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Planar Chiral P,O-Compounds Derived from Ferrocenyl Aryl Ethers

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Dedicated to Professor Wolfgang Kläui on the occasion of his 65th birthday

Keywords: Ferrocenes / C–C coupling / Planar chirality / Phosphanes / Metalation

The *ortho*-directed lithiation of $FcOC_6H_4$-4-*t*Bu (**1**) [Fc = (η^5-C_5H_4)(η^5-C_5H_5)Fe] with *n*BuLi/tmeda is reported (tmeda = tetramethylethylenediamine). In this reaction, multimetalation occurs to yield novel 1,2-functionalized P,O-derivatives that contain up to four phosphanyl moieties as determined by NMR spectroscopic studies and single-crystal X-ray diffraction analysis. Thus available planar chiral P,O-ferrocenes can successfully be applied in the palladium-catalyzed Suzuki coupling of diverse aryl halides and aryl boronic acids. The aforementioned systems allow the activation of carbon–chlorine bonds in an efficient way and tolerate catalyst loadings as low as 10 ppm. Noteworthy is their remarkable ability to economically generate hindered biaryls under mild reaction conditions.

Introduction

Ferrocene-based phosphanes have widely been applied as donor ligands both in organometallic chemistry and in homogeneous catalysis.[1] Among this family of compounds planar chiral ferrocenylphosphanes, such as Josiphos and *trans*-chelating bisphosphane ligands (TRAPs), are of particular interest in asymmetric synthesis and catalysis.[2] To date, the most prominent synthesis methodology utilizes the diastereoselective *ortho*-directed metalation of chiral ferrocenes and is strongly affiliated with the pioneering work of Ugi, Togni, Hayashi et al.[3]

Ortho-metalation was independently described by Wittig[4] and Gilman[5] in the late 1930s in the example of the deprotonation of anisole by *n*BuLi. However, to the best of our knowledge, alkoxy or aryloxy ferrocenes have never been applied in such reactions. So far, the synthesis of such molecules relies on the etherification of hydroxyferrocene FcOH [Fc = (η^5-C_5H_4)(η^5-C_5H_5)Fe] as demonstrated by Nesmejanow et al.[6] For the synthesis of ferrocenyl aryl ethers, Rausch exerted the Ullmann coupling of haloferrocenes with alkaline phenolates in the presence of copper, however, which afforded several byproducts.[7] Recently, Plenio and co-workers reported a straightforward copper(I)-catalyzed synthesis of diverse ferrocenyl aryl ethers starting from iodoferrocene and various phenols.[8] To our surprise, this class of organometallics has not been studied further yet.

This prompted us to examine the *ortho*-directed metalation of ferrocenyl aryl ethers. Thus available hemilabile P,O-compounds can be considered to be promising ligands in a palladium-catalyzed Suzuki reaction (Figure 1).[9]

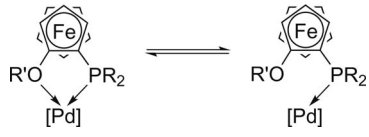

Figure 1. Concept of a hemilabile P,O compound.

Results and Discussion

The most commonly used synthesis protocol for *ortho*-directed metalations utilizes lithium diisopropylamide (LDA) or BuLi in tetrahydrofuran or diethyl ether at low temperature.[10] However, in the case of ferrocene $FcOC_6H_4$-4-*t*Bu (**1**) [Fc = (η^5-C_5H_4)(η^5-C_5H_5)Fe], no metalation occurs within hours under similar reaction conditions even in the presence of tetramethylethylenediamine (tmeda). Running the reaction at ambient temperature along with a change of the solvent to *n*-hexane resulted in a 90% conversion of **1** within twelve hours. Successful conversion of the lithiated species to the corresponding ferrocenylphosphanes was possible by addition of $ClPPh_2$ (**2a**) at –78 °C (Scheme 1). After appropriate workup, we were astonished to isolate three products, **3a**, **4a**, and **5a**, of which **3a** is clearly dominating. The substitution pattern of **3a**–**5a** is in accordance with *ortho*-directed metalation at the cyclopentadienyl and the aryl moiety.

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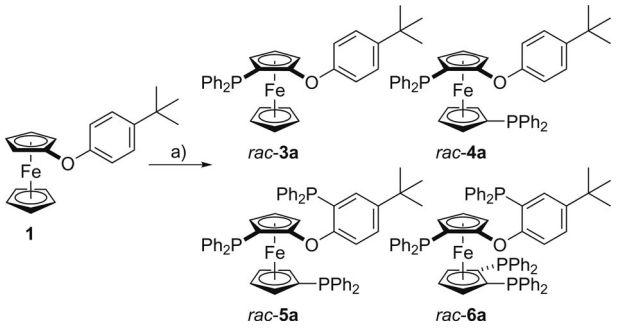
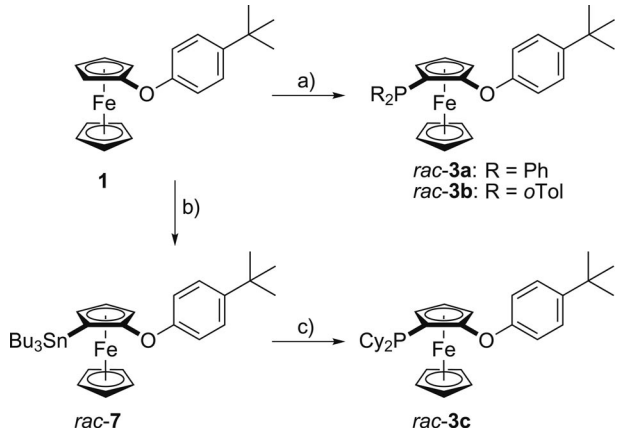


Scheme 1. Synthesis of **3a**–**6a**. (a) 1. *n*BuLi, tmeda, *n*-hexane, 25 °C, 12 h; 2. $ClPPh_2$ (**2a**), –78 °C, 1 h.



Scheme 2. Synthesis of **3a**–**3c**. (a) 1. *n*BuLi, tmeda, *n*-hexane, 25 °C, 12 h; 2. $ClPR_2$ (**2**), tetrahydrofuran, –78 °C, 1 h (**3a**: 64%; **3b**: 55%). (b) 1. *n*BuLi, tmeda, *n*-hexane, 25 °C, 12 h; 2. nBu_3SnCl, tetrahydrofuran, –78 °C, 1 h (23%). (c) 1. *n*BuLi, tetrahydrofuran, –78 °C, 1 h; 2. $ClPCy_2$ (**2c**), tetrahydrofuran, –78 °C, 1 h (91%).

Attempts to prepare **4a** and **5a** in a more efficient way prompted us to use *n*BuLi/tmeda in excess amounts. Changing the molar ratio of **1**/*n*BuLi from 1:1 to 1:2 resulted in the selective formation of **4a** as frequently observed in ferrocene chemistry.[11] However, with a ratio of 1:5 only **5a** and **6a**, respectively, could be obtained after column chromatography, thus proving multimetalation of **1**. Such dilithiation processes at one cyclopentadienyl ligand were recently observed by several groups.[12] It must be emphasized that **5a** and **6a** could only be isolated on a milligram scale. Further products could not be identified, which points to significant decomposition of the multimetalated species.

The synthesis methodology for the preparation of **3a** could successfully be transferred to $ClPoTol_2$ (Tol = tolyl; **2b**) as outlined in Scheme 2. Desired product **3b** could be separated from the multiple substituted side products by column chromatography. In the case of the alkylphosphane $ClPCy_2$ (Cy = cC_6H_{11}) (**2c**), this separation failed. Analytical pure **3c** could neither be obtained by column chromatography nor crystallization.[13] Therefore we developed another synthesis route that utilized organometallic **7** (Scheme 2). Transmetalation of dark red **7** with *n*BuLi and subsequent treatment with **2c** afforded the desired orange **3c** in almost quantitative yield and in analytical pure form.

Replacement of the nonchiral base tmeda by the chiral alkaloid (–)-sparteine induces[14] 37–40% enantiomeric excess (*ee*) in **3a**.[15]

All ferrocenes synthesized are pale orange solids that dissolve in common organic solvents. Ferrocenes **3a**–**3c** are stable in air both in the solid state and in solution.

Identification of compounds **3a**–**3c**, **4a**, **5a**, **6a**, and **7** described herein was deduced from their spectroscopic data (IR, NMR ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) and the structures of **3a**, **4a**, and **5a** were confirmed by single-crystal X-ray diffraction analysis. Correct elemental microanalyses were obtained. As expected, IR studies are less informative, whereas NMR spectroscopy is most capable of unambiguously determining the identity of the ferrocenes.

