Supporting information

to

Biferrocene-based diphosphine ligands: Synthesis and application of Walphos-analogs in asymmetric hydrogenations

Afrooz Zirakzadeh, Manuela Groß, Yaping Wang, Kurt Mereiter, Felix Spindler, and Walter Weissensteiner*

General Considerations S2
General atom numbering schemes for NMR assignment S2
Synthesis of compounds S3
Synthesis of complexes S17
Hydrogenation S19
X-ray structure determination S23
General considerations

All reactions except oxidations with H2O2 were carried out under an argon atmosphere using standard Schlenk techniques and dry solvents. Ugi’s amine and some of the phosphines were kindly provided by Solvias AG. Solvents were dried according to standard procedures under argon atmosphere and distilled freshly prior to use. Tetrahydrofuran (THF) was dried over sodium/benzophenone, dichloromethane (DCM) and acetone were dried over P2O5, Et2O over LiAlH4, MeOH and EtOH over magnesiumalkoxide, and toluene was dried over sodium. Column chromatography was performed either on silica gel (Merck, 40–63 µm) or on aluminium oxide (Merck, aluminium oxide 90). Petroleum ether (PE, boiling range 60–80 °C), ethyl acetate (EA) and triethyl amine (TEA) were used as the eluents. The following compounds were purchased and were used without further purification: acetophenone (FLUKA), 2-acetamidoacrylic acid methyl ester (TCI), itaconic acid dimethyl ester (TCI), α-methylcinnamic acid (ALDRICH), α-phenylcinnamic acid (ALDRICH), benzoylformic acid methyl ester (TCI), ethyl propionylacetate (ALDRICH), acetylacetone (FLUKA). Ugi’s amine was kindly provided by SOLVIAS AG. Elemental analyses were carried out by 'Mikroanalytisches Laboratorium der Universität Wien'.

NMR spectra were recorded either on a Bruker DRX-400, a Bruker Avance-500 or on a Bruker DRX-600 spectrometer in CDCl3, CD2Cl2 or acetone-d6. Chemical shifts are referenced to: CHCl3 (1H: 7.26 ppm) and CDCl3 (13C: 77.0 ppm); CDHCl2 (1H: 5.32 ppm) and CD2Cl2 (13C: 53.7 ppm); and to acetone-d5 (1H: 2.07 ppm) and acetone-d6 (13C: 30.3 ppm). 31P NMR spectra were referenced to 85% H3PO4 (31P: 0 ppm). For the assignment of peaks, the following abbreviations were used: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet and bm = broad multiplet. Coupling constants in 13C NMR are due to 31P-13C or 19F-13C coupling. High resolution mass spectra were recorded on a Bruker ESI-Qq aoTOF MS spectrometer. Optical rotations were measured on a Perkin Elmer 241 or a Jasko P-1020 polarimeter in CHCl3. Melting points were measured either on a Kofler or on a Boif X-4 melting point apparatus. Conversion and e.e. values were measured with use of an Agilent 7890 A GC or an Agilent 1200 HPLC.

General atom numbering schemes for NMR assignment:
Synthesis of the compounds:

**(SFc)**-2-Bromo-1-iodoferrocene, (SFc)-2 and (SFc)-2-bromo-1-tributylstannylferrocene, (SFc)-5

To a degassed solution of (R,SFc)-2-(4-methylphenylsulfinyl)-1-tributylstannylferrocene, (R,SFc)-4, (1.12 g, 1.83 mmol) in dry Et2O (8 mL) at –78 °C was added tert-butyllithium (1.6 M in pentane, 1.14 mL, 1.82 mmol) and the resulting dark red solution was stirred for 5 min before it was transferred at –78 °C into a degassed solution of 1,1,2,2-tetrabromoethane (1.89 g, 5.46 mmol) in dry Et2O (8 mL). The red reaction mixture was stirred for one additional hour at –78 °C and was subsequently quenched with saturated aqueous solutions of Na2S2O3 and NaHCO3. The products were extracted with Et2O and the combined organic phases were washed with water and brine. The organics were dried over MgSO4 and the crude product was obtained after filtration and evaporation of the solvents. Excess reagents and a small amount of byproduct were removed by chromatography (aluminium oxide, PE) and 1.2 g of products was isolated as a mixture of the desired product (SFc)-5 and tributylstannylferrocene in a ratio of 87:13. This mixture of products was used without further separation in the next step. An analytical sample of (SFc)-5 was purified by an additional chromatography (aluminium oxide, PE).

**(SFc)**-5: 1H NMR (400 MHz, CDCl3): δ 0.92 (t, \(J = 7.3\) Hz, 9H, CH3), 1.00–1.20 (m, 6H, CH2), 1.33–1.43 (m, 6H, CH2), 1.54–1.64 (m, 6H, CH2), 3.91 (dd, \(J_1 = 2.4\) Hz, \(J_2 = 1.2\) Hz, 1H, H5), 4.16 (s, 5H, Cp′), 4.21 (t, \(J = 2.4\) Hz, 1H, H4), 4.54 (dd, \(J_1 = 2.4\) Hz, \(J_2 = 1.2\) Hz, 1H, H3). 13C{1H} NMR (100.6 MHz, CDCl3): \(\delta\) 10.7 (3C, CH2), 13.7 (3C, CH3), 27.4 (3C, CH2), 29.2 (3C, CH2), 69.4 (C4), 70.4 (Cp′), 72.3 (C3), 72.9 (C1), 73.5 (C5), 86.1 (C2).

HR-MS (ESI in MeOH/MeCN): \(m/z\) [M]+ calcd. 554.0294 for C22H35BrFeSn; found: 554.0283; [M – Br + H]+ calcd. 476.1188 for C22H36FeSn; found: 476.1192.

\([\alpha]^{20}_D\): +26 (589), +27.5 (578), +32.5 (546) (c 0.25, CHCl3).

To a degassed 87:13 mixture of (SFc)-5 and tributylstannylferrocene (1.2 g) in DCM (10 mL) was added a degassed solution of iodine (0.66 g, 2.60 mmol) in DCM (10 mL) and the resulting reaction mixture was stirred for 17 h. Subsequently, the reaction was quenched with a saturated aqueous solution of Na2S2O3. The phases were separated and the organics were filtered through neutral aluminium oxide. After evaporation of the solvents, the residue
was taken up in MeOH and to this solution was added 350 mg of KF. This mixture was stirred for 15 min and again filtered through neutral alumina. The solvent was removed and the residue was dissolved in Et₂O. The organics were washed with water and brine, and then dried over MgSO₄. Filtration and evaporation of the solvents provided the crude product. Three consecutive column chromatographies (aluminium oxide, heptane) afforded the desired pure product (S₂Fc)-2 in 60% yield (based on (R,S₂Fc)-4, 424 mg, 1.085 mmol) and 99% chemical purity. An analytical sample was further purified by column chromatography (aluminium oxide, heptane) and gave (S₂Fc)-2 in >99.5% chemical purity.

(S₂Fc)-2: Mp.: 74 ºC

¹H NMR (400 MHz, CDCl₃): δ 4.19 (t, 2.6 Hz, 1H, H₄), 4.22 (s, 5H, Cp'), 4.43 (dd, J₁ = 2.6 Hz, J₂ = 1.4 Hz, 1H, H₅), 4.52 (dd, J₁ = 2.6 Hz, J₂ = 1.4 Hz, 1H, H₃). The spectrum matched the previously reported data for rac-2 (Butler, I. R. Inorg. Chem. Commun. 2008, 11, 15–19).

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 46.2 (C₁), 68.4 (C₄), 69.6 (C₃), 73.59 (C₅), 73.62 (5C, Cp'), 84.5 (C₂).

HR-MS (ESI in MeOH/MeCN): m/z [M]+ calcd. 389.8204 for C₁₀H₈BrFeI; found: 389.8204. [α]₂₀λ: −26 (589), −29 (578), −43 (546) (c 0.25; CHCl₃).

Anal. calcd. for: C₁₀H₈BrI C, 30.73; H, 2.06. Found: C, 30.74; H, 2.01.

(RFc)-2'-Bromo-(SFc)-2-((R)-1-N,N-dimethylaminoethyl)-1,1''-biferrocene, (R,SFc,RFc)-3

To a degassed solution of (R)-1 (292 mg, 1.14 mmol) in THF (1.5 mL) at −78 ºC was added dropwise sec-BuLi (1.4 M in cyclohexane, 0.9 mL, 1.26 mmol). The resulting deep red solution was stirred for 1 h at −78 ºC and for 2 h at 0 ºC. A solution of ZnBr₂ in THF (1.3 M, 1.15 mL, 1.49 mmol) was added and the reaction mixture was stirred for further 40 min at 0 ºC. A solution of [Pd₂(dba)₃]·CHCl₃ (52.2 mg, 0.057 mmol) and tri(2-furyl)phosphine (106.8 mg, 0.46 mmol) in THF was prepared. After degassing it was stirred for 20 min at r.t. to give a dark green clear solution. To this catalyst solution were transferred a degassed solution of (S₂Fc)-2 (288.5 mg, 0.738 mmol) in THF (1 mL) and the freshly prepared ferrocenyl-zinc compound. The resulting solution was heated under argon at 75 ºC for 19 h. The reaction mixture was cooled to r.t., quenched with 5 M NaOH (3 mL), diluted with water and extracted with Et₂O (3 x 50 mL). The combined organic phases were washed with water (3 x 50 mL) and brine (2 x 50 mL) and dried over MgSO₄. The mixture was filtered and the solvent was evaporated. The crude product was purified by column chromatography (aluminium oxide; eluents: PE to elute excess tfp, and PE/Et₂O/NEt₃ = 5/5/1 to elute product (R,S₂Fc,RFc)-3 (yield: 300 mg, 0.577 mmol, 78%).
M.p.: 89–94 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.51 (d, $J = 6.9$ Hz, 3H, CH$_3$CH), 1.70 (s, 6H, N(CH$_3$)$_2$), 3.42 (q, $J = 6.9$ Hz, 1H, CH$_3$C), 4.18 (dd, $J_1 = 2.5$ Hz, $J_2 = 1.4$ Hz, 1H, H3), 4.26 (dd, $J_1 = J_2 = 2.6$ Hz, 1H, H4$''$), 4.28 (s, 5H, Cp$'$), 4.36 (bs, 6H, Cp$''''$ + H4), 4.39 (dd, $J_1 = 2.6$ Hz, $J_2 = 1.5$ Hz, 1H, H5$''$), 4.45 (dd, $J_1 = 2.6$ Hz, $J_2 = 1.5$ Hz, 1H, H3$''$), 4.60 (dd, $J_1 = 2.5$ Hz, $J_2 = 1.4$ Hz, 1H, H5).

$^{13}$C{1H} NMR (100.6 MHz, CDCl$_3$): $\delta$ 20.1 (C$_H$3CH), 41.1 (2C, N(CH$_3$)$_2$), 55.3 (CH$_3$C), 66.1 (C4$''$), 66.5 (C4), 67.0 (C3), 69.6 (5C, Cp$'$), 69.8 (C3$''$), 70.1 (C5$''$), 71.5 (5C, Cp$''''$), 71.6 (C5), 82.6 (C$_q$), 82.7 (C$_q$), 85.7 (C$_q$), 88.7 (C2).

HR-MS (ESI, MeOH/MeCN): m/z [M+H]$^+$ calcd. 520.0026 for C$_{24}$H$_{27}$BrFe$_2$N; found: 520.0022.

$[\alpha]_{20}^{\lambda}$ (nm): –950 (589), –1062 (578), –1631 (546) (c 0.283, CHCl$_3$).

Anal. calcd. for: C$_{24}$H$_{26}$BrFe$_2$N C, 55.43; H, 5.04; N 2.69. Found: C, 55.53; H, 4.98; N, 2.68.

**(RFc)-2$''$-Bromo-(SFc)-2-((R)-1-N,N-dimethylaminoethyl-$\kappa$N)-1,1$''$-biferrocene trihydridoboron, (RSFc,RFc)-3·BH$_3$**

To a stirred solution of (RSFc,RFc)-3 (100 mg, 0.19 mmol) in THF (3 mL) was added BH$_3$·THF in THF (1 M, 0.7 mL, 0.7 mmol) at 0 °C. Stirring was continued for 1 h at r.t. before the reaction mixture was quenched at 0 °C by dropwise addition of water. The organics were extracted with DCM, the combined solutions were washed with water and dried with MgSO$_4$. The solvents were removed and the residue was purified by chromatography (aluminium oxide, eluent CH$_2$Cl$_2$; yield: 136 mg 0.255 mmol, 91%).

M.p.: 162–165 °C.

$^1$H NMR (500.1 MHz, CDCl$_3$): $\delta$ 1.46–1.70 (bm, 3H, BH$_3$), 1.78 (s, 3H, NCH$_3$A), 1.85 (d, $J = 6.9$ Hz, 3H, CH$_3$CH), 2.14 (s, 3H, NCH$_3$B), 3.82 (q, $J = 6.9$ Hz, 1H, CH$_3$C), 4.31–4.33 (m, 1H, H3), 4.33 (s, 5H, Cp$'$), 4.34 (dd, $J_1 = J_2 = 2.6$ Hz, 1H, H4$''$), 4.36 (s, 5H, Cp$''''$), 4.38 (dd, $J_1 = 2.6$ Hz, $J_2 = 1.6$ Hz, 1H, H5$''$), 4.47–4.50 (bm, 2H, H3$''$ + H4), 4.70 (dd, $J_1 = 2.4$ Hz, $J_2 = 1.4$ Hz, 1H, H5).

$^{13}$C{1H} NMR (125.8 MHz, CDCl$_3$): $\delta$ 18.0 (CH$_3$CH), 43.6 (NCH$_3$B), 52.1 (NCH$_3$A), 62.4 (CH$_3$CH), 66.9 (C4$''$), 67.6 (C4), 68.2 (C3), 69.9 (C4), 70.2 (5C, Cp$'$), 70.3 (C3$''$), 71.7 (5C, Cp$''''$), 72.5 (C5), 82.5 (C$_q$), 83.9 (C$_q$), 84.9 (C$_q$), 86.3 (C2).

HR-MS (ESI, MeOH/MeCN): m/z [M+Na]$^+$ calcd. 556.0173 for C$_{24}$H$_{29}$BBrFe$_2$NNa; found: 556.0194.

$[\alpha]_{23}^{\lambda}$ (nm): –839 (589) (c 0.321, CHCl$_3$).
To a degassed solution of \((R,S_{\text{Fc}},R_{\text{Fc}})\)-3 (188 mg, 0.361 mmol) in 2.4 mL of THF was added dropwise at –40 °C a solution of \(n\)-BuLi (1.6 M in hexane, 0.27 mL, 0.434 mmol). The color of the reaction mixture changed immediately to dark red. After stirring for 40 min at –40 °C was the solution warmed up to r.t., before chlorodiphenylphosphine (107 mg, 0.487 mmol) was added. The mixture was stirred for 18 h at r.t. and for 1 h at 35 °C. The reaction was quenched with 5 mL of saturated aqueous NaHCO₃. The product was extracted twice with ethyl acetate and the combined organic phases were washed with water and brine. After drying over MgSO₄, filtration and evaporation of the solvents, the crude product was obtained as an orange solid. The pure product was obtained after chromatography (aluminium oxide, PE/EE/NET₃ = 50/5/1) as orange foam (yield: 146 mg, 0.233 mmol, 65%).

M.p.: 182–184 °C.

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 1.29 (d, \(J = 6.8\) Hz, 3H, \(\text{CH}_3\text{CH}\)), 1.59 (s, 6H, \(\text{N(CH}_3\text{)}_2\)), 3.68 (q, \(J = 6.8\) Hz, 1H, \(\text{CH}_2\text{CH}\)), 3.99 (s, 5H, \(\text{Cp}''\)), 4.12 (m, 2H, H₃ + H₃′′), 4.25 (s, 5H, Cp′), 4.29 (dd, \(J_1 = J_2 = 2.4\) Hz, 1H, H₄), 4.47 (dd, \(J_1 = J_2 = 2.3\) Hz, 1H, H₄′′), 4.67 (m, 1H, H₅), 4.71 (m, 1H, H₅′′), 7.08–7.13 (m, 5H, \(\text{PhB-ortho} + \text{PhB-meta} + \text{PhB-para}\)), 7.38 (m, 3H, \(\text{PhA-meta} + \text{PhA-para}\))

\(^{13}\)C\(^{\text{[1H]}}\) NMR (100.6 MHz, CDCl₃): \(\delta\) 11.9 (CH₃CH), 39.8 (2C, \(\text{N(CH}_3\text{)}_2\)), 55.5 (CH₃CH), 65.7 (C₄), 66.7 (C₃), 69.6 (5C, Cp′), 69.7 (C₄″), 69.9 (5C, Cp″), 71.6 (d, \(J = 5.1\) Hz, C₃″), 73.4 (d, \(J = 9.1\) Hz, C₅), 73.6 (d, \(J = 4.6\) Hz, C₅″), 84.5 (C₁), 91.2 (C₂), 92.6 (C₁″/C₂″), 126.9 (bs, \(\text{PhB-para}\)), 127.3 (d, \(J = 5.5\) Hz, 2C, \(\text{PhB-meta}\)), 128.0 (d, \(J = 8.4\) Hz, 2C, \(\text{PhA-meta}\)), 129.0 (bs, \(\text{PhA-para}\)), 132.4 (d, \(J = 17.6\) Hz, 2C, \(\text{PhB-ortho}\)), 135.5 (d, \(J = 22.9\) Hz, 2C, \(\text{PhA-ortho}\)), 139.7, 139.8, 140.5, 140.6 (2C, \(\text{PhA-ipsa} + \text{PhB-ipsa}\))

\(^{31}\)P\(^{\text{[1H]}}\) NMR (162 MHz, CDCl₃): \(\delta\) –22.7.

