



Communication Planar-Chiral P and N-bridged Diferrocenes

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Abstract: We describe the synthesis of planar-chiral diferrocene compounds **4**, **7** and **12**, intended as key precursors for a new family of asymmetric catalyst ligands with less complex structures than their popular equivalents. In contrast to conventional 1,2-disubstituted ferrocenes containing center-chiral and planar-chiral elements, these compounds are purely planar-chiral due to the absence of α -substituted ethyl groups. The title compounds **4**, **7** and **12** were obtained from known precursors in 87%, 59% and 60% yields, respectively.

Keywords: ferrocene; transition metal ligand; planar chirality; diferrocene

1. Introduction

Disubstituted ferrocenyl compounds have been used as powerful asymmetry-inducing units in organic synthesis; if one cyclopentadienyl ring is substituted with two different functional groups, the resulting compound displays planar chirality [1,2]. Ferrocene-based ligands have been used successfully in asymmetric catalysis [3–7]. Their range of applications is impressive, and beyond academic research, ligands like Xyliphos (Scheme 1) have been employed in industrial-scale asymmetric hydrogenations [8].



Scheme 1. Ferrocene-based catalysts Xyliphos (i), Pigiphos (ii), NHC-Pigiphos (iii) and Stanphos (iv), and pincer ligands recently developed by Zirakzadeh et al. (v–viii).

The majority of their syntheses are based on 1-*N*,*N*-dimethylamino-ethylferrocene, well known as Ugi's amine. Its popularity is based on simple large-scale preparation of both enantiomerically pure forms

and perfect stereocontrol of ortho-metallation/substitution, enabling the diastereoselective synthesis of planar-chiral disubstituted ferrocenyl compounds [9]. In a subsequent reaction, the dimethylamino group at the α -carbon of the ethyl side chain can be displaced by other nucleophiles stereo-retentively [10]. This is shown in Scheme 2.



Scheme 2. Stereochemical properties of Ugi's amine: diastereoselective lithiation followed by reaction with electrophile E [9] and stereo-retentive $S_N 1$ reaction with nucleophile Nu at the α -carbon of the alkyl sidechain [10].

In many cases, the asymmetric induction may be even improved further by combining two of these asymmetric ferrocene units in one molecule. For instance, the P,P,P-diferrocene ligand Pigiphos [11] (Scheme 1) has been employed in asymmetric acetalization [12], hydroamination [13–16], hydrophosphination [17], carbonyl reduction [18,19], 1,3-dipolar cycloaddition [20], olefin cyclopropanation [21] and Nazarov cyclization [22]. Stanphos (Scheme 1) is the cyclized version of Pigiphos [23] and has been used as a P,P-ligand in asymmetric hydroalkoxylations [24] and the α -hydroxylation of 1,3-ketoesters [25]. Zirakzadeh et al. developed ferrocene-based PNP-pincer ligands for Fe(II)-catalyzed asymmetric hydrogenation [26]. Their diferrocene compounds are linked by a secondary amine, imine [27] or two secondary imines [28] (Scheme 1).

We attempted to access similar compounds containing oxygen, nitrogen or sulfur at the ethyl side chain. However, we noticed that when replacing phosphorous (R_2PPh) with sulfur (R_2S) or nitrogen (R_2NPh), eliminations yielding vinylferrocenes as decay products become a serious side reaction [29], thereby limiting the practical value of such compounds. In this article, we present two possible synthetic workarounds:

Designing diferrocenyl compounds with methyl instead of ethyl chains, effectively removing the possibility of elimination. As we cannot use the convenient diastereoselective *ortho*-lithiation nor the stereo-retentive S_N1 reaction of Ugi's amine, Xiao et al. have developed a diastereoselective *ortho*-lithiation protocol of the chiral methylferrocene equivalent with a homochiral *O*-methylephedrine auxiliary attached to the amino group [30]. This approach will yield compounds 4 and 7.

