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($2S_p$,4*R*,6*R*,$8S_p$)-4,6-Dimethyl-1-phenyl-diferroceno-1-phosphines

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Abstract: Ferrocene-based compounds are powerful asymmetric ligands usable for chemical catalysis. We present the synthesis of six new homochiral diferroceno cycles potentially useful as P,O-, P,N- or P,S-ligands. Due to the stereoconservative nature of the S_N1 reaction at carbons adjacent to ferrocene units, we obtained a single diastereomer of the 8-membered diferroceno[*c*,*f*]heterophosphocines in all cases.

Keywords: ferrocene; asymmetric compound; planar chirality; macrocycle

1. Introduction

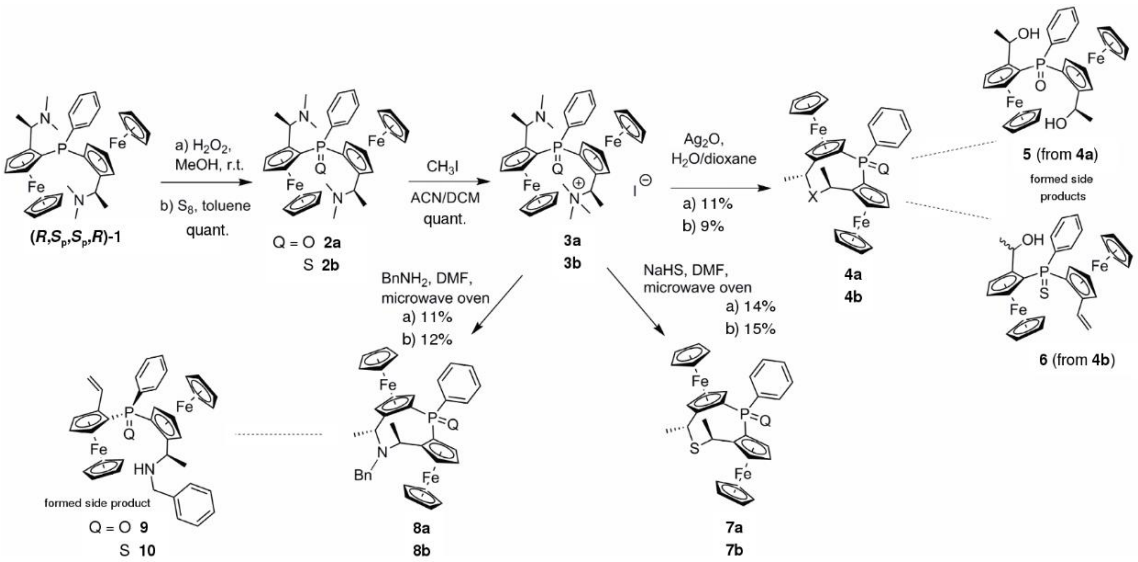
Ferrocenes have been used successfully for decades in asymmetric transition-metal catalysis [1]. Metallocenes can be planar-chiral if the same Cp ring is decorated with different substituents [2]. In addition to academic research, ferrocenes have been employed industrially as well. The homochiral P,P-ligand Xyliphos is used in the industrial asymmetric hydrogenation of a metolachlor precursor [3].

With the expectation to increase the asymmetric induction, the chiral array was extended with the introduction of two ferrocene units. To date, there have been diferrocenyl ligands reported acting as N,N-ligands for Rh(I) [4], P,S-ligands for Pd [5], P,P-ligands for Rh(I) [6] and P,P,P-ligands for Ru(II) [7], Rh(III) [8] and Ni(II) [9] catalyzed reactions.

The asymmetric capabilities may be improved further by constraining the conformational freedom of the two ferrocene moieties, e.g., by ring-closing to end up with a diferroceno cycle, which would incorporate two planar-chiral ferrocene units. Xiao et al. have developed 7-membered P,N-ligands for Pd(II) and with these complexes achieved up to 86% e.e. in asymmetric allylic amination [10]. Smith et al. [11] and Barreiro et al. [12] developed 8-membered P & P,P-ligands applied in Au(I)-catalyzed hydroalkoxylation. In this article, we report the synthesis of six 8-membered cyclic phosphine ligands with two annelated ferrocene moieties and similar structural features.

2. Results and Discussion

The synthetic route towards homoannularly bridged diferrocenes **4** is shown in Scheme 1. We obtained the enantiopure diferrocenyl precursor (*R*,S_p,S_p,*R*)-**1** [13,14] according to a known efficient literature procedure [12]. The phosphorous atom was protected quantitatively as phosphine oxide **2a** using hydrogen peroxide or as phosphine sulfide **2b** with elemental sulfur. The preparation of precursor **2b** is reported in Reference [15].



Scheme 1. Synthesis of 8-membered diferroceno[*c*,*f*]heterophosphocines. All of the shown compounds possess a (S_p,S_p)-configuration unless otherwise noted.

Nucleophilic substitutions at the α-carbon adjacent to a ferrocene unit proceed via a carbenium ion stabilized by the aromatic system. In constrast to typical S_N1 reactions, however, these substitutions on the α-carbon take place stereo-conservatively [16]. Since preliminary experiments showed that the tertiary amino groups were inert to nucleophilic substitution, we attempted transformation of **2a** and **2b** to better leaving groups by methylation. Despite using a large excess (6 equiv) of methyl iodide, HRMS showed that only monoammonium salts **3a** and **3b**, respectively, were formed quantitatively. These salts could not be characterized by NMR, since they proved to be poorly soluble in $CDCl_3$, D_2O and DMSO-d_6 and were used without further purification in the follow-up experiments.

