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Reactivity of Ferrocenyl Phosphates Bearing (Hetero-)Aromatics and [3]Ferrocenophanes toward Anionic Phospho-Fries Rearrangements

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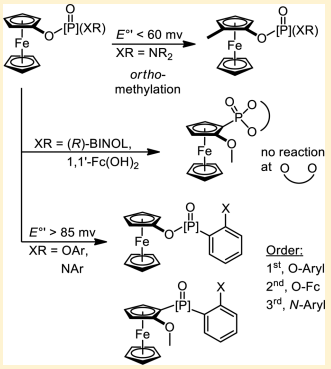
Supporting Information

ABSTRACT: The temperature-dependent behavior within anionic phospho-Fries rearrangements (apFr) of $P(O)(OFc)_n(EAr)_{3-n}$ (Fc = $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$; E = O; Ar = phenyl, naphthyls, (*R*)-BINOL, [3]ferrocenophanyl; E = N, 1*H*-pyrrolyl, 1*H*-indolyl, 9*H*-carbazolyl; *n* = 1−3) is reported. While Fc undergoes one, the Ph-based apFr depends on temperature. First, the aryls are lithiated and rearranged, followed by Fc and N-heterocycles. Addition of Me_2SO_4 thus gave methylated Fc, contrary to non-organometallic aromatics giving mixtures of HO and MeO derivatives. The (*R*)-BINOL Fc phosphate gave Fc-rearranged phosphonate in 91% de. Exchanging O- with N-aliphatics prevented apFr, due to higher electron density at P. Also 1,2-N→C migrations were observed. X-ray analysis confirms 1D H bridge bonds for OH and NH derivatives. The differences in reactivity between N-aliphatic and N-aromatic phosphoramidates were verified by electrochemistry. The redox potentials revealed lower values for the electron-rich aliphatics, showing no apFr, preventing a nucleophilic attack at P after lithiation. Redox separations for multiple Fc molecules are based on electrostatic interactions.



INTRODUCTION

Anionic phospho-Fries rearrangements (apFr) are crucial reactions within the synthesis of *ortho*-hydroxyl-functionalized aromatics.[1,2] They proceed regioselectively, which is beneficial especially within the synthesis of natural products.[3] The selectivity is caused by the low reaction temperatures, compared to cationic alternative synthetic methodologies.[4] Particularly, the use of phosphorus-containing groups, as the 1,3-O→C migrating fragments, enables their conversion to phosphines, which are otherwise difficult to prepare.[5] Thereby, it is beneficial that a chiral phosphorus group rearranges under retention.[6] The resulting *ortho*-oxygen functionalities enhance the catalytic activity by acting as hemilabile bidendate ligands within, for example, the Suzuki−Miyaura C−C cross-coupling reaction.[5,7] Chiral BINOL backbones, containing an *ortho*-hydroxy phosphine oxide substitution pattern, for example, catalyze asymmetric additions of $ZnEt_2$ to aldehydes, giving the respective alcohols in up to 99% ee.[8] The first anionic phospho modification was reported by Melvin in 1981 by converting *O*,*O*′-dialkyl-*O*″-aryl phosphates into *O*,*O*′-dialkylarylphosphonates.[9] We successfully adopted this 1,3-O→C migration on different ferrocenyl-based organometallic compounds,[2,5,10] whereby the highest yields were obtained for phosphates as the starting materials. The usage of ferrocenyl phosphates derived from chiral-pool-based alcohols allowed a diastereoselective process and gave products with up to 96% de.[11] Recently, the progress of anionic phospho-Fries rearrangements was summarized and showed the great applicability and regioselective aspects of the rearrangement.[1,12]

Until now, anionic phospho-, thia-, sila-, and carbo-Fries rearrangements concentrated on rearrangements at the same type of heteroatom-bonded aromatics within one molecule, such as phenyls/naphthyls,[13] tricarbonylchromium-complexed compounds,[14] and ferrocenes.[15] It was found that molecules containing more than one O-bonded aromatic unit rearrange within one reaction step, as shown for phosphates[16] and phosphonates.[12,17] A similar reactivity is observed for non-Fries 1,3-S→C shifts that are also known to proceed at ferrocenes.[18]

Anionic-induced rearrangements solely proceed at X-bonded (X = O, N) aromatics, whereas for X = C, an *ortho*-lithiation and no subsequent intramolecular migration occur, such as for arylsulfonamides.[19−21] Stable C-bonded aromatics including phosphine oxides are solely attacked by singlet oxygen[22] or under basic conditions at >200 °C.[23]

Besides OH and SH functionalities, *ortho*-NH substituents are also accessible by 1,2-N→C rearrangements to the α-position as it could be shown for pyrroles.[24,25] If the α-positions are blocked, then 1,3-[26] or 1,5-migrations occurred.[27] The less stable N−P bond, compared to O−P or C−P units, readily allows 1,2-migrations in the presence of aldehydes,[28,29] aziridines,[30] oximes,[31] and even pyrroles.[25]

Investigations of mixed X = O-, N-bonded compounds (e.g., *O*,*O*′-bonded bridging BINOLS,[32] ephedrine-based compounds,[1a,33] *N*-phenyltetrazoles,[34] and 2,8-dimethylphenoxaphosphine[35]) revealed that only the *O*-phenyl substituents underwent anionic-induced rearrangements.

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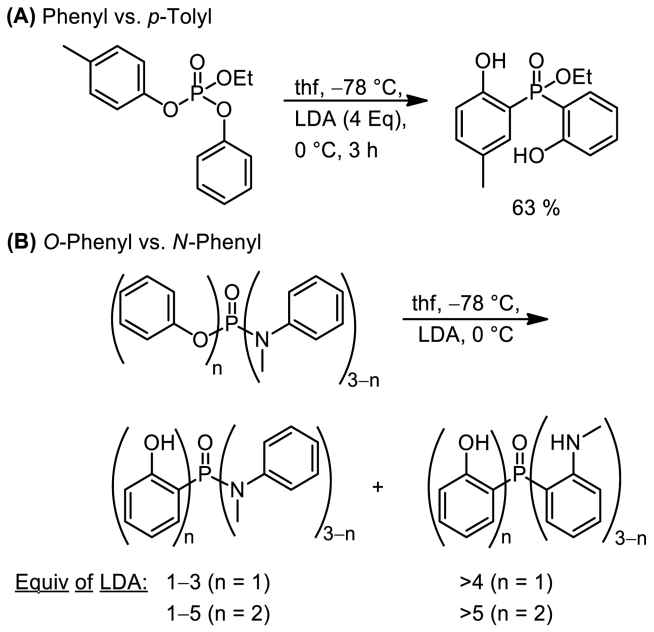
The reported examples of rearrangements proceeding at different types of aromatics within one molecule are summarized in Scheme 1. Electronically and chemically similar

Scheme 1. Examples of Recently Reported Migrations of Differently Substituted Phosphates: (A) Simultaneous Rearrangement for Phenyl vs Tolyl[16f] and (B) Consecutive Rearrangement of O- vs N-Bonded Phenyls[3b,36]



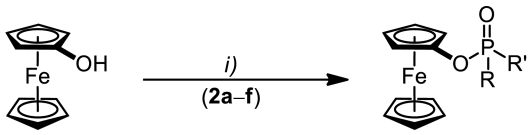
substituents, such as phenyl and *p*-tolyl (reaction A), Scheme 1), rearrange within one reaction step without any reactivity differences between both groups.[16f] In compounds bearing both O- and N-bonded aromatics, the first lithiation and 1,3-X→C migration take place at the O-bonded substituent (reaction B, Scheme 1).[3b,36] Using excess LDA forced the formation of the phosphane oxide species, however, as a minor product.

Thus, studies investigating the selectivity of apFr for different substituents are still pending. The widely used reaction protocols for anionic phospho-Fries rearrangements include stirring with LDA at −70 °C for 1 h and subsequent warming of the reaction mixture to ambient temperature, without knowing whether the reaction occurs at low or high temperatures.[37] A comparison between phenyl and the electronically enriched ferrocenyl groups would allow an activation energy estimation of the respective groups. Thus, investigations on triferrocenyl phosphate, $(FcO)_3P(O)$(**3**)[2] (Fc = Fe(η^5-C_5H_5)(η^5-C_5H_4)), which was first described by Herberhold et al. in 1998,[38,39] in combination with phenyl, naphthyl, BINOL, and N-heterocyclic aromatics are reported herein (Scheme 1C). Temperature-dependent studies are included to estimate the minimum temperature required for the first lithiation process. The dependency between electron density and reactivity is evidenced by electrochemical investigations, whereby the ferrocenyl unit is well-suited as a probe.[10]

RESULTS AND DISCUSSION

The ferrocenyl phosphates **3**−**7** were synthesized by reacting lithiated ferrocenol **1**-Li with $POCl_3$ (**2a**) or chlorophosphates $Cl_2P(O)(OR)$ (**2b**−**2e**) (Scheme 2). The usage of BuLi as the

Scheme 2. Synthesis of Ferrocenyl Phosphates 3−8*



1	**2a** ($POCl_3$)	**3** (R = R' = OFc),	92 %
	2b ($Cl_2P(O)OPh$)	**4** (R = OFc, R' = OPh),	63 %
	2c ($ClP(O)(OPh)_2$)	**5** (R = R' = OPh),	99 %
	2d ($Cl_2P(O)R^1$)	**6** (R = OFc, R' = R^1),	25 %
	2e ($Cl_2P(O)R^2$)	**7** (R = OFc, R' = R^2),	65 %
	2f ($Cl_2P(O)R^3$)	**8** (R = OFc, R' = R^3),	0 %[a]

R^1 = R^2 = R^3 =

*Conditions: (*i*) Et_2O (**3**−**5**)[2]/THF (**6**−**8**), −30 °C, BuLi, −70 °C, 0.33 equiv of **2a**, 0.5 equiv of **2b**,**d**−**f**, or 1 equiv of **2c**. Yields are based on 2 (**3**, **4**, **7**) or 1 (**5**, **6**). [a]Instead of **8**, **3** was formed in 58% yield.

metalation reagent, instead of widely used nitrogen bases, increased the yield, that is for **3** from 36[38,39] to 92% and for **5** from 62 to 99%[5] (Scheme 2, Experimental Section). However, the reaction of **1**-Li with the 3-hydroxypyridyl derivative **2f** did not result in desired phosphate **8**, but rather gave **3** in 58 (tetrahydrofuran) or 25% yield (diethyl ether), showing that the solvent plays a crucial role within the appropriate reaction. Although a 2:1 ratio of **1**/**2f** was present, the 3-hydroxypyridyl substituent was replaced by a third nucleophilic substitution of **1**-Li. The properties of R^3 as the leaving group are due to the excellent stabilization of a negative charge within the electron-poor heterocycle. The formation of a keto-amino tautomeric structure, as possible for the 2- and 4-hydroxypyridine, is excluded, and thus, a P−N formation is rather disfavored compared to a P−O bonding of the pyridine derivative. Nevertheless, pyridyl triflates have been investigated for anionic 1,3-O→C migrations. The electron-withdrawing character and their different chemical structure increase their stability toward the attack of a nucleophile.[40]

Treatment of $P(O)(OFc)_3$ (**3**) (Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)) with LDA at various temperatures (−70 to 25 °C) resulted in the expected 1,3-O→C migration of the phosphorus fragment, which is initialized by an *ortho*-lithiation, producing **9** and **10** (Scheme 3). After optimizing the reaction conditions for the apFr of **3**[2], we obtained the highest yield for **9** of 86% at a temperature of −30 °C. Lower temperatures reduced the conversion of **3**. Above −30 °C, partial decomposition takes place, lowering the yield. Nevertheless, the double rearranged

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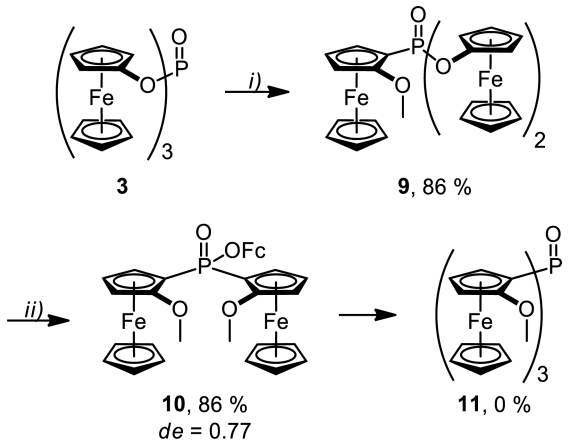
Scheme 3. Consecutive Anionic Phospho-Fries Rearrangement of Triferrocenyl Phosphate 3 To Afford Phosphonate 9 and Phosphinate 10*



*Conditions: (*i*) LDA, THF, −30 °C, 3 h, Me_2SO_4, 86% (based on **3**); (*ii*) LDA, THF, 0 °C, 3 h, Me_2SO_4, 86% (based on **9**).

product **10** was not formed within this reaction step, even using excess LDA (Scheme 3).

An apFr of **9** by treating it with LDA gave phosphinate **10** in 86% yield at 0 °C. The increased temperature required for the lithiation reaction of **9** is due to the increased electron density at the ferrocenyl backbone (vide infra). Phosphinate **10** was formed as a 0.89:0.11 diastereomeric mixture, which was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. Based on an X-ray measurement (Figure 1), where a similar ratio of two

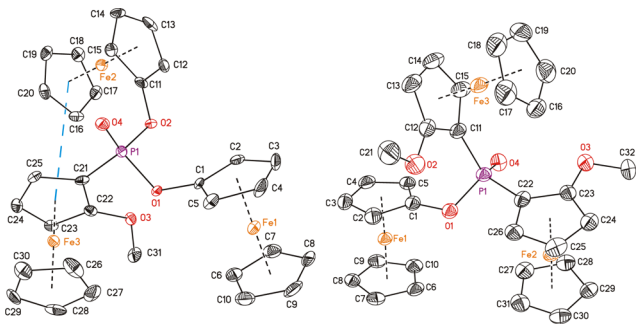


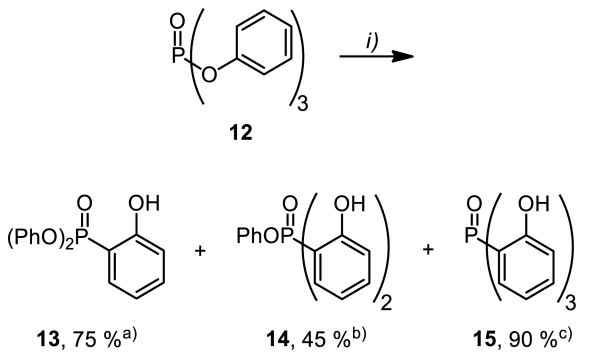
Figure 1. ORTEP (50% probability level) of the molecular structures of **9** (left) and **10** (right) with the atom-numbering scheme. All hydrogen atoms and disordered parts of **10** (10%) have been omitted for clarity. Intramolecular T-shaped π interactions (blue): Ct−Ct = 4.585(3) Å, α = 72.6(3)° (Ct = centroids of the C_5 rings; α = angle between the respective planes).

diastereomers was observed, the mainly formed diastereomer should be assigned as the *meso*-enantiomers R_p,S_p,r^P and S_p,R_p,s^P. The *rac*-enantiomers $R_p,R_p/S_p,S_p$ only cocrystallized in a similar ratio and are refined as a disorder. The *meso*-isomers should give two sets of signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra; however, only one set was present.

However, the formation of phosphine oxide **11** was not observed because, by the reaction of **10** with LDA at −10 °C, the starting material could be recovered in 86% yield. In contrast, when the reaction was run at 50 °C, the educt **10** was not present and probably decomposed during the course of the reaction or by a nucleophilic attack at the phosphorus atom.

The incomplete reaction of ferrocenyls toward apFr is contrary to triphenyl phosphate **12**, giving phosphine oxide **15** within one reaction step (Scheme 4).[9,16] Until now, the apFr of

Scheme 4. Anionic Phospho-Fries Rearrangement of Triphenyl Phosphate 12 To Give 13−15*



*Conditions: (*i*) THF, LDA, 2 h, H^+/H_2O. Yields are based on **12**. [a]At −70 °C with 2 equiv of LDA. [b]At −70 °C with 6 equiv of LDA. [c]At 0 °C with 12 equiv of LDA.

phenyl derivatives were warmed to 0 °C or even ambient temperature before being terminated with HCl or H_2O.[37] Thus, the intermediately formed phosphonates (e.g., **13**) and phosphinates (e.g., **14**) have not been isolated and reported yet. However, adding the scavenger, while keeping the reaction temperature at −80 °C, allowed the isolation of **13**.[2] Increasing the temperature, at which the scavenger is added, consecutively shifts the product ratio from **13** over **14** to **15** at 0 °C. The identity of **13** was verified by using single-crystal X-ray diffraction analysis (Figure 3). Initially, lithiation and

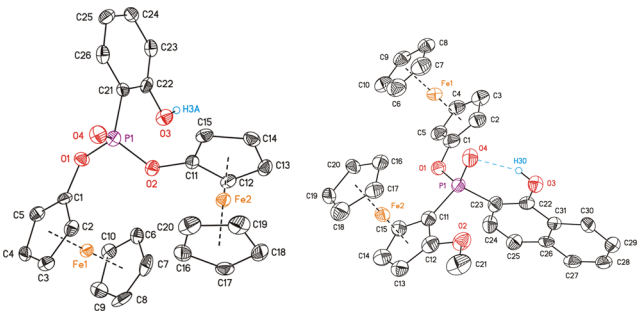


Figure 2. ORTEP (50% probability level) of the molecular structures of **16a** (left) and **24** (right) with the atom-numbering scheme. All C-bonded hydrogen atoms and the disordered parts in **24** (occupancy ratio of 0.722:0.278) have been omitted for clarity. Intramolecular hydrogen bridge bond: O3···O4, 2.624(10) Å; O3−H_3O···O4, 153°.

subsequent rearrangement of **12** to form phosphonate **13** occurred at −70 °C. Gradually, increasing the temperature exceeds the activation energy for the lithiation of **13**-Li, resulting in the formation of phosphinate **14** and finally phosphine oxide **15** (Scheme 4). Thus, the number of rearrangements solely depends on the temperature required for the lithiation process, due to the absence of any non-rearranged but *ortho*-methylated product derived from **12**. The amount of LDA used for the synthesis of **15** was taken from reported procedures.[9,16]

Obviously, the phenylic hydroxyl groups in **13**-Li and **14**-Li_2 do not prevent a further deprotonation by LDA. Contrary,

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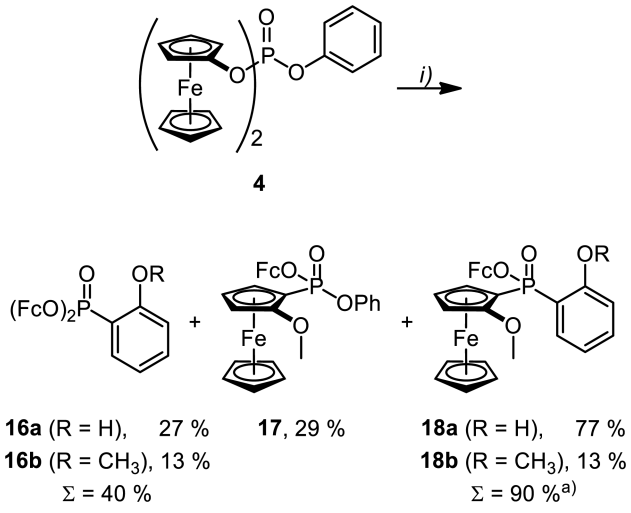
starting at **3**, the presence of already one ferrocenylic hydroxyl group in **9**-Li inhibits further lithiation to **10** with even a 6-fold excess of LDA (Scheme 3). To complex the lithium ions by phenyl- instead of ferrocenyl-based hydroxyls, 12 equiv of PhOLi was added, which increased the yield of **10** from 0 to 46% and the de from 0.77 to 0.99.

If both phenyl and ferrocenyl groups are present in a phosphate, as shown for **4** (Scheme 5) and **5** (Scheme 6), the

Scheme 5. Anionic Phospho-Fries Rearrangement of Diferrocenylphenyl Phosphate 4 To Afford Phosphonates 16a,b and 17 and Phosphinate 18a,b*



*Conditions: (*i*) THF, LDA (4 equiv), −60 °C, Me_2SO_4. Yields are based on **4**. [a]At 0 °C with 7 equiv of LDA.

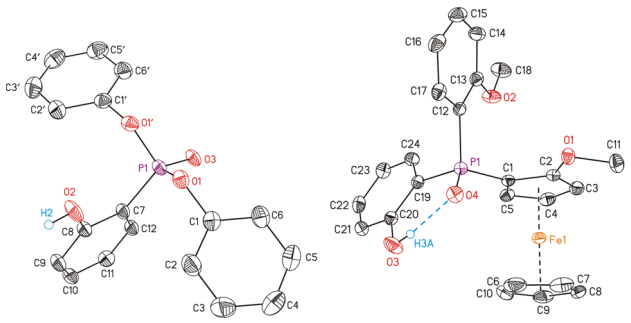


Figure 3. ORTEP (50% probability level) of the molecular structures of **13** (left) and **22b** (right) with their atom-numbering scheme and the intramolecular hydrogen bridge bond (blue). All C-bonded hydrogen atoms and the disordered C_5H_5 unit in **22b** (occupancy ratio of 0.73:0.27) have been omitted for clarity. Symmetry operation for generating equivalent atoms (′): *x*, −*y* + 1/2, *z*. Intramolecular hydrogen bridge bond: O3···O4, 2.597(2) Å; O3−H_3A···O4, 157°.

reactivity toward the lithiation and subsequent 1,3-O→C migration is reduced compared to that of **12** (recovered starting materials: 0% of **12** at −70 °C; 25% of **4** at −60 °C, 80% at −75 °C; 0% of **5** at −70 °C, 25% at −80 °C).