Instead of the α -substituted ethyl group, we changed to a β -substituted one in order to disfavor elimination processes. To date, there are barely any examples of said type of ferrocene compounds in the literature. With such structures, we get rid of stereocenters at the ethylene side chains, simplifying the stereochemistry to pure planar chirality. This approach would yield compounds like **12**.

2. Results

2.1. N-bridged Diferrocenyl Compound 4

Our synthetic route towards precursors for compounds resembling Pigiphos [11] is illustrated in Scheme 3. First, the ferrocenyl-O-methylephedrine derivative 1 was diastereoselectively lithiated and converted to bromide 2 using a modified procedure with $C_2Br_2Cl_4$ instead of $C_2Br_2F_4$ [30]. For removal of the auxiliary ammonium iodide, salt 3 was prepared under standard conditions [30].



Scheme 3. Synthesis of diferrocenes 4 and 7.

The activated leaving group enabled the coupling of two homochiral ferrocene units of configuration R_p with bidentate nucleophiles to yield purely planar-chiral diferrocenyl compounds. We used 0.5 equiv of benzyl amine as a nucleophile to obtain diferrocene amine 4 from 3 following a modified procedure [30], but were not able to obtain the desired compound, instead diferrocenyl amine 4 was obtained in 65% yield in DMF under microwave irradiation (supporting information document, Figures S1–S3).

Encouraged by the outcome, we optimized the yield by performing this transformation in two steps. First, ammonium salt **3** was treated with a large excess of benzyl amine, yielding 90% of monoferrocenyl amine **5** (supporting information document, Figures S4–S7). Subsequently, **5** was coupled with one equiv. of **3** to give **4** in 87% yield over two steps.

2.2. P-bridged Diferrocenyl Compound 7

Similar to diferrocene **8**, as published by Hayashi et al. [24,31,32], we planned to couple two auxiliary-substituted ferrocene molecules **1** via Cl₂PPh to obtain a phosphorous-linked diferrocene. However, our preliminary experiments failed, possibly due to the steric repulsion of the large ephedrine auxiliary. Instead, we present an efficient workaround to obtain a similar diferrocene precursor.

To overcome the problem of steric hindrance in **1** we replaced the bulky auxiliary prior to coupling with a smaller substituent. The sterically less demanding and purely planar-chiral amine **6** was obtained from ammonium salt **3** and dimethylamine in an autoclave according to reference [30]. We then followed an optimized ortho-lithiation protocol [30] to couple **6** with 0.5 equiv of Cl_2PPh and obtained a compound identified as the desired homochiral phosphorous-linked diferrocene (R_p , R_p)-7 in 59% yield (supporting information document, Figures S8–S11) and some dehalogenated product of **6**.

Compound 7 strongly resembles Hayashi's diamine diferrocene compound 8 [24,31,32], but the stereochemical complexity is reduced from configuration ($S_rS_rR_p, R_p$) to (R_p, R_p), since it is entirely planar-chiral. We thus propose compound 7 as a new key precursor for less complicated equivalents of ferrocene-based ligands, such as Gipiphos [33] and Stanphos [23–25], with the additional advantage of hindered elimination at the alkyl chains.

2.3. 1,2-Substituted Diferrocenyl Phosphinsulfide 12

In order to synthesize further purely planar-chiral diferrocenyl phosphines (Scheme 4), divinyl substituted diferrocenylphosphine 9 was chosen as a key intermediate, easily accessible from diamine (R,R,S_p,S_p)-8 [34] (Scheme 4). To introduce substituents at terminal carbon atoms, hydroboration of the double bond is well established, leading predominantly to anti-Markownikow products.



Scheme 4. Synthesis of diferrocene 12.

Since we noticed in a pre-experiment that treatment of **9** with BH_3^*THF followed by oxidative work-up yielded an inseparable mixture of P-borane complexes with primary and secondary OH groups, we changed to 9-borabicyclo(3.3.1)nonane (9-BBN) to improve the regioselectivity. Treatment with H_2O_2/OH^- afforded the desired diol isolated as phosphine oxide(S_p, S_p)-**10** (supporting information document, Figures S12–S15), but in moderate yield (25%) and difficult to purify chromatographically due to its high polarity. In contrast, with P-sulfide **11** (supportung information document, Figures S16 and S17) the hydroboration step proceeded more efficiently giving diol (S_p, S_p)-**12** in 60% yield (supporting information document, Figures S18–S21). Both new 1,2-substituted diferrocenyl phosphines contained some residual eluent moisture which could not be removed in high vacuum. Drying by heating was not possible since we observed product decomposition.

We have thus produced new homochiral compounds **10** and **12** with the unusual 1,2-substitution pattern rarely published for ethylferrocenes. In contrast to Hayashi's diferrocenyl precursor **8** with (R,R,S_p,S_p) , these only include two planar chiral moieties with (S_p,S_p) configuration, thereby reducing the stereochemical complexity.

3. Materials and Methods

3.1. General

Routine NMR spectra were recorded on a 400 MHz Bruker AVIII 400 spectrometer operating at 400.27 MHz (¹H), 100.66 MHz (¹³C) and 162.04 MHz (³¹P) with an autosampler. ¹H-NMR spectra and ¹³C{¹H}-NMR spectra used for substance characterization were recorded on a Bruker AVIII 700 spectrometer (Bruker Biospin, Billerica, MA, USA) at 700.40 MHz (¹H) and 176.13 MHz (¹³C). ¹³C{¹H}-NMR spectra were recorded in J-modulated mode. NMR chemical shifts are referenced to non-deuterated CHCl₃ residual shifts: at 7.26 ppm for ¹H-NMR, at 77.00 ppm for CDCl₃ for ¹³C-NMR and at 0.00 ppm for 85% H₃PO₄ for ³¹P-NMR. HR-MS were recorded by a Bruker Maxis ESI oa-RTOF mass spectrometer equipped with a quadrupole analyzer ion guide. Melting points were measured on a Reichelt Thermovar Kofler apparatus, uncorrected.

Absolute THF was dried by distillation from sodium benzophenonketyl under Ar. Et_2O and n-pentane were dried by distillation over $LiAlH_4$. Reaction progress was monitored by TLC, SiO_2 sheets with F_{254} fluorescent indicator. Heating by microwave irradiation was performed in a START-1500 oven (EMLS microwave laboratory systems, Leutkirch, Germany). Preparative column chromatography was carried out using a Biotage Isolera One automated flash chromatography instrument with self-packed columns (Macherey-Nagel silica gel 60M, particle size 40–63 μ m). All the other chemicals were analytical grade and used without further purification.

Published procedures were followed to obtain 3 [30], 6 [30], 8 [24] and 9 [34].

3.2. Synthesis

3.2.1. N-(2Rp-Bromoferrocenylmethyl)-N-methyl-1-methoxy-1-phenylprop-2-ylamine 2

Ferrocenyl compound **1** (synthesized according to reference [30]) (3.396 g, 9.00 mmol) was dissolved in 90 mL of dry n-pentane under Ar. The solution was cooled to -78 °C. To the suspension 6.4 mL of *tert*-BuLi (1.7 M, 10.9 mmol, 1.2 eq) was added dropwise and the reaction mixture was stirred for 1.5 h at -78 °C, then for 2.5 h at -30 °C. The reaction mixture was cooled to -78 °C, and 4.40 g of 1,2-dibromotetrachloroethane (13.50 mmol, 1.5 eq) dissolved in 13.5 mL of dry THF was added dropwise. The mixture was stirred at -78 °C for 20 min and allowed to warm up to RT overnight. To the reaction mixture, 90 mL of saturated aqueous NaHCO₃ solution was added and the organic layer was separated. The aqueous layer was repeatedly extracted with Et₂O (2 × 100 mL, 1 × 50 mL). The combined organic fractions were washed with water and brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO₂; 17% (Et₂O + 1.5% Et₃N) in heptane) yielding 3.513 g of **2** (86%) as a dark orange oil. NMR spectra are in agreement with reference [30].

3.2.2. N,N-Bis(2Rp-bromoferrocenylmethyl)benzylamine 4

Route 1: Ammonium iodide salt **3** [30] (100 mg, 0.17 mmol) was suspended in 8 mL of benzene and 2 mL of DMF in a glass tube. To the suspension, 9 μ L BnNH₂ (0.08 mmol, 0.5 eq) was added and the suspension was stirred under microwave irradiation at 110 °C for 10 min. The reaction mixture was cooled to RT, volatiles were removed under reduced pressure and 25 mL of Et₂O was added. The organic mixture was washed with water (2 × 30 mL) and brine (1 × 30 mL), and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified via column chromatography (SiO₂; 5–15% (Et₂O + 1.5% Et₃N) in heptane) yielding 35.7 mg of amine **4** (65%) as an orange glassy solid.

Route 2: Amine 5 (250 mg, 0.65 mmol) was dissolved in 8 mL of benzene and 2 mL of DMF in a glass tube. To the suspension, 389 mg of ammonium iodide salt 3 (0.65 mmol, 1.00 eq) was added and the mixture was stirred under microwave irradiation at 110 °C for 15 min. The reaction mixture was cooled to RT, volatiles were removed under reduced pressure and 35 mL of Et₂O was added. The organic layer was washed with water (2 × 40 mL) and brine (1 × 40 mL), and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂, 5–15% (Et₂O + 1.5% Et₃N) in heptane) yielding 417 mg of amine 4 (97%).

¹H-NMR (700 MHz, CDCl₃) δ = 7.35 (m, 2H); 7.30 (m, 2H); 7.22 (m, 1H); 4.40 (m, 2H); 4.22 (m, 2H); 4.06 (m, 2H); 4.04 (s, 10H); 3.60 (d, *J* = 14.2 Hz, 1H); 3.57 (s, 4H); 3.47 (d, *J* = 14.1 Hz, 1H) ppm. ¹³C-NMR (700 MHz, CDCl₃) δ = 140.16 (C_q); 128.64 (CH); 128.06 (CH); 126.68 (CH); 83.66 (C_q); 80.45 (C_q); 71.12 (CH); 69.95 (CH); 68.35 (CH); 66.03 (CH); 56.71 (CH₂); 51.74 (CH₂) ppm. HR-MS: m/z calculated for C₂₉H₂₇Br₂Fe₂N; [M]⁺ 658.9209, found: 658.9226.

3.2.3. N-(2Rp-Bromoferrocenylmethyl)benzylamine 5

Ammonium iodide salt 3 (100 mg, 0.17 mmol) was suspended in 8 mL of benzene and 1 mL of DMF in a glass tube, and 182 μ L of BnNH₂ (1.67 mmol, 10 eq) was added. The suspension was

stirred under microwave irradiation at 110 °C for 15 min. The reaction mixture was cooled to RT, volatiles were removed under reduced pressure and 25 mL of Et₂O was added. The organic layer was washed with water (2 × 30 mL) and brine (1 × 30 mL), and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂; 10–30% (Et₂O + 1.5% Et₃N) in heptane) yielding 58 mg of amine **5** (90%) as a yellow oil. ¹H-NMR (700 MHz, CDCl₃) δ = 7.36–7.32 (m, 4H); 7.28–7.24 (m, 1H); 4.42 (m, 1H); 4.21 (m, 1H); 4.14 (s, 5H); 4.09 (pt, *J* = 2.5 Hz, 1H); 3.84 (d, *J* = 13.3 Hz, 1H); 3.79 (d, *J* = 13.4 Hz, 1H); 3.78 (d, *J* = 13.3 Hz, 1H); 3.55 (d, *J* = 13.4 Hz, 1H) ppm. ¹³C-NMR (700 MHz, CDCl₃) δ = 140.24 (C_q); 128.38 (CH); 128.09 (CH); 126.91 (CH); 84.90 (C_q); 70.98 (C_q); 70.11 (CH); 67.32 (CH); 65.98 (CH); 53.06 (CH₂); 46.94 (CH₂) ppm. HR-MS: m/z calculated for C₁₈H₁₈BrFeN; [M + H]⁺ 384.0050, found: 384.0042.

3.2.4. 1,1"-(Phenylphosphinidene)bis[(2Rp)-2-[(dimethylamino)-methyl]]ferrocene 7

Amine 6 [30] (1.042 g, 3.236 mmol) was dissolved in 3 mL of dry Et₂O under Ar. The yellow-to-orange solution was cooled to -40 °C and 2 mL of n-BuLi (1.6 M; 3.2 mmol, 1.0 eq) was added dropwise to the reaction mixture. The solution was stirred at this temperature for 2 h, and then cooled to -78 °C. To the solution, 220 µL of Cl₂PPh (1.62 mmol, 0.50 eq) was added. The suspension was stirred for another 20 min at this temperature and allowed to warm to RT overnight. The reaction mixture was quenched with 5 mL of aqueous saturated NaHCO₃ solution. Residues were dissolved by adding some DCM and the aqueous layer was extracted with DCM (2×10 mL). The combined organic fractions were washed with water (3×35 mL) and brine $(3 \times 35 \text{ mL})$, and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO₂, 65–100% (Et₂O + 1.5% Et₃N) in heptane) yielding 561 mg diaminophosphine 7 (59%) as a brown oil. ¹H-NMR (600 MHz, CDCl₃) δ = 7.65–7.61 (m, 2H); 7.31–7.26 (m, 3H); 4.47 (m, 1H); 4.41 (m, 1H); 4.33 (pt, *J* = 2.4 Hz, 1H); 4.29 (m, 1H); 4.19 (pt, *J* = 2.4 Hz, 1H); 4.12 (m, 1H); 4.06 (s, 5H); 3.97 (dd, *J* = 13.2, 2.2 Hz, 1H); 3.67 (s, 5H); 3.47 (d, J = 13.2 Hz, 1H); 3.30 (d, J = 13.3 Hz, 1H); 3.19 (dd, J = 13.2, 1.7 Hz, 1H); 2.36 (s, 6H); 1.76 (s, 6H) ppm. ¹³C-NMR (600 MHz, CDCl₃) δ = 140.57 (d, J_{CP} = 6.5 Hz, C_q); 134.38 (d, J_{CP} = 23.0 Hz, CH); 128.48 (d, $J_{CP} = 0.9$ Hz, CH); 127.51 (d, $J_{CP} = 8.6$ Hz, CH); 91.18 (d, $J_{CP} = 31.5$ Hz, C_q); 88.46 $(d, J_{CP} = 23.0 \text{ Hz}, C_q)$; 80.17 $(d, J_{CP} = 5.9 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 12.9 \text{ Hz}, C_q)$; 72.50 $(d, J_{CP} = 5.4 \text{ Hz}, C_q)$; 72.50 $(d, J_{CP} = 5.4 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 12.9 \text{ Hz}, C_q)$; 72.50 $(d, J_{CP} = 5.4 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 12.9 \text{ Hz}, C_q)$; 72.50 $(d, J_{CP} = 5.4 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 12.9 \text{ Hz}, C_q)$; 72.50 $(d, J_{CP} = 5.4 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 12.9 \text{ Hz}, C_q)$; 72.50 $(d, J_{CP} = 5.4 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 12.9 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 12.9 \text{ Hz}, C_q)$; 72.50 $(d, J_{CP} = 5.4 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 12.9 \text{ Hz}, C_q)$; 72.50 $(d, J_{CP} = 5.4 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 12.9 \text{ Hz}, C_q)$; 72.50 $(d, J_{CP} = 5.4 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 12.9 \text{ Hz}, C_q)$; 75.92 $(d, J_{CP} = 1$ CH); 71.71 (d, *J*_{CP} = 5.3 Hz, CH); 71.64 (d, *J*_{CP} = 3.4 Hz, CH); 70.31 (d, *J*_{CP} = 3.5 Hz, CH); 69.92 (CH); 69.60 (CH); 69.41 (CH); 67.99 (CH); 58.63 (d, $J_{CP} = 11.2$ Hz, CH₂); 57.73 (d, $J_{CP} = 8.4$ Hz, CH₂); 46.02 (CH₃); 44.74 (CH₃) ppm. ³¹P-NMR δ = -44.15 (s) ppm. HRMS: m/z calculated for C₃₂H₃₇Fe₂N₂P; [M + H]⁺ 593.1471, found: 593.1457.

3.2.5. 1,1"-(Phenylphosphinideneoxide)di[(2S_p)-2-(-1-hydroxy-2-ethyl)]ferrocene 10

1,1"-(Phenylphosphinideneoxide)di[(2S_p)-2-(-1-hydroxy-2-ethyl)]ferrocene 10 [35]: Divinylphosphine **9** (56 mg, 0.11 mmol) was dissolved in 1 mL of absolute THF under Ar. The orange solution was cooled in an ice bath and 4 mL of 9-BBN solution (0.5 M in THF, 2 mmol, 19 eq) was added dropwise. The solution was stirred under Ar at RT for 24 h; then 0.7 mL of aqueous 3 M KOAc and 6 mL of aqueous H₂O₂ (30%, 59 mmol, 554 eq) were added in that order, and the solution was stirred for another 24 h. The solution was extracted with DCM (2 × 5 mL). The combined organic fractions were washed with water (15 mL) and brine (15 mL), and dried over MgSO₄. The solvent was removed under reduced pressure and the product was purified by column chromatography (Al₂O₃, 50–100% EtOAc in heptane, 0–20% MeOH in EtOAc) yielding 16 mg of dihydroxyphosphineoxide **10** (25%). ¹H-NMR (600 MHz, CDCl₃) δ = 7.77-7.73 (m, 2H); 7.53-7.44 (m, 3H); 4.55 (m, 1H); 4.45 (m, 1H); 4.36 (m, 1H); 4.31 (q, *J* = 2.3 Hz, 1H); 4.30–4.26 (m, 2H); 4.28 (s, 5H); 4.11 (q, *J* = 7.2 Hz, 1H); 4.09 (m, 1H); 4.00 (m, 1H); 3.94 (s, 5H); 3.39–3.24 (m, 3H); 3.05–2.92 (m, 2H); 2.57–2.43 (m, 2H) ppm. ¹³C-NMR δ = 135.89 (d, *J*_{CP} = 108.9 Hz, C_q); 131.28 (d, *J*_{CP} = 2.7 Hz, CH); 130.82 (d, *J*_{CP} = 9.6 Hz, CH); 128.05 (d, *J*_{CP} = 12.0 Hz, CH); 91.69 (d, *J*_{CP} = 10.8 Hz, C_q); 88.18 (d, *J*_{CP} = 11.8 Hz, C_q); 76.09 (d, *J*_{CP} = 115.6 Hz, C_q); 73.29 (d, *J*_{CP} = 15.0 Hz, CH); 72.36 (d, *J*_{CP} = 10.1 Hz, CH); 72.09 (d, *J*_{CP} = 10.2 Hz, CH); 71.25 (d, *J*_{CP} = 118.1 Hz, C_q); 71.24 (d, *J*_{CP} = 15.7 Hz, CH); 70.20 (CH); 70.11 (CH); 69.91 (d, J_{CP} = 11.0 Hz, CH); 68.98 (d, J_{CP} = 11.2 Hz, CH); 64.01 (CH₂); 62.54 (CH₂); 31.73 (CH₂); 31.10 (CH₂) ppm. ³¹P-NMR δ = 32.70 (s) ppm. HR-MS: m/z calculated for C₃₀H₃₁Fe₂O₃P; [M + Na]⁺ 605.0602, found: 605.0592; [M + K]⁺ 621.0341, found: 621.0327.

3.2.6. 1,1"-(Phenylphosphinidenesulfide)di[(2Sp)-2-vinyl]ferrocene 11

1,1"-(Phenylphosphinidenesulfide)di[(2S_p)-2-vinyl]ferrocene 11 [36]: Divinylphosphine **9** (240 mg, 0.45 mmol) and sulfur (92 mg, 2.87 mmol, 6.34 eq) were dissolved in 3.6 mL of toluene under Ar. The solution was stirred and heated under reflux for 4 h, and then cooled to RT. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO₂; 0–10% EtOAc in heptane), yielding 255 mg of divinylphosphinesulfide **11** (quantitative) as orange crystals. M.p.: 191–192 °C (decomposition). ¹H-NMR (600 MHz, CDCl₃) δ = 8.11–8.04 (m, 1H); 7.73–7.67 (m, 2H); 7.47–7.37 (m, 3H); 6.95–6.88 (m, 1H); 5.52–5.46 (m, 1H); 5.24–5.17 (m, 1H); 5.21 (m, 1H); 4.86–4.82 (m, 2H); 4.71 (m, 1H); 4.36 (s, 5H); 4.28 (m, 1H); 4.26 (m, 1H); 4.23 (s, 5H); 3.72 (m, 1H); 3.51 (m, 1H) ppm. ¹³C-NMR δ = 134.63 (d, *J_{CP}* = 87.8 Hz, C_q); 134.37 (CH); 132.97 (CH); 132.18 (d, *J_{CP}* = 10.6 Hz, CH); 130.92 (d, *J_{CP}* = 2.9 Hz, CH); 127.58 (d, *J_{CP}* = 12.3 Hz, CH); 112.13 (CH₂); 111.61 (CH₂); 88.19 (d, *J_{CP}* = 11.6 Hz, C_q); 86.45 (d, *J_{CP}* = 11.5 Hz, C_q); 79.27 (C_q); 78.63 (C_q); 75.62 (d, *J_{CP}* = 11.8 Hz, CH); 74.48 (d, *J_{CP}* = 12.7 Hz, CH); 71.10 (CH); 67.70 (d, *J_{CP}* = 9.1 Hz, CH) ppm. ³¹P-NMR (400 MHz, CDCl₃) δ = 40.54 (s) ppm. HR-MS: m/z calculated for C₃₀H₂₇Fe₂PS; [M]⁺ 562.0270, found: 562.0270.

3.2.7. 1,1"-(Phenylphosphinidenesulfide)di[(2S_p)-2-(-1-hydroxy-2-ethyl)]ferrocene 12

Divinylphosphinesulfide 11 (530 mg, 0.94 mmol) was dissolved in 10 mL of absolute THF under Ar. The orange solution was cooled in an ice bath and 16 mL of 9-BBN solution (0.5 M in THF, 8 mmol, 8.5 eq) was added dropwise. The solution was stirred under Ar at RT for 24 h, and then cooled in an ice bath; 7 mL of aqueous 3 M KOAc and 5 mL of aqueous H₂O₂ (30%, 49 mmol, 52 eq) were added in that order and the solution was stirred at RT for another 24 h. The solution was extracted with DCM $(2 \times 12 \text{ mL})$. The combined organic fractions were washed with water (50 mL) and brine (50 mL) and dried over MgSO₄. The solvent was removed under reduced pressure and the product was purified by column chromatography (SiO₂, 0–50% EtOAc in heptane) yielding 337 mg of dihydroxide 12 (60%) as an orange oil. Residual eluent moisture (heptane) could not be removed in high vacuum. Solvent removal by heating was not possible due to decomposition of the product (visible by formation of a black solid). ¹H-NMR (700 MHz, CDCl₃) δ = 7.79 (dd, *J* = 13.0, 7.6 Hz, 2H); 7.49 (pt, *J* = 7.5 Hz, 1H); 7.44 (pt, J = 7.9 Hz, 2H); 4.53 (s, 1H); 4.42 (s, 1H); 4.35 (s, 5H); 4.22 (s, 1H); 4.20 (s, 1H); 4.12 (s, 5H); 4.09 (m, 2H); 3.93 (s, 1H); 3.70 (s, 1H); 3.66 (dt, J = 15.3, 6.5 Hz, 1H); 3.28 (m, 1H); 3.14 (m, 1H); 3.13 (m, 1H); 2.70–2.64 (m, 1H); 2.53–2.48 (m, 1H) ppm. ¹³C-NMR δ = 134.90 (d, J_{CP} = 87.1 Hz, C_q); 132.13 (d, J_{CP} = 10.4 Hz, CH); 131.11 (d, J_{CP} = 2.8 Hz, CH); 127.69 (d, J_{CP} = 12.2 Hz, CH); 90.48 (d, J_{CP} = 13.0 Hz, C_q); 87.45 (d, $J_{CP} = 12.7$ Hz, C_a); 80.25 (d, $J_{CP} = 95.7$ Hz, C_a); 74.13 (d, $J_{CP} = 12.8$ Hz, CH); 74.04 (d, J_{CP} = 12.8 Hz, CH); 74.04 (d, J_{CP} = 12.8 Hz, CH); 74.04 (d, J 95.6 Hz, C_q); 72.99 (d, J_{CP} = 12.9 Hz, CH); 72.26 (d, J_{CP} = 9.4 Hz, CH); 71.97 (d, J_{CP} = 9.8 Hz, CH); 70.70 (CH); 70.44 (CH); 68.82 (d, *J*_{CP} = 10.2 Hz, CH); 67.67 (d, *J*_{CP} = 10.6 Hz, CH); 63.26 (CH₂); 62.07 (CH₂); 31.19 (CH₂); 30.78 (CH₂) ppm. ³¹P-NMR δ = 40.32 (s) ppm. HR-MS: m/z calculated for C₃₀H₃₁Fe₂O₂PS; [M]⁺ 598.0481, found: 598.0479.

Supplementary Materials: Figure S1: ¹H-NMR spectrum of compound **4**. Figure S2: ¹³C-NMR spectrum of compound **4**. Figure S3: HR-MS spectrum of compound **4**. Figure S4: ¹H-NMR spectrum of compound **5**. Figure S5: ¹³C-NMR spectrum of compound **5**. Figure S6: HR-MS of compound **5**. Figure S7: HR-MS of compound **5** (detailed). Figure S8: ¹H-NMR spectrum of compound **7**. Figure S9: ¹³C-NMR spectrum of compound **7**. Figure S10: ³¹P-NMR spectrum of compound **7**. Figure S11: HR-MS of compound **7**. Figure S12: ¹H-NMR spectrum of compound **7**. Figure S12: ¹³C-NMR spectrum of compound **10**. Figure S13: ¹³C-NMR spectrum of compound **10**. Figure S15: HR-MS of compound **10**. Figure S16: ¹H-NMR spectrum of compound **11**. Figure S17: ¹³C-NMR spectrum of compound **11**. Figure S18: ¹H-NMR spectrum of compound **12**. Figure S19: ¹³C-NMR spectrum of compound **12**. Figure S20: ¹³C-NMR spectrum of compound **12**. Figure S21: HR-MS of compound **12**.

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