2N_2\cdot 2C_4H_8O$, M = 722.45, red crystal 0.45 × 0.10 × 0.10 mm, a = 13.063(2), c = 20.881(2) Å, V = 3563.2 (8) Å^3, ρ_{calc} = 1.347 g cm^{-3}, μ = 7.088 mm^{-1}, empirical absorption correction (0.143 ≤ T ≤ 0.538), Z = 4, tetragonal, space group $P4_3$ (No. 78), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 11 731 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 4043 independent (R_{int} = 0.096) and 2493 observed reflections [$I \geq 2\sigma(I)$], 358 refined parameters, R = 0.087, wR^2 = 0.244, Flack parameter 0.055(16), max. (min.) residual electron density 0.40 (−0.39) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, due to crystal shape and disordered solvent molecules the quality of the analysis is poor. CCDC 762155.

4.4.5. Preparation of (*S*,*S*,*S*$_p$,*S*$_p$)-*6b*

The diol (*S*,*S*,*S*$_p$,*S*$_p$)-**3b** (102 mg, 0.190 mmol, 1 eq) was dissolved in dichloromethane (5 ml) and diethylaluminumchloride was added (199 µl of a 1 M solution in hexanes, 0.199 mmol, 1.05 eq). The mixture was stirred overnight and filtered. Removal of the solvent gave complex (*S*,*S*,*S*$_p$,*S*$_p$)-**6b** as a pink solid (90.7 mg, 0.152 mmol, 80.2%). X-ray quality crystals could be obtained by diffusion of pentane into a solution of (*S*,*S*,*S*$_p$,*S*$_p$)-**6b** in tetrahydrofurane at −30 °C. M.p.: 262 °C (DSC); $[\alpha]_D^{20}$ = +1780 (436 nm, c = 0.020, CH_2Cl_2); ^{1}H NMR (600 MHz, CD_2Cl_2, 188 K, TMS): δ = 8.53 (bs, 1H, C*H*N^A), 8.40 (bs, 1H, C*H*N^B), 4.55 (bs, 1H, H-3^A), 4.47 (bs, 1H, H-3^B), 4.19 (bs, 5H, Cp^1), 4.17 (bs, 1H, H-5^A), 4.15 (bs, 1H, H-5^B), 4.11 (bs, 1H, H-4^A), 4.07 (bs, 1H, H-4^B),[1] 4.06 (bs, 5H, Cp^2), 3.42 (m, 1H, H-6^B), 2.84 (m, 1H, H-6^A), 2.44 (m, 1H, H-7^A), 2.32 (m, 1H, H-7^B), 2.00−1.90 (m, 2H, H-8^A, H-8^B), 1.43−1.26 (m, 4H, H-7$^{A'}$, H-7$^{B'}$, H-8$^{A'}$, H-8$^{B'}$), [all resonances were broad]; ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2,

[1] The signal of H-4^B appears as a shoulder within the signal of Cp^2.

188 K, TMS): $\delta = 169.5$ (*C*HN^{A}), 168.7 (*C*HN^{B}), 130.2 (C-1^{A}), 128.5 (C-1^{B}), 69.2 (Cp^{1}), 69.1 (Cp^{2}), 66.2 (C-4^{A}), 65.3 (C-4^{B}), 63.7 (C-6^{A}), 62.5 (C-5^{A}), 61.6 (C-6^{B}), 61.5, (C-2^{A}, C-5^{B}), 60.0 (C-3^{A}), 59.9 (C-3^{B}), 59.8 (C-2^{B}), 27.3 (C-7^{A}), 26.7 (C-7^{B}), 22.9, 22.5 (C-8^{A}, C8^{B}), [all resonances were broad]; IR (KBr): ν bar = 1626 cm^{-1} (C═N); elemental analysis calcd (%) for $C_{28}H_{28}AlClFe_2N_2O_2$ (598.66 g/mol): C, 56.18; H, 4.71; N, 4.68; found: C, 56.70; H, 4.51; N, 4.53.

X-ray crystal structure analysis of (*S*,*S*,*S*$_p$,*S*$_p$)-**6b**: formula $C_{28}H_{28}AlClFe_2O_2N_2 \cdot 2/2C_4H_8O$, $M = 670.76$, red crystal 0.40 × 0.07 × 0.07 mm, $a = 12.6115(5)$, $c = 21.7821(9)$ Å, $V = 3464.4(2)$ Å^3, $\rho_{calc} = 1.286$ g cm^{-3}, $\mu = 7.923$ mm^{-1}, empirical absorption correction ($0.144 \leq T \leq 0.607$), $Z = 4$, tetragonal, space group $P4_3$ (No. 78), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and φ scans, 37 188 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 4540 independent ($R_{int} = 0.155$) and 2809 observed reflections [$I \geq 2\sigma(I)$], 365 refined parameters, $R = 0.083$, $wR^2 = 0.245$, Flack parameter 0.002(10), max. (min.) residual electron density 0.58 (−0.37) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, due to crystal shape and disordered solvent molecules the quality of the analysis is poor. CCDC 762156.

