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("Ferrocene-salaldiminato")zirconium Complexes for Ethylene Polymerization Catalysis: The Role of the Bulky Substituents

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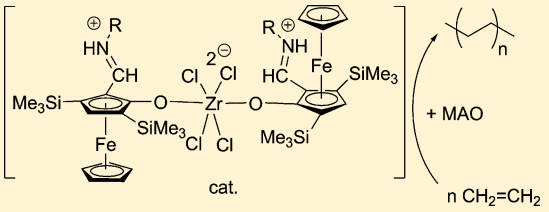
Supporting Information

ABSTRACT: We prepared the 2-hydroxy-5-trimethylsilylferrocenecarbaldimine systems **13** enantioselectively by a short synthetic route starting from the chiral ferrocene carbaldehyde acetal **5**. The imines **13a–c** were used to synthesize the zwitterionic ("ferrocene-salaldiminato")$_2$ZrCl$_4$ complexes **14a–c**. Activation with MAO gave homogeneous Ziegler–Natta catalysts, which showed only a moderate ethylene polymerization activity, similar to the unsubstituted parent "ferrocene-salaldiminato" zirconium systems. Consequently, a synthetic route was devised and carried out to make the corresponding 2-hydroxy-3,5-bis(trimethylsilyl)ferrocenecarbaldimines (**21**) available. The enantiomerically highly enriched ligands (*pS*)-**21a** and -**d** derived from the aldehyde and aniline or cyclohexylamine, respectively, were used to synthesize the corresponding ("ferrocene-salaldiminato")$_2$ZrCl$_4$ complexes **22a,d**. Both gave highly active homogeneous Ziegler–Natta catalysts upon activation with MAO for the formation of linear low molecular weight polyethylene. Complex **22d** and many ligand precusors from both sequences were characterized by X-ray diffraction.



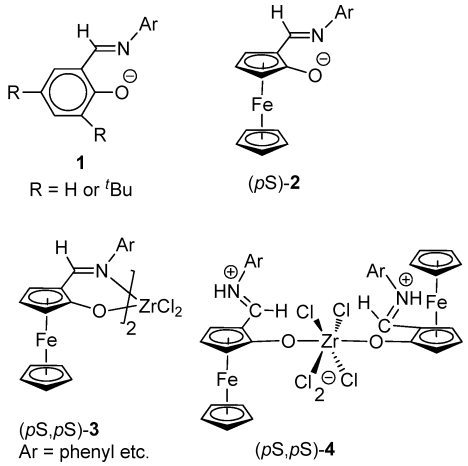
INTRODUCTION

Homogeneous Ziegler–Natta olefin polymerization catalysis based on group 4 metal complexes has undergone much development during the last decades. An enormous number of publications have described the various metallocene catalysts,[1] different types of mono-Cp metal systems including the Cp/amido ("constrained geometry") systems,[2] and a variety of non-Cp ("postmetallocene")[3] catalyst developments. Among the latter the salicyl-aldiminato-derived group 4 complexes[4] constitute an interesting and important subclass in homogeneous olefin polymerization catalysis.

We had introduced the salicylaldimine-related 2-hydroxyferrocenecarbaldimine ligands **2** (in this account for simplicity termed as "ferrocene-salaldiminato" or "Fe-salaldiminato").[5−8] In contrast to the systems **1**, their nonplanar structure introduces an element of planar chirality into this chemistry. We had developed viable syntheses of the homochiral bis-κ*O*,*N*["Fe-salaldiminato"]-chelate zirconium dichloride complexes **3** as well as the related zwitterionic octahedral bis κ*O*["Fe-salaldiminato"]ZrCl$_4$ complexes **4**. We were able to synthesize both the (*pS*, *pS*) and (*pR*, *pR*) enantiomers selectively (Scheme 1).[5−8]

Activation of both systems **3** and **4** with excess MAO gave ethylene polymerization catalysts of almost equal activity. They formed linear polyethylene at temperatures up to 125 °C but with rather low catalytic activities. It was previously shown that the catalyst activities of the bis(salicylaldiminato)ZrCl$_2$-derived systems [(**1**)$_2$ZrCl$_2$] dependend critically on the substituents at the arene moieties of the chelate ligand.

Scheme 1



The parent compound (R = H) showed low polymerization activities,[9] whereas systems bearing bulky substituents (R = ^{t}Bu) gave highly active ethylene polymerization catalysts upon activation.[10] Therefore, we have now carried out a benchmark study on our ferrocene-derived "three-dimensional" analogues of the (salicylaldiminato)zirconium systems and attached bulky substituents at the functionalized Cp-ring of the "Fe-

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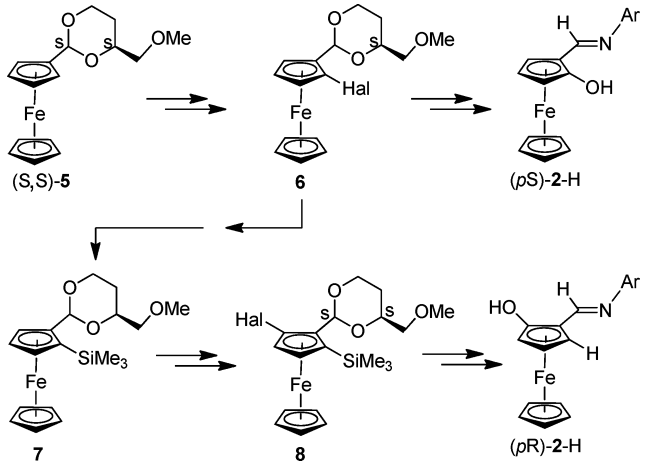
salaldiminato" systems (**2**) in order to investigate the crucial role of steric bulk in different positions of these systems. For reasons of easy synthetic feasibility, we chose $-SiMe_3$ substituents for this study.

RESULTS AND DISCUSSION

Attachment of a Bulky Trimethylsilyl Substituent at a Site Adjacent to the Aldimine Group. We had previously used variants of the Kagan route[8] for the selective synthesis of the hydroxyferrocenecarbaldimine enantiomers (*pS*)-**2**-H and (*pR*)-**2**-H, respectively. Both started from the ferrocene aldehyde acetal **5**. The (*pS*)-OH group was introduced by means of a directed metalation, halogenation, and oxidation sequence. For the synthesis of the (*pR*)-OH isomer, we also started from **5**, used a similar metalation/halogenation/metalation sequence to block the "*o*-(*pS*) position" by the $-SiMe_3$ substituent, and then introduced the −OH substituent at the remaining *o*-position by a similar sequence[5] (see Scheme 2), which involved fluoride-induced removal of the $-SiMe_3$ placeholder at some intermediate stage.

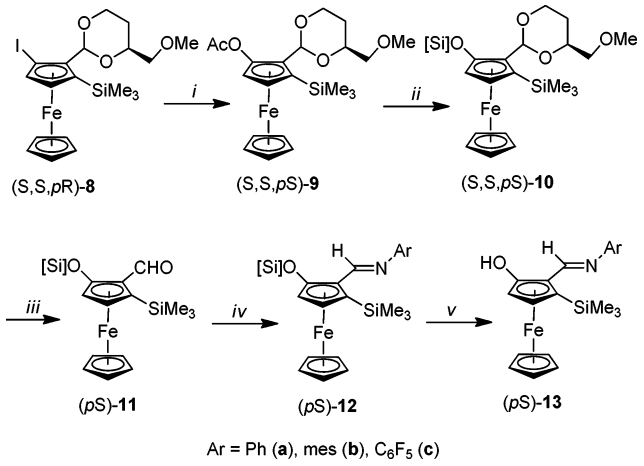
Scheme 2



Starting material of this synthesis was the ferrocene derivative (*S,S,pR*)-**8**. This iodoferrocene was heated with Cu_2O/acetic acid in acetonitrile[11] at elevated temperature to yield the acetoxyferrocene acetal (*S,S,pS*)-**9** (see Scheme 3). Compound **9** was isolated in >70% yield (see the Experiment Section and the Supporting Information for its characterization). Subsequent treatment with sodium methoxide followed by tert-butyl(chloro)diphenylsilane then gave the *O*-silyl-protected *α*-hydroxylferrocene carbaldehyde acetal (*S,S,pS*)-**10** in 84% yield. The acetal was converted to the free aldehyde **11** by treatment with *p*-toluene sulfonic acid. The $Ph_2{}^tBuSi$-protected aldehyde (*pS*)-**11** was then converted to three aldimine derivatives [**12a** (Ar = Ph), **12b** (Ar = mesityl), **12c** (Ar = C_6F_5)] by acid-catalyzed condensation with the respective primary aromatic amines. The ligand synthesis was then successfully finished by $Et_3N{\cdot}3HF$-induced deprotection to give the respective free 2-hydroxy-5-trimethylsilylferrocene carbaldimines (*pS*)-**13a** (Ar = Ph), (*pS*)-**13b** (Ar = mesityl), and (*pS*)-**13c** (Ar = C_6F_5) (see Scheme 3).

The compounds **13** were characterized by spectroscopy and C,H,N-elemental analysis. Compound (*pS*)-**13a** (Ar = Ph) was also characterized by X-ray diffraction. The X-ray crystal structure analysis confirmed the specific arrangement of the

Scheme 3. [a]



[a]Conditions: (*i*) Cu_2O/AcOH, 80 °C, 74%, (*ii*) NaOMe, dmf, then $Ph_2{}^tBuSiCl$ ([Si] = $Ph_2{}^tBuSi$, 84%), (*iii*) *p*-TsOH/H_2O, 87%, (*iv*) $ArNH_2$, *p*-TsOH, 80 °C (a, Ar = Ph, quant, b, Ar = Mes, 89%, c, Ar = C_6F_5, 60%), (*v*) $Et_3N{\cdot}3HF$/THF (a, Ar = Ph, 77%, b, Ar = Mes, 65%, c, Ar = C_6F_5, 74%).

three substituents at the "upper" Cp ring of the ferrocene framework of compound (*pS*)-**13a**: the −OH group (C2−O1: 1.349(2) Å) is in 1,2-position to the carbaldimine function (C3−C11: 1.443(2) Å) and in 1,3-position to the $-SiMe_3$ group (C4−Si1: 1.876(2) Å). The carbaldimine moiety (C11−N1: 1.286(2) Å) is oriented in-plane with the Cp-ring and oriented toward the adjacent −OH group (θ O1−C3−C2−C9 = 1.50°, C2−C3−C11−N1 = 4.05°, C3−C11−N1−C21 = 177.57°). There is evidence for internal hydrogen bonding between the −OH group and the imino-nitrogen (see Figure 1).

In solution compound (*pS*)-**13a** features the ^1H NMR −OH resonance at δ 9.88 (benzene-d_6). It shows the $^1H/^{13}C$ NMR signals of the aldimine $-CH{=}[N]$ unit at δ 8.78/166.3, and it

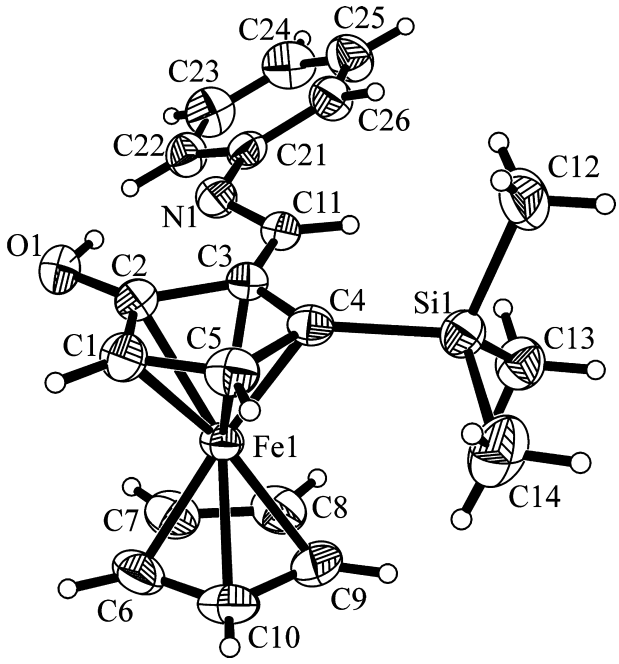


Figure 1. Molecular structure of (*pS*)-**13a**.

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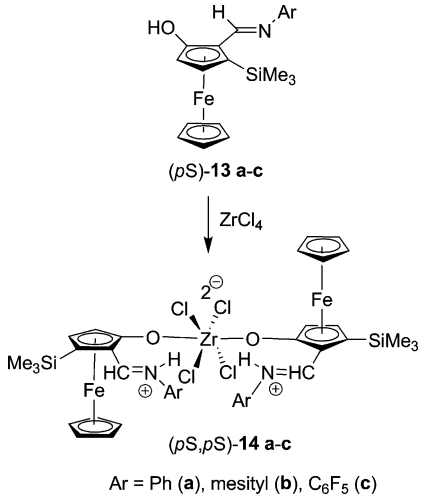
features the NMR signals of the $-SiMe_3$ substituent at δ 0.18 (1H, s, 9 H) and −0.4 (^{29}Si).

The ligand system (*pS*)-**13a** reacted at room temperature in dichloromethane (2 h) with zirconium tetrachloride in a molar ratio of 2:1 to yield the blue zwitterionic pseudooctahedral complex **14a** (91%). A closely related example of this general complex type will be described below. Complex (*pS,pS*)-**14a** shows the typical ^{1}H/^{13}C NMR features of the symmetry equivalent pair of $-CH{=}NPhH^+$ iminium funtional groups at δ 8.87/161.3 (=CH, d, $^3J_{HH}$ = 14.8 Hz) and 12.2 (broad, NH), respectively. The ligands (*pS*)-**13b** and (*pS*)-**13c** reacted analogously with $ZrCl_4$ to give the corresponding zwitterionic complexes (*pS,pS*)-**14b** (Ar = mesity, 76%), and (*pS,pS*)-**14c** (Ar = C_6F_5, 79%) as deep blue solids. Since we employed highly enantiomerically enriched, chiral O,N-chelated complexes, we obtained in each case a single diastereomer of the (κO-ligand)$_2ZrCl_4$ systems as single enantiomers (see Scheme 4). Consequently, complex (*pS,pS*)-**14c** features a single set of ^{19}F NMR resonances at δ −147.8 (*o*), −154.0 (*p*), and −160.3 (*m* F of C_6F_5).