Typical of all compounds is the 1,2-substitution pattern of the oxygen-bearing cyclopentadienyl rings, which is evidenced from the *J*(H,H) and *J*(C,P) coupling constants. In the $^1H\{^{31}P\}$ NMR spectra of **3**–**6** two doublets-of-doublets [^3J(H,H) = 2.6 Hz and ^4J(H,H) = 1.5 Hz] and one pseudotriplet [^3J(H,H) = 2.6 Hz] are observed (Figure 2). The 1,2-P,O-substitution is further confirmed by the *J*(C,P) coupling constants of C1, the carbon atom that bears the aryloxy functionality. The values vary between 15 and 20 Hz, which can be considered typical for ^2J(C,P) constants. Similar coupling *J*(C,P) constants [15 (**5a**), 17 Hz (**6a**)] are found for the corresponding *i*C atom of the benzene moiety. Additional proof for 1,2-P,O-substitution also comes from the coupling pattern and chemical shifts of the three remaining aryloxy hydrogen atoms (Figure 2).

The second cyclopentadienyl ring shows resonance signals characteristic for non-, mono-, and disubstitution. The 1,2-P,P-substitution is verified by *J*(H,H), *J*(C,P), and *J*(P,P) constants, of which the latter is 97 Hz.[16] This coupling constant is very impressive as only a few ferrocene compounds with *J*(P,P) are described [i.e. 75 Hz in 2-(diphenylphosphanyl)-1-(dicyclohexylphosphanyl)ferrocene].[17] In addition, ferrocenes **5a** and **6a** exhibit a through-space rather than scalar coupling of 5 and 7 Hz between P1 and P3 (Figure 3).

The molecular structures of **3a**, **4a**, and **5a** predicted by NMR spectroscopy (vide supra) were additionally confirmed by single-crystal X-ray diffraction analyses. Due to the poor crystallization behavior of **3a** and **5a**, we converted these compounds with elemental selenium to the respective selenophosphanes **3a-Se** and **5a-Se$_3$**. Graphical representations are given in Figures 4 (**3a-Se**), 5 (**4a**), and 6 (**5a-Se$_3$**). Selected bond lengths [Å] and angles [°] are listed in the captions of these figures. The crystal and structure refinement data for all ferrocenes are summarized in Table 4 in the Exp. Section.

The palladium-catalyzed Suzuki reaction, the carbon–carbon cross-coupling of aryl and vinyl halides/triflates with boronic acids, is among the most essential transformations in organic and organometallic chemistry[18] and has been applied industrially for the production of fine chemi-

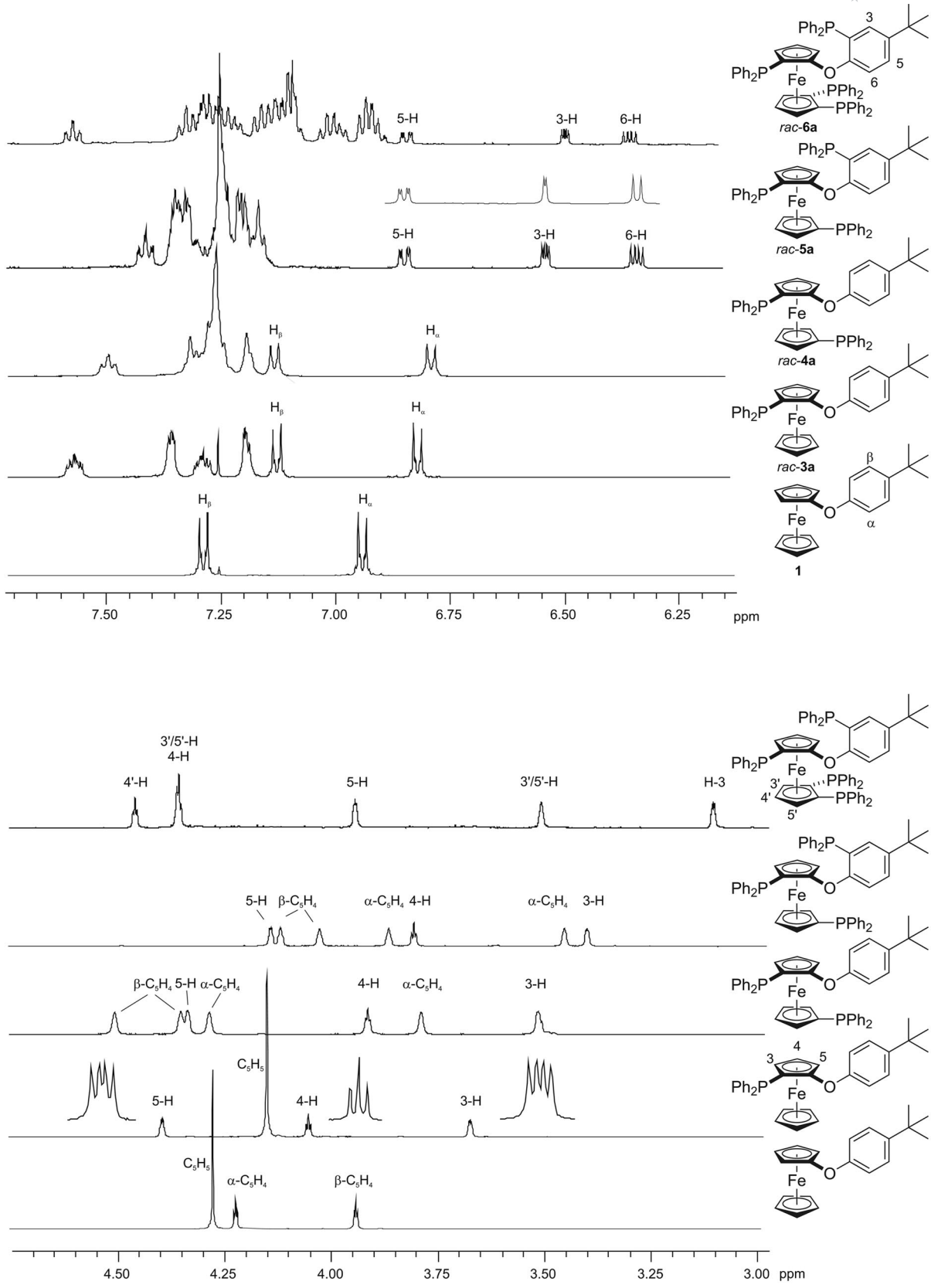


Figure 2. Parts of the ^1H NMR spectra of **1** and **3a**–**6a** between δ = 6–8 ppm (top) and δ = 3–4.5 ppm (bottom) with the signal shape of 3-H, 4-H, and 5-H of **3a** from the $^1H\{^{31}P\}$ NMR spectra, and a part of the $^1H\{^{31}P\}$ NMR spectra of **5a** that shows protons 3-H, 5-H, and 6-H ($CDCl_3$, 25 °C).

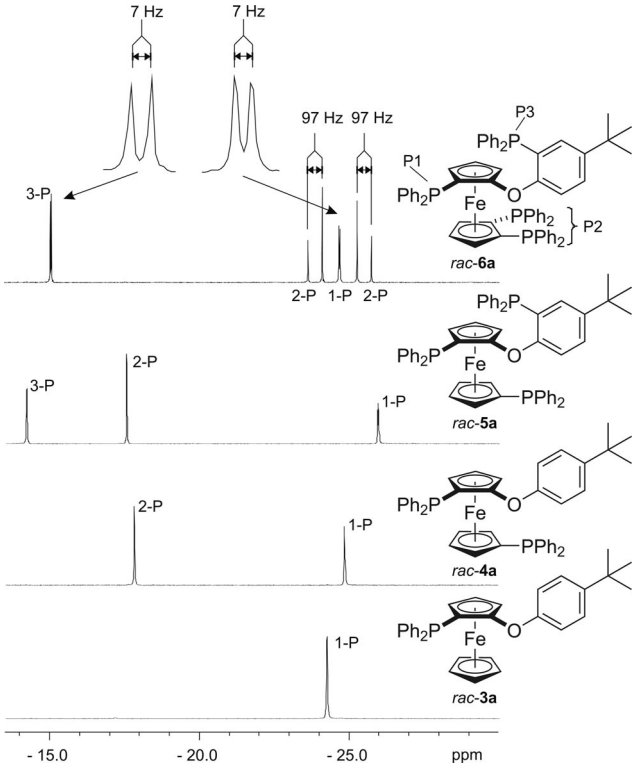


Figure 3. Part of the $^{31}P\{^{1}H\}$ NMR spectra of **3a**–**6a** between δ = –30 and –10 ppm ($CDCl_3$, 25 °C).

cals and pharmaceuticals.[19–21] Recently, very active organometallic and metal–organic systems for a wide variety of applications have been presented.[22,23]

As generally accepted in literature, hybrid P,O ligands are superior over monophosphane or diphosphane ligands in the Suzuki reaction.[9] This is why we applied phosphanes **3a**–**3c** in the coupling of different aryl halides with diverse boronic acids (see Tables 1, 2, and 3).