4.4.6. Preparation of (*R*,*R*,*S*$_p$,*S*$_p$)-**6c**

The diol (*R*,*R*,*S*$_p$,*S*$_p$)-**3c** (102 mg, 0.190 mmol, 1 eq) was dissolved in dichloromethane (5 ml) and diethylaluminumchloride was added (199 µl of a 1 M solution in hexanes, 0.199 mmol, 1.05 eq). The mixture was stirred overnight and filtered. Removal of the solvent gave complex (*R*,*R*,*S*$_p$,*S*$_p$)-**6c** as a pink solid (98.0 mg, 0.164 mmol, 86.2%). X-ray quality crystals could be obtained by diffusion of pentane into a solution of (*R*,*R*,*S*$_p$,*S*$_p$)-**6c** in tetrahydrofurane at −30 °C. M.p.: 222 °C (DSC); $[\alpha]_D^{20} = +863$ (436 nm, $c = 0.020$, CH_2Cl_2); ^{1}H NMR (600 MHz, CD_2Cl_2, 188 K, TMS): $\delta = 8.71$ (bs, 1H, C*H*N^{A}), 8.33 (bs, 1H, C*H*N^{B}), 4.54, 4.53 (each m, each 1H, H-3^{A}, H-3^{B}), 4.21 (bs, 5H, Cp^{1}), 4.20, 4.18 (each m, each 1H, H-4^{A}, H-5^{A}), 4.16 (bs, 1H, H-5^{B}), 4.02 (m, 1H, H-4^{B}), 3.96 (bs, 5H, Cp^{2}), 3.57 (m, 1H, H-6^{B}), 2.71 (m, 1H, H-6^{A}), 2.54 (m, 1H, H-7^{A}), 2.32 (m, 1H, H-7^{B}), 2.05–1.94 (m, 2H, H-8^{A}, H-8^{B}), 1.51–1.35 (m, 4H, H-7$^{A'}$, H-7$^{B'}$, H-8$^{A'}$, H-8$^{B'}$); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 188 K, TMS): $\delta = 175.5$ (*C*HN^{A}), 164.3 (CHN^{B}), 129.8 (C-1^{A}), 128.7 (C-1^{B}), 69.4 (Cp^{1}, Cp^{2}), 66.7, 61.5 (C-4^{A}, C-5^{A}), 65.5 (C-6^{A}), 65.1 (C-4^{B}), 62.5 (C-5^{B}), 61.0 (C-2^{B}), 60.6 (C-3^{B}), 60.5 (C-6^{B}), 59.9 (C-3^{A}), 59.2 (C-2^{A}), 28.2 (C-7^{A}), 26.5 (C-7^{B}), 23.3, 22.6 (C-8^{A}, C-8^{B}); IR (KBr): ν bar = 1630 cm^{-1} (C═N); elemental analysis calcd (%) for $C_{28}H_{28}AlClFe_2N_2O_2$ (598.66 g/mol): C, 56.18; H, 4.71; N, 4.68; found: C, 56.83; H, 4.87; N, 4.38.

X-ray crystal structure analysis of (*R*,*R*,*S*$_p$,*S*$_p$)-**6c**: formula $C_{28}H_{28}AlClFe_2O_2N_2 \cdot 2C_4H_8O$, $M = 742.86$, red crystal 0.30 × 0.05 × 0.03 mm, $a = 13.0043(6)$, $c = 20.8756(10)$ Å, $V = 3530.3(3)$ Å^3, $\rho_{calc} = 1.398$ g cm^{-3}, $\mu = 7.851$ mm^{-1}, empirical absorption correction ($0.202 \leq T \leq 0.799$), $Z = 4$, tetragonal, space group $P4_3$ (No. 78), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and φ scans, 16 676 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 4313 independent ($R_{int} = 0.104$) and 2616 observed reflections [$I \geq 2\sigma(I)$], 357 refined parameters, $R = 0.085$, $wR^2 = 0.240$, Flack parameter 0.060(15), max. (min.) residual electron density 0.63 (−0.53) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, due to crystal shape and disordered solvent molecules the quality of the analysis is poor. CCDC 762157.

4.5. Asymmetric trimethylsilylcyanation reactions

4.5.1. General procedure for the asymmetric trimethylsilylcyanations using (ferro-salen)AlMe complexes

The corresponding metal complex (0.05 eq), benzaldehyde (1 eq) and trioctylphosphine oxide (1 eq) were dissolved in dichloromethane (0.5 ml). Trimethylsilylcyanide (2.5 eq) was added and the reaction flask was quickly cooled to −20 °C. After complete consumption of benzaldehyde (according to TLC analysis) the solvent was removed and the residue was purified by column chromatography (ca. 15 × 2 cm, cyclohexanes:ethyl acetate = 4:1). Removal of the solvent gave the product as a colourless oil.

4.5.2. General procedure for the asymmetric trimethylsilylcyanations using (ferro-salen)AlCl complexes

The corresponding metal complex (0.01 eq), benzaldehyde (1 eq) and trioctylphosphine oxide (0.05 eq) were dissolved in dichloromethane (0.5 ml). Trimethylsilylcyanide (2.5 eq) was added and the reaction flask was quickly cooled to −20 °C. After complete consumption of benzaldehyde (according to TLC analysis) the solvent was removed and the residue was purified by filtration through a short plug of silica gel (ca. 3 × 0.5 cm) using chloroform as the eluent. Removal of the solvent gave the product as a colourless oil.

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Appendix. Supporting information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.04.008.

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