Scheme 4



The complexes (*pS,pS*)-**14a−c** were activated by treatment with an excess of methylaluminoxane (MAO) to give homogeneous Ziegler−Natta catalysts for the polymerization of ethene. The polymerization reactions were carried out in toluene solution at 2 bar ethene pressure at two different temperatures. In all cases, linear polyethylene (PE) was obtained (see Table 1) that was close to insoluble in chlorobenzene at 80 °C. We assume that the (*pS,pS*)-**14**/MAO catalysts produced ultrahigh linear PE[12] under these conditions. However, the catalyst activities at all three catalysts were quite low (see Table 1), similar to that observed using the unsubstituted parent **3**/**4** plus MAO systems.[6]

These results indicated that the attachment of the bulky trimethylsilyl substituents at the carbaldimine side of the "Fe-salaldiminato" ligands had almost no influence on the behavior of the polymerization catalysts derived from the hydroxyferrocene carbaldimine ligands. We, therefore, consequently introduced the bulky $-SiMe_3$ substituent at the α position adjacent to the −OH group.

Attachment of a Bulky Substituent ($-SiMe_3$) at a Site Adjacent to the −OH Group. We used the established ability of the bromo substituent at arenes[13] and ferrocenes[14] to direct

Table 1. Ethene Polymerization with the (*pS,pS*)-14/MAO Catalyst Systems[a]

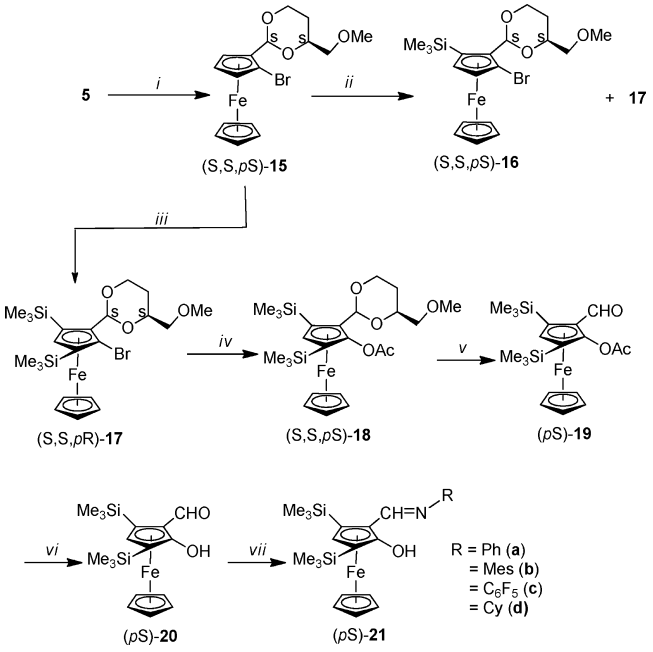
complex	*T* (°C)	yield (g PE)	activity[b]	T_m (°C)[c]
14a	25	0.28	14	137
14a	80	0.25	12	138
14b	25	0.68	34	139
14b	80	0.48	24	137
14c	25	1.26	63	136
14c	80	1.13	56	n.o.

[a]Polymerization conditions: *P*(ethene) = 2 bar, toluene = 200 mL, 2 h. Polymerizations were carried out in 1 L autoclave reactors with 5 μmol of Zr (**14a** 4.5 mg, **14b** 5.4 mg, **14c** 5.8 mg) preactivated with 400 equiv of MAO in 5 mL of toluene. The remaining 1600 equiv of MAO was then added. [b]In g/(mmol × bar × h). [c]DSC, second run.

metalation for the introduction of the $-SiMe_3$ substituent at the alternative site adjacent to the −OH group in the "Fe-salaldiminato" ligand system.

Again, the Kagan methodology was employed to introduce a bromo substituent stereoselectively at the ferrocene carbaldehyde nucleus. The chiral acetal (*S,S*)-**5** was treated with ^{t}BuLi, followed by α,α'-dibromoxylene[15] to yield (*S,S,pS*)-**15** (see Scheme 5). Its stereochemistry was confirmed by an X-ray crystal structure analysis (for details see the Supporting Information).

Scheme 5[a]



[a]Conditions: (*i*) ^{t}BuLi, ether, then $C_6H_4(CH_2Br)_2$, 83%, (*ii*) LiTMP 1 equiv, then Me_3SiCl, (*iii*) LiTMP 2.5 equiv, then Me_3SiCl, 68%, (*iv*) Cu_2O, AcOH, CH_3CN reflux, 58%, (*v*) *p*-TsOH/H_2O, 98%, (*vi*) 10% KOH, C_2H_5OH, rt, 85%, (*vii*) R-NH_2, *p*-TsOH, R = Ph (a) 84%, R = Mes (b) quant, R = C_6F_5 (c) 83%, R = cyclohexyl (d) 89%.

We then treated (*S,S,pS*)-**15** with the Li-TMP base (TMPH = 2,2,6,6-tetramethylpiperidine), followed by treatment with trimethylsilyl chloride. The reaction in an equimolar ratio gave a mixture of the mono- and disilylated product (**16** or potentially an isomer and **17**). They were hard to separate. Therefore, we treated (*S,S,pS*)-**15** with a 2.5 molar excess of the

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Li-TMP base and obtained the disilylated product (*S*,*S*,*pR*)-**17** selectively and in good yield (68%). From then on, we tried a few protocols (for details see the Supporting Information) and eventually arrived at the synthetic sequence depicted in Scheme 5.

The bromo substituent in **17** was exchanged for acetoxy by the established Cu_2O/AcOH reaction. Then the acetal auxiliary was removed by treatment with acid/water to give the aldehyde **19**. Saponification of the acetate eventually gave the free α-hydroxyferrocene-carbaldehyde product (*pS*)-**20** bearing a bulky trimethylsilyl group adjacent to the −OH functionality at the "upper" ferrocene Cp-ring.

Compound (*pS*)-**20** was characterized spectroscopically [^{1}H/^{13}C NMR: δ 10.20/199.0 (−CHO), 8.00 (−OH), 0.36 and 0.11 (^{1}H of −SiMe$_3$; IR (KBr): $\tilde{\nu}$ 3420 (bs, OH), 1635 cm^{-1} (C═O)], by C,H elemental analysis, and by X-ray diffraction. The X-ray crystal structure analysis of (*pS*)-**20** (see Figure 2) shows a pair of Me_3Si− substituents at the "upper"

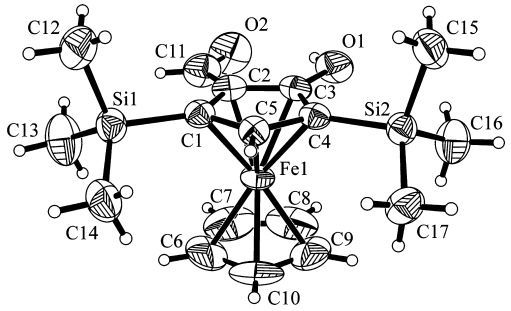


Figure 2. View of the molecular structure of compound (*pS*)-**20**.

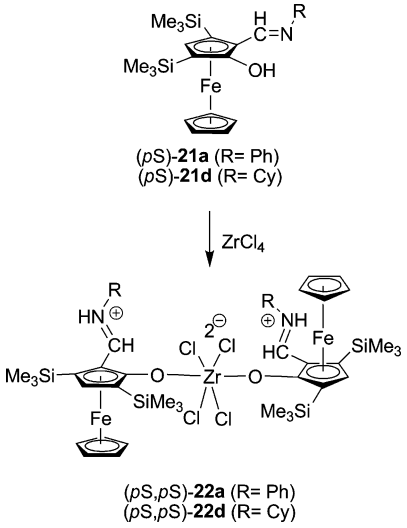
ferrocene Cp-ring, one directly adjacent to the −CHO unit (C1−Si1: 1.865(3) Å) and one in ortho position to the −OH group (C4−Si2: 1.860(3) Å). The aldehyde carbonyl group lies in the Cp-plane (θ C3−C2−C11−O2: −3.22°; C11−O2 = 1.216(5) Å), and it is oriented toward the −OH group (C3−O1 = 1.361(4) Å), probably because of the formation of an intramolecular hydrogen bond.

We then prepared a series of corresponding "Fe-salaldimines" (**21**) by condensation of the doubly Me_3Si-substituted hydroxy-ferrocene carbaldehyde (*pS*)-**20** with the primary amines aniline (**a**), mesityl amine (**b**), pentafluoroaniline (**c**), and cyclohexylamine (**d**), respectively. The corresponding imines **21a−d** were obtained in good yield (see Scheme 6). Both compounds (*pS*)-**21a** (R = Ph) and (*pS*)-**21d** (R = Cy) were characterized by X-ray crystal structure analysis (see Figure 3). In (*pS*)-**21a**, the hydrogen bridge between −OH and the imine nitrogen leads to a syn orientation of the −CH═N unit toward the hydroxyl group in-plane with the substituted ferrocene Cp-ring. The phenyl substituent at nitrogen is rotated slightly outside the imine plane [C11−N1: 1.272(3) Å, θ C11−N1−C21−C26 = 33.63°]. The structure of the cyclohexylimine derivative (*pS*)-**21d** features a similar overall structural composition [C11−N1 = 1.266(7) Å, C11−N1−C21−C26 = −119.29°].

The C_6F_5-substituted imine (*pS*)-**21c** was also characterized by X-ray diffraction. For details including a scheme of the structure see the Supporting Information.

Treatment of the *N*-cyclohexyl-substituted bulky hydroxyferrocene carbaldimine (*pS*)-**21d** with zirconium tetrachloride in a 2:1 molar ratio gave bis κO-ligand-substituted Zr complex (*pS*,*pS*)-**22d**. The zwitterionic complex **22d** was isolated as a

Scheme 6



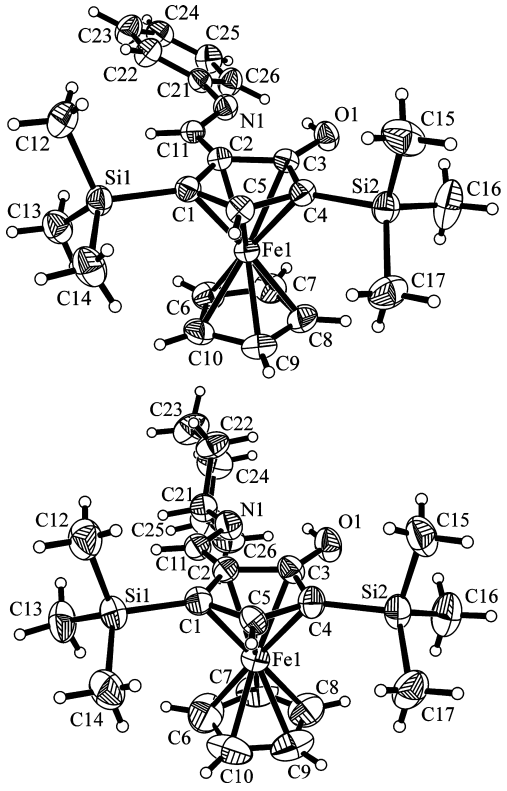


Figure 3. Molecular structure of the "Fe-salaldimines" (*pS*)-**21a** (R= Ph; top) and (*pS*)-**21d** (R = cyclohexyl; bottom).

deep blue solid in 76% yield. In solution, the C_2-symmetric complex features a single set of ^{1}H/^{13}C NMR ligand signals [e.g., δ 8.35 (d $^3J_{HH}$ = 16.8 Hz)/167.1 (−CH═[N])]. It shows a broad ═NH-Cy ^{1}H NMR resonance at δ 11.19.

Single crystals of (*pS*,*pS*)-**22d** suitable for the X-ray crystal structure analysis were obtained from an ether solution by slow evaporation of the solvent. Complex (*pS*,*pS*)-**22d** possesses C_2-symmetry in the crystal. It features a pseudo-octahedral coordination geometry at the central zirconium atom with both "Fe-salaldiminato" ligands trans-κ,O-coordinated (Zr1−O1: 1.992(6) Å) and the four chloride ligands in the meridial positions. The "Fe-salaldiminato" ligands are found as their

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C=NHCy$^+$ tautomeric iminium forms (C11−N1: 1.239(10) Å). Both the ferrocene units are arranged at the linear −O−Zr−O−core such that their substituted Cp-rings are syn-oriented in the overall C_2-symmetric arrangement (see Figure 4).

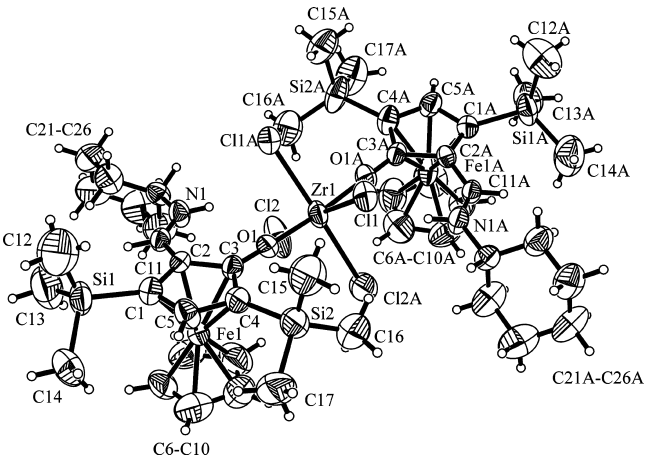

Figure 4. Projection of the molecular structure of complex (*pS,pS*)-**22d**.