In general, the rearrangement at the phenyl rings is favored compared to that at the ferrocenyls, as clarified by the higher yields of **16** and **19** at lower temperatures when compared to the rearrangement products **9**, **17**, **19**, and **20**−**22**.[2] However, the formation of **17** indicates a low-energy difference between lithiation at a phenyl and a ferrocenyl fragment. Furthermore, the possibility of an *ortho*-lithiation is higher at the ferrocenyls, due to the presence of 4-*ortho*-hydrogens in contrast to 2-*ortho*-hydrogen atoms at the phenyl groups. As a consequence of the different behavior of ferrocenyl (stepwise) and phenyl groups (temperature-dependent), phosphinate **18** was formed at 0 °C as the final rearranged product. In contrast, **5** gave phosphine oxide **22** at 0 °C (Scheme 6), although excess LDA was used.

To prevent the decomposition of oxygen-sensitive hydroxy ferrocenes,[2,5,10,11,15,41] the lithiation and rearrangement reactions were quenched by the addition of excess Me_2SO_4, resulting in the methylation of all ferrocenyl-related hydroxy functionalities. However, the in situ methylation of phenols is rather slow and, moreover, gave mixtures of the methylated and non-methylated derivatives, **16**, **18**, and **20**−**22** (Schemes 5 and 6). For phosphine oxide **22**, a kinetic resolution was observed (Scheme 6). Most likely **22a** was initially formed as a racemic mixture (R_p/S_p enantiomers), due to the absence of external and internal chiral information. For **22b** (>85% de), one set of signals was observed in the ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra, confirming the diastereoselective process. The absolute configuration could be assigned as S_p,S^P/R_p,R^P by single-crystal X-ray diffraction analysis (Figure 3).

The differences between ferrocenyls and phenyls toward apFr prompted us to extend the substrate scope to condensed aromatics, which also allows us to investigate the regioselectivity of the 1,3-O→C migrations. To reduce the number of possible rearrangement products, phosphates bearing two ferrocenyls instead of one ferrocenyl were applied.

The anionic phospho-Fries rearrangement of 1-naphthyl derivative **6** resulted in the formation of a 1,2-substitution pattern, both at the naphthyl and at the ferrocenyl moieties, giving phosphonate **23** and phosphinate **24**, respectively, as shown in Scheme 7. Phosphinate **24** was formed in a scalemic mixture (ratio of both diastereomers of 1:0.78), as it was observed for **18** (Scheme 5). Similar to triferrocenyl **3** and diferrocenyl phosphate **4**, the lithiation of **6** required higher temperatures. Thus, 90% of the starting material **6** was recovered at −70 °C.

Replacement of the 1-naphthyl derivative **6** (Scheme 7) with its 2-isomer **7** (Scheme 8), however, allowed the anionic phospho-Fries rearrangement at −80 °C (Scheme 8, Experimental Section). Thus, phosphonate **25** reveals an increased reactivity toward the lithiation process at the 2-position of the naphthyl moiety when compared with that of the 1-substituted compound **6**. Lithiation selectively occurred at the more acidic 3-position and not at the electronically richer 1-position, which is in accordance with similar rearrangements of 2-naphthyl alkyl phosphonates and phosphates, where the 2,3-substitution pattern was present in the predominantly formed products.[21,42] If the reaction temperature is increased to 0 °C, the 1,3-O→C migration occurred at both types of aromatics, resulting in **26** with a **26a**/**26b** ratio of 1:0.43 (Scheme 8, Experimental Section). Within this reaction, the phosphonate **25** could not be isolated.

Phosphonate **27a**[38,39] was obtained by the reaction of lithiated 1,1′-ferrocenediol (1,1′-Fc(OLi)$_2$; **29**-Li_2) with $POCl_3$ and subsequent addition of **1**-Li (Scheme 11). However, **27a** was only produced in a yield of 20%, which is attributed to the reaction protocol applied (vide infra, Experimental Section). Phosphate (*R*)-**27b**, possessing a chiral (*R*)-BINOL bridging backbone, was accessible by treatment of **1**-Li with chlorophosphate (*R*)-**2g** (Scheme 9).

After appropriate workup, (*R*)-**27b** could be isolated in a yield of 49% (Scheme 9, Experimental Section). It was found

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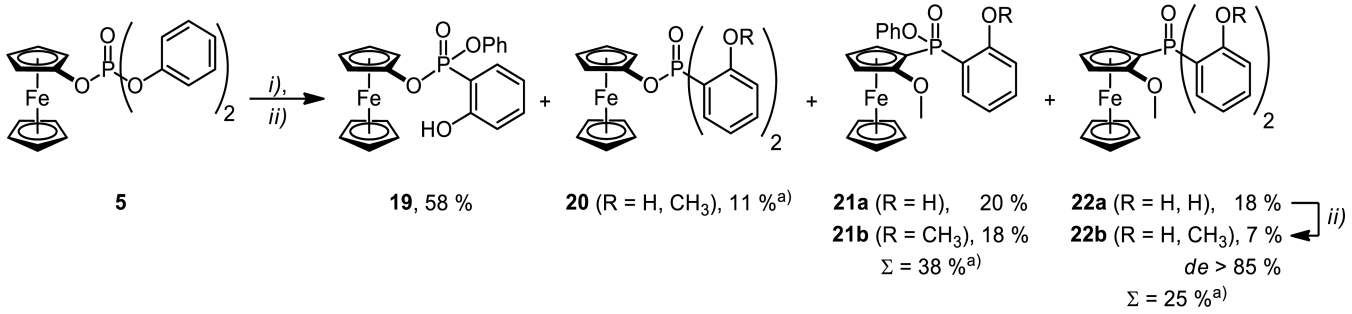
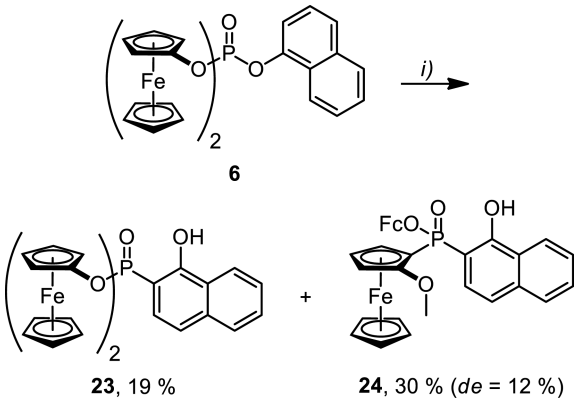
Scheme 6. Anionic Phospho-Fries Rearrangement of Ferrocenyldiphenyl Phosphate 5 To Give Phosphonate 19, Phosphinates 20 and 21a,b, and Phosphine Oxides 22a,b*



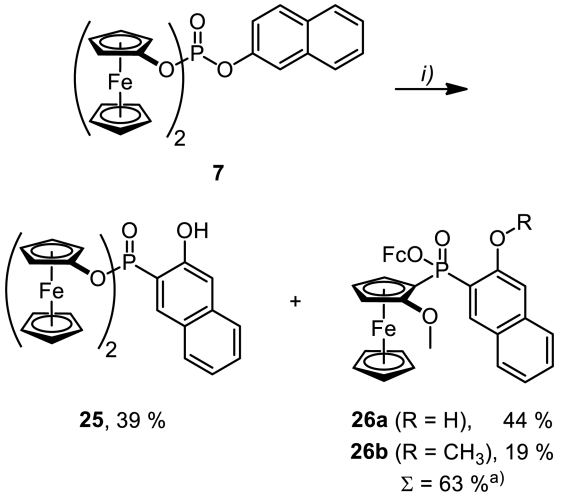
*Conditions: (*i*) THF, LDA (8 equiv), −70 °C, 2 h; (*ii*) addition of Me_2SO_4 (12 equiv). Yields are based on **5**. [a]At 0 °C.

Scheme 7. Anionic Phospho-Fries Rearrangement of Diferrocenyl(1-naphthyl) Phosphate 6 To Give Phosphonate 23 and Phosphinate 24*



*Conditions: (*i*) THF, LDA (6 equiv), 0 °C, 2 h, Me_2SO_4 (8 equiv). Yields are based on **6**.

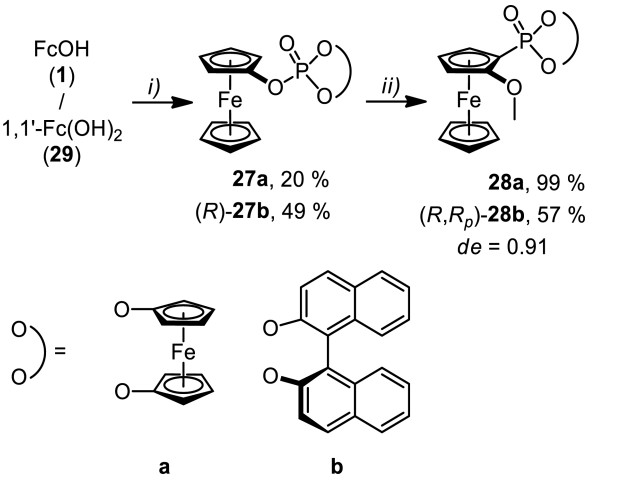
Scheme 8. Anionic Phospho-Fries Rearrangement of Diferrocenyl(2-naphthyl) Phosphate 7 To Give Phosphonate 25 and Phosphinates 26a,b*



*Conditions: (*i*) THF, LDA (6 equiv), −80 °C, 2 h, Me_2SO_4 (8 equiv). Yields are based on **7**. [a]At 0 °C.

that the addition of 2 equiv of $POCl_3$ within the synthesis of (*R*)-**2g** did not result in the formation of a bisphosphorylated BINOL. Treatment of phosphates **27a,b** with excess LDA (6 equiv) at −70 °C allowed anionic phospho-Fries rearrangements at the single substituted ferrocenyls. The formation of compounds that were lithiated at the bridging backbones of **27a,b** were not observed, which is in accordance with the result obtained with the phenyl derivative of **27b**.[32]

Scheme 9. Anionic Phospho-Fries Rearrangement of Phosphates 27a and (*R*)-BINOL-Based (*R*)-27b*



*Conditions: (*i*) **27a**/**29**, BuLi (2 equiv), $POCl_3$, THF, **1**-Li, yield based on **29**; **27b**, **1**, BuLi (1 equiv), Et_2O, P(O)Cl((*R*)-BINOL) (**2g**), yield based on **1**; (*ii*) THF, LDA, −10 °C (**28a**)/−70 °C (**28b**), 2 h, Me_2SO_4, yields are based on **27a**/**27b**.

The non-rotatable P═O bond prevents a stabilization of the negative charge in the 3-position of the naphthyl ring. Therefore, an attack at the phosphorus atom is excluded. Phosphonate **28a** (Scheme 9) was isolated in virtually quantitative yield.

The chiral information in the backbone of **27b** resulted in a diastereoselective lithiation, owing to a preferable rotation of the P═O building block to one site of the ferrocenyl unit.

After subsequent 1,3-O→C migration, phosphonate **28b** was isolated as the (R,R_p) diastereomer with a de of 91%, as confirmed by single-crystal X-ray diffraction (Figure 4) in 57% yield. Within this reaction, 38% of the starting material (*R*)-**27b** could be recovered. Increasing the temperature to −20 °C for 2 h reduced the yield of (R,R_p)-**28b** to 37%, whereas the de remained at 89%. Thus, the P═O is directed to one site of cyclopentadienyl, where the lithiation occurred.

To force metalation at the 1,3-dioxa[3]ferrocenophane backbone, phosphate (1*R*)-**30** was synthesized by reacting

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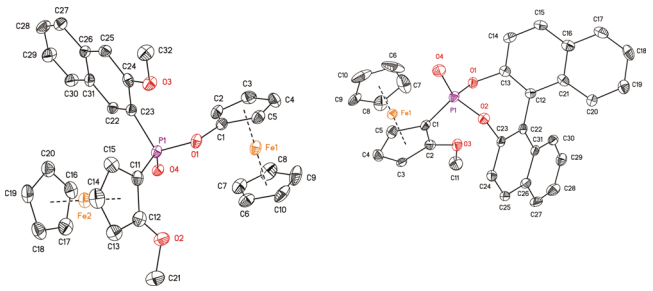
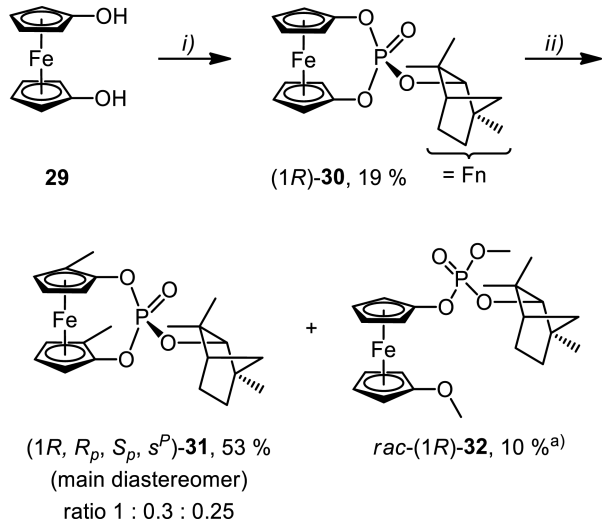


Figure 4. ORTEP (50% probability level) of the molecular structures of **26b** (left) and (R,R_p)-**28b** (right) with the atom-numbering scheme. All hydrogen atoms and one molecule of $CHCl_3$ (**28b**) have been omitted for clarity.

$(Li)_2$-**29** with the chiral dichloro (1*R*)-*α*-fenchyl phosphate (**2h**),[11] whereby the aliphatic substituent does not undergo lithiation reactions (Scheme 10). The fenchyl methyl groups in

Scheme 10. Anionic Phospho-Fries Rearrangement of the Chiral-Pool-Based Phosphate (1*R*)-30*



*Conditions: (*i*) BuLi, $Cl_2P(O)((1R)$-*α*-Fn) (**2h**), Et_2O. Yield based on **29**; (*ii*) THF, LiTMP, −10 °C, Me_2SO_4. Yields are based on (*R*)-**30**. [a]Stirring for 18 h at ambient temperature; formation of **31** in 53% yield, 1,1′-$Fc(OMe)_2$ in 20% yield, formation of **32** in 10% yield; *rac* refers to the configuration at the phosphorus atom.

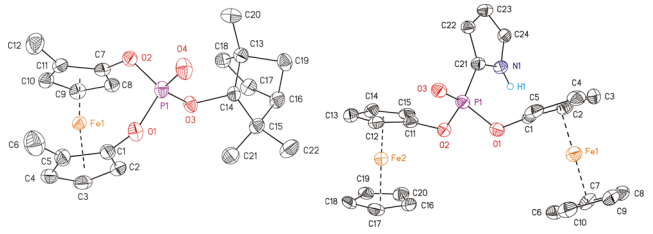


Figure 5. ORTEP of the two crystallographically independent molecules of the asymmetric unit of (1*R*-*α*,R_p,S_p,s^P)-**31** (left, 50% probability level) and **52** (right, 30% probability level) with the atom-numbering scheme. All C-bonded hydrogen atoms have been omitted for clarity.

the 1- and 3-positions of the bicycle enhance the stereoselectivity within such types of reactions, when compared to other chiral pool alcohols (Scheme 10).[11]

Within the synthesis of (1*R*)-**30**, the formation of a [3,3]ferrocenophane, containing two phosphate bridged ferrocenyls, was not observed. Treatment of (1*R*)-**30** with the sterically demanding base LiTMP (TMP = tetramethylpiperidide) at −10 °C resulted only in the *ortho*-lithiation at both cyclopentadienyls. Subsequent addition of Me_2SO_4 gave the 1,1′-double-methylated phosphate **31** (Scheme 10). This *ansa*-compound was obtained as a mixture of three non-separable diastereomers in a ratio of 1:0.25:0.3. Single-crystal X-ray diffraction analysis allowed the determination of the absolute configuration of one diastereomer, which could be assigned to ($1R$,R_p,S_p,s^P) containing a pseudochiral phosphorus atom (Figure 5). We assume that the ($1R$,R_p,S_p,s^P)-**31** isomer is the main diastereomer formed within this reaction. This can be explained by the steric hindrance of the two methyl groups at C3 at one site of the ferrocenyl backbone, as shown in the crystal packing (Figure 5). Furthermore, the P═O bond is fixed at one site and favors a pseudo-*meso*-lithiation. However, the absolute configuration of the other two diastereomers could not be unequivocally determined. Most likely the pseudo-*racemic* (R_p,R_p) and (S_p,S_p) isomers were formed since their ratio within the product mixture is similar (Experimental Section). Increasing the temperature within the reaction of (1*R*)-**30** with LDA to ambient conditions did not change the dr of (1*R*)-**31**, whereby the amount of the recovered starting material (1*R*)-**30** increased from 0 to 6%. This can be explained by the deprotonation and cleavage of tetrahydrofuran.[5,43] The addition of the methylation reagent Me_2SO_4 also resulted in an activation of the P═O bond, which favors a nucleophilic attack of water during the workup procedure and hence the cleavage of the ferrocenophane. Methylation of the thus-formed 1′-hydroxy moiety gave (1*R*)-**32** as a racemic mixture concerning the configuration of the phosphorus atom. Additionally, 20% of 1,1′-$Fc(OMe)_2$ was isolated, indicating hydrolysis of the [3]ferrocenophane backbone of (1*R*)-**30**.

The usage of ferrocene diol **29** could allow for the consecutive preparation of the super-ferrocenophane **35** as depicted in Scheme 11. In this respect, **29** was metalated by using BuLi and the thus-formed corresponding lithiated species gave **29**-$P_2O_2Cl_4$ with 2 equiv of $POCl_3$. It was expected that the stepwise addition of $(Li)_2$-**29** to the latter compound should result in the formation of phosphate **35**. However, instead, only 12% of the bis[3]ferrocenophane **34** could be isolated (Scheme 11). To investigate if the intermediate bisphosphate **29**-$P_2O_2Cl_4$ or a mixture of the 1,3-dioxa[3]ferrocenophane **29**-POCl and $POCl_3$ was formed, **1**-Li was added instead of $(Li)_2$-**29**. After appropriate workup, **3** (42%), **27a** (20%), and bisphosphate **33** (11%) could be isolated, revealing that the respective reaction mixture contained $POCl_3$, **29**-$P_2O_2Cl_4$, and **29**-POCl. The ratio of **3**/**27a**/**33** also indicated that **29**-POCl was predominantly formed.

Treatment of **33** with LDA at −30 °C resulted in complete decomposition of this compound by producing an insoluble residue during column chromatographic workup. In contrast, bis[3]ferrocenophane **34** gave the double rearranged bisphosphonate **36**, which was isolated in a yield of 62% (Scheme 11, Experimental Section). Compared to previous results of anionic phospho-[5,11] and thia-Fries[15b] rearrangements, the *meso*-(R_p,S_p)-isomer should be exclusively formed.

Since investigations about apFr at phosphoramidates are pending, compounds **37**−**41** with P−N bonds were studied. The family of organophosphorus Fc−O−P−N compounds[44] has sparsely been investigated, including four-membered

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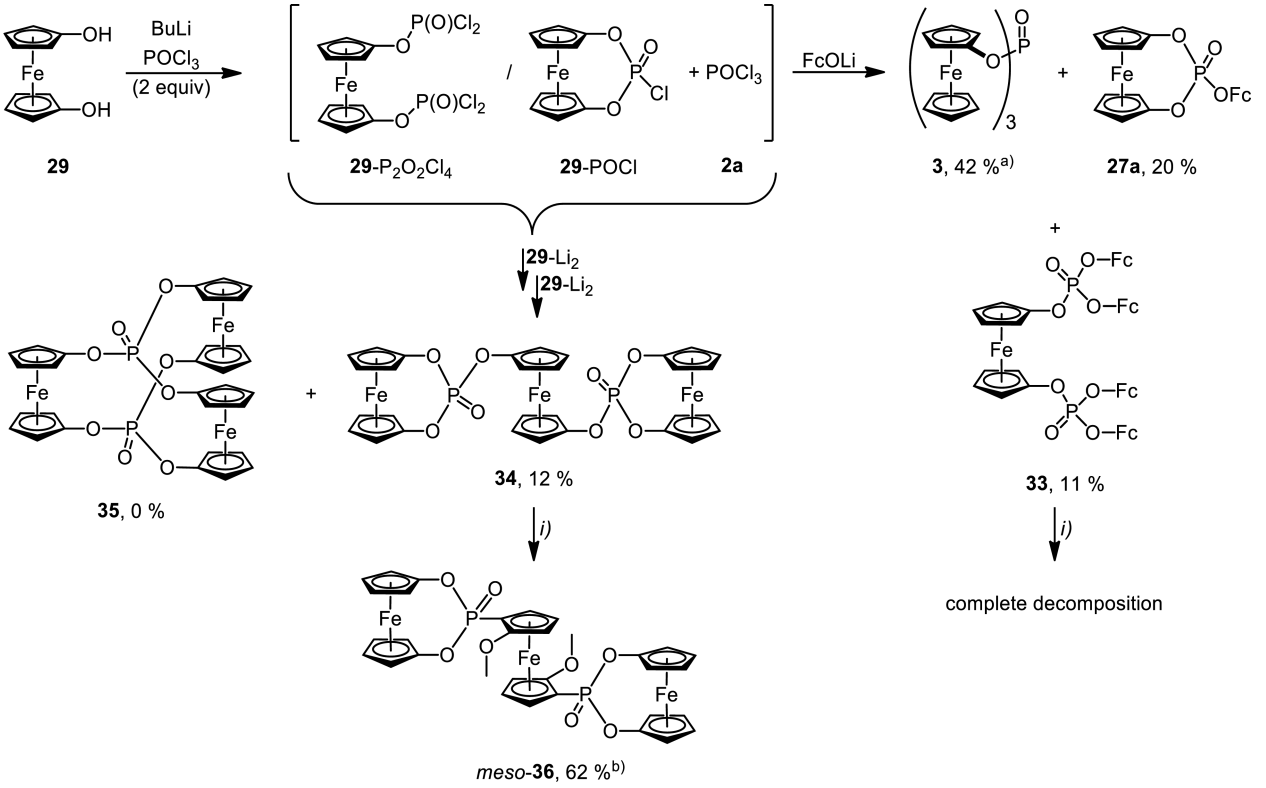
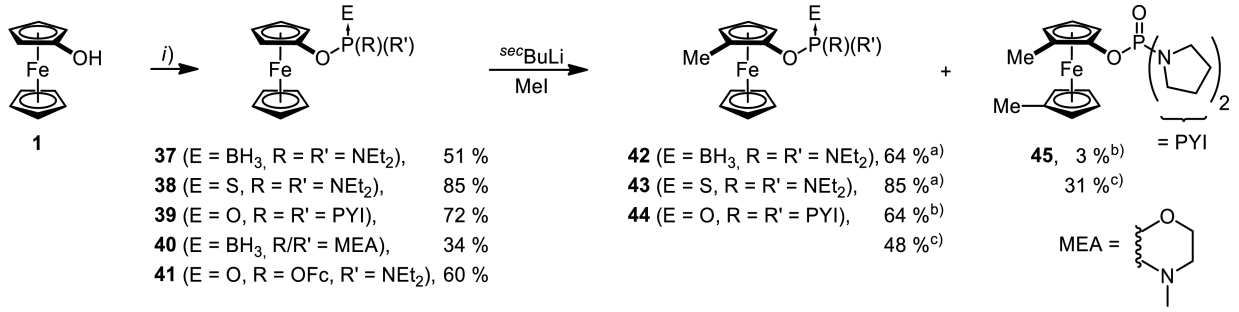
Scheme 11. Reaction of 29 with $POCl_3$ and/or FcOLi for the Synthesis of [3]Ferrocenophanes 27a and 34 and Phosphate 33 (Yields Are Based on 29)*



*Conditions: (*i*) THF, LDA (4 equiv), −30 °C, 2 h, Me_2SO_4 (8 equiv). [a]Yield based on **1**. [b]Yield based on **34**.

Scheme 12. Synthesis of Ferrocenyl Phosphoramidates 37−41 and Their Treatment with *s*-BuLi (Yields Are Based on 37−41)*



37 (E = BH_3, R = R' = NEt_2), 51 %
38 (E = S, R = R' = NEt_2), 85 %
39 (E = O, R = R' = PYI), 72 %
40 (E = BH_3, R/R' = MEA), 34 %
41 (E = O, R = OFc, R' = NEt_2), 60 %

42 (E = BH_3, R = R' = NEt_2), 64 %[a]
43 (E = S, R = R' = NEt_2), 85 %[a]
44 (E = O, R = R' = PYI), 64 %[b]
48 %[c]

45, 3 %[b]
31 %[c]

*Conditions: (*i*) NEt_3 (**37**, **38**, **40**, **41**)/BuLi (**39**), **2i−l**, [BH_3·THF] (**37**, **40**)/S_8 (**38**). Yields are based on **1**. [a]THF, ≤−10 °C, 3.5 h. [b]Hexane, ambient temperature, 18 h. [c]Et_2O, ≤−30 °C, 4 h.

diazadiphosphetidine cycles[39] and six- and eight-membered cyclic phosphazenes.[45]

The aliphatic phosphoramidates **39** and **41**, thiophosphoramidate **38**, and borane adducts **37** and **40** were synthesized, differing between one (**40**, **41**) and two N-bonded substituents (**37**−**39**). They were accessible by the reaction of **1** (in the presence of a base) with chlorophosphineamines **2i,l**, chloropyrrolidine phosphinate **2j**, or the 2-chloro-3-methyl-1,3,2-oxazaphospholidine **2k** (Scheme 12). The P^{III} derivatives were subsequently treated with either the [BH_3·THF] complex (**37**, **40**) or S_8 (**38**).

Consecutive treatment of **37**−**41** with LDA and MeI did not result in the lithiation of these species, and hence, >80% of the starting material could be recovered. The high basicity of the ferrocenyl backbone is caused by an increased electron density, due to the electron-donating N-bonded substituents, as it could be confirmed by electrochemical investigations (Figure S3 and Table 1). Replacing LDA with the stronger base *s*-BuLi allowed the synthesis of the *ortho*-methylated derivatives **42**−**45** (starting from **37**−**39**). Within these reactions, lithiation occurred at the *ortho*-position, whereby the lithium ion is stabilized by the oxygen atom of the ferrocenyl entity. An involvement of the P→E moiety is possible for E = O and S; however, in the case of the borane adduct **43** (E = BH_3), it failed. Nevertheless, the *ortho*-methylated species **42**−**45** could not be separated from their starting materials **37**−**39** due to their similar properties within the column chromatographic workup. However, they could be identified by inter alia ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (vide infra) and are highlighted in Figures S1 and S2 (also see Experimental Section). The lithiation behavior strongly depends on the solvent applied, as it

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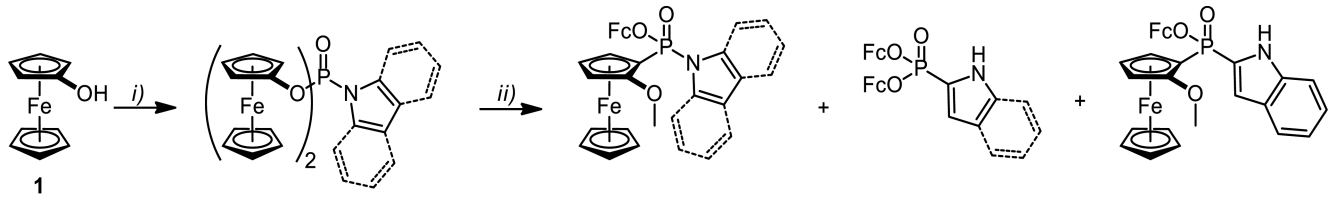
Scheme 13. Synthesis of Ferrocenyl Phosphonates 46−48 and Their Treatment with LDA Causing 1,3-O→C and 1,2-N→C Rearrangements for the Synthesis of 49−54*



46 (1*H*-pyrrol-1-yl), 44 %
47 (1*H*-indol-1-yl), 81 %
48 (9*H*-carbazol-9-yl), 27 %

49 (1*H*-pyrrol-1-yl), 24 %[a)]
50 (1*H*-indol-1-yl), 24 %
51 (9*H*-carbazol-9-yl), 56 %[b)]

52 (1*H*-pyrrol-2-yl), 27 %
53 (1*H*-indol-2-yl), 31 %

54, 67 %[c)]

*Conditions: (*i*) THF, −30 °C, BuLi, **2m−o**; yields are based on **1**; (*ii*) THF, LDA (6 equiv), −40 °C, 2 h, Me_2SO_4 (8 equiv); yields are based on **46−48**. [a]At −70 °C. [b]At −60 °C. [c]At 0 °C.

could be shown for pyrrolidine containing **39**. Thus, running the reaction in hexane gave **44** in a mixture along with **39** and **45** in a ratio of 1:0.24:<0.05, whereas in diethyl ether, a ratio of 1:0.06:0.65 is characteristic, due to the increased reactivity of *s*-BuLi. The methyl group should be substituted in the *ortho*-position to the oxygen atom (1,2-substitution), due to a stabilization of the lithium ion, as found for derivatives possessing a Fc−P bond.[46] To the best of our knowledge, 1,3-disubstituted products can merely be obtained by multiple-step lithiations including reactions with electrophiles[47] or are formed in a negligible yield compared to that with the main 1,2-product.[48] Hence, a 1,3-substitution pattern is rather expected for electrophilic aromatic substitution reactions and not for lithiation reactions as depicted in Scheme 12.[49]

The results of the reactivity of N-bonded, aliphatic Fc−O−P compounds and our previous investigations within this field of chemistry[5] revealed that electron-withdrawing phosphorus groups increase the possibility of a lithiation and the occurrence of an apFr. Thus, we replaced the aliphatic by N-bonded nitrogen heterocycles. The lone pair of the nitrogen is rather involved in the aromatic system, which decreases the transfer of electron density to phosphorus and the ferrocenyls. Thus, their stability toward acidic media is increased.[50]

Phosphonates **46−48** were accessible by the reaction of **1**-Li with dichlorophosphonates **2m−o**, whereby the size of the aromatic systems increased from 1*H*-pyrrole (**46**) to 1*H*-indole (**47**) and 9*H*-carbazole (**48**) (Scheme 13). A wide range of

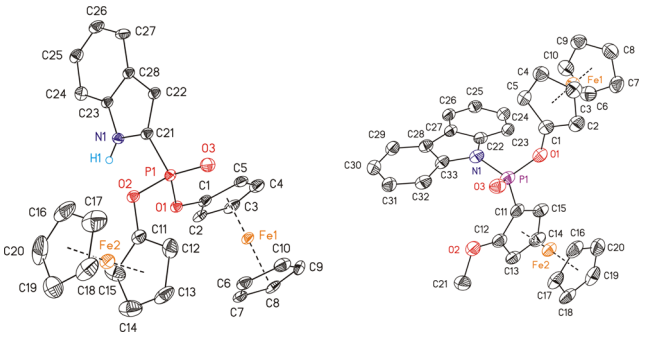


Figure 6. ORTEP (50% probability level) of the molecular structures of **53** (left, 50% probability) and **51** (right, 30% probability level) with their atom-numbering scheme. All C-bonded hydrogen atoms, the disordered atoms (occupancy ratio of 0.88:0.12) in **53**, one disordered molecule of $CHCl_3$ in **53**, and disordered packing solvent in **51** (0.9·CH_2Cl_2) have been omitted for clarity.

pyrrole- and indole-based phosphonates are known, whereas carbazole derivatives are sparsely investigated.[51] This is clarified by reported procedures for the synthesis of **2m−o**, of which only the indolyl derivative **2n** has been reported.[52] Treatment of lithiated carbazole with excess $POCl_3$ in tetrahydrofuran at −80 °C resulted in the formation of **2o**. In contrast, the decreased steric demand and thus the increased reactivity of lithiated pyrrole toward $POCl_3$ required a dropwise addition of pyrrole into a tetrahydrofuran solution containing >10 equiv of $POCl_3$ at −80 °C.

In contrast to the aliphatic derivatives **37−41**, the reaction of **46−48** with LDA followed by the addition of Me_2SO_4 gave several 1,3-O→C (**49−51**, **54**) anionic phospho-Fries and 1,2-N→C (**52−54**) rearranged products (Scheme 13). The latter ones are the first examples of rearrangements of phosphonato moieties. Shifts at thiaphosphonates,[24] chiral phosphine oxides, and sulfides[6] at pyrrole have been reported, whereas indoles have not been investigated. It should be noted that within the synthesis of the indole systems **50** and **53**, 18% of FcOMe could also be isolated, probably due to a nucleophilic attack at the phosphorus atom, combined with the good stabilization of a negative charge at the heterocycle. The reaction of **46** even resulted in the formation of 32% of FcOMe and 45% of recovered starting material at −70 °C, which supports the assumption of a nucleophilic attack.

Contrary to the phenyl and naphthyl phosphates **4−7**, the first rearrangements occurred at the ferrocenyl substituent, resulting in the formation of phosphinates **49−51** (Scheme 13). Increasing the temperature to 0 °C accelerated the rearrangements at the heterocycles, and phosphonates **52** and **53** and phosphinate **54** could be isolated after appropriate workup. The chemical properties toward lithiation reactions could also be derived from electrochemical measurements (Table 1).

The configuration of the predominantly formed diastereomers in **51** could be assigned as R_p,S^P/S_p,R^P based on single-crystal X-ray diffraction analysis (Figure 1). Phosphinate **54** was formed in a ratio of 1:0.098 (0.82 de). It remains unclear whether the diastereoselective process in the case of **54** is caused by steric effects of the heterocycle or by a stabilization of the lithium ions by the aromatic π-system.

Most of the heterocyclic phosphonates and phosphinates showed no sign of decomposition in solution, except for **49**, which rapidly decomposed due to either a nucleophilic attack at the phosphorus atom or oxidation reactions occurring at the pyrrole substituent. Compound **52** was hardly soluble in

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$CDCl_3$, due to the formation of intermolecular hydrogen bridge bonds, as evidenced from in the crystal packing (Figure S30). Thus, a mixture of $CHCl_3$ and DMSO was required for NMR investigations. The structure of **52** could be verified by single-crystal X-ray diffraction analysis (Figure 5).

NMR Spectroscopy. In the ^1H NMR spectra of all ferrocene sandwich compounds, an AA′XX′ signal pattern for the C_5H_4 cyclopentadienyl protons with $^{3,4}J_{H,H}$ coupling constants of ∼2 Hz[53] is observed, which is characteristic of recently reported ferrocenyl phosphates and their rearrangement species (Tables S1 and S2).[2,5,11] The assignment of all resonances is supported by 2D experiments such as COSY, HSQC, and HMBC that are included in the Supporting Information. For **24** and **52**, $^{13}C\{^1H\}$ shifts were taken from HMBC and 90 DEPT measurements, due to their low solubility. In general, diastereomeric ratios were obtained from fitted integrals of the $^{31}P\{^1H\}$ or selected signals in the ^1H spectra to exclude baseline inaccuracies.

The OCH_3 resonances in the 1,3-O→C anionic phospho-Fries rearranged species **9**, **10**, **17**, **18**, **21**, **22**, **24**, **26**, **28**, **36**, **49**−**51**, and **54** appeared as singlets in the ^1H NMR spectra between 3.5 and 4.0 ppm, as expected.[2,5,11]

In contrast, the respective signal in the (*R*)-BINOL phosphonate **28b** occurred somewhat high-field-shifted at 2.63 ppm. The resonances for the C-bonded methyl groups in methylated **31** and **42**−**45** occurred as singlets at ∼2.05 ppm in the ^1H and at 12−14 ppm in the $^{13}C\{^1H\}$ NMR spectra. The coupling pattern and the distribution of the related proton and carbon resonances of the C_5H_3 units support a 1,2-substitution pattern for **42**−**45** (vide supra).

Compounds **13**−**15**, **16a**, **18a**, **19**, **20**, **21a**, **22a,b**, **23**−**25**, and **26a** containing OH and **52**−**54** with NH functionalities showed signals between 9 and 12 ppm, occurring as singlets or as doublets with a $^4J_{H,P}$ coupling of ≤1 Hz.

The ^1H NMR resonances of the methyl groups of **32** occurred as a singlet at 3.37 ppm for the $C_5H_4(OCH_3)$ fragment. In contrast, the P−O−CH_3 fragment was observed as a doublet at 3.82 ppm with a $^3J_{H,P}$ coupling constant of 8.4−11.3 Hz.

A successful 1,3-O→C migration is evidenced by the appearance of doublets in the $^{13}C\{^1H\}$ NMR spectra for formed C_{Fc}−P bonds at 51−59 ppm for the phosphonates **9**, **17**, **28a,b**, **36**, and **49**−**53** and 60−63 ppm for the phosphinates **10**, **18a,b**, **21a,b**, **24**, **26a,b**, and **54** and phosphine oxides **22a,b**. The signals for phenyl-related C_{Ph}−P units occurred between 100 and 122 ppm, independent of the type of the phosphorus compound. However, the trend of the $^1J_{C,P}$ coupling constants follows the order phosphonates (229−206 ppm) > phosphinates (163−184 ppm) > phosphine oxides (111−107 ppm) for the ferrocenyl-related carbons. Non-ferrocenyl-related C−P couplings decrease from N-heterocyclic phosphonates (**52** and **53**; 236−227 ppm) > non-heterocyclic phosphonates (**13**, **16a,b**, **19**, **23**, and **25**; 181−190 ppm) > N-heterocyclic phosphinates (**54**; 172 ppm) > non-heterocyclic phosphinates (**14**, **18a,b**, **20**, **21a,b**, **24**, and **26a,b**; 132−147 ppm) > phosphine oxides **15** and **22** (107−111 ppm) (Tables S1 and S2).

The *ipso*-carbon atoms of the C−O−Me and C−O−P moieties could also be distinguished. Independent from a single or 1,2-double substitution, the C−O−P carbon atoms appear between 116 and 119 ppm, whereas the C−O−CH_3 groups occurred downfield shifted at 126−130 ppm. In contrast, the signals in 1,3-dioxa[3]ferrocenophanes **27a**, **28a**, **30**, **31**, **34**, and **36** are observed at higher fields between 109 and 111 ppm for the C−O−P and 129 and 131 ppm for the C−O−CH_3 fragments.

Phosphates containing three freely rotatable P−O bonds, which is typical for **3**−**7** and **33**, exhibit $^{31}P\{^1H\}$ shifts from −15.3 to −16.9 ppm. *N*-Aryl phosphonates **46**−**48**, showing a similar chemical behavior, are slightly downfield shifted to −11 ppm. Replacement of the *N*-aryl with an *N*-alkyl substituent, as characteristic for **41**, shifts the signal downfield to 2.5 ppm. Phosphorus atoms that are included in 1,3-dioxa[3]-ferrocenophane moieties, in general, showed downfield shifted $^{31}P\{^1H\}$ resonances compared to non-bridged derivatives. Thus, the signals for exclusively ferrocenyl-containing **27a** and **34** occurred at −5.6 ppm, at −2.5 ppm for the (*R*)-BINOL derivative **27b**, and at −4 to 1 ppm for **30** and **31** bearing an aliphatic (1*R*)-*α*-fenchyl substituent. An additional methyl substituent at the cyclopentadienyl ring, as present in **31**, does not influence the ^{31}P shift compared to their non-methylated derivative **30**. The ^{31}P shift also increased from 23 ppm for **39**, **44**, and **45**, bearing two *N*-alkyl groups, to 91 ppm for the P = S derivatives **39** and **43** and to 122−132 ppm for the borane adducts **37**, **40**, and **42**.

Within the synthesized phosphonates, the $^{31}P\{^1H\}$ NMR shift allows a differentiation between O-/N-bonded non-bridged (**17**, **19**, **23**, **25**, **49**−**51**; 14−19 ppm), O-bonded [3]ferrocenophanes (**28a,b**, **36**; 30−35 ppm), and molecules bearing a C-bonded N-heterocycles (**52**, **53**; 4.0−4.5 ppm). The $^{31}P\{^1H\}$ NMR resonances for phosphinates **10**, **14**, **18**, **20**, **21**, **24**, **26**, and **54** range between 25 and 45 ppm. Phosphine oxides **15** and **22** were observed at 38−51 ppm, whereas a trend within the presence of an OCH_3 or OH group could be observed. Thus, the comparison of between the **a** (OH containing) with the respective **b** derivatives (OMe instead of OH) in **16**, **18**, **21**, **26**, and oxide **22** reveals $\Delta\delta$ values of 4 ppm for **16**, more than 9 ppm for **18**, **21**, and **26**, and 11 ppm for **22**. This is probably due to the formation of intramolecular hydrogen bridge bonds that are present in the solid state (Figures 3 and 4 and Figures S10, S12, S25, and S27), in $CDCl_3$ involving the P═O bond, which lowers the electron density at the phosphorus atom. Within the series of the dichlorophosphates of the N-bonded heterocycles, the ^{31}P shifts decrease from 1*H*-pyrrol-1-yl (**2m**, 5.5 ppm) > 1*H*-indolyl-1-yl (**2n**, 2.7 ppm) > 9*H*-carbazol-9-yl (**2o**, 0.5 ppm), whereas this trend is not observed for the respective diferrocenyl phosphates **46**−**48**.

The ^{11}B NMR values for the borane adducts **37**, **40**, and **42** slightly differ between the $(NEt_2)_2$-functionalized compounds **40** and **42** with −39.5 ppm and the cyclic 2-aminoethanol containing species **37** (−42.6 ppm). The appropriate signals appear as doublets with a $^1J_{B,P}$ coupling constant of ∼90 Hz.

Ferrocene **22b** exhibits one signal (>99% de) in the $^{31}P\{^1H\}$ NMR spectrum at 38.2 ppm and two sets of signals in the ^1H and $^{31}C\{^1H\}$ NMR spectra, revealing the formation of two diastereomers. Therefore, the de could be calculated by using the integrals of the OCH_3 (85% de) and the OH (87% de) resonances. This leads to the conclusion that the ^{31}P resonances of both diastereomers occurred isochronically.

The methylated ferrocenes **42**−**45** could be identified within their mixtures with their starting materials (18% of **37** for **42**, 7% of **38** for **43**, and 6% of **39** for **44** and **45**; Scheme 12). The methyl groups were observed at ∼2 ppm in the ^1H and at ∼12 ppm in the $^{13}C\{^1H\}$ NMR spectra, which are characteristic for methylferrocene.[54] The The cyclopentadienyl carbons bearing CH_3 groups showed resonances between 74 and 75 ppm. For

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the 2,1′-functionalized ferrocene **45**, the additional methyl group at the 1′-position was observed at 13.9 ppm. The respective *ipso* signal of the cyclopentadienyls occurred at 85.0 ppm.

Molecular Solid-State Structures. The molecular structures of **4**, **6**, **9**, **10**, **13**, **16a**, **22b**, **24**, **26a**, **27a**, **28b**, **31**, **34**, **40**, **41**, **47**, **48**, and **51**−**53** in the solid state have been determined by single-crystal X-ray diffraction analysis (Figures 1−6). Suitable crystals were obtained by crystallization by slowly cooling hot solutions or by solvent evaporation at ambient temperature (for more details, see the Experimental Section).

The compounds crystallized in the centrosymmetric triclinic space group $P\bar{1}$ (**9**, **24**, **26a**, **34**, **48**, and **51**), the monoclinic space groups $P2_1/n$ (**4** and **53**), $P2_1/c$ (**6**, **10**, **16a**, **22b** and **47**), $C2/c$ (**41**, **52**), and the orthorhombic space groups *Pnma* (**13**) and *Pbca* (**40**). Ferrocenes **27a**, **28b**, and **31** crystallized in the non-centrosymmetric monoclinic space group $P2_1$ (**31**, abs. struct. parameter[55] = 0.002(8)) and the orthorhombic space groups *Fdd*2 (**27a**, abs. struct. parameter = −0.01(2)) and $P2_12_12_1$ (**28b**, abs. struct. parameter = 0.012(16)).

In the asymmetric unit, these compounds are present with one (**4**, **6**, **9**, **10**, **16a**, **22b**, **24**, **26a**, **27a**, **28b**, **40**, **41**, **47**, **48**, and **51**−**53**) two (**31**), or one-half (**13** and **34**) of crystallographically independent molecule(s). The two molecules of **31** differ by the rotation of the (1*R*)-*α*-fenchyl moiety around its P−O bond, as confirmed by the $C1_{Fn}$−$C2_{Fn}$−O_{Fn}−P torsions of −90.8(4) and −151.6(3)° (Figure S21).

This also explains the favored formation of one diastereomer, due to this free rotation of the sterically demanding methyl groups at C3 and also the possibility for lithiation if they are slightly bended in one direction. In phosphonate **13**, a mirror plane is present in the phenyl plane, including the P1, O2, and O3 atoms (Figure 3). The formula unit of phosphate **34** can be calculated by the inversion through the Fe2 atom (Figure S22).

The O−P−O bridge also decreases the Cp···Fe···Cp′ angle (Cp = C_5H_5; Cp′ = C_5H_4 or C_5H_3) from 175.59(4)°, which is the smallest value found in the MeO-substituted moiety in **9**, to 170.41(4)−171.8(10)° in **27a**, **31**, and **34**. These values are in accordance with 171.1° for the only reported example of a solid-state structure of an O−P−O-bridged 1,3-dioxa-2-phospha[3]ferrocenophane.[39]

In further examples of solid-state structures containing 1,1′-disubstituted ferrocenes in an O−M−O moiety, the ferrocenyl backbone acts as a chelating ligand for metals,[56] for compounds of 1,1′-ferrocenediol and related macrocyclic diethers,[57] exhibiting significantly increased Cp···Fe···Cp′ angles toward the oxygen coordination site with a minimum of 174.5°.[56]

The bite angle of the 1,1′-substituted ferrocenes strongly depends on the number of bridging atoms (Supporting Information).

The absolute configuration of phosphonate **10** of the predominantly formed diastereomer (0.77 de, Scheme 3) could be assigned to the pair of the *meso*-diastereomers R_p,S_p,R^P and S_p,R_p,S^P (Figure 1). The pair of racemic enantiomers ($R_p,R_p/S_p,S_p$) was present in solution (0.89:0.11, Experimental Section) and cocrystallized (ratio 0.9:0.1), resulting in a disorder of the structure (omitted in Figure 1).

Phosphinate **24** predominantly crystallized as the S_p,S^P isomer, whereas the disordered part occurred in a R_p,R^P configuration (ratio of 0.722:0.278). With regard to the centrosymmetric space group $P\bar{1}$, a diastereoselective crystallization of **24** took place. The other set of diastereomers ($S_p,R^P/R_p,S^P$), present in solution in a ratio of 1:0.78 (Experimental Section), was, however, not observed.

A diastereoselective crystallization process also occurred in the case of phosphinate **26b**. NMR investigations (vide supra) revealed a ratio of both diastereomers of 1:0.5, whereas single crystals of **26b** appeared as a mixture of both enantiomers R_p,S^P and S_p,R^P, respectively, which are the most predominantly formed configurations.

Phosphate **31** possesses, similar to *meso*-**10**, a pseudochiral phosphorus atom, due to the different configurations of the C_5H_3Me moieties, resulting in the (1*R*-*α*,R_p,S_p,s^P)-**31** isomer.

We conclude that this is the predominantly formed configuration within the mixture of isomers, based on NMR investigations, which showed an isomeric mixture of 1:0.25:0.3 (Experimental Section). In the carbazole derivative **51** a dr of 1:0.28 is characteristic, as evidenced by NMR experiments (vide supra), while single crystals of the R_p,S^P- and S_p,R^P-configured molecules were obtained. The kinetic resolution of **22a** to **22b** within the methylation reaction (Scheme 6) resulted in the formation of $S_p,S^P/R_p,R^P$ isomers.

Interestingly, the P═O bond in **22b** (1.5013(15) Å) is enlarged compared to the other P^V compounds reported herein (1.441(8)−1.477(2) Å). In the P^{III} species **40**, the P−B bond distance is further increased to 1.881(5) Å, which is in the range of reported structures (1.868−1.899 Å)[58,59] for this type of compound (vide infra).

Compound **26b** exhibits the shortest Fe···Cp′ distance of 1.6279(6) Å compared to all other compounds reported herein (Tables S3−S5) but is typical for other ferrocenes bearing phosphole or benzannelated moieties.[60] This is evidenced by the formation of an intermolecular T-shaped *π* interaction with the naphthyl ring of an adjacent molecule, resulting in the formation of a dimer (Figure S18). This behavior is supported by a *π*−*π* interaction of 3.277(7) Å between the C25 atoms of adjacent coplanar naphthyl rings (*α* = 0°).

Ferrocene **28b** is the third example of a binaphthyl-related phosphonate; one has been reported with the same configuration at the BINOL (*R*)[28] and one as the racemic mixture.[61]

The bridging of the BINOL moiety to a phosphepine structure shifts the oxygen atoms by 0.154(6) (O1) and 0.039(6) Å (O2) out of the $C_{10}H_6$ plane. However, the bending of the naphthalene entities out of their planarity is rather low (5.7(4) and 4.4(5)°; Tables S3−S5). Both planes of the two naphthyls are rotated by 54.6 (2)°.

Indoles that are not bearing stabilizing substituents in 3-position are also rarely described in the solid state, that is, one example of a 1*H*-indole phosphate/phosphonate with a P−N bond.[62]

Furthermore, the molecular structure of a 2-indanone derivative in the solid state was reported.[63] Compound **53** is the first example of a molecular solid-state structure of a 1*H*-indol bearing a phosphorus moiety in the 2-position.

Additional features in the packing of the solid-state structures of the compounds described herein are graphically described in Figures S5−S33 (Supporting Information).

Electrochemistry. The electrochemical behavior of the ferrocenyl phosphates **3**−**7**, **27a**,**b**, **30**, **31**, **33**, and **34**, the phosphonates **9** and **28b**, the phosphinate **10** (Figure 7 and Supporting Information Figure S3), and the nitrogen-containing ferrocenyl phosphoramidates **37**−**41**, **46**−**48**, and **51** were investigated by cyclic voltammetry (CV) and square-wave voltammetry (SWV). The charge transfer behavior of the

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Table 1. Cyclic Voltammetry Data of Compounds 3−7, 9, 10, 27a,b, 28b, 30, 31, 33, 34, 37−41, 46−48, and 51[a]

compound	$E_1^{\circ\prime}$[b] (ΔE_p)[c]	$E_2^{\circ\prime}$[b] (ΔE_p)[c]	$E_3^{\circ\prime}$[b] (ΔE_p)[c]	$\Delta E^{\circ\prime}$[d]
3	30 (64)	235 (66)	435 (68)	205/200
4	85 (60)	250 (65)		165
5	106 (60)			
6	85 (60)	250 (66)		165
7	90 (68)	260 (70)		170
9	−20 (64)	200 (62)	520 (76)	220/320
10	−60 (66)	205 (70)	510 (80)	265/305
27a	110 (62)	535 (72)		425
27b	142 (64)			
28b	152 (68)			
30	302 (64)			
31	254 (60)			
33	90 (70)	270 (60)	800 (135)	180/530
34	225 (70)	540 (125)[e]		315
37	−29 (65)			
38	−50 (62)			
39	−63 (62)			
40	62 (64)			
41	−14 (74)	202 (106)		216
46	100 (58)	260 (66)		160
47	95 (60)	255 (62)		160
48	90 (62)	250 (66)		160
51	40 (60)	290 (64)		250

[a]All potentials are given in mV. [b]$E^{\circ\prime}$ = formal potential of the respective redox process. [c]ΔE_p = difference between oxidation and reduction potentials. [d]$\Delta E^{\circ\prime}$ = potential difference between the ferrocenyl-related redox processes. Potentials vs FcH/FcH^+, scan rate of 100 mV s^{-1} at a glassy carbon electrode of 1.0 mmol L^{-1} solutions in anhydrous dichloromethane containing 0.1 mol L^{-1} of $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte at 25 °C. [e]Broad two-electron process.

oxidized products of **3** and **10** were studied in an exemplary manner in more detail by in situ UV−vis/NIR spectroelectrochemistry (Supporting Information, Figure S4). Selected CV and SWV of individual monoferrocenes are presented in the Supporting Information (Figure S3).

The CV data are summarized in Table 1. All measured compounds, except **33** and **34**, show for each ferrocenyl moiety one well-separated reversible one-electron redox event. For compound **3**, with its three OFc units, three separated redox processes with the first one at $E_1^{\circ\prime}$ = 30 mV were found (Figure 7), due to the weak coordinating electrolyte $[^nBu_4N][B(C_6F_5)_4]$, which is known to stabilize highly charged species and minimize ion pairing effects.[64−66] However, this differs when $[^nBu_4N][ClO_4]$ as electrolyte was used, as reported by Herberhold et al. There, only two reversible events were observed with a two-electron step for the first and a one-electron step for the second oxidation.[38]

When one ferrocenyl group in **3** is replaced by an electron-poorer phenyl moiety, as is typical in **4**, the first redox process is shifted to a higher redox potential ($E_1^{\circ\prime}$ = 85 mV) (Table 1), as expected. The same trend is observed for **5** in which two ferrocenyl moieties are replaced by two phenyl units ($E_1^{\circ\prime}$ = 106 mV) (Table 1). A replacement of the phenyl group in **4** by a naphthyl moiety, as is characteristic for **6** or **7**, however, does not have any notable influence on the first (**4** and **6**, $E_1^{\circ\prime}$ = 85 mV; **7**, $E_1^{\circ\prime}$ = 90 mV) or second redox potential (**4** and **6**, $E_2^{\circ\prime}$ = 250 mV; **7**, $E_2^{\circ\prime}$ = 260 mV).

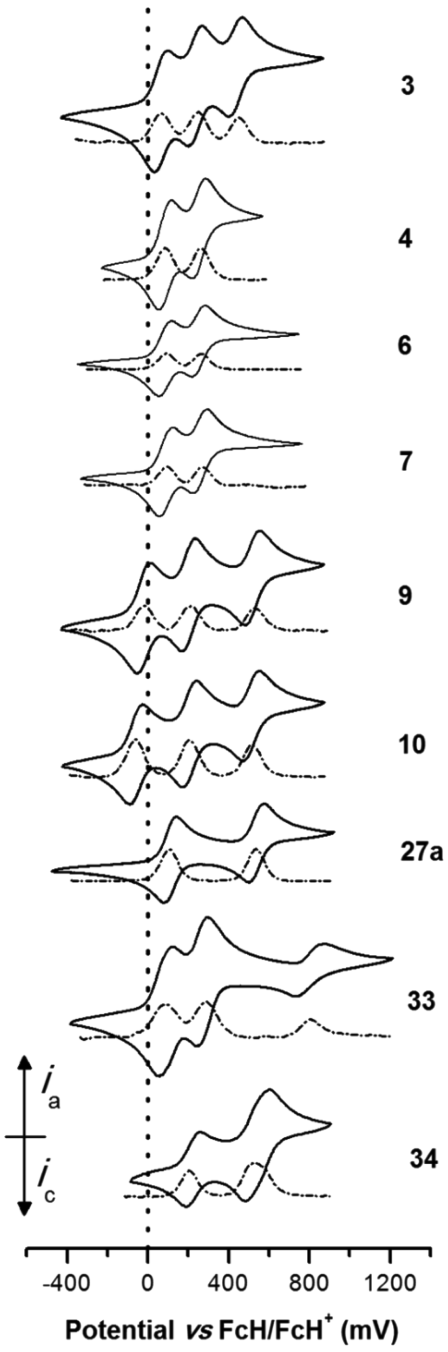

Figure 7. Cyclic voltammograms (solid lines, scan rate 100 mV s^{-1}) and square-wave voltammograms (dotted lines, step height 25 mV, pulse width 5 s, amplitude 5 mV) ferrocenyl phosphates **3**, **4**, **6**, **7**, **27a**, **33**, **34**, phosphonate **9**, and phosphinate **10** in dichloromethane solutions (1.0 mmol L^{-1}) at 25 °C using a glassy carbon working electrode. Supporting electrolyte is 0.1 mol L^{-1} of $[N^nBu_4][B(C_6F_5)_4]$.

The anionic phospho-Fries rearrangement of **3** to give **9** led to a decrease of the first redox potential, due to the more electron-donating methoxy group, which increases the electron density at the ferrocenyl (**3**, $E_1^{\circ\prime}$ = 30 mV; **9**, $E_1^{\circ\prime}$ = −20 mV).

A second rearrangement to form compound **10** leads to a similar reduction of the first redox event from $E_1^{\circ\prime}$ = −20 mV (**9**) to $E_1^{\circ\prime}$ = −60 mV (**10**), whereas the second and third redox processes have not been influenced. The reason, therefore, is the lower electron-withdrawing effect of the

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phosphonate group in methoxy ferrocene **10**, leading to a higher electron density at the ferrocenyl moiety, and as a result thereof, this compound can more easily be oxidized.

In situ UV−vis/NIR spectroelectrochemical measurements were additionally carried out for compounds **3** and **10**. However, no intervalence charge transfer absorptions were found (Supporting Information, Figure S4). This shows that no direct electronic communication between the Fc and Fc^+ units occurs, indicating significant electrostatic interaction among the terminal Fc/Fc^+ groups as oxidation progresses.[2,10]

Replacing the electron-rich [3]ferrocenophane group in **27a** with a chelating (*R*)-BINOL substituent in **27b** increased the first redox potential from $E_1^{\circ\prime}$ = 110 mV to $E_1^{\circ\prime}$ = 142 mV. A series of ferrocenophanes inter alia **27b** were electrochemically investigated by Herberhold using $[^nBu_4N][ClO_4]$ as electrolyte.[38] There, a lower redox separation of $\Delta E^{\circ\prime}$ = 300 mV ($E_1^{\circ\prime}$ = 550 mV, $E_2^{\circ\prime}$ = 850 mV vs SCE) was observed, which is attributed to the stronger coordinating character of the electrolyte (vide supra). Zanello et al. studied the redox behavior of tri- and ditellura-ferrocenophanes and described an unambiguous assignment of the molecule orbitals in the redox process.[67]

The apFr of **27b** leading to **28b** shows a similar redox behavior (Supporting Information, Figure S3). The electron-donating effect of the methoxy group to the ferrocenyl moiety in **28b** is superimposed by the electron-withdrawing effect of the phosphonate moiety.

The methyl groups in the 2,2′-position in **31** shift the redox potential, in comparison to **30**, to lower values ($E_1^{\circ\prime}$ = 254 mV for **31**, $E_1^{\circ\prime}$ = 302 mV for **30**) due to their electron-donating effect. Compound **33**, bearing five ferrocenyls, showed three redox processes. The four OFc groups are represented by the first two redox events at $E_1^{\circ\prime}$ = 90 mV and $E_2^{\circ\prime}$ = 270 mV. Both consist of two nonseparated one-electron processes of one ferrocenyl at each phosphate fragment. The one-electron redox wave at $E_3^{\circ\prime}$ = 800 mV represents the 1,1′-substituted ferrocenyl (Table 1). The difference between the anodic and cathodic potential of ΔE_p = 135 mV indicates an electrochemical irreversibility of the third redox event. The redox potential at $E_3^{\circ\prime}$ = 800 mV leads to the conclusion that both phosphate groups, each bearing two oxidized ferrocenyl, exerts a high electron-withdrawing effect. It is known, for example, for formyl-substituted ferrocenes that a second substitution of a monofunctionalized ferrocene with the same functionality leads to a summation of the electronic effects and, therefore, to a linear increase or decrease of the redox potential.[68] Molecule **34** containing two [3]ferrocenophane motifs, compared to two ferrocenyls at the phosphorus atom (**33**), showed two redox processes: a one-electron event for the non-bridged and a redox process with a shoulder including two one-electron processes for both [3]ferrocenophanes (Figure 7).

Electrochemical measurements of ferrocenyl phosphoramidates **46**−**48** and **51** display two reversible one-electron redox processes (Table 1). The nature of the N-heterocycle in **46**−**48** has negligible influence on the redox potential (Table 1), and as consequence thereof, the redox separation is $\Delta E^{\circ\prime}$ = 160 mV, identical for all three compounds. A further redox process for the N-heterocycle was not observed under the applied measurement conditions. The first redox process for **51** is found at $E_1^{\circ\prime}$ = 40 mV (for comparison, for **48**, $E_1^{\circ\prime}$ = 90 mV), which is attributed to the electron-donating methoxy substituent (Table 1). The second redox event is $E_2^{\circ\prime}$ = 290 mV for **51**, 40 mV higher than in **48**, which can be explained by the more electron-withdrawing influence of the directly to phosphorus-bonded Fc^+ moiety.

Besides the importance of the electron density at the ferrocenyls for limiting a lithiation process, also the nature of the substituent is relevant. Thus, triferrocenyl phosphate **3** (30 mV, Table 1) underwent an apFr, whereas the borane adduct **40** (62 mV) showed no attack at the phosphorus atom, although it contained a ferrocenyl unit with a decreased electron density. Obviously, the strongly electron-donating cyclic *N*-alkyl group shields the phosphorus atom and thus prevents a nucleophilic attack. Compared to *N*-aryl phosphates **46**−**48**, this is due to the electron-rich *N*-alkyl substituents, enabling a better orbital overlap between the N and the P atoms.

In contrast to the compounds described above, phosphoramidates **37**−**41** did not undergo an apFr, although lithiation reactions were observed by using the stronger base *s*-BuLi instead of LDA (Scheme 12). This indicates that a higher electron density is present at the ferrocenyls in **37**−**41**, which is verified by the lower redox potentials of up to 62 mV for the borane adduct **40**. In contrast, the aromatic derivatives and the [3]ferrocenophanes **30** and **31** are observed at higher values of 90 mV (Table 1). The low values for phosphonate **9** (−20 mV) and phosphinate **10** (−60 mV) are misleading, as the first redox event refers to the methoxy-substituted ferrocenyl, which is not able to undergo an apFr. Within the series of aliphatic ferrocenyl phosphates, the replacement of a P═O (**39**, −63 mV) by a P═S (**38**, −50 mV) and furthermore a P→BH_3 (**37**, −29 mV) group decreases the electron density at the ferrocenyl, while increasing the redox potential. This is contrary to the results obtained by apFr within the series of $P(E)(OFc)(OEt)_2$,[5] with decreasing yields for E = O (94%) > E = BH_3 (37%) > E = S (0%). The latter one could only be converted by using *s*-BuLi (50%). Replacement of an *N*-alkyl (**39**) by an FcO moiety (**41**) shifts the potential for the first redox event from −63 to −14 mV.

CONCLUSIONS

A series of *O*-ferrocenyl-*O*′-aryl phosphates have been synthesized and investigated within anionic phospho-Fries rearrangements (apFr). This 1,3-O→C migration is limited to one ferrocenyl group within one reaction step, enabling the phosphonate and phosphinate of triferrocenyl phosphate $P(O)(OFc)_3$ (Fc = $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$) to be easily accessible. In contrast, the number of phenyl-based rearrangements solely depends on the temperature, requiring a strict temperature regime within one reaction step. We could show for the first time that in the presence of different types of aromatics, combined within one molecule, the first lithiation and migration process, moreover, take place at the phenyl units, due to the higher electron density at the ferrocene backbone and thus their lower basicity. Scavenging of the reactions with Me_2SO_4 also showed a complete methylation of ferrocenyls, whereas phenyls rather remain with a hydroxy functionality. The presence of a 1,3-dioxa-[3]ferrocenophane moiety limits the rearrangements to the non-bridging substituent. In case of a chiral (*R*)-BINOL derivative, this proceeds with a >91% de, resulting in an (R_p) configuration at the ferrocenyl backbone, as evidenced by single-crystal X-ray diffraction analysis. If rearrangements were excluded, *ortho*-lithiations took place, resulting in the presence of an electrophile *ortho* to the oxygens. Ferrocenylic P^V and P^{III} derivatives bearing N- instead of O-bonded aliphatics do not undergo an apFr, whereas they are

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lithiated in *ortho*-position. This could be proven by electrochemical investigations, revealing a lower value for the first redox potential and, thus, a higher electron density at the ferrocenyls and the phosphorus atoms. Replacing *N*-aliphatic with *N*-aromatic 1*H*-pyrrole, 1*H*-indole, and 9*H*-carbazole moieties allowed 1,3-O→C rearrangements and coincidently increased the value for the first redox event. However, besides the electron density at the ferrocenyls, clarified by the first redox potential, the shielding of the phosphorus atom toward a nucleophilic attack is also important. Therefore, triferrocenyl phosphate **3** ($E_1^{\circ\prime}$ = 30 mV) as a unique example undergoes an apFr, whereas the borane adduct **40**, possessing a higher potential of $E_1^{\circ\prime}$ = 62 mV, could not be lithiated under identical reaction conditions. The absence of a lithiation reaction at *N*-alkyl-substituted phosphoramidates is due to the higher electron density of the lone pair of the electrons at the nitrogen atom, compared to aromatic derivatives. Changing the base from LDA to *s*-BuLi resulted in an *ortho*-lithiation, whereas an 1,3-O→C rearrangement did not occur, due to the shielding of the phosphorus atom.

Besides apFr, the 1,2-N→C migrations also occurred for the pyrrole and indole derivatives. The identity and absolute configuration of some compounds could inter alia be verified by using single-crystal X-ray diffraction analysis. The measurements confirmed the formation of intra- or intermolecular hydrogen bridge bonds for compounds possessing OH and NH functionalities.

EXPERIMENTAL SECTION

General. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. For column chromatography, either silica with a particle size of 40−60 μm (230−400 mesh (ASTM)) or alumina with a particle size of 90 μm was used. The assignment and labeling of the H and C atoms in the NMR follows the IUPAC recommendations.[69]

Reagents. Tetrahydrofuran and hexane were purified by distillation from sodium/benzophenone ketyl, diethyl ether by distillation from sodium, and *N*,*N*-diisopropyl amine by distillation from calcium hydride. $POCl_3$ (**2a**) was distilled prior to usage.

Ferrocene, $ClSn(^nBu)_3$, iodine, 1*H*-pyrrole, 1*H*-indole, 9*H*-carbazole, [BH_3·THF] (1 M), ^{t}BuOOH (5.5 M in decane), 1-naphthol, 2 naphthol, 3-hydroxypyridine, 2-(methylamino)ethanol, butyllithium (2.5 M solution in hexane), *s*-BuLi (1.3 M in cyclohexane), LiTMP, dimethyl sulfate, triphenylphosphate, pyrrolidine, sulfur, (*R*)-[1,1′-binaphthalene]-2,2′-diol, (1*R*)-*α*-fenchol, dichlorophenyl phosphate (**2b**), and chlorodiphenyl phosphate (**2c**) were purchased from commercial suppliers and were used without further purification.

Ferrocenol (**1**),[5,41] 1,1′-ferrocenediol (**29**),[5,41] dichloro(1*R*)-*α*-fenchyl phosphate (**2h**),[11] 1-chloro-*N*,*N*,*N*′,*N*′-tetraethylphosphinediamine (**2i**),[70] chlorodi(pyrrolidin-1-yl)phosphinate (**2j**),[71] dichloro-*N*,*N*-diethylphosphinamine (**2l**),[72] 2-chloro-3-methyl-1,3,2-oxazaphospholidine (**2k**),[73] and [NBu_4][$B(C_6F_5)_4$][71] were synthesized according to literature procedures reported elsewhere.

The chlorophosphates **2d**,**e**,**g**,**n**,**j** have already been described, however, by using BuLi as the base instead of an amine. The spectroscopic data are in agreement with those reported in literature: dichloro-1-naphthylphosphate (**2d**),[74] dichloro-2-naphthylphosphate (**2e**),[75] (11b*R*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine 4-oxide (**2g**),[76] and dichloro(1*H*-indol-1-yl) phosphonate (**2n**).[52a] The synthesis and behavior toward anionic phospho-Fries rearrangements of **3**, **4**, and **5** as well as the spectroscopic data of all their rearrangement products have been described.[2]

Instruments. NMR spectra were recorded with a Bruker Avance III 500 spectrometer (500.3 MHz for ^{1}H, 160.4 MHz for ^{11}B, 125.8 MHz for ^{13}C, and 202.5 MHz for ^{31}P) and are reported with chemical shifts in *δ* (ppm) units downfield from tetramethylsilane with the solvent as the reference signal (chloroform-d_1: ^{1}H at 7.26 ppm and ^{13}C{^{1}H} at 77.00 ppm; benzene-d_6: ^{1}H at 7.16 ppm and ^{13}C{^{1}H} at 128.06 ppm; dimethylsulfoxide-d_6: ^{1}H at 2.50 ppm and ^{13}C{^{1}H} at 39.52 ppm), by external standards (^{31}P{^{1}H} relative to 85% H_3PO_4, 0.0 ppm and $P(OMe)_3$, 139.0 ppm), or by the ^{2}H solvent lock signal.[77] For compounds consisting of mixtures of different diastereomers, the main diastereomer was assigned to be the major (ma) and the remaining diastereomer to be the minor (mi) stereoisomer.

The melting or decomposition points were determined by using a Gallenkamp MFB 595 010 M melting point apparatus. Elemental analyses were performed with a Thermo FlashAE 1112 instrument. High-resolution mass spectra were recorded with a Bruker Daltonik micrOTOF-QII spectrometer.

Electrochemistry. Electrochemical measurements on **3**−**7**, **9**, **10**, **27a**,**b**, **28a**,**b**, **30**, **31**, **33**, **34**, **37**−**41**, **46**−**48**, and **51** (1.0 mmol·L^{-1}) using 0.1 mol·L^{-1} [NBu_4][$B(C_6F_5)_4$] as the supporting electrolyte[78] in anhydrous, oxygen-free dichloromethane were performed in a argon-purged cell at 25 °C with a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer.[70,79] Spectroelectrochemical measurements (Figure S4) were performed in an optically transparent thin-layer electrochemical cell placed in a Varian Cary 5000 UV/vis−NIR absorption spectrometer using anhydrous dichloromethane solutions containing 2.0 mmol L^{-1} of the analyte and 0.1 mol L^{-1} of [N^nBu_4][$B(C_6F_5)_4$] as supporting electrolyte at 25 °C.[80] Between the spectroscopic measurements, the applied potentials have been increased stepwise using step heights of 25, 50, or 100 mV. At the end of the measurements, the analyte was reduced at −400 mV for 30 min and an additional spectrum was recorded to prove the reversibility of the oxidations.

For the voltammetric measurements, a three-electrode cell containing a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm^2), and a Ag/Ag$^+$ (0.01 mmol L^{-1} [$AgNO_3$]) reference electrode fixed on a Luggin capillary was used. The working electrode was pretreated by being polished on a Buehler microcloth first with 1 μm and then with a 1/4 μm diamond paste. The reference electrode was constructed from a silver wire inserted into a 0.01 mmol L^{-1} solution of [$AgNO_3$] and 0.1 mol L^{-1} of an [NBu_4][$B(C_6F_5)_4$] acetonitrile solution in a Luggin capillary with a CoralPor tip. This Luggin capillary was inserted in a second Luggin capillary containing a 0.1 mol L^{-1} [NBu_4][$B(C_6F_5)_4$] dichloromethane solution and a CoralPor tip. Experiments under the same conditions showed that all reduction and oxidation potentials were reproducible within ±5 mV. Experimental potentials were referenced against a Ag/Ag$^+$ reference electrode, but the presented results are referenced against ferrocene as an internal standard as required by IUPAC.[81] To achieve this, each experiment was repeated in the presence of 1 mmol L^{-1} of decamethylferrocene (Fc*). Data were processed on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH$^+$ couple to 0.0 V.[82] Under our conditions, the Fc*/Fc*$^+$ couple was at −614 mV vs FcH/FcH$^+$, ΔE_p = 60 mV, while the FcH/FcH$^+$ couple was at 220 mV vs Ag/Ag$^+$, ΔE_p = 61 mV.

Single-Crystal X-ray Diffraction Analysis. Data of **4**, **6**, **9**, **10**, **13**, **16a**, **22b**, **24**, **26b**, **27a**, **28b**, **31**, **34**, **40**, **47**, **48**, **51**, **52**, and **53** were collected with an Oxford Gemini S diffractometer at ≤120 K with graphite-monochromated Mo K*α* radiation (*λ* = 0.71073 Å). The molecular structures were solved by direct methods using SHELXS-13[83] and refined by full-matrix least-squares procedures on F^2 using SHELXL-13.[58,84] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the treatment of the hydrogen atom positions, unless otherwise noted. Graphics of the molecular structures were created using ORTEP.[85]

Synthesis of Ferrocenyl Phosphates and Phosphonates: General Procedure. In a Schlenk tube, the respective amount of ferrocenol (**1**) or 1,1′-ferrocenediol (**29**) was dissolved in 20 mL of tetrahydrofuran, and the obtained solution was cooled to −30 °C. BuLi (**1**, 1 equiv; **29**, 2 equiv) was added dropwise, and the suspension was stirred for 10 min at this temperature. The mixture was cooled to −70 °C, and 1 equiv of the respective chlorophosphates **2g**,**i**−**k** or 0.5 equiv of the respective dichlorophosphates **2d**−**f**,**h**,**l**−**o** was added with a Pasteur pipet in a single portion. After allowing the reaction mixture

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to warm to ambient temperature, we continued stirring for 18 h, and all volatiles were removed in vacuum. The crude products were filtered through 5 cm of alumina using a 1:1 dichloromethane/ethyl acetate (v/v) mixture as the eluent to remove unreacted **1**. Purification was realized by column chromatography (silica or alumina; for column size, see below) using different solvent mixtures (see below). After removal of all volatiles in vacuum, the respective phosphates were obtained as orange solids or oils.

*Diferrocenyl(1-naphthyl) Phosphate (**6**).* Ferrocenol (**1**, 600 mg, 2.97 mmol), BuLi (1.2 mL, 3.0 mmol), and dichloro(1-naphthyl) phosphate (**2d**, 388 mg, 1.5 mmol) were reacted according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 15 cm) using a 9:1 dichloromethane/hexane mixture (v/v) as the eluent. The title compound **6** was obtained as an orange solid. Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by crystallization from a boiling hexane solution containing **6**. Yield: 195 mg (0.364 mmol, 25% based on **1**). Anal. Calcd for $C_{30}H_{25}Fe_2O_4P{\cdot}1/6C_6H_{14}$ (592.18·1/6 86.18 g/mol): C, 61.39; H, 4.54. Found: C, 61.39; H, 4.63. Mp: 130−134 °C. ^{1}H NMR ($CDCl_3$, δ): 3.91 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 4 H, H3,4$_{C5H4}$), 4.21 (s, 10 H, C_5H_5), 4.44−4.46 (m, 4 H, H2,5$_{C5H4}$), 7.45 (t, $J_{H,H}$ = 7.9 Hz, 1 H, H3$_{C10H7}$), 7.53−7.56 (m, 3 H, H2/6/7$_{C10H7}$), 7.72 (d, $J_{H,H}$ = 8.1 Hz, 1 H, H4$_{C10H7}$), 7.86−7.88 (m, 1 H, H5$_{C10H7}$), 8.11−8.13 (m, 1 H, H8$_{C10H7}$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.86 (d, $^3J_{C,P}$ = 3.9 Hz, C2/5$_{C5H4}$), 59.90 (d, $^3J_{C,P}$ = 3.7 Hz, C2/5$_{C5H4}$), 62.9 (C3/4$_{C5H4}$), 69.6 (C_5H_5), 115.1 (d, $^3J_{C,P}$ = 2.9 Hz, C2$_{C10H7}$), 117.9 (d, $^2J_{C,P}$ = 5.3 Hz, C$_{C5H4}$−O), 121.7 (C8$_{C10H7}$), 125.39 (C3$_{C10H7}$), 125.40 (C4$_{C10H7}$), 126.3 (d, $^3J_{C,P}$ = 6.9 Hz, C8a$_{C10H7}$), 126.5 (C6/7$_{C10H7}$), 126.8 (C6/7$_{C10H7}$), 127.7 (C5$_{C10H7}$), 134.8 (C4a$_{C10H7}$), 146.4 (d, $^2J_{C,P}$ = 7.6 Hz, C1$_{C10H7}$). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −15.6. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{25}Fe_2O_4P$ 592.0185; found 592.0160.

*Diferrocenyl(2-naphthyl) Phosphate (**7**).* Ferrocenol (**1**, 836 mg, 4.138 mmol), BuLi (1.7 mL, 4.25 mmol), NEt_3 (0.6 mL, 4.3 mmol), and dichloro(2-naphthyl) phosphate (**2e**, 515 mg, 1.973 mmol) were reacted according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 35 cm) using chloroform as the eluent. The title compound was obtained as an orange oil. Yield: 380 mg (0.64 mmol, 65% based on **2e**). Anal. Calcd for $C_{30}H_{25}Fe_2O_8P_2{\cdot}1/3\ C_6H_{14}$ (741.99·1/3 86.18 g/mol): C, 49.87; H, 3.75. Found: C, 49.65; H, 3.59. Mp: >230 °C (decomp.). ^{1}H NMR ($CDCl_3$, δ): 3.93 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, H3,4$_{C5H4}$), 4.26 (s, 10 H, C_5H_5), 4.46−4.48 (m, 4 H, H2,5$_{C5H4}$), 7.39 (dd, $^3J_{H,H}$= 8.9 Hz, $^4J_{H,H}$ = 2.4 Hz, 1 H, H3), 7.45−7.53 (m, 2 H, $C_{10}H_7$), 7.73−7.75 (m, 1 H, H1), 7.82−7.87 (m, 3 H, $C_{10}H_7$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.76 (d, $^3J_{C,P}$ = 4.1 Hz, C2/5$_{C5H4}$), 59.77 (d, $^3J_{C,P}$ = 4.0 Hz, C2/5$_{C5H4}$), 62.9 (s, C_5H_4), 69.7 (s, C_5H_5), 116.5 (d, $^3J_{C,P}$ = 5.0 Hz, C1), 117.9 (d, $^2J_{C,P}$ = 5.4 Hz, C$_{C5H4}$−O), 119.8 (d, $^3J_{C,P}$ = 5.0 Hz, C3), 125.7 ($C_{10}H_7$), 126.9 ($C_{10}H_7$), 127.6 ($C_{10}H_7$), 127.7 ($C_{10}H_7$), 130.0 (C4), 131.1 (C8a), 133.8 (C4a), 148.0 (d, $^2J_{C,P}$ = 7.4 Hz, C2). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −16.0. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{25}Fe_2O_4P$ 592.0185; found 592.0160.

*(R)-1,1′-Binaphthyl-2,2′-diylferrocenyl phosphate (**27b**).* Ferrocenol (**1**, 235 mg, 1.16 mmol), BuLi (0.47 mL, 1.18 mmol), and (*R*)-1,1′-binaphthyl-2,2′-diyl chlorophosphate (**2g**, 427 mg, 1.16 mmol) were reacted according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 8 cm) using a 99:1 dichloromethane/ethyl acetate mixture (v/v) as the eluent (R_f = 0.26). The title compound was obtained as an orange solid. Yield: 305 mg (0.57 mmol, 49% based on **1**). Anal. Calcd for $C_{30}H_{21}FeO_4P{\cdot}1/3\ C_6H_{14}$ (532.31·1/3 86.18 g/mol): C, 68.51; H, 4.61. Found: C, 68.56; H, 4.48. Mp: 247 °C. ^{1}H NMR ($CDCl_3$, δ): 3.89−3.91 (m, 1 H, H3/4-C_5H_4), 3.93−3.94 (m, 1 H, H3/4-C_5H_4), 4.31 (s, 5 H, C_5H_5), 4.34−4.40 (m, 1 H, H2/5-C_5H_4), 4.54−4.56 (m, 1 H, H2/5-C_5H_4), 7.30−7.41 (m, 4 H, $C_{10}H_8$), 7.14−7.52 (m, 3 H, $C_{10}H_8$), 7.65 (d, $J_{H,H}$ = 8.8 Hz, 1 H, $C_{10}H_8$), 7.96−7.98 (m, 2 H, $C_{10}H_8$), 8.03 (d, $J_{H,H}$ = 8.9 Hz, 1 H, $C_{10}H_8$), 8.07 (d, $J_{H,H}$ = 8.9 Hz, 1 H, $C_{10}H_8$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.8 (d, $J_{C,P}$ = 4.6 Hz, C_5H_4), 59.9 (d, $J_{C,P}$ = 3.5 Hz, C_5H_4), 62.9 (C_5H_4), 63.0 (C_5H_4), 69.8 (C_5H_5), 117.9 (d, $^2J_{C,P}$ = 5.0 Hz, C$_{C5H4}$−O), 120.2 (d, $J_{C,P}$ = 3.3 Hz, CH), 120.6 (d, $J_{C,P}$ = 2.9 Hz, CH), 121.2 (d, $J_{C,P}$ = 2.1 Hz, ^{q}C), 121.5 (d, $J_{C,P}$ = 2.3 Hz, ^{q}C), 125.89 (CH), 125.92 (CH), 126.9 (CH), 127.0 (CH), 127.2 (CH), 128.45 (CH), 128.54 (CH), 131.1 (CH), 131.6 (CH), 131.7 (d, $J_{C,P}$ = 0.9 Hz, ^{q}C), 132.0 (d, $J_{C,P}$ = 1.1 Hz, ^{q}C), 132.26 (d, $J_{C,P}$ = 0.8 Hz, ^{q}C), 132.27 (d, $J_{C,P}$ = 1.0 Hz, ^{q}C), 146.1 (d, $^2J_{C,P}$ = 8.2 Hz, C2/2′), 147.4 (d, $^2J_{C,P}$ = 11.4 Hz, C2/2′). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −2.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{30}H_{21}FeO_4P$ + Na 555.0419; found 555.0401.

*1,3-Dioxa-2-((1R)-α-fenchyl)(oxo)phospha-[3]ferrocenophane (**30**).* Ferrocene-1,1′-diol (**29**, 600 mg, 2.75 mmol), BuLi (2.20 mL, 5.50 mmol), and dichloro-(1*R*)-α-fenchyl phosphate (**2h**, 749 mg, 2.752 mmol) were reacted according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 12 cm) using a 95:5 dichloromethane/ethyl acetate (v/v) mixture as the eluent. The title compound was obtained as an orange solid. Yield: 214 mg (0.51 mmol, 19% based on **29**). Anal. Calcd for $C_{20}H_{25}FeO_4P$ (416.23 g/mol): C, 57.71; H, 6.05. Found: C, 58.04; H, 6.35. Mp: 130−133 °C. ^{1}H NMR ($CDCl_3$, δ): 1.01 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 1.13−1.17 (m, 1 H, H5/6), 1.20 (s, 3 H, CH_3), 1.22−1.24 (m, 1 H, H7), 1.46−1.52 (m, 1 H, H5/6), 1.56 (ddd, $J_{H,H}$ = 10.5 Hz, $J_{H,H}$ = 3.8 Hz, $J_{H,H}$ = 2.2 Hz, 1 H, H7), 1.74−1.85 (m, 3 H, H5/6, H4), 4.01 (ddd, $J_{H,P}$ = 3.9 Hz, $J_{H,H}$ = 2.6 Hz, $J_{H,H}$ = 1.3 Hz, 2 H, C_5H_4), 4.05−4.06 (m, 2 H, C_5H_4), 4.20 (dd, $^3J_{H,P}$ = 8.2 Hz, 1 H, H2), 4.38 (dtd, $J_{H,P}$ = 4.4 Hz, $J_{H,H}$ = 2.6 Hz, $J_{H,H}$ = 1.3 Hz, 2 H, C_5H_4), 4.63−4.64 (m, 2 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.1 (CH_3), 20.8 (CH_3), 25.83 (C5/6), 25.87 (C5/6), 29.8 (CH_3), 39.7 (d, $^3J_{C,P}$ = 2.6 Hz, C3), 40.9 (C7), 47.9 (C4), 49.3 (d, $^3J_{C,P}$ = 5.5 Hz, C1), 63.30 (C_5H_4), 63.32 (C_5H_4), 63.35 (C_5H_4), 63.36 (C_5H_4), 66.0 (C_5H_4), 66.92 (C_5H_4), 66.93 (C_5H_4), 93.9 (d, $^2J_{C,P}$ = 7.7 Hz, C2), 109.4 (d, $^2J_{C,P}$ = 10.3 Hz, C$_{C5H4}$−O), 109.5 (d, $^2J_{C,P}$ = 10.4 Hz, C$_{C5H4}$−O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 0.3. HRMS (ESI-TOF) m/z: $[M_2 + Na]^+$ calcd for $(C_{20}H_{25}FeO_4P)_2$ + Na 855.1574; found 855.1581.

Synthesis of 27a and 33. 1,1′-Ferrocenediol (**29**, 150 mg, 0.688 mmol) was dissolved in 30 mL of diethyl ether, and the solution was cooled to −30 °C. BuLi (0.55 mL, 1.375 mmol) was dropwise added, and stirring was continued for 10 min at this temperature. Afterward, the mixture was cooled to −70 °C and $POCl_3$ (**2a**, 0.125 mL, 1.376 mmol) was added in a single portion. Separately, ferrocenol (**1**, 603 mg, 2.98 mmol) was dissolved in 30 mL of diethyl ether and cooled to −30 °C, and BuLi (1.2 mL, 3 mmol) was dropwise added. Both reaction mixtures were tempered at −30 °C, and the mixture containing **1** was slowly added to the one containing **29** by using a transfer cannula. The cooling bath was removed, and stirring was continued for 18 h, followed by the removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, 2 × 15 cm), resulting three fractions. Fraction 1 (dichloromethane, R_f = 0.52) contained $P(O)(OFc)_3$ (**3**, 330 mg, 0.415 mmol, 42% based on **1**); fraction 2 contained compound **27a** (95:5 dichloromethane/ethyl acetate (v/v) mixture, R_f = 0.57), and fraction 3 contained **33** (95:5 dichloromethane/ethyl acetate (v/v) mixture, R_f = 0.41).

*1,3-Dioxa-2-(ferrocenyloxy)(oxo)phospha-[3]ferrocenophane (**27a**).* The spectroscopic data of this compound are in agreement with those reported in ref 38. Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by crystallization from a boiling hexane solution containing **27a**. Yield: 63 mg (0.136 mmol, 20% based on **29**). ^{1}H NMR ($CDCl_3$, δ): 3.96 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 Hz, C_5H_4, FcO), 4.07 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 Hz, C_5H_4, ansa), 4.33 (s, 5 H, C_5H_5), 4.41−4.42 (m, 2 H, C_5H_4, ansa), 4.50 (pt, $^{3,4}J_{H,H}$ = 1.8 Hz, 2 Hz, C_5H_4, FcO), 4.58−4.59 (m, 2 H, C_5H_4, ansa). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.4 (d, $J_{C,P}$ = 4.4 Hz, C_5H_4, FcO), 62.8 (d, $J_{C,P}$ = 3.1 Hz, C_5H_4, ansa), 63.0 (s, C_5H_4, FcO), 63.7 (d, $J_{C,P}$ = 3.4 Hz, C_5H_4, ansa), 66.8 (s, C_5H_4, ansa), 69.8 (C_5H_5), 109.9 (d, $^2J_{C,P}$ = 12.5 Hz, C−O, ansa), 118.0 (d, $^2J_{C,P}$ = 6.1 Hz, C−O, FcO). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −5.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}Fe_2O_4P$ + H 464.9636; found 464.9608.

*(1,1′-Ferrocenediyl)tetraferrocenyl Bis(phosphate) (**33**).* Yield: 86 mg (0.077 mmol, 11% based on **29**). Mp: 167 °C. ^{1}H NMR ($CDCl_3$, δ): 3.93 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 8 H, FcO), 4.05 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, FcO_2), 4.28 (s, 20 H, C_5H_5), 4.44 (dd, $J_{H,P}$ = 4.4 Hz, $J_{H,H}$ = 2.1 Hz, 8 H, FcO), 4.52 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, FcO_2). ^{13}C{^{1}H} NMR

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($CDCl_3$, δ): 59.65 (C_5H_4, FcO), 59.66 (C_5H_4, FcO), 59.69, (C_5H_4, FcO), 59.70 (C_5H_4, FcO), 61.16 (C_5H_4, FcO_2), 61.20 (C_5H_4, FcO_2), 62.93 (C_5H_4, FcO), 62.94 (C_5H_4, FcO), 65.1 (C_5H_4, FcO_2), 69.7 (C_5H_5), 117.8 (d, $^2J_{C,P}$ = 5.5 Hz, C−O, FcO), 118.1 (d, $^2J_{C,P}$ = 5.4 Hz, C−O, FcO_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −15.3. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{50}H_{44}Fe_5O_8P_2$ 1113.9260; found 1113.9205.

*1,1′-Bis(1,3-dioxa-2-(oxo)phospha-[3]ferrocenophan-2-yloxy)-ferrocene (**34**).* 1,1′-Ferrocenediol (**29**, 642 mg, 2.94 mmol) was split in three portions of 214 mg (0.982 mmol), and each of them was dissolved in 10 mL of diethyl ether. The solutions were cooled to −30 °C, and BuLi (0.79 mL, 1.96 mmol) was dropwise added. The first portion was cooled to −70 °C, $POCl_3$ (**2a**, 0.18 mL, 1.96 mmol) was added quickly via syringe, and the reaction mixture was slowly warmed to ambient temperature. After being stirred for 10 min at this temperature, the reaction mixture was cooled again to −70 °C and the second portion of lithiated 1,1′-$Fc(OH)_2$ (**29**-Li_2) was added via a transfer cannula. The same procedure was repeated for the third fraction of **29**-Li_2. Afterward, the mixture was allowed to warm to ambient temperature and stirred for 18 h. All volatiles were removed in vacuum. Purification was realized using column chromatography (silica, column size 2 × 12 cm) using a 95:5 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **34** was obtained as an orange solid. The spectroscopic data are in agreement with those reported in ref 38. Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by crystallization from a boiling hexane solution containing **34**. Yield: 94 mg (0.127 mmol, 12% based on **29**). Anal. Calcd for $C_{30}H_{24}Fe_2O_8P_2 \cdot 1/3\ C_6H_{14}$ (741.99·1/3 86.18 g/mol): C, 49.87; H, 3.75. Found: C, 49.65; H, 3.59. Mp: >230 °C (decomp.). ^1H NMR ($CDCl_3$, δ): 4.06−4.07 (m, 8 H, ansa), 4.17 (pt, $^{3,4}J_{H,H}$= 2.0 Hz, 4 H, open), 4.44−4.45 (m, 4 H, ansa), 4.56−4.57 (m, 4 H, ansa), 4.66 (pt, $^{3,4}J_{H,H}$= 1.9 Hz, 4 H, open). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 61.2 (d, $J_{C,P}$ = 4.5 Hz, open), 62.9 (d, $J_{C,P}$ = 3.0 Hz, ansa), 63.7 (d, $J_{C,P}$ = 3.6 Hz, ansa), 65.2 (open), 66.8 (ansa), 66.9 (ansa), 109.9 (d, $^2J_{C,P}$ = 12.8 Hz, C_{C5H4}−O, ansa), 118.3 (d, $^2J_{C,P}$ = 6.0 Hz, C_{C5H4}−O, open). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −5.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{30}H_{24}Fe_3O_8P_2$ + Na 764.8889; found 764.8862.

*N,N,N′,N′-Tetraethyl-1-(ferrocenyloxy)phosphinediamine·BH_3 (**37**).* Ferrocenol (**1**, 1.037 g, 5.13 mmol), triethylamine (0.75 mL, 5.41 mmol), and $ClP(NEt_2)_2$ (**2i**, 1.09 mL, 5.17 mmol) were reacted according to the general procedure described above. After stirring for 12 h, a 1 M solution of BH_3 in tetrahydrofuran (5.2 mL, 5.2 mmol) was added in a single portion and stirring was continued for an additional 2 h. Purification was realized by column chromatography (alumina, column size 3.5 × 13 cm) using a 8:2 hexane/diethyl ether mixture (v/v) as the eluent. Compound **37** was obtained as an orange oil. Yield: 1.02 g (2.61 mmol, 51% based on **1**). Anal. Calcd for $C_{18}H_{32}BFeN_2OP$ (390.09 g/mol): C, 55.42; H, 8.27; N, 7.18. Found: C, 55.55; H, 8.08; N, 6.92. IR data (NaCl, ν/cm^{-1}): 3067, w, 3020 w, 2942 s, 2905 s, 2852 s, 2353 s (BH_3), 1446 s, 1399 w, 1366 s, 1285 m. ^1H NMR (C_6D_6, δ): 0.93 (t, $^3J_{H,H}$ = 7.1 Hz, 12 H, CH_3), 1.01−1.72 (br m, 3 H, BH_3), 2.86−3.03 (m, 8 H, CH_2), 3.67 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.19 (s, 5 H, C_5H_5), 4.42 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 14.3 (d, $^3J_{C,P}$ = 1.7 Hz, CH_3), 39.2 (d, $^2J_{C,P}$ = 6.3 Hz, CH_2), 61.4 (d, $J_{C,P}$ = 2.7 Hz, C_5H_4), 63.0 (C_5H_4), 69.7 (C_5H_5), 118.1 (d, $^2J_{C,P}$ = 1.4 Hz, C_{C5H4}−O). $^{11}B\{^1H\}$ NMR (C_6D_6, δ): −39.5 (d, $^1J_{B,P}$ = 95 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 130.7−132.1 (br m). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{32}BFeN_2OP$ 390.1693; found 390.1702.

*N,N,N′,N′-Tetraethyl-1-(ferrocenyloxy)phosphinediamine sulfide (**38**).* Ferrocenol (**1**, 1.102 g, 5.46 mmol), triethylamine (0.77 mL, 5.55 mmol), and $ClP(NEt_2)_2$ (**2i**, 1.26 g, 5.98 mmol) were reacted according to the general procedure described above. After stirring for 12 h, sulfur (210 mg, 6.55 mmol) was added in a single portion and stirring was continued for an additional 2 h. Purification was realized by column chromatography (alumina, column size 2.5 × 32 cm) using first hexane, to remove the excess of sulfur, followed by a 7:3 hexane/dichloromethane mixture (v/v) as the eluent. Compound **38** was obtained as an orange oil. Yield: 1.900 g (4.65 mmol, 85% based on **1**). Anal. Calcd for $C_{18}H_{29}FeN_2OPS$ (408.32 g/mol): C, 52.95; H, 7.16; N, 6.86. Found: C, 53.17; H, 7.55; N, 6.30. ^1H NMR (C_6D_6, δ): 0.99 (t, $^3J_{H,H}$ = 7.1 Hz, 12 H, CH_3), 3.00−3.09 (m, 8 H, CH_2), 3.70 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.22 (s, 5 H, C_5H_5), 4.50 (ptd, $^{3,4}J_{H,H}$ = 2.1 Hz, $J_{H,H}$ = 0.6 Hz, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 14.2 (d, $^4J_{C,P}$ = 3.2 Hz, CH_3), 40.6 (d, $^3J_{C,P}$ = 5.0 Hz, CH_2), 61.4 (d, $J_{C,P}$ = 3.6 Hz, C_5H_4), 62.9 (C_5H_4), 69.8 (C_5H_5), 117.6 (d, $^2J_{C,P}$ = 1.9 Hz, C_{C5H4}−O). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 90.9. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{29}FeN_2OPS$ 408.1082; found 408.1109.

*Ferrocenyl Di(pyrrolidin-1-yl)phosphinate (**39**).* Ferrocenol (**1**, 370 mg, 1.83 mmol), BuLi (0.73 mL, 1.83 mmol), and chlorodi-(pyrrolidin-1-yl) phosphinate (**2j**, 408 mg, 1.83 mmol) were reacted at −80 °C according to the general procedure described above. Purification was realized by column chromatography (alumina, column size 4 × 8 cm) using a 1:1 dichloromethane/ethyl acetate mixture (v/v) as the eluent. The title compound was obtained as an orange solid. Yield: 512 mg (1.319 mmol, 72% based on **1**). Anal. Calcd for $C_{18}H_{25}FeN_2O_2P$ (388.22 g/mol): C, 55.69; H, 6.49; N, 7.27. Found: C, 55.67; H, 6.54; N, 7.09. Mp: 76−78 °C. ^1H NMR (C_6D_6, δ): 1.40−1.43 (m, 8 H, H3,H4−C_4N), 3.11−3.15 (m, 8 H, H2,H5−C_4N), 3.71 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.27 (s, 5 H, C_5H_5), 4.60 (ptd, $^{3,4}J_{H,H}$ = 1.9 Hz, $J_{H,P}$ = 0.6 Hz, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 26.5 (d, $^3J_{C,P}$ = 8.9 Hz, C3,C4−C_4N), 46.8 (d, $^2J_{C,P}$ = 4.6 Hz, C2,C5−C_4N), 60.3 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 62.8 (C_5H_4), 69.9 (C_5H_5), 118.5 (d, $^2J_{C,P}$ = 4.3 Hz, C_{C5H4}−O). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 22.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{25}FeN_2O_2P$ + Na 411.0895; found 411.0895.

*2-Ferrocenyloxy-3-methyl-1,3,2-oxaphospholidine·BH_3 (**40**).* Ferrocenol (**1**, 508 mg, 2.51 mmol), triethylamine (0.39 mL, 2.81 mmol), and 2-chloro-3-methyl-1,3,2-oxazaphospholidine (**2k**, 350 mg, 2.51 mmol) were reacted according to the general procedure described above. After stirring for 12 h, a 1 M solution of BH_3 in tetrahydrofuran (2.8 mL, 2.8 mmol) was added in a single portion and stirring was continued for an additional 2 h. Purification was realized by column chromatography (alumina, column size 3.5 × 13 cm) using a 1:3 hexane/dichloromethane mixture (v/v) as the eluent. The title compound **40** was obtained as an orange oil. Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by evaporation of a hexane solution at ambient temperature containing **40**. Yield: 270 mg (0.847 mmol, 34% based on **1**). Anal. Calcd for $C_{13}H_{19}BFeNO_2P$ (318.92 g/mol): C, 48.96; H, 6.00; N, 4.39. Found: C, 49.28; H, 6.08; N, 4.35. Mp: 153 °C. ^1H NMR ($CDCl_3$, δ): 0.31−0.86 (br m, 3 H, BH_3), 2.79 (d, $^3J_{H,P}$ = 10.1 Hz, 3 H, CH_3), 2.97 (ddd, $^3J_{H,P}$ = 13.1 Hz, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 4.8 Hz, 1 H, CH_2−N), 3.08 (dtd, $^3J_{H,P}$ = 11.9 Hz, $J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 5.9 Hz, 1 H, CH_2−N), 3.89 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.14−4.25 (m, 8 H, C_5H_5, C_5H_4, CH_2−O), 4.29−4.30 (m, 1 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 31.2 (d, $^2J_{C,P}$ = 9.9 Hz, CH_3), 49.2 (d, $^2J_{C,P}$ = 2.2 Hz, CH_2−N), 60.6 (d, $J_{C,P}$ = 1.4 Hz, C_5H_4), 61.2 (d, $J_{C,P}$ = 1.8 Hz, C_5H_4), 63.2 (d, $J_{C,P}$ = 19.1 Hz, C_5H_4), 67.9 (d, $^2J_{C,P}$ = 10.5 Hz, CH_2−O), 69.6 (C_5H_5), 116.5 (d, $^2J_{C,P}$ = 11.2 Hz, C_{C5H4}−O). $^{11}B\{^1H\}$ NMR ($CDCl_3$, δ): −42.6 (d, $^1J_{B,P}$ = 92 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 122.0 (br m). HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{19}BFeNO_2P$ + Na 342.0491; found 342.0499.

*Diferrocenyl-N,N-diethyphosphoramidate (**41**).* Ferrocenol (**1**, 414 mg, 2.05 mmol), triethylamine (0.29 mL, 2.05 mmol), and Cl_2PNEt_2 (**2l**, 178 mg, 1.025 mmol) were reacted according to the general procedure described above. After stirring for 12 h, ^{t}BuOOH (0.38 mL, 2.09 mmol) was added and stirring was continued for an additional 2 h. Purification was realized by column chromatography (alumina, column size 4.5 × 12 cm) using dichloromethane as the eluent. The title compound **41** was obtained as an orange solid. Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by evaporation of a hexane solution at ambient temperature containing **41**. Yield: 253 mg (0.618 mmol, 60% based on **1**). Anal. Calcd for $C_{24}H_{28}Fe_2NO_3P$ (521.15 g/mol): C, 55.31; H, 5.42; N, 2.69. Found: C, 55.04; H, 5.74; N, 2.64. Mp: 103 °C. ^1H NMR ($CDCl_3$, δ): 1.03 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 3.07 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2), 3.09 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2), 3.87−3.90 (m, 4 H, C_5H_4), 4.27 (s, 10 H, C_5H_5), 4.34−4.35 (m, 2 H, C_5H_4), 4.50−4.51 (m, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 13.9 (d, $^3J_{C,P}$ = 2.0 Hz, CH_3), 39.7 (d, $^2J_{C,P}$ = 4.5 Hz, CH_2), 59.6 (d, $J_{C,P}$ = 4.5 Hz, C_5H_4), 60.2 (d, $J_{C,P}$ = 3.3 Hz,

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C_5H_4), 62.6 (C_5H_4), 62.7 (C_5H_4), 69.5 (C_5H_5), 117.4 (d, $^2J_{C,P}$ = 4.3 Hz, C_{C5H4}–O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 2.5. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{24}H_{28}Fe_2NO_3P$ 521.0501; found 521.0486.

*Diferrocenyl 1H-Pyrrol-1-ylphosphonate (**46**).* Ferrocenol (**1**, 836 mg, 4.14 mmol), BuLi (1.7 mL, 4.25 mmol), and dichloro(1*H*-pyrrol-1-yl)phosphonate (**2m**, 380 mg, 2.07 mmol) were reacted according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 12 cm) using a 98:2 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **46** was obtained as an orange solid. Yield: 468 mg (0.91 mmol, 44% based on **1**). Anal. Calcd for $C_{24}H_{22}Fe_2NO_3P$ (515.10 g/mol): C, 55.96; H, 4.30; N, 2.72. Found: C. 55.48; H, 4.48; N, 2.67. Mp: 184 °C. ^1H NMR ($CDCl_3$, δ): 3.87–3.89 (m, 4 H, C_5H_4), 4.21 (s, 10 H, C_5H_5), 4.27–4.28 (m, 2 H, C_5H_4), 4.30–4.31 (m, 2 H, C_5H_4), 6.40 (ddd, $^4J_{H,P}$ = 4.7 Hz, $J_{H,H}$ = 2.2 Hz, $J_{H,H}$ = 2.2 Hz, 2 H, C3/4), 7.09 (ddd, $J_{H,H}$ = 2.2 Hz, $J_{H,H}$ = 2.2 Hz, $^3J_{H,P}$ = 2.2 Hz, 2 H, C2/5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.4 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 59.6 (d, $J_{C,P}$ = 4.6 Hz, C_5H_4), 62.96 (C_5H_4), 63.00 (C_5H_4), 69.7 (C_5H_5), 113.3 (d, $^3J_{C,P}$ = 11.5 Hz, C3/4), 117.3 (d, $^2J_{C,P}$ = 4.5 Hz, C_{C5H4}–O), 122.8 (d, $^2J_{C,P}$ = 6.5 Hz, C2/5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −11.5. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{24}H_{22}Fe_2NO_3P$ 515.0031; found 515.0014.

*Diferrocenyl(1H-indol-1-yl)phosphonate (**47**).* Ferrocenol (**1**, 836 mg, 4.14 mmol), BuLi (1.7 mL, 4.25 mmol), and dichloro(1*H*-indol-1-yl) phosphonate (**2n**) (484 mg, 2.07 mmol) were reacted according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 12 cm) using a 98:2 dichloromethane/ethyl acetate (v/v) mixture as the eluent. The title compound was obtained as an orange solid. Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by crystallization from a boiling hexane solution containing **47**. Yield: 945 mg (1.67 mmol, 81% based on **1**). Anal. Calcd for $C_{28}H_{24}Fe_2NO_3P$ (565.16 g/mol): C, 59.51; H, 4.28; N, 2.48. Found: C, 59.51; H, 4.30; N, 2.60. Mp: ∼25 °C. ^1H NMR ($CDCl_3$, δ): 3.82 (ddd, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 2.7 Hz, $J_{H,H}$ = 1.5 Hz, 2 H, C_5H_4), 3.85 (ddd, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 2.7 Hz, $J_{H,H}$ = 1.5 Hz, 2 H, C_5H_4), 4.13 (s, 10 H, C_5H_5), 4.15–4.16 (m, 2 H, C_5H_4), 4.34–4.35 (m, 2 H, C_5H_4), 6.72 (ddd, $^4J_{H,P}$ = 3.6 Hz, $^3J_{H,H}$ = 2.7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H3), 7.29 (ddd, $J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.0 Hz, 1 H, H5/6), 7.39 (ddd, $J_{H,H}$ = 8.4 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.2 Hz, 1 H, H5/6), 7.46 (dd, $^3J_{H,H}$ = 3.5 Hz, $^3J_{H,P}$ = 2.1 Hz, 1 H, H2), 7.64–7.66 (m, 1 H, H4), 7.87 (d, $J_{H,H}$ = 8.3 Hz, 1 H, C7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.3 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 59.6 (d, $J_{C,P}$ = 4.5 Hz, C_5H_4), 62.95 (C_5H_4), 62.98 (C_5H_4), 69.6 (C_5H_5), 108.3 (d, $^3J_{C,P}$ = 9.2 Hz, C3), 113.9 (C7), 117. Two (d, $^2J_{C,P}$ = 4.0 Hz, C_{C5H4}–O), 121.3 (C4), 122.7 (C5/6), 123.9 (C5/6), 128.5 (d, $^2J_{C,P}$ = 7.4 Hz, C2), 131.1 (d, $^3J_{C,P}$ = 10.9 Hz, C3a), 136.9 (d, $^2J_{C,P}$ = 5.0 Hz, C7a). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −11.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{28}H_{24}Fe_2NO_3P$ + Na 588.0086; found 588.0102.

*Diferrocenyl 9H-Carbazol-9-yl phosphonate (**48**).* Ferrocenol (**1**) (835 mg, 4.13 mmol), BuLi (1.8 mL, 4.5 mmol), and 9*H*-carbazol-9-yl dichloro phosphate (**2o**) (580 mg, 2.04 mmol) were reacted according to the general procedure described above. Purification was realized by column chromatography (silica, column size 3.5 × 8 cm) using dichloromethane as the eluent. Compound **48** was obtained as an orange solid. Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by crystallization from a boiling hexane solution containing **48**. Yield: 340 mg (0.553 mmol, 27% based on **1**). Anal. Calcd for $C_{32}H_{26}Fe_2NO_3P$ (615.22 g/mol): C, 62.47; H, 4.26; N, 2.28. Found: C, 62.69; H, 4.40; N, 2.29. Mp: 160 °C. ^1H NMR ($CDCl_3$, δ): 3.76 (ddd, $J_{H,H}$ = 2.7 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 1.4 Hz, 2 H, C_5H_4), 3.81 (ddd, $J_{H,H}$ = 2.7 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 1.4 Hz, 2 H, C_5H_4), 4.07 (s, 10 H, C_5H_5), 4.12–4.14 (m, 2 H, C_5H_4), 4.35–4.36 (m, 2 H, C_5H_4), 7.40 (ddd, $J_{H,H}$ = 7.9 Hz, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 0.9 Hz, 2 H, $C_{12}H_8N$), 7.53 (ddd, $J_{H,H}$ = 8.5 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.3 Hz, 2 H, $C_{12}H_8N$), 8.04–8.06 (m, 2 H, $C_{12}H_8N$), 8.17 (d, $J_{H,H}$ = 8.4 Hz, 2 H, $C_{12}H_8N$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.3 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 59.5 (d, $J_{C,P}$ = 4.8 Hz, C_5H_4), 62.89 (C_5H_4), 62.94 (C_5H_4), 69.5 (C_5H_5), 114.9 (C1, C8), 117.2 (d, $^2J_{C,P}$ = 3.9 Hz, C_{C5H4}–O), 120.1, 122.8, 126.2 (d, $J_{C,P}$ = 9.2 Hz, C4a, C4b), 127.0, 140.15 (d, $J_{C,P}$ = 6.6 Hz, C8a, C9a). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −11.8. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{32}H_{26}Fe_2NO_3P$ 615.0345; found 615.0332.

Anionic Phospho-Fries Rearrangement: General Procedure. In a Schlenk tube, tetrahydrofuran (3 mL) and diisopropylamine (amount see below) were placed, and the solution was cooled to −30 °C. Afterward, BuLi (amount see below) was added dropwise and the mixture was stirred for 10 min at −30 °C. Depending on the reaction temperature required for each rearrangement, the respective temperature was adjusted. Afterward, the corresponding ferrocenyl phosphate (1 equiv) was added in a single portion, and stirring was continued for 2–4 h. Dimethyl sulfate (see below for amount) was added in a single portion, and the reaction mixture was allowed to warm to ambient temperature, where stirring was continued overnight. All volatiles were removed under reduced pressure. Purification was realized using column chromatography on silica or alumina (see below) using different solvent mixtures as eluents (see below).

Anionic Phospho-Fries Rearrangement of 6: Synthesis of 23 and 24. Phosphate **6** (70 mg, 0.131 mmol), diisopropylamine (0.11 mL, 0.783 mmol), BuLi (0.31 mL, 0.78 mmol), and dimethyl sulfate (0.1 mL, 1.05 mmol) were reacted at 0 °C for 2 h, according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 12 cm) using a 95:5 dichloromethane/ethyl acetate mixture (v/v) as the eluent, resulting in the elution of two fractions. At first, the phosphonate **23** was eluted followed by the phosphinate **24**.

*O,O′-Diferrocenyl(1-hydroxynaphth-2-yl)phosphonate (**23**).* Orange solid. Yield: 13 mg (0.024 mmol, 19% based on **6**). Anal. Calcd for $C_{30}H_{25}Fe_2O_4P$ (592.18 g/mol): C, 60.85; H, 4.26. Found: C, 61.27; H, 4.56. Mp: 163–168 °C. ^1H NMR ($CDCl_3$, δ): 3.83–3.84 (m, 2 H, C_5H_4), 3.85–3.86 (m, 2 H, C_5H_4), 4.19 (s, 10 H, C_5H_5), 4.30–4.31 (m, 2 H, C_5H_4), 4.38–4.39 (m, 2 H, C_5H_4), 7.32–7.40 (m, 2 H, H3/4), 7.54 (ddd, $J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 6.8 Hz, $J_{H,H}$ = 1.2 Hz, 1 H, C_6H_4), 7.62 (ddd, $J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 6.9 Hz, $J_{H,H}$ = 1.3 Hz, 1 H, C_6H_4), 7.77 (d, $J_{H,H}$ = 8.1 Hz, 1 H, C_6H_4), 8.40 (d, $J_{H,H}$ = 8.3 Hz, 1 H, C_6H_4), 10.99 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.6 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 59.9 (d, $J_{C,P}$ = 4.2 Hz, C_5H_4), 62.9 (C_5H_4), 63.0 (C_5H_4), 69.6 (C_5H_5), 99.5 (d, $^1J_{C,P}$ = 185.2 Hz, C1), 117.1 (d, $^2J_{C,P}$ = 4.2 Hz, C_{C5H4}–O), 119.5 (d, $J_{C,P}$ = 14.1 Hz, C4), 123.7 (C_6H_4), 124.8 (d, $^3J_{C,P}$ = 14.4 Hz, C8a), 125.4 (d, $J_{C,P}$ = 6.4 Hz, C3), 126.2 (C_6H_4), 127.6 (C_6H_4), 129.5 (C_6H_4), 137.2 (d, $^4J_{C,P}$ = 2.1 Hz, C4a), 161.5 (d, $^2J_{C,P}$ = 8.1 Hz, C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 17.7. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{25}Fe_2O_4P$ 592.0185; found 592.0202.

*O-Ferrocenyl(2-methoxyferrocenyl)(1-hydroxynaphth-2-yl)-phosphinate (**24**).* Orange solid. The compound was obtained in a ratio of both diastereomers of 1:0.78. Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by slow evaporation of a hexane solution containing **24** at ambient temperature. Yield: 24 mg (0.040 mmol, 30% based on **6**). Anal. Calcd for $C_{31}H_{27}Fe_2O_4P$ (606.21 g/mol): C, 61.42; H, 4.49. Found: C, 61.58; H, 4.73. Mp: 194–196 °C. ^1H NMR ($CDCl_3$, δ): 3.66 (s, 3 H, OCH_3, ma), 3.74–3.76 (m, 1.7 H, ma, mi), 3.76–3.79 (m, 1.7 H, ma, mi), 3.86 (s, 2.1 H, OCH_3, mi), 4.10 (dd, $J_{H,H}$ = 2.8 H, $J_{H,H}$ = 2.8 H, 0.7 H, C_5H_3, mi), 4.16 (dd, $J_{H,H}$ = 2.6 H, $J_{H,H}$ = 2.6 H, 1 H, C_5H_3, ma), 4.17–4.18 (m, 5.7 H, C_5H_5 ma, $C_5H_{3/4}$ mi), 4.19–4.21 (m, 9.5 H, C_5H_5 ma, C_5H_5 mi, $C_5H_{3/4}$ ma), 4.23 (ddd, $J_{H,H}$ = 2.7 Hz, $J_{H,P}$ = 2.2 Hz, $J_{H,H}$ = 1.5 Hz, 0.7 H, C_5H_3 mi), 4.26 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,P}$ = 2.8 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3 ma), 4.32 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 0.7 H, C_5H_3 mi), 4.36 (dddd, J = 2.7 Hz, J = 1.4 Hz, J = 1.4 Hz, J = 0.7 Hz, 1 H, ma), 4.42 (s, 3.5 H, C_5H_5, mi), 4.45 (dddd, J = 2.7 Hz, J = 1.4 Hz, J = 1.4 Hz, J = 0.6 Hz, 0.7 H, mi), 4.51 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,H}$ = 1.7 Hz, $J_{H,P}$ = 1.7 Hz, 1 H, ma), 7.26 (dd, $J_{H,H}$ = 8.5 Hz, $J_{H,P}$ = 3.0 Hz, 0.7 H, H3/4 mi), 7.30 (dd, $J_{H,H}$ = 8.6 Hz, $J_{H,P}$ = 2.9 Hz, 1 H, H3/4 ma), 7.39 (dd, $J_{H,P}$ = 12.8 Hz, $J_{H,H}$ = 8.6 Hz, 0.7 H, H3/4 mi), 7.44 (dd, $J_{H,P}$ = 13.1 Hz, $J_{H,H}$ = 8.6 Hz, 1 H, H3/4 ma), 7.48–7.52 (m, 1.7 H, ma, mi), 7.54–7.58 (m, 1.7 H, ma, mi), 7.71 (d, $J_{H,H}$ = 8.9 Hz, 0.7 H, mi), 7.73 (d, $J_{H,H}$ = 8.6 Hz, 1 H, ma), 7.38 (d, $J_{H,H}$ = 8.4 Hz, 0.7 H, mi), 8.42 (d, $J_{H,H}$ = 8.4 Hz, 1 H, ma), 11.96 (s, 0.7 H, OH, mi), 11.99 (s, 1 H, OH, ma). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.7* (d, $J_{C,P}$ = 10.1 Hz, C_5H_3), 55.8* (d, $J_{C,P}$ = 10.2 Hz, C_5H_3), 58.3 (OCH_3), 58.3 (OCH_3), 59.9 (d, $J_{C,P}$ = 4.3 Hz, C_5H_4), 60.0 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 60.1 (d, $J_{C,P}$ = 4.0 Hz, C_5H_4), 60.4 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 60.6 (C_{C5H3}–P, *), 60.9 (C_{C5H3}–P, *the second signal of the doublet overlaps), 62.68

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(C_5H_4), 62.76 (C_5H_4), 62.77 (C_5H_4), 62.9 (C_5H_4), 64.4 (d, $J_{C,P}$ = 12.2 Hz, C_5H_3), 64.6 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 67.0* (d, $J_{C,P}$ = 15.9 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 10.8 Hz, C_5H_3), 69.48 (C_5H_5), 69.49 (C_5H_5), 70.0 (C_5H_5), 70.2 (C_5H_5), 103.7 (C2, HMBC), 117.1 (d, $^2J_{C,P}$ = 6.8 Hz, C_{C5H4}–O), 128.3 (d, $^2J_{C,P}$ = 11.5 Hz, C_{C5H3}–O), 118.5* (d, $J_{C,P}$ = 13.5 Hz, $C_{10}H_6$), 118.7* (d, $J_{C,P}$ = 13.5 Hz, $C_{10}H_6$), 123.5* ($C_{10}H_6$), 123.68* ($C_{10}H_6$), 123.69* ($C_{10}H_6$), 125.5* ($C_{10}H_6$), 125.6* ($C_{10}H_6$), 125.62* ($C_{10}H_6$), 125.67* ($C_{10}H_6$), 126.2* ($C_{10}H_6$), 126.3* ($C_{10}H_6$), 127.3* ($C_{10}H_6$), 127.4* ($C_{10}H_6$), 128.1 (C_{C5H3}–O, HMBC), 128.5 (C_{C5H3}–O, HMBC), 136.5 (C4a/C8a, HMBC), 160.8 (C1, HMBC). (*Obtained from DEPT90 measurements). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 44.6 (ma), 44.7 (mi). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{31}H_{27}Fe_2O_4P$ + H 607.0373; found 607.0376.

Anionic Phospho-Fries Rearrangement of 7: Synthesis of 25 and 26a,b. Phosphate 7 (82 mg, 0.17 mmol), diisopropylamine (0.14 mL, 1.01 mmol), BuLi (0.41 mL, 1.03 mmol), and dimethyl sulfate (0.3 mL, 3.15 mmol) were reacted at −80 °C (**24**) or 0 °C (**25**) for 2 h according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 12 cm) using a 95:5 dichloromethane/ethyl acetate mixture (v/v) for **25** and **26b** or a 2:3 dichloromethane/ethyl acetate mixture (v/v) for **26b** as the eluents.

*O,O′-Diferrocenyl(3-hydroxynaphth-2-yl)phosphonate (**25**).* Orange oil. Yield: 32 mg (0.066 mmol, 39% based on **7**). Anal. Calcd for $C_{30}H_{25}Fe_2O_4P{\cdot}0.25\ CHCl_3$ (592.18·119.38 g/mol): C, 58.41; H, 4.09. Found: C, 58.58; H, 4.43. ^1H NMR ($CDCl_3$, δ): 3.85–3.88 (m, 4 H, C_5H_4), 4.19 (s, 10 H, C_5H_5), 4.31–4.32 (m, 2 H, C_5H_4), 4.38–4.39 (m, 2 H, C_5H_4), 7.33–7.36 (m, 2 H, H4, H5/6/7/8), 7.51 (ddd, $J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 6.8 Hz, $J_{H,H}$ = 1.0 Hz, C_6H_4), 7.71 (d, $J_{H,H}$ = 8.3 Hz, C_6H_4), 7.80 (d, $J_{H,H}$ = 8.2 Hz, C_6H_4), 8.08 (d, $^3J_{H,P}$ = 17.0 Hz, H1), 9.70 (d, $^4J_{H,P}$ = 0.9 Hz, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.7 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 59.87 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 63.0 (C_5H_4), 63.1 (C_5H_4), 69.6 (C_5H_5), 112.1 (d, $^3J_{C,P}$ = 11.9 Hz, C4), 117.2 (d, $^2J_{C,P}$ = 4.6 Hz, C_{C5H4}–O), 122.4 (d, $^1J_{C,P}$ = 181.3 Hz, C2), 124.3 (C_6H_4), 126.7 (C_6H_4), 128.7 (C_6H_4), 129.2 (C_6H_4), 134.8 (d, $^2J_{C,P}$ = 5.5 Hz, C1), 138.0 (C4a/C8a), 139.6 (C4a/C8a), 156.6 (d, $^2J_{C,P}$ = 7.8 Hz, C3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 14.6. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{25}Fe_2O_4P$ 592.0185; found 592.0156.

*O-Ferrocenyl(2-methoxyferrocenyl)(3-hydroxynaphth-2-yl) phosphinate (**26a**).* Compound **26a** was obtained as an orange oil with a ratio of two diastereomers of 1:0.51. Yield: 45 mg (0.074 mmol, 44% based on **7**). Anal. Calcd for $C_{31}H_{27}Fe_2O_4P$ (606.21 g/mol): C, 61.42; H, 4.49. Found: C, 61.21; H, 4.94. Mp: >250 °C (decomp.) ^1H NMR ($CDCl_3$, δ): 3.667 (s, 1.5 H, OCH_3, mi), 3.68 (d, $J_{H,H}$ = 3.2 Hz, 1 H, C_5H_3, ma), 3.75–3.77 (m, 1.5 H, $C_5H_{3/4}$, mi, ma), 3.78–3.81 (m, 1.5 H, $C_5H_{3/4}$, mi, ma), 3.88 (s, 3 H, OCH_3, ma), 4.10–4.12 (m, 1 H, $C_5H_{3/4}$, ma), 4.17–4.20 (m, 11 H, C_5H_5 ma, C_5H_5 mi, $C_5H_{3/4}$ mi), 4.21–4.23 (m, 1 H, $C_5H_{3/4}$, ma), 4.26–4.28 (m, 0.5 H, $C_5H_{3/4}$, mi), 4.34–4.35 (m, 1.5 H, $C_5H_{3/4}$, ma, mi), 4.43 (s, 5 H, C_5H_5, ma), 4.44–4.46 (m, 1 H, $C_5H_{3/4}$, ma), 4.54–4.55 (m, 0.5 H, $C_5H_{3/4}$, mi), 7.26–7–32 (m, 3 H, H4, H5/6/7/8, ma, mi), 7.42–7.48 (m, 1.5 H, H5/6/7/8, ma, mi), 7.66 (d, $J_{H,H}$ = 8.2 Hz, 1 H, H5/6/7/8, ma), 7.69 (d, $J_{H,H}$ = 8.2 Hz, 0.5 H, H5/6/7/8, mi), 7.71 (d, $J_{H,H}$ = 8.2 Hz, 1 H, H5/6/7/8, ma), 7.75 (d, $J_{H,H}$ = 8.3 Hz, 0.5 H, H5/6/7/8, mi), 8.07 (d, $^3J_{H,P}$ = 16.5 Hz, 1 H, H1, ma), 8.16 (d, $^3J_{H,P}$ = 16.8 Hz, 0.5 H, H1, mi), 10.75 (d, $^4J_{H,P}$ = 0.9 Hz, 1 H, OH, ma), 10.83 (d, $^4J_{H,P}$ = 0.9 Hz, 0.5 H, OH, mi). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.89 (d, $J_{C,P}$ = 10.5 Hz, C_5H_3, mi), 55.92 (d, $J_{C,P}$ = 10.2 Hz, C_5H_3, ma), 58.3 (OCH_3, mi), 58.4 (OCH_3, ma), 59.97 (d, $^1J_{C,P}$ = 167.3 Hz, C_{C5H3}–P, ma), 59.98 (d, $J_{C,P}$ = 4.4 Hz, C_5H_4, mi), 60.03 (d, $J_{C,P}$ = 4.3 Hz, C_5H_4, ma), 60.05 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4, mi), 60.3 (d, $J_{C,P}$ = 4.0 Hz, C_5H_4, ma), 62.77 (C_5H_4, mi), 62.80 (C_5H_4, mi), 62.86 (C_5H_4, ma), 62.91 (C_5H_4, ma), 64.5 (d, $J_{C,P}$ = 12.1 Hz, C_5H_3, mi), 64.8 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3, ma), 67.1 (d, $J_{C,P}$ = 16.0 Hz, C_5H_3, ma), 67.4 (d, $J_{C,P}$ = 10.9 Hz, C_5H_3, ma), 69.62 (C_5H_5, ma), 69.54 (C_5H_5, mi), 70.0 (C_5H_5, mi), 70.2 (C_5H_5, ma), 111.42 (d, $^3J_{C,P}$ = 8.6 Hz, C4, mi), 111.48 (d, $^3J_{C,P}$ = 9.2 Hz, C4, ma), 115.6 (d, $^1J_{C,P}$ = 132.0 Hz, C2, ma), 117.32 (C_{C5H4}–O), 117.33 (C_{C5H4}–O), 117.37 (C_{C5H4}–O), 123.61 (C5/6/7/8, ma), 123.65 (C5/6/7/8, mi), 126.49 (C5/6/7/8, ma), 126.55 (C5/6/7/8, mi), 127.2 (d, $^2J_{C,P}$ = 14.6 Hz, C_{C5H3}–O, ma), 128.4 (C5/6/7/8, ma), 128.6 (C5/6/7/8, mi), 128.65 (C5/6/7/8, mi), 128.71 (C5/6/7/8, ma), 133.8 (d, $^2J_{C,P}$ = 9.9 Hz, C_1, ma), 134.8 (d, $^2J_{C,P}$ = 9.3 Hz, C_1, mi), 137.4 (C4a/C8a), 137.46 (C4a/C8a), 137.48 (C4a/C8a), 157.4 (d, $^2J_{C,P}$ = 6.1 Hz, C3, ma). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 42.6 (ma), 42.7 (mi). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{31}H_{27}Fe_2O_4P$ 606.0341; found 606.0316.

*O-Ferrocenyl(2-methoxyferrocenyl)(3-methoxy-2-naphthyl)-phosphinate (**26b**).* Compound **26b** was obtained as an orange solid with a dr of 1:0.97. Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by slow evaporation of a hexane solution containing **26b** at ambient temperature. Yield: 20 mg (0.032 mmol, 19% based on **7**). Anal. Calcd for $C_{32}H_{29}Fe_2O_4P{\cdot}5/6\ C_6H_{14}$ (620.24·5/6 86.18 g/mol): C, 64.22; H, 5.92. Found: C, 64.00; H, 6.14. Mp: 179 °C. ^1H NMR ($CDCl_3$, δ): 3.57 (s, mi, 3 H, OCH_3(Fc)), 3.72–3.76 (m, 4 H, C_5H_4), 3.77 (s, ma, 3 H, OCH_3(Fc)), 3.82 (s, ma, 3 H, $OCH_3(C_{10}H_6)$), 3.91 (s, mi, 3 H, $OCH_3(C_{10}H_6)$), 4.02 (dd, mi, $J_{H,P}$ = 5.4 Hz, $J_{H,H}$ = 2.7 Hz, 1 H, C_5H_3), 4.07 (dd, ma, $J_{H,P}$ = 5.2 Hz, $J_{H,H}$ = 2.6 Hz, 1 H, C_5H_3), 4.02 (td, mi, J = 2.7 Hz, J = 1.5 Hz, 1 H, C_5H_3), 4.17–4.19 (m, 1 H, C_5H_3), 4.20 (s, 5 H, C_5H_5), 4.21 (s, 5 H, C_5H_5), 4.22–4.26 (m, 7 H, C_5H_5, C_5H_4, C_5H_3), 4.34–4.36 (m, 1 H, C_5H_4), 4.44–4.45 (m, 2 H, C_5H_3, C_5H_4), 4.47–4.48 (m, 6 H, C_5H_5, C_5H_4), 7.02 (d, $^4J_{H,P}$ = 5.7 Hz, 1 H, H4), 7.12 (d, $^4J_{H,P}$ = 5.8 Hz, 1 H, H4), 7.33–7.40 (m, 2 H, $C_{10}H_7$), 7.47 (ddd, $^3J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 6.9 Hz, J = 1.3 Hz, 1 H, $C_{10}H_7$), 7.52 (ddd, $^3J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 6.9 Hz, J = 1.3 Hz, 1 H, $C_{10}H_7$), 7.67 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, $C_{10}H_7$), 7.73 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, $C_{10}H_7$), 7.87 (d, $J_{H,H}$ = 8.2 Hz, 1 H, $C_{10}H_7$), 7.90 (d, $J_{H,H}$ = 8.2 Hz, 1 H, $C_{10}H_7$), 8.60 (d, $^2J_{H,H}$ = 15.7 Hz, 1 H, H1), 8.63 (d, $^2J_{H,P}$ = 15.5 Hz, 1 H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.0 (d, $J_{C,P}$ = 10.8, C_5H_3), 55.2 (s, $OCH_3(C_{10}H_6)$), 55.32 (d, $J_{C,P}$ = 10.8, C_5H_3), 55.34 (s, $OCH_3(C_{10}H_6)$), 58.2 (s, OCH_3(Fc)), 58.3 (s, OCH_3(Fc)), 60.0 (d, $^3J_{C,P}$ = 3.6 Hz, C2/5_{C5H4}), 60.2 (d, $^1J_{C,P}$ = 45.1 Hz, C–P), 60.4 (d, $^3J_{C,P}$ = 3.7 Hz, C2/5_{C5H4}), 60.71 (d, $^1J_{C,P}$ = 164.4 Hz, C–P), 60.74 (d, $^3J_{C,P}$ = 3.9 Hz, C2/5_{C5H4}), 60.8 (d, $^3J_{C,P}$ = 4.3 Hz, C2/5_{C5H4}), 61.1 (d, $^1J_{C,P}$ = 166.2 Hz, C–P), 62.36 (s, C3/4_{C5H4}), 62.40 (s, C3/4_{C5H4}), 62.43 (s, C3/4_{C5H4}), 62.5 (s, C3/4_{C5H4}), 63.5 (d, $J_{C,P}$ = 12.6 Hz, C_5H_3), 63.9 (d, $J_{C,P}$ = 13.7 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 16.5 Hz, C_5H_3), 67.8 (d, $J_{C,P}$ = 10.4 Hz, C_5H_3), 69.35 (s, C_5H_5), 69.38 (s, C_5H_5), 70.0 (s, C_5H_5), 70.1 (s, C_5H_5), 105.6 (d, $^3J_{C,P}$ = 7.3 Hz, C4), 105.8 (d, $^3J_{C,P}$ = 7.4 Hz, C4), 117.3 (d, $^2J_{C,P}$ = 5.7 Hz, C_{C5H4}–O), 117.8 (d, $^2J_{C,P}$ = 6.1 Hz, C_{C5H4}–O), 121.4 (d, $^1J_{C,P}$ = 133.2 Hz, C2), 122.0 (d, $^1J_{C,P}$ = 136.2 Hz, C2), 124.1 ($C_{10}H_7$), 124.2 ($C_{10}H_7$), 126.3 ($C_{10}H_7$), 126.4 ($C_{10}H_7$), 128.3 ($C_{10}H_7$), 128.5 ($C_{10}H_7$), 129.08 ($C_{10}H_7$), 129.14 ($C_{10}H_7$), 128.0 (d, $^3J_{C,P}$ = 8.2 Hz, C4a), 128.1 (d, $^3J_{C,P}$ = 8.1 Hz, C4a), 129.3 (d, $^2J_{C,P}$ = 7.6 Hz, C_{C5H3}–O), 129.9 (d, $^2J_{C,P}$ = 13.1 Hz, C_{C5H3}–O), 136.76 (C8a), 136.77 (C8a), 137.7 (d, $^2J_{C,P}$ = 7.3 Hz, C1), 138.2 (d, $^2J_{C,P}$ = 7.2 Hz, C1), 157.3 (d, $^2J_{C,P}$ = 4.3 Hz, C3–O), 157.5 (d, $^2J_{C,P}$ = 4.0 Hz, C3–O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 29.4 (ma), 33.5 (mi). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{32}H_{29}Fe_2O_4P$ 620.0502; found 620.0508.

*1,3-Dioxa-2-((1R)-α-fenchyl)(oxo)phospha-[3](2,2′-dimethyl)-ferrocenophane ((1R)-**31**).* LiTMP (212 mg, 1.44 mmol) was dissolved in 10 mL of tetrahydrofuran and cooled to −50 °C. Compound **30** (150 mg, 0.36 mmol) was added in a single portion, and stirring was continued for 4 h in a temperature range of −30 to −10 °C. Dimethyl sulfate (0.3 mL, 3.2 mmol) was added in a single portion, and the reaction mixture was allowed to warm to ambient temperature. After 18 h, all volatiles were removed in vacuum. Purification was realized using column chromatography (silica, column size 2 × 25 cm) and dichloromethane as the eluent. Compound **31** was obtained as an orange solid as a mixture of three diastereomers in a ratio of 1:0.25:0.3. Single crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by slow evaporation of a hexane solution containing **31** at ambient temperature. Yield: 84 mg (0.189 mmol, 53% based on (1*R*)-**30**). Anal. Calcd for $C_{22}H_{29}FeO_4P$ (444.28 g/mol): C, 59.48; H, 6.58. Found: C, 59.46; H, 6.86. Mp: 84 °C. ^1H NMR ($CDCl_3$, δ): An assignment of the signals to hydrogen atoms is hardly possible, due to an overlap of all three diastereomers and their different ratio. For spectra, see the Supporting Information. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 9.1 (d, $^4J_{C,P}$ = 5.9 Hz, $CH_{3(C5H3)}$), 11.5 (d, $^4J_{C,P}$ = 3.8 Hz, $CH_{3(C5H3)}$), 19.24 (CH_3), 19.26 (CH_3), 21.15 (CH_3), 21.17 (CH_3), 21.3 (CH_3), 25.96 (C5/6), 26.01 (C5/6), 26.32 (C5/6), 26.34

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(C5/6), 26.6 (C5/6), 29.59 (CH_3), 29.66 (CH_3), 29.71 (CH_3), 39.78 (d, $^3J_{C,P}$ = 2.6 Hz, C3), 39.80 (d, $^3J_{C,P}$ = 2.4 Hz, C3), 39.85 (d, $^3J_{C,P}$ = 2.1 Hz, C3), 40.92 (C7), 40.97 (C7), 47.67 (C4), 47.74 (C4), 49.11 (d, $^3J_{C,P}$ = 5.9 Hz, C1), 49.15 (d, $^3J_{C,P}$ = 5.6 Hz, C1), 49.18 (d, $^3J_{C,P}$ = 5.6 Hz, C1), 60.14 (d, $J_{C,P}$ = 8.7 Hz), 61.2 (d, $J_{C,P}$ = 1.8 Hz), 61.3 (d, $J_{C,P}$ = 2.4 Hz), 64.08, 64.10, 64.14, 65.9, 66.55, 66.60, 67.4 (d, $J_{C,P}$ = 5.4 Hz), 68.1, 68.5 (d, $J_{C,P}$ = 4.2 Hz), 68.6 (d, $J_{C,P}$ = 4.1 Hz), 78.8 (d, $^3J_{C,P}$ = 5.4 Hz, C_{C5H3}–CH_3), 78.95 (d, $^3J_{C,P}$ = 5.9 Hz, C_{C5H3}–CH_3), 79.01 (d, $^3J_{C,P}$ = 5.6 Hz, C_{C5H3}–CH_3), 94.5 (d, $^2J_{C,P}$ = 8.0 Hz, C2), 94.6 (d, $^2J_{C,P}$ = 7.9 Hz, C2), 94.9 (d, $^2J_{C,P}$ = 8.1 Hz, C2), 109.40 (d, $^2J_{C,P}$ = 14.8 Hz, C_{C5H3}–O), 109.49 (d, $^2J_{C,P}$ = 13.9 Hz, C_{C5H3}–O), 109.58 (d, $^2J_{C,P}$ = 14.9 Hz, C_{C5H3}–O), 109.64 (d, $^2J_{C,P}$ = 14.1 Hz, C_{C5H3}–O), 110.8 (d, $^2J_{C,P}$ = 13.0 Hz, C_{C5H3}–O), 111.0 (d, $^2J_{C,P}$ = 13.1 Hz, C_{C5H3}–O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 0.77 (30%), 0.87 (25%), 0.96 (100%). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{22}H_{29}FeO_4P$ 444.1148; found 444.1118.

*(1R)-α-Fenchyl(1′-methoxyferrocenyl)methyl phosphate (**32**).* LiTMP (212 mg, 1.44 mmol) was dissolved in 10 mL of tetrahydrofuran and cooled to −50 °C. Compound (1*R*)-**30** (150 mg, 0.36 mmol) was added in a single portion, and the reaction mixture was allowed to warm to ambient temperature. After being stirred for 18 h, dimethyl sulfate (0.3 mL, 3.2 mmol) was added in a single portion and stirring was continued for an additional 6 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, column size 2 × 18 cm) using a 95:5 dichloromethane/ethyl acetate mixture (v/v) for the elution of 1,1′-$Fc(OMe)_2$ (18 mg, 0.073 mmol, 20% based on (1*R*)-**30**). Compound **32** was eluted using a 9:1 dichloromethane/ethyl acetate mixture (v/v) as the eluent (R_f = 0.37). The title compound was obtained as an orange oil as a mixture of two diastereomers in a 1:1 ratio. Yield: 17 mg (0.037 mmol, 10% based on (1*R*)-**30**). ^1H NMR ($CDCl_3$, δ): 0.89 (s, 3H, CH_3), 0.92 (s, 3 H, CH_3), 1.05−1.07 (m, 8 H, CH_3, H5/6), 1.10 (s, 3 H, CH_3), 1.13 (s, 3 H, CH_3), 1.15−1.16 (m, 1 H, H7), 1.18−1.19 (m, 1 H, H7), 1.41−1.46 (m, 2 H, H5/6), 1.49−1.52 (m, 2 H, H7), 1.69−1.71 (m, 6 H, H5/6, H4), 3.366 (s, 3 H, C−O−CH_3), 3.370 (s, 3 H, C−O−CH_3), 3.808 (d, $^3J_{H,P}$ = 11.3 Hz, 3 H, P−O−CH_3), 3.815 (d, $^3J_{H,P}$ = 11.3 Hz, 3 H, P−O−CH_3), 3.91−3.93 (m, 8 H, C_5H_4), 3.99 (dd, $^3J_{H,P}$ = 8.4 Hz, $J_{H,H}$ = 1.9 Hz, 1 H, H2), 4.00 (dd, $^3J_{H,P}$ = 8.4 Hz, $J_{H,H}$ = 1.8 Hz, 1 H, H2), 4.14−4.15 (m, 4 H, C_5H_4), 4.41 (dd, $J_{H,P}$ = 3.5 Hz, $J_{H,P}$ = 1.8 Hz, 1 H, C_5H_4), 4.42−4.43 (m, 2 H, C_5H_4), 4.46 (dd, $J_{H,P}$ = 3.3 Hz, $J_{H,P}$ = 1.6 Hz, 1 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.2 (CH_3), 20.74 (CH_3), 20.75 (CH_3), 25.62 (C5/6), 25.65 (C5/6), 25.89 (C5/6), 25.90 (C5/6), 29.8 (CH_3), 39.53 (C3), 39.55 (C3), 40.92 (C7), 47.9 (C4), 49.21 (C1), 49.22 (C1), 49.25 (C1), 49.26 (C1), 54.58 (P−O−CH_3), 54.60 (P−O−CH_3), 54.63 (P−O−CH_3), 54.65 (P−O−CH_3), 56.31 (C_5H_4), 57.5 (C−O−CH_3), 60.29 (C_5H_4), 60.32 (C_5H_4), 60.35 (C_5H_4), 60.36 (C_5H_4), 60.37 (C_5H_4), 63.10 (C_5H_4), 63.12 (C_5H_4), 63.15 (C_5H_4), 63.15 (C_5H_4), 63.40 (C_5H_4), 63.41 (C_5H_4), 91.57 (C2), 91.60 (C2), 91.63 (C2), 91.66 (C2), 117.84 (C_{C5H4}–O–P), 117.85 (C_{C5H4}–O–P), 117.88 (C_{C5H4}–O–P), 117.89 (C_{C5H4}–O–P), 128.1 (C_{C5H4}–O–C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −3.95, −3.91. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{22}H_{29}FeO_5P$ 462.1259; found 462.1246.

*meso-2,2′-Dimethoxy-1,1′-bis(1,3-dioxa-2-(oxo)phospha-[3]-ferrocenophan-2-yl)-ferrocene (**36**).* Phosphate **34** (36 mg, 0.067 mmol), diisopropylamine (0.04 mL, 0.27 mmol), BuLi (0.11 mL, 0.275 mmol), and dimethyl sulfate (0.05 mL, 0.527 mmol) were reacted at −30 °C for 2 h according to the general procedure described above. Purification was realized by column chromatography (silica, column size, 2 × 12 cm) using a 1:1 dichloromethane/ethyl acetate (v/v) mixture as the eluent. The title compound was obtained as an orange oil. Yield: 32 mg (0.042 mmol, 62% based on **34**). Anal. Calcd for $C_{32}H_{28}Fe_3O_8P_2$ (770.04 g/mol): C, 49.91; H, 3.67. Found: C, 53.46; H, 6.34. (*best match, too less compound) ^1H NMR ($CDCl_3$, δ): 3.82 (s, 6 H, OCH_3), 4.01−4.02 (m, 4 H, C_5H_4), 4.08−4.10 (m, 4 H, C_5H_4), 4.34−4.35 (m, 4 H, C_5H_4), 4.52 (dd, $J_{H,P}$ = 6.0 Hz, $J_{H,H}$ = 2.9 Hz, 2 H, C_5H_3), 4.66−4.68 (m, 4 H, C_5H_3), 4.71−4.72 (m, 2 H, C_5H_4), 4.73−4.74 (m, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 52.9 (d, $^1J_{C,P}$ = 227.4 Hz, C−P), 58.4 (d, $J_{C,P}$ = 12.1 Hz, C_5H_3), 58.6 (s, OCH_3), 63.78 (C_5H_4), 63.82 (C_5H_4), 63.86 (C_5H_4), 63.88 (C_5H_4), 65.66 (C_5H_4), 65.69 (C_5H_4), 67.02 (C_5H_4), 67.04 (C_5H_4), 69.3 (d, $J_{C,P}$ = 15.0 Hz, C_5H_3), 69.4 (d, $J_{C,P}$ = 14.0 Hz, C_5H_3), 109.06 (d, $^2J_{C,P}$ = 11.8 Hz, C_{C5H4}–O), 109.12 (d, $^2J_{C,P}$ = 12.1 Hz, C_{C5H4}–O), 130.5 (d, $^2J_{C,P}$ = 10.5 Hz, C_{C5H3}–O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 30.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{32}H_{28}Fe_3O_8P_2$ + Na 792.9202; found 792.9191.

*1,3-Dioxa-2-(2-methoxyferrocenyl) (oxo)phospha-[3]ferrocenophane (**28a**).* Phosphate **27a** (30 mg, 0.065 mmol), diisopropylamine (0.04 mL, 0.27 mmol), BuLi (0.11 mL, 0.27 mmol), and dimethyl sulfate (0.1 mL, 1.05 mmol) were reacted between −30 and −10 °C for 2 h according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 12 cm) using a 95:5 dichloromethane/ethyl acetate mixture (v/v) as the eluent. The title compound **28a** was obtained as an orange solid. Yield: 31 mg (0.0.065 mmol, 99% based on **27a**). Anal. Calcd for $C_{21}H_{19}Fe_2O_8P_2$ (478.04 g/mol): C, 52.76; H, 4.01. Found: C, 52.02; H, 4.52. (*best match). Mp: >230 °C (decomp.). ^1H NMR ($CDCl_3$, δ): 3.76 (s, 3 H, OCH_3), 4.00−4.01 (m, 2 H, C_5H_4), 4.07−4.09 (m, 2 H, C_5H_4), 4.17 (dd, $J_{H,P}$ = 5.9 Hz, $J_{H,H}$ = 2.8 Hz, 1 H, C_5H_3), 4.32−4.35 (m, 3 H, C_5H_4, C_5H_3), 4.40 (s, 5 H, C_5H_5), 4.41−4.43 (m, 1 H, C_5H_3), 4.73−4.75 (m, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 52.9 (d, $^1J_{C,P}$ = 228.6 Hz, C−P), 56.0 (d, $J_{C,P}$ = 12.3 Hz, C_5H_3), 58.5 (s, CH_3), 63.74 (d, $J_{C,P}$ = 5.7 Hz, C_5H_4), 63.78 (d, $J_{C,P}$ = 5.6 Hz, C_5H_4), 63.9 (d, $J_{C,P}$ = 6.2 Hz, C_5H_4), 64.9 (d, $J_{C,P}$ = 15.3 Hz, C_5H_3), 65.49 (C_5H_4), 65.52 (C_5H_4), 66.93 (C_5H_4), 67.2 (d, $J_{C,P}$ = 14.1 Hz, C_5H_3), 70.5 (s, C_5H_5), 109.1 (d, $^2J_{C,P}$ = 11.8 Hz, C_{C5H4}–O), 109.3 (d, $^2J_{C,P}$ = 11.8 Hz, C_{C5H4}–O), 129.4 (d, $^2J_{C,P}$ = 10.8 Hz, C_{C5H3}–O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 31.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{28}Fe_3O_8P_2$ + H 770.9382; found 770.9391.

*(R,R$_p$)-1,1′-Binaphthyl-2,2′-diyl(2-methoxyferrocenyl)phosphonate (**28b**).* Phosphate **27b** (100 mg, 0.188 mmol), diisopropyl amine (0.16 mL, 1.15 mmol), BuLi (0.45 mL, 1.125 mmol), and dimethyl sulfate (0.3 mL, 3.16 mmol) were reacted in tetrahydrofuran at −70 °C for 2 h according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2 × 8 cm) using a 9:1 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **28b** was obtained as an orange solid with a dr of both diastereomers of 1:0.045 (de = 0.91). Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by crystallization from a boiling chloroform solution containing **28b**. Yield: 59 mg (0.108 mmol, 57% based on **27b**). Anal. Calcd for $C_{31}H_{23}FeO_4P \cdot 1/4\ CH_2Cl_2$ (546.33 · 1/4 84.93 g/mol): C, 66.13; H, 4.17. Found: C, 66.50; H, 4.37. Mp: >290 °C (decomp.). ^1H NMR ($CDCl_3$, δ): 2.63 (s, 3 H, OCH_3), 4.10 (ddd, $J_{H,P}$ = 3.2 Hz, $J_{H,H}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 4.15 (ddd, $J_{H,P}$ = 2.9 Hz, $J_{H,H}$ = 2.8 Hz, $J_{H,H}$ = 2.8 Hz, 1 H, C_5H_3), 4.37 (s, 5 H, C_5H_5), 4.54 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,P}$ = 2.2 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 7.15 (dd, $^3J_{H,H}$ = 8.8 Hz, $^3J_{H,P}$ = 0.9 Hz, 1 H, H3), 7.27−7.31 (m, 2 H, C_6H_4), 7.37−7.39 (m, 1 H, C_6H_4), 7.43−7.49 (m, 3 H, C_6H_4), 7.73 (dd, $^3J_{H,H}$ = 8.8 Hz, $^3J_{H,P}$ = 8.8 Hz, 1 H, H3′), 7.81 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, H4), 7.87−7.89 (m, 1 H, C_6H_4), 7.96−7.97 (m, 1 H, C_6H_4), 8.06 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, H4′). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 51.1 (d, $^1J_{C,P}$ = 214.3 Hz, C_{C5H3}–P), 55.9 (d, $J_{C,P}$ = 12.2 Hz, C_5H_3), 57.0 (s, OCH_3), 65.0 (d, $J_{C,P}$ = 15.3 Hz, C_5H_3), 67.7 (d, $J_{C,P}$ = 15.9 Hz, C_5H_3), 70.5 (s, C_5H_5), 121.2 (d, $^2J_{C,P}$ = 3.1 Hz, C3), 121.6 (d, $^2J_{C,P}$ = 2.3 Hz, C3′), 121.8 (d, $^3J_{C,P}$ = 2.4 Hz, C1/C1′), 122.3 (d, $^3J_{C,P}$ = 2.6 Hz, C1/C1′), 125.2, 125.4, 126.2, 126.5, 127.1, 127.2, 128.1, 128.4, 128.6 (d, $^2J_{C,P}$ = 9.8 Hz, C_{C5H3}–O), 130.0 (d, $^4J_{C,P}$ = 1.4 Hz, C4/C4′), 130.8 (d, $^4J_{C,P}$ = 0.9 Hz, C4/C4′), 131.5 (d, $^4J_{C,P}$ = 1.2 Hz, C4a/C4a′), 131.7 (d, $^4J_{C,P}$ = 1.2 Hz, C4a/C4a′), 132.60 (C8a/C8a′), 132.61 (C8a/C8a′), 146.7 (d, $^2J_{C,P}$ = 9.9 Hz, C2/C2′), 147.5 (d, $^2J_{C,P}$ = 10.0 Hz, C2/C2′). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 33.7 (4.5%), 34.6 (95.5%). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{31}H_{23}FeO_4P$ 547.0757; found 547.0764.

*N,N,N′,N′-Tetraethyl-1-(2-methylferrocenyloxy)phosphinediamine·BH$_3$ (**42**).* Compound **37** (519 mg, 1.33 mmol), *s*-BuLi (1.23 mL, 1.60 mmol), and MeI (0.16 mL, 2.60 mmol) were reacted according to the general procedure between −20 and −10 °C for 3.5 h as described above. Purification was realized by column chromatography (alumina, column size 3.5 × 13 cm) using a 8:2 hexane/diethyl ether mixture (v/v) as the eluent. Compound **42** was obtained as a mixture in 436 mg

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consisting of the starting material **37** (91 mg, 0.24 mmol, 18%) and **42**. Both compounds could not be separated from each other by column chromatography occurring in a ratio of 1:0.28. Yield: 343 mg (0.85 mmol, 64% based on **37**). ^{1}H NMR (C_6D_6, δ): 0.90 (t, $^{3}J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 1.01 (t, $^{3}J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 2.02 (s, 3 H, C_{C5H3}–CH_3), 2.87–3.00 (m, 8 H, CH_2), 3.62 (pt, $^{3,4}J_{H,H}$ = 2.6 Hz, 1 H, C_5H_4), 3.69–3.70 (m, 1 H, C_5H_4), 4.12 (s, 5 H, C_5H_5), 4.53 (dd, $J_{H,H}$ = 2.5 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6, δ): 12.4 (C_{C5H3}–CH_3), 14.2 (d, $^{4}J_{C,P}$ = 1.7 Hz, CH_3), 14.5 (d, $^{4}J_{C,P}$ = 1.7 Hz, CH_3), 39.3 (d, $^{3}J_{C,P}$ = 6.4 Hz, CH_2), 39.5 (d, $^{3}J_{C,P}$ = 6.4 Hz, CH_2), 60.7 (C_5H_3), 60.95 (d, $J_{C,P}$ = 3.0 Hz, C_5H_3), 64.5 (C_5H_3), 70.3 (C_5H_5), 74.6 (d, $^{3}J_{C,P}$ = 2.6 Hz, C_{C5H3}–CH_3), 117.4 (d, $^{2}J_{C,P}$ = 1.8 Hz, C_{C5H3}–O). ^{31}P{^{1}H} NMR (C_6D_6, δ): 130.8–131.7 (br m). ^{11}B{^{1}H} NMR (C_6D_6, δ): −39.6 (d, $^{1}J_{B,P}$ = 91.3 Hz). HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{19}H_{34}BFeN_2OP$ + Na 427.1747; found 427.1724.

*N,N,N′,N′-Tetraethyl-1-(2-methylferrocenyloxy)phosphinediamine sulfide (**43**).* Compound **38** (250 mg, 0.61 mmol), *s*-BuLi (0.75 mL, 0.98 mmol), and MeI (0.10 mL, 1.59 mmol) were reacted according to the general procedure between −20 and −10 °C for 3.5 h as described above. Purification was realized by column chromatography (alumina, column size 2.5 × 17 cm) using an 85:15 hexane/dichloromethane mixture (v/v) as the eluent. Compound **43** was obtained in a mixture of 135 mg along with the starting material **38**. Both compounds could not be separated from each other by column chromatography occurring in a ratio of 1:0.07. Yield: 128 mg (0.302 mmol, 50% based on **38**). ^{1}H NMR (C_6D_6, δ): 0.97 (t, $^{3}J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 1.06 (t, $^{3}J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 2.04 (s, 3 H, C_{C5H3}–CH_3), 2.99–3.11 (m, 8 H, CH_2), 3.64 (pt, $^{3,4}J_{H,H}$ = 2.6 Hz, 1 H, C_5H_3), 3.71–3.72 (m, 1 H, C_5H_3), 4.14 (s, 5 H, C_5H_5), 4.61–4.62 (m, 1 H, C_5H_3). ^{13}C{^{1}H} NMR (C_6D_6, δ): 12.5 (C_{C5H3}–CH_3), 14.1 (d, $^{4}J_{C,P}$ = 3.3 Hz, CH_3), 14.4 (d, $^{4}J_{C,P}$ = 3.0 Hz, CH_3), 40.6 (d, $^{3}J_{C,P}$ = 5.0 Hz, CH_2), 40.9 (d, $^{3}J_{C,P}$ = 5.1 Hz, CH_2), 60.9 (C_5H_3), 61.0 (d, $J_{C,P}$ = 3.0 Hz, C_5H_3), 64.5 (C_5H_3), 70.3 (C_5H_5), 74.9 (d, $^{3}J_{C,P}$ = 4.0 Hz, C_{C5H3}–CH_3), 116.8 (d, $^{2}J_{C,P}$ = 1.3 Hz, C_{C5H3}–O). ^{31}P{^{1}H} NMR (C_6D_6, δ): 90.9. HRMS (ESI-TOF) m/z: [M]$^+$ calcd for $C_{19}H_{31}FeN_2OPS$ 422.1239; found 422.1262.

*(2-Methylferrocenyl)di(pyrrolidin-1-yl)phosphinate (**44**) and (1′,2-Dimethylferrocenyl)di(pyrrolidinin-1-yl)phosphinate (**45**).* Compound **39** (206 mg, 0.53 mmol) was dissolved in hexane (A)/diethyl ether (B) and cooled to −30 °C, and *s*-BuLi (0.54 mL, 0.69 mmol) was dropwise added. The mixture was stirred for 18 h at ambient temperature (A) or 4 h between −40 and −30 °C (B). Afterward, MeI (0.10 mL, 1.59 mmol) was added in a single portion, and the reaction mixture was allowed to warm to ambient temperature, where stirring was continued for 18 h. Purification was realized by column chromatography (alumina, column size 2.5 × 17 cm) using a 9:1 dichloromethane/ethyl acetate mixture (v/v) as the eluent. The title compounds **44** and **45** were obtained as mixtures (A, **39**/**44**/**45** = 0.24:1:<0.05; B, **39**/**44**/**45** = 0.06:1:0.65) and could not be separated from each other by column chromatography.

*Compound **44**.* