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Anionic Phospho-Fries Rearrangement at Ferrocene: One-Pot Approach to P,O-Substituted Ferrocenes

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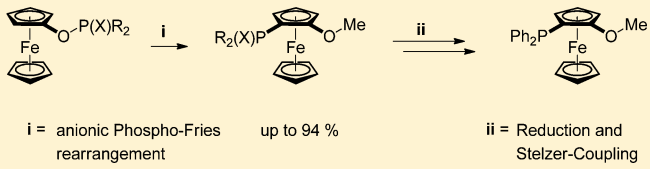
Supporting Information

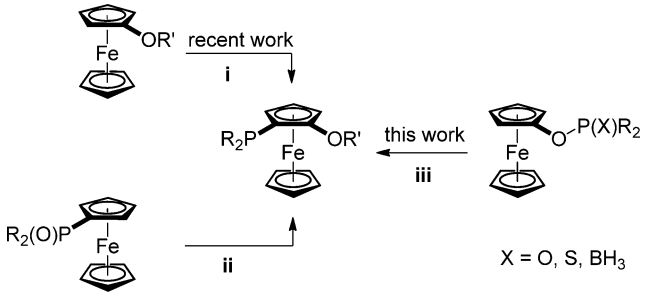
ABSTRACT: For the first time the anionic phospho-Fries rearrangement has been successfully applied in ferrocene chemistry, giving access to 1,2-P,O-substituted ferrocenes. The 1,3 (O → C)-migration occurs at ferrocenyl phosphates, thiophosphates, phosphite−borane adducts, and phosphinates by treatment with a base such as lithium diisopropylamide at low temperature, whereas the highest yields were obtained starting from diethylferrocenyl phosphate. Complete reduction of the phosphonate to a primary phosphine and subsequent Stelzer P,C cross coupling allowed the synthesis of Fe(η^5-C_5H_3-2-OMe-PPh_2)(η^5-C_5H_5) (**1**). The qualification of **1** as a supporting ligand in palladium-catalyzed Suzuki−Miyaura C,C couplings has been proven by the synthesis of sterically congested tri-ortho-substituted biaryls under mild reaction conditions in good to excellent yields.



INTRODUCTION

Planar-chiral ferrocenes are undoubtedly of major importance in asymmetric catalytic transformations in academia as well as in industry.[1] Most frequently their synthetic methodology relies on the ortho-directed metalation of substituted ferrocenes followed by the addition of an electrophile.[2,3] Just a few of these ortho-directing groups contain a heteroatom directly bonded to ferrocene, thus limiting the diversity of accessible ferrocenes carrying two heteroatoms in 1,2-positions. The synthesis of 1,2-P,O-substituted ferrocenes can be realized by ortho-directed metalation starting either from ferrocenyl ethers (Scheme 1, path i) or ferrocenyl phosphine oxides (path ii). The first path suffers from the formation of several byproducts due to di- and polymetalation of ferrocenyl aryl ethers, requiring an elaborate purification,[4] while for the respective alkyl derivatives lithiation occurs almost exclusively at the heretofore unsubstituted cyclopentadienyl ring.[4,5] The small number of oxygen electrophiles not affecting the ferrocene backbone or the questionable success of an Ullman-type coupling limits the use of ferrocenyl phosphine oxides[6,7] as starting materials for this approach, which has therefore not been realized yet. In contrast, intramolecular transformations, e.g. anionic hetero-Fries or Fries-like rearrangements, would allow the straightforward synthesis of such metallocenes; however, the scope of this reaction has been scarcely explored, as there are only three reports in ferrocene chemistry so far.[5c,8] In principle, it should be possible to access 1,2-P,O-substituted ferrocenes exerting an anionic phospho-Fries rearrangement (Scheme 1, path iii), circumventing difficulties in the synthesis of these molecules via the ortho-directed metalation of ferrocenyl ethers.

Scheme 1. Different Pathways for the Synthesis of 1,2-P,O-Substituted Ferrocenes



Recently, we demonstrated that P,O-ferrocene ligands show high activities in the synthesis of sterically congested biaryls via Suzuki−Miyaura C,C couplings.[3,4a] We assume that the ferrocene substitution pattern represents a promising structural motif for this challenging catalytic transformation. Herein, we report for the first time on an anionic phospho-Fries rearrangement at ferrocene as the key step in the preparation of 1,2-P,O-substituted ferrocenes and their successful application as ligands in the synthesis of tri-ortho-substituted biaryls.

RESULTS AND DISCUSSION

Accidentally discovered by Melvin in 1981,[9] the anionic phospho-Fries rearrangement is a well-established protocol for access to phenyl-based phosphonates and related compounds.[10] It was used, for example, for the preparation of chiral binol derivatives for asymmetric catalysis[11] and is in consideration for the synthesis of natural product analogues.[12] The 1,3 (O → C)-migration is usually base-induced, requiring deprotonation at the ortho position. Depending on the base as

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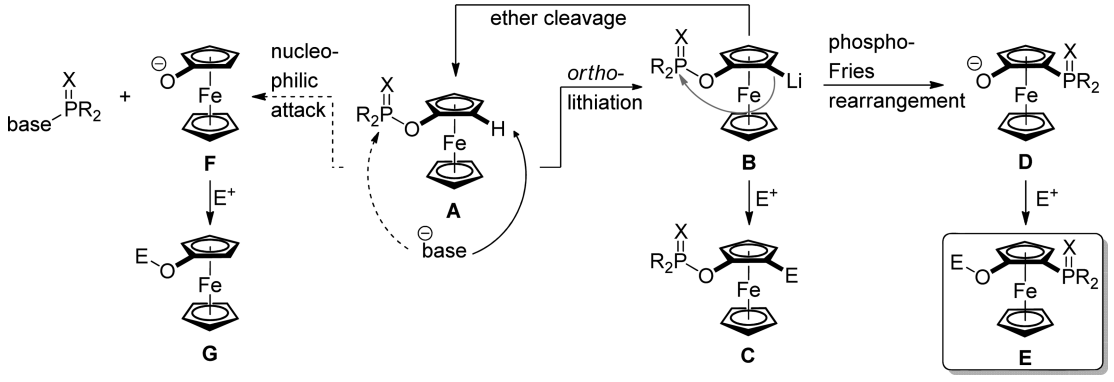
Scheme 2. Possible Reactions of Phosphorous-Ferrocenolates Treated with a Base and Subsequently with an Electrophile



well as the substituents X and R at the phosphorus atom (Scheme 2), ortho-directed metalation at ferrocene (**B**) or a nucleophilic attack at the phosphorus atom (**F**) may occur. Without doubt this process requires the use of a sterically hindered, non-nucleophilic base. In contrast, no clear conclusion regarding X and R can be drawn, as electron-withdrawing substituents facilitate the deprotonation of the ferrocene as well as a nucleophilic attack at phosphorus. The different ring sizes of ferrocene and benzene as well as the different C−C bond lengths,[13] resulting in an increased separation of two substituents at the 1,2-positions, should decrease the rate of the Fries rearrangement at ferrocene-based compounds and might therefore require a higher reaction temperature. However, lithiated ferrocenes exhibit a lower stability in comparison to corresponding benzene derivatives regarding ether cleavage,[14] which makes strict temperature control necessary. Otherwise, ferrocene **A** will (seemingly) be converted incompletely or undesired **C** may be formed to a greater extent (Scheme 2).

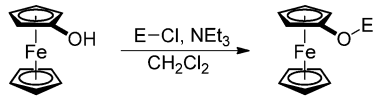
The ferrocenolato P(III) and P(V) compounds **4**−**10** were synthesized starting from ferrocenol (**3**) (Table 1).[15] The organometallic analogue of phenol was reacted with the respective chlorophosphorous derivatives (Table 1) in the presence of triethylamine. The ferrocenolato P(III) compounds were additionally either treated with [BH_3·thf] (Table 1, entry 4) or oxidized using H_2O_2 (Table 1, entry 6) or elemental sulfur (entry 7), respectively. Except for the less electrophilic thio derivative **6** (entry 3), the products can typically be isolated in good to excellent yields.

When a solution of phosphate **4** in tetrahydrofuran was treated at temperatures below −40 °C for 4 h with 2 equiv of freshly prepared LDA (lithium diisopropylamide) with subsequent addition of excess dimethyl sulfate, almost all starting material could be recovered, strongly indicating that no ortho-directed lithiation took place. At −30 °C, however, disubstituted ferrocene **12** could be isolated in 94% yield as the only product (Scheme 3).

The absences of phosphate **4** and an ortho-methylated ferrocene (Scheme 2, **C**) indicate that the rate of the anionic phospho-Fries rearrangement is sufficiently high under these conditions.[10,17] Replacement of the P═O oxygen atom by a BH_3 protecting group decreases the yield for ferrocene **14** to 37%. The recovery of only 31% of the starting material may be due to partial decomposition during the reaction. Thiophosphate **6** gives under these conditions only recovered starting material. If the stronger base ^{s}BuLi is used at −30 °C, however, thiophosphonate **13** can be isolated in 50% yield. Running this reaction at 0 °C decreases the yield to 11% (35% recovered starting material).