Complex (*pS,pS*)-**22a** (R = Ph) was formed analogously by reaction of the neutral ligand (*pS,pS*)-**21a** with $ZrCl_4$ in a 2:1 molar ratio. The deep blue product was isolated in ca. 70% yield.

The C_2-symmetric complex (*pS,pS*)-**22a** shows a broad NH ^{1}H NMR resonance at δ 12.30 in solution and the typical ^{1}H/^{13}C NMR signals of the pair of −CH=NHPh units at the ferrocene framework [δ 8.80 (d, $^3J_{HH}$ = 15.4 Hz)/161.7]. The pair of unsubstituted ferrocene Cp-ligands gives rise to a sharp ^{1}H NMR signal at δ 4.58, and we monitored ^{1}H NMR signals of the pairs of $-SiMe_3$ substituents at δ 0.58 and 0.38.

Complexes (*pS,pS*)-**22a** and -**d** were used for the generation of homogeneous ethene polymerization catalysts. We first activated the system (*pS,pS*)-**22d** (R = cyclohexyl) by treatment with excess MAO and performed polymerization reactions at three different temperatures (0, 25, 50 °C, toluene solution, 2 bar ethylene pressure); under the three conditions, the "Fe-salaldiminato" Zr/MAO systems were very active catalysts. They produced linear low molecular weight polyethylene with vinyl end groups (determined by ^{1}H NMR).[16] We noticed the influence of the Al/Zr ratio on the catalyst performance (see Table 2), with an optimized situation being achieved at Al/Zr ratios between 1000 and 500.

At low reaction times (30 min to 1 h), the corresponding (*pS,pS*)-**22a**/MAO ethene polymerization catalyst (R = Ph) shows a similar performance in the 0 to 50 °C temperature range. Again, we notice a tendency toward even higher catalyst activities at low Al/Zr ratios (see Table 3). The (*pS,pS*)-**22a**/MAO catalyst exibits high catalytic activity. It forms rather low molecular weight linear polyethylene with a vinyl end group.

A comparison of the polymerization results obtained with the (*pS,pS*)-**22a**, **22d**/MAO catalysts, having a bulky $-SiMe_3$ group adjacent to the −O[Zr] moiety of the ("Fe-salaldiminato")$_2$Zr complexes, with those of the less substituted **14**/MAO systems clearly confirms the crucial role of the presence of steric bulk near the oxygen site of these catalyst systems.

The doubly silyl-substituted "Fe-salaldiminato"-derived catalyst (*pS,pS*)-**22a** (R = Ph)/MAO system shows another peculiarity; at longer reaction times (≥2 h, see Table 3), it increasingly forms polyethylene with a pronounced bimodal distribution. Along with the low molecular weight PE, we observed the formation of a high molecular weight linear PE fraction as a minor byproduct (ca. 10% to 30%). Preactivation with MAO over a long period of time (6 h, entry 8 in Table 3) leads to a situation where the usual major low molecular weight PE formation has become completely suppressed in favor of the sole formation of the high molecular weight PE product, albeit at the cost of a substantial reduction of the catalyst activity. A comparison with the low activity/high molecular weight producing less substituted **14**/MAO catalyst system (see above) lets us assume that the **22a**/MAO system is not stable for prolonged times under our typical polymerization reaction conditions potentially due to loss of the "proximate" $-SiMe_3$ substituent.

CONCLUSIONS

Our study shows that the three-dimensional analogues of the salicylaldiminato metal complexes, the "Fe-salaldiminato" complexes, can readily be synthesized. In contrast to their "flat" aromatic analogues, these di- and multisubstituted ferrocene derivatives are planarly chiral. A combination of

Table 2. Ethene Polymerization with the (*pS,pS*)-22d/MAO Catalyst System

entry[a]	[Al]/[Zr]	T_p (°C)	time (h)	yield (g PE)	A^b	$T_m{}^c$	$M_n{}^d$	$M_w{}^d$	PDI
1	2000	0	0.5	3.2	650	128	1480	4920	3.3
2	2000	0	1	7.2	720	125	1400	5130	3.7
3	2000	25	0.5	3.4	670	129	1870	4490	2.4
4	2000	25	1	5.9	590	130	1240	4930	4.0
5	2000	50	0.5	4.8	960	125	1200	3730	3.1
6	2000	50	1	7.4	740	127	1160	3460	3.0
7	1000	25	0.5	6.0	1200	124	1680	6420	3.8
8	1000	25	1	11.0	1100	132	1400	5130	3.7
9	1000	50	0.5	3.6	720	130	5150	14 020	2.8
10	500	25	0.5	5.2	1050	130	2370	11 270	4.7
11	500	25	0.25	3.4	1340	130	2200	8990	4.0
12	250	25	0.5	0.8	160	130	3960	11 120	2.8

[a]Polymerization conditions: *P*(ethene) = 2 bar, toluene = 200 mL. Polymerizations were carried out in 1 L autoclave reactors with 5 μmol of Zr complex (5.7 mg) preactivated with 400 equiv of MAO in 5 mL of toluene; the remaining 1600 equiv of MAO was added with an addition funnel while the autoclave was charged with Ar. Values of selected representative experiments are listed. [b]g/(mmol·bar·h). [c]°C, DSC, second run. [d]g/mol.

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Table 3. Ethene Polymerization with the (*pS*,*pS*)-22a/MAO Catalyst System

entry[a]	[Al]/[Zr]	*T* (°C)	time (h)	yield (g PE)	A^b	$T_m{}^c$	$M_n{}^d$	$M_w{}^d$	PDI
1	2000	0	0.5	4.6	580	117	750	1600	2.1
2	2000	25	0.5	4.9	980	118	860	1960	2.3
3	2000	25	1	9.0	900	122	1100	3100	2.8
4	2000	25	2	16.2	810	127	1440	4260	2.9
							120 000 (84:16)	250 000	2.1
5	2000	50	0.5	5.3	1060	122	1010	3490	3.5
6	2000	50	1	11.3	1130	125	1130	3120	2.8
							93 000 (84:16)	260 000	2.8
7	2000	50	2	15.9	800	127	1180	3620	3.1
							140 000 (72:28)	640 000	4.5
8[e]	2000	50	0.5	0.14	30	137	397 000	1 230 000	3.1
9	1000	25	0.5	4.6	920	123	1380	4190	3.0
10	1000	25	1	8.4	840	126	1690	5530	3.3
							190 000 (91:9)	520 000	2.7
11	500	25	0.5	2.8	550	127	2080	5470	2.6

[a]Polymerization conditions: *P*(ethene) = 2 bar, toluene = 200 mL. Polymerizations were carried out in 1 L autoclave reactors with 5 μmol of Zr complex (5.7 mg) preactivated with 400 equiv of MAO in 5 mL of toluene; the remaining 1600 equiv of MAO was added with an addition funnel while the autoclave was charged with Ar. Values of selected representative experiments are listed. [b]g/(mmol·bar·h). [c]°C, DSC, second run. [d]g/mol. [e]5 μmol of Zr complex in 5 mL of toluene activated with 400 equiv of MAO; the solution was stirred at rt for 6 h and then injected into the autoclave. The remaining 1600 equiv of MAO was subsequently injected.

two imine ligands at a group 4 metal center as commonly takes place in the respective homogeneous Ziegler–Natta catalyst precursors would result in the formation of a mixture of diastereomers if starting from the racemic ligand systems. Therefore, we have from the beginning used highly enantiomerically enriched "Fe-salaldiminato" ligands. The enantioselective synthesis of these ligands proved no problem, and they have become available by straightforward variations of literature routes from stereoselective synthetic ferrocene chemistry.[8,17] The polymerization results from this and previous studies showed broad parallels between established salicylaldiminato group 4 catalyst chemistry[10,18] and the catalytic behavior of the new "Fe-salaldiminato" zirconium systems. In both series, the unsubstituted parent compounds gave at best catalysts of mediocre activities. However, this is changed drastically upon attachment of bulky substituents at the right position or the arene (or ferrocene) ring systems, namely, directly adjacent to the −OH (or −O[M]) functionality. In our case, we used the $-SiMe_3$ group for reasons of synthetic simplification, but this was sufficient for proof of principle, although our new catalyst systems may have been somewhat hampered due to the potential instability of this substituent under actual catalytic reaction upon prolonged exposure. It might be that the respective *tert*-butyl-substituted "Fe-salaldiminato" catalyst systems will be more stable. It will be interesting to see whether such ferrocene-derived ligands might become useful additions to the broad catalyst repertoire in homogeneous "postmetallocene" Ziegler–Natta chemistry.

EXPERIMENTAL SECTION

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. All solvents were dried and degassed before use, if necessary, for the respective reaction. Attention should be paid to the purification of the ferrocene hydroxyl derivatives due to their facile oxidation. Dichloromethane, diethyl ether, pentane, tetrahydrofuran, and toluene were dried using a solvent drying system as described by Grubbs.[19] Dimethylformamide was stirred over calcium hydride and distilled prior to use. Deuterated solvents used for NMR spectroscopy were dried if necessary. *Chemicals:* Unless otherwise noted all chemicals were used as purchased. 2,6-Diisopropylaniline and 2,4,6-trimethylaniline were stirred over calcium hydride and distilled prior to use. Trimethyl chlorosilane, dimethylformamide, and acetonitrile were purified according to the standard purification method.[20] The following instruments were used for physical characterization of the compounds: melting points: TA-Instruments DSC Q-20; elemental analyses: Foss–Heraeus CHNO-Rapid; IR: Varian 1300 FT-IR; NMR: Bruker AC-200 P-FT (^{1}H, 200 MHz), Bruker AV 300 (^{1}H, 300 MHz; ^{29}Si, 60 MHz, dept based on $^nJ_{SiH}$ = 7 Hz, δ^{29}Si(SiMe$_4$) = 0), Bruker AMX-400 (^{1}H, 400 MHz), Varian 500 MHz INOVA (^{1}H, 500 MHz; ^{13}C, 126 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz). [NMR chemical shifts were referenced to the respective solvent signal; numbering of the compounds see the Supporting Information.] X-ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction, Denzo-SMN;[21] absorption correction, Denzo;[22] structure solution, SHELXS-97;[23] structure refinement, SHELXL-97;[24] and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 50% probability, *R*-values are given for observed reflections, and wR_2 values are given for all reflections. The optical rotations were determined using a Perkin-Elmer 341 polarimeter. The measurements were performed at room temperature using a Na lamp. The solvent and the respective wavelength used for the measurement are indicated within the experimental details. The unit for all values of optical rotation is [deg × cm^2 × g^{-1}]; the respective concentration is given in units of [g × mL^{-1}].[25]

Polymer samples were dissolved at 140 °C before GPC on a Polymer Laboratories PL-GPC 220 high-temperature chromatograph, equipped with 2 Olexis 300·7.5 mm columns and triple detection by a differential refractive index detector, a PL-BV 400 HT viscometer, and a Precision Detectors model 2040 light scattering detector (15°, 90°). The solvent was 1,2,4-trichlorbenzene (BHT stabilized) at 160 °C, with a PE standard.

Materials. Compound **5** was synthesized according to the literature.[8b] Ferrocenecarboxaldehyde and (*S*)-1,2,4-butanetriol were purchased from Sigma-Aldrich and Alfa Aesar, respectively, and used without further purification. Ferrocenes (*S*,*S*,*pS*)-**7**, (*S*,*S*,p*R*)-**8** and **15** were prepared according to literature procedures.[1] The syntheses of the ferrocenes (*S*,*S*,*pS*)-**9**, **10**, **16**, (*S*,*S*,p*R*)-**17**, **18**, and (*pS*)-**11**, **12a**, **12b**, **12c**, **13a**, **13b**, **13c**, **20**, **21a**, **21b**, **21c**, and **21d** were independently developed analogously to published procedures, and optimized modifications are presented here. In particular, dilithiation

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conditions of compound **15** with TMP-Li were well developed, and we present the optimized conditions. Caution: triethylamine trihydrofluoride is very toxic and causes severe burns; alkyllithium reagents are extremely pyrophoric. All such reagents must be handled with due care.

Preparation of Compound (*S,S,pS*)-9. The iodoferrocene (*S,S,pR*)-**8** (15.63 g, 30.4 mmol, 1 equiv) and copper(I) oxide (1.01 g, 7.08 mmol, 1.5 equiv) were suspended in acetonitrile (300 mL). After addition of acetic acid (9.13 g, 152 mmol, 5 equiv), the mixture was heated to 80 °C for 3 h under an argon atmosphere. The solvent was removed, and the crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 4:1) to yield 10.09 g (22.6 mmol, 74%) of the desired product as a yellow oil. Anal. Calcd for $C_{21}H_{30}FeO_5Si$: C, 56.50; H, 6.77. Found: C, 56.74; H, 6.77. ^{1}H NMR (600 MHz, [D$_6$]-benzene, 298 K): δ 5.45 (s, 1H, 6-H), 4.72 (d, $^3J_{HH}$ = 2.6 Hz, 1H, 4H)^t, 4.33 (s, 5H, C_5H_5), 3.84 (d, $^3J_{HH}$ = 2.6 Hz, 1H, 5H)^t, 3.82 (ddd, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 1.3 Hz, 1H, 10-H$_{eq}$), 3.77 (m, 1H, 8-H), 3.44 (ddd, $^3J_{HH}$ = 12.4 Hz, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 2.6 Hz, 1H, 10-H$_{ax}$), 3.35 (dd, $^2J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 6.4 Hz, 1H, 12-H), 3.10 (dd, $^2J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 4.4 Hz, 1H, 12-H′), 3.10 (s, 3H, OCH_3), 1.81 (s, 3H, $^{Ac}CH_3$), 1.56 (dddd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, 9-H$_{ax}$), 0.93 (dtd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 2.6 Hz, $^3J_{HH}$ = 1.3 Hz, 1H, 9-H$_{eq}$), 0.40 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, $SiMe_3$), [^{t} tentative assignment]. ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 298 K): δ 168.3 (C═O), 117.0 (C3)^t, 99.6 (C6), 82.3 (C2)^t, 76.2 (C8), 75.9 (C12), 70.7 (C_5H_5), 69.3 (C5), 66.6 (C10), 66.2 (C1), 63.8 (C4), 58.8 (OMe), 28.1 (C9), 20.7 ($^{Ac}CH_3$), 1.2 ($SiMe_3$) [^{t} tentative assignment]. $[\alpha]_D^{20}$ = +8.1 (*c* 0.01055, dichloromethane).