HR-MS (ESI, MeOH/MeCN): \(m/z\) [M+H]⁺ calcd. 626.1362 for \(\text{C}_{36}\text{H}_{37}\text{Fe}_2\text{NP}\); found: 626.1367.

\([\alpha]_{D}^{20}\) (nm): –447 (589), –518 (578), –886 (546) (c 0.219, CHCl₃).

\((S_{\text{Fc}})-2-((R)-1-N,N\text{-Dimethylaminoethyl})-(R_{\text{Fc}})-2''\text{-diphenylphosphino-1,1''-biferrocene, (R,S}_{\text{Fc}},R_{\text{Fc}})-6\)

\((S_{\text{Fc}})-2-((R)-1-N,N\text{-Dimethylaminoethyl})-(R_{\text{Fc}})-2''\text{-bis(3,5-dimethyl-4-methoxyphenyl)-phosphino-1,1''-biferrocene, (R,S}_{\text{Fc}},R_{\text{Fc}})-7\)
Synthesis as described for \((R,S_{Fc},R_{Fc})-\alpha\): \((R,S_{Fc},R_{Fc})-(3) (1.01 \text{ g}, 1.95 \text{ mmol})\) in THF (13 mL); \(n\)-BuLi (1.6M in hexane, 1.46 mL, 2.34 mmol); chloro-bis(3,5-dimethyl-4-methoxy)phenylphosphine (0.891 g, 2.65 mmol) dissolved in THF (5 mL). Purification by column chromatography (aluminium oxide, PE/EE/NEt\(_3\) = 90:10:1 → 80:20:1) provided the pure product as orange foam (yield: 1.020 g, 1.38 mmol, 71%).

M.p.: 41–42 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.35 (d, 3H, \(J = 6.8\) Hz, CH\(_3\)CH), 1.47 (s, 6H, N(CH\(_3\))\(_2\)), 2.11 (s, 6H, Ph\(^B\)-CH\(_3\)), 2.31 (s, 6H, Ph\(^A\)-CH\(_3\)), 3.51 (q, \(J = 6.8\) Hz, 1H, CH\(_3\)CH), 3.61 (s, 3H, Ph\(^B\)-OCH\(_3\)), 3.73 (s, 3H, Ph\(^A\)-OCH\(_3\)), 4.00 (s, 5H, Cp\(^{''''}\)), 4.11 (dd, \(J_1 = 2.4\) Hz, \(J_2 = 1.4\) Hz, 1H, H3), 4.18 (m, 1H, H3\(^{''}\)), 4.26 (s, 5H, Cp\(^{\prime}\)), 4.29 (dd, \(J_1 = J_2 = 2.4\) Hz, 1H, H4), 4.47 (dd, \(J_1 = J_2 = 2.4\) Hz, 1H, H4\(^{''}\)), 4.65-4.68 (m, 2H, H5 + H5\(^{''}\)), 6.80 (d, \(J = 7.5\) Hz, 2H, Ph\(^B\)-ortho), 7.29 (d, \(J = 8.1\) Hz, 2H, Ph\(^A\)-ortho).

\(^{13}\)C{\(^1\)H} NMR (100.6 MHz, CDCl\(_3\)): \(\delta\) 15.3 (CH\(_3\)CH), 16.1 (2C, Ph\(^{A/B}\)-CH\(_3\)), 16.2 (2C, Ph\(^{A/B}\)-CH\(_3\)), 40.3 (2C, N(CH\(_3\))\(_2\)), 55.6 (CH\(_3\)CH), 59.5 (Ph\(^B\)-OCH\(_3\)), 59.7 (Ph\(^A\)-OCH\(_3\)), 65.8 (C4), 66.7 (C3), 69.3 (C4\(^{''''}\)), 69.7 (5C, Cp\(^{\prime}\)), 69.9 (5C, Cp\(^{''''}\)), 71.8 (d, \(J = 5.0\), C3\(^{''}\)), 73.4 (d, \(J = 9.4\) Hz, C5\(^{''''}/\)C5), 73.6 (d, \(J = 4.5\) Hz, C5\(^{''''}/\)C5), 78.6 (d, \(J = 13.2\) Hz, C1\(^{''}\)), 84.7 (d, \(J = 2.7\) Hz, C1), 90.5 (C2), 92.4 (d, \(J = 30.5\) Hz, C2\(^{''''}\)), 129.8 (d, \(J = 58.0\) Hz, Ph\(^{A/B}\)-ipso), 129.9 (d, \(J = 59.4\) Hz, Ph\(^{A/B}\)-ipso), 133.4 (d, \(J = 19.9\) Hz, 2C, Ph\(^{H/ortho}\)), 134.2–134.4 (4C, Ph\(^{A/B-meta}\)), 135.8 (d, \(J = 23.7\) Hz, 2C, Ph\(^A\)-ortho), 156.7 (Ph\(^B\)-para), 157.8 (Ph\(^A\)-para). Assignments of Ph\(^A\)/Ph\(^B\) are interchangeable.

\(^{31}\)P{\(^1\)H} NMR (162 MHz, CDCl\(_3\)): \(\delta\) –26.6.

HR-MS (ESI, MeOH/MeCN): \(m/z\) [M+H\(^+\)] \(^+\) calcd. 742.2200 for C\(_{42}\)H\(_{49}\)Fe\(_2\)NO\(_2\)P; found: 742.2190.

\([\alpha]^{20}_d\) (nm): –356 (589), –416 (578), –739 (546) (c 0.210, CHCl\(_3\)).

\((S_{Fc})-2-((R)-1-N,N-Dimethylaminoethyl)-(R_{Fc})-2'''-diphenylphosphinyl-1,1'''-biferrocene,\n\((R,S_{Fc},R_{Fc})-8\)
From \((R,S_{Fc},R_{Fc})-3\) with use of ClP(O)Ph₂: Synthesis procedure as described for \((R,S_{Fc},S_{Fc})-6\). \((R,S_{Fc},R_{Fc})-3\) (603 mg, 1.16 mmol) in THF (7.7 mL); n-BuLi (1.6 M in hexane, 0.87 mL, 1.39 mmol); diphenylphosphinylchloride (371.5 mg, 0.3 mL, 1.57 mmol). Purification by column chromatography (aluminium oxide, PE/EE/NEt₃ 10/10/1) provided the pure product as orange foam (yield: 529 mg, 0.825 mmol, 71%).

From \((R,S_{Fc},R_{Fc})-6\) with use of \(\text{H}_2\text{O}_2\): To a solution of \((R,S_{Fc},R_{Fc})-6\) (1.11 g, 1.78 mmol) in acetone (150 mL) was added an aqueous solution of \(\text{H}_2\text{O}_2\) (30%, 10 mL). The reaction mixture was stirred for 50 min at r.t. Subsequently, it was quenched with saturated aqueous \(\text{Na}_2\text{S}_2\text{O}_3\). The organics were extracted with EA and the combined organic phases were washed with water and brine, dried over \(\text{MgSO}_4\), filtered and the solvents evaporated. The crude product was purified by chromatography (aluminium oxide, PE/EA/TEA = 5/1/1) and the pure product was obtained as a red-orange solid (yield: 1.04 g, 1.62 mmol, 92%).

M.p.: 78–81 °C.

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 1.25 (d, \(J = 6.8\) Hz, 3H, \(\text{CH}_3\)), 1.72 (s, 6H, \(N(\text{CH}_3)²\)), 3.72 (q, \(J = 6.8\) Hz, 1H, \(\text{CH}_3\)), 3.88 (dd, \(J_1 = J_2 = 2.4\) Hz, 1H, H4), 3.95 (dd, \(J_1 = 2.4\) Hz, \(J_2 = 1.4\) Hz, 1H, H3), 4.17 (s, 5H, Cp'), 4.42 (dd, \(J_1 = 2.5\) Hz, \(J_2 = 1.5\) Hz, 1H, H3'), 4.46 (s, 5H, Cp''), 4.52 (m, 1H, H4''), 4.73 (m, 1H, H5''), 7.17 (m, 2H, Ph⁴-m), 7.26–7.30 (m, 1H, Ph⁴-para), 7.36–7.43 (m, 3H, Ph⁴-meta + Ph⁴-para), 7.44–7.50 (m, 2H, Ph⁴-ortho), 7.72–7.78 (m, 2H, Ph⁴-ortho).

\(^{13}\)C\{{\(^1\)H}\} NMR (100.6 MHz, CDCl₃): \(\delta\) 10.3 (CH₃), 39.8 (2C, N(CH₃)₂), 55.4 (CH₃), 65.6 (C₄), 66.1 (C₃), 69.5 (5C, Cp'), 70.1 (d, \(J = 11.5\) Hz, C⁴'), 70.7 (5C, Cp''), 73.7 (C₅), 73.8 (d, \(J = 14.1\) Hz, C₃''), 75.7 (d, \(J = 9.8\) Hz, C⁵''), 83.5 (C₁), 89.8 (d, \(J = 10.7\) Hz, C₁'/C₂''), 91.5 (C₂), 127.7 (d, \(J = 12.2\) Hz, 2C, Ph⁴-meta), 127.8 (d, \(J = 12.2\) Hz, 2C, Ph⁴-meta), 130.6 (d, \(J = 2.8\) Hz, Ph⁴-para), 130.9 (d, \(J = 2.2\) Hz, Ph⁴-para), 131.7 (d, \(J = 9.4\) Hz, 2C, Ph⁴-ortho), 132.0 (d, \(J = 10.2\) Hz, 2C, Ph²-ortho), 133.7 (d, \(J = 105.8\) Hz, Ph²-ipso), 135.9 (d, \(J = 104.9\) Hz, Ph²-ipso); 1 Cq (C₁'/C₂'') not observed; Ph⁴ and Ph⁴ interchangeabe. \(^{31}\)P\{{\(^1\)H}\} NMR (162 MHz, CDCl₃): \(\delta\) 28.95.

HR-MS (ESI, MeOH/MeCN): \(m/z\) \([M+H]^+\) calcd. 642.1312 for \(C_{36}H_{37}Fe_2NOP\); found: 624.1316.

\([\alpha]^{20}_D\) (nm): −733 (589), −829 (578), −1314 (546) (c 0.222, CHCl₃).

\((S_{Fc})-2-((R)-1-N,N-Dimethylaminoethyl)-(R_{Fc})-2''-bis(3,5-dimethyl-4-methoxyphenyl)-phosphinyl-1,1''-biferrocene, (R,S_{Fc},R_{Fc})-9\)
Synthesis as described for \((R,S_{Fc},R_{Fc})-8\). \((R,S_{Fc},R_{Fc})-8\) (156 mg, 0.210 mmol) was dissolved in acetone (11 mL); \(H_2O_2\) (30%, 1 mL); chromatography (aluminium oxide, PE/EA/NEt3 = 10/10/1); the pure product was obtained as orange foam (yield: 140 mg, 0.185 mmol, 88%).

M.p.: 35–37 °C.

\(^1\)H NMR (400 MHz, CDCl3): \(\delta\) 1.30 (d, \(J = 6.8\) Hz, 3H, \(C_2H_3CH\)), 1.49 (s, 6H, N(\(\text{CH}_3\))2), 2.15 (s, 6H, \(\text{Ph}^B\)-\(\text{CH}_3\)), 2.29 (s, 6H, \(\text{Ph}^A\)-\(\text{CH}_3\)), 3.58 (q, \(J = 6.8\) Hz, 1H, \(\text{CH}_3\CH\)), 3.64 (s, 3H, \(\text{Ph}^B\)-O\(\text{CH}_3\)), 3.72 (s, 3H, \(\text{Ph}^A\)-O\(\text{CH}_3\)), 3.97 (dd, \(J_1 = 2.5\) Hz, \(J_2 = 1.5\) Hz, 1H, H3)), 4.03 (dd, 1H, \(J_1 = J_2 = 2.5\) Hz, H4)), 4.19 (s, 5H, C3′), 4.23–4.25 (m, 1H, H3′′), 4.42 (s, 5H, C3′′), 4.50–4.52 (m, 1H, H4′′), 4.69–4.71 (m, 2H, H5′′ + H5), 7.14 (d, \(J = 12.0\) Hz, 2H, \(\text{Ph}^B\)-ortho), 7.42 (d, \(J = 11.6\) Hz, 2H, \(\text{Ph}^A\)-ortho).

\(^{13}\)C\(^{1}\)H NMR (100.6 MHz, CDCl3): \(\delta\) 14.0 (CH\(_3\)CH), 16.2 (2C, Ph\(^A/B\)-\(\text{CH}_3\)), 16.3 (2C, Ph\(^A/B\)-\(\text{CH}_3\)), 40.1 (2C, N(\(\text{CH}_3\))2), 55.6 (CH\(_3\)CH), 59.4 (Ph\(^B\)-O\(\text{CH}_3\)), 59.7 (Ph\(^A\)-O\(\text{CH}_3\)), 65.3 (C4), 66.2 (C3), 69.6 (5C, C3′), 69.8 (d, \(J = 11.3\) Hz, C4′′), 70.7 (5C, C3′′), 73.8 (d, \(J = 14.6\) Hz, C3′′), 74.1 (C5), 75.6 (d, \(J = 9.9\) Hz, C5′), 83.7 (C1), 90.0 (d, \(J = 11.1\) Hz, C1′′/C2′′), 90.7 (C2), 128.7 (d, \(J = 107.0\) Hz, Ph\(^A/B\)-ipso), 130.2–130.5 (4C, Ph\(^A\)-meta + Ph\(^B\)-meta), 130.7 (d, \(J = 107.3\) Hz, Ph\(^A/B\)-ipso), 132.2–132.5 (4C, Ph\(^A\)-ortho + Ph\(^B\)-ortho), 159.3 (2C, m, Ph\(^A\)-para + Ph\(^B\)-para). One Fe-Cq (C1′′/C2′′) not observed; assignment of Ph\(^A\)/Ph\(^B\) are interchangeable.

\(^{31}\)P\(^{1}\)H NMR (162 MHz, CDCl3): \(\delta\) 26.4.

HR-MS (ESI, MeOH/MeCN): \(m/z\) [M+H]\(^+\) calcd. 758.2149 for \(\text{C}_{42}\text{H}_{49}\text{Fe}_2\text{O}_2\text{P}_2\); found: 758.2128.

[\(\alpha\)]\(^{20}\)_D (nm): –679 (589), –772 (578), –1243 (546) (c 0.239, CHCl\(_3\)).

**Synthesis of derivatives 10–13**

General procedure A: Phosphineoxide \((R,S_{Fc},R_{Fc})-8\) (for \(10–12\)) or \((R,S_{Fc},R_{Fc})-9\) (for \(13\)) was transferred into a Schlenk flask and dissolved under Ar in freshly distilled acetic acid through which Ar had been bubbled for several hours. The resulting solution was again degassed and subsequently heated under Ar to 70 or 75 °C for 18 h. After cooling to room temperature, the acetic acid was removed under vacuum, the residue was taken up in DCM and saturated aqueous NaHCO\(_3\) was added. The phases were separated and the aqueous phase was extracted with DCM. The combined organic phases were washed with water and brine, and dried over MgSO\(_4\). After filtration and evaporation of the solvents, the crude product was purified by column chromatography.

\(\text{(S}_{Fc}\)\(_2\))-2-(\((R)\)-1-Cyclohexylphosphinylethyl)-(\(R_{Fc}\)\(_2\))-2\"-diphenylphosphinyl-1,1\"-biferrocene, \(\text{(R}_{Fc},\text{R}_{Fc})-(10b)\)
Synthesis according to general procedure A: \((R,S\text{Fc},R\text{Fc})-8\) (425 mg, 0.663 mmol) in acetic acid (8 mL), dicyclohexylphosphine (0.53 mL, 2.62 mmol), reaction temperature 70 °C, column chromatography (aluminium oxide, PE/EA = 2:1 → EA) yielded a mixture of \((R,S\text{Fc},R\text{Fc})-10b\) and traces of \((R,S\text{Fc},R\text{Fc})-10a\) which was used in the next step without further separation (441 mg, 0.544 mmol, 82%).

\((R,S\text{Fc},R\text{Fc})-10a\)

HR-MS (ESI, MeOH/MeCN): \(m/z [M]^+\) calcd. 794.2192 for \(C_{46}H_{52}Fe_2OP_2\); found: 794.2181.

\((R,S\text{Fc},R\text{Fc})-10b\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 0.45–0.58\) (m, 1H, Cy-CH), 0.70–1.88 (m, 21H, Cy), 1.70 (dd, \(J_1 = 13.7\) Hz, \(J_2 = 7.6\) Hz, 3H, CH\(_3\)CH), 2.89 (dq, \(J_1 = 13.3\) Hz, \(J_2 = 7.6\) Hz, 1H, CH\(_3\)CH), 4.10 (t, \(J = 2.6\) Hz, 1H, H4), 4.24–4.26 (m, 1H, H3), 4.26–4.28 (m, 1H, H3”), 4.28 (s, 5H, Cp’), 4.33 (s, 5H, Cp’’), 4.57–4.60 (m, 1H, H4”), 4.85–4.88 (m, 1H, H5”), 4.97–5.00 (m, 1H, H5), 7.21–7.29 (m, 2H, Ph\(^{\text{A-meta}}\)), 7.30–7.37 (m, 1H, Ph\(^{\text{A-para}}\)), 7.41–7.53 (m, 3H, Ph\(^{\text{B-meta}}\)), 7.67–7.75 (m, 2H, Ph\(^{\text{A-ortho}}\)), 7.82–7.90 (m, 2H, Ph\(^{\text{B-ortho}}\)). Ph\(^{\text{A}:}\) up, Ph\(^{\text{B}:}\) down, pointing towards Cp’’).