Replacement of LDA by the Simpkins base (+)-bis[(*R*)-1-phenylethyl]amine in the rearrangement of **4** resulted in a very low enantioenrichment (<5% ee) of phosphonate **12**, as

Table 1. Reaction of Ferrocenol (3) with Different Phosphorous Electrophiles to Afford 4−10



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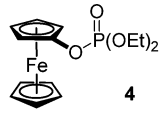
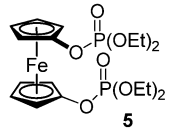
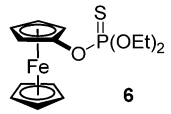
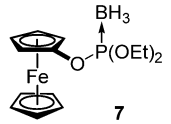
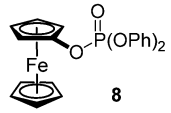
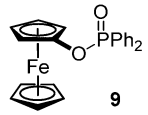
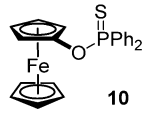
Entry	E–Cl	Product	Yield
1	ClP(O)(OEt)$_2$	 **4**	90 %
2 [a]	ClP(O)(OEt)$_2$	 **5**	60 %
3	ClP(S)(OEt)$_2$	 **6**	31 %
4 [b]	Cl(OEt)$_2$	 **7**	76 %
5	ClP(O)(OPh)$_2$	 **8**	62 %
6 [c]	ClPPh$_2$	 **9**	85 %
7 [d]	ClPPh$_2$	 **10**	95 %

[a] 1,1′-Ferrocenediol **11**[15,16] was used instead of **3**. [b] [BH_3·thf] was added. [c] H_2O_2 was added. [d] Sulfur was added.

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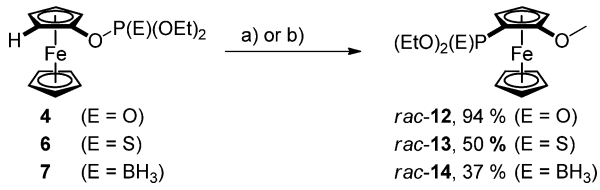
Scheme 3. Anionic Phospho-Fries Rearrangement of Ferrocenylphosphate 4, Ferrocenylhiophosphate 6, and Borane Adduct 7[a]



4 (E = O) *rac*-**12**, 94 % (E = O)
6 (E = S) *rac*-**13**, 50 % (E = S)
7 (E = BH_3) *rac*-**14**, 37 % (E = BH_3)

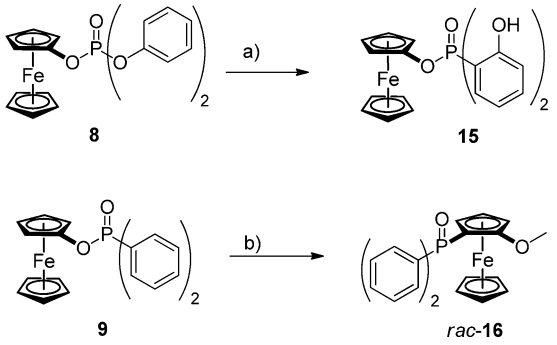
[a]Legend: (a) E = O, BH_3, (1) LDA, thf, −30 °C, 4 h, (2) Me_2SO_4 or MeI; (b) E = S, (1) ^{s}BuLi, thf, −30 °C, 4 h, (2) MeI.

evinced by chiral HPLC. This is in accordance with other ortho-directed lithiations at ferrocene, where a mere change of the base without further adoptions of the reaction conditions had only a small effect.[8b,18]

The formation of the phospho-Fries rearrangement products **12**−**14** can be unambiguously proven using NMR spectroscopy. On the one hand, the resonance in the $^{31}P\{^1H\}$ NMR spectra is shifted downfield from −5.4 (**4**), 63.8 (**6**), and 128.2 ppm (**7**) to 36.4 (**12**), 89.6 (**13**), and 135.4 ppm (**14**), respectively. Additionally, a singlet for the methoxy group for all three compounds was observed at 3.7 ppm (**12**,[19] **13**, **14**) in the ^1H NMR spectra (Supporting Information). Due to the established planar chirality at ferrocene the two ethoxy moieties become diastereotopic, resulting in a doubling of all their resonances in ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. The C−P ipso-carbon atom gives a doublet in the $^{13}C\{^1H\}$ NMR spectra at 59.2 ppm with a large $^1J_{C,P}$ coupling constant of 213 Hz (**12**), in agreement with the values for similar compounds.[20]

Replacing the ethoxy (**4**) by phenoxy substituents in ferrocenyl phosphonate **8** opens two different reaction pathways, as an anionic phospho-Fries rearrangement can take place at ferrocene and at the benzene rings (Scheme 4).

Scheme 4. Anionic Phospho-Fries Rearrangement of Phenyl-Substituted Ferrocenylphosphate 8 and Phosphinate 9[a]



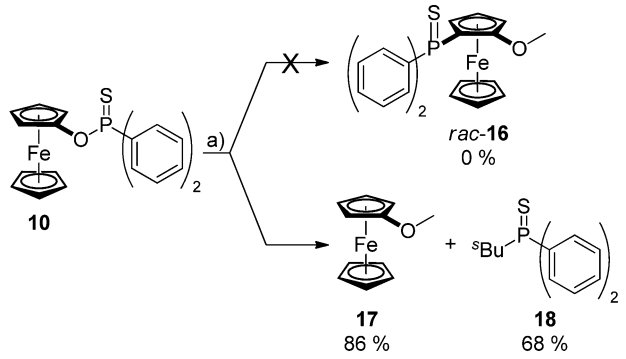
[a]Legend: (a) (1) LDA, thf, −40 °C, 4 h, (2) MeI, 8%; (b) (1) LDA, −30 °C, 4 h, (2) MeI, 8%.

When phosphate **8** was treated with LDA at −40 °C, double phospho-Fries rearrangement was observed at the two benzene moieties, and phosphinate **15** could be isolated in 8% yield. Although further products were formed, as evinced by $^{31}P\{^1H\}$ NMR spectroscopy, no additional compound could be either isolated in pure form or identified.

This result discouraged us from investigating this transformation further. Likewise, phosphinate **9** gave a complex product mixture when similar reaction conditions were applied (Scheme 4), from which desired phosphine oxide **16** was isolated in 8% yield. However, for this transformation partial nucleophilic attack of the base occurred at the phosphorus atoms, which results in the formation of ferrocenyl methyl ether (**17**; 16%).

In the case of the corresponding thiophosphinate **10**, LDA turned out to be a too weak base, as the starting material could be recovered completely. The stronger base ^{s}BuLi exclusively resulted in nucleophilic attack at the phosphorus atom, and hence only ferrocenyl methyl ether (**17**) and *sec*-butyldiphenylphosphane sulfide (**18**) were formed (Scheme 5). For compounds **10** and **18** single-crystal structures could be obtained (Figure SI1, Supporting Information).

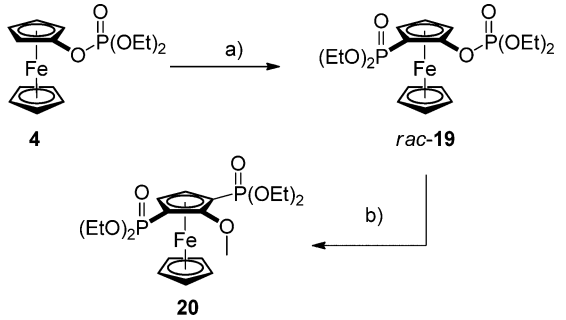
Scheme 5. Reaction of Thiophosphinate 10 with ^{s}BuLi[a]



[a]Legend: (a) (1) ^{s}BuLi, −30 °C, 4 h, (2) MeI.

Two subsequent anionic phospho-Fries rearrangements could be performed when the intermediate of the reaction of phosphate **4** and LDA was quenched with chlorodiethylphosphate to give ferrocene **19** (Scheme 6). Both transformations

Scheme 6. Anionic Phospho-Fries Rearrangement of Ferrocenylphosphate 4 and Intermediately Formed Phosphate 19[a]



[a]Legend: (a) (1) LDA, thf, −20 °C, 4 h, (2) $ClP(O)(OEt)_2$, 33%; (b) (1) LDA, thf, −30 °C, 4 h, (2) MeI, 21%.

proceeded as expected; no further ferrocene compounds could be identified. The considerably lower yields in comparison to that for the synthesis of **12** (Scheme 3) are due to the lower stabilities of **19** and **20**; partial decomposition has been observed for both compounds even after purification. It is interesting to note that the conversion of ferrocene **19** into bisphosphonate **20** clearly simplified the NMR spectra, due to the higher symmetry of the latter compound. For the rearrangement of 1,1′-diphosphate **5** a complex mixture of

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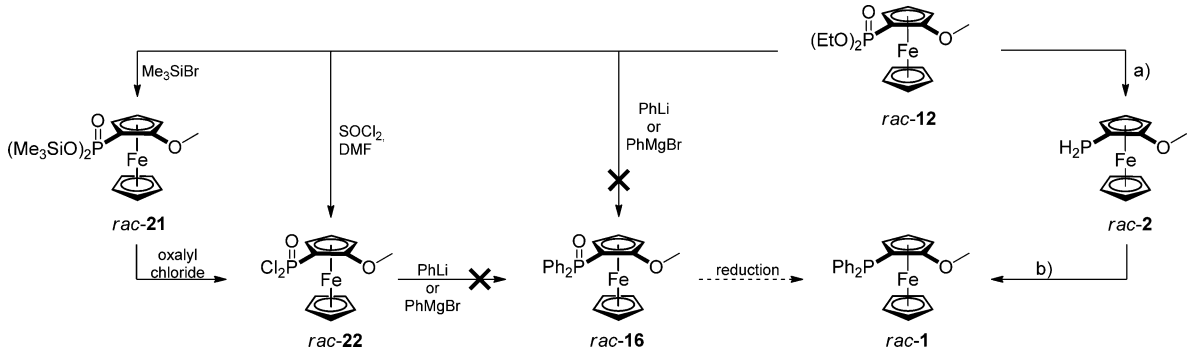
Scheme 7. Possible Pathways for the Transformation of Phosphonate 12 into Phosphine 1[a]



[a]Legend: (a) (1) Li[AlH_4] (4 equiv), Me_3SiCl (4 equiv), thf, 25 °C, (2) **12**, 40 °C, 12 h, 99%; (b) PhI (2 equiv), K_3PO_4 (2 equiv), [Pd(dppf)Cl_2] (4 mol %), toluene, 110 °C, 12 h, 52%.

several phosphorus-containing molecules was obtained, from which no product could be identified or isolated in pure form.