Excellent catalysts (i) are able to activate aryl chlorides independently of their electronic properties, (ii) can couple substrates at very low catalyst loadings, and (iii) are able to prepare sterically hindered biaryls (iv) under mild reaction conditions.

As shown in Table 1, strongly basic **3c** is able to couple activated (entry 1), non- (entries 2–4), and deactivated (entries 5–7) aryl chlorides with different boronic acids. Coupling of *ortho*-functionalized substrates is also possible (entries 2, 4, and 7). Unfortunately, the catalyst loadings cannot be decreased without significant loss of activity (entry 8).[24]

When it comes to the commercial application of coupling reactions, the costs of the noble-metal catalysts have to be considered. We studied the influence of lowering the catalyst concentration in the coupling of 2-bromotoluene (Table 2, entries 1–4) and 4′-chloroacetophenone (entries 5 and 6) with phenylboronic acid. It was found that quantitative yields of the appropriate coupling products can only be achieved for the synthesis of 2-methylbiphenyl at 0.1 and 0.01 mol-% (entries 1 and 2), otherwise the yields are between 31 and 85%. Furthermore, the results show that for the conversion of 2-bromotoluene the catalyst loading can be reduced to 0.001 mol-% (δ = 10 ppm, entry 4) with a turnover number (TON) > 30000 and turnover frequency (TOF) > 1000 h^{-1}. In the case of less active 4′-chloroacetophenone, the presented strategy is less successful. Catalyst concentrations lower than 0.01 mol-% cannot be reached effectively.

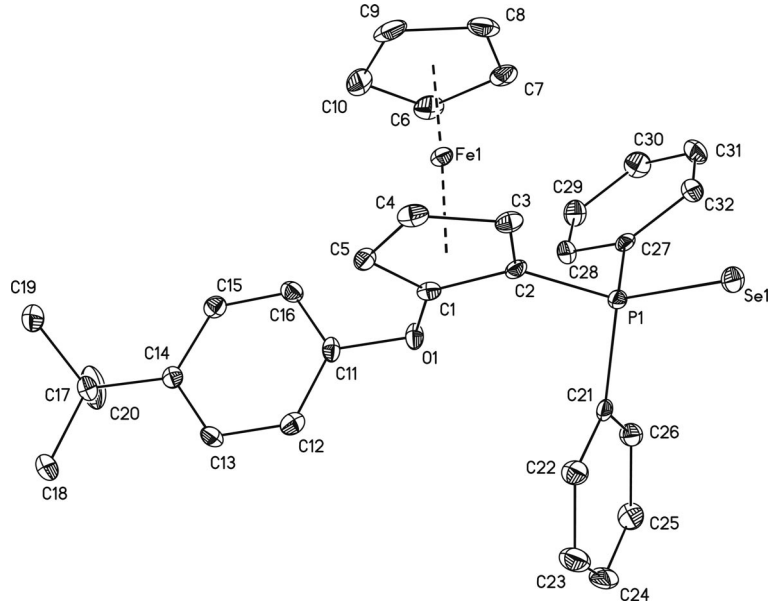


Figure 4. ORTEP diagram (50% probability level) of **3a-Se** with atom numbering scheme. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: D1–Fe1 1.6516(3), D2–Fe1 1.6560(3), C1–O1 1.370(2), C2–P1 1.806(2), P1–Se1 2.1101(5); D1–Fe1–D2 177.57(2), O1–C1–C2–P1 2.4(3), C1–D1–D2–C6 9.3(1) (D1 = centroid C1–C5, D2 = centroid C6–C10). The figure in parentheses after each calculated value represents the standard deviation in units of the last significant digits.

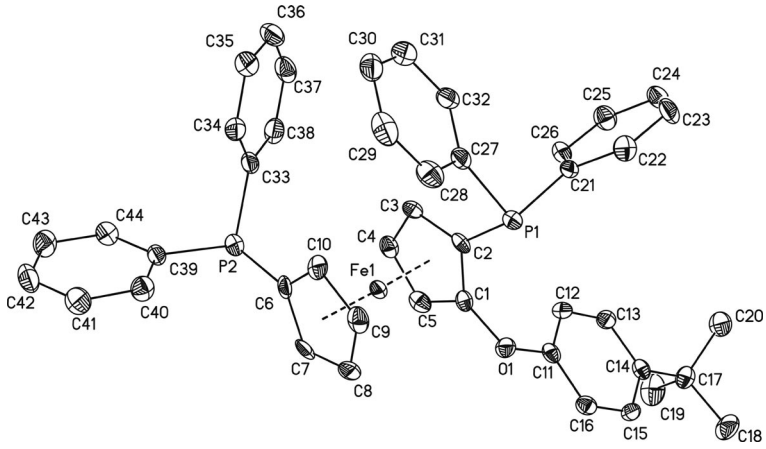


Figure 5. ORTEP diagram (50% probability level) of **4a** with atom numbering scheme. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: D1–Fe1 1.6376(3), D2–Fe1 1.6447(3), C1–O1 1.377(3), C2–P1 1.830(2), C6–P2 1.821(2); D1–Fe1–D2 177.74(2), O1–C1–C2–P1 2.3(3), C1–D1–D2–C8 17.5(2), P1–D1–D2–P2 131.03(2) (D1 = centroid C1–C5, D2 = centroid C6–C10). The figure in parentheses after each calculated value represents the standard deviation in units of the last significant digits.

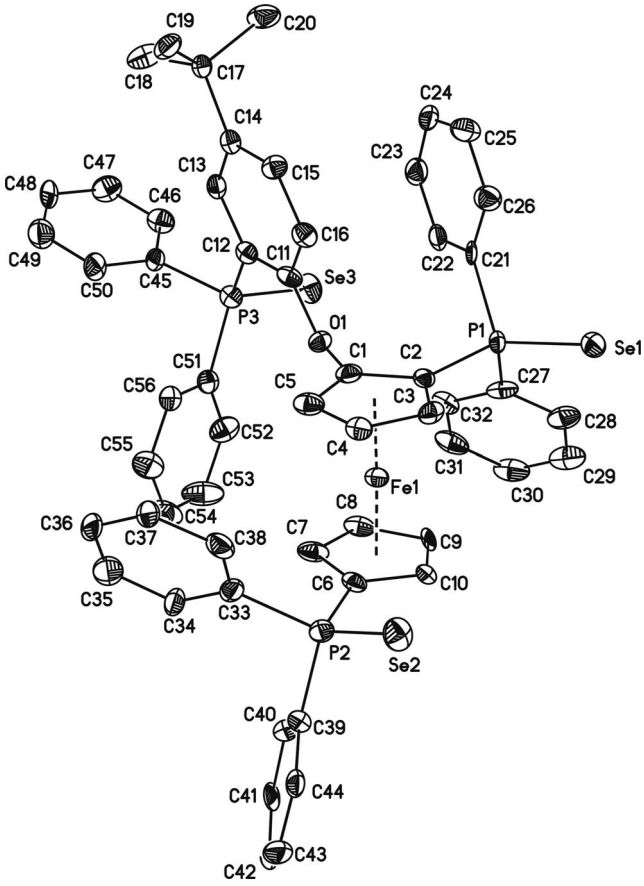


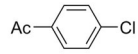
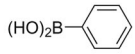
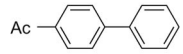
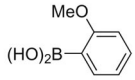
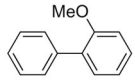
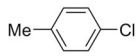
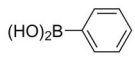
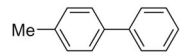
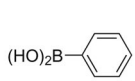
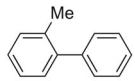
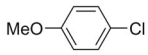
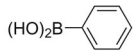
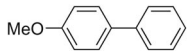
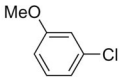
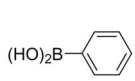
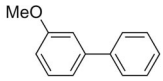
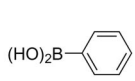
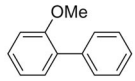
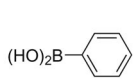
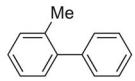
Figure 6. ORTEP diagram (50% probability level) of **5a-Se$_3$** with atom numbering scheme. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: D1–Fe1 1.6517(11), D2–Fe1 1.6554(11), C1–O1 1.391(9), C2–P1 1.813(8), C6–P2 1.801(7), C12–P3 1.825(7), P1–Se1 2.110(2), P2–Se2 2.105(2), P3–Se3 2.110(2); D1–Fe1–D2 177.27(8), O1–C1–C2–P1 3.6(12), C1–D1–D2–C8 7.8(6), P1–D1–D2–P2 148.50(5) (D1 = centroid C1–C5, D2 = centroid C6–C10). The figure in parentheses after each calculated value represents the standard deviation in units of the last significant digits.