Preparation of Compound (*S,S,pS*)-10. The acetate (*S,S,pS*)-**9** (10.09 g, 22.6 mmol, 1 equiv) was dissolved in *N,N*-dimethylformamide (100 mL), and sodium methoxide (1.34 g, 24.9 mmol, 1.1 equiv) was added in one portion, yielding a dark red solution. After 90 min, *tert*-butylchlorodiphenylsilane (6.83 g, 24.9 mmol, 1.1 equiv) was added, and the bright yellow mixture was stirred overnight. The solvent was removed, and the residue was purified by column chromatography to yield 12.26 g (19.1 mmol, 84%) of a yellow oil (silica gel, cyclohexane/ethyl acetate, 15:1). Anal. Calcd for $C_{35}H_{46}FeO_4Si_2$: C, 65.40; H, 7.21. Found: C, 65.61; H, 7.16. ^{1}H NMR (600 MHz, [D$_6$]-benzene, 298 K): δ 7.99 (m, 2 H, *o*-Ph), 7.75 (m, 2 H, *o*-Ph′), 7.28 (m, 2 H, *m*-Ph), 7.26 (m, 1H, *p*-Ph), 7.11(m, 1H, *p*-Ph′), 7.10 (m, 2H, *m*-Ph′), 5.84 (s, 1H, 6-H), 4.23 (s, 5H, C_5H_5), 3.95 (m, 1H, 10-H′), 3.92 (m, 1H, 8-H), 3.76 (d, $^3J_{HH}$ =2.6, 1H, 4-H), 3.63 (m, 1H, 10-H), 3.52 (d, $^3J_{HH}$ =2.6, 1H, 5-H), 3.46 (dd, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 6.4 Hz, 1H, 12-H), 3.22 (dd, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 4.7 Hz, 1H, 12-H′), 3.16 (s, 1H, OMe), 1.67 (m, 1H, 9-H), 1.21 (s, 9H, ^{t}Bu), 1.05 (dm, $^2J_{HH}$ = 13.2 Hz, 1H, 9-H′), 0.44 (s, $^2J_{SiH}$ = 6.8 Hz, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 298 K): δ 136.1 (*o*-Ph, *o*-Ph′), 134.2 ($^1J_{SiC}$ = 75.1 Hz, *i*-Ph), 132.6 ($^1J_{SiC}$ = 74.4 Hz, *i*-Ph′), 130.4 (*p*-Ph), 130.1 (*p*-Ph′), 128.1 (*m*-Ph), 128.0 (*m*-Ph′), 123.7 (C3)^t, 100.4 (C6), 79.9 (C2)^t, 76.7 (C8), 75.9 (C12), 70.3 (C_5H_5), 67.3 (C5), 67.0 (C10), 64.0 ($^1J_{SiC}$ = 71.8 Hz, C1), 61.6 (C4), 58.8 (OMe), 28.3 (C9), 26.9 (^{t}Bu), 19.7 ($^1J_{SiC}$ = 69.1 Hz, ^{t}Bu), 1.4 ($^1J_{SiC}$ = 53.2 Hz, $SiMe_3$) [^{t} tentative assignment]. $[\alpha]_D^{20}$ = +10.8 (*c* 0.01, dichloromethane).

Preparation of Compound (*pS*)-11. The acetal (*S,S,pS*)-**10** (11.64 g, 18.1 mmol, 1 equiv) and *p*-toluenesulfonic acid (6.90 g, 36.3 mmol, 2 equiv) were dissolved in a two-phase mixture of dichloromethane (80 mL) and water (20 mL). The mixture was heated to reflux for 3 h under vigorous stirring. The phases were separated, and the organic phase was dried over magnesium sulfate. Filtration and removal of the solvent gave the crude product, which was purified by filtration on silica gel (cyclohexane/ethyl acetate, 4:1). Attempts to crystallize the product in pentane did not yield the compound, so further purification was achieved by column chromatography on silica gel (cyclohexane/ethyl acetate/triethylamine, 66:1:1), yielding 7.72 g (76%) of a red oil after removal of the solvent. Anal. Calcd for $C_{30}H_{36}FeO_2Si_2$: C, 66.65; H, 6.71. Found: C, 67.02; H, 6.90. ^{1}H NMR (600 MHz, [D$_6$]-benzene, 298 K): δ 10.80 (d, $^5J_{HH}$ = 0.7 Hz, 1H, CHO), 7.83 (m, 2H, *o*-Ph), 7.58 (m, 2 H, *o*-Ph′), 7.22 (m, 1H, *p*-Ph), 7.20 (m, 2H, *m*-Ph), 7.13 (m, 1H, *p*-Ph′), 7.07 (m, 2H, *m*-Ph′), 3.97 (s, 5H, C_5H_5), 3.96 (d, $^3J_{HH}$ = 2.6 Hz, 1H, 4-H), 3.76 (dd, $^3J_{HH}$ = 2.6 Hz, $^5J_{HH}$ = 0.7 Hz, 1H, 5-H), 1.07 (s, 9H, ^{t}Bu), 0.40 (s, $^2J_{SiH}$ = 6.8 Hz, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 298 K): δ 192.2 (CHO), 136.1 (*o*-Ph), 135.9 (*o*-Ph′), 133.3 (*i*-Ph), 131.9 (*i*-Ph′), 130.7 (*p*-Ph), 130.5 (*p*-Ph′), 128.2 (*m*-Ph), 128.2 (*m*-Ph′), 128.5 (C2), 73.7 (C3), 71.9 (C5), 70.6 (C_5H_5), 65.9 (C1), 65.1 (C4), 26.8 (^{t}Bu), 19.6 (^{t}Bu), 0.2 ($SiMe_3$). $[\alpha]_D^{20}$ = −30.7 (*c* 0.00215, dichloromethane).

Preparation of Compound (*pS*)-12a. The aldehyde (*pS*)-**11** (483 mg, 0.89 mmol, 1 equiv), aniline (0.40 mL, 4.5 mmol, 5 equiv), and *p*-toluenesulfonic acid (16.9 mg, 0.089 mmol, 0.1 equiv) were dissolved in dry toluene (10 mL) in a Schlenk vessel and heated at 80 °C for 18 h. Removal of the solvent gave the crude product, which was purified by column chromatography (cyclohexane/triethylamine/ethyl acetate, 66:1:1, R_f = 0.74) to give a red oil quantitatively. Anal. Calcd for $C_{36}H_{41}FeNOSi_2$: C, 70.22; H, 6.71; N, 2.27. Found: C, 70.09; H, 6.80; N, 2.04. ^{1}H NMR (600 MHz, [D$_6$]-benzene, 298 K): δ 9.09 (d, $^5J_{HH}$ = 0.5 Hz, 1H, CHN), 7.88 (m, 2 H, *o*-Ph), 7.62 (m, 2H, *o*-Ph′), 7.34 (m, 2 H, *o*-Ph^N), 7.222 (m, 2H, *m*-Ph^N)[1], 7.215 (m, 1H, *p*-Ph)[1], 7.22 (m, 2H, *m*-Ph)[1], 7.12 (m, 1H, *p*-Ph′), 7.07 (m, 2H, *m*-Ph′), 7.04 (m, 1H, *p*-Ph^N), 4.05 (s, 5H, C_5H_5), 4.02 (d, $^3J_{HH}$ = 2.6 Hz, 1H, 4-H), 3.80 (dd, $^3J_{HH}$ = 2.6 Hz, $^5J_{HH}$ = 0.6 Hz, 1H, 5-H), 1.1 (s, 9H, ^{t}Bu), 0.50 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, $SiMe_3$), [^{1} from the ghsqc NMR experiment].[26] ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 298 K): δ 159.1 (CHN), 153.7 (*i*-Ph^N), 136.2 (*o*-Ph), 136.0 (*o*-Ph′), 133.6 (*i*-Ph), 132.3 (*i*-Ph′), 130.6 (*p*-Ph), 130.4 (*p*-Ph′), 129.6 (*m*-Ph^N), 128.2 (*m*-Ph), 128.1 (*m*-Ph′), 126.9 (C2), 125.4 (*p*-Ph^N), 120.9 (*o*-Ph^N), 75.6 (C3), 70.6 (C5), 70.5 (C_5H_5), 64.9 (C1), 64.0 (C4), 26.9 (^{t}Bu), 19.6 (^{t}Bu), 1.0 ($SiMe_3$). $[\alpha]_D^{20}$ = −4.3 (*c* 0.01, dichloromethane).

Preparation of Compound (*pS*)-13a. The imine (*pS*)-**12a** (0.519 g, 0.84 mmol, 1 equiv) and triethylamine trihydrofluoride (0.09 mL, 0.56 mmol, 2/3 equiv) were dissolved in tetrahydrofuran (20 mL), and the solution was stirred for 2 h. The solvent was removed, and the crude product was purified by column chromatography under argon (silica gel, cyclohexane/ethyl acetate/triethylamine, 20:1:1, solvents were degassed before use). Removal of the solvent under vacuum gave quantitative (*pS*)-**13a**. X-ray quality crystals were obtained from a solution in pentane at −30 °C. Anal. Calcd for $C_{20}H_{23}FeNOSi$: C, 63.66; H, 6.14; N, 3.71. Found: C, 64.00; H, 6.34; N, 3.54. Mp: 102 °C (DSC). ^{1}H NMR (600 MHz, [D$_6$]-benzene, 298 K): δ 9.88 (bs, 1H, OH), 8.78 (d, $^5J_{HH}$ = 0.5 Hz, 1H, CHN), 7.12 (m, 2H, *m*-Ph^N), 7.07 (m, 2H, *o*-Ph^N), 7.01 (m, 1H, *p*-Ph^N), 4.69 (dm, 1H, $^3J_{HH}$ = 2.6 Hz, 4-H), 4.03 (s, 5H, C_5H_5), 3.74 (d, 1H, $^3J_{HH}$ = 2.6 Hz, 5-H), 0.18 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 298 K): δ 166.3 (CHN), 151.0 (*i*-Ph^N), 130.9 (C2)^t, 129.7 (*m*-Ph^N), 126.1 (*p*-Ph^N), 120.8 (*o*-Ph^N), 70.4 (C5), 70.3 (C_5H_5), 68.3 (C3)^t, 66.0 (C1), 61.6 (C4), 0.8 ($^1J_{SiC}$ = 52.6 Hz, $SiMe_3$) [^{1} tentative assignment]. $[\alpha]_D^{20}$ = +0.7 (*c* 0.001, dichloromethane).

X-ray crystal structure analysis of 13a: formula $C_{20}H_{23}FeNOSi$, M = 377.33, red crystal, 0.45 × 0.20 × 0.10 mm, a = 7.8042(2), b = 10.3403(3), c = 22.6773(6) Å, V = 1830.01(9) Å^3, ρ_{calc} = 1.370 g cm^{-3}, μ = 0.895 mm^{-1}, empirical absorption correction (0.688 ≤ T ≤ 0.915), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 31 085 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.60 Å^{-1}, 4532 independent (R_{int} = 0.030) and 4317 observed reflections [$I > 2\sigma(I)$], 223 refined parameters, R = 0.022, wR_2 = 0.062, max. (min.) residual electron density 0.27 (−0.17) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, Flack parameter −0.008(10).

Preparation of Compound (*pS*)-12b. The aldehyde (*pS*)-**11** (1.70 g, 3.15 mmol), 2,4,6-trimethylaniline (2.2 mL, 15.7 mmol, 5 equiv), and *p*-toluenesulfonic acid (60 mg, 0.315 mmol, 0.1 equiv) were dissolved in dry toluene (40 mL) in a Schlenk vessel and heated at 125 °C for 7 h. Removal of the solvent gave the crude product, which was purified by column chromatography (cyclohexane/triethylamine/ethyl acetate, 66:1:1, R_f = 0.74) to give 1.85 g (89%) of the imine as an orange foam solid. Anal. Calcd for $C_{39}H_{47}FeNSi_2O$: C, 71.21; H, 7.20; N, 2.13. Found: C, 71.84; H, 7.61; N, 2.20. ^{1}H NMR (500 MHz, [D$_6$]-benzene, 298 K): δ 8.84 (m, 1H, CHN), 7.86 (m,

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2H, *o*-Ph), 7.64 (m, 2H, *o*-Ph′), 6.84 (s, 2H, *m*-Mes), 7.20 (m, 2H, *m*,*p*-Ph), 7.12 (m, 1H, *p*-Ph′)[1], 7.09 (m, 2H, *m*-Ph′)[1], 4.17 (s, 5H, C_5H_5), 3.98 (d, $^3J_{HH}$ = 2.6 Hz, 1H, 4H), 3.77 (d, $^3J_{HH}$ = 2.6 Hz, 1H, 5H), 2.35 (s, 6H, *o*-CH_3^{Mes}), 2.19 (s, 3H, *p*-CH_3^{Mes}), 1.02 (s, 9H, ^{t}Bu), 0.46 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, $SiMe_3$) [[1] from the ghsqc NMR experiment].[26] $^{13}C\{^1H\}$ NMR (126 MHz, [D_6]-benzene, 298 K): δ 162.4 (CHN), 151.1 (*i*-Mes), 136.0 (*o*-Ph), 135.9 (*o*-Ph′), 133.8 (*i*-Ph), 132.5 (*i*-Ph′), 132.2 (*p*-Mes), 130.5 (*p*-Ph), 130.3 (*p*-Ph′), 129.4 (*m*-Mes), 128.2 (*m*-Ph), 128.1 (*m*-Ph′), 127.0 (C2)^t, 126.8 (*o*-Mes), 74.8 (C3)^t, 70.5 (C5), 70.3 (C_5H_5), 64.9 (C1), 63.8 (C4), 26.8 (^{t}Bu), 20.8 (*p*-CH_3^{Mes}), 19.6 (^{t}Bu), 19.0 (*o*-CH_3^{Mes}), 1.0 ($SiMe_3$), [^{t} tentative assignment]. $[\alpha]_D^{20}$ = −20.7 (*c* 0.0115, dichloromethane).