Next, we attempted to perform a Hoffmann elimination of salts **3a** and **3b** using Ag_2O in a water/dioxane mixture at mild conditions (50 °C) [17]. Instead of the expected mono-eliminated products, we obtained oxa-cycles **4a** and **4b** identified by NMR (see Supplementary Materials) in 11% and 9% yield, respectively, thus inadvertently producing 8-membered cycles potentially useful as P,O-ligands. Apparently, the Hoffmann elimination is disfavored compared to the reaction with the nucleophilic solvent. Presumably, these oxa-cycles were formed by a water molecule displacing the ammonium group intermolecularly and then displacing the amine group at the other ferrocenyl alkyl chain intramolecularly. In both cases, side products were formed as well, possibly by ring opening of the oxa cycles. In the first case, we obtained the dihydroxy hydrolytic side product **5** in 6% yield; in the latter case, we isolated the mono-eliminated decay product **6** in 6% yield.

Inspired by this finding, we attempted to cyclize mono-ammonium salts **3a** and **3b** with other bidentate nucleophiles. We intended to synthesize sulfur-bridged cycles **7a** and **7b** as well as nitrogen-bridged P,N cycles **8a** and **8b** by using NaHS and $BnNH_2$ as nucleophiles. We heated the respective nucleophile and crude ammonium salts **3a** or **3b** dissolved in water or ACN in a Schlenk tube following standard procedures ([10,18], respectively). In both cases we detected the desired diferroceno[*c*,*f*]heterophosphocines in the crude reaction mixture by HRMS but attempted purification via SiO_2 column chromatography merely yielded decay products formed by elimination.

A modified procedure (DMF, microwave heating) yielded less decomposed material and desired cycles were obtained by chromatography on the less acidic sorbens Al_2O_3. This allowed us to isolate and characterize all four intended cycles **7a** (14%), **7b** (15%), **8a** (11%) and **8b** (12%). In case of the *N*-benzyl cycles **8a** and **8b**, mono-eliminated side products **9** and **10** were isolated in 8% and 13% yield. In all six diferrocenocycles, impurities were detected by NMR. Repeated filtration or chromatography did not yield pure fractions.

3. Materials and Methods

3.1. General

Melting points were measured on a Reichelt Thermovar Kofler apparatus, uncorrected. Routine NMR spectra were recorded on a 400 MHz Bruker AVIII 400 spectrometer operating at 400.27 MHz (^{1}H), 100.66 MHz (^{13}C) and 162.04 MHz (^{31}P) with autosampler. ^{1}H-NMR spectra and ^{13}C-NMR spectra used for substance characterization were recorded either on a 600 MHz Bruker AVIII 600 spectrometer operating (Bruker Biospin, Billerica, MA, USA) at 600.25 MHz (^{1}H) and 150.95 MHz (^{13}C) or on a Bruker AVIII 700 spectrometer at 700.40 MHz (^{1}H) and 176.13 MHz (^{13}C). ^{13}C-NMR spectra were recorded in *J*-modulated mode. NMR chemical shifts are referenced to non-deuterated $CHCl_3$ residual shifts: At 7.26 ppm for ^{1}H-NMR, at 77.00 ppm to $CDCl_3$ for ^{13}C-NMR and at 0.00 ppm to 85% H_3PO_4 for ^{31}P-NMR. HRMS were recorded by a Bruker Maxis ESI oa-RTOF mass spectrometer equipped with a quadrupole analyzer ion guide.

MeCN and DCM were distilled from CaH_2. Reaction progress was monitored by TLC (SiO_2 or Al_2O_3 sheets with F 254 fluorescent indicator). Preparative column chromatography (MPLC) was carried out by an Biotage Isolera One automated flash chromatography instrument using self-packed columns containing either SiO_2–Macherey-Nagel silica gel 60 M (particle size 40–63 μm) or Al_2O_3–Merck aluminum oxide 90 standardized (activation grade II-III). All the other chemicals were analytical grade and used without further purification.

3.2. Synthesis

Bis{[(2S$_p$)-2-[(1R)-1-(dimethylamino)-ethyl]]ferrocenyl}phenyl phosphineoxide **2a**: [19]

Diaminophosphine **1** (630 mg, 1.02 mmol) was dissolved in MeOH (8.0 mL) and cooled in an ice bath. Aqueous H_2O_2 (30%; 210 μL, 1.85 mmol, 1.82 equiv.) was added to the orange solution. The solution was warmed to r.t. and stirred for 40 min. The reaction mixture was quenched by adding 10% aqueous $NaHSO_3$ solution followed by sufficient aqueous $NaHCO_3$ solution until pH 7 was reached. The aqueous suspension was extracted using DCM (3 × 8 mL). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure to yield diaminophosphineoxide **2a** (647 mg, quant.) as an orange solid. The highly polar product was pure enough for the next step.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.80 (dd, *J* = 11.4, 8.0 Hz, 2H, C_6H_5); 7.43–7.35 (m, 3H, C_6H_5); 4.52 (q, *J* = 6.8 Hz, 1H, C_2H_4); 4.49 (m, 1H, C_5H_3); 4.44 (m, 1H, C_5H_3); 4.36 (m, 1H, C_5H_3); 4.33 (m, 1H, C_5H_3); 4.28 (m, 1H, C_5H_3); 4.25 (m, 1H, C_5H_3); 4.23 (s, 5H, C_5H_5); 3.73 (s, 5H, C_5H_5); 3.31–3.26 (m, 1H, C_2H_4); 2.26 (s, 6H, NCH_3); 1.53 (s, 6H, NCH_3); 1.47 (d, *J* = 6.8 Hz, 3H, C_2H_4); 1.21–1.15 (m, 3H, C_2H_4) ppm. ^{13}C-NMR δ = 130.07 (d, J_{CP} = 9.2 Hz, CH, C_6H_5); 129.44 (CH, C_6H_5); 127.20 (CH, C_6H_5); 89.90 (C_q, C_5H_3); 85.23 (C_q, C_5H_3); 75.14 (C_q, C_5H_3); 73.60 (CH, C_5H_3); 71.89 (CH, C_5H_3); 71.25 (C_q, C_5H_3); 71.72 (d, J_{CP} = 14.9 Hz, CH, C_5H_3); 70.34 (CH, C_5H_5); 70.20 (CH, C_5H_5); 69.59 (d, J_{CP} = 9.8 Hz, CH, C_5H_3); 69.32 (CH, C_5H_3); 67.91 (CH, C_5H_3); 55.17 (CH, C_2H_4); 40.97 (CH_3, NCH_3); 34.66 (CH, C_2H_4); 14.93 (CH_3, NCH_3); 13.05 (CH_3, C_2H_4); 13.04 (CH_3, C_2H_4) ppm; 1 C_q not observed. ^{31}P-NMR δ = 29.59 (s) ppm. HRMS: *m*/*z* calculated for $C_{34}H_{41}Fe_2N_2OP$ $[M + H]^+$: 637.1734, found: 637.1726.

{[(2S$_p$)-2-[(1R)-1-(dimethylamino)-ethyl]]ferrocenyl}{[(2S$_p$)-2-[(1R)-1-(trimethylammonium)-ethyl]]ferrocenyl} phenyl phosphineoxide iodide (**3a**): [20]

Diaminophosphineoxide **2a** (642 mg, 1.01 mmol) was dissolved in 15 mL of dry MeCN and 15 mL of dry DCM in a flame-dried Schlenk tube under Ar. MeI (375 μL, 6.00 mmol, 5.94 equiv.) was added to the solution and stirred for 2 h at r.t. Precipitation of ammonium iodide **3a** was induced by adding Et_2O (10 mL) yielding the salt as an orange powder (780 mg, quant.). HRMS: *m*/*z* calculated for $C_{35}H_{44}Fe_2IN_2OP$ $[M - I]^+$: 651.1885, found: 651.1868.

{[(2S_p)-2-[(1R)-1-(dimethylamino)-ethyl]]ferrocenyl}{[(2S_p)-2-[(1R)-1-(trimethylammonium)-ethyl]]ferrocenyl} phenyl phosphinesulfide iodide (**3b**):

Similar procedure as given for **3a** yielded **3b** from **2b** in quantitative yield.
HRMS: *m*/*z* calculated for $C_{35}H_{44}Fe_2IN_2PS$ $[M - I]^+$: 667.1662, found: 667.1644.

(2S_p,4R,6R,8S_p)-4,6-Dimethyl-1-phenyl-diferroceno-5-oxa-1-phosphineoxide (**4a**):

Ammonium iodide salt **3a** (87 mg, 0.11 mmol) was dissolved in water (1.5 mL) and dioxane (1 mL). The solution was warmed to 50 °C and Ag_2O (19 mg, 0.08 mmol, 1.5 equiv.) was added. The resulting suspension was stirred for 1 h. After complete consumption of the ammonium iodide salt **3a** the mixture was cooled to r.t. and the solid material was removed by filtration. The solution was extracted with DCM (3 × 3 mL) and the combined organic fractions were washed with water (10 mL) and brine (10 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by MPLC (SiO_2, 75→100% EtOAc in heptane) yielding oxa cycle **4a** (7 mg, 11%) as a glassy orange solid and dihydroxyphosphineoxide **5** (4 mg, 6%).

4a: ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.02–7.95 (m, 2H, C_6H_5); 7.51–7.47 (m, 3H, C_6H_5); 5.13 (s, 1H, C_5H_3); 4.65 (q, *J* = 6.5 Hz, 1H, C_2H_4); 4.52 (s, 1H, C_5H_3); 4.45 (s, 1H, C_5H_3); 4.43 (s, 1H, C_5H_3); 4.38–4.36 (m, 1H, C_5H_3); 4.36–4.34 (m, 1H, C_5H_3); 4.24 (s, 5H, C_5H_5); 4.12 (q, *J* = 7.2 Hz, 1H, C_2H_4); 3.73 (s, 5H, C_5H_5); 1.53 (d, *J* = 6.5 Hz, 3H, C_2H_4); 1.51 (d, *J* = 6.4 Hz, 3H, C_2H_4) ppm. ^{13}C-NMR δ = 138.11 (d, J_{CP} = 112.4 Hz, C_q, C_6H_5); 131.56 (d, J_{CP} = 10.0 Hz, CH, C_6H_5); 131.14 (d, J_{CP} = 2.6 Hz, CH, C_6H_5); 127.79 (d, J_{CP} = 12.3 Hz, CH, C_6H_5); 91.83 (d, J_{CP} = 13.2 Hz, C_q, C_5H_3); 88.93 (d, J_{CP} = 14.1 Hz, C_q, C_5H_3); 76.12 (d, J_{CP} = 10.2 Hz, C_q, C_5H_3); 75.32 (C_q, C_5H_3); 74.74 (d, J_{CP} = 10.6 Hz, CH, C_5H_3); 73.78 (d, J_{CP} = 13.5 Hz, CH, C_5H_3); 70.44 (CH, C_5H_5); 70.17 (d, J_{CP} = 11.1 Hz, CH, C_5H_3); 70.16 (CH, C_5H_5); 69.88 (d, J_{CP} = 10.2 Hz, CH, C_5H_3); 69.15 (d, J_{CP} = 9.8 Hz, CH, C_5H_3); 69.01 (d, J_{CP} = 10.1, CH, C_5H_3); 68.31 (CH, C_2H_4); 66.13 (CH, C_2H_4); 20.93 (CH_3, C_2H_4); 20.78 (CH_3, C_2H_4) ppm. ^{31}P-NMR δ = 31.13 (s) ppm. HRMS: *m*/*z* calculated for $C_{30}H_{29}Fe_2O_2P$ $[M + Na]^+$: 587.0502, found: 587.0507; $[2M + Na]^+$ 1151.1106, found: 1151.1113.

5: ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.95–7.90 (m, 2H, C_6H_5); 7.55–7.50 (m, 3H, C_6H_5); 5.93 (d, *J* = 5.4 Hz, 1H, OH); 5.22 (m, 1H, C_5H_3); 4.76 (m, 1H, C_2H_4); 4.57 (d, *J* = 5.4 Hz, 1H, C_5H_3); 4.56 (s, 1H, OH); 4.48 (pq, *J* = 2.4 Hz, 1H, C_5H_3); 4.44 (m, 1H, C_5H_3); 4.41 (m, 2H, C_5H_3, C_2H_4); 4.38 (pq, *J* = 2.4 Hz, 1H, C_5H_3); 4.17 (s, 5H, C_5H_5); 3.75 (s, 5H, C_5H_5); 1.64 (d, *J* = 6.7 Hz, 3H, C_2H_4); 1.21 (d, *J* = 6.7 Hz, 3H, C_2H_4) ppm. ^{13}C-NMR δ = 136.54 (d, J_{CP} = 110.2 Hz, C_q, C_6H_5); 131.55 (d, J_{CP} = 2.9 Hz, CH, C_6H_5); 129.93 (d, J_{CP} = 9.5 Hz, CH, C_6H_5); 128.45 (d, J_{CP} = 12.1 Hz, CH, C_6H_5); 98.73 (d, J_{CP} = 10.4 Hz, C_q, C_5H_3); 97.57 (d, J_{CP} = 11.3 Hz, C_q, C_5H_3); 72.64 (C_q, C_5H_3); 71.85 (C_q, C_5H_3); 71.75 (d, J_{CP} = 14.6 Hz, CH, C_5H_3); 70.97 (d, J_{CP} = 15.0 Hz, CH, C_5H_3); 70.81 (d, J_{CP} = 10.0 Hz, CH, C_5H_3); 70.46 (CH, C_5H_5); 70.45 (CH, C_5H_5); 70.27 (d, J_{CP} = 11.0 Hz, CH, C_5H_3); 69.86 (d, J_{CP} = 11.0 Hz, CH, C_5H_3); 69.64 (d, J_{CP} = 9.8 Hz, CH, C_5H_3); 65.35 (CH, C_2H_4); 65.30 (CH, C_2H_4); 22.98 (CH_3, C_2H_4); 21.95 (CH_3), C_2H_4) ppm. ^{31}P-NMR δ = 38.45 (s) ppm. HRMS: *m*/*z* calculated for $C_{30}H_{31}Fe_2O_3P$ $[M + Na]^+$: 605.0607, found: 605.0595; $[2M + Na]^+$: 1187.1317, found: 1187.1295.

(2S_p,4R,6R,8S_p)-4,6-Dimethyl-1-phenyl-diferroceno-5-oxa-1-phosphinesulfide (**4b**):

Similar procedure as given for **4a** yielded cycle **4b** from 3**b** in 9% yield and 6% of eliminated side product **6**.

4b: ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.13–8.07 (m, 2H, C_6H_5); 7.45–7.38 (m, 3H, C_6H_5); 5.44 (m, 1H, C_5H_3); 4.61 (m, 1H, C_5H_3); 4.59–4.55 (m, 2H, C_2H_4); 4.47 (m, 1H, C_5H_3); 4.45–4.39 (m, 2H, C_5H_3); 4.37 (m, 1H, C_5H_3); 4.16 (s, 5H, C_5H_5); 4.00 (s, 5H, C_5H_5); 1.45 (d, *J* = 6.4 Hz, 3H, C_2H_4); 1.41 (d, *J* = 6.7 Hz, 3H, C_2H_4) ppm. ^{13}C-NMR δ = 137.31 (d, J_{CP} = 90.0 Hz, C_q, C_6H_5); 132.51 (d, J_{CP} = 11.2 Hz, CH, C_6H_5); 130.82 (d, J_{CP} = 3.0 Hz, CH, C_6H_5); 127.33 (d, J_{CP} = 12.7 Hz, CH, C_6H_5); 92.84 (d, J_{CP} = 9.9 Hz, C_q, C_5H_3); 89.73 (d, J_{CP} = 10.2 Hz, C_q, C_5H_3); 77.97 (C_q, C_5H_3); 77.42 (d, J_{CP} = 15.5 Hz, CH, C_5H_3); 76.15 (C_q, C_5H_3); 75.04 (d, J_{CP} = 15.2 Hz, CH, C_5H_3); 70.82 (d, J_{CP} = 8.8 Hz, CH, C_5H_3); 70.81 (CH, C_5H_5); 70.41 (CH, C_5H_5); 69.58 (d, J_{CP} = 11.7 Hz, CH, C_5H_3); 69.41 (d, J_{CP} = 11.5 Hz, CH, C_5H_3); 69.33

(d, J_{CP} = 9.0 Hz, CH, C_5H_3); 65.79 (2 CH, C_2H_4); 21.22 (CH_3, C_2H_4); 20.56 (CH_3, C_2H_4) ppm. ^{31}P-NMR δ = 43.82 (s) ppm. HRMS: *m/z* calculated for $C_{30}H_{29}Fe_2OPS$ $[M + Na]^+$: 603.0273, found: 603.0279; $[2M + Na]^+$ 1183.0649, found: 1183.0662.