The ability to synthesize sterically hindered biaryls by Suzuki coupling is still a challenge. Reaction protocols that can convert hindered substrates under mild conditions are of great interest and could provide convenient access to axial-chiral biaryls.[25] As can be seen from Table 3, biaryls with up to three *ortho* substituents (entries 3 and 5) are accessible in excellent yields at 50 °C and 0.1 mol% [Pd]. Even the highly hindered 2,4,6-triisopropylbromobenzene can be coupled smoothly (entry 7). Attempts to utilize *ortho*-disubstituted boronic acids for the synthesis of tetrafunctionalized biphenyls were not satisfactory so far as the catalyst is clearly very sensitive towards steric hindrance at the boronic acid.

Recapitulating the aforementioned results, only strongly Lewis basic **3c** in combination with [$Pd_2(dba)_3$] can successfully be applied in the catalytic coupling of chloroarenes with boronic acids. It was found that less basic **3b** is highly sensitive towards the activation of carbon–halide bonds. Although nonactivated bromoarenes are coupled smoothly, significant loss of activity is observed when deactivated bromoarenes or activated aryl chlorides are used.[26] These results are in accordance with similar systems described in literature that show that the catalytic behavior towards chloroarenes strongly corresponds to the electron richness of the phosphane ligands.[27] However, less-electron-rich diarylphosphanes such as **3a** and **3b** are beneficial for homogeneous catalysis as well. We were able to demonstrate that **3a** can be applied to the coupling of bromoarenes with boronic acids at very low catalyst levels and that **3b** is remarkably qualified for the synthesis of sterically hindered biaryls.[28]

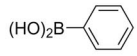
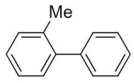
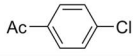
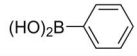
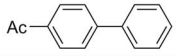
The application of enantiomerically enriched **3a** (vide supra) in an asymmetric Suzuki coupling has been so far unsuccessful,[29] presumably due to the low enantiomeric excess of the planar chiral phosphane or a negative nonlinear effect.[30]

Table 1. Suzuki coupling of aryl chlorides.[a]

Entry	Aryl chloride	Boronic acid	Product	Yield / % [b]
1				98
2				82
3				97
4				99
5				87
6				99
7				88
8				25 [c]

[a] Reaction conditions: aryl chloride (1.0 equiv.), boronic acid (1.5 equiv.), K_3PO_4 (3.0 equiv.), toluene (2 mL mmol^{-1} halide), [$Pd_2(dba)_3$]/**3c** (dba = dibenzylideneacetone), 1.0 mol-% [Pd], 100 °C, 24 h. Reaction times were not minimized. [b] NMR spectroscopic yields based upon an average of two runs. [c] 0.1 mol-% [Pd].

Table 2. Suzuki coupling at low catalyst loadings.[a]

Aryl halide	Boronic acid	Product	Entry	[Pd] / mol-%	Yield / % [b]	TON	TOF / h^{-1}
			1	0.1	99	990	41.3
			2	0.01	98	9 800	408
			3	0.005	68	13 600	567
			4	0.001	34	34 000	1417
			5	0.1	85	850	35.4
			6	0.01	31	3 100	129

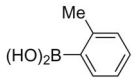
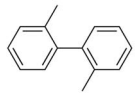
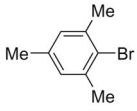
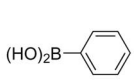
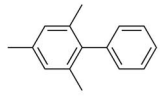
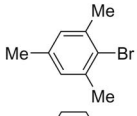
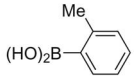
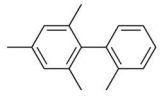
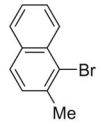
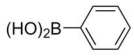
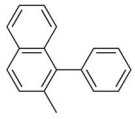
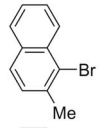
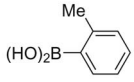
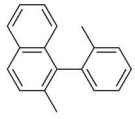
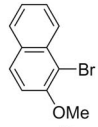
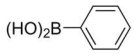
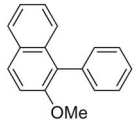
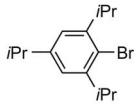
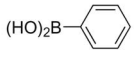
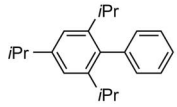
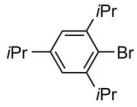
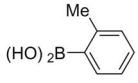
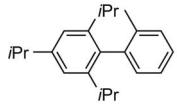
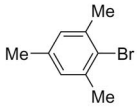
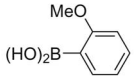
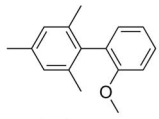
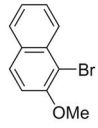
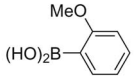
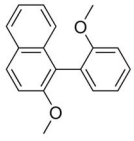
[a] Reaction conditions: aryl halide (1.0 equiv.), boronic acid (1.5 equiv.), K_3PO_4 (3.0 equiv.), toluene (2 mL mmol^{-1} halide), [$Pd_2(dba)_3$]/**3a**, 100 °C, 24 h. Reaction times were not minimized. [b] NMR spectroscopic yields based upon an average of two runs.

Conclusion

Within this study the straightforward synthesis methodology for planar chiral 1,2-functionalized P,O-ferrocenes has been developed. Starting from $FcOC_6H_4$-4-*t*Bu (**1**) [Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)], the ability of ferrocenyl aryl ethers to undergo *ortho*-directed lithiation was proven for the first time. Surprisingly, besides the monophosphanes, which could be isolated as dominating products (yields up to 64%), other ferrocenes with up to four phosphanyl moieties are formed as side products, thereby indicating multimetalation processes. The substitution pattern of the phosphanes obtained is associated with the *ortho*-directing effect of the ether functionality, as confirmed by NMR spectroscopy and single-crystal X-ray diffraction analysis.

P,O-Ferrocenes Fe(η^5-C_5H_5)[η^5-C_5H_3(OC_6H_4-4-*t*Bu-C_6H_4)-2-PR_2] [R = Ph (**3a**), *o*Tol (**3b**), Cy (**3c**)] were successfully applied in the palladium-catalyzed Suzuki cross-coupling of diverse aryl halides with aryl boronic acids. Solely **3c** allows the activation of carbon–chlorine bonds independently of the electronic properties of the aryl chlorides in an efficient way. Less Lewis basic phosphanes **3a** and **3b**, however, can be exerted for (i) coupling reactions at low catalyst levels, and (ii) the synthesis of sterically hindered biaryls. The catalyst system **3a**/[$Pd_2(dba)_3$] tolerates loadings as low as 10 ppm in the synthesis of 2-methylbiphenyl (TON > 30 000; TOF > 1 000 h^{-1}). For the coupling of *ortho*-functionalized arenes, the couple **3b**/[$Pd_2(dba)_3$] has turned out to be a remarkably efficient system. At mild reaction conditions (50 °C, 0.1 mol-% [Pd]) biaryls with up to

Table 3. Suzuki coupling of sterically hindered substrates.[a]

Entry	Aryl halide	Boronic acid	Product	Yield / % [b]
1				99
2				99
3				92
4				91
5				94
6				76
7				99
8				25
9				22 [c], 49 [c,d]
10				50 [c,d]

[a] Reaction conditions: aryl chloride (1.0 equiv.), boronic acid (1.5 equiv.), K_3PO_4 (3.0 equiv.), toluene (2 mL mmol^{-1} halide), [$Pd_2(dba)_3$]/**3b**, 0.1 mol% [Pd], 50 °C, 24 h. Reaction times were not minimized. [b] NMR spectroscopic yields based upon an average of two runs. [c] 2.0 equiv. boronic acid, 100 °C. [d] 0.5 mol-% [Pd].

three *ortho* substituents are accessible in excellent yields. Even the highly hindered 2,4,6-triisopropylbromobenzene can be coupled smoothly.