Preparation of Compound (*pS*)-13b. The imine (*pS*)-**12b** (1.23 g, 1.87 mmol, 1 equiv) and triethylamine trihydrofluoride (201 μL, 1.24 mmol, 2/3 equiv) were dissolved in tetrahydrofuran (30 mL), and the solution was stirred for 2 h. The solvent was removed, and the crude dark red oil product was purified by column chromatography under argon (silical gel, cyclohexane/ethyl acetate/triethylamine, 20:1:1, solvents were degassed before use). Deep red solid of (S_p)-**13b** was isolated by removal of solvents, yield: 0.52 g (1.23 mmol, 66%). Anal. Calcd for $C_{23}H_{29}FeNSiO$: C 65.86; H 6.97; N 3.34. Found: C, 65.23; H, 7.18; N, 3.23. Mp: 131 °C (DSC). ^1H NMR (600 MHz, [D_6]-benzene, 298 K): δ 9.91 (bs, 1H, OH), 8.50 (m, 1H, CHN), 6.78 (m, 2H, *m*-Mes), 4.66 (d, $^3J_{HH}$ = 2.6 Hz, 1H, 4-H), 4.10 (s, 5H, C_5H_5), 3.74 (d, $^3J_{HH}$ = 2.6 Hz, 1H, 5-H), 2.15 (s, 3H, *p*-CH_3^{Mes}), 2.14 (s, 6H, *o*-CH_3^{Mes}), 0.14 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_6]-benzene, 298 K): δ 169.5 (CHN), 147.9 (*i*-Mes), 133.8 (*p*-Mes), 131.0 (C2)^t, 129.5 (*m*-Mes), 127.7 (*o*-Mes), 70.2 (C_5H_5), 69.9 (C5), 68.1 (C3)^t, 65.8 (C1), 61.2 (C4), 20.8 (*p*-CH_3^{Mes}), 18.7 (*o*-CH_3^{Mes}), 0.7 ($SiMe_3$), [^{t} tentative assignment]. $[\alpha]_D^{20}$ = +158.2 (*c* 0.00045, dichloromethane).

Preparation of Compound (*pS*)-12c. The aldehyde (*pS*)-**11** (1.70 g, 3.15 mmol, 1 equiv), 2,3,4,5,6-pentafluoroaniline (2.95 g, 16.1 mmol, 5 equiv), and *p*-toluenesulfonic acid (61.3 mg, 0.32 mmol, 0.1 equiv) were dissolved in dry toluene (40 mL) in a Schlenk vessel and heated at 125 °C for 7 h. Removal of the solvent gave the crude product, which was purified by column chromatography (silica gel, cyclohexane/triethylamine/ethyl acetate, 66:1:1, R_f = 0.74) to give the imine **12c** as an purple-red foam solid; yield 1.37 g, 1.90 mmol, 60.3%. Anal. Calcd for $C_{36}H_{36}F_5NFeOSi_2$: C, 61.27; H, 5.14; N, 1.98. Found: C, 61.58; H, 5.26; N, 1.93. ^1H NMR (600 MHz, [D_6]-benzene, 298 K): δ 9.12 (bs, 1H, CHN), 7.85 (m, 2H, *o*-Ph), 7.60 (m, 2H, *o*-Ph′), 7.22 (m, 3H, *m*,*p*-Ph), 7.12 (m, 1H, *p*-Ph′), 7.07 (m, 2H, *m*-Ph′), 4.08 (s, 5H, C_5H_5), 4.06 (d, $^3J_{HH}$ = 2.7 Hz, 1H, 4-H), 3.88 (dd, $^3J_{HH}$ = 2.6 Hz, $^5J_{HH}$ = 0.5 Hz, 5-H), 1.11 (s, 9H, ^{t}Bu), 0.45 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_6]-benzene, 298 K): δ 169.0 (br, CHN), 136.1 (*o*-Ph), 135.9 (*o*-Ph′), 133.2 (*i*-Ph), 131.9 (*i*-Ph′), 130.8 (*p*-Ph), 130.5 (*p*-Ph′), 128.3 (*m*-Ph), 128.2 (*m*-Ph′), 127.8 (C2)^t, 73.5 (C3)^t, 72.2 (C5), 70.9 (C_5H_5), 65.4 (C1), 64.7 (C4), 26.8 (^{t}Bu), 19.6 (^{t}Bu), 0.5 ($SiMe_3$), n.o. (C_6F_5) [^{t} tentative assignment]. ^{19}F NMR (564 MHz, [D_6]-benzene, 298 K): δ −155.3 (m, 2F, *o*-C_6F_5), −163.2 (t, $^3J_{FF}$ = 21.9 Hz, 1F, *p*-C_6F_5), −164.0 (m, 2F, *m*-C_6F_5). $[\alpha]_D^{20}$ = −14.0 (*c* 0.00205, dichloromethane).

Preparation of Compound (*pS*)-13c. The imine (*pS*)-**12c** (0.54 g, 0.76 mmol, 1 equiv) and triethylamine trihydrofluoride (41 μL, 0.25 mmol, 1/3 equiv) were dissolved in tetrahydrofuran (15 mL), and the solution was stirred for 2 h. The solvent was removed, and the purple oily residues were dissolved in pentane (10 mL) and filtered. Evaporation of pentane gave a crude purple product, which was further purified by column chromatography under Ar (silical gel, cyclohexane/ethyl acetate/triethylamine, 20:1:1, solvents were degassed before use). Purple solids of (*pS*)-**13c** were isolated by removal of solvents; yield 264.5 mg, 0.566 mmol, 74%. Anal. Calcd for $C_{20}H_{18}F_5FeNOSi$: C, 51.41; H, 3.88; N, 3.00. Found: C, 51.90; H, 3.68; N, 2.80. Mp: 85 °C. ^1H NMR (600 MHz, [D_2]-dichloromethane, 298 K): δ 8.96 (s, 1H, CHN), 8.60 (s, 1H, OH), 4.86 (d, $^3J_{HH}$ = 2.7 Hz, 1H, 4-H), 4.22 (s, 5H, C_5H_5), 4.15 (d, $^3J_{HH}$ = 2.7 Hz, 5-H), 0.31 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_2]-dichloromethane, 298 K): δ 175.7 (CHN), 130.3 (C2)^t, 72.1 (C5), 71.0 (C_5H_5), 68.0 (C1), 67.2 (C3)^t, 62.7 (C4), 0.6 ($SiMe_3$), n.o. (C_6F_5) [^{t} tentative assignment]. ^{19}F NMR (564 MHz, [D_2]-dichloromethane, 298 K): δ −154.6 (m, 2F, *o*-C_6F_5), −161.7 (t, $^3J_{FF}$ = 21.3 Hz, 1F, *p*-C_6F_5), −164.0 (m, 2F, *m*-C_6F_5). $[\alpha]_D^{20}$ = +38.9 (*c* 0.00115, dichloromethane).

Preparation of Compound (*pS*,*pS*)-14a. The alcohol (*pS*)-**13a** (125.4 mg, 0.33 mmol, 2 equiv) and zirconium tetrachloride (38.7 mg, 0.17 mmol, 1 equiv) were dissolved in dichloromethane (5 mL), instantly giving a deep blue solution. The mixture was stirred for 2 h, and the solvent was removed. The dark blue solid can be washed with pentane or ether (1 mL). This gave 187 mg (0.15 mmol, 91%) of complex (*pS*,*pS*)-**14a** as a deep blue solid. Anal. Calcd for $C_{40}H_{46}Cl_4Fe_2N_2O_2Si_2Zr$: C, 48.64; H, 4.69; N, 2.84. Found: C, 46.82 ; H, 4.84; N, 2.52. Mp: 215 °C. ^1H NMR (600 MHz, [D_2]-dichloromethane, 298 K): δ 12.17 (d, $^3J_{HH}$ = 14.8 Hz, 1H, NH), 8.87 (d, $^3J_{HH}$ = 14.8 Hz, 1H, CHN), 7.75 (m, 2H, *o*-Ph^N), 7.53 (m, 2H, *m*-Ph^N), 7.46 (m, 1H, *p*-Ph^N), 6.04 (br, 1H, 4-H), 4.92 (br, 1H, 5-H), 4.66 (s, 5H, C_5H_5), 0.35 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_2]-dichloromethane, 298 K): δ 161.3 (CHN), 138.4 (*i*-Ph^N), 130.7 (*m*-Ph^N), 128.6 (*p*-Ph^N), 119.6 (*o*-Ph^N), 135.3 (C3)^t, 81.3 (br, C5), 73.2 (C_5H_5), 72.3 (br, C4), 70.0 (C1), 64.9 (C2)^t, 0.6 ($^1J_{SiC}$ = 53.8 Hz, $SiMe_3$) [^{t} tentative assignment]. $[\alpha]_D^{20}$ = +1.9 (*c* 0.00085, dichloromethane).

Preparation of Compound (*pS*,*pS*)-14b. The alcohol (*pS*)-**13b** (46.0 mg, 0.11 mmol, 2 equiv) and zirconium tetrachloride (13.1 mg, 0.056 mmol, 1 equiv) were dissolved in dichloromethane (3 mL), instantly giving a deep blue solution. The mixture was stirred overnight and the solvent was removed to afford 46.0 mg (0.086 mmol, 76%) of complex (*pS*,*pS*)-**14b** as a deep blue solid. Anal. Calcd for $C_{46}H_{58}Cl_4Fe_2N_2O_2Si_2Zr$: C, 51.55; H, 5.45; N, 2.61. Found: C, 51.68; H, 5.57; N, 2.52. Mp: 129 °C. ^1H NMR (600 MHz, [D_2]-dichloromethane, 298 K): δ 11.99 (d, $^3J_{HH}$ = 15.4 Hz, 1H, NH), 8.30 (d, ^3J = 15.4 Hz, 1H, CHN), 7.02 (s, 2H, *m*-Mes), 5.98 (br, 1H, 4-H), 4.80 (d, $^3J_{HH}$ = 2.3 Hz, 1H, 5-H), 4.60 (s, 5H, C_5H_5), 2.42 (bs, 6H, *o*-CH_3^{Mes}), 2.34 (s, 3H, *p*-CH_3^{Mes}), 0.28 ($SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_2]-dichloromethane, 298 K): δ 173.5 (CHN), 139.8 (*p*-Mes), 135.0 (*i*-Mes), 134.9 (C-3)^t, 133.2 (*o*-Mes), 129.9 (*m*-Mes), 79.7 (C5), 72.1 (C_5H_5), 70.7 (br, C4), 70.2 (C1), 63.2 (C2)^t, 21.0 (*p*-CH_3^{Mes}), 18.8 (*o*-CH_3^{Mes}), 0.5 ($^1J_{SiC}$ = 53.2 Hz, $SiMe_3$) [^{t} tentative assignment]. $[\alpha]_D^{20}$ = +14.4 (*c* 0.00125, dichloromethane).

Preparation of Compound (*pS*,*pS*)-14c. The alcohol (*pS*)-**13c** (52.8 mg, 0.11 mmol, 2 equiv) and zirconium tetrachloride (13.2 mg, 0.056 mmol, 1 equiv) were dissolved in dichloromethane (3 mL), instantly giving a deep blue solution. The mixture was stirred overnight, and the solvent was removed, giving 52 mg (0.045 mmol, 79%) of complex (*pS*,*pS*)-**14c** as a deep purple solid. Anal. Calcd for $C_{40}H_{36}Cl_4F_{10}Fe_2N_2O_2Si_2Zr$: C, 41.15; H, 3.11; N, 2.40. Found: C, 40.40; H, 3.15; N, 2.41. Mp: 147 °C. ^1H NMR (600 MHz, [D_2]-dichloromethane, 298 K): δ 11.32 (d, $^3J_{HH}$ = 14.4 Hz, 1H, NH), 8.58 (d, $^3J_{HH}$ = 14.4 Hz, 1H, CHN), 6.28 (br, 1H, 4-H), 5.16 (d, $^3J_{HH}$ = 2.7 Hz, 5-H), 4.72 (s, 5H, C_5H_5), 0.26 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_2]-dichloromethane, 298 K): δ 163.3 (CHN), 136.1 (C-3)^t, 84.6 (C5), 74.8 (C_5H_5), 74.0 (br, C4), 70.3 (C1), 63.3 (C2)^t, 0.3 ($SiMe_3$) [^{t} tentative assignment; C_6F_5 not listed]. ^{19}F NMR (564 MHz, [D_2]-dichloromethane, 298 K): δ −147.8 (br, 2F, *o*-C_6F_5), −154.0 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), −160.3 (br, 2F, *m*-C_6F_5).