6: ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.10 (dd, *J* = 17.6, 10.8 Hz, 1H, C_2H_3); 7.87–7.81 (m, 2H, C_6H_5); 7.51–7.42 (m, 3H, C_6H_5); 5.49 (dd, *J* = 17.6, 1.6 Hz; 1H, C_2H_3); 5.23–5.17 (m, 1H, C_5H_3); 5.20 (dd, *J* = 10.8, 1.7 Hz, 1H, C_2H_3); 4.88 (m, 1H, C_5H_3); 4.49 (m, 1H, C_5H_3); 4.34 (s, 5H, C_5H_5); 4.33 (m, 1H, C_5H_3); 4.24 (m, 1H, C_5H_3); 4.17 (s, 5H, C_5H_5); 3.77 (m, 1H, C_5H_3); 3.71 (m, 1H, OH); 2.41 (d, *J* = 5.3 Hz; 1H, C_2H_4); 1.26 (d, *J* = 6.6 Hz, 3H, C_2H_4) ppm. ^{13}C-NMR δ = 135.30 (d, J_{CP} = 87.1 Hz, C_q, C_6H_5); 134.25 (CH, C_6H_5); 132.10 (d, J_{CP} = 10.3 Hz, CH, C_6H_5); 131.38 (d, J_{CP} = 2.8 Hz, CH, C_6H_5); 127.96 (d, J_{CP} = 12.1 Hz, CH, C_2H_3); 111.74 (CH_2, C_2H_3); 94.90 (d, J_{CP} = 12.3 Hz, C_q, C_5H_3); 88.43 (d, J_{CP} = 11.8 Hz, C_q, C_5H_3); 78.56 (d, J_{CP} = 95.4 Hz, C_q, C_5H_3); 75.05 (d, J_{CP} = 12.0 Hz, CH, C_5H_3); 74.97 (d, J_{CP} = 12.6 Hz, CH, C_5H_3); 73.48 (d, J_{CP} = 96.0 Hz, C_q, C_5H_3); 71.22 (CH, C_5H_5); 71.00 (d, J_{CP} = 9.7 Hz, CH, C_5H_3); 70.72 (CH, C_5H_5); 70.10 (d, J_{CP} = 10.4 Hz, CH, C_5H_3); 68.38 (d, J_{CP} = 9.1 Hz, CH, C_5H_3); 68.04 (d, J_{CP} = 10.5 Hz, CH, C_5H_3); 64.38 (CH, C_2H_4); 21.91 (CH_3, C_2H_4) ppm. ^{31}P-NMR δ = 40.51 (s) ppm. HRMS: *m/z* calculated for $C_{30}H_{29}Fe_2OPS$ $[M]^+$ 580.0376, found: 580.0360; $[M + Na]^+$ 603.0273, found: 603.0273; $[M + K]^+$ 619.0013, found: 619.0018.

(2S_p,4R,6R,8S_p)-4,6-Dimethyl-1-phenyl-diferroceno-5-sulfa-1-phosphineoxide (**7a**):

Ammonium iodide salt **3a** (75 mg, 0.10 mmol) and $NaHS{\cdot}H_2O$ (7.5 mg, 0.10 mmol, 1.0 equiv.) were dissolved in 8 mL of DMF and heated for 8 min at 100 °C in a microwave oven. The mixture was cooled to r.t., 10 mL of DCM were added and the organic layer was washed four times with 50 mL of water each, once with 20 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Al_2O_3; 0→100% EtOAc in heptane) yielding 14% of the intended sulfidephosphineoxide diferrocenyl cycle **7a** (8 mg) as a glassy orange solid.

^{1}H-NMR(700 MHz, $CDCl_3$) δ = 7.92–7.85 (m, 2H, C_6H_5); 7.52–7.48 (m, 3H, C_6H_5); 5.30 (s, 1H, C_5H_3); 5.11 (s, 1H, C_5H_3); 4.52 (s, 1H, C_5H_3); 4.37 (s, 1H, C_5H_3); 4.36 (s, 1H, C_5H_3); 4.35 (s, 5H, C_5H_5); 4.24 (s, 1H, C_5H_3); 3.83 (s, 5H, C_5H_5); 3.74 (q, *J* = 6.9 Hz, 1H, C_2H_4); 3.21 (q, *J* = 7.1 Hz, 1H, C_2H_4); 1.58 (d, *J* = 7.2 Hz, 3H, C_2H_4); 1.51 (d, *J* = 7.0 Hz, 3H, C_2H_4) ppm. ^{13}C-NMR δ = 138.59 (d, J_{CP} = 111.7 Hz, C_q, C_6H_5); 131.81 (d, J_{CP} = 9.8 Hz, CH, C_6H_5); 131.17 (d, J_{CP} = 2.7 Hz, CH, C_6H_5); 127.66 (d, J_{CP} = 12.1 Hz, CH, C_6H_5); 96.88 (d, J_{CP} = 13.2 Hz, C_q, C_5H_3); 92.56 (d, J_{CP} = 13.8 Hz, C_q, C_5H_3); 74.83 (d, J_{CP} = 37.5 Hz, C_q, C_5H_3); 74.20 (d, J_{CP} = 42.9 Hz, C_q, C_5H_3); 73.50 (d, J_{CP} = 10.7 Hz, CH, C_5H_3); 73.32 (d, J_{CP} = 13.8 Hz, CH, C_5H_3); 70.36 (CH, C_5H_5); 70.32 (d, J_{CP} = 11.8 Hz, CH, C_5H_3); 70.11 (d, J_{CP} = 10.1 Hz, CH, C_5H_3); 69.95 (CH, C_5H_5); 67.45 (d, J_{CP} = 9.6 Hz, CH, C_5H_3); 67.43 (d, J_{CP} = 10.0 Hz, CH, C_5H_3); 36.62 (CH, C_2H_4); 35.71 (CH, C_2H_4); 20.28 (CH_3, C_2H_4); 20.20 (CH_3, C_2H_4) ppm. ^{31}P-NMR δ = 29.47 (s) ppm. HRMS: *m/z* calculated for $C_{30}H_{29}Fe_2OPS$ $[M]^+$: 580.0376, found: 580.0369.