\(^{31}\)P\(_{({^1}\text{H})}\) NMR (162 MHz, CD\(_2\)Cl\(_2\)): \(\delta –27.2\) (P(O)Ph\(_2\)), 52.9 (P(O)Cy\(_2\)).

HR-MS (ESI, MeOH/MeCN): \(m/z [M+Na]^+\) calcd. 833.2039 for \(C_{46}H_{52}Fe_2NaO_2P_2\); found: 833.2030.

\((S\text{Fc})-2-((R)-1\text{-Diphenylphosphinoethyl})-(R\text{Fc})-2''\text{-diphenylphosphinyl}-1,1''\text{-biferrocene, (R,S\text{Fc},R\text{Fc})-(11a), and (S\text{Fc})-2-((R)-1\text{-diphenylphosphinylethyl})-(R\text{Fc})-2''\text{-diphenylphosphinyl}-1,1''\text{-biferrocene, (R,S\text{Fc},R\text{Fc})-(11b)}}\)

Synthesis according to general procedure A: \((R,S\text{Fc},R\text{Fc})-8\) (300 mg, 0.468 mmol) in acetic acid (7 mL), diphenylphosphine (348 mg, 1.87 mmol), reaction temperature 70 °C, column chromatography (aluminium oxide, PE/EA = 2:1 → EE) yielded a mixture of 74% \((R,S\text{Fc},R\text{Fc})-11a\) and 16% of \((R,S\text{Fc},R\text{Fc})-11b\) (includes traces of an unidentified byproduct) which was used in the next step without further separation.

\((R,S\text{Fc},R\text{Fc})-11a\): \n
\(^1\)H NMR (600 MHz, CD\(_2\)Cl\(_2\)): \(\delta 1.24\) (dd, \(J_1 = J_2 = 5.7\) Hz, 3H, CHCH\(_3\)), 3.34–3.41 (m, 1H, CHCH\(_3\)), 3.45 (bs, 1H, H3), 3.92 (t, \(J = 2.4\) Hz, 1H, H4), 4.15 (bs, 1H, H’’), 4.20 (s, 5H, Cp’), 4.49 (s, 5H, Cp’’), 4.61 (bs, 1H, H’’), 4.78 (bs, 1H, H5), 4.93 (bs, 1H, H’’), 6.77–6.88 (m, 2H,
$^{13}$C $\{^1\text{H}\}$ NMR (150.9 MHz, CD$_2$Cl$_2$): $\delta$ 15.2 (d, J = 2.4 Hz, CH$_3$), 28.8 (d, J = 18.0 Hz, CHCH$_3$), 65.5 (C4), 66.3 (d, J = 3.1 Hz, C3), 69.6 (5C, Cp'), 70.4 (d, J = 10.8 Hz, Cp") , 70.9 (5C, Cp"'), 73.4 (C5), 74.9 (d, J = 14.7 Hz, Cp"), 75.9 (d, J = 9.5 Hz, Cp"'), 82.6 (d, J = 3.2 Hz, Cp), 89.8 (d, J = 11.2 Hz, Cp), 127.5 (d, J = 6.7 Hz, 2C, Ph$^{\text{D-ortho}}$), 127.7–127.9 (m, 5C, Ph), 128.4 (d, J = 4.6 Hz, 2C, Ph-meta), 128.7–128.8 (m, Ph-para), 131.1–131.2 (m, 2C, Ph-meta), 131.7–131.9 (m, 4C, Ph-ortho), 132.3 (dd, J$_1$ = 6.0 Hz, J$_2$ = 10.2 Hz, 2C, Ph-ortho), 134.9 (d, J = 18.5 Hz, 2C, Ph$^{\text{D-ortho}}$).

$^{31}$P $\{^1\text{H}\}$ NMR (243 MHz, CD$_2$Cl$_2$): $\delta$ 3.2 (PPh$_2$), 29.1 (P(O)Ph$_2$).

(S$\text{Fc}$)-2-{(R)-1-Bis[3,5-bis(trifluoromethyl)phenyl]phosphinoethyl}-(R$\text{Fc}$)-2''-diphenylphosphinyl-1,1''-biferrocene, (R$\text{S}_{\text{Fc}},R\text{Fc}$)-(12a), and (S$\text{Fc}$)-2-{(R)-1-bis[3,5-bis(trifluoromethyl)phenyl]phosphinylethyl}-(R$\text{Fc}$)-2''-diphenylphosphinyl-1,1''-biferrocene, (R$\text{S}_{\text{Fc}},R\text{Fc}$)-(12b)

Synthesis according to general procedure A: (R$\text{S}_{\text{Fc}},R\text{Fc}$)-8 (1 g, 1.56 mmol) in acetic acid (10 mL), bis-(3,5-trifluoromethyl)phenylphosphine (1.07 g, 2.34 mmol), reaction temperature 70 °C for 18 h, column chromatography on aluminium oxide (PE/EE = 2:1) resulted in a mixture of 95% of 12a and 5% of bisphosphineoxide 12b which was used in the next step without further separation (yield: 1.07 g, 1.01 mmol, 65%, orange foam).
(RSFc,RFc)-12a:
$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 1.16 (dd, $J_1 = 4.9$ Hz, $J_2 = 6.9$ Hz, 3H, CH$_3$CH), 3.34–3.39 (m, 1H, CH$_3$CH), 3.40 (bs, 1H, Cp), 4.14–4.17 (m, 2H, 2 Cp), 4.23 (s, 5H, Cp), 4.50 (s, 5H, Cp), 4.58–4.61 (m, 1H, Cp), 4.81–4.84 (m, 1H, Cp), 5.31–5.34 (m, 1H, Cp), 6.87–6.93 (m, 2H, Ph), 6.94–6.99 (m, 1H, Ph), 7.03 (d, $J = 4.9$ Hz, 2H, Ph$^{CD-ortho}$), 7.41–7.51 (m, 3H, Ph), 7.58 (d, $J = 4.9$ Hz, 2H, Ph$^{CD-ortho}$), 7.62–7.69 (m, 2H, Ph), 7.76 (s, 1H, Ph$^{CD-para}$), 7.83–7.90 (m, 3H, Ph + Ph$^{CD-para}$).

$^{13}$C{$^1$H} NMR (150.9 MHz, CDCl$_3$): $\delta$ 13.6 (CH$_3$CH), 30.5 (d, $J = 23.1$ Hz, CHCH$_3$), 65.5 (Cp), 66.3 (2C, Cp), 69.8 (5C, Cp), 70.0 (d, $J = 11.7$ Hz, Cp), 71.0 (5C, Cp), 74.7 (Cp), 75.2 (Cp), 82.7 (Cp), 89.9 (d, $J = 20.6$ Hz, Cp), 121.8–140.7 (Ph), 2 Fe-C$_4$ not observed.

$^{31}$P{$^1$H} NMR (243 MHz, CDCl$_3$): $\delta$ 3.7 (CH$_3$CHP$_2$), 24.6 (Fc-P(O)Ph$_2$).

HR-MS (ESI, MeOH/MeCN): m/z [M+Na]$^+$ calcd. 1077.0646 for C$_{50}$H$_{36}$F$_{12}$Fe$_2$NaOP$_2$; found: 1077.0669.

(R,SFc,RFc)-12b: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.37 (dd, $J_1 = 18.2$ Hz, $J_2 = 7.2$ Hz, 3H, CH$_3$CHP), 4.01 (m, 1H, Cp), 4.15 (s, 5H, Cp), 4.18 (m, 1H, Cp), 4.20 (m, 1H, Cp), 4.37 (s, 5H, Cp), 4.38 (m, 1H, Cp), 4.40 (m, 1H, Cp), 4.75 (dq, $J_1 = 7.56$ Hz, $J_2 = 6.98$ Hz, 1H, CH$_3$CHP), 4.89 (m, 1H, Cp), 7.16–7.22 (m, 2H, Ph), 7.22–7.29 (m, 2H, Ph), 7.34–7.40 (m, 1H, Ph), 7.46–7.52 (m, 2H, Ph), 7.54–7.59 (m, 1H, Ph), 7.87 (s, 1H, Ph$^{CD-para}$), 7.95 (s, 1H, Ph$^{CD-ortho}$), 8.00–8.06 (m, 2H, Ph), 8.49 (d, $J = 10.3$ Hz, 2H, Ph$^{CD-ortho}$), 8.76 (d, $J = 10.8$ Hz, 2H, Ph$^{CD-ortho}$).

$^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$): $\delta$ 28.2; 32.3.

HR-MS (ESI, MeOH/MeCN): m/z [M+H]$^+$ calcd. 1071.0776 for C$_{50}$H$_{37}$F$_{12}$Fe$_2$O$_2$P$_2$; found: 1071.0785.

(SFc)-2-{(R)-1-Bis[3,5-bis(trifluoromethyl)phenyl]phosphinoethyl}-(RFc)-2′′-bis(3,5-dimethyl-4-methoxyphenyl)-phosphinyl-1,1′′-biferrocene, (RSFc,RFc)-(13a)

Synthesis according to general procedure A: (RSFc,RFc)-9 (423 mg, 0.56 mmol), bis-(3,5-trifluoromethyl)phenyl phosphine (1.02 g, 2.23 mmol) were dissolved in acetic acid (15 mL), reaction temperature 75 °C for 18 h, column chromatography (aluminium oxide, PE/EA = 4:1; yield: 430 mg, 0.367 mmol, 66%).

M.p.: 36–38 °C.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.11 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.9$ Hz, 3H, CH$_3$CH), 1.85 (s, 6H, Ph$^B$-CH$_2$), 2.30 (s, 6H, Ph$^A$-CH$_3$), 3.18 (m, 1H, H3), 3.33 (s, 3H, Ph$^{10}$-OCH$_3$), 3.40 (dq, $J_1 = J_2 = 6.8$ Hz, 1H, CH$_3$), 3.73 (s, 3H, Ph$^A$-OCH$_3$), 4.14-4.15 (m, 1H, H3'), 4.16 (dd, $J_1 = J_2 = 2.6$ Hz, 1H, H4), 4.22 (s, 5H, Cp'), 4.45 (s, 5H, Cp''), 4.59 (dt, $J_1 = J_2 = 2.6$ Hz, 1H, H4''), 4.81 (m, 1H, H5''), 5.31 (dd, $J_1 = J_2 = 1.3$ Hz, 1H, H5), 7.01 (d, $J = 5.3$ Hz, 2H, Ph$^C$-ortho), 7.26 (d, $J = 11.9$ Hz, 2H, Ph$^B$-ortho), 7.49 (d, $J = 11.4$ Hz, 2H, Ph$^A$-ortho), 7.53 (d, $J = 4.0$ Hz, 2H, Ph$^D$-ortho), 7.76 (bs, 1H, Ph$^C$-para), 7.83 (bs, 1H, Ph$^A$-para).

$^{13}$C{1H} NMR (100.6 MHz, CDCl$_3$): $\delta$ 13.8 (d, $J = 3.9$ Hz, CH$_3$CH), 15.8 (2C, Ph$^B$-CH$_3$), 30.3 (d, $J = 13.3$ Hz, 2C, Ph$^D$-meta), 31.0 (d, $J = 12.9$ Hz, 2C, Ph$^A$-meta), 31.1 (dm, $J = 19.0$ Hz, 2C, Ph$^D$-ortho), 31.2 (dq, $J_1 = 32.6$ Hz, $J_2 = 2.7$ Hz, 4C, Ph$^A$-meta + Ph$^D$-meta), 32.2 (d, $J = 10.0$ Hz, 2C, Ph$^A$-ortho), 33.7 (dm, $J = 19.1$ Hz, 2C, Ph$^C$-ortho), 33.8 (d, $J = 31.9$ Hz, 2C, Ph$^C$-para), 34.7 (d, $J = 32.4$ Hz, 2C, Ph$^D$-ortho) 1 C$_q$ not observed (C1''/C2'''); assignment of phenyl units: Ph$^A$ down, Ph$^B$ up, Ph$^C$ front, Ph$^D$ back.

$^{31}$P{1H} NMR (162 MHz, CDCl$_3$): $\delta$ 5.8 (CH$_3$CH-P$^A$Ar$_2$), 25.5 (Fc-P(O)Ar$_2$).

HR-MS (ESI, MeOH/MeCN): m/z [M+Na]$^+$ calcd. 1193.1484 for C$_{56}$H$_{48}$F$_{12}$Fe$_2$NaO$_3$P$_2$; found: 1193.1500.

[α]$^20$_D (nm): −393 (589), −448 (578), −735 (546) (c 0.287, CHCl$_3$).

### Synthesis of ligands 14–17

#### General procedure B:

Each phosphineoxide 10–13 was dissolved in THF and the solution was degassed. PMHS and Ti(O-iPr)$_4$ were added and the resulting mixture was refluxed under argon at 75 °C for 90 min. The solution turned dark green immediately after starting the reaction. The reaction mixture was transferred onto a column (aluminium oxide, PE/EA/EtOH = 85:15:1) without prior workup. The orange product was eluted and the solvents were removed to give the crude products as orange solids.

(S$_{Fe}$)-2-((R)-1-Cyclohexylphosphinoethyl)-(R$_{Fe}$)-2''-diphenylphosphino-1,1''-biferrocene, (R,S$_{Fe}$,R$_{Fe}$)-(14)
Synthesis according to general procedure B: 390 mg \((R,S_{Fc},R_{Fc})-12b\) (0.48 mmol) in THF (4 mL), PMHS (0.4 mL) and Ti(O-iPr)\(_4\) (690 mg, 2.4 mmol), reaction time 16 h, chromatography: aluminium oxide, PE/EE/EtOH = 90:10:1. In order to remove excess of PMHS, the crude product was purified by two further chromatographies (aluminium oxide, PE/EA = 10:1) which gave the pure product as orange foam (yield: 206 mg, 0.26 mmol, 55%).

M.p.: 84–87 °C.

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 0.54–0.53 (m, 1H, Cy-CH), 0.76–1.80 (m, 21H, Cy), 1.45 (dd, \(J_1 = 7.4\) Hz, \(J_2 = 3.8\) Hz, 3H, CH\(_3\)CH), 2.89 (bq, \(J = 7.4\) Hz, 1H, CH\(_2\)CH), 3.93 (s, 5H, Cp'''), 4.09–4.11 (m, 1H, H3), 4.21 (t, \(J = 2.5\) Hz, 1H, H4), 4.23–4.26 (m, 1H, H3''), 4.25 (s, 5H, Cp'), 4.52 (t, \(J = 2.5\) Hz, 1H, H4''), 4.66–4.69 (m, 1H, H5), 4.70–4.73 (m, 1H, H5''), 7.04–7.10 (m, 3H, PhA-\(\text{meta} + \text{PhA-para}\)), 7.24–7.32 (m, 2H, Ph\(A\)-\(\text{ortho}\)), 7.37–7.44 (m, 3H, PhB-\(\text{meta} + \text{PhB-para}\)), 7.65–7.72 (m, 2H, Ph\(B\)-\(\text{ortho}\)). Ph\(A\): up, Ph\(B\): down, pointing towards Cp''').

\(^13\)C\{\(^1\)H\} NMR (100.6 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 15.2 (CH\(_3\)CH), 26.2 (d, \(J = 25.2\) Hz, CH\(_3\)CH), 26.7, 27.0 (2C, 2 CH\(_2\)), 27.3 (d, \(J = 11.7\) Hz, CH\(_2\)), 27.56, 72.62, 27.84, 27.90 (3C, 3 CH\(_2\)), 29.74, 29.86, 29.87, 29.93 (2C, 2 CH\(_2\)), 31.3 (d, \(J = 23.7\) Hz, Cy-CH), 32.2 (d, \(J = 20.1\) Hz, CH\(_2\)), 32.4 (d, \(J = 21.9\) Hz, Cy-CH), 32.6 (d, \(J = 21.6\) Hz, CH\(_2\)), 65.1 (C4), 66.7 (d, \(J = 2.4\) Hz, C3), 69.8 (5C, Cp'), 69.9 (C4'''), 70.2 (5C, Cp'''), 72.4 (d, \(J = 4.8\) Hz, C3'''), 73.6 (d, \(J = 9.8\) Hz, C5), 73.8–73.9 (m, C5''), 78.7 (C1'''), 84.2 (C1), 93.4 (C2''), 95.2 (d, \(J = 19.8\) Hz, C2), 126.9 (Ph\(A\)-\(\text{para}\)), 127.4 (d, \(J = 5.4\) Hz, 2C, Ph\(A\)-\(\text{meta}\)), 128.2 (d, \(J = 8.5\) Hz, 2C, Ph\(B\)-\(\text{meta}\)), 129.9 (Ph\(B\)-\(\text{para}\)), 133.3 (dd, \(J_1 = 17.6\) Hz, \(J_2 = 7.3\) Hz, 2C, Ph\(A\)-\(\text{ortho}\)), 136.1 (d, \(J = 23.6\) Hz, 2C, Ph\(B\)-\(\text{ortho}\)), 140.9 (d, \(J = 10.0\) Hz, Ph\(A\)-ipso), 141.2 (d, \(J = 10.7\) Hz, Ph\(B\)-ipso).