Preparation of Compound (*S*,*S*,*pS*)-16. To a degassed solution of bromo-substituted ferrocene acetal (*S*,*S*,*pS*)-**15** (2.68 g, 6.8 mmol, 1 equiv) in THF (40 mL) was added dropwise at −78 °C Li-TMP in THF/hexane (prepared *in situ*, 7.5 mmol, 1.1 equiv). The reaction mixture was subsequently stirred for 30 min at −78 °C followed by 3 h at −30 °C. The temperature was again lowed to −78 °C, and $ClSiMe_3$ was injected. The temperature was raised to 0 °C, and stirring was continued for 16 h. The reaction was quenched with saturated aqueous Na_2CO_3 (30 mL) before diethyl ether was added, and the phases were separated. The aqueous phase was extracted three times with diethyl ether (each time 10 mL). The combined organic phases were dried over $MgSO_4$, and the solvents were removed under reduced pressure. The orange residue was chromatographed on silica gel (cyclohexane/ethyl acetate, 20:1) to afford a bright yellow oil (0.85 g, 27%). Anal. Calcd for $C_{19}H_{27}FeBrO_3Si$: C, 48.84; H, 5.82. Found: C, 44.60; H, 5.84. ^1H NMR (600 MHz, [D_6]-benzene, 298 K): δ 5.51 (s, 1H, 6-H),

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4.38 (d, $^3J_{HH}$ = 2.4 Hz, 1H, 5-H), 4.17 (s, 5H, C_5H_5), 3.89 (m, 1H, 10-H_{eq}), 3.87 (d, $^3J_{HH}$ = 2.4 Hz, 1H, 4-H), 3.75 (m, 1H, 8-H), 3.51 (m, 1H, 10-H_{ax}), 3.30 (dd, $^2J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, 12-H), 3.16 (m, $^2J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, 12-H′), 3.06 (s, 3H, OCH_3), 1.68 (ddd, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 12.1 Hz, $^3J_{HH}$ = 5.3 Hz, 1H, 9-H_{ax}), 1.05 (dm, $^2J_{HH}$ = 13.3 Hz, 1H, 9-H_{eq}), 0.41 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_6]-benzene, 298 K): δ 100.5 (C6), 89.0 (C2)^t, 81.8 (C1)^t, 76.5 (C8), 75.5 (C12), 73.1 (C4), 72.4 (C5), 71.8 (C_5H_5), 70.1 (C3), 66.7 (C10), 58.8 (OCH_3), 28.2 (C9), 1.2 ($SiMe_3$) [^{t} tentative assignment]. $[\alpha]_D^{20}$ = −3.5 (*c* 0.00225, dichloromethane).

Preparation of Compound (*S*,*S*,*p*R)-17. To a degassed solution of the bromo-substituted ferrocene acetal (*S*,*S*,*pS*)-**15** (1.32 g, 3.35 mmol, 1 equiv) in THF (15 mL) was added dropwise at −78 °C Li-TMP in THF/hexane (prepared *in situ*, 8.37 mmol, 2.5 equiv). The reaction mixture was subsequently stirred for 30 min at −78 °C followed by 6 h at −30 °C. The temperature was again cooled to −78 °C, and $ClSiMe_3$ was injected. The temperature was raised to 0 °C, and stirring was continued for 16 h. The reaction was quenched with saturated aqueous Na_2CO_3 (30 mL) before diethyl ether was added, and the phases were separated. The aqueous phase was extracted three times with diethyl ether (each time 10 mL). The combined organic phases were dried over $MgSO_4$, and the solvents were removed under reduced pressure. The orange residue was chromatographed on silica gel to yield 1.23 g (68%) of a yellow oil (cyclohexane/ethyl acetate, 20:1). Anal. Calcd for $C_{22}H_{35}BrFeO_3Si_2$: C, 48.98; H, 6.54. Found: C, 49.00; H, 6.41. ^1H NMR (600 MHz, [D_6]-benzene, 298 K): δ 5.57 (s, 1H, 6-H), 4.25 (s, 5H, C_5H_5), 4.09 (s, 1H, 5-H), 3.88 (ddd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 5.3 Hz, $^3J_{HH}$ = 1.3 Hz, 1H, 10-H_{eq}), 3.76 (m, 1H, 8-H), 3.52 (ddd, $^3J_{HH}$ = 12.6 Hz, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 2.6 Hz, 1H, 10-H_{ax}), 3.29 (dd, $^2J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 5.3 Hz, 1H, 12-H), 3.15 (m, $^2J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 5.3 Hz, 1H, 12-H′), 3.04 (s, 3H, OCH_3), 1.69 (dddd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 5.3 Hz, 1H, 9-H_{ax}), 1.05 (dm, $^2J_{HH}$ = 13.2 Hz, 1H, 9-H_{eq}), 0.44 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, 4-$SiMe_3$), 0.35 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, 1-$SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_6]-benzene, 298 K): δ 100.7 (C6), 92.0 (C3)^t, 87.9 (C2)^t, 78.7 (C5), 76.5 (C8), 75.5 (C12), 74.2 (C1), 72.5 (C4), 71.9 (C_5H_5), 66.7 (C10), 58.8 (OCH_3), 28.2 (C9), 1.3 ($^1J_{SiC}$ = 53.6 Hz, 4-$SiMe_3$), 0.1 ($^1J_{SiC}$ = 53.3 Hz, 1-$SiMe_3$) [^{t} tentative assignment]. $[\alpha]_D^{20}$ = +0.7 (*c* 0.00095, dichloromethane).

Preparation of Compound (*S*,*S*,*pS*)-18. A mixture of compound (*S*,*S*,*pR*)-**17** (1.02 g, 1.89 mmol, 1 equiv), acetic acid (0.54 mL, 9.45 mmol, 5 equiv, previously dried over 4 Å molecular sieves), and Cu_2O (0.30 g, 2.08 mmol, 1.1 equiv) was heated to reflux in CH_3CN (25 mL) for 15 h under nitrogen. After cooling to room temperature, CH_2Cl_2 (30 mL) was added, and the reaction mixture was filtered over Celite. The residue was then washed with additional CH_2Cl_2 (20 mL). The filtrate and washings were combined, washed with water (20 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the resultant crude yellow crystalline solid was purified by column chromatography (silica gel, hexane/EtOAc, 10:1) to yield the product as a yellow oil in 58.9% yield (0.58 g, 1.1 mmol).

Improved Method. A mixture of the bromo acetal (*S*,*S*,*p*R)-**17** (21.20 g, 39.3 mmol, 1 equiv), acetic acid, and acetic anhydride (acetic acid 5.63 mL, 98.3 mmol, 2.5 equiv, acetic anhydride 9.23 mL, 98.3 mmol, 2.5 equiv, previously mixed and heated at 80 °C for 1 h) and Cu_2O (6.19 g, 43.2 mmol, 1.1 equiv) was heated to reflux in CH_3CN (130 mL) for 15 h under nitrogen. After cooling to rt, CH_2Cl_2 (30 mL) was added and the reaction mixture was filtered over Celite. The residue was then washed with additional CH_2Cl_2 (100 mL). The filtrate and washings were combined and extracted with water (50 mL), and the green-yellow organic phase was dried over $MgSO_4$. The solvent was removed *in vacuo*, and the resultant crude yellow crystalline solid was purified by column chromatography (silica gel, hexane/etheyl acetate, 10:1) to yield the product as a yellow oil in 78.6% yield (16.026 g, 30.9 mmol). Anal. Calcd for $C_{24}H_{38}FeO_5Si_2$: C, 55.59; H, 7.39. Found: C, 55.49; H, 7.44. ^1H NMR (600 MHz, [D_6]-benzene, 298 K): δ 5.42 (s, 1H, 6-H), 4.33 (s, 5H, C_5H_5), 3.93 (s, 1H, 5-H), 3.81 (ddd, $^2J_{HH}$ =11.3 Hz, $^3J_{HH}$ = 5.1 Hz, $^3J_{HH}$ = 1.3 Hz, 1H, 10-H_{eq}), 3.64 (m, 1H, 8-H), 3.42 (ddd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 2.6 Hz, 1H, 10-H_{ax}), 3.25 (dd, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 5.7 Hz, 1H, H-12), 3.11 (dd, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 4.7 Hz, 1H, H-12′), 3.07 (s, 3H, OCH_3), 1.92 (s, 3H, $COCH_3$), 1.58 (dddd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 5.1 Hz, 1H, 9-H_{ax}), 0.96 (dtd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 2.6 Hz, $^3J_{HH}$ = 1.3 Hz, 1H, 9-H_{eq}), 0.37 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, 4-$SiMe_3$), 0.33 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, 1-$SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_6]-benzene, 298 K): δ 169.1 (C═O), 120.9 (C2)^t, 100.0 (C6), 85.4 (C3)^t, 76.3 (C8), 75.6 (C12), 74.1 (C5), 70.9 (C_5H_5), 69.7 (C4), 67.8 (C1), 66.3 (C10), 58.9 (OCH_3), 28.2 (C9), 20.5 ($^{Ac}CH_3$), 1.1 (4-$SiMe_3$), −0.1 (1-$SiMe_3$) [^{t} tentative assignment]. ^{29}Si dept (60 MHz, [D_6]-benzene, 298 K): δ −2.4, −4.0. $[\alpha]_D^{20}$ = −3.4 (*c* 0.00555, dichloromethane).

Preparation of Compound (*pS*)-19. The acetoxyl acetal (2*S*,4*S*,*pS*)-**18** (10.50 g, 20.3 mmol) was dissolved under Ar in dichloromethane (100 mL), and water (40 mL) was added, followed by addition of *p*-toluenesulfonic acid monohydrate (7.70 g, 40.5 mmol, 2 equiv). The mixture was heated to reflux for 3 h under vigorous stirring, the phases were separated, and the organic phase was dried over magnesium sulfate. Filtration and removal of the solvent gave the crude product, which was purified by column chromatography on silica gel (cyclohexane/ethyl acetate/triethylamine, 15:1:1). The desired product was isolated as orange crystalline needles in a 98% yield (8.27 g, 19.9 mmol). X-ray quality crystals were obtained from a solution in diethyl ether at −30 °C. Anal. Calcd for $C_{19}H_{28}FeO_3Si_2$: C, 54.80; H, 6.78. Found: C, 55.10; H, 7.00. Mp: 86.6 °C. ^1H NMR (500 MHz, [D_6]-benzene, 298 K): δ 10.18 (m, 1H, CHO), 4.19 (m, 1H, 5-H), 4.10 (s, 5H, C_5H_5), 1.75 (s, 3H, $^{Ac}CH_3$), 0.32 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, 4-$SiMe_3$), 0.21 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, 1-$SiMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, [D_6]-benzene, 298 K): δ 191.5 (CHO), 169.5 (C═O), 124.6 (C2)^t, 78.3 (C3)^t, 78.0 (C5), 72.9 (C1), 72.7 (C4), 71.1 (C_5H_5), 20.2 ($^{Ac}CH_3$), 0.3 ($^1J_{SiC}$ = 53.5 Hz, 4-$SiMe_3$), −0.5 ($^1J_{SiC}$ = 53.8 Hz, 1-$SiMe_3$) [^{t} tentative assignment]. ^{29}Si dept (60 MHz, [D_6]-benzene, 298 K): δ −2.4, −3.9. $[\alpha]_D^{20}$ = +14.1 (*c* 0.0021, dichloromethane).

X-ray crystal structure analysis of (*pS*)-19: formula $C_{19}H_{28}FeO_3Si_2$, *M* = 416.44, orange crystal, 0.35 × 0.07 × 0.05 mm, *a* = 23.4373(5) Å, *b* = 23.4373(5) Å, *c* = 7.6500(1) Å, γ = 120.00°, *V* = 3639.21(12) Å^3, ρ_{calc} = 1.140 g cm^{-3}, μ = 0.733 mm^{-1}, empirical absorption correction (0.783 ≤ *T* ≤ 0.964), *Z* = 6, trigonal, space group *P*65 (No. 170), λ = 0.71073 Å, *T* = 223(2) K, ω and φ scans, 23 609 reflections collected (±*h*, ±*k*, ±*l*), (sin θ)/λ = 0.66 Å^{-1}, 5364 independent (R_{int} = 0.041) and 4728 observed reflections [$I > 2\sigma(I)$], 233 refined parameters, *R* = 0.058, wR_2 = 0.158, max. (min.) residual electron density 0.87 (−0.32) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, Flack parameter 0.07(3).

Preparation of Compound (*pS*)-20. A Schlenk vessel was charged with the acetoxy aldehyde (*pS*)-**19** (8.27 g, 19.9 mmol, 1 equiv) under Ar, and 10% KOH (100 mL) and ethanol (120 mL) were added subsequently. The reaction mixture immediately became a dark purple-red suspension. The reaction mixture was allowed to stir at rt for 1 h before the evaporation of ethanol. The residue was extracted with pentane (100 mL × 3). The combined organic phases were extracted with water (100 mL) and quickly dried over $MgSO_4$. Evaporation of the solvent gave a dark red crystalline solid. The crude hydroxyl aldehyde was purified by FC on silica gel (cyclohexane/ethylacetate/triethylamine, 15:1:1). The fraction should be collected under argon. The pure oxygen-sensitive compound was isolated as a bright red solid in 85% yield (6.35 g, 17.0 mmol). Anal. Calcd for $C_{17}H_{26}FeO_2Si_2$: C, 54.54; H, 7.00. Found: C, 54.64; H, 6.94. Mp: 88 °C. ^1H NMR (600 MHz, [D_6]-benzene, 298 K): δ 10.20 (m, 1H, CHO), 8.00 (br, 1H, OH), 4.00 (s, 5H, C_5H_5), 3.91 (s, 1H, 5-H), 0.36 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, 1-$SiMe_3$), 0.11 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, 4-$SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_6]-benzene, 298 K): δ 199.9 (CHO), 135.8 (C2)^t, 77.1 (C5), 70.5 (C_5H_5), 70.2 (C3)^t, 69.3 (C4), 67.0 (C1), 0.7 ($^1J_{SiC}$ = 53.2 Hz, 4-$SiMe_3$), −0.4 ($^1J_{SiC}$ = 53.3 Hz, 1-$SiMe_3$) [^{t} tentative assignment]. ^{29}Si dept (60 MHz, [D_6]-benzene, 298 K): δ −3.0, −3.8. $[\alpha]_D^{20}$ = −124.7 (*c* 0.00105, dichloromethane).