Experimental Section

***rac*-1-(4-*tert*-Butylphenoxy)-2-(diphenylphosphanyl)ferrocene (3a):** *n*BuLi (2.5 M in *n*-hexane, 0.6 mL, 1.5 mmol, 1.0 equiv.) was added dropwise over 5 min to a solution of **1** (0.50 g, 1.5 mmol) and tmeda (0.22 mL, 1.5 mmol, 1.0 equiv.) in anhydrous *n*-hexane (30 mL). The mixture was stirred for 12 h at ambient temperature. After cooling to –78 °C, neat **2a** (0.33 g, 1.5 mmol, 1.0 equiv.) was added in a single portion, stirred for 30 min at –78 °C and then for 90 min at ambient temperature. The reaction mixture was diluted with water (50 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on alumina [*n*-hexane/diethyl ether = 95:5 (v/v)]. Ferrocene **3a** was isolated as an orange solid (0.50 g, 0.96 mmol, 64% based on **1**); m.p. 96–98 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.25 [s, 9 H, $C(CH_3)_3$], 3.66–3.68 (m, 1 H, 3-H/C_5H_3), 4.05 [pt, ^3J(H,H) = 2.6 Hz, 1 H, 4-H/C_5H_3], 4.15 (s, 5 H, C_5H_5), 4.38–4.40 (m, 1 H, 5-H/C_5H_3), 6.81–6.84 (m, 2 H, *o*-C_6H_4), 7.11–7.15 (m, 2 H, *m*-C_6H_4), 7.18–7.22 (m, 3 H, C_6H_5), 7.27–7.32 (m, 2 H, C_6H_5), 7.34–7.38 (m, 3 H, C_6H_5),

7.55–7.60 (m, 2 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C, TMS): δ = 31.4 [s, 3 C, C(CH_3)$_3$], 34.0 [s, 1 C, $C(CH_3)_3$], 61.9 (s, 1 C, 5-C/C_5H_3), 64.0 (s, 1 C, 4-C/C_5H_3), 66.5 (s, 1 C, 3-C/C_5H_3), 67.3 [d, ^1J(C,P) = 9.7 Hz, 1 C, 2-C/C_5H_3], 70.2 (s, 5 C, C_5H_5), 117.2 (s, 2 C, *o*-C_6H_4), 125.7 (s, 2 C, *m*-C_6H_4), 126.6 [d, ^2J(C,P) = 18.6 Hz, 1 C, 1-C/C_5H_3], 127.8 [d, ^3J(C,P) = 6.5 Hz, 2 C, *m*-C_6H_5], 127.9 (s, 1 C, *p*-C_6H_5), 128.0 [d, ^3J(C,P) = 7.4 Hz, 2 C, *m*-C_6H_5], 128.7 (s, 1 C, *p*-C_6H_5), 132.8 [d, ^2J(C,P) = 19.5 Hz, 2 C, *o*-C_6H_5], 134.5 [d, ^2J(C,P) = 20.8 Hz, 2 C, *o*-C_6H_5], 137.4 [d, ^1J(C,P) = 9.1 Hz, 1 C, *i*-C_6H_5], 138.9 [d, ^1J(C,P) = 10.8 Hz, 1 C, *i*-C_6H_5], 145.1 (s, 1 C, *p*-C_6H_4), 155.9 (s, 1 C, *i*-C_6H_4) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = –24.3 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3099, 3066 (=C–H), 2960, 2867 (CH_3), 1508 (C=C), 1372, 1362 [C(CH_3)$_3$], 1245 (=C–O–C), 828, 813, 747, 739, 696 (=C–H) cm^{-1}. $C_{32}H_{31}FeOP$ (518.41): calcd. C 74.14, H 6.03; found C 74.06, H 6.26.

***rac*-1-(4-*tert*-Butylphenoxy)-2-[bis(2-tolyl)phosphanyl]ferrocene (3b):** Same procedure as described for **3a** but **2b** (0.37 g, 1.5 mmol, 1.0 equiv.) was used instead of **2a**. The product was purified by column chromatography on alumina [*n*-hexane/diethyl ether = 95:5 (v/v)] and **3b** was isolated as an orange solid (0.45 g, 0.82 mmol, 55% based on **1**); m.p. 119–122 °C. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.30 [s, 9 H, C(CH_3)$_3$], 2.21 [d, ^4J(P,H) = 1.6 Hz, 3 H, $C_6H_4CH_3$], 2.91 (s, 3 H, $C_6H_4CH_3$), 3.76–3.78 (m, 1 H, 3-H/C_5H_3), 4.08 [dpt, ^3J(H,H) = 2.6, ^4J(P,H) = 0.5 Hz, 1 H, 4-H/C_5H_3], 4.15 (s, 5 H, C_5H_5), 4.39–4.41 (m, 1 H, 5-H/C_5H_3), 6.96–7.00 [m, 2 H, *o*-$C_6H_4OC(CH_3)_3$], 7.00–7.15 (m, 4 H, $C_6H_4CH_3$), 7.16–7.20 (m, 1 H, $C_6H_4CH_3$), 7.22–7.32 [m, 5 H, $C_6H_4CH_3$ and *m*-$C_6H_4OC(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.8 [d, ^3J(C,P) = 20.3 Hz, 1 C, $C_6H_4CH_3$], 22.0 [d, ^3J(C,P) = 24.3 Hz, 1 C, $C_6H_4CH_3$], 31.5 [s, 3 C, C(CH_3)$_3$], 34.2 [s, 1 C, $C(CH_3)_3$], 61.3 [d, ^3J(C,P) = 2.0 Hz, 1 C, 5-C/C_5H_3], 63.9 (s, 1 C, 4-C/C_5H_3), 66.2 [d, ^1J(C,P) = 9.4 Hz, 1 C, 2-C/C_5H_3], 66.8 (s, 1 C; 3-C/C_5H_3), 70.0 (s, 5 C, C_5H_5), 118.3 (s, 2 C, *o*-C_6H_4), 125.2 (s, 1 C, $C_6H_4CH_3$), 125.5 [d, J(C,P) = 1.3 Hz, 1 C, $C_6H_4CH_3$], 125.9 (s, 2 C, *m*-C_6H_4), 127.7 (s, 1 C, $C_6H_4CH_3$), 127.8 [d, ^2J(C,P) = 18.9 Hz, 1 C, 1-C/C_5H_3], 129.0 (s, 1 C, $C_6H_4CH_3$), 129.7 [d, ^3J(C,P) = 4.3 Hz, 1 C, 6-C/$C_6H_4CH_3$], 129.9 [d, ^3J(C,P) = 5.7 Hz, 1 C, 6-C/$C_6H_4CH_3$], 131.6 (s, 1 C, $C_6H_4CH_3$), 134.8 [d, ^1J(C,P) = 9.2 Hz, 1 C, 2-C/$C_6H_4CH_3$], 135.7 (s, 1 C, $C_6H_4CH_3$), 138.8 [d, ^1J(C,P) = 13.5 Hz, 1 C, 2-C/$C_6H_4CH_3$], 140.6 [d, ^2J(C,P) = 25.6 Hz, 1 C, 1-C/$C_6H_4CH_3$], 143.2 [d, ^2J(C,P) = 29.2 Hz, 1 C, 1-C/$C_6H_4CH_3$], 145.7 (s, 1 C, *p*-C_6H_4), 155.6 (s, 1 C, *i*-C_6H_4) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = –44.0 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3098, 3058, 3003 (=C–H), 2960, 2864 (CH_3), 1509 (C=C), 1373, 1362 [C(CH_3)$_3$], 1242 (=C–O–C), 837, 818, 802, 750 (=C–H) cm^{-1}. HRMS: *m*/*z*: calcd. for $C_{34}H_{35}FeOP$: 546.1770; found 546.1684 [M]$^+$. $C_{34}H_{35}FeOP$ (546.46): calcd. C 74.73, H 6.46; found C 74.28, H 6.66.