\(^{31}\)P\{\(^1\)H\} NMR (162 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) –22.2 (d, \(J = 3.9\) Hz, Fe-PPh\(_2\)), 7.4 (bs, CH\(_3\)CH-PCy\(_2\)).

HR-MS (ESI, MeOH/MeCN): \(m/z\) [M+H]\(^+\) calcd. 779.2321 for C\(_{46}\)H\(_{53}\)Fe\(_2\)P\(_2\); found: 779.2337.

\([\alpha]^{20}_D\) (nm): – 345 (589), – 396 (578), – 677 (546) (c 0.22, CHCl\(_3\)).

\((S_{Fc})-2-(((R)-1-Diphenylphosphinoethyl)-(R_{Fc})-2''-diphenylphosphino-1,1''-biferrocene, (R,S_{Fc},R_{Fc})-(15)\)

\[
\begin{align*}
\text{Fe} & \quad \text{PPh}_2 \\
\text{Fe} & \quad \text{C}_{46}\text{H}_{53}\text{Fe}_2\text{P}_2 \\
\text{Mol. Wt.: 766.45} 
\end{align*}
\]

Synthesis according to general procedure B: mixture of 84% \((R,S_{Fc},R_{Fc})-11a\) and 16% \((R,S_{Fc},R_{Fc})-11b\) (423 mg, 0.541 mmol) in 4.8 mL of THF, PMHS (0.44 mL) and Ti(O-iPr)\(_4\) (767 mg, 2.7 mmol), reaction time 90 min, chromatography: aluminium oxide, PE/EE/EtOH = 85:15:1. For further purification from excess PMHS, the crude product was suspended in PE/EA (95:5) and filtered. The product was washed several times with the same solvent mixture and was dried \textit{in vacuo} (yield: 139 mg, 0.181 mmol, 34%).
M.p.: 72–73 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.28 (dd, $J_1 = J_2 = 7.0$ Hz, 3H, CH$_3$CH), 3.22 (q, $J = 7.0$ Hz, 1H), 3.59 (m, 1H, H3), 4.05 (s, 5H, Cp‴), 4.11 (m, 1H, H3″), 4.13 (dd, $J_1 = J_2 = 2.5$ Hz, 1H, H4), 4.27 (s, 5H, Cp'), 4.48 (dd, $J_1 = J_2 = 2.4$ Hz, 1H, H4″), 4.70 (m, 1H, H5), 4.82 (m, 1H, H5″), 6.87–6.91 (m, 2H, Ph$^D$-ortho), 6.92–7.00 (m, 3H, Ph$^B$-ortho+Ph$^C$-meta+Ph$^C$-para+Ph$^D$-para), 7.05–7.09 (m, 2H, Ph$^C$-ortho), 7.09–7.14 (m, 2H, Ph$^D$-meta), 7.17–7.25 (m, 6H, Ph$^B$-ortho+Ph$^C$-meta+Ph$^C$-para+Ph$^D$-para), 7.38–7.39 (m, 3H, Ph$^A$-meta+Ph$^A$-para), 7.63–7.67 (m, 2H, Ph$^A$-ortho).

$^{13}$C{1H} NMR (100.6 MHz, CDCl$_3$): $\delta$ 16.8 (d, $J = 1.9$ Hz, CH$_3$CH), 28.4 (d, $J = 19.1$ Hz, CH$_3$CH), 65.4 (C4), 67.3 (d, $J = 6.9$ Hz, C3), 69.4 (5C, Cp’), 69.8 (bs, C4″), 70.0 (5C, Cp‴), 72.1 (d, $J = 5.1$ Hz, C3″), 73.0 (d, $J = 8.5$ Hz, C5), 74.0 (d, $J = 4.6$ Hz, C5″), 92.8 (d, $J = 19.6$ Hz, C2), 126.9 (Ph-para), 127.2 (Ph-para), 127.3–127.4 (4C, Ph-meta), 127.9–128.0 (4C, Ph-meta), 128.6 (Ph-para), 129.0 (Ph-para), 131.5 (d, $J = 15.3$ Hz, 2C, Ph$^C$-ortho), 132.9 (dd, $J_1 = 17.7$ Hz, $J_2 = 4.8$ Hz, 2C, Ph$^B$-ortho), 135.4 (d, $J = 6.9$ Hz, 2C, Ph$^{A/D}$-ortho), 135.6 (d, $J = 8.8$ Hz, 2C, Ph$^{A/D}$-ortho), 139.8 (d, $J = 23.2$ Hz, Ph$^A$-ipso). 6 Cq were not observed; Ph$^A$/Ph$^B$ and Ph$^C$/Ph$^D$ interchangeable.

$^{31}$P{1H} NMR (162 MHz, CDCl$_3$): $\delta$ −22.8 (Fe-PPh$_2$), 3.6 (CH$_3$CH-PPh$_2$).

HR-MS (ESI, MeOH/MeCN): m/z [M$^+$] calcd. 766.1304 for C$_{46}$H$_{40}$Fe$_2$P$_2$; found: 766.1305.

[α]$^\text{D}$ (nm): −326 (589), −370 (578), −624 (546) (c 0.244, CHCl$_3$).

Anal. calcd. for: C$_{46}$H$_{40}$Fe$_2$P$_2$  C, 72.08; H, 5.26. Found: C, 71.79; H, 5.10.

(S$_{Fe}$)-2-{(R)-1-Bis[3,5-bis(trifluoromethyl)phenyl]phosphinoethyl}-(RF$_{Fe}$)-2′′-diphenylphosphino-1,1′′-biferrocene, (R,$S_{Fe}$,R$_{Fe}$)-(16)

![Chemical Structure](image)

Mol. Wt.: 1038.44

Synthesis according to general procedure B: mixture of 95% ($R$,$S_{Fe}$,$R_{Fe}$)-12a and 5% ($R$,$S_{Fe}$,$R_{Fe}$)-12b (971 mg, 0.921 mmol) in THF (10 mL), PMHS (4.05 mL) and Ti(O-iPr)$_4$ (2.1 g, 7.37 mmol), reaction time 16 h, chromatography: aluminium oxide, PE/EA/EtOH = 90:10:1. In order to remove excess of PMHS, the crude product was purified by a second chromatography (aluminium oxide, PE/EA = 10:1) which gave the pure product as orange foam (yield: 139 mg, 0.134 mmol, 34%).

M.p.: 82–84 °C.
\[^{1}\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3): \delta \ 1.17 \ (dd, J_1 = 5.5 \text{ Hz}, J_2 = 6.6 \text{ Hz}, 3\text{H}, \text{CH}_2\text{CH}), \ 3.35 \ (s, 1\text{H}, \text{CH}_3), \ 3.43 \ (dq, J_1 = J_2 = 6.6 \text{ Hz}, 1\text{H}, \text{CH}_3\text{CH}), \ 4.11 \ (s, 5\text{H}, \text{Cp}'''), \ 4.22 \ (bs, 1\text{H}, \text{H}^3), \ 4.25 \ (t, J = 2.5 \text{ Hz}, 1\text{H}, \text{H}^4), \ 4.28 \ (s, 5\text{H}, \text{Cp}'), \ 4.58 \ (t, J = 2.4 \text{ Hz}, 1\text{H}, \text{H}^4'), \ 4.76 \ (bs, 1\text{H}, \text{H}^5'), \ 4.91 \ (bs, 1\text{H}, \text{H}^5), \ 6.79–6.89 \ (m, 3\text{H}, \text{Ph}^\text{B-meta} + \text{Ph}^\text{B-para}), \ 7.10 \ (d, J = 5.5 \text{ Hz}, 2\text{H}, \text{Ph}^\text{D-ortho}), \ 7.24–7.30 \ (m, 2\text{H}, \text{Ph}^\text{D-ortho}), \ 7.35–7.42 \ (m, 3\text{H}, \text{Ph}^\text{A-meta} + \text{Ph}^\text{A-para}), \ 7.46 \ (d, J = 3.8 \text{ Hz}, 2\text{H}, \text{Ph}^\text{C-ortho}), \ 7.63–7.70 \ (m, 2\text{H}, \text{Ph}^\text{A-ortho}), \ 7.75 \ (s, 1\text{H}, \text{Ph}^\text{D-para}).

\[^{13}\text{C} \{^1\text{H} \} \text{NMR} \ (100.6 \text{ MHz, CDCl}_3): \delta \ 13.8 \ (bs, \text{CH}_3\text{CH}), \ 29.6 \ (d, J = 23.4 \text{ Hz}, \text{CH}_3\text{CH}), \ 65.8 \ (\text{C}3), \ 66.2 \ (\text{C}4), \ 69.7 \ (5\text{C}, \text{Cp}'), \ 69.9 \ (\text{C}4''), \ 70.2 \ (\text{C}5, \text{Cp}'''), \ 72.5 \ (d, J = 2.6 \text{ Hz}, \text{C}3''), \ 73.2 \ (d, J = 3.7 \text{ Hz}, \text{C}5'), \ 74.0 \ (d, J = 9.5 \text{ Hz}, \text{C}5), \ 78.6 \ (d, J = 12.2 \text{ Hz}, \text{C}1''), \ 83.9 \ (bs, \text{C}1), \ 89.3 \ (d, J = 20.2 \text{ Hz}, \text{C}2), \ 90.9 \ (d, J = 29.3 \text{ Hz}, \text{C}2''), \ 121.7 \ (\text{Ph}^\text{C-para}), \ 122.8 \ (\text{Ph}^\text{D-para}), \ 123.0 \ (q, J_{\text{F-C}} = 272.5 \text{ Hz}, 2\text{C}, \text{CF}_3), \ 123.1 \ (q, J_{\text{F-C}} = 272.5 \text{ Hz}, 2\text{C}, \text{CF}_3), \ 127.6 \ (\text{Ph}^\text{B-meta}), \ 127.8 \ (\text{Ph}^\text{B-para}), \ 128.0 \ (d, J = 7.4 \text{ Hz}, 2\text{C}, \text{Ph}^\text{A-meta}), \ 129.0 \ (\text{Ph}^\text{A-para}), \ 130.3–131.2 \ (m, 2\text{C}, \text{Ph}^\text{CD-meta}), \ 131.1 \ (d, J = 16.5 \text{ Hz}, 2\text{C}, \text{Ph}^\text{C-ortho}), \ 131.8 \ (q, J = 32.9 \text{ Hz}, 2\text{C}, \text{Ph}^\text{CD-meta}), \ 133.7 \ (d, J = 19.9 \text{ Hz}, 2\text{C}, \text{Ph}^\text{B-ortho}), \ 134.5 \ (d, J = 20.2 \text{ Hz}, 2\text{C}, \text{Ph}^\text{D-ortho}), \ 135.2 \ (d, J = 22.5 \text{ Hz}, 2\text{C}, \text{Ph}^\text{A-ortho}), \ 136.5–136.9 \ (m, 1\text{C}, \text{Ph}^\text{CD-ipso}), \ 138.3–139.0 \ (m, 2\text{C}, \text{Ph}^\text{A-ipso} + \text{Ph}^\text{A-ipso}), \ 140.7 \ (d, J = 31.9 \text{ Hz}, 1\text{C}, \text{Ph}^\text{CD-ipso}).

\[^{31}\text{P} \{^1\text{H} \} \text{NMR} \ (162 \text{ MHz, CDCl}_3): \delta \ -24.7 \ (d, J = 4.0 \text{ Hz}, \text{CH}_3\text{CH}^\text{P}R_2), \ 5.1 \ (d, J = 4.0 \text{ Hz}, \text{Fe}^\text{PPh}_2).\n
HR-MS (ESI, MeOH/MeCN): m/z [M+H\]^+ \ \text{calcd.} \ 1039.0878 \ \text{for} \ C_{50}H_{37}F_{12}Fe_2P_2; \ \text{found:} \ 1039.0869.

[\alpha]_{20}^\lambda (\text{nm}): -290 (589), -332 (578), -551 (546) (c \ 0.309, \text{CHCl}_3).

\text{Anal. calcd. for:} \ C_{50}H_{36}F_{12}Fe_2P_2 \ C, 57.83; \ H, 3.49; \ P 5.97. \ \text{Found:} \ C, 57.88; \ H, 3.43; \ P 6.06.

(S_{Fc})-2-{(R)}-1-Bis[3,5-bis(trifluoromethyl)phenyl]phosphinoethyl]-phosphino-1,1'-biferrocene, (R,S_{Fc},R_{Fc})-(17)

Synthesis according to general procedure B: phosphine oxide (R,S_{Fc},R_{Fc})-\text{13a} \ (617 \text{ mg}, \ 0.527 \text{ mmol}) \ in \ 4.8 \text{ mL of THF, PMHS (0.34 mL) and Ti(O-iPr)_4 (600 mg, 2.11 mmol), 75} ^\circ\text{C for 22 h, chromatography: aluminium oxide, PE/EA/EtOH = 90:10:1. After evaporation of the solvents, the crude product was precipitated upon addition of small amounts of Et}_2\text{O. To remove excess PMHS, the solid crude product was suspended in a mixture of PE/EA (95:5)}}
and filtered off; this was repeated for several times. After drying in vacuo, the pure product was obtained as an orange solid (yield: 295 mg, 0.255 mmol, 49%).

M.p.: 58–60 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.13 (dd, $J_1 = 6.9$ Hz, $J_2 = 5.0$ Hz, 3H, CH$_3$), 1.79 (s, 6H, PhB-C$_3$H$_3$), 2.31 (s, 6H, PhA-C$_3$H$_3$-meta), 3.18 (m, 1H, H$_3$), 3.30 (s, 3H, PhB-OC$_3$H$_3$), 3.44 (dq, $J_1 = J_2 = 6.9$ Hz, 1H, CH$_3$C$_3$H), 3.74 (s, 3H, PhA-OC$_3$H$_3$), 4.12 (s, 5H, Cp$''''$), 4.18 (m, 1H, H$_3''$), 4.20 (dd, $J_1 = J_2 = 2.5$ Hz, 1H, H$_4$), 4.25 (s, 5H, Cp$'$), 4.56 (dd, $J_1 = J_2 = 2.3$ Hz, 1H, H$_4''$), 4.72 (m, 1H, H$_5''$), 4.90 (m, 1H, H$_5$), 6.91 (d, $J = 7.6$ Hz, 2H, PhB-ortho), 7.30 (d, $J = 8.1$ Hz, 2H, Ph$''$-ortho), 7.49 (d, $J = 3.8$ Hz, 2H, PhD-ortho), 7.75 (s, 1H, Ph$^D$-para), 7.81 (s, 1H, Ph$^D$-para).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$): $\delta$ 13.6 (d, $J = 3.2$ Hz, CH$_3$), 15.7 (2C, PhB-$C_3$H$_3$), 16.2 (2C, PhA-$C_3$H$_3$-meta), 30.1 (d, $J = 23.7$ Hz, CH$_3$CH), 59.1 (PhB-OCH$_3$), 59.7 (PhA-OCH$_3$), 65.7 (bs, C3), 66.2 (C4), 69.7 (6C, C$_p$+C$''$$''$), 70.1 (5C, C$_p'''$), 72.5 (d, $J = 5.4$ Hz, C3$''$), 72.9 (d, $J = 4.9$ Hz, C5$''$), 73.9 (d, $J = 10.5$ Hz, C5), 79.5 (d, $J = 11.3$ Hz, C1$''$), 84.0 (C1), 88.8 (d, $J = 19.9$ Hz, C2), 90.6 (d, $J = 29.0$ Hz, C2$''$), 121.6 (bm, Ph$^D$-para), 123.0 (bm, Ph$^C$-para), 123.0 (q, $J = 273$ Hz, 2C, Ph$^{CD}$-CF$_3$), 123.1 (q, $J = 273$ Hz, 2C, Ph$^{CD}$-CF$_3$), 129.5 (d, $J = 7.5$ Hz, 2C, PhA$^B$-meta), 130.3 (d, $J = 9.1$ Hz, 2C, PhA$^{VB}$-meta), 130.8 (dm, $J = 16.8$ Hz, 2C, PhA-ortho), 131.9 (dq, $J_1 = 33.2$ Hz, $J_2 = 2.5$ Hz, 4C, Ph$^{CD}$-meta), 132.7, 132.8, 133.2, 133.4 (2C, PhA$^{B}$-ipso), 134.3 (dm, $J = 20.7$ Hz, 2C, Ph$^C$-ortho), 134.4 (dd, $J_1 = 20.6$ Hz, $J_2 = 4.5$ Hz, 2C, Ph$^B$-ortho), 135.7 (d, $J = 22.9$ Hz, 2C, PhA$^B$-ortho), 136.1 (d, $J = 32.3$ Hz, Ph$^{CD}$-ipso), 141.0 (d, $J = 33.0$ Hz, Ph$^{CD}$-ipso), 156.9 (Ph$^B$-para), 157.8 (Ph$^A$-para).

Assignment of phenyl units: PhA down, PhB up, PhC front, PhD back.

$^{31}$P ($^1$H) NMR (162 MHz, CDCl$_3$): $\delta$ −27.6 (Fc-PAr$_2$), 5.2 (CH$_3$CHPAr$_2$).

HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcd. 1154.1637 for C$_{56}$H$_{48}$F$_{12}$Fe$_2$O$_2$P$_2$; found: 1154.1643.

[α]$_{20}^\lambda$ (nm): −281 (589), −321 (578), −537 (546) (c 0.25, CHCl$_3$).

Anal. calcd. for: C$_{56}$H$_{48}$F$_{12}$Fe$_2$O$_2$P$_2$: C, 58.25; H, 4.19. Found: C, 58.19; H, 3.92.

$^3$P $^1$H NMR (162 MHz, CDCl$_3$): $\delta$ −27.6 (Fc-PAr$_2$), 5.2 (CH$_3$CHPAr$_2$).

HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcd. 1154.1637 for C$_{56}$H$_{48}$F$_{12}$Fe$_2$O$_2$P$_2$; found: 1154.1643.

[α]$_{20}^\lambda$ (nm): −281 (589), −321 (578), −537 (546) (c 0.25, CHCl$_3$).

Anal. calcd. for: C$_{56}$H$_{48}$F$_{12}$Fe$_2$O$_2$P$_2$: C, 58.25; H, 4.19. Found: C, 58.19; H, 3.92.

**Dichloro-{$(S_{Fc}, R_{Fc})$}-2-((R)-1-diphenylphosphinoethyl-κP)-{(R$_{Fc}$)-2''-diphenylphosphino-κP-1,1''-biferrocene} palladium(II), [PdCl$_2$$(R,S_{Fc}, R_{Fc})$]-{(15)}**

![Diagram](image_url)

To a mixture of $(R,S_{Fc}, R_{Fc})$-{(15)} (50 mg, 0.065 mmol) and diacetonitrildichloropalladium(II) (16.9 mg, 0.065 mmol) were added 3 mL of degassed DCM. The dark red solution was stirred under argon at r.t. overnight. The solution was filtered under inert conditions over a cellite pad. The solvent was removed completely and the dark red solid residue was dried in vacuo (yield: 61 mg, 0.065 mmol, >99%).
Single crystals suitable for X-ray structure determination were grown from a CHCl₃/toluene solution by slow evaporation of the solvents.

M.p.: 190 °C (dec.).

1H NMR (400 MHz, CD₂Cl₂): δ 1.17 (dd, J₁ = 12.7 Hz, J₂ = 7.2 Hz, 3H, CH₃CH), 3.26 (bs, 1H, H3""), 3.98 (m, 1H, H4""), 4.07 (s, 5H, Cp""), 4.18 (m, 1H, H5""), 4.23 (s, 5H, Cp'), 4.25 (dd, J₁ = J₂ = 2.5 Hz, 1H, H4), 4.41 (bs, 1H, H4""), 4.74 (bs, 1H, H5""), 7.34–7.42 (m, 6H, Ph-H), 7.44–7.50 (m, 6H, Ph-H), 7.50–7.55 (m, 2H, PhD-ortho), 7.61–7.66 (m, 2H, PhC-ortho), 7.81–7.86 (m, 2H, PhA-ortho).

13C{1H} NMR (100.6 MHz, CD₂Cl₂): δ 20.3 (d, J = 3.3 Hz, CH₃CH), 28.8 (dd, J₁ = 20.6 Hz, J₂ = 3.3 Hz, CH₃CH), 66.4 (C4), 67.6 (d, J = 2.7 Hz, C3), 69.7 (5, Cp''), 69.9 (d, J = 8.0 Hz, C4""), 70.9 (5, Cp''), 72.7 (C5), 77.7 (d, J = 8.6 Hz, C3""), 78.0 (d, J = 8.0 Hz, C5""), 81.7 (C1""/C2""), 83.5 (C1), 86.6 (C1""/C2""), 93.0 (C2), 127.1 (d, J = 12.2 Hz, 2C, Ph-meta), 127.3 (d, J = 12.2 Hz, 2C, Ph-meta), 127.9 (d, J = 11.3 Hz, 2C, Ph-meta), 129.1 (d, J = 10.0 Hz, 2C, Ph-meta), 130.6 (d, J = 3.3 Hz, Ph-para), 130.9 (2C, 2 Ph-para), 131.0 (d, J = 2.7 Hz, Ph-para), 132.1 (d, J = 8.6 Hz, 2C, PhD-ortho), 135.2 (d, J = 11.5 Hz, 2C, PhB-ortho), 135.5 (d, J = 10.0 Hz, 2C, PhC-ortho), 135.9 (d, J = 12.0 Hz, 2C, PhA-ortho), 4C Ph-ipso were not observed. Assignment of phenyl units corresponding to crystal structure: PhA (C35–C40), PhB (C41–C46), PhC (C23–C28), PhD (C29–C34).

31P {1H} NMR (162 MHz, CD₂Cl₂): δ 25.5 (Fc-PPh₂), 38.8 (CH₃CHPPh₂).

HR-MS (ESI, MeOH/MeCN): m/z [M-Cl]+ calcd. 907.0027 for C₄₆H₄₀ClFe₂P₂Pd; found: 907.0006.

Specific rotation: [α]₂₀λ (nm): −1113 (589), −1286 (578), −1819 (546) (c 0.024, CHCl₃).

Chloro-{[(SFc)-2-((R)-1-diphenylphosphinoethyl-κP)-(RFc)-2""-diphenylphosphino-κP-1,1""-biferrocene-(η⁶-p-cymene)}ruthenium(II)-hexafluorophosphate, [RuCl(p-cymene)-((R,SFc,RFc)-(15))PF₆]

[RuCl₂(p-cymene)]₂ (19.96 mg, 0.0326 mmol) and AgNO₃ (11.08 mg, 0.065 mmol) were dissolved in degassed MeOH (2 mL) and stirred at r.t. for 1 h. The yellow suspension was filtered under inert conditions over a cellite pad into a Schlenk flask containing (R,SFc,RFc)-(15) (50 mg, 0.065 mmol). The solvent was removed in vacuo and the residue was dissolved in degassed DCM. The dark red solution was stirred for 20 min at r.t. and then a solution of
NH₄PF₆ (31.9 mg, 0.196 mmol) in degassed MeOH (0.5 mL) was added. The solution was stirred for further 20 min at room temperature and then the solvent was removed completely. The residue was dissolved in a minimum of degassed DCM and then the complex was precipitated by the addition of Et₂O. The red solid was filtered and washed with cold MeOH and cold Et₂O (yield: 58 mg, 0.056 mmol, 75%).

Single crystals suitable for X-ray crystallography were obtained by slow diffusion of Et₂O into a saturated DCM solution.

¹H NMR (400 MHz, CD₃COCD₃): δ 0.63 (d, J = 6.9 Hz, 3H, CH(CH₃)₃(CH₃)B), 1.11 (d, J = 6.9 Hz, 3H, -CH(CH₃)₃(CH₃)B), 1.47 (bs, 3H, (p-cymene)-CH₃), 1.62 (bs, 3H, CHCH₃), 2.43 (q, J = 6.9 Hz, 1H, (p-cymene)-CH(CH₃)₂), 3.42 (bs, 1H, CH₃), 3.74 (bs, 1H, Cp), 3.77 (bs, 1H, Cp), 3.81 (bs, 1H, Cp), 4.03 (bs, 1H, (p-cymene)-H), 4.18 (s, 5H, Cp/Cp″), 4.25 (bs, 5H, Cp′/Cp‴), 4.46 (bs, 2H, Cp), 4.95 (bd, J = 5.6 Hz, 1H, (p-cymene)-H), 5.08 (bs, 1H, Cp), 5.69 (bs, 1H, (p-cymene)-H), 5.76 (bs, 1H, (p-cymene)-H), 7.43–7.48 (m, 2H, Ph), 7.54–7.60 (m, 4H, Ph), 7.69–7.79 (m, 8H, Ph), 7.94 (bs, 2H, Ph), 8.27 (bs, 4H, Ph).

¹³C{¹H} NMR (150.9 MHz, CD₃COCD₃): δ 17.1 ((p-cymene)-CH₃), 20.3 ((p-cymene)-CHCH₃A), 23.2 ((p-cymene)-CHCH₃B), 29.3 (bs, CH₃CHP), 32.3 (bs, (p-cymene)-CH(CH₃)₂), 66.5 (Cp), 70.0 (Cp), 71.6 (Cp′/Cp‴), 80.2 (Cp), 86.3–86.5 (m, Fe-C₃), 88.6 (p-cymene), 89.7 (p-cymene), 98.0 (p-cymene), 98.4 (p-cymene), 128.8 (bs, Ph-meta), 129.0 (bs, Ph-meta), 129.2 (bs, Ph-meta), 131.5 (Ph-para), 132.6 (Ph-para), 132.7 (Ph-para), 133.5 (s, Ph-para), 136.9 (d, J = 51.0 Hz, Ph-ipso), 136.9–137.0 (4C, Ph-ortho), 139.5 (d, J = 43.4 Hz, Ph-ipso); several Fe-Cp and Ph-signals not observed.

³¹P{¹H} NMR (242.9 MHz, CD₃COCD₃): δ −143.1 (sept., J = 699.9 Hz, PF₆⁻), 32.2 (Fe-PPPh₂ + CH₃CH-PPh₂).

HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcld. 1037.1132 for C₅₆H₅₄ClFe₂P₂Ru; found: 1037.1091.

Specific rotation: [α]²₀° (nm): −570 (589), −627 (578), −912 (546) (c 0.03, CHCl₃).

**Hydrogenations**

**Table 1S.** Selected high throughput screening results obtained with ligands (R,Fc,R,Fc)-14–17 in the iridium and ruthenium catalysed hydrogenation of double bonds.

| Entry | Substrate | Metal precursor | Ligand | Solvent | Conv. % | e.e. % |
|-------|-----------|----------------|--------|---------|---------|--------|
| 1     | MAC       | [Ir(COD)₂]BARF | 16     | THF     | 20      | 40     |
| 2     | MAC       | [Ir(COD)₂]BARF | 17     | THF     | 29      | 42     |
| 3     | MAA       | [Ir(COD)₂]BARF | 14     | THF     | 92      | 14     |
| 4     | MAA       | [Ir(COD)₂]BARF | 15     | THF     | 40      | 19     |
| 5     | DMI       | [Ir(COD)₂]BARF | 14     | THF     | 99      | 28     |
| 6     | DMI       | [Ir(COD)₂]BARF | 16     | THF     | 99      | 9      |
| 7     | MCA       | [Ir(COD)₂]BARF | 15     | THF     | 100     | 20     |
| 8     | MCA       | [Ir(COD)₂]BARF | 17     | THF     | 100     | 20     |
|   |     |                          |   |       |       |
|---|-----|--------------------------|---|-------|-------|
| 9 | AllylOH | [Ir(COD)₂]BARF          | 14| THF   | 100   |
| 10| AllylOH | [Ir(COD)₂]BARF          | 16| THF   | 100   |
| 11| EAAC    | [Ir(COD)₂]BARF          | 15| THF   | 65    |
| 12| EAAC    | [Ir(COD)₂]BARF          | 15| THF   | 60    |
| 13| DHNAA   | [Ir(COD)₂]BARF          | 16| THF   | 27    |
| 14| DHNAA   | [Ir(COD)₂]BARF          | 16| THF   | 27    |
| 15| MPG     | [Ir(COD)₂]BARF          | 14| THF   | 100   |
| 16| MPG     | [Ir(COD)₂]BARF          | 15| THF   | 99    |
| 17| MAC     | [Ru(COD)(OOCF₃)₂]       | 15| MeOH  | 100   |
| 18| MAC     | [Ru(COD)(OOCF₃)₂]       | 16| MeOH  | 100   |
| 19| MAA     | [Ru(COD)(OOCF₃)₂]       | 15| MeOH  | 100   |
| 20| MAA     | [Ru(COD)(OOCF₃)₂]       | 16| MeOH  | 100   |
| 21| DMI     | [Ru(COD)(OOCF₃)₂]       | 15| MeOH  | 98    |
| 22| DMI     | [Ru(COD)(OOCF₃)₂]       | 17| MeOH  | 99    |
| 23| MCA     | [Ru(COD)(OOCF₃)₂]       | 14| MeOH  | 99    |
| 24| MCA     | [Ru(COD)(OOCF₃)₂]       | 15| MeOH  | 99    |
| 25| AllylOH | [Ru(COD)(OOCF₃)₂]       | 14| MeOH  | 12    |
| 26| AllylOH | [Ru(COD)(OOCF₃)₂]       | 17| MeOH  | 19    |
| 27| EAAC    | [Ru(COD)(OOCF₃)₂]       | 16| MeOH  | 78    |
| 28| EAAC    | [Ru(COD)(OOCF₃)₂]       | 17| MeOH  | 100   |
| 29| DHNAA   | [Ru(COD)(OOCF₃)₂]       | 14| MeOH  | 100   |
| 30| DHNAA   | [Ru(COD)(OOCF₃)₂]       | 16| MeOH  | 100   |
| 31| MPG     | [Ru(COD)(OOCF₃)₂]       | 16| MeOH  | 74    |
| 32| MPG     | [Ru(COD)(OOCF₃)₂]       | 17| MeOH  | 82    |
| 33| MAC     | [RuCl₂(p-cymene)₂]      | 15| MeOH  | 60    |
| 34| MAC     | [RuCl₂(p-cymene)₂]      | 17| MeOH  | 12    |
| 35| MAA     | [RuCl₂(p-cymene)₂]      | 14| MeOH  | 100   |
| 36| MAA     | [RuCl₂(p-cymene)₂]      | 15| MeOH  | <10   |
| 37| DMI     | [RuCl₂(p-cymene)₂]      | 14| MeOH  | 98    |
| 38| DMI     | [RuCl₂(p-cymene)₂]      | 15| MeOH  | 88    |
| 39| MCA     | [RuCl₂(p-cymene)₂]      | 15| MeOH  | 65    |
| 40| MCA     | [RuCl₂(p-cymene)₂]      | 16| MeOH  | <10   |
| 41| AllylOH | [RuCl₂(p-cymene)₂]      | 15| MeOH  | <10   |
| 42| AllylOH | [RuCl₂(p-cymene)₂]      | 16| MeOH  | <10   |
| 43| EAAC    | [RuCl₂(p-cymene)₂]      | 14| MeOH  | 74    |
| 44| EAAC    | [RuCl₂(p-cymene)₂]      | 17| MeOH  | 42    |
| 45| DHNAA   | [RuCl₂(p-cymene)₂]      | 14| MeOH  | 59    |
| 46| DHNAA   | [RuCl₂(p-cymene)₂]      | 17| MeOH  | 13    |
| 47| MPG     | [RuCl₂(p-cymene)₂]      | 15| MeOH  | 17    |
| 48| MPG     | [RuCl₂(p-cymene)₂]      | 16| MeOH  | 16    |
Hydrogenations – experimental procedures

High throughput screening

All reactions were carried out on a Symyx high throughput screening instrument with use of the following reaction conditions: substrate 41.67 μmol; catalyst 1.67 μmol; catalyst loading: S/C: 25; 4 mol%; V total 500 μL; Pressure for substrates MAC, MAA, DMI, E-EAAC 1 bar H₂, MCA, Allyl-OH, DHNAA and MPG 50 bar H₂; reaction time: 16 h.

Single experiments

A solution of the substrate (1 mmol) was dissolved under argon in a degassed solvent (2.5 mL). The catalyst was formed in situ by stirring a mixture of ligand and metal precursor in a degassed solvent (2.5 mL) for 30 minutes at r.t. Both the catalyst and the substrate solution were transferred through a stainless steel capillary into either a glass or a steel autoclave. The argon gas was then replaced by hydrogen gas (3–5 cycles) and the pressure was set. After completion of the reaction, the reaction mixture was filtering through a plug of silica. Conversions and e.e. values of the product were determined by either gas chromatography or HPLC.

The following reaction conditions and methods were applied:

**MAC:** MAC (219.2 mg, 1 mmol); [Rh(NBD)₂][BF₄] + 1.1eq. ligand; S/C = 100; solvent: MeOH (5 mL); p(H₂): 1 bar; 20 ºC; reaction time: 16 h. Analysis data: GC, column: PERMABOND®- L-Chirasil-Val (25m); 160 ºC isothermal. MAC = 11.1 min, (R) = 25.4 min, (S) = 28.6 min.

**MAA:** MAA (143.1 mg, 1 mmol); [Rh(NBD)₂][BF₄] + 1.1eq. ligand; S/C = 100; solvent: MeOH (5 mL); p(H₂): 1 bar; 20 ºC; reaction time: 16 h. Analysis data: GC, column: PERMABOND®- L-Chirasil-Val (25m); 110 ºC isothermal. MAA = 5.3 min, (R) = 8.8 min, (S) = 10.9 min.

**DMI:** DMI (158.2 mg, 1 mmol); [Rh(NBD)₂][BF₄] + 1.1eq. ligand; S/C = 100; solvent: MeOH (5 mL); p(H₂): 1 bar; 20 ºC; reaction time: 16 h. Analysis data: GC, column: LIPODEX-E (50m); 85 ºC isothermal. DMI = 46.2 min, (S) = 29.5 min, (R) = 30.7 min.