X-ray crystal structure analysis of (*pS*)-20: formula $C_{17}H_{26}FeO_2Si_2$, *M* = 374.41, red crystal, 0.30 × 0.17 × 0.10 mm, *a* = 12.2088(2) Å, *b* = 19.7299(4) Å, *c* = 8.1404(1) Å, *V* = 1960.85(6) Å^3, ρ_{calc} = 1.268 g cm^{-3}, μ = 0.895 mm^{-1}, empirical absorption

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correction ($0.775 \leq T \leq 0.915$), $Z = 4$, orthorhombic, space group $P2_12_12$ (No. 18), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 12 101 reflections collected ($\pm h, \pm k, \pm l$), $(\sin\theta)/\lambda = 0.60$ Å^{-1}, 4594 independent ($R_{int} = 0.046$) and 4163 observed reflections [$I > 2\sigma(I)$], 206 refined parameters, $R = 0.042$, $wR_2 = 0.094$, max. (min.) residual electron density 0.29 (−0.28) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, Flack parameter −0.07(2).

Preparation of Compound (*pS*)-21a. The aldehyde (*pS*)-**20** (1.57 g, 4.2 mmol, 1 equiv), aniline (1.92 mL, 21 mmol, 5 equiv), and *p*-toluenesulfonic acid (80 mg, 0.42 mmol, 0.1 equiv) were dissolved in dry toluene (50 mL) in a Schlenk vessel and heated at 125 °C for 2.5 h. Removal of the solvent gave the crude dark red product, which was purified by column chromatography under argon (silica gel, cyclohexane/triethylamine/ethyl acetate, 10:1:1) to give the bright red product in a 84.0% yield (1.59 g, 3.5 mmol). X-ray quality crystals were obtained from a solution in pentane at −30 °C. Anal. Calcd for $C_{23}H_{31}FeNOSi_2$: C 61.45; H 6.95; N 3.12. Found: C, 62.04; H, 7.03; N, 2.67. Mp: 120 °C. ^{1}H NMR (500 MHz, [D_2]-dichloromethane, 298 K): δ 9.59 (br, 1H, OH), 8.83 (s, 1H, CHN), 7.41 (m, 2H, *m*-Ph), 7.26 (m, 1H, *p*-Ph), 7.22 (m, 2H, *o*-Ph), 4.15 (s, 5H, C_5H_5), 3.89 (s, 1H, 5-H), 0.37 (s, $^2J_{SiH}$ = 6.8 Hz, 9H, 1-$SiMe_3$), 0.35 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, 4-$SiMe_3$). ^{13}C{^{1}H} NMR (126 MHz, [D_2]-dichloromethane, 298 K): δ 166.6 (CHN), 150.8 (*i*-Ph), 135.0 (C2)^t, 129.7 (*m*-Ph), 126.2 (*p*-Ph), 120.9 (*o*-Ph), 75.3 (C5), 70.3 (C_5H_5), 69.9 (C3)^t, 68.8 (C4), 64.9 (C1), 0.8 ($^1J_{SiC}$ = 52.9 Hz, 4-$SiMe_3$), −0.3 ($^1J_{SiC}$ = 53.3 Hz,1-$SiMe_3$) [^{t} tentative assignment]. ^{29}Si dept (60 MHz, [D_2]-dichloromethane, 298 K): δ −2.8, −3.7. $[\alpha]_D^{20}$ = −106.4 (*c* 0.0007, dichloromethane).

X-ray crystal structure analysis of (*pS*)-21a: formula $C_{23}H_{31}FeNOSi_2$, $M = 449.52$, red crystal, 0.35 × 0.20 × 0.04 mm, $a = 8.3549(2)$ Å, $b = 10.0008(2)$ Å, $c = 28.5722(7)$ Å, $V = 2387.37(9)$ Å^3, $\rho_{calc} = 1.251$ g cm^{-3}, $\mu = 0.745$ mm^{-1}, empirical absorption correction ($0.780 \leq T \leq 0.971$), $Z = 4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 15 610 reflections collected ($\pm h, \pm k, \pm l$), $(\sin\theta)/\lambda = 0.60$ Å^{-1}, 5312 independent ($R_{int} = 0.048$) and 5035 observed reflections [$I > 2\sigma(I)$], 260 refined parameters, $R = 0.039$, $wR_2 = 0.088$, max. (min.) residual electron density 0.31 (−0.33) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, Flack parameter 0.002(16).

Preparation of Compound (*pS*)-21b. The aldehyde (*pS*)-**20** (0.51 g, 1.35 mmol), 2,4,6-trimethylaniline (0.95 mL, 6.76 mmol, 5 equiv), and *p*-toluenesulfonic acid (25.7 mg, 0.14 mmol, 0.1 equiv) were dissolved in dry toluene (20 mL) in a Schlenk vessel and heated at 125 °C for 4.5 h. Removal of the solvent gave the crude dark red product, which was purified by column chromatography under argon (silica gel, cyclohexane/triethylamine/ethyl acetate, 10:1:1) to give the bright red product in a quantitative yield (0.66 g, 1.35 mmol). Anal. Calcd for $C_{26}H_{37}FeNOSi_2$: C 63.52; H 7.59; N 2.85. Found: C, 63.49; H, 7.72; N, 2.76. Mp: 111 °C. ^{1}H NMR (600 MHz, [D_6]-benzene, 298 K): δ 9.92 (br, 1H, OH), 8.53 (s, 1H, CHN), 6.76 (m, 2H, *m*-Mes), 4.16 (s, 5H, C_5H_5), 3.92 (s, 1H, 5-H), 2.15 (s, 3H, *p*-CH_3^{Mes}), 2.13 (s, 6H, *o*-CH_3^{Mes}), 0.48 (s, 9H, 1-$SiMe_3$), 0.17 (s, 9H, 4-$SiMe_3$). ^{13}C{^{1}H} NMR (151 MHz, [D_6]-benzene, 298 K): δ 169.5 (CHN), 147.8 (*i*-*Mes*), 135.7 (C2)^t, 133.7 (*p*-Mes), 129.5 (*m*-Mes); 127.7 (*o*-Mes), 74.5 (C5), 70.3 (C_5H_5), 69.9 (C3)^t, 68.3 (C4), 64.6 (C1), 20.8 (*p*-CH_3^{Mes}), 18.8 (*o*-CH_3^{Mes}), 0.7 ($^1J_{SiC}$ = 52.9 Hz, 4-$SiMe_3$), −0.1 ($^1J_{SiC}$ = 53.1 Hz, 1-$SiMe_3$) [^{t} tentative assignment]. ^{29}Si dept (60 MHz, [D_6]-benzene, 298 K): δ −3.3, −3.7. $[\alpha]_D^{20}$ = −164.1 (*c* 0.00085, dichloromethane).

Preparation of Compound (*pS*)-21c. The aldehyde (*pS*)-**20** (1.2 g, 3.2 mmol, 1 equiv), 2,3,4,5,6-pentafluoroaniline (3.0 g, 16 mmol, 5 equiv), and *p*-toluenesulfonic acid (61 mg, 0.32 mmol, 0.1 equiv) were dissolved in dry toluene (40 mL) in a Schlenk vessel and heated at 125 °C for 2.5 h. Removal of the solvent gave the crude purple-red product, which was purified by column chromatography under argon (silica gel, cyclohexane/triethylamine/ethyl acetate, 10:1:1) to give a purple solid in 84% yield (1.44 g, 2.7 mmol). X-ray quality crystals were obtained from a solution in pentane at −30 °C. Anal. Calcd for $C_{23}H_{26}F_5FeNOSi_2$: C, 51.21; H, 4.86; N, 2.60. Found: C, 51.55; H, 5.09; N, 2.37. Mp: 97 °C. ^{1}H NMR (600 MHz, [D_6]-benzene, 298 K): δ 9.01 (s, 1H, OH), 8.90 (br, 1H, CHN), 4.13 (s, 5H, C_5H_5), 4.02 (s, 1H, 5-H), 0.45 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, 1-$SiMe_3$), 0.22 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, 4-$SiMe_3$). ^{13}C{^{1}H} NMR (151 MHz, [D_6]-benzene, 298 K): δ 175.2 (CHN), 135.6 (C2)^t, 76.7 (C5), 70.8 (C_5H_5), 69.5 (C4), 69.1 (C3)^t, 66.8 (C1), 0.7 ($^1J_{SiC}$ = 53.0 Hz, 4-$SiMe_3$), −0.3 ($^1J_{SiC}$ = 53.2 Hz, 1-$SiMe_3$) [^{t} tentative assignment; C_6F_5 not listed]. ^{19}F NMR (470 MHz, [D_6]-benzene, 298 K): δ −154.8 (m, 2F, *o*-C_6F_5), −161.5 (t, $^3J_{FF}$ = 21.3 Hz, 1F, *p*-C_6F_5), −163.5 (m, 2F, *m*-C_6F_5). ^{29}Si dept (60 MHz, [D_6]-benzene, 298 K): δ −3.1, −3.6. $[\alpha]_D^{20}$ = −1.0 (*c* 0.0011, dichloromethane).

X-ray crystal structure analysis of (*pS*)-21c: formula $C_{23}H_{26}F_5FeNOSi_2$, $M = 539.48$, red crystal, 0.40 × 0.30 × 0.10 mm, $a = 10.9331(2)$ Å, $b = 11.0599(2)$ Å, $c = 21.0231(3)$ Å, $V = 2542.09(7)$ Å^3, $\rho_{calc} = 1.410$ g cm^{-3}, $\mu = 0.740$ mm^{-1}, empirical absorption correction ($0.756 \leq T \leq 0.929$), $Z = 4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 15 873 reflections collected ($\pm h, \pm k, \pm l$), $(\sin\theta)/\lambda = 0.66$ Å^{-1}, 5958 independent ($R_{int} = 0.037$) and 5650 observed reflections [$I > 2\sigma(I)$], 305 refined parameters, $R = 0.037$, $wR_2 = 0.086$, max. (min.) residual electron density 0.37 (−0.22) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, Flack parameter 0.103(15).

Preparation of Compound (*pS*)-21d. The aldehyde (*pS*)-**20** (1.59 g, 4.3 mmol, 1 equiv), cyclohexylamine (2.4 mL, 21.3 mmol, 5 equiv), and *p*-toluenesulfonic acid (81 mg, 0.43 mmol, 0.1 equiv) were dissolved in dry toluene (30 mL) in a Schlenk vessel and heated at 125 °C for 3 h. Removal of the solvent gave the crude purple-red product, which was purified by column chromatography under argon (silical gel, cyclohexane/triethylamine/ethyl acetate, 10:1:1) to give a purple solid in 89% yield (1.73 g, 3.8 mmol). X-ray quality crystals were obtained from a solution in pentane at −30 °C. Anal. Calcd for $C_{23}H_{37}FeNOSi_2$: C, 60.64; H, 8.19; N, 3.07. Found: C, 61.30; H, 7.92; N, 2.95. Mp: 140 °C. ^{1}H NMR (500 MHz, [D_6]-benzene, 298 K): δ 10.39 (s, 1H, OH), 8.53 (s, 1H, CHN), 4.11 (s, 5H, C_5H_5), 3.83 (s, 1H, 5-H), 2.86 (m, 1H, 8-H), 1.63/1.18 (10-H)^{t,1}, 1.62/1.38 (13-H)^{t,1}, 1.60/1.13 (12-H)^{t,1}, 1.57/1.32 (9-H)^{t,1}, 1.44/1.09 (11-H)^{t,1}, 0.48 (s, 9H, 1-$SiMe_3$), 0.25 (s, 9H, 4-$SiMe_3$) [^{t} tentative assignment; ^{1} from ghsqc NMR experiment].[26] ^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 298 K): δ 164.0 (CHN), 135.7 (C2)^t, 73.7 (C5), 70.3 (C_5H_5), 70.0 (C3)^t, 68.5 (C8), 67.1 (C4), 63.9 (C1), 35.2 (C9)^{t,1}, 34.3 (C13)^{t,1}, 25.8 (C11)^{t,1}, 24.5 (C10)^{t,1}, 24.7 (C12)^{t,1}, 0.9 ($^1J_{SiC}$ = 52.7 Hz, 4-$SiMe_3$), −0.1 ($^1J_{SiC}$ = 52.8 Hz, 1-$SiMe_3$) [^{t} tentative assignment; ^{1} from ghsqc NMR experiment].[26] ^{29}Si dept (60 MHz, [D_6]-benzene, 298 K): δ −3.2, −3.8. $[\alpha]_D^{20}$ = −106.3 (*c* 0.0006, dichloromethane)

X-ray crystal structure analysis of (*pS*)-21d: formula $C_{23}H_{37}FeNOSi_2$, $M = 449.52$, red crystal, 0.55 × 0.30 × 0.25 mm, $a = 7.4546(3)$ Å, $b = 15.3671(6)$ Å, $c = 10.8018(4)$ Å, $\beta = 92.031(2)°$, $V = 1236.63(8)$ Å^3, $\rho_{calc} = 1.223$ g cm^{-3}, $\mu = 0.720$ mm^{-1}, empirical absorption correction ($0.693 \leq T \leq 0.840$), $Z = 2$, monoclinic, space group $P2_1$ (No. 4), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 5865 reflections collected ($\pm h, \pm k, \pm l$), $(\sin\theta)/\lambda = 0.60$ Å^{-1}, 4766 independent ($R_{int} = 0.039$) and 4625 observed reflections [$I > 2\sigma(I)$], 260 refined parameters, $R = 0.064$, $wR_2 = 0.168$, max. (min.) residual electron density 1.21 (−0.70) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, Flack parameter 0.02(3).

Preparation of Compound (*pS*,*pS*)-22a. A solution of the alcohol (*pS*)-**21a** (170.3 mg, 0.38 mmol, 2 equiv) in dichloromethane (8 mL) was slowly added to a suspension of zirconium tetrachloride (44.1 mg, 0.19 mmol, 1 equiv) in dichloromethane (5 mL), instantly giving a deep blue solution. The mixture was stirred overnight, and the solvent was evaporated, giving a deep blue solid. The deep blue solid was washed with pentane (5 mL), and removal of the pentane solution gave 150.6 mg (0.13 mmol, 70%) of complex (*pS*,*pS*)-**22a** as a deep blue solid. Anal. Calcd for $C_{46}H_{62}Cl_4Fe_2N_2O_2Si_4Zr$: C, 48.80; H, 5.52; N, 2.47. Found: C, 48.81; H, 5.49; N, 2.30. Mp: 159 °C. ^{1}H NMR (500 MHz, [d_2]-dichloromethane, 298 K): δ 12.30 (br, 1H, NH), 8.80 (d, $^3J_{HH}$ = 15.4 Hz, 1H, CHN), 7.73 (m, 2H, *o*-Ph), 7.49 (m, 2H, *m*-Ph), 7.45 (m, 1H, *p*-Ph), 4.71 (s, 1H, 5-H), 4.58 (s, 5H, C_5H_5), 0.58 (s, 9H, 1-$SiMe_3$), 0.38 (s, 9H, 4-$SiMe_3$). ^{13}C{^{1}H} NMR (126 MHz, [d_2]-dichloromethane, 298 K): δ 161.7 (CHN), 138.8 (*i*-Ph), 138.2 (br, C2)^t, 130.4 (*m*-Ph), 128.6 (*p*-Ph_C), 120.1 (*o*-Ph), 87.4 (C5). 76.8 (C1), 74.4 (br, C4), 72.8 (C_5H_5), 67.2 (C3)^t, 1.0 (1-$SiMe_3$), 0.8 (4-

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$SiMe_3$) [^{t} tentative assignment]. ^{29}Si dept (60 MHz, [d_2]-dichloromethane, 298 K): δ −2.54, −2.55. $[\alpha]_D^{20}$ = +1.6 (c 0.0007, dichloromethane).

Preparation of Compound (*pS*,*pS*)-22d. A solution of the alcohol (*pS*)-**21d** (230.3 mg, 0.51 mmol, 2 equiv) in dichloromethane (15 mL) was slowly added to a suspension of zirconium tetrachloride (58.9 mg, 0.25 mmol, 1 equiv) in dichloromethane (5 mL), instantly giving a deep blue solution. The mixture was stirred overnight, and the solvent was evaporated, giving a purple solid. The purple solid was washed with pentane (5 mL), and removal of the pentane solution gave 220.6 mg (0.193 mmol, 76.3%) of complex (*pS*,*pS*)-**22d** as a deep purple solid. X-ray quality crystals were obtained from a solution in ether/toluene at room temperature. Anal. Calcd for $C_{46}H_{74}Cl_4Fe_2N_2O_2Si_4Zr$: C, 48.29; H, 6.52; N, 2.45. Found: C, 49.13; H, 6.75; N, 2.23. Mp: >350 °C. ^{1}H NMR (500 MHz, [d_2]-dichloromethane, 298 K): δ 11.19 (br, 1H, NH), 8.35 (d, $^3J_{HH}$ = 16.8 Hz, 1H, CHN), 4.44 (s, 5H, C_5H_5), 4.40 (s, 1H, 5-H), 3.62 (m, 1H, 8-H), 2.23/1.67 (9-H)^{t,1}, 2.22/1.71 (13-H)^{t,1}, 1.92, 1.90/1.42, 1.40 (10,12-H)^{t,1}, 1.73/1.25 (11-H)^{t,1}, 0.53 (s, 9H, 1-$SiMe_3$), 0.34 (s, 9H, 4-$SiMe_3$) [^{t} tentative assignment; ^{1} from ghsqc NMR experiment].[26] ^{13}C{^{1}H} NMR (126 MHz, [d_2]-dichloromethane, 298 K): δ 167.1 (CHN), 137.6 (C2)^t, 84.4 (C5), 74.3 (C1), 73.0 (C4), 72.1 (C_5H_5), 65.2 (C3)^t, 61.9 (C8), 32.1 (C9)^{t,1}, 33.2 (C13)^{t,1}, 25.25, 25.28 (C10, 12)^{t,1}, 25.31 (C11)^{t,1}, 1.1 (1-$SiMe_3$), 0.8 (4-$SiMe_3$). ^{29}Si dept (60 MHz, [d_2]-dichloromethane, 298 K): δ −2.8, −2.9.

X-ray crystal structure analysis of (*pS*,*pS*)-22d: formula $C_{50}H_{84}Cl_4FeN_2O_3Si_4Zr$, M = 1218.27, red crystal, 0.25 × 0.20 × 0.10 mm, a = 12.2271(3) Å, b = 17.1048(4) Å, c = 29.5106(7) Å, V = 6171.9(3) Å^3, ρ_{calc} = 1.311 g cm^{-3}, μ = 0.918 mm^{-1}, empirical absorption correction (0.803 ≤ T ≤ 0.914), Z = 4, orthorhombic, space group $C2221$ (No. 20), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 18 787 reflections collected ($\pm h$, $\pm k$, $\pm l$), (sin θ)/λ = 0.66 Å^{-1}, 7131 independent (R_{int} = 0.056) and 6553 observed reflections [I > 2σ(I)], 306 refined parameters, R = 0.103, wR_2 = 0.246, max. (min.) residual electron density 0.63 (−0.83) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, Flack parameter 0.33(6).

■ ASSOCIATED CONTENT

Supporting Information

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[§]X-ray crystal structure analyses.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143−1170.

(2) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587−2598.

(3) Britovsek, G. J. P. V.; Gibson, C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.

(4) (a) Garnovskii, A. D.; Nivorozhkin, A. L.; Minkin, V. I. *Coord. Chem. Rev.* **1993**, *126*, 1−69. (b) Yamada, S. *Coord. Chem. Rev.* **1999**, *190−192*, 537−555. (c) Vigato, P. A.; Tamburini, S. *Coord. Chem. Rev.* **2004**, *248*, 1717−2128. (d) Drozdzak, R.; Allaert, B.; Ledoux, N.; Dragutan, I.; Dragutan, V.; Verpoort, F. *Adv. Synth. Catal.* **2005**, *347*, 1721−1743.

(5) (a) Niemeyer, J.; Kehr, G.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2009**, 3716−3730. (b) Niemeyer, J.; Kehr, G.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2009**, 3731−3741.

(6) Niemeyer, J.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem.—Eur. J.* **2008**, *14*, 9499−9502.

(7) See also: (a) Niemeyer, J.; Kehr, G.; Fröhlich, R.; Erker, G. *Eur. J. Inorg. Chem.* **2010**, 680−684. (b) Niemeyer, J.; Cloppenburg, J.; Frölich, R.; Kehr, G.; Erker, G. *J. Organomet. Chem.* **2010**, *695*, 1801−1812.

(8) (a) Riant, O.; Samuel, O.; Kagan, H. B. *J. Am. Chem. Soc.* **1993**, *115*, 5835−5836. (b) Riant, O.; Samuel, O.; Flessner, T.; Taudien, S.; Kagan, H. B. *J. Org. Chem.* **1997**, *62*, 6733−6745. (c) Masson-Szymczak, A.; Riant, O.; Gref., A.; Kagan, H. B. *J. Organomet. Chem.* **1996**, *511*, 193−197.

(9) Strauch, J.; Warren, T. H.; Erker, G.; Fröhlich, R.; Saarenketo, P. *Inorg. Chim. Acta* **2000**, *300−302*, 810−821.

(10) (a) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Tanaka, H.; Fujita, T. *Chem. Lett.* **1999**, *28*, 1263−1264. (b) Matsui, S.; Tohi, Y.; Mitani, M.; Saito, J.; Makio, H.; Tanaka, H.; Nitabaru, M.; Nakano, T.; Fujita, T. *Chem. Lett.* **1999**, *28*, 1065−1066. (c) Mitani, M.; Mohri, J.-I.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.-I.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 3327−3336. (d) Mitani, M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Nakano, T.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc.* **2003**, *125*, 4293−4305. (e) Matsugi, T.; Fujita, T. *Chem. Soc. Rev.* **2008**, *37*, 1264−1277. (f) Makio, H.; Terao, H.; Iwashita, A.; M., T.; Fujita, T. *Chem. Rev.* **2011**, *111*, 2363−2449.

(11) (a) Sato, M.; Motoyama, I.; Hata, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2213−2217. (b) Akabori, S. *Synthesis* **1981**, 278−280.

(12) (a) Vickers, M. E. *Polymer* **1995**, *36*, 2667−2670. (b) Bartczak, Z.; Galeski, A. *Polymer* **1996**, *37*, 2113−2123. (c) Russell, K. E.; Hunter, B. K.; Heyding, R. D. *Polymer* **1997**, *38*, 1409−1414. (d) Malmberg, A.; Kokko, E.; Lehmus, P.; Löfgren, B.; Seppälä, J. V. *Macromolecules* **1998**, *31*, 8448−8454. (e) Wang, W.; Yan, D.; Zhu, S.; Hamielec, A. E. *Macromolecules* **1998**, *31*, 8677−8683. (f) Kooko, E.; Lehmus, P.; Leino, R.; Luttikhedde, H. J. G.; Ekholm, P. J.; Näsman, H.; Seppälä, J. V. *Macromolecules* **2000**, *33*, 9200−9204. (g) Sun, M. T.; Xu, T. Q.; Cao, W.; Liu, Y.; Wu, Q. L.; Mu, Y.; Ye, L. *Dalton Trans.* **2011**, *40*, 10184−10194.

(13) (a) Huffman, J. W.; Keith, L. H.; Asbury, R. L. *J. Org. Chem.* **1965**, *30*, 1600−1604. (b) Slocum, D. W.; Jennings, C. A.; Engelmann, T. R.; Rockett, B. W.; Hauser, C. R. *J. Org. Chem.* **1971**, *36*, 377−381. (c) Slocum, D. W.; Koonsvitsky, B. P.; Ernst, C. R. *J. Organomet. Chem.* **1972**, *38*, 125−132. (d) Mongin, F.; Schlosser, M. *Tetrahedron Lett.* **1996**, *37*, 6551−6554.

(14) (a) Butler, I. R.; Drew, M. G. B. *Inorg. Chem. Commun.* **1999**, *2*, 234−237. (b) Butler, I. R.; Drew, M. G. B.; Plath, M. *Inorg. Chem. Commun.* **1999**, *2*, 424−427. (c) Butler, I. R.; Drew, M. G. B. C.; Greenwell, H.; Lewis, E.; Plath, M.; Müssig, S.; Szewczyk, J. *Inorg. Chem. Commun.* **1999**, *2*, 576−580. (d) Steurer, M.; Wang, Y. P.; Mereiter, K.; Weissensteiner, W. *Organometallics* **2007**, *26*, 3850−3859.

(15) (a) Holger, S.; Fritz, V. *Synthesis* **1999**, 295−305. (b) Nasser, I. *Eur. J. Org. Chem.* **2006**, 483−488. (c) Marjan, J. *Helv. Chim. Acta* **2009**, *92*, 555−566. (d) Ramin, G. V. *Tetrahedron Lett.* **2009**, *50*, 1861−1865.

(16) Galland, G. B.; Quijada, R.; Rojas, R.; Bazan, G.; Komon, Z. J. A. *Macromolecules* **2002**, *35*, 339−345.

(17) (a) *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A.; Hayashi, T., Eds.; VCH: Weinheim, 1995. (b) Štěpnička, P.; Blaser, H.-U.; Chen, W.; Camponovo, F.; Togni, A. In *Ferrocenes: Ligands, Materials and Biomolecules*; Štěpnička, P., Ed.; VCH: Weinheim, 2008; pp 117−237.

(18) (a) Matsugi, H.; Kashiwa, N.; Fujita, T. *Adv. Synth. Catal.* **2002**, *344*, 477−493. (b) Mitani, M.; Nakano, T.; Fujita, T. *Chem.−Eur. J.* **2003**, *9*, 2396−2403. (c) Suzuki, Y.; Terao, H.; Fujita, T. *Bull. Chem.*

Soc. Jpn. **2003**, *76*, 1493−1517. (d) Nakayama, Y; Bando, H.; Sonobe, Y.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 617−625. (e) Mitani, M.; Saito, J.; Nakayama, Y.; Markio, H.; Matsukawa, N.; Natsui, S.; Mohri, J.; Furuyama, R.; Terao, H.; Bando, H.; Tanaka, H.; Fujita, T. *Chem. Rec.* **2004**, *4*, 137−158. (f) Makio, H.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 52−66. (g) Matsugi, T.; Fujita, T. *Chem. Soc. Rev.* **2008**, *37*, 1264−1277.

(19) Pangborn, A. B.; Giradello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

(20) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann, Elsevier Science: Oxford, 2003; pp 85, 215.

(21) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326.

(22) Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, *A59*, 228−234.

(23) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

(24) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.

(25) Eliel, E. L.; Wilen, S. H.; Doyle, M. P. *Basic Organic Stereochemistry*; Wiley-Interscience: New York, 2001; pp 1−7.

(26) Berger, S.; Braun, S. *200 and More NMR Experiments*; Wiley-VCH: Weinheim, 2004.

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