The transformation of phosphonate **12** into phosphine **1**, which has been considered as auxiliary ligand for palladium in Suzuki C,C cross-couplings, was thoroughly investigated, as outlined in Scheme 7. The attempted direct conversion of phosphonate **12** into phosphine oxide **16** by treatment with phenylmagnesium bromide or phenyllithium gave only unreacted starting materials. Likewise, the conversion into the dichlorophosphonate intermediate **22**[21−23] with subsequent introduction of the phenyl moieties[17e,24] in a "one-pot" reaction turned out to be unsuccessful in the case of ferrocene **12**. In contrast, reduction of this phosphonate in the presence of an excess of Li[AlH_4] and trimethylsilyl chloride followed by acidic workup under anaerobic conditions yielded phosphine **2** quantitatively.[24−27] Successive palladium-catalyzed Stelzer P,C cross-coupling[28] was chosen for the conversion of the primary phosphine into the title compound **1**. As this transformation has, to the best of our knowledge, never been applied in ferrocene chemistry, the coupling of ferrocenylphosphine (**25**) with phenyl iodide in presence of [$Pd(PPh_3)_4$] was selected as a test reaction. Optimization of the reaction conditions furnished diphenylphosphinoferrocene (**26**) in up to 72% yield (Table SI1, Supporting Information). Application onto 1,2-disubstituted ferrocene **2**, however, gave ferrocenyl methyl ether (**17**) as the only product, which was formed due to a P,C_{Cp} bond cleavage during the catalytic transformation.[29] The utilization of 1,1′-bis(diphenylphosphino)ferrocene (dppf) as a sterically demanding, chelating ligand for palladium and avoidance of an excess of phenyl iodide circumvented this side reaction, giving access to the desired ferrocene **1** in 52% yield.[30]

Single crystals of ferrocene **1** suitable for X-ray diffraction studies were obtained by crystallization from boiling *n*-hexane. The molecular structure along with important bond distances and bond and torsion angles is shown in Figure 1.

Phosphine **1** crystallizes in the monoclinic space group $P2_1/c$. The solid-state structure unambiguously confirms the 1,2-substitution pattern of the metallocene backbone, as already deduced from NMR spectroscopy (vide supra). The ferrocenyl substituent adopts an eclipsed conformation; as expected, the phosphorus and oxygen atoms are both located in the plane of the cyclopentadienyl ring (rms deviation 0.0008 Å, distance of P1 −0.0010(3) Å and distance of O1 −0.079(3) Å). The methyl and one phenyl group point in opposite directions; consequently, the free electron pairs are directed into the vacant space between the two substituents, which in principle

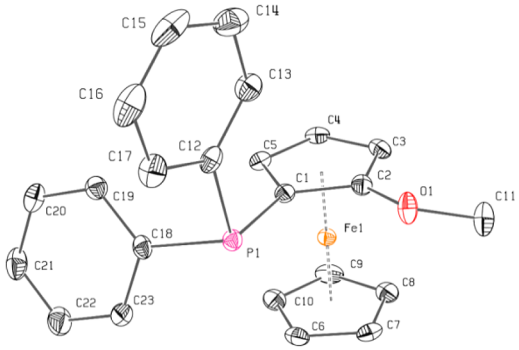


Figure 1. ORTEP diagram (50% probability level) of the molecular structure of *rac*-**1** with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg): C1−P1 1.8160(17), C12−P1 1.8388(18), C18−P1 1.8395(18), C2−O1 1.366(2), C11−O1 1.430(2), D1−Fe1 1.6443(2), D2−Fe1 1.6515(2); D1−Fe1−D2 179.10(2); P1−C1−C2−C3 −179.70(12), C5−C1−P1−C12 −90.73(17), C5−C1−P1−C18 11.54(17), C5−C1−C2−O1 176.16(15), C3−C2−O1−C11 −24.6(2), C1−D1−D2−C6 1.43(12), C2−D1−D2−C7 1.70(12). D1 denotes the centroid of C_5H_3; D2 denotes the centroid of C_5H_5.

should allow for a chelating complexation of a suitable transition metal, e.g. palladium.

P,O-ferrocenes show high activities in the synthesis of sterically congested biaryls via Suzuki−Miyaura C,C couplings, as demonstrated recently.[3,4] This prompted us to investigate the performance of phosphine **1** as a ligand in the palladium-catalyzed synthesis of racemic tri-ortho-substituted biaryls, starting from 1-bromonaphthalenes **23** and ortho-substituted phenylboronic acids **24** (Figure 2).

At a catalyst concentration of 0.5 mol % and a reaction temperature of 70 °C the respective biaryls **25** could typically be isolated in good to excellent yields (Figure 2). A slightly higher temperature was required to obtain biphenyl **25g** quantitatively. For the sterically more demanding 9-phenanthryl derivative **25h** only a moderate yield of 43% was achieved.[31]

These results demonstrate that P,O-substituted ferrocenes, accessible through an anionic phospho-Fries rearrangement, are catalytically active for the synthesis of axial-chiral biaryls via Suzuki−Miyaura C,C couplings in the presence of palladium. Enantioenriched phosphine **1**, which enables the performance of these biaryl couplings in an atropselective manner, may be accessible by exerting a stereoselective ortho-directed metal-

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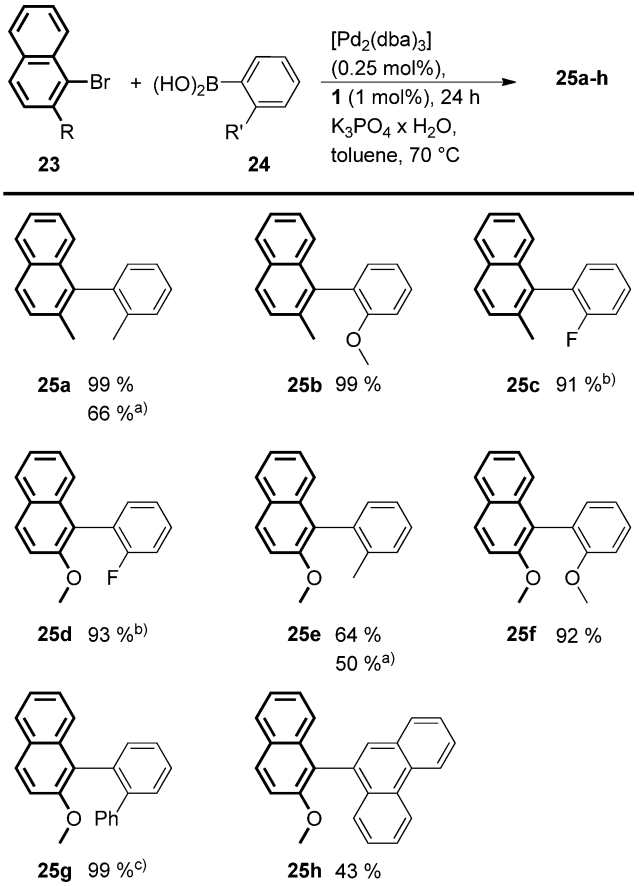

Figure 2. Application of phosphine **1** to the palladium-catalyzed synthesis of tri-ortho-substituted biaryls via Suzuki–Miyaura C,C couplings. Legend: (a) 50 °C; (b) $K_3PO_4 \cdot 3H_2O$; (c) 100 °C. Yields are based on isolated material; reaction times were not minimized.

ation of ferrocenyl phosphates; this will be investigated in due course.

The anionic phospho-Fries rearrangement was successfully applied in ferrocene chemistry for the first time, giving straightforward access to planar-chiral 1,2-P,O-disubstituted derivatives. Treatment of diethylferrocenylphosphate (**4**) with LDA and subsequent *O*-methylation yielded diethyl(2-methoxyferrocenyl)phosphonate (**12**) as the only product. 1,3 (O → C)-Migrations proceeded at structurally related ferrocenes as well; however, for the corresponding phosphite–borane adduct (**7**) a lower yield was observed and diethylferrocenylthiophosphate (**6**) required the use of the stronger base ^{s}BuLi. In contrast, the related diphenylphosphate **8**, phosphinate **9**, and thiophosphinate **10** are essentially unsuited for an anionic phospho-Fries rearrangement, as side reactions occur, including but not limited to a nucleophilic attack of the base at the phosphorus atom.