***rac*-1-(4-*tert*-Butylphenoxy)-2-(dicyclohexylphosphanyl)ferrocene (3c):** A solution of **7** (0.21 g, 0.34 mmol) in anhydrous tetrahydrofuran (10 mL) was cooled to –78 °C and *n*BuLi (2.5 M in *n*-hexane, 0.13 mL, 0.34 mmol, 1.0 equiv.) was added slowly. The mixture was stirred for 30 min at –78 °C. Afterwards, neat **2c** (0.08 g, 0.34 mmol, 1.0 equiv.) was added in a single portion. The reaction was stirred for 30 min at –78 °C and 90 min at ambient temperature. After addition of water (50 mL) the organic layer was separated and the aqueous phase was extracted with diethyl ether (3 × 50 mL). The combined organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on alumina [*n*-hexane/diethyl ether = 95:5 (v/v)]. Compound **3c** was isolated as an orange solid (0.16 g, 0.31 mmol, 91% based on **7**); m.p. 132–134 °C. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.32 [s, 9 H, C(CH_3)$_3$], 1.11–1.35 (m, 10 H, C_6H_{11}), 1.57–2.10 (m, 12 H, C_6H_{11}), 3.94–3.96 (m, 1 H, 3-H/C_5H_3), 3.99 [pt, ^3J(H,H) = 2.6 Hz, 1 H, 4-H/C_5H_3], 4.21 (s, 5 H, C_5H_5), 4.25–4.26 (m, 1 H, 5-H/C_5H_3), 6.97–7.01 (m, 2 H, *o*-C_6H_4), 7.28–7.32 (m, 2 H, *m*-C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.42 [d, ^4J(C,P) = 1.0 Hz, 1 C, 4-C/C_6H_{11}], 26.45 [d, ^4J(C,P) = 0.9 Hz, 1 C, 4-C/C_6H_{11}], 27.30 [d, J(C,P) = 10.4 Hz, 1 C, C_6H_{11}], 27.39 [d, J(C,P) = 9.3 Hz, 1 C, C_6H_{11}], 27.47 [d, J(C,P) = 8.3 Hz, 1 C, C_6H_{11}], 27.48 [d, J(C,P) = 10.4 Hz, 1 C, C_6H_{11}], 30.0 [d, J(C,P) = 13.1 Hz, 1 C, C_6H_{11}], 30.7 [d, J(C,P) = 12.8 Hz, 1 C, C_6H_{11}], 31.1 [d, J(C,P) = 9.7 Hz, 1 C, C_6H_{11}], 31.2 [d, J(C,P) = 10.6 Hz, 1 C, C_6H_{11}], 31.5 [s, 3 C, C(CH_3)$_3$], 33.54 [d, ^1J(C,P) = 11.3 Hz, 1 C, 1-C/C_6H_{11}], 33.55 [d, ^1J(C,P) = 11.5 Hz, 1 C, 1-C/C_6H_{11}], 34.2 [s, 1 C, $C(CH_3)_3$], 60.4 (s, 1 C, 5-C/C_5H_3), 62.9 [d, ^3J(C,P) = 2.7 Hz, 1 C, 4-C/C_5H_3], 66.5 [d, ^1J(C,P) = 21.2 Hz, 1 C, 2-C/C_5H_3], 67.0 [d, ^3J(C,P) = 11.2 Hz, 1 C, 3-C/C_5H_3], 70.2 (s, 5 C, C_5H_5), 117.5 (s, 2 C, *o*-C_6H_4), 125.4 [d, ^2J(C,P) = 6.4 Hz, 1 C, 1-C/C_5H_3], 126.0 (s, 2 C, *m*-C_6H_4), 145.5 (s, 1 C, *p*-C_6H_4), 155.6 (s, 1 C, *i*-C_6H_4) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = –8.6 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3097, 3055 (=C–H), 2955, 2871 (CH_3), 2919, 2848 (CH_2), 1509 (C=C), 1376, 1362 [C(CH_3)$_3$], 1238 (=C–O–C), 834, 817 (=C–H) cm^{-1}. HRMS: *m*/*z*: calcd. for $C_{32}H_{43}FeOP$: 531.2474; found 531.2374 [M + H]$^+$. $C_{32}H_{43}FeOP$ (530.50): calcd. C 72.45, H 8.17; found C 71.60, H 8.02.

***rac*-1-(4-*tert*-Butylphenoxy)-2,1′-bis(diphenylphosphanyl)ferrocene (4a):** *n*BuLi (2.5 M in *n*-hexane, 1.2 mL, 3.0 mmol, 2.0 equiv.) was added dropwise over 5 min to a solution of **1** (0.50 g, 1.5 mmol) and tmeda (0.45 mL, 3.0 mmol, 2.0 equiv.) in anhydrous *n*-hexane (30 mL). The mixture was stirred for 12 h at ambient temperature. After cooling to –78 °C, neat **2a** (0.66 g, 3.0 mmol, 2.0 equiv.) was added in a single portion, and the reaction was stirred for 30 min at –78 °C and then for 90 min at ambient temperature. The reaction mixture was diluted with water (50 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on alumina [*n*-hexane/diethyl ether = 90:10 (v/v)]. Compound **4a** was isolated as a yellow solid (0.70 g, 1.00 mmol, 67% based on **1**). Single crystals of **4a** could be obtained by recrystallization from $CHCl_3$; m.p. 186–188 °C. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.26 [s, 9 H, C(CH_3)$_3$], 3.50–3.53 (m, 1 H, 3-H/C_5H_3), 3.77–3.81 (m, 1 H, H_α-C_5H_4), 3.91 [pt, ^3J(H,H) = 2.5 Hz, 1 H, 4-H/C_5H_3], 4.26–4.30 (m, 1 H, H_α-C_5H_4), 4.32–4.37 (m, 2 H, 5-H/C_5H_3 and H_β-C_5H_4), 4.48–4.53 (m, 1 H, H_β-C_5H_4), 6.78–6.83 (m, 2 H, *o*-C_6H_4), 7.11–7.16 (m, 2 H, *m*-C_6H_4), 7.17–7.22 (m, 3 H, C_6H_5), 7.22–7.36 (m, 15 H, C_6H_5), 7.48–7.53 (m, 2 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C, TMS): δ = 31.4 [s, 3 C, C(CH_3)$_3$], 34.1 [s, 1 C, $C(CH_3)_3$], 63.6 (s, 1 C, 5-C/C_5H_3), 66.2 [d, ^3J(C,P) = 1.7 Hz, 1 C, 4-C/C_5H_3], 67.4 (s, 1 C, 3-C/C_5H_3), 67.9 [d, ^1J(C,P) = 10.9 Hz, 1 C, 2-C/C_5H_3], 73.6 [d, ^2J(C,P) = 11.4 Hz, 1 C, *o*-C_5H_4], 74.0 (m, 1 C, *m*-C_5H_4), 74.7 [d, ^3J(C,P) = 4.2 Hz, 1 C, *m*-C_5H_4], 75.4 [d, ^2J(C,P) = 17.9 Hz, 1 C, *o*-C_5H_4], 77.3 [d, ^1J(C,P) = 8.3 Hz, 1 C, *i*-C_5H_4], 117.3 (s, 2 C, *o*-C_6H_4), 125.8 (s, 2 C, *m*-C_6H_4), 126.8 [d, ^2J(C,P) = 18.4 Hz, 1 C, 1-C/C_5H_3], 127.9 [d, ^3J(C,P) = 6.7 Hz, 2 C, *m*-C_6H_5], 128.0 [d, ^3J(C,P) = 7.3 Hz, 2 C, *m*-C_6H_5], 128.0–128.1 (m, 5 C, *m*-C_6H_5 and *p*-C_6H_5), 128.3 (s, 1 C, *p*-C_6H_5), 128.5 (s, 1 C, *p*-C_6H_5), 128.9 (s, 1 C, *p*-C_6H_5), 132.9 [d, ^2J(C,P) = 19.3 Hz, 2 C, *o*-C_6H_5], 133.1 [d, ^2J(C,P) = 19.1 Hz, 2 C, *o*-C_6H_5], 133.6 [d, ^2J(C,P) = 19.9 Hz, 2 C, *o*-C_6H_5], 134.5 [d, ^2J(C,P) = 20.9 Hz, 2 C, *o*-C_6H_5], 137.1 [d, ^1J(C,P) = 9.0 Hz, 1 C, *i*-C_6H_5], 138.7 [d, ^1J(C,P) = 9.9 Hz, 1 C, *i*-C_6H_5], 138.8 [d, ^1J(C,P) = 10.7 Hz, 1 C, *i*-C_6H_5], 139.2 [d, ^1J(C,P) = 10.0 Hz, 1 C, *i*-C_6H_5], 145.4 (s, 1 C, *p*-C_6H_4),

155.8 (s, 1 C, *i*-C_6H_4) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = –17.8 (s, 1 P, C_5H_4P), –24.3 (s, 1 P, C_5H_3P) ppm. IR (KBr): $\tilde{\nu}$ = 3066, 3044, 3026 (=C–H), 2964, 2950, 2900, 2864 (CH_3), 1509 (C=C), 1361 [$C(CH_3)_3$], 1242 (=C–O–C), 826, 742, 698 (=C–H) cm^{-1}. $C_{44}H_{40}FeOP_2$ (702.58): calcd. C 75.22, H 5.74; found C 75.10, H 5.90.

***rac*-1-(2-Diphenylphosphanyl-4-*tert*-butylphenoxy)-2,1′-bis(diphenylphosphanyl)ferrocene (5a):** Triphosphane **5a** and tetraphosphane **6a** were formed as side products when **1** was treated with *n*BuLi and **2a** in excess amounts. The development of a straightforward synthesis protocols failed; m.p. 100–102 °C. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.01 [s, 9 H, $C(CH_3)_3$], 3.46–3.49 (m, 1 H, 3-H/C_5H_3), 3.51–3.54 (m, 1 H, H_α-C_5H_4), 3.88 [pt, ^3J(H,H) = 2.6 Hz, 1 H, 4-H/C_5H_3], 3.92–3.95 (m, 1 H, H_α-C_5H_4), 4.08–4.11 (m, 1 H, H_β-C_5H_4), 4.18–4.20 (m, 1 H, H_β-C_5H_4), 4.20–4.23 (m, 1 H, 5-H/C_5H_3), 6.34 [dd, ^3J(H,H) = 8.5, ^4J(P,H) = 4.6 Hz, 1 H, 6-H/C_6H_3], 6.54 [dd, ^3J(P,H) = 5.3, ^4J(H,H) = 2.4 Hz, 1 H, 3-H/C_6H_3], 6.85 [dd, ^3J(H,H) = 8.5, ^4J(H,H) = 2.4 Hz, 1 H, 5-H/C_6H_3], 7.13–7.39 (m, 28 H, C_6H_5), 7.39–7.45 (m, 2 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C, TMS): δ = 31.2 [s, 3 C, $C(CH_3)_3$], 34.1 [s, 1 C, $C(CH_3)_3$], 64.9 [d, ^3J(C,P) = 1.5 Hz, 1 C, 5-C/C_5H_3], 67.2 [d, ^3J(C,P) = 3.0 Hz, 1 C, 4-C/C_5H_3], 68.0 (s, 1 C, 3-C/C_5H_3), 69.5 [d, ^1J(C,P) = 14.4 Hz, 1 C, 2-C/C_5H_3], 73.9 [d, ^2J(C,P) = 11.2 Hz, 1 C, *o*-C_5H_4], 75.1 (m, 1 C, *m*-C_5H_4), 75.2 [d, ^2J(C,P) = 18.3 Hz, 1 C, *o*-C_5H_4], 75.5 [d, ^3J(C,P) = 3.9 Hz, 1 C, *m*-C_5H_4], 113.6 (s, 1 C, 6-C/C_6H_3), 124.9 [d, ^2J(C,P) = 20.3 Hz, 1 C, 1-C/C_5H_3], 125.3 [d, ^1J(C,P) = 14.4 Hz, 1 C, 2-C/C_6H_3], 126.2 (s, 1 C, 5-C/C_6H_3), 127.8–128.6 (m, 18 C, *m*-C_6H_5 and *p*-C_6H_5), 130.6 [d, ^2J(C,P) = 1.6 Hz, 1 C, 3-C/C_6H_3], 133.1 [d, ^2J(C,P) = 19.1 Hz, 2 C, *o*-C_6H_5], 133.3 [d, ^2J(C,P) = 20.2 Hz, 2 C, *o*-C_6H_5], 133.5 [d, ^2J(C,P) = 19.6 Hz, 2 C, *o*-C_6H_5], 133.8 [d, ^2J(C,P) = 20.4 Hz, 2 C, *o*-C_6H_5], 134.2 [d, ^2J(C,P) = 20.2 Hz, 2 C, *o*-C_6H_5], 134.3 [d, ^2J(C,P) = 21.0 Hz, 2 C, *o*-C_6H_5], 136.9 [d, ^1J(C,P) = 11.8 Hz, 1 C, *i*-C_6H_5], 137.2 [d, ^1J(C,P) = 11.8 Hz, 1 C, *i*-C_6H_5], 137.6 [d, ^1J(C,P) = 10.9 Hz, 1 C, *i*-C_6H_5], 138.7 [d, ^1J(C,P) = 9.5 Hz, 1 C, *i*-C_6H_5], 139.1 [d, ^1J(C,P) = 11.6 Hz, 1 C, *i*-C_6H_5], 139.3 [d, ^1J(C,P) = 10.0 Hz, 1 C, *i*-C_6H_5], 144.6 (s, 1 C, 4-C/C_6H_3), 158.4 [d, ^2J(C,P) = 15.4 Hz, 1 C, 1-C/C_6H_3] (carbon *i*-C_5H_4 was not observed) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = –14.3 [d, ^6J(P,P) = 4.8 Hz, 1 P, C_6H_3P], –17.6 (s, 1 P, C_5H_4P), –26.0 ppm [d, ^6J(P,P) = 4.8 Hz, 1 P, C_5H_3P]. IR (NaCl): $\tilde{\nu}$ = 3070, 3055, 3001 (=C–H), 2962, 2927, 2860 (CH_3), 1585 (C=C), 1361 [$C(CH_3)_3$], 1244 (=C–O–C), 908, 824, 735, 696 (=C–H) cm^{-1}. HRMS: *m*/*z*: calcd. for $C_{56}H_{49}FeOP_3$: 444.1246; found 444.1235 $[M + 2H]^{2+}$.