(2S_p,4R,6R,8S_p)-4,6-Dimethyl-1-phenyl-diferroceno-5-sulfa-1-phosphinesulfide (**7b**):

Similar procedure as given for **7a** yielded cycle **7b** from **3b** in 15% yield.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.95–7.90 (m, 2H, C_6H_5); 7.47–7.43 (m, 1H, C_6H_5); 7.43–7.38 (m, 2H, C_6H_5); 5.38 (m, 1H, C_5H_3); 4.64 (q, *J* = 2.2 Hz, 1H, C_5H_3); 4.50 (m, 1H, C_5H_3); 4.42–4.40 (m, 1H, C_5H_3); 4.40–4.38 (m, 2H, C_5H_3); 4.28 (s, 5H, C_5H_5); 4.20 (s, 5H, C_5H_5); 3.63 (q, *J* = 6.8 Hz, 1H, C_2H_4); 2.96 (q, *J* = 7.3 Hz, 1H, C_2H_4); 1.54 (d, *J* = 7.3 Hz, 3H, C_2H_4); 1.31 (d, *J* = 6.8 Hz, 3H, C_2H_4) ppm. ^{13}C-NMR δ = 137.96 (d, J_{CP} = 88.8 Hz, C_q, C_6H_5); 132.57 (d, J_{CP} = 11.0 Hz, CH, C_6H_5); 131.13 (d, J_{CP} = 3.1 Hz, CH, C_6H_5); 127.45 (d, J_{CP} = 12.5 Hz, CH, C_6H_5); 96.94 (d, J_{CP} = 11.0 Hz, C_q, C_5H_3); 92.90 (d, J_{CP} = 10.6 Hz, C_q, C_5H_3); 75.32 (d, J_{CP} = 15.6 Hz, CH, C_5H_3); 75.02 (C_q, C_5H_3); 74.42 (C_q, C_5H_3); 73.75 (d, J_{CP} = 15.0 Hz, CH, C_5H_3); 70.91 (CH, C_5H_5); 70.29 (CH, C_5H_5); 70.22 (d, J_{CP} = 11.5 Hz, CH, C_5H_3); 70.05 (d, J_{CP} = 11.5 Hz, CH, C_5H_3); 68.58 (d, J_{CP} = 8.6 Hz, CH, C_5H_3); 68.34 (d, J_{CP} = 9.1 Hz, CH, C_5H_3); 37.27 (CH, C_2H_4); 35.39 (CH, C_2H_4); 20.82 (CH_3, C_2H_4); 20.79 (CH_3, C_2H_4) ppm. ^{31}P-NMR δ = 42.92 (s) ppm. HRMS: *m/z* calculated for $C_{30}H_{29}Fe_2PS_2$ $[M]^+$: 596.0147, found: 596.0141.

($2S_p$,4R,6R,$8S_p$)-4,6-Dimethyl-5-benzyl-1-phenyl-diferroceno-5-amino-1-phosphineoxide (**8a**):

Ammonium iodide salt **3a** (77 mg, 0.10 mmol) and $BnNH_2$ (11 µL, 0.10 mmol, 1.0 equiv.) were dissolved in 8 mL of DMF and heated for 8 min at 100 °C in a microwave oven. The reaction mixture was cooled to r.t., 10 mL of DCM were added and the organic solution was washed four times with 50 mL of water each, once with 20 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Al_2O_3; 0→100% EtOAc in heptane) yielding 11% of the intended benzylic aminephosphineoxide diferroceno cycle **8a** (7 mg) as a glassy orange solid as well as 8% of the sec. amine elimination product **9** (5 mg).

8a: ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.11–8.06 (m, 2H, C_6H_5); 7.57–7.50 (m, 3H, C_6H_5); 7.41 (d, *J* = 7.4 Hz, 2H, C_7H_7); 7.28–7.24 (m, 2H, C_7H_7); 7.17 (pt, *J* = 7.3 Hz, 1H, C_7H_7); 4.80 (m, 1H, C_5H_3); 4.47 (m, 1H, C_5H_3); 4.39 (m, 2H, C_5H_3); 4.35 (m, 1H, C_5H_3); 4.29 (m, 1H, C_5H_3); 4.24 (s, 5H, C_5H_5); 4.04 (q, *J* = 6.8 Hz, 1H, C_2H_4); 3.94 (d, *J* = 16.4 Hz, 1H, C_7H_7); 3.90 (s, 5H, C_5H_5); 3.73 (q, *J* = 6.6 Hz, 1H, C_2H_4); 3.39 (d, *J* = 16.3 Hz, 1H, C_7H_7); 1.26 (d, *J* = 6.5 Hz, 3H, C_2H_4); 1.25 (d, *J* = 6.9 Hz, 3H, C_2H_4) ppm. ^{13}C-NMR δ = 143.69 (C_q, C_7H_7); 137.02 (d, J_{CP} = 110.2 Hz, C_q, C_6H_5); 132.35 (d, J_{CP} = 9.38 Hz, CH, C_6H_5); 131.20 (d, J_{CP} = 2.7 Hz, CH, C_6H_5); 127.82 (CH, C_7H_7); 127.63 (d, J_{CP} = 5.5 Hz, CH, C_6H_5); 127.54 (d, J_{CP} = 6.6, CH, C_7H_7); 126.01 (CH, C_7H_7); 93.20 (d, J_{CP} = 13.2 Hz, C_q, C_5H_3); 93.06 (d, J_{CP} = 13.6 Hz, C_q, C_5H_3); 75.38 (d, J_{CP} = 22.2 Hz, C_q, C_5H_3); 74.62 (d, J_{CP} = 18.2 Hz, C_q, C_5H_3); 73.65 (d, J_{CP} = 11.4 Hz, CH, C_5H_3); 72.64 (d, J_{CP} = 13.9 Hz, CH, C_5H_3); 70.45 (CH, C_5H_5); 70.39 (d, J_{CP} = 10.6 Hz, CH, C_5H_3); 70.17 (CH, C_5H_5); 69.81 (d, J_{CP} = 11.2 Hz, CH, C_5H_3); 69.58 (d, J_{CP} = 9.6 Hz, 2 CH, C_5H_3); 54.66 (CH, C_2H_4); 53.55 (CH, C_2H_4); 53.12 (CH_2, C_7H_7); 21.44 (CH_3, C_2H_4); 20.52 (CH_3, C_2H_4) ppm. ^{31}P-NMR δ = 29.63 (s) ppm. HRMS: *m*/*z* calculated for $C_{37}H_{36}Fe_2NOP$ $[M + H]^+$: 654.1306, found: 654.1306; $[M + Na]^+$: 676.1126, found: 676.1129.

9: ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.80–7.69 (m, 3H, C_6H_5); 7.55–7.34 (m, 2H, C_6H_5); 7.33–7.27 (m, 3H, C_7H_7); 7.16–7.10 (m, 2H, C_7H_7); 6.84–6.80 (m, 1H, C_2H_3); 5.46 (dd, *J* = 17.7, 1.6 Hz, 1H, C_2H_3); 5.16 (dd, *J* = 10.8, 10.6 Hz, 1H, C_2H_3); 4.86 (m, 1H, C_5H_3); 4.49 (m, 1H, C_2H_4); 4.41 (pq, *J* = 2.4 Hz, 1H, C_5H_3); 4.39 (pt, *J* = 2.0 Hz, 1H, C_5H_3); 4.36 (m, 1H, C_5H_3); 4.27 (s, 5H, C_5H_5); 4.24 (s, 1H, C_5H_3); 3.93 (s, 5H, C_5H_5); 3.89 (d, *J* = 4.3 Hz, 1H, C_5H_3); 3.20 (s, 2H, C_7H_7); 1.43 (d, *J* = 6.6, 3H, C_2H_4) ppm. ^{13}C-NMR δ = 133.52 (C_q, C_6H_5); 131.28 (CH, C_6H_5); 130.29 (CH, C_6H_5); 128.38 (CH, C_6H_5); 128.26 (CH, C_7H_7); 128.15 (CH, C_7H_7); 127.95 (CH, C_7H_7); 111.43 (CH_2, C_2H_3); 90.13 (C_q, C_2H_3); 86.08 (C_q, C_5H_3); 71.65 (CH, C_5H_3); 71.26 (CH, C_5H_3); 71.17 (CH, C_5H_3); 70.81 (CH, C_5H_3); 70.73 (CH, C_5H_5); 70.31 (CH, C_5H_5); 70.28 (CH, C_5H_3); 69.58 (CH, C_5H_3); 67.25 (CH, C_2H_4); 53.15 (CH_2, C_7H_7); 20.56 (CH_3, C_2H_4) ppm; 4 C_q not observed. ^{31}P-NMR δ = 30.54 (s) ppm. HRMS: *m*/*z* calculated for $C_{37}H_{36}Fe_2NOP$ $[M + H]^+$: 654.1306, found: 654.1314.

($2S_p$,4R,6R,$8S_p$)-4,6-Dimethyl-5-benzyl-1-phenyl-diferroceno-5-amino-1-phosphinesulfide (**8b**):

Similar procedure as given for **8a** yielded cycle **8b** from **3b** in 12% yield and side product **10** in 13% yield.

8b: ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.91 (ddd, *J* = 13.6, 7.8, 1.5 Hz, 2H, C_6H_5); 7.47–7.41 (m, 3H, C_6H_5); 7.31 (d, *J* = 7.5 Hz, 2H, C_7H_7); 7.28–7.24 (m, 2H, C_7H_7); 7.17 (pt, *J* = 7.2 Hz, 1H, C_7H_7); 5.36 (m, 1H, C_5H_3); 4.65 (dd, *J* = 4.3, 2.4 Hz, 1H, C_5H_3); 4.57 (m, 1H, C_5H_3); 4.48 (m, 1H, C_5H_3); 4.46 (m, 1H, C_5H_3); 4.38 (m, 1H, C_5H_3); 4.21 (s, 5H, C_5H_5); 4.14 (s, 5H, C_5H_5); 3.98 (s, 1H, C_7H_7); 3.73 (q, *J* = 6.9 Hz, 1H, C_2H_4); 3.46 (q, *J* = 6.3 Hz, 1H, C_2H_4); 3.19 (d, *J* = 16.9 Hz, 1H, C_7H_7); 1.19 (d, *J* = 7.0 Hz, 3H, C_2H_4); 1.09 (d, *J* = 6.4 Hz, 3H, C_2H_4) ppm. ^{13}C–NMR δ = 144.18 (C_q, C_7H_7); 138.58 (d, J_{CP} = 89.2 Hz, C_q, C_6H_5); 132.79 (d, J_{CP} = 11.3 Hz, CH, C_6H_5); 130.88 (d, J_{CP} = 3.0 Hz, CH, C_6H_5); 127.88 (CH, C_7H_7); 127.32 (d, J_{CP} = 12.4 Hz, CH, C_6H_5); 127.00 (CH, C_7H_7); 126.05 (CH, C_7H_7); 93.39 (d, J_{CP} = 11.1 Hz, C_q, C_5H_3); 92.56 (d, J_{CP} = 12.1 Hz, C_q, C_5H_3); 75.55 (C_q, C_5H_3); 75.47 (d, J_{CP} = 15.6 Hz, CH, C_5H_3); 74.93 (C_q, C_5H_3); 73.93 (d, J_{CP} = 15.0 Hz, CH, C_5H_3); 71.41 (d, J_{CP} = 9.7 Hz, CH, C_5H_3); 71.01 (CH, C_5H_5); 70.35 (CH, C_5H_5); 70.07 (d, J_{CP} = 11.5 Hz, CH, C_5H_3); 69.96 (d, J_{CP} = 9.1 Hz, CH, C_5H_3); 69.85 (d, J_{CP} = 11.4 Hz, CH, C_5H_3); 55.79 (CH, C_2H_4); 53.18 (CH_2, C_7H_7); 52.14 (CH, C_2H_4); 22.12 (CH_3, C_2H_4); 21.35

(CH_3, C_2H_4) ppm. ^{31}P-NMR δ = 43.41 (s) ppm. HRMS: *m*/*z* calculated for $C_{37}H_{36}Fe_2NPS$ $[M + H]^+$: 670.1078, found: 670.1068.

10: M.p.: 179–180 °C (decomposition). ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.82 (dd, *J* = 12.7, 6.5 Hz, 2H, C_6H_5); 7.29–7.23 (m, 3H, C_6H_5); 7.13–7.08 (m, 3H, C_7H_7); 6.80–6.76 (m, 3H, C_7H_7, C_2H_3); 5.47 (dd, *J* = 17.7, 1.6 Hz, 1H, C_2H_3); 5.17 (dd, *J* = 10.8, 1.6 Hz, 1H, C_2H_3); 4.86 (m, 1H, C_5H_3); 4.62 (q, *J* = 6.7 Hz, 1H, C_2H_4); 4.56 (m, 1H, C_5H_3); 4.33 (s, 5H, C_5H_5); 4.30 (m, 1H, C_5H_3); 4.24 (dd, *J* = 4.1, 2.6 Hz, 1H, C_5H_3); 4.12 (s, 5H, C_5H_5); 3.77 (m, 1H, C_5H_3); 3.67 (m, 1H, C_5H_3); 3.21 (dd, *J* = 23.6, 12.8 Hz, 2H, C_7H_7); 1.45 (d, *J* = 6.6 Hz, 3H, C_2H_4) ppm. ^{13}C-NMR δ = 140.46 (C_q, C_7H_7); 135.15 (d, J_{CP} = 86.3 Hz, C_q, C_6H_5); 134.47 (CH, C_7H_7); 131.80 (d, J_{CP} = 10.2 Hz, CH, C_6H_5); 131.14 (d, J_{CP} = 2.9 Hz, CH, C_6H_5); 127.85 (CH, C_7H_7); 127.82 (d, J_{CP} = 11.4 Hz, CH, C_6H_5); 127.78 (CH, C_7H_7); 126.14 (CH, C_2H_3); 111.48 (CH_2, C_2H_3); 95.12 (d, J_{CP} = 12.7 Hz, C_q, C_5H_3); 88.55 (d, J_{CP} = 12.0 Hz, C_q, C_5H_3); 77.91 (d, J_{CP} = 95.5 Hz, C_q, C_5H_3); 75.03 (d, J_{CP} = 12.2 Hz, CH, C_5H_3); 74.42 (d, J_{CP} = 12.1 Hz, CH, C_5H_3); 73.98 (d, J_{CP} = 95.4 Hz, C_q, C_5H_3); 71.15 (CH, C_5H_5); 71.10 (d, J_{CP} = 10.1 Hz, CH, C_5H_3); 70.67 (CH, C_5H_5); 69.97 (d, J_{CP} = 10.2 Hz, CH, C_5H_3); 68.22 (d, J_{CP} = 9.1 Hz, CH, C_5H_3); 67.94 (d, J_{CP} = 10.6 Hz, CH, C_5H_3); 50.71 (CH_2, C_7H_7); 50.08 (CH, C_2H_4); 19.53 (CH_3, C_2H_4) ppm. ^{31}P-NMR δ = 39.55 (s) ppm. HRMS: *m*/*z* calculated for $C_{37}H_{36}Fe_2NPS$ $[M + H]^+$: 670.1078, found: 670.1075.

Supplementary Materials: The following are available online, Figure S1: ^{1}H-NMR spectrum of compound **2a**, Figure S2: ^{13}C-NMR spectrum of compound **2a**, Figure S3: ^{31}P-NMR spectrum of compound **2a**, Figure S4: ^{1}H-NMR spectrum of compound **4a**, Figure S5: ^{13}C-NMR spectrum of compound **4a**, Figure S6: ^{31}P-NMR spectrum of compound **4a**, Figure S7: ^{1}H-NMR spectrum of compound **4b**, Figure S8: ^{13}C-NMR spectrum of compound **4b**, Figure S9: ^{31}P-NMR spectrum of compound **4b**, Figure S10: ^{1}H-NMR spectrum of compound **7a**, Figure S11: ^{13}C-NMR spectrum of compound **7a**, Figure S12: ^{31}P-NMR spectrum of compound **7a**, Figure S13: ^{1}H-NMR spectrum of compound **7b**, Figure S14: ^{13}C-NMR spectrum of compound **7b**, Figure S15: ^{31}P-NMR spectrum of compound **7b**, Figure S16: ^{1}H-NMR spectrum of compound **8a**, Figure S17: ^{13}C-NMR spectrum of compound **8a**, Figure S18: ^{31}P-NMR spectrum of compound **8a**, Figure S19: ^{1}H-NMR spectrum of compound **8b**, Figure S20: ^{13}C-NMR spectrum of compound **8b**, Figure S21: ^{31}P-NMR spectrum of compound **8b**, Figure S22: ^{1}H-NMR spectrum of compound **5**, Figure S23: ^{13}C-NMR spectrum of compound **5**, Figure S24: ^{31}P-NMR spectrum of compound **5**, Figure S25: ^{1}H-NMR spectrum of compound **6**, Figure S26: ^{13}C-NMR spectrum of compound **6**, Figure S27: ^{31}P-NMR spectrum of compound **6**, Figure S28: ^{1}H-NMR spectrum of compound **9**, Figure S29: ^{13}C-NMR spectrum of compound **9**, Figure S30: ^{31}P-NMR spectrum of compound **9**, Figure S31: ^{1}H-NMR spectrum of compound **10**, Figure S32: ^{13}C-NMR spectrum of compound **10**.

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