Planar-chiral diethyl(2-methoxyferrocenyl)phosphonate (**12**) was further converted into Fe(η^5-C_5H_3-2-OMe-PPh_2)(η^5-C_5H_5) (**1**) by complete reduction of the phosphonate moiety and subsequent P,C cross-coupling (Stelzer coupling). The qualification of phosphine **1** as a supporting ligand in palladium-catalyzed Suzuki–Miyaura C,C couplings has been proven by the synthesis of sterically congested tri-ortho-substituted biaryls under mild reaction conditions in good to excellent yields.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under an argon or nitrogen atmosphere using standard Schlenk techniques. Reaction vessels were heated at reduced pressure with a heat gun and flushed with argon. This procedure was repeated three times. If necessary, solvents were deoxygenated by standard procedures. For column chromatography either silica with a particle size of 40–60 μm (230–400 mesh (ASTM), Fa. Macherey-Nagel) or alumina with a particle size of 90 μm was used.

Instruments. FT IR spectra were recorded between NaCl crystals or as KBr pellets. NMR spectra (500.3 MHz for ^{1}H, 125.7 MHz for $^{13}C\{^1H\}$, 160.5 MHz for $^{11}B\{^1H\}$ and 202.5 MHz for $^{31}P\{^1H\}$ spectra) are reported with chemical shifts in δ (ppm) downfield from tetramethylsilane with the solvent as reference signal (^{1}H NMR, $CHCl_3$ δ 7.26, C_6HD_5 δ 7.16; $^{13}C\{^1H\}$ NMR, $CDCl_3$ δ 77.00, C_6D_6 δ 128.06; $^{31}P\{^1H\}$ NMR, standard external relative to 85% H_3PO_4 δ 0.0, $P(OMe)_3$ δ 139.0).

Single-Crystal X-ray Diffraction Analysis. Single crystals of **1**, **10**, and **18** suitable for X-ray diffraction analysis were obtained by recrystallization from *n*-hexane at ambient temperature. Data were collected at 100 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2.[32] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the treatment of the hydrogen atom positions.

The HPLC measurements were performed with an UV detector operating at 245 nm equipped with a Chiralcel OD-H column (4.6 × 250 mm) using a 9/1 (v/v) hexane/2-propanol mixture (0.5 mL/min) as the solvent. Retention times *t* are reported in minutes.

Reagents. Tetrahydrofuran was purified by distillation from sodium/benzophenone ketyl and dichloromethane from calcium hydride.

All starting materials were obtained from commercial suppliers and used without further purification. Acetoxyferrocene,[15] ferrocenol,[8,15,33] 1,1-bis(acetoxy)ferrocene,[15] and 1,1′-ferrocenediol[15] were prepared according to published procedures.

Synthesis of (2-Methoxyferrocenyl)diphenylphosphane (1). (2-Methoxyferrocenyl)phosphine (**2**; 480 mg, 1.94 mmol), iodobenzene (0.43 mL, 3.90 mmol), K_3PO_4 (825 mg, 3.90 mmol), and [(dppf)$PdCl_2$] (55 mg, 4 mol %) were dissolved in 6 mL of toluene. The reaction mixture was degassed and stirred for 18 h at 110 °C. After the mixture was cooled to ambient temperature, water (30 mL) was added in a single portion and the mixture was extracted with diethyl ether (3 × 20 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (column size 2 × 6 cm, silica) using a 7/3 (v/v) hexane/CH_2Cl_2 mixture to give **1** (R_f = 0.14) as an orange solid. Yield: 410 mg (1.01 mmol, 52% based on **2**). Anal. Calcd for $C_{23}H_{21}FeOP$ (400.23): C, 69.02; H, 5.29. Found: C, 68.48; H, 5.28. Mp: 147 °C. ^{1}H NMR ($CDCl_3$, δ): 3.50 (ddd, $^3J_{H,H}$ = 2.5 Hz, $^4J_{H,H}$ = 1.4 Hz, $^3J_{H,P}$ = 1.3 Hz, 1H, *o*-PPh_2), 3.67 (s, 3H, OCH_3), 3.98 (dpt, $^4J_{H,P}$ = 0.5 Hz, $^3J_{H,H}$ = 2.5 Hz, 1H, *m*-OCH_3), 4.11 (s, 5H, C_5H_5), 4.26 (ddd, $^4J_{H,P}$ = 1.5 Hz, $^4J_{H,H}$ = 1.4 Hz, $^3J_{H,H}$ = 2.5 Hz, 1H, *o*-OCH_3), 7.24–7.29 (m, 5H, *o,m*-Ph), 7.36–7.39 (m, 3H, *o,m*-Ph), 7.53–7.58 (m, 2H, *p*-Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 54.7 (d, $^3J_{C,P}$ = 2.6 Hz, *o*-OCH_3), 58.0 (s, OCH_3), 63.1 (s, *m*-OCH_3), 65.0 (d, $^1J_{C,P}$ = 7.6 Hz, C–PPh_2), 65.7 (d, $^2J_{C,P}$ = 2.0 Hz, *o*-PPh_2), 69.3 (s, C_5H_5), 127.8 (s, *p*-Ph), 128.05 (d, $^3J_{C,P}$ = 6.0 Hz, *m*-Ph), 128.10 (d, $^3J_{C,P}$ = 7.7 Hz, *m*-Ph), 129.0 (s, *p*-Ph), 131.1 (d, $^2J_{C,P}$ = 18.0 Hz, C–OCH_3), 132.3 (d, $J_{C,P}$ = 18.4 Hz, *o*-Ph), 134.9 (d, $J_{C,P}$ = 21.1 Hz, *o*-Ph), 137.3 (d, $^1J_{C,P}$ = 8.7 Hz, C^i-Ph), 139.6 (d, $^1J_{C,P}$ = 11.1 Hz, C^i-Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −23.97 (s). HRMS (ESI-TOF, *m/z*): calcd for $C_{23}H_{21}FeOP$ 400.0674, found 400.0754 $[M]^+$.

Crystal Data for **1**: $C_{23}H_{21}FeOP$, M = 400.22, monoclinic, $P2_1/c$, λ = 0.71073 Å, a = 8.1036(2) Å, b = 19.4551(4) Å, c = 12.1025(3) Å, β = 100.958(2)°, V = 1873.25(8) Å^3, Z = 4, ρ_{calcd} =1.419 Mg m^{-3}, μ = 0.899 mm^{-1}, T = 107.1(2) K, θ range 2.99–25.99°, 8695 reflections collected, 3655 independent reflections (R_{int} = 0.0240), R1 = 0.0275, wR2 = 0.0633 ($I > 2\sigma(I)$).

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Synthesis of (2-Methoxyferrocenyl)phosphine (2). In tetrahydrofuran (20 mL) an excess of $Li[AlH_4]$ (0.6 g, 16 mmol) was treated with trimethylchlorosilane (1.65 mL, 12.9 mmol) at −30 °C. After the suspension was stirred for 5 min, phosphonate **12** (645 mg, 1.83 mmol) was added dropwise. The mixture was slowly heated to 45 °C until gas evaporation was no longer detectable. Afterward, the oil bath was replaced by an ice bath. Acidification was realized by dropwise addition of oxygen-free H_2SO_4 (3 mL, ω = 30%). *Caution!* During the addition an immense gas emission occurs. The mixture was extracted three times with oxygen-free diethyl ether (3 × 20 mL) under an argon atmosphere. The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Phosphine **2** was obtained as an orange oil and subsequently used in further reactions (see above). Yield: 450 mg (1.82 mmol, 99% based on **12**). ^{1}H NMR ($CDCl_3$, δ): 3.62 (dd, $^1J_{H,P}$ = 202.6 Hz, $^2J_{H,H}$ = 12.6 Hz, 1H, PH), 3.70 (s, 3H, OCH_3), 3.81 (dd, $^1J_{H,P}$ = 207.8 Hz, $^2J_{H,H}$ = 12.6 Hz, 1H, PH), 3.94 (ptd, $^{3+4}J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 0.84 Hz, 1H, *o*-OCH_3), 4.01 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 1.4 Hz, $J_{H,H}$ = 1.4 Hz, 1H, *o*-PH_2), 4.15 (dd, $J_{H,H}$ = 2.6 Hz, $J_{H,H}$ = 1.4 Hz, 1H, *m*-OCH_3), 4.16 (s, 5H, C_5H_5).^{13}C{^{1}H} NMR ($CDCl_3$, δ, HMBC): 54.0 (d, $^3J_{C,P}$ = 0.86, *m*-OCH_3), 57.9 (s, OCH_3), 62.9 (d, $^3J_{C,P}$ = 5.0 Hz, *o*-OCH_3), 69.5 (s, C_5H_5), 70.0 (d, $^2J_{C,P}$ = 19.9 Hz, *o*-PH_2), 129.8 (C−OCH_3).[34] ^{31}P NMR ($CDCl_3$, δ): −159.9 (dd, $^1J_{H,P}$ = 202.6 Hz, $^1J_{H,P}$ = 207.8 Hz).

Synthesis of Ferrocenol (3).[8,15,33] Ferrocenylacetate[15] (1.00 g, 4.10 mmol) was dissolved in ethanol (30 mL), and 2 M oxygen-free aqueous KOH (2.5 mL, 5.00 mmol) was added with a syringe in a single portion. The reaction solution was heated to 70 °C and stirred for 15 min. After addition of 2 M oxygen-free aqueous HCl (2.5 mL, 5.00 mmol) in a single portion, all volatiles were removed under reduced pressure. The precipitate was dissolved in diethyl ether (30 mL) and filtered through a layer of Celite (5 cm). Subsequent removal of the solvent under reduced pressure gave **3** as an orange solid. Yield: 805 mg (4.00 mmol, 97% based on ferrocenylacetate).

Synthesis of *O,O*-Diethyl-*O*-ferrocenylphosphate (4). Ferrocenol (**3**; 1.00 g, 4.1 mmol) was dissolved in CH_2Cl_2 (30 mL). This solution was cooled to −30 °C, and NEt_3 (0.63 mL, 4.5 mmol) was added. After 5 min, *O,O*-diethylchlorophosphate (0.65 mL, 4.5 mmol) was added in a single portion with a syringe and the reaction solution was stirred overnight at ambient temperature. After removal of all volatiles, the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Column chromatography (column size 3.5 × 14.5 cm, alumina) using CH_2Cl_2 as the eluent afforded **4** as an orange oil. Yield: 1.032 g (3.05 mmol, 90% based on **3**). Anal. Calcd for $C_{14}H_{19}FeO_4P$ (338.12): C, 49.73; H, 5.66. Found: C, 49.86; H, 5.79. IR data (NaCl, ν/cm^{-1}): 3098 w, 2986 m, 2932 w, 2909 w, 2871 w, 1793 w, 1711 w, 1647 w, 1460 s, 1412 w, 1394 m, 1373 m, 1278 s, 1241 m, 1166 m, 1106 m, 1065 w, 1033 s, 959 s, 887 s, 820 s, 757 m, 640 m. ^{1}H NMR ($CDCl_3$, δ): 1.36 (td, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,P}$ = 0.9 Hz, 6H, CH_3), 3.88 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 2H, C_5H_4), 4.13−4.21 (m, 4H, CH_2), 4.25 (s, 5H, C_5H_5), 4.39 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 2H, C_5H_4).^{13}C{^{1}H} NMR ($CDCl_3$, δ): 16.1 (d, $^3J_{C,P}$ = 6.9 Hz, CH_3), 59.6 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 62.7 (s, C_5H_4), 64.3 (d, $^2J_{C,P}$ = 6.2 Hz, 2C, CH_2), 69.5 (s, C_5H_5), 117.7 (d, $^2J_{C,P}$ = 4.8 Hz, C_5H_4−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −5.4. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{14}H_{19}FeO_4P$ 338.0365, found 338.0367 $[M]^+$.

Synthesis of 1,1′-Bis(*O,O*-diethylphosphato)ferrocene (5). 1,1′-Ferrocenediol **11** was prepared in accordance with the method for ferrocenol[8,15,33] using 1,1′-diacetoxyferrocene[15] (655 mg, 2.2 mmol) and KOH (2.5 mL, 4.8 mmol) followed by HCl (2.5 mL, 4.8 mmol) addition. The resulting orange solid was subsequently treated with NEt_3 (0.60 mL, 4.8 mmol) and chlorodiethylphosphate (0.73 mL, 4.8 mmol) in CH_2Cl_2 at −30 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. After removal of all volatiles the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Purification was realized by column chromatography (column size 3 × 10 cm, silica) using a 3/1 (v/v) CH_2Cl_2/ethyl acetate mixture as the eluent. Product **5** was obtained as an orange oil. Yield: 635 mg (1.30 mmol, 60% based on **11**). ^{1}H NMR ($CDCl_3$, δ): 1.36 (td, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,P}$ = 1.0 Hz, 12H, CH_3), 3.99 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 4H, C_5H_4), 4.14−4.21 (m, 8H, CH_2), 4.46 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 4H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 16.1 (d, $^3J_{C,P}$ = 6.7 Hz, CH_3), 61.1 (d, $^3J_{C,P}$ = 3.8 Hz, *o*-C_5H_4), 64.4 (d, $^2J_{C,P}$ = 5.6 Hz, CH_2), 64.6 (s, *m*-C_5H_4), 118.0 (d, $^2J_{C,P}$ = 4.6 Hz, C_5H_4−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −5.4. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{18}H_{28}FeO_8P_2$ 490.0604, found 490.0633 $[M]^+$.

Synthesis of *O,O*-Diethyl-*O*-ferrocenylthiophosphate (6). Ferrocenol (**3**; 1.00 g, 4.1 mmol) was dissolved in CH_2Cl_2 (30 mL), cooled to −30 °C, and treated with NEt_3 (0.63 mL, 4.5 mmol) in a single portion. After 5 min, *O,O*-diethylchlorothiophosphate (0.71 mL, 4.5 mmol) was added with a syringe and the solution was stirred overnight at ambient temperature. After removal of all volatiles the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Column chromatography (column size 3.5 × 14.5 cm, silica) using toluene as the eluent afforded **6** as an orange oil. Yield: 450 mg (1.27 mmol, 31% based on **3**). IR data (NaCl, ν/cm^{-1}): 3095 m, 2982 s, 2931 w, 2904 w, 2867 w, 1629 w, 1452 s, 1390 m, 1371 m, 1352 w, 1236 s, 1162 m, 1105 m, 1025 s, 945 s, 885 s, 818 s. ^{1}H NMR ($CDCl_3$, δ): 1.35 (td, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,P}$ = 0.4 Hz, 6H, CH_3), 3.89 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 2H, *m*-C_5H_4), 4.13−4.22 (m, 4H, CH_2), 4.25 (s, 5H, C_5H_5), 4.40 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 2H, *o*-C_5H_4).^{13}C{^{1}H} NMR ($CDCl_3$, δ): 15.9 (d, $^3J_{C,P}$ = 7.4 Hz, CH_3), 60.4 (d, $^3J_{C,P}$ = 3.5 Hz, *o*-C_5H_4), 62.8 (s, *m*-C_5H_4), 64.9 (d, $^2J_{C,P}$ = 5.7 Hz, CH_2), 69.5 (s, C_5H_5), 117.5 (d, $^2J_{C,P}$ = 4.7 Hz, C_5H_4−O).^{31}P{^{1}H} NMR ($CDCl_3$, δ): 63.8. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{14}H_{19}FePSO_3$ 354.0136, found 354.0170 $[M]^+$.

Synthesis of *O,O*-Diethyl-*O*-ferrocenylphosphite−Borane (7). Ferrocenol (**3**; 728 mg, 3.60 mmol) was dissolved in CH_2Cl_2 (30 mL), cooled to −30 °C, and treated with NEt_3 (0.55 mL, 3.96 mmol) in a single portion. After 5 min, chlorodiethylphosphite (0.57 mL, 4.5 mmol) was added with a syringe and the solution was stirred for 12 h. Borane−tetrahydrofuran (4.00 mL, 3.95 mmol) was added, and stirring was continued for 12 h. After removal of all volatiles, the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Purification was realized by column chromatography (column size 3 × 16 cm, silica) using a 1/1 (v/v) hexane/toluene mixture as the eluent. Product **7** (R_f = 0.39) was obtained as an orange oil. Yield: 910 mg (2.70 mmol, 76% based on **3**). ^{1}H NMR (C_6D_6, δ): 1.06 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, CH_3), 3.92−4.03 (m, 4H, CH_2), 3.72 (pt, $^{3+4}J_{H,H}$ = 2.0 Hz, 2H, *m*-C_5H_4), 4.22 (s, 5H, C_5H_5), 4.46 (pt, $^{3+4}J_{H,H}$ = 2.0, 2H, *o*-C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6, δ): 16.1 (d, $^3J_{C,P}$ = 5.5 Hz, CH_3), 60.8 (d, $^3J_{C,P}$ = 2.8 Hz, *o*-C_5H_4), 63.1 (s, *m*-C_5H_4), 63.4 (d, $^2J_{C,P}$ = 3.1 Hz, CH_2), 70.0 (s, C_5H_5), 117.7 (d, $^2J_{C,P}$ = 4.3 Hz, C_5H_4−O). ^{11}B{^{1}H} NMR (C_6D_6, δ): −42.7 (d, $^1J_{B,P}$ = 92 Hz). ^{31}P{^{1}H} NMR (C_6D_6, δ): 128.2 (q, $^1J_{P,B}$ = 92 Hz). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{14}H_{22}BFeO_3P$ − BH_3 322.0416, found 322.0403 $[M - BH_3]^+$.

Synthesis of *O*-Ferrocenyl-*O,O*-diphenylphosphate (8). Ferrocenol (**3**; 1.080 g, 5.3 mmol) was dissolved in CH_2Cl_2 (30 mL), cooled to −30 °C, and treated with NEt_3 (0.81 mL, 5.8 mmol) in a single portion. After 5 min, *O,O*-diphenylchlorophosphate (1.2 mL, 5.9 mmol) was added with a syringe and the solution was stirred overnight at ambient temperature. After removal of all volatiles the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Column chromatography (column size 4 × 18 cm, alumina) using CH_2Cl_2 as the eluent afforded **8** as an orange solid. Yield: 1.45 g (3.3 mmol, 62% based on **3**). Anal. Calcd for $C_{22}H_{19}FeO_4P$ (434.04): C, 60.86; H, 4.41. Found: C, 60.86; H, 4.29. Mp: 67 °C. ^{1}H NMR ($CDCl_3$, δ): 3.91 (pt, $^{3+4}J_{H,H}$ = 2.0 Hz, 2H, *m*-C_5H_4), 4.22 (s, 5H, C_5H_5), 4.44 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 2H, *o*-C_5H_4), 7.18−7.27 (m, 6H, *o,p*-Ph), 7.36 (t, $^3J_{H,H}$ = 7.9 Hz, 4H, *m*-Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.8 (d, $^3J_{C,P}$ = 3.8 Hz, *o*-C_5H_4), 62.9 (s, *m*-C_5H_4), 69.6 (s, C_5H_5), 117.9 (d, $^2J_{C,P}$ = 5.4 Hz, C_5H_4−O), 120.1 (d, $^3J_{C,P}$ = 5.3 Hz, 2 Hz, *o*-Ph), 125.5 (s, *p*-Ph), 129.8 (s, *m*-Ph), 150.5 (d, $^2J_{C,P}$ = 7.4 Hz, Ph−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −16.9. HRMS

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(ESI-TOF, m/z): calcd for $C_{22}H_{19}FeO_4P$ 434.0365, found 434.0362 $[M]^+$.

Synthesis of *O*-Ferrocenyldiphenylphosphinate (9). Ferrocenol (**3**; 830 mg, 4.1 mmol) was dissolved in CH_2Cl_2 (30 mL), cooled to −30 °C, and treated with NEt_3 (0.63 mL, 4.5 mmol) in a single portion. After 5 min, chlorodiphenylphosphane (0.83 mL, 4.5 mmol) was added in a single portion with a syringe and the solution was stirred overnight at ambient temperature. Oxidation was realized by adding a H_2O_2 solution (0.40 mL, ω = 35%, 4.5 mmol), whereupon the reaction mixture turned slightly darker. After removal of all volatiles, the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Column chromatography (column size 4 × 18 cm, silica) using a 4/1 (v/v) CH_2Cl_2/ethyl acetate mixture as the eluent afforded **9** as a yellow solid. Yield: 1.41 g (3.5 mmol, 85% based on **3**). ^{1}H NMR ($CDCl_3$, δ): 3.80 (s, 2H, *m*-C_5H_4), 4.18 (s, 5H, C_5H_5), 4.30 (s, 2H, *o*-C_5H_4), 7.46 (td, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,P}$ = 3.6 Hz, 4H, *m*-Ph), 7.54 (t, $^3J_{H,H}$ = 6.9 Hz, 2H, *p*-Ph), 7.85 (dd, $^2J_{H,P}$ = 12.4 Hz, $^3J_{H,H}$ = 7.3 Hz, 4H, *o*-Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 60.3 (d, $^3J_{C,P}$ = 3.7 Hz, *o*-C_5H_4), 62.7 (s, *m*-C_5H_4), 69.5 (s, C_5H_5), 117.5 (d, $^2J_{C,P}$ = 6.7 Hz, C_5H_4−O), 128.5 (d, $^3J_{C,P}$ = 13.1 Hz, *m*-Ph), 130.7 (s, Ph−P (HMBC); 132.8 (C_6D_6) (d, $^1J_{C,P}$ = 130.0 Hz, Ph−P)),[35] 131.8 (d, $^2J_{C,P}$ = 10.2 Hz, *o*-Ph), 132.3 (d, $^4J_{C,P}$ = 2.7 Hz, *p*-Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 30.1. HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{19}FeO_2P$ 402.0467, found 402.0465 $[M]^+$.

Synthesis of *O*-Ferrocenyldiphenylthiaphosphinate (10). Ferrocenol (**3**; 828 mg, 4.1 mmol) was dissolved in CH_2Cl_2 (30 mL), cooled to −30 °C, and treated with NEt_3 (0.63 mL, 4.5 mmol) in a single portion. After 5 min, chlorodiphenylphosphane (0.83 mL, 4.5 mmol) was added with a syringe and the solution was stirred overnight at ambient temperature. Sulfur (160 mg, 4.9 mmol) was added, and the mixture was stirred for an additional 10 min. After removal of all volatiles, the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Purification was realized by column chromatography (column size 3 × 10 cm, alumina) using first hexane to elute the excess sulfur and then changing to CH_2Cl_2 to elute the title compound as a yellow solid. Yield: 1.65 g (3.9 mmol, 95% based on **10**). Anal. Calcd for $C_{22}H_{19}FeOPS$ (418.27): C, 63.17; H, 4.58. Found: C, 63.03; H, 4.71. ^{1}H NMR ($CDCl_3$, δ): 3.82 (pt, $^{3+4}J_{H,H}$ = 2.0 Hz, 2H, *m*-C_5H_4), 4.20 (s, 5H, C_5H_5), 4.24 (pt, $^{3+4}J_{H,H}$ = 1.8 Hz, 2H, *o*-C_5H_4), 7.44−7.50 (m, 4H, *o*-Ph), 7.50−7.56 (m, 2H, *p*-Ph), 7.88−7.96 (m, 4H, *m*-Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 61.1 (d, $^3J_{C,P}$ = 3.9 Hz, *o*-C_5H_4), 62.8 (s, *m*-C_5H_4), 69.5 (s, C_5H_5), 117.4 (d, $^2J_{C,P}$ = 5.6 Hz, C_5H_4−O), 128.4 (d, $J_{C,P}$ = 13.4 Hz, Ph), 131.4 (d, $J_{C,P}$ = 11.2 Hz, Ph), 132.0 (d, $^4J_{C,P}$ = 2.8 Hz, *p*-Ph), 134.2 (d, $^1J_{C,P}$ = 110.3 Hz, Ph−P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 81.5. Mp: 147−149 °C.

Crystal Data for ***10****:* $C_{22}H_{19}FeOPS$, M = 418.25, monoclinic, $P2_1/c$, λ = 0.71073 Å, a = 10.6166(6) Å, b = 30.5540(17) Å, c = 11.5573(7) Å, β = 97.308(6)°, V = 3718.5(4) Å^3, Z = 8, ρ_{calcd} =1.494 Mg m^{-3}, μ = 1.017 mm^{-1}, T = 110 K, θ range 2.87−26.00°, 17774 reflections collected, 7148 independent reflections (R_{int} =0.0389), R1 = 0.0436, wR2 = 0.1031 ($I > 2\sigma(I)$).

Synthesis of Diethyl(2-methoxyferrocenyl)phosphonate (12). LDA was prepared by treating diisopropylamine (1.25 mL, 8.9 mmol) with ^{n}BuLi (3.6 mL, 9.0 mmol) in tetrahydrofuran (20 mL) at −60 °C. After the mixture was stirred for 10 min at −60 °C, phosphate **4** (1.5 g, 4.4 mmol) was added dropwise. The yellow solution was stirred for 4 h between −30 and −15 °C and the color changed from orange to red. The reaction was stopped by adding Me_2SO_4 (1.3 mL, 13.7 mmol) in a single portion. The mixture was warmed to room temperature and subsequently heated to 50 °C for 1 h to complete the methylation. After removal of all volatiles, the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Purification by column chromatography (column size 2 × 8 cm, alumina) using ethyl acetate as the eluent afforded **12** as an orange oil. Yield: 1.46 g (4.14 mmol, 94% based on **4**). IR data (NaCl, ν/cm^{-1}): 3095 m, 2980 s, 2931 w, 2905 w, 2865 w, 1639 m, 1482 s, 1412 s, 1388 w, 1340 m, 1254 s, 1168 m, 1106 s, 1051 s, 1029 s, 964 s, 801 s, 753 m. ^{1}H NMR (C_6D_6, δ): 1.11 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 1.17 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 3.25 (s, 3H, OCH_3), 3.71 (dd, $^3J_{H,H}$ = 2.7 Hz, 1H, *m*-OCH_3), 3.76 (m, 1H, *o*-OCH_3), 4.07 (m, 2H, CH_2), 4.15 (m, 2H, CH_2), 4.30 (s, 5H, C_5H_5), 4.36 (m, 1H, *o*-P(O)). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 16.6 (m, CH_3), 55.4 (d, $^3J_{C,P}$ = 11 Hz, *o*-OCH_3), 57.8 (s, OCH_3), 59.2 (d, $^1J_{C,P}$ = 213.7 Hz, C−P), 61.6 (m, CH_2), 63.8 (d, $^3J_{C,P}$ = 13.7 Hz, *m*-OCH_3), 67.7 (d, $^2J_{C,P}$ = 12.8 Hz, *o*-P(O)), 70.4 (s, C_5H_5), 129.0 (d, $^2J_{C,P}$ = 10.3 Hz, C−OCH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 36.4. HRMS (ESI-TOF, m/z): calcd for $C_{15}H_{21}FeO_4P$ 352.0521, found 352.0602 $[M]^+$. HPLC (t): 19.6, 20.6.

Synthesis of *O,O*-Diethyl(2-methoxyferrocenyl)-thiaphosphonate (13). An *O,O*-diethyl-*O*-ferrocenylthiophosphate solution (**6**; 250 mg, 0.71 mmol) in 10 mL of tetrahydrofuran was treated with ^{s}BuLi (0.65 mL, 0.85 mmol) at −60 °C. The mixture was stirred for 4 h between −30 and −20 °C, and iodomethane (0.1 mL, 1.6 mmol) was added in a single portion. Additional stirring for 18 h and removal of all volatiles afforded a residue, which was chromatographed (column size 3.5 × 6 cm, silica). First, unreacted **6** (46%) was eluted with a 3/1 (v/v) toluene/hexane mixture. Afterward, the eluent was changed to pure toluene and the product **13** (R_f = 0.35) was obtained as an orange oil. Yield: 130 mg (0.35 mmol, 49% based on **6**). ^{1}H NMR ($CDCl_3$, δ): 1.30 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 1.39 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 3.70 (s, 3H, OCH_3), 4.03 (m, 1H, C_5H_3), 4.09−4.37 (m, 11H, CH_2, C_5H_5, C_5H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 16.1 (d, $^3J_{C,P}$ = 7.9 Hz, CH_3), 16.2 (d, $^3J_{C,P}$ = 7.9 Hz, CH_3), 55.3 (d, $J_{C,P}$ = 10.1 Hz, C_5H_3), 58.2 (s, OCH_3), 62.1 (d, $^2J_{C,P}$ = 6.4 Hz, CH_2), 62.6 (d, $^2J_{C,P}$ = 5.7 Hz, CH_2), 63.4 (d, $J_{C,P}$ = 14.1 Hz, C_5H_3), 64.6 (d, $^1J_{C,P}$ = 174.6 Hz, C_5H_3−P), 67.7 (d, $J_{C,P}$ = 15.7 Hz, C_5H_3), 70.2 (s, C_5H_5), 127.7 (d, $^2J_{C,P}$ = 9.0 Hz, C−OCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 89.6. HRMS (ESI-TOF, m/z): calcd for $C_{15}H_{21}FeO_3PS$ 368.0293, found 368.0310 $[M]^+$.

Synthesis of *O,O*-Diethyl(2-methoxyferrocenyl)-phosphonite−Borane (14). LDA was prepared by treating diisopropylamine (0.42 mL, 2.98 mmol) with ^{n}BuLi (1.20 mL, 3.0 mmol) in tetrahydrofuran (10 mL) at −60 °C. After the mixture was stirred for 10 min, **7** (500 mg, 1.49 mmol) in tetrahydrofuran (2 mL) was added with a syringe in a single portion. Stirring was continued for 4 h between −30 and −20 °C, while the solution turned dark. The reaction was stopped by adding iodomethane (0.30 mL, 4.8 mmol) in a single portion. The reaction mixture was warmed to room temperature. After removal of all volatiles the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Purification by column chromatography (column size 2 × 16 cm, silica) using a 2/1 (v/v) hexane/toluene mixture as the eluent afforded first unreacted **7** (31%) and second **14** as an orange oil. Yield: 190 mg (0.55 mmol, 37% based on **7**). ^{1}H NMR ($CDCl_3$, δ): 1.29 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 1.33 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 3.69 (s, 3H, OCH_3), 3.99−4.07 (m, 2H, CH_2), 4.08−4.10 (m, 1H, C_5H_3), 4.11−4.16 (m, 2H, CH_2), 4.23−4.24 (m, 1H, C_5H_3), 4.26−4.27 (m, 1H, C_5H_3), 4.32 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 16.5 (d, $^3J_{C,P}$ = 5.8 Hz, CH_3), 55.3 (d, $J_{C,P}$ = 6.5 Hz, C_5H_3), 58.2 (s, OCH_3), 60.1 (d, $^1J_{C,P}$ = 90.1 Hz, C−P), 62.6 (d, $^2J_{C,P}$ = 5.5 Hz, CH_2), 62.8 (d, $^2J_{C,P}$ = 4.9 Hz, CH_2), 64.2 (d, $J_{C,P}$ = 10.0 Hz, C_5H_3), 70.2 (s, C_5H_5), 128.7 (d, $^2J_{C,P}$ = 6.2 Hz, C−OCH_3). $^{11}B\{^1H\}$ NMR (C_6D_6, δ): −40.8 (d, $^1J_{B,P}$ = 89 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 135.4 (q, $^1J_{P,B}$ = 89 Hz). HRMS (ESI-TOF, m/z): calcd for $C_{15}H_{24}BFeO_3P$+H 350.0903, found 350.0856 $[M + H]^+$.

Synthesis of Bis(2-hydroxyphenyl)-*O*-ferrocenylphosphinate (15). LDA was prepared by treating diisopropylamine (0.98 mL, 7.07 mmol) with ^{n}BuLi (2.75 mL, 6.90 mmol) in tetrahydrofuran (10 mL) at −60 °C. After the mixture was stirred for 10 min, **8** (500 mg, 1.15 mmol) was added in a single portion. The solution was stirred for 5 h between −60 and −40 °C, while the solution turned dark. The reaction was stopped by adding iodomethane (0.43 mL, 1.6 mmol) in a single portion. The reaction mixture was allowed to warm to room temperature. After removal of all volatiles the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Purification by column chromatography

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(column size 3 × 18 cm, silica) using a 3/1 (v/v) CH_2Cl_2/ethyl acetate mixture as the eluent afforded **15** as an orange oil. Yield: 40 mg (0.10 mmol, 8% based on **8**). ^{1}H NMR ($CDCl_3$, δ): 3.85 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 2H, C_5H_4), 4.22 (s, 5H, C_5H_5), 4.29 (pt, $^{3+4}J_{H,H}$ = 1.9 Hz, 2H, C_5H_4), 6.92−6.98 (m, 4H, Ph), 7.42−7.47 (m, 3H, Ph), 7.48 (dd, $J_{H,H}$ = 7.8 Hz, $J_{H,H}$ = 1.6 Hz, 1H, Ph), 9.86 (s, 2H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 60.0 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 63.1 (s, C_5H_4), 69.7 (C_5H_5), 111.1 (d, $^1J_{C,P}$ = 139.9 Hz, Ph−P), 117.1 (d, $^2J_{C,P}$ = 6.9 Hz, C_5H_4−O), 118.6 (d, $J_{C,P}$ = 9.4 Hz), 119.9 (d, $J_{C,P}$ = 12.8 Hz), 131.6 (d, $J_{C,P}$ = 8.0 Hz), 135.6 (d, $J_{C,P}$ = 1.8 Hz), 162.1 (d, $^2J_{C,P}$ = 5.9 Hz, C−OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 42.3. HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{19}FeO_4P$ 434.0365, found 434.0364 $[M]^+$.

Synthesis of (2-Methoxyferrocenyl)diphenylphosphane Oxide (16). LDA was prepared by treating diisopropylamine (0.33 mL, 2.35 mmol) with ^{n}BuLi (0.92 mL, 2.30 mmol) in tetrahydrofuran (10 mL) at −60 °C. After the mixture was stirred for 10 min, compound **9** (500 mg, 1.24 mmol) was added in a single portion. The solution was stirred for 4 h between −30 and −20 °C, while the reaction solution turned dark. The reaction was stopped by adding iodomethane (0.30 mL, 4.8 mmol) in a single portion. The reaction mixture was warmed to room temperature. After removal of all volatiles the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Purification by column chromatography (column size 3 × 14 cm, silica) using a 2/1 (v/v) CH_2Cl_2/ethyl acetate mixture as the eluent afforded **16** as an orange oil. Yield: 45 mg (0.10 mmol, 8% based on **9**). ^{1}H NMR ($CDCl_3$, δ): 3.58 (s, 3H, OCH_3), 4.03−4.05 (m, 1H, C_5H_3), 4.08 (dd, $J_{H,P}$ = 4.6 Hz, $J_{H,H}$ = 2.4 Hz, 1H, C_5H_3), 4.20 (s, 5H, C_5H_5), 4.28 (dd, $J_{H,P}$ = 3.6 Hz, $J_{H,H}$ = 1.9 Hz, 1H, C_5H_3), 7.40 (td, $J_{H,H}$ = 7.4 Hz, J = 2.7 Hz, 2H, Ph), 7.42−7.53 (m, 4H, Ph), 7.63−7.68 (m, 2H, Ph), 7.84−7.90 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.5 (d, $J_{C,P}$ = 8.0 Hz, C_5H_3), 58.1 (s, OCH_3), 62.4 (d, $^1J_{C,P}$ = 116.1 Hz, C_5H_3−P), 63.9 (d, $J_{C,P}$ = 10.8 Hz, C_5H_3), 68.3 (d, $J_{C,P}$ = 11.0 Hz, C_5H_3), 69.8 (s, C_5H_5), 127.9−128.1 (m, Ph), 128.4−128.6 (m, C−OCH_3), 131.3−131.4 (m, Ph), 131.9 (d, $J_{C,P}$ = 10.0 Hz, Ph), 133.6−135.0 (m, P−Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 28.3. HRMS (ESI-TOF, m/z): calcd for $C_{23}H_{21}FePO_2$ 416.0623, found 416.0658 $[M]^+$.

Synthesis of *sec*-Butyldiphenylphosphine Sulfide (18). *O*-Ferrocenyldiphenylthiaphosphinate (**10**; 620 mg, 1.48 mmol) was dissolved in tetrahydrofuran (10 mL) and cooled to −60 °C. After dropwise addition of ^{s}BuLi (1.80 mL, 2.37 mmol) the reaction mixture was stirred for 4 h at −40 °C and the reaction subsequently stopped by adding iodomethane (0.15 mL, 2.37 mmol) in a single portion. All volatiles were removed under reduced pressure, and the residue was taken up in CH_2Cl_2 (30 mL) and washed with water (100 mL). After the organic layer was dried over $MgSO_4$, all volatiles were removed under reduced pressure and purified by column chromatography (column size 3.5 × 11 cm, silica). Ferrocenyl methyl ether (86%) was eluted using a 1/1 (v/v) hexane/toluene mixture, followed by **18** using pure toluene as eluent. Yield: 280 mg (1.01 mmol, 68% based on **10**). Anal. Calcd for $C_{16}H_{19}PS$ (274.36): C, 70.04; H, 6.98. Found: C, 70.15; H, 6.93. Mp: 93 °C. ^{1}H NMR ($CDCl_3$, δ): 0.97 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_2CH_3), 1.15 (dq, $^2J_{H,P}$ = 19.4 Hz, $^3J_{H,H}$ = 6.8 Hz, 3H, $CHCH_3$), 1.43−1.67 (m, 2H, CH_2), 2.56−2.66 (m, 1H, CH), 7.41−7.51 (m, 6H, *m*,*p*-Ph), 7.89−7.97 (m, 4H, *o*-Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 12.0 (s, $CHCH_3$), 12.1 (d, $^3J_{C,P}$ = 15.2 Hz, CH_2CH_3), 22.6 (s, CH_2), 34.8 (d, $^1J_{C,P}$ = 55.7 Hz, CH), 128.4−128.6 (m, *m*-Ph), 131.18−131.25 (m, *p*-Ph), 131.3−131.4 (m, *o*-Ph), 131.9 (d, $^1J_{C,P}$ = 76.4 Hz, Ph−P), 132.1 (d, $^1J_{C,P}$ = 76.3 Hz, Ph−P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 52.8. HRMS (ESI-TOF, m/z): calcd for $C_{16}H_{19}PS$+H 275.1018, found 275.1005 $[M+H]^+$.

Crystal Data for ***18****:* $C_{16}H_{19}PS$, M = 274.34, triclinic, $P\bar{1}$, λ = 0.71073 Å, a = 9.1715(7) Å, b = 11.9513(8) Å, c = 13.8640(10) Å, α = 86.089(6)°, β = 88.870(6)°, γ = 76.849(6) °, V = 1476.34(18) Å^3, Z = 4, ρ_{calcd} = 1.234 Mg m^{-3}, μ = 0.308 mm^{-1}, T = 110.00(10) K, θ range 3.00−25.00°, 9738 reflections collected, 5158 independent reflections (R_{int} =0.0700), R1 = 0.0907, wR2 = 0.2353 ($I > 2\sigma(I)$).

Synthesis of (2-(Diethoxyphosphoryl)ferrocenyl)-*O*,*O*-diethylphosphate (19). LDA was prepared by treating diisopropylamine (0.5 mL, 3.6 mmol) with ^{n}BuLi (1.45 mL, 3.6 mmol) in tetrahydrofuran (20 mL) at −60 °C. After the mixture was stirred for 10 min at this temperature, phosphate **4** (600 mg, 1.8 mmol) was added dropwise. The solution was stirred for 4 h between −30 and −15 °C, during which the color changed from orange to red. The reaction was stopped by adding *O*,*O*-diethylchlorophosphate (0.75 mL, 5.2 mmol) in a single portion. The reaction mixture was warmed to room temperature. After removal of all volatiles the residue was collected in CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$, and all volatiles were removed under reduced pressure. Purification by column chromatography (column size 3 × 8 cm, silica) using a 9/1 (v/v) ethyl acetate/methanol mixture as the eluent afforded **19** as an orange oil. Yield: 290 mg (0.6 mmol, 33% based on **4**). ^{1}H NMR ($CDCl_3$, δ): 1.33 (td, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,P}$ = 0.9 Hz, 3H, CH_3), 1.34 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 1.38 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 1.43 (td, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,P}$ = 1.1 Hz, 3H, CH_3), 4.09−4.33 (m, 10H, CH_2, C_5H_3), 4.39 (s, 5H, C_5H_5), 4.79 (ddd, $J_{H,P}$ = 2.3 Hz, $J_{H,H}$ = 2.3 Hz, $J_{H,H}$ = 1.5 Hz, 2H C_5H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 15.8−16.0 (m, CH_3), 16.2−16.3 (m, CH_3), 58.1 (dd, $^1J_{C,P}$ = 208.7 Hz, $^3J_{C,P}$ = 7.1 Hz, C−P), 61.6 (d, $^2J_{C,P}$ = 5.7 Hz, CH_2), 61.8 (d, $^2J_{C,P}$ = 5.7 Hz, CH_2), 62.3 (d, $J_{C,P}$ = 10.2 Hz, C_5H_3), 64.4 (d, $^2J_{C,P}$ = 6.4 Hz, CH_2), 64.5 (d, $^2J_{C,P}$ = 6.4 Hz, CH_2), 65.0 (d, $J_{C,P}$ = 13.7 Hz, C_5H_3), 67.2 (d, $J_{C,P}$ = C_5H_3), 71.1 (s, C_5H_5), 118.3 (dd, $^2J_{C,P}$ = 9.1 Hz, $^2J_{C,P}$ = 4.5 Hz, C−O).$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −6.1 (s, O−P(O)$(OEt)_2$), 22.2 (C−P(O)$(OEt)_2$). HRMS (ESI-TOF, m/z): calcd for $C_{18}H_{28}FeO_7P_2$ 497.0552, found 497.0635 $[M]^+$.

Synthesis of 1,3-Bis(*O*,*O*-diethylphosphonato)-2-methoxyferrocene (20). LDA was prepared by treating diisopropylamine (0.11 mL, 0.78 mmol) with ^{n}BuLi (0.31 mL, 0.75 mmol) in tetrahydrofuran (10 mL) at −60 °C. After the mixture was stirred for 10 min at this temperature, **19** (183 mg, 0.39 mmol) was added in a single portion. The solution was stirred for 4 h between −30 and −20 °C, while the solution turned dark. The reaction was stopped by adding iodomethane (0.1 mL, 1.6 mmol) in a single portion. The reaction mixture was warmed to room temperature. After removal of all volatiles the residue was collected in CH_2Cl_2 (30 mL) and purified by column chromatography (column size 2 × 15 cm, silica) using a 9/1 (v/v) ethyl acetate/methanol mixture as the eluent, which afforded **20** as an orange oil. Yield: 40 mg (0.08 mmol, 21% based on **19**). ^{1}H NMR ($CDCl_3$, δ): 1.35 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 1.38 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, CH_3), 3.89 (s, 3H, OCH_3), 4.13−4.26 (m, 8H, CH_2), 4.43 (t, $^3J_{H,P}$ = 2.55 Hz, 2H, C_5H_2), 4.49 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 16.4−16.5 (m, CH_3), 62.1 (t, $^2J_{C,P}$ = 5.5 Hz, CH_2), 63.1 (dd, $^1J_{C,P}$ = 211.9 Hz, $^3J_{C,P}$ = 10.7 Hz, C−P), 64.0 (s, OCH_3), 69.4 (t, $^2J_{C,P}$ = 13.6 Hz, C_5H_2), 128.7 (t, $^2J_{C,P}$ = 63.2 Hz, C−OCH_3).$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 22.1. HRMS (ESI-TOF, m/z): calcd for $C_{19}H_{30}P_2O_7$ + Na 511.0709, found 511.0747 $[M + Na]^+$.

General Procedure for Suzuki−Miyaura Cross-Coupling Reactions. A glass vessel (4 mL size) was charged with $[Pd_2(dba)_3]$ (0.25 mol %), compound **1** (Pd/P ratio 1/2 (n/n)), boronic acid (1.5 mmol), powdered $K_3PO_4{\cdot}xH_2O$ (690 mg, 3.0 mmol), the appropriate aryl halide (1.0 mmol), and dry toluene (3 mL). The vessel was purged with argon and closed. The reaction mixture was heated at 70 °C, except as otherwise noted, with vigorous stirring for 24 h. After it was cooled 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 filtered through alumina and concentrated under reduced pressure. The obtained crude material was purified by flash chromatography on silica (hexane/diethyl ether mixtures).

Further spectroscopic details for **25a−h** are given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving full experimental and spectroscopic details for all compounds and X-ray crystallographic data for **1**, **10**, and **18**. This material is available free of charge via the

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Internet at http://pubs.acs.org. Crystallographic data are also available from the Cambridge Crystallographic Database as file numbers CCDC 978226 (**1**), 978248 (**10**), and 978227 (**18**).

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Notes

The authors declare no competing financial interest.

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(35) In the ^{13}C{^{1}H} NMR spectrum of a concentrated sample solution in $CDCl_3$ the signal of this carbon atom could not be observed. However, the corresponding ^{1}H,^{13}C-HMBC spectrum was measured, from which the resonance was received. The spectrum of an additional measurement in C_6D_6 exhibited the resonance of this carbon atom as well as the C,P-coupling constant.