***rac*-1-(2-Diphenylphosphanyl-4-*tert*-butylphenoxy)-2,1′,2′-tris(diphenylphosphanyl)ferrocene (6a):** ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.04 [s, 9 H, $C(CH_3)_3$], 3.09–3.11 (m, 1 H, 3-H/C_5H_3OP), 3.49–3.52 (m, 1 H, 3-H or 5-H/$C_5H_3P_2$), 3.93–3.95 (m, 1 H, 5-H/C_5H_3OP), 4.34–4.37 (m, 2 H, 4-H/C_5H_3OP and 3-H or 5-H/$C_5H_3P_2$), 4.46 [pt, ^3J(H,H) = 2.5 Hz, 1 H, 4-H/$C_5H_4P_2$], 6.36 [dd, ^3J(H,H) = 8.5 Hz, ^4J(P,H) = 4.8 Hz, 1 H, 6-H/C_6H_3], 6.51 [dd, ^3J(P,H) = 4.8 Hz, ^4J(H,H) = 2.4 Hz, 1 H, 3-H/C_6H_3], 6.85 [ddd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.5 Hz, ^5J(P,H) = 0.6 Hz, 1 H, 5-H/C_6H_3], 6.89–6.97 (m, 6 H, C_6H_5), 6.98–7.05 (m, 4 H, C_6H_5), 7.07–7.36 (m, 28 H, C_6H_5), 7.56–7.61 ppm (m, 2 H, C_6H_5); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C, TMS): δ = 31.2 [s, 3 C, $C(CH_3)_3$], 34.1 [s, 1 C, $C(CH_3)_3$], 66.7 (m, 1 C, 5-C/C_5H_3OP), 67.0 (m, 1 C, 4-C/C_5H_3OP), 69.1 [d, ^1J(C,P) = 17.5 Hz, 1 C, 2-C/C_5H_3OP], 69.9 [d, ^2J(C,P) = 4.9 Hz, 1 C, 3-C/C_5H_3OP], 75.6 [pt, ^{2+3}J(C,P) = 4.1 Hz, 1 C, 3-C or 5-C/$C_5H_3P_2$], 77.2 [d, ^3J(C,P) = 4.4 Hz, 1 C, 4-C/$C_5H_3P_2$], 78.5 [dd, ^2J(C,P) = 8.7 Hz, ^3J(C,P) = 4.1 Hz, 1 C, 3-C or 5-C/$C_5H_3P_2$], 83.8 [dd, ^2J(C,P) = 29.2 Hz, ^1J(C,P) = 7.4 Hz, 1 C, 1-C or 2-C/$C_5H_3P_2$], 85.1 [dd, ^2J(C,P) = 28.5 Hz, ^1J(C,P) = 8.6 Hz, 1 C, 1-C or 2-C/$C_5H_3P_2$], 113.8 [d, ^3J(C,P) = 1.1 Hz, 1 C, 6-C/C_6H_3], 124.9 [d, ^2J(C,P) = 15.0 Hz, 1 C, 1-C/C_5H_3OP], 125.8 [d, ^1J(C,P) = 15.5 Hz, 1 C, 2-C/C_6H_3], 125.9 (s, 1 C, 5-C/C_6H_3), 127.5–128.8 (m, 24 C, *m*-C_6H_5 and *p*-C_6H_5), 130.3 (s, 1 C, 3-C/C_6H_3), 132.6 [d, ^2J(C,P) = 19.0 Hz, 2 C, *o*-C_6H_5], 133.0 [d, ^2J(C,P) = 19.4 Hz, 2 C, *o*-C_6H_5], 133.3 [d, ^2J(C,P) = 20.6 Hz, 2 C, *o*-C_6H_5], 133.8 [d, ^2J(C,P) = 21.5 Hz, 2 C, *o*-C_6H_5], 134.0 [d, ^2J(C,P) = 21.8 Hz, 2 C, *o*-C_6H_5], 134.3 [d, ^2J(C,P) = 20.7 Hz, 2 C, *o*-C_6H_5], 134.58 [d, ^2J(C,P) = 20.8 Hz, 2 C, *o*-C_6H_5], 134.63 [d, ^2J(C,P) = 21.3 Hz, 2 C, *o*-C_6H_5], 137.0 [d, ^1J(C,P) = 12.0 Hz, 1 C, *i*-C_6H_5], 137.2 [d, ^1J(C,P) = 12.8 Hz, 1 C, *i*-C_6H_5], 137.4 [d, ^1J(C,P) = 11.7 Hz, 1 C, *i*-C_6H_5], 137.6 [dd, ^1J(C,P) = 9.9 Hz, ^4J(C,P) = 5.3 Hz, 1 C, *i*-C_6H_5], 137.9 [dd, ^1J(C,P) = 10.3 Hz, ^4J(C,P) = 4.8 Hz, 1 C, *i*-C_6H_5], 138.5 [d, ^1J(C,P) = 12.4 Hz, 1 C, *i*-C_6H_5], 138.6 [d, ^1J(C,P) = 9.0 Hz, 1 C, *i*-C_6H_5], 139.0 [d, ^1J(C,P) = 9.2 Hz, 1 C, *i*-C_6H_5], 144.6 (s, 1 C, 4-C/C_6H_3), 157.1 [d, ^2J(C,P) = 16.6 Hz, 1 C, 1-C/C_6H_3] ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = –15.1 [d, ^6J(P,P) = 6.9 Hz, 1 P, C_6H_3P], –23.9 [d, ^3J(P,P) = 96.4 Hz, 1 P, $C_5H_3P_2$], –24.7 [d, ^6J(P,P) = 6.9 Hz, 1 P, C_5H_3OP], –25.5 [d, ^3J(P,P) = 96.4 Hz, 1 P, $C_5H_3P_2$] ppm. IR (NaCl): $\tilde{\nu}$ = 3068, 3053, 3001 (=C–H), 2960, 2925, 2868 (CH_3), 1585 (C=C), 1248 (=C–O–C), 908, 824, 739, 696 (=C–H) cm^{-1}. HRMS: *m*/*z*: calcd. for $C_{68}H_{58}FeOP_4$: 1071.2862; found 1071.2839 $[M + H]^+$.

Single-Crystal X-ray Diffraction Analysis: Crystal data for **3a-Se**, **4a**, and **5a-Se$_3$** are summarized in Table 4. Data were collected with an Oxford Gemini S diffractometer at 100 K using Mo-K_α (λ = 0.71073 Å for **3a-Se**) and Cu-K_α (λ = 1.54184 Å for **4a**, **5a-Se$_3$**) radiation. The structures were solved by direct methods and refined by full-matrix least-square procedures on F^2.[31] All non-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions.

CCDC-760050 (for **3a-Se**), -760051 (for **4a**), and -760052 (for **5a-Se$_3$**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for Suzuki Cross-Coupling: An oven-dried Schlenk tube was charged with $[Pd_2(dba)_3]$, **3** [Pd/P = 1:2 (n/n)], boronic acid (1.5 mmol, 1.5 equiv.), powdered, anhydrous K_3PO_4 (637 mg, 3.0 mmol, 3.0 equiv.), and acenaphthene (154 mg, 1.0 mmol) as internal standard. The Schlenk tube was capped with a rubber septum, evacuated and refilled with argon. This sequence was repeated three times. Dry toluene (2 mL) was added through the septum with a syringe and the resulting mixture was stirred at room temperature for 5 min. The aryl halide (1.0 mmol, 1.0 equiv.) was added with a syringe (solid aryl halides were added during the initial charge). The reaction mixture was heated at the given temperature with vigorous stirring for 24 h. After cooling to room temperature, the reaction mixture was diluted with water (25 mL) and extracted with diethyl ether (3 × 25 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica (diethyl ether).

For reactions conducted at low catalyst loadings (≤0.5 mol% Pd) stoichiometric solutions of $[Pd_2(dba)_3]$ and **3** in toluene were prepared and were added to the Schlenk tube instead of the solvent.

Supporting Information (see also the footnote on the first page of this article): Full experimental details as well as ^1H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra for all compounds.

Table 4. Crystal and intensity collection data for **3a-Se**, **4a**, and **5a-Se$_3$**.

	3a-Se	**4a**	**5a-Se$_3$**
Formula weight	597.35	702.55	1123.59
Chemical formula	$C_{32}H_{31}FeOPSe$	$C_{44}H_{40}Fe_2OP_2$	$C_{56}H_{49}FeOP_3Se_3$
Crystal system, space group	monoclinic, $P2_1/c$	orthorhombic, $Pna2_1$	monoclinic, $C2/c$
a [Å]	10.3138(2)	21.2970(2)	21.4815(10)
b [Å]	30.3315(7)	9.68120(10)	12.3484(11)
c [Å]	8.4704(2)	17.2355(2)	38.2575(13)
α, β, γ [°]	90.0, 91.432(2), 90.0	90.0, 90.0, 90.0	90.0, 103.853(2), 90.0
V [Å^3]	2648.99(10)	3553.62(6)	9853.1(10)
$\rho_{calcd.}$ [g cm^{-3}]	1.498	1.313	1.515
$F(000)$	1224	1472	4528
Crystal dimensions [mm]	0.20 × 0.20 × 0.20	0.30 × 0.25 × 0.20	0.20 × 0.20 × 0.05
Z	4	4	8
Max., min. transmission	0.658, 0.673	1.000, 0.659	1.000, 0.650
μ [mm^{-1}]	2.028	4.508	6.212
θ [°]	2.81–29.06	4.15–62.50	4.16–61.99
Index ranges	$-12 \le h \le 12$	$-24 \le h \le 24$	$-24 \le h \le 24$
	$-37 \le k \le 37$	$-10 \le k \le 11$	$-12 \le k \le 14$
	$-10 \le l \le 10$	$-19 \le l \le 19$	$-43 \le l \le 43$
Total/unique reflections	32950/5198	14838/5020	22453/7681
Data/restraints/parameters	5198/0/325	5020/1/433	7681/0/577
R_{int}	0.0343	0.0367	0.0571
R_1, wR_2 [$I \ge 2\sigma(I)$][a]	0.0260, 0.0617	0.0274, 0.0665	0.0588, 0.1565
R_1, wR_2 (all data)	0.0332, 0.0630	0.0296, 0.0670	0.0795, 0.1714
Goodness-of-fit (S) on F^2 [b]	1.034	0.981	1.125
Largest diff. peak, hole [e Å^{-3}]	0.442, –0.355	0.268, –0.221	1.054, –1.430
Absolute structure parameter[32]	–	–0.001(3)	–

[a] $R_1 = \frac{\sum_{hkl}\left\|F_o\right|-\left|F_c\right\|}{\sum_{hkl}\left|F_o\right|}$, $wR_2 = \sqrt{\frac{\sum_{hkl} w\left(F_o^2 - F_c^2\right)^2}{\sum_{hkl} w\left(F_o^2\right)^2}}$, $w = \frac{1}{\sigma^2\left(F_o^2\right) + (a \cdot P)^2 + b \cdot P}$, $P = \frac{\max\left(0, F_o^2\right) + 2 \cdot F_c^2}{3}$.

[b] $S = \sqrt{\frac{\sum_{hkl} w\left(F_o^2 - F_c^2\right)^2}{m - n}}$, m = number of reflections, n = parameters used.

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