**MCA:** Cationic precursor: MCA (162.2 mg, 1 mmol); [Rh(NBD)₂][BF₄] + 1.1eq. ligand; S/C = 100; solvent MeOH (5 mL); p(H₂): 20 bar; 20 ºC; reaction time: 20 h. Neutral precursor: MCA (162.2 mg, 1 mmol); [RhCl(NBD)]₂ + 1.011 eq. ligand; S/C = 25 or 100; solvent: THF (5 mL); p(H₂): 20 bar; 20 ºC; reaction time: 20 h; Work up: After removing the solvent under reduced pressure, the crude product was dissolved in DCM and extracted with NaOH (2M). The organic phase was discarded. The aqueous phase was made acidic by addition of aqueous HCl solution (to pH=1) and the acid was extracted with DCM (2 x 25 mL). The combined organics were washed with brine, dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was transformed into the corresponding methyl ester. The residue was dissolved in MeOH and diazomethane in Et₂O was added until the colour of the solution turned permanently into light yellow. After stirring for 20 minutes at r.t., the solvent was removed carefully under reduced pressure and the remaining residue was filtered over a short plug of Silica which had been wetted with MeOH. Analysis data: HPLC, column:
Daicel, Chiraldex OB-H, temperature: 25 °C, eluent: hexane/iPrOH 97:3, flow rate: 0.5 mL/min, detector: DAD, Sig = 230 nm. Substrate = 15.8 min, (R) = 10.7 min, (S) = 11.6 min.

**PCA:** PCA (224.2 mg, 1 mmol); [Rh(NBD)\(_2\)][BF\(_4\)] + 1.1 eq. ligand; S/C = 100; solvent: MeOH (5 mL); \(p(H_2)\): 50 bar; 20 °C; reaction time: 19 h; esterification to the methyl ester: see MCA. Analysis data: HPLC, column: Daicel, Chiraldex OD-H, temperature: 25 °C, eluent: hexane/iPrOH 97:3, flow rate: 0.5 mL/min, detector: DAD, Sig = 230 nm. Substrate = 20 min, (R) = 18 min, (S) = 18.7 min.

**IPCA-D:** Cationic precursor: IPCA-D (308.4 mg, 1 mmol); [Rh(NBD)\(_2\)][BF\(_4\)] + 1.1 eq. ligand; S/C = 100; solvent: MeOH (5 mL); \(p(H_2)\): 50 bar; 20 °C; reaction time: 20 h. Neutral precursor: IPCA-D (308.4 mg, 1 mmol); [RhCl(NBD)]\(_2\) + 1.011 eq. ligand; S/C = 25 or 100; solvent: THF (5 mL); \(p(H_2)\): 50 bar; 20 °C; reaction time: 20 h. Analysis data: HPLC, column: Chiralpak IC, temperature: 25 °C, solvent: heptane/EtOH/TFA = 90/10/0.1, flow rate: 1.0 mL/min, detector: DAD, Sig = 230 nm. IPCA-D = 5.6 min, (S) = 8.7 min, (R) = 10.3 min.

**EOCA-D:** Cationic precursor: EOCA-D (298.3 mg, 1 mmol); [Rh(NBD)\(_2\)][BF\(_4\)] + 1.01 eq. ligand; S/C = 25 or 40; solvent: MeOH (5 mL); additive: NaOMe (5.3 mg, 0.0985 mmol); \(p(H_2)\): 3.5 bar; 20 °C; reaction time: 20 h. Neutral precursor: EOCA-D (298.3 mg, 1 mmol); [RhCl(NBD)]\(_2\) + 1.011 eq. ligand; S/C = 25; solvent: THF (5 mL); additive: NaOMe (5.3 mg, 0.0985 mmol); \(p(H_2)\): 20 bar; 20 °C; reaction time: 17 h. Analysis data: HPLC, column: Chiralpak IA, temperature: 25 °C, solvent: heptane/EtOH/TFA = 90/10/0.1, flow rate: 0.5 mL/min, detector: DAD, Sig = 230 nm. EOCA-D = 13.6 min, (R) = 9.7 min, (S) = 11.3 min.

**ACA:** ACA (253.3 mg, 2.53 mmol); [RuI\(_2\)(p-cymene)]\(_2\) + 1.1 eq. ligand; S/C = 500; solvent: MeOH (10 mL); additive: HCl\(_{aq}\) (240 μL, 1N); \(p(H_2)\): 80 bar; 80 °C; reaction time: 17 h. Analysis data: GC, Column: PERMABOND®- L-Chirasil-Val (25m); 88 °C isothermal. ACA = 2.0 min, (R) = 8.3 min, (S) = 9.1 min.

**EOP:** EOP (144.2 mg, 1 mmol); [RuI\(_2\)(p-cymene)]\(_2\) + 1.1 eq. ligand; S/C = 100; solvent: EtOH (10 mL); additive: HCl\(_{aq}\) (47.4 μL, 1N); \(p(H_2)\): 80 bar; 80 °C; reaction time: 16 h; formation of trifluoroacetate derivative: after removing the solvent and drying under reduced pressure, to the remaining residue was added trifluoroacetic anhydride (2 mL). After stirring for 20 minutes, excess of trifluoroacetic anhydride was removed by blowing argon over the solution and the remaining residue was filtered over a short plug of Silica that had been wetted with MeOH. Analysis data: GC, column: LIPODEX-E (50m); 80 °C isothermal. Substrate = 15.6 min, (R) = 26.6 min, (S) = 29.7 min.
X-ray structure determination of (S_Fc)-2, (R,S_Fc,R_Fc)-3 BH₃, (R,S_Fc,R_Fc)-16, (R,S_Fc,R_Fc)-17, [PdCl₂(12)], and [RuCl(p-cymene)(12)]PF₆.

Single crystals for X-ray diffraction were obtained as follows: (S_Fc)-2 from acetonitrile by evaporation; (R,S_Fc,R_Fc)-3 BH₃ from ethyl acetate by slow evaporation at room temperature; (R,S_Fc,R_Fc)-16 by prolonged standing of a supersaturated ethyl acetate solution at 4 °C; (R,S_Fc,R_Fc)-17 from dichloromethane by evaporation; [PdCl₂(12)] as the solvate [PdCl₂(12)]·C₇H₈·½(H₂O) from wet toluene by evaporation; [RuCl(p-cymene)(12)]PF₆ from dichloromethane by layering with diethyl ether. The colour of the crystals varied from orange to red brown. Single crystal X-ray data were collected on a Bruker Kappa APEX-2 CCD diffractometer with a cryostream cooler (Oxford Cryosystems) using graphite-monochromatised Mo-Kα radiation (λ = 0.71073 Å) and 0.5° ϕ- and ω-scan frames covering complete Ewald spheres with θ_max = 30°. Because of a 46 Å c-axis (R,S_Fc,R_Fc)-16 needed special data collection conditions with narrower frames and a larger detector distance. The frames were integrated with program SAINT and corrections for absorption and λ/2 effects were applied with program SADABS. After structure solution with program SHELXS97 and direct methods, refinement on F² was carried out with the program SHELXL97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions and thereafter refined as riding. The absolute structures of all compounds could be unambiguously determined by anomalous dispersion effects and the Flack absolute structure parameter. Variata: In (R,S_Fc,R_Fc)-16 two of the four CF₃ groups of showed partial orientation disorder and needed splitted F positions. In (R,S_Fc,R_Fc)-17, on the contrary, the CF₃ groups were well-ordered. In [PdCl₂(12)]·C₇H₈·½(H₂O), which contains two Pd complexes, two toluene molecules, and one water molecule in the asymmetric unit, the toluene solvent molecules were surprisingly well-ordered. This solid contained in addition a water molecule with a refined partial occupancy of 0.731(8). The given chemical formula was idealized to full occupation. All crystal structures were checked with program PLATON (Spek, 2003). Crystallographic data are compiled in Table S5 and atomic parameters are provided in CIF-format in the Supporting. Structural diagrams of complexes (Fig. S1 – S6) and Tables (Tab. S6 – S11) with selected geometric parameters are given below. For molecular graphics the programs XP (Bruker) and MERCURY (Macrae et al., 2006) were used.

Bruker programs: APEX2; SAINT, version 7.68A; SADABS, version 2008/1; SHELXTL, version 2008/4; XP, version 5 (Bruker AXS Inc., Madison, WI, 2009).

SHELXS97 and SHELXL97: G. M. Sheldrick, Acta Cryst. 2008, A64, 112–122.

PLATON: Spek, A. L. J. Appl. Cryst. 2003, 36, 7–13.

MERCURY: Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. J. Appl. Cryst. 2006, 39, 453–457.
Table S2. Crystal data and structure refinement for the six investigated compounds \((S_{Fe})-2\), \((R,S_{Fe},R_{Fe})-3\) BH₃, \((R,S_{Fe},R_{Fe})-16\), \((R,S_{Fe},R_{Fe})-17\), \([PdCl_2(12)]·C_7H₈·½(H₂O)\), and \([RuCl(p-cymene)(12)]PF₆\).

|                      | \((S_{Fe})-2\) | \((R,S_{Fe},R_{Fe})-3\) BH₃ | \((R,S_{Fe},R_{Fe})-16\) | \((R,S_{Fe},R_{Fe})-17\) |
|----------------------|----------------|-----------------------------|--------------------------|--------------------------|
| formula              | C₁₄H₈BrFel     | C₂₁H₃BBrFe₂N                | C₂₀H₁₇Fe₂P₂              | C₂₁H₉Fe₂O₂P₂             |
| fw                   | 390.82         | 533.90                      | 1038.43                  | 1154.58                  |
| cryst.size, mm       | 0.38 × 0.24 × 0.12 | 0.38 × 0.18 × 0.09          | 0.40 × 0.35 × 0.30       | 0.41 × 0.22 × 0.11       |
| crystal system       | orthorhombic   | orthorhombic                | orthorhombic             | monoclinic               |
| space group           | P₂₁₂₁ (no. 19) | P₂₁₂₁ (no. 19)              | P₂₁₂₁ (no. 19)           | P₂₁ (no. 4)              |
| a, Å                  | 9.6837(5)      | 8.5531(2)                   | 9.7275(4)                | 9.3995(3)                |
| b, Å                  | 10.3437(5)     | 10.3363(2)                  | 9.9670(5)                | 15.5949(4)               |
| c, Å                  | 10.3664(5)     | 26.0765(5)                  | 46.626(2)                | 17.1152(5)               |
| α, deg               | 90             | 90                          | 90                       | 90                       |
| β, deg               | 90             | 90                          | 90                       | 90                       |
| γ, deg               | 90             | 90                          | 90                       | 90                       |
| V, Å³                | 1038.35(9)     | 2305.36(8)                  | 4520.6(4)                | 2504.43(13)              |
| T, K                  | 100            | 100                         | 100                      | 100                      |
| Z                    | 4              | 4                           | 4                        | 2                        |
| ρabs, g cm⁻³         | 2.500          | 1.538                       | 1.526                    | 1.531                    |
| μ, mm⁻¹ (MoKα)       | 8.221          | 3.002                       | 0.798                    | 0.731                    |
| F(000)               | 728            | 1088                        | 2104                     | 1180                     |
| absorption corrections | multi-scan, 0.25-0.43 | multi-scan, 0.62-0.77                 | multi-scan, 0.74-0.79                | multi-scan, 0.82-0.92                |
| θ range, deg         | 2.8 - 30.0     | 2.1 - 30.0                  | 1.7 – 30.0               | 2.4 - 30.0               |
| no. of rflns measd / Ru₄ | 21500 / 0.028    | 59062 / 0.035               | 107854 / 0.020           | 72597 / 0.037            |
| no. of rflns unique   | 3026           | 6701                        | 13134                    | 14551                    |
| no. of rflns F>2σ(I)  | 3010           | 6423                        | 13071                    | 13358                    |
| Data completeness, %  | 99.9           | 99.7                        | 99.6                     | 99.4                     |
| no. of params/restraints | 118 / 0          | 266 / 0                     | 616 / 15                 | 671 / 1                  |
| R₁ (I > 2σ(I))       | 0.0139         | 0.0214                      | 0.0255                   | 0.0265                   |
| R₁ (all data)        | 0.0141         | 0.0233                      | 0.0256                   | 0.0326                   |
| wR₂ (I > 2σ(I))      | 0.0347         | 0.0524                      | 0.0638                   | 0.0597                   |
| wR₂ (all data)       | 0.0348         | 0.0531                      | 0.0639                   | 0.0623                   |
| Flack abs.str. param. | 0.020(6)        | 0.001(5)                    | 0.012(6)                 | -0.006(6)                |
| Diff.Four.peaks min/max, eÅ⁻³ | -0.72 / 0.34 | -0.23 / 0.97 | -0.50 / 0.65 | -0.39 / 0.57 |
Table S2, continued with crystal data of [PdCl₂(12)]·C₇H₈·½(H₂O), and [RuCl(p-cymene)(12)]PF₆.

|                              | [PdCl₂(12)]·C₇H₈·½(H₂O) | [RuCl(p-cymene)(12)]PF₆ |
|------------------------------|--------------------------|-------------------------|
| formula                      | C₄₆H₄₀Cl₂Fe₂P₂Pd·C₇H₈·½(H₂O) | C₅₆H₅₄Cl₆Fe₂P₃Ru         |
| fw                           | 1044.86                  | 1182.12                 |
| cryst.size, mm               | 0.32 × 0.26 × 0.22       | 0.54 × 0.32 × 0.20      |
| crystal system               | triclinic                | orthorhombic            |
| space group                  | P1 (no. 1)               | P₂₁₂₁₂₁ (no. 19)        |
| a, Å                         | 11.2688(4)               | 11.5426(2)              |
| b, Å                         | 14.6804(5)               | 18.4163(3)              |
| c, Å                         | 15.1107(4)               | 22.5369(4)              |
| α, deg                       | 109.367(2)               | 90                      |
| β, deg                       | 90.523(2)                | 90                      |
| γ, deg                       | 104.076(2)               | 90                      |
| V, Å³                        | 2276.47(13)              | 4790.71(14)             |
| T, K                         | 100                      | 100                     |
| Z                            | 2                        | 4                       |
| ρcalc, g cm⁻³                | 1.524                    | 1.639                   |
| μ, mm⁻¹ (MoKα)               | 1.245                    | 1.128                   |
| F(000)                       | 1066                     | 2408                    |
| absorption corrections      | multi-scan, 0.68-0.77     | multi-scan, 0.68-0.80    |
| θ range, deg                | 2.1 - 30.0               | 2.1 – 30.0              |
| no. of rflns measd / Rint    | 80353 / 0.026            | 122473 / 0.032          |
| no. of rflns unique         | 24452                    | 13953                   |
| no. of rflns F>2σ(I)         | 23710                    | 13482                   |
| Data completeness, %         | 94.1                     | 99.8                    |
| no. of params/restraints     | 1095 / 3                 | 626 / 0                 |
| R₁ (I > 2σ(I))               | 0.0231                   | 0.0233                  |
| R₁ (all data)                | 0.0246                   | 0.0251                  |
| wR₂ (I > 2σ(I))              | 0.0568                   | 0.0599                  |
| wR₂ (all data)               | 0.0581                   | 0.0616                  |
| Flack abs.str. param.        | -0.013(6)                | -0.012(7)               |
| Diff.Four.peaks min/max, eÅ³ | -0.54 / 0.83             | -0.37 / 0.94            |
Crystal structure of (S

Figure S1. Structural diagram of the asymmetric unit of (S

Table S3. Selected geometric data (Å, deg) of (S

Comment: Crystalline (S

26
structures, GUFIW and \((S_{Fc})\cdot2\), differ (see deposited CIF). Interestingly it was recently reported that racemic 1-bromo-2-iodoferrocene crystallizes in a triclinic form: CCDC – NUTWIJ, Dayaker, G.; Sreeshailam, A.; Chevallier, F.; Roisnel, T.; Krishna, P. R.; Mongin, F. Chem. Commun. 2010, 46, 2862–2864; space group \(P-1\), \(a = 9.8917(4), b = 10.0527(5), c = 10.8535(5) \text{Å}, \alpha = 81.390(2), \beta = 82.628(2), \gamma = 84.345(2)^\circ\). According to this reference, the crystal lattice of NUTWIJ contains two independent molecules of which one has an ordered and one a disordered Br/I arrangement.
Crystal structure of (R,S\textsubscript{Fc},R\textsubscript{Fc})-3\textsubscript{BH}\textsubscript{3}

Figure S2. Structural diagram of the asymmetric unit of (R,S\textsubscript{Fc},R\textsubscript{Fc})-3\textsubscript{BH}\textsubscript{3}, (R\textsubscript{Fc})-2''-bromo-(S\textsubscript{Fc})-2-[(R)-1,N,N-dimethylaminoethyl-\kappa\text{N}]-1,1''-biferrocene trihydridoboron, showing 50\% ellipsoids and the atom numbering.

Table S4. Selected geometric data (Å, deg) of (R,S\textsubscript{Fc},R\textsubscript{Fc})-3\textsubscript{BH}\textsubscript{3}.

| Bond 1          | Length (Å) | Bond 2          | Length (Å) |
|-----------------|------------|-----------------|------------|
| Fe(1)-C(1)      | 2.039(2)   | C(1)-C(5)       | 1.428(2)   |
| Fe(1)-C(2)      | 2.042(2)   | C(1)-C(11)      | 1.471(2)   |
| Fe(1)-C(3)      | 2.037(2)   | C(2)-C(3)       | 1.436(2)   |
| Fe(1)-C(4)      | 2.044(2)   | C(2)-C(21)      | 1.510(2)   |
| Fe(1)-C(5)      | 2.048(2)   | C(3)-C(4)       | 1.426(2)   |
| Fe(1)-C(6)      | 2.053(2)   | C(4)-C(5)       | 1.424(2)   |
| Fe(1)-C(7)      | 2.053(2)   | C(6)-C(7)       | 1.421(3)   |
| Fe(1)-C(8)      | 2.043(2)   | C(6)-C(10)      | 1.430(3)   |
| Fe(1)-C(9)      | 2.042(2)   | C(7)-C(8)       | 1.423(3)   |
| Fe(1)-C(10)     | 2.050(2)   | C(8)-C(9)       | 1.414(3)   |
|                 |            | C(9)-C(10)      | 1.425(3)   |
| Fe(2)-C(11)     | 2.057(2)   | C(11)-C(12)     | 1.437(2)   |
| Fe(2)-C(12)     | 2.002(2)   | C(11)-C(15)     | 1.430(3)   |
| Fe(2)-C(13)     | 2.037(2)   | C(12)-C(13)     | 1.426(2)   |
| Fe(2)-C(14)     | 2.054(2)   | C(12)-C(13)     | 1.418(2)   |
| Fe(2)-C(15)     | 2.058(2)   | C(13)-C(14)     | 1.429(2)   |
| Fe(2)-C(16)     | 2.053(2)   | C(14)-C(15)     | 1.409(3)   |
| Fe(2)-C(17)     | 2.039(2)   | C(15)-C(16)     | 1.415(3)   |
| Fe(2)-C(18)     | 2.037(2)   | C(16)-C(20)     | 1.429(3)   |
| Fe(2)-C(19)     | 2.046(2)   | C(17)-C(18)     | 1.413(3)   |
| Fe(2)-C(20)     | 2.056(2)   | C(18)-C(19)     | 1.414(3)   |
|                 |            | C(19)-C(20)     | 1.414(3)   |
| Br(1)-C(12)     | 1.889(2)   | C(5)-C(1)-C(2)  | 107.87(14) |
| C(21)-C(22)     | 1.532(2)   | C(5)-C(1)-C(11) | 125.20(14) |
| N(1)-C(21)      | 1.532(2)   | C(2)-C(1)-C(11) | 126.67(14) |
| N(1)-C(23)      | 1.484(2)   | C(2)-C(1)-C(11) | 106.97(14) |
| N(1)-C(24)      | 1.493(3)   | C(3)-C(2)-C(21) | 125.96(14) |
| N(1)-B(1)       | 1.630(2)   | C(1)-C(2)-C(21) | 127.05(14) |
| C(1)-C(2)       | 1.449(2)   | C(4)-C(3)-C(2)  | 108.62(15) |
|                 |            | C(5)-C(4)-C(3)  | 108.08(14) |
Comment: \((R,S_{Fc},R_{Fc})-3\)BH\(_3\) is the diastereomer of \((R,S_{Fc},S_{Fc})-3\)BH\(_3\), of which a crystal structure was recently reported (Wang, Y.; Zirakzadeh, A.; Weissensteiner, W.; Mereiter, K. Acta Cryst. 2011, E67, m1806–m1807). Both compounds crystallize in the orthorhombic space group \(P2_12_12_1\) with similar lattice dimensions but different structures (data for \(T = 100\) K):

\((R,S_{Fc},R_{Fc})-3\)BH\(_3\): \(a = 8.5531(2), b = 10.3363(2), c = 26.0765(5)\) Å, \(V = 2305.36(8)\) Å\(^3\), \(D_x = 1.538\)

\((R,S_{Fc},S_{Fc})-3\)BH\(_3\): \(a = 8.8791(2), b = 9.2210(2), c = 27.1292(6)\) Å, \(V = 2221.18(9)\) Å\(^3\), \(D_x = 1.597\).

The density and packing efficiency of \((R,S_{Fc},S_{Fc})-3\)BH\(_3\) is notably higher.
Crystal structure of \((R,S_{\text{Fc}},R_{\text{Fc}})\)-16

Figure S3. Structural diagram of the asymmetric unit of \((R,S_{\text{Fc}},R_{\text{Fc}})\)-16 showing 50% ellipsoids and the atom numbering. Six partly occupied F positions of two orientation disordered CF₃ groups (C(29) and C(30)) were omitted for clarity.

Table S5. Selected geometric data (Å, deg) of \((R,S_{\text{Fc}},R_{\text{Fc}})\)-16.

| Bond                  | Distance (Å) | Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|-----------------------|--------------|
| Fe(1)-C(1)            | 2.0430(13)   | C(2)-C(3)             | 1.438(2)     | C(2)-C(3)             | 1.438(2)     |
| Fe(1)-C(2)            | 2.0355(14)   | C(3)-C(4)             | 1.418(2)     | C(3)-C(4)             | 1.418(2)     |
| Fe(1)-C(3)            | 2.0446(14)   | C(4)-C(5)             | 1.429(2)     | C(4)-C(5)             | 1.429(2)     |
| Fe(1)-C(4)            | 2.0466(15)   | C(5)-C(6)             | 1.438(2)     | C(5)-C(6)             | 1.438(2)     |
| Fe(1)-C(5)            | 2.0457(14)   | C(6)-C(7)             | 1.420(3)     | C(6)-C(7)             | 1.420(3)     |
| Fe(1)-C(6)            | 2.0417(15)   | C(7)-C(8)             | 1.420(3)     | C(7)-C(8)             | 1.420(3)     |
| Fe(1)-C(7)            | 2.0400(16)   | C(8)-C(9)             | 1.425(2)     | C(8)-C(9)             | 1.425(2)     |
| Fe(1)-C(8)            | 2.0436(16)   | C(9)-C(10)            | 1.425(2)     | C(9)-C(10)            | 1.425(2)     |
| Fe(1)-C(9)            | 2.0481(16)   | C(10)-C(11)           | 1.469(2)     | C(10)-C(11)           | 1.469(2)     |
| Fe(1)-C(10)           | 2.0477(15)   | C(11)-C(12)           | 1.447(2)     | C(11)-C(12)           | 1.447(2)     |
| Fe(2)-C(11)           | 2.0550(12)   | C(12)-C(13)           | 1.438(2)     | C(12)-C(13)           | 1.438(2)     |
| Fe(2)-C(12)           | 2.0555(12)   | C(13)-C(14)           | 1.426(2)     | C(13)-C(14)           | 1.426(2)     |
| Fe(2)-C(13)           | 2.0450(13)   | C(14)-C(15)           | 1.432(2)     | C(14)-C(15)           | 1.432(2)     |
| Fe(2)-C(14)           | 2.0482(14)   | C(15)-C(16)           | 1.428(2)     | C(15)-C(16)           | 1.428(2)     |
| Fe(2)-C(15)           | 2.0526(13)   | C(16)-C(17)           | 1.422(2)     | C(16)-C(17)           | 1.422(2)     |
| Fe(2)-C(16)           | 2.0480(14)   | C(17)-C(18)           | 1.421(2)     | C(17)-C(18)           | 1.421(2)     |
| Fe(2)-C(17)           | 2.0502(14)   | C(18)-C(19)           | 1.426(2)     | C(18)-C(19)           | 1.426(2)     |
| Fe(2)-C(18)           | 2.0523(14)   | C(19)-C(20)           | 1.428(2)     | C(19)-C(20)           | 1.428(2)     |
| Fe(2)-C(19)           | 2.0550(14)   | C(20)-C(21)           | 1.427(2)     | C(20)-C(21)           | 1.427(2)     |
| P(1)-C(21)            | 1.8885(14)   | C(21)-C(22)           | 1.531(2)     | C(21)-C(22)           | 1.531(2)     |
| P(1)-C(23)            | 1.8421(16)   | C(22)-C(23)           | 1.396(2)     | C(22)-C(23)           | 1.396(2)     |
| P(1)-C(31)            | 1.8337(15)   | C(23)-C(24)           | 1.398(2)     | C(23)-C(24)           | 1.398(2)     |
| P(2)-C(12)            | 1.8188(13)   | C(24)-C(25)           | 1.395(2)     | C(24)-C(25)           | 1.395(2)     |
| P(2)-C(45)            | 1.8263(14)   | C(25)-C(26)           | 1.383(3)     | C(25)-C(26)           | 1.383(3)     |
| P(2)-C(39)            | 1.8353(14)   | C(26)-C(27)           | 1.385(3)     | C(26)-C(27)           | 1.385(3)     |
| C(1)-C(2)             | 1.438(2)     | C(27)-C(28)           | 1.392(3)     | C(27)-C(28)           | 1.392(3)     |
| C(2)-C(3)             | 1.431(2)     | C(28)-C(30)           | 1.513(3)     | C(28)-C(30)           | 1.513(3)     |
C(29)-F(1)         1.358(4)  C(2)-C(1)-C(5)        107.65(12)
C(29)-F(2)         1.306(3)  C(2)-C(1)-C(11)       126.38(12)
C(29)-F(3)         1.318(3)  C(5)-C(1)-C(11)       125.49(12)
C(30)-F(4)         1.313(3)  C(3)-C(2)-C(1)        107.53(12)
C(30)-F(5)         1.301(3)  C(3)-C(2)-C(21)       125.33(12)
C(30)-F(6)         1.326(4)  C(1)-C(2)-C(21)       127.10(12)
C(31)-C(36)        1.398(2)  C(4)-C(3)-C(2)        108.70(12)
C(31)-C(32)        1.400(2)  C(3)-C(4)-C(5)        108.11(13)
C(32)-C(33)        1.385(2)  C(4)-C(5)-C(1)        107.99(12)
C(33)-C(34)        1.387(2)  C(10)-C(6)-C(7)       108.10(15)
C(33)-C(37)        1.507(2)  C(8)-C(7)-C(6)        107.63(16)
C(34)-C(35)        1.387(2)  C(7)-C(8)-C(9)        108.52(15)
C(35)-C(36)        1.390(2)  C(8)-C(9)-C(10)       107.95(16)
C(35)-C(38)        1.502(2)  C(6)-C(10)-C(9)       107.80(15)
C(37)-F(9)         1.300(3)  C(15)-C(11)-C(12)     107.80(11)
C(37)-F(8)         1.305(4)  C(15)-C(11)-C(1)      129.14(12)
C(37)-F(7)         1.324(2)  C(12)-C(11)-C(1)      122.86(11)
C(38)-F(11)        1.336(2)  C(13)-C(12)-C(11)     107.41(11)
C(38)-F(10)        1.336(2)  C(13)-C(12)-P(2)      129.75(10)
C(38)-F(12)        1.345(2)  C(11)-C(12)-P(2)      122.06(9)
C(39)-C(44)        1.398(2)  C(14)-C(13)-C(12)     108.34(12)
C(39)-C(40)        1.401(2)  C(13)-C(14)-C(15)     108.08(12)
C(40)-C(41)        1.392(2)  C(11)-C(15)-C(14)     108.37(12)
C(41)-C(42)        1.395(2)  C(17)-C(16)-C(20)     108.04(13)
C(42)-C(43)        1.383(3)  C(18)-C(17)-C(16)     108.23(13)
C(43)-C(44)        1.400(2)  C(17)-C(18)-C(19)     107.99(13)
C(45)-C(46)        1.396(2)  C(16)-C(19)-C(20)     107.79(13)
C(45)-C(50)        1.400(2)  C(2)-C(21)-C(22)      111.51(12)
C(46)-C(47)        1.395(2)  C(2)-C(21)-P(1)       107.27(9)
C(47)-C(48)        1.390(2)  C(22)-C(21)-P(1)      115.32(10)
C(48)-C(49)        1.388(2)  Fe1-C1-C11-Fe2        -57.32(17)
C(49)-C(50)        1.391(2)  Fe1-C2-C21-P1        -160.58(8)
C(31)-P(1)-C(23)   104.09(7)  Fe1-C2-C21-C22       -60.82(14)
C(31)-P(1)-C(21)   98.24(6)  Fe1-C2-C21-P1-C23    -171.16(9)
C(23)-P(1)-C(21)   102.14(7)  C2-C21-P1-C23        -64.73(10)
C(12)-P(2)-C(45)   101.89(6)  Fe2-C12-P2-C39       -22.82(11)
C(12)-P(2)-C(39)   105.41(6)  Fe2-C12-P2-C45       127.97(10)
Crystal structure of (R,S\textsubscript{Fc},R\textsubscript{Fc})-17

Figure S4. Structural diagram of the asymmetric unit of (R,S\textsubscript{Fc},R\textsubscript{Fc})-17 showing 50% ellipsoids and the atom numbering.

Table S6. Selected geometric data (Å, deg) of (R,S\textsubscript{Fc},R\textsubscript{Fc})-17.

| Bond                        | Distance (Å)        | Bond                        | Distance (Å)        |
|-----------------------------|---------------------|-----------------------------|---------------------|
| Fe(1)–C(1)                  | 2.0630 (15)         | C(1)–C(5)                   | 1.427 (2)           |
| Fe(1)–C(2)                  | 2.0288 (15)         | C(1)–C(2)                   | 1.451 (2)           |
| Fe(1)–C(3)                  | 2.0368 (16)         | C(1)–C(11)                  | 1.472 (2)           |
| Fe(1)–C(4)                  | 2.0535 (16)         | C(2)–C(3)                   | 1.432 (2)           |
| Fe(1)–C(5)                  | 2.0628 (16)         | C(2)–C(21)                  | 1.511 (2)           |
| Fe(1)–C(6)                  | 2.0523 (17)         | C(3)–C(4)                   | 1.425 (2)           |
| Fe(1)–C(7)                  | 2.0476 (17)         | C(4)–C(5)                   | 1.422 (2)           |
| Fe(1)–C(8)                  | 2.0481 (18)         | C(6)–C(10)                  | 1.424 (3)           |
| Fe(1)–C(9)                  | 2.0600 (17)         | C(6)–C(7)                   | 1.424 (3)           |
| Fe(1)–C(10)                 | 2.0547 (16)         | C(7)–C(8)                   | 1.423 (3)           |
|                            |                     | C(8)–C(9)                   | 1.418 (2)           |
| Fe(2)–C(11)                 | 2.0551 (14)         |                             |                     |
| Fe(2)–C(12)                 | 2.0386 (15)         |                             |                     |
| Fe(2)–C(13)                 | 2.0301 (15)         | C(11)–C(15)                 | 1.431 (2)           |
| Fe(2)–C(14)                 | 2.0552 (16)         | C(11)–C(12)                 | 1.455 (2)           |
| Fe(2)–C(15)                 | 2.0642 (15)         | C(12)–C(13)                 | 1.437 (2)           |
| Fe(2)–C(16)                 | 2.0583 (16)         | C(13)–C(14)                 | 1.420 (2)           |
| Fe(2)–C(17)                 | 2.0475 (16)         | C(14)–C(15)                 | 1.427 (2)           |
| Fe(2)–C(18)                 | 2.0381 (16)         | C(16)–C(20)                 | 1.419 (3)           |
| Fe(2)–C(19)                 | 2.0526 (17)         | C(16)–C(17)                 | 1.421 (3)           |
| Fe(2)–C(20)                 | 2.0636 (17)         | C(17)–C(18)                 | 1.420 (3)           |
|                            |                     | C(18)–C(19)                 | 1.422 (3)           |
| P(1)–C(21)                  | 1.8839 (16)         | C(19)–C(20)                 | 1.424 (3)           |
| P(1)–C(23)                  | 1.8395 (15)         | C(21)–C(22)                 | 1.535 (2)           |
| P(1)–C(31)                  | 1.8363 (16)         |                             |                     |
| P(2)–C(12)                  | 1.8260 (16)         | C(23)–C(24)                 | 1.398 (2)           |
| P(2)–C(39)                  | 1.8412 (16)         | C(23)–C(28)                 | 1.402 (2)           |
| P(2)–C(48)                  | 1.8346 (16)         | C(24)–C(25)                 | 1.389 (2)           |
|                            |                     | C(25)–C(26)                 | 1.390 (2)           |
| Bond | Length (Å) | Bond | Length (Å) |
|------|-----------|------|-----------|
| C(25)-C(29) | 1.496 (2) | C(43)-C(47) | 1.508 (2) |
| C(26)-C(27) | 1.391 (2) | C(46)-O(1) | 1.435 (2) |
| C(27)-C(28) | 1.386 (2) | C(29)-F(1) | 1.335 (2) |
| C(27)-C(30) | 1.503 (2) | C(29)-F(2) | 1.339 (2) |
| C(29)-F(1) | 1.335 (2) | C(29)-F(3) | 1.341 (2) |
| C(29)-F(2) | 1.339 (2) | C(29)-F(4) | 1.338 (2) |
| C(29)-F(3) | 1.341 (2) | C(30)-F(5) | 1.339 (2) |
| C(29)-F(4) | 1.338 (2) | C(31)-C(32) | 1.389 (2) |
| C(30)-F(5) | 1.339 (2) | C(31)-C(34) | 1.387 (2) |
| C(31)-P(1)-C(23) | 102.53 (7) | C(31)-P(1)-C(21) | 98.05 (7) |
| C(31)-P(1)-C(21) | 103.05 (7) | C(32)-C(33) | 1.407 (2) |
| C(33)-P(1)-C(21) | 103.41 (7) | C(32)-C(33) | 1.426 (2) |
| C(34)-C(35) | 1.504 (2) | C(34)-C(36) | 1.386 (2) |
| C(35)-C(36) | 1.388 (2) | C(35)-C(37) | 1.501 (2) |
| C(35)-C(38) | 1.308 (2) | C(35)-C(39) | 1.307 (2) |
| C(37)-P(1)-C(23) | 102.53 (7) | C(37)-P(1)-C(21) | 98.05 (7) |
| C(37)-P(1)-C(21) | 103.05 (7) | C(38)-C(39) | 1.407 (2) |
| C(38)-C(40) | 1.392 (2) | C(38)-P(2)-C(39) | 100.54 (7) |
| C(39)-C(40) | 1.392 (2) | C(39)-P(2)-C(39) | 100.54 (7) |
| C(40)-C(41) | 1.394 (2) | C(40)-C(41) | 1.394 (2) |
| C(41)-P(1)-C(21) | 107.29 (11) | C(41)-P(1)-C(23) | 111.62 (13) |
| C(41)-P(1)-C(23) | 115.33 (10) | C(41)-P(1)-C(23) | 115.33 (10) |
| C(42)-O(1) | 1.391 (2) | Fe1-C1-C11-Fe2 | -55.84 (19) |
| C(42)-C(43) | 1.395 (2) | Fe1-C2-C21-C22 | 69.98 (16) |
| C(43)-C(44) | 1.392 (2) | Fe1-C2-C21-P1 | -162.76 (8) |
| C(44)-C(45) | 1.499 (2) | C2-C21-P1-C23 | -179.56 (10)|
Crystal structure of $[\text{PdCl}_2(15)]\cdot\text{C}_7\text{H}_8\cdot\frac{1}{2}(\text{H}_2\text{O})$

**Figure S5.** Structural diagram of the asymmetric unit of the crystal structure of $[\text{PdCl}_2(15)]\cdot\text{C}_7\text{H}_8\cdot\frac{1}{2}(\text{H}_2\text{O})$ showing 50% ellipsoids and the atom numbering. The structure contains two independent Pd-complexes, two toluene solvent molecules, and one water molecule in the asymmetric unit. The two Pd-complexes are similar in bond lengths, bond angles and conformation. Hydrogen atoms were omitted for clarity. O1w represents a water molecule that is hydrogen bonded to Cl1 (O1w…Cl1 = 3.219(3) Å) and Cl2 (O1w…Cl2 = 3.461(3) Å).

**Table S7.** Selected geometric data (Å, deg) of $[\text{PdCl}_2(15)]\cdot\text{C}_7\text{H}_8\cdot\frac{1}{2}(\text{H}_2\text{O})$.

| Bond                  | Distance (Å) |
|-----------------------|--------------|
| Pd(1)–P(1)            | 2.2747(5)    |
| Pd(1)–P(2)            | 2.2927(5)    |
| Pd(1)–Cl(1)           | 2.3535(5)    |
| Pd(1)–Cl(2)           | 2.3487(5)    |
| Fe(1)–C(1)            | 2.060(2)     |
| Fe(1)–C(2)            | 2.072(2)     |
| Fe(1)–C(3)            | 2.051(2)     |
| Fe(1)–C(4)            | 2.032(2)     |
| Fe(1)–C(5)            | 2.040(2)     |
| Fe(1)–C(6)            | 2.055(3)     |
| Fe(1)–C(7)            | 2.053(2)     |
| Fe(1)–C(8)            | 2.046(3)     |
| Fe(1)–C(9)            | 2.046(2)     |
| Fe(1)–C(10)           | 2.028(2)     |
| Fe(1)–C(11)           | 2.044(2)     |
| Fe(1)–C(12)           | 2.051(2)     |
| Fe(1)–C(13)           | 2.064(2)     |
| Fe(1)–C(14)           | 2.064(2)     |
| Fe(1)–C(15)           | 2.054(2)     |
| Fe(1)–C(16)           | 2.070(2)     |
| Fe(1)–C(17)           | 2.062(2)     |
| Fe(1)–C(18)           | 2.034(3)     |
| Fe(1)–C(19)           | 2.037(3)     |
| Fe(1)–C(20)           | 2.071(2)     |
| Fe(1)–C(21)           | 2.081(2)     |
| Fe(1)–C(22)           | 2.047(2)     |
| Fe(1)–C(23)           | 2.024(2)     |
Fe(1A) - C(5A)       2.028(2)  
P(2A) - C(12A)       1.818(2)  
Fe(1A) - C(6A)       2.052(3)  
P(2A) - C(35A)       1.826(2)  
Fe(1A) - C(7A)       2.040(3)  
P(2A) - C(41A)       1.820(2)  
Fe(1A) - C(8A)       2.041(2)  
Fe(1A) - C(9A)       2.047(3)  
P(1) - Pd(1) - P(2)   104.09(2)  
Fe(1A) - C(10A)      2.059(3)  
P(1) - Pd(1) - Cl(1)  86.36(2)  
P(1) - Pd(1) - Cl(2)  174.58(2)  
Fe(2A) - C(11A)      2.048(2)  
P(1) - Pd(1) - Cl(1)  167.86(2)  
Fe(2A) - C(12A)      2.053(2)  
P(2) - Pd(1) - Cl(2)  81.15(2)  
Fe(2A) - C(13A)      2.056(2)  
Cl(1) - Pd(1) - Cl(2) 88.28(2)  
Fe(2A) - C(14A)      2.049(2)  
Fe(2A) - C(15A)      2.042(2)  
P(1A) - Pd(1A) - P(2A) 104.42(2)  
Fe(2A) - C(16A)      2.062(3)  
P(1A) - Pd(1A) - Cl(1A) 85.71(2)  
Fe(2A) - C(17A)      2.069(2)  
P(1A) - Pd(1A) - Cl(2A) 173.12(2)  
Fe(2A) - C(18A)      2.055(2)  
P(2A) - Pd(1A) - Cl(1A) 168.22(2)  
Fe(2A) - C(19A)      2.046(2)  
P(2A) - Pd(1A) - Cl(2A) 82.15(2)  
Fe(2A) - C(20A)      2.048(2)  
Cl(1A) - Pd(1A) - Cl(2A) 87.54(2)  
P(1) - C(21)         1.860(2)  

P(1A) - C(21A)       1.862(2)  
P(1A) - C(23A)       1.828(2)  
P(1A) - C(29A)       1.827(2)  
P(1A) - C(29A)       1.827(2)  
P(1A) - C(21A)       1.862(2)  
P(1A) - C(23A)       1.828(2)  
P(1A) - C(29A)       1.827(2)  
P(1A) - C(29A)       1.827(2)
Crystal structure of \([\text{RuCl}(p\text{-cymene})(15)]\text{PF}_6\)

**Figure S6.** Structural diagram of the asymmetric unit of \([\text{RuCl}(p\text{-cymene})(15)]\) showing 50% ellipsoids and the atom numbering.

**Table S8.** Selected geometric data (Å, deg) of \([\text{RuCl}(p\text{-cymene})(15)]\).

| Bond          | Distance (Å) |
|---------------|--------------|
| Ru(1) - Cl(1) | 2.3818 (4)   |
| Ru(1) - P(1)  | 2.3824 (4)   |
| Ru(1) - P(2)  | 2.3808 (5)   |
| Ru(1) - C(47) | 2.325 (2)    |
| Ru(1) - C(48) | 2.286 (2)    |
| Ru(1) - C(49) | 2.239 (2)    |
| Ru(1) - C(50) | 2.292 (2)    |
| Ru(1) - C(51) | 2.228 (2)    |
| Fe(1) - C(1)  | 2.078 (2)    |
| Fe(1) - C(2)  | 2.085 (2)    |
| Fe(1) - C(3)  | 2.051 (2)    |
| Fe(1) - C(4)  | 2.034 (2)    |
| Fe(1) - C(5)  | 2.029 (2)    |
| Fe(1) - C(6)  | 2.063 (2)    |
| Fe(1) - C(7)  | 2.056 (2)    |
| Fe(1) - C(8)  | 2.057 (2)    |
| Fe(1) - C(9)  | 2.062 (2)    |
| Fe(1) - C(10) | 2.052 (2)    |
| Fe(2) - C(11) | 2.070 (2)    |
| P(1) - C(21)  | 1.885 (2)    |
| P(1) - C(23)  | 1.824 (2)    |
| P(1) - C(29)  | 1.836 (2)    |
| P(1) - C(12)  | 1.834 (2)    |
| P(2) - C(35)  | 1.832 (2)    |
| P(2) - C(41)  | 1.836 (2)    |
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|--------------|--------------|--------------|--------------|
| C(3)-C(4)   | 1.424(3)     | P(3)-F(2)    | 1.589(2)     |
| C(4)-C(5)   | 1.421(3)     | P(3)-F(3)    | 1.578(2)     |
| C(6)-C(10)  | 1.416(3)     | P(3)-F(4)    | 1.612(2)     |
| C(6)-C(7)   | 1.432(3)     | P(3)-F(5)    | 1.604(2)     |
| C(7)-C(8)   | 1.422(3)     | P(3)-F(6)    | 1.584(2)     |
| C(8)-C(9)   | 1.419(3)     |              |              |
| C(9)-C(10)  | 1.431(3)     | Cl(1)-Ru(1)-P(1) | 84.934(15)  |
| C(11)-C(15) | 1.433(2)     | Cl(1)-Ru(1)-P(2) | 85.102(15)  |
| C(11)-C(12) | 1.460(2)     | P(1)-Ru(1)-P(2) | 99.118(15)  |
| C(12)-C(13) | 1.449(2)     |              |              |
| C(13)-C(14) | 1.409(3)     | C(21)-P(1)-C(23) | 104.39(8)   |
| C(14)-C(15) | 1.420(3)     | C(21)-P(1)-C(29) | 105.49(8)   |
| C(16)-C(20) | 1.416(4)     | C(23)-P(1)-C(29) | 102.27(8)   |
| C(16)-C(17) | 1.418(4)     | C(21)-P(1)-Ru(1) | 121.59(6)   |
| C(17)-C(18) | 1.418(3)     | C(23)-P(1)-Ru(1) | 116.85(6)   |
| C(18)-C(19) | 1.421(3)     | C(29)-P(1)-Ru(1) | 104.04(6)   |
| C(19)-C(20) | 1.427(4)     | C(12)-P(2)-C(35) | 111.33(8)   |
| C(21)-C(22) | 1.540(2)     | C(12)-P(2)-C(41) | 97.81(8)    |
| C(23)-C(24) | 1.389(3)     | C(35)-P(2)-C(41) | 103.44(8)   |
| C(23)-C(28) | 1.406(3)     | C(12)-P(2)-Ru(1) | 119.08(5)   |
| C(24)-C(25) | 1.392(3)     | C(35)-P(2)-Ru(1) | 112.63(6)   |
| C(25)-C(26) | 1.381(3)     | Fe1-C1-C11-Fe2 | -101.37(17) |
| C(26)-C(27) | 1.394(3)     | C2-C1-C11-C12 | 73.5(2)     |
| C(27)-C(28) | 1.386(3)     | Fe1-C2-C21-C22 | 43.8(2)     |
| C(29)-C(30) | 1.398(3)     | C2-C2-C21-P1  | 169.65(9)   |
| C(29)-C(34) | 1.396(3)     | C2-C21-P1-C23 | -43.98(13)  |
| C(30)-C(31) | 1.392(3)     | C2-C21-P1-C29 | -151.37(12) |
| C(31)-C(32) | 1.381(3)     | Fe2-C12-P2-C35 | -44.85(14)  |
| C(32)-C(33) | 1.394(3)     | Fe2-C12-P2-C41 | 62.93(13)   |
| C(33)-C(34) | 1.390(3)     |              |              |
| C(35)-C(36) | 1.407(3)     |              |              |
| C(35)-C(40) | 1.399(3)     |              |              |
| C(36)-C(37) | 1.391(3)     |              |              |
| C(37)-C(38) | 1.389(3)     |              |              |
| C(38)-C(39) | 1.389(3)     |              |              |
| C(39)-C(40) | 1.395(3)     |              |              |
| C(41)-C(42) | 1.400(3)     |              |              |
| C(41)-C(46) | 1.398(2)     |              |              |
| C(42)-C(43) | 1.391(3)     |              |              |
| C(43)-C(44) | 1.395(3)     |              |              |
| C(44)-C(45) | 1.384(3)     |              |              |
| C(45)-C(46) | 1.390(3)     |              |              |
| C(47)-C(48) | 1.424(2)     |              |              |
| C(47)-C(52) | 1.408(2)     |              |              |
| C(48)-C(49) | 1.416(3)     |              |              |
| C(49)-C(50) | 1.417(3)     |              |              |
| C(50)-C(51) | 1.414(3)     |              |              |
| C(51)-C(52) | 1.420(3)     |              |              |
| C(47)-C(53) | 1.514(3)     |              |              |
| C(53)-C(54) | 1.506(3)     |              |              |
| C(53)-C(55) | 1.537(3)     |              |              |
| C(50)-C(56) | 1.507(3)     |              |              |

P(3)-F(1) | 1.587(2)
Table S9. Comparison of geometrical parameters of biferrocenes 3, 16, 17 and complexes [PdCl$_2$(15)] and [RuCl(p-cymene)(15)]PF$_6$ (for numbering scheme see Figures S5 and S6)

|                           | 3  | 16  | 17  | [PdCl$_2$(15)] | [RuCl(p-cymene)(15)]PF$_6$ |
|---------------------------|----|-----|-----|----------------|---------------------------|
|                           |    |     |     | molec. 1      | molec. 2                  |
| Distance (Å)              |    |     |     |                |                           |
| C11/Cp                    | 0.102 | 0.171 | 0.137 | 0.045 | 0.077 | 0.086 |
| C1/Cp"                   | 0.142 | 0.093 | 0.087 | 0.241 | 0.309 | 0.085 |
| M/Cp (M= Pd, Ru)          | -- | -- | -- | 3.646 | 3.683 | 3.224 |
| C1/Cp                     | -- | -- | -- | 4.804 | 4.905 | 1.289 |
| Cl2/Cp                    | -- | -- | -- | 5.702 | 5.768 | --    |
| P1/Cp                     | 1.474 | 1.728 | 1.688 | 1.767 | 1.782 | 1.721 |
| P2/Cp                     | 2.639 | 2.383 | 2.936 | 2.990 | 2.909 |       |
| P2/ Cp"                   | 0.258 | -0.183 | 0.108 | 0.085 | 0.225 |       |
| Angle (°)                 |    |     |     |                |                           |
| 2/1/11                    | 126.7 | 126.4 | 126.8 | 119.7 | 120.1 | 124.8 |
| 5/1/11                    | 125.2 | 125.5 | 125.6 | 131.9 | 132.0 | 127.8 |
| 1/11/12                   | 124.9 | 122.7 | 125.3 | 124.7 | 125.0 | 128.5 |
| 1/11/15                   | 129.0 | 129.2 | 126.9 | 125.7 | 125.7 | 124.2 |
| 11/12/P2/35               | -- | -- | -- | 67.6 | 62.3 | 59.7 |
| 11/12/P2/41               | -- | -- | -- | 177.8 | 177.8 | 167.5 |
| Cp/ Cp"                   | 123.0 | 124.3 | 126.0 | 83.5 | 82.3 | 76.9 |
| Cp/ plane P1-M-P2         | -- | -- | -- | 78.4 | 80.5 | 137.7 |

S38
Table S10. Comparison of geometrical parameters of Walphos complexes \([\text{PdCl}_2(\text{SL-W002-1})]\) and \([\text{RuCl}(p\text{-cymene})( \text{SL-W002-1})]\text{PF}_6\) (for numbering scheme see Figures S5 and S6)

| Distance (Å) | [\text{PdCl}_2(\text{SL-W002-1})]_{\text{JOFYAF}^{22}} | QODHIB$^{11a}$ | [\text{RuCl}(p\text{-cymene})( \text{SL-W002-1})]\text{PF}_6^{2+} | molecule 1 | molecule 2 |
|--------------|----------------------------------------------------|-----------------|-------------------------------------------------|-----------|-----------|
| C11/Cp       | 0.090                                              | 0.119           | 0.049                                           | 0.069     |           |
| C1/Ph (backbone) | 0.292                                             | 0.162           | -0.041                                          | -0.017    |           |
| M/Cp (M= Pd, Ru) |                                                  |                 |                                                 |           |           |
| P1/Cp        | 1.784                                              | 1.876           | 1.776                                           | 1.668     |           |
| P2/Cp        | 2.842                                              | 2.907           | 2.854                                           | 2.850     |           |
| P2/Ph (backbone) | -0.225                                            | -0.352          | -0.213                                          | -0.346    |           |
| C11/Cp       | 4.703                                              | 4.648           | 2.022                                           | 2.095     |           |
| C12/Cp       | 5.530                                              | 5.494           | --                                              | --        |           |
| Angle (°)    |                                                    |                 |                                                 |           |           |
| 2/1/11       | 120.8                                              | 122.3           | 129.1                                           | 128.5     |           |
| 5/1/11       | 131.4                                              | 129.8           | 123.2                                           | 123.8     |           |
| 1/11/12      | 120.6                                              | 121.3           | 117.7                                           | 118.2     |           |
| 1/11/16      | 120.8                                              | 120.0           | 124.0                                           | 123.2     |           |
| Cp/Ph (backbone) | 78.8                                              | 78.3            | 74.1                                            | 68.3      |           |
| Cp/plane P1-M-P2 | 69.9                                              | 59.1            | 118.3                                           | 115.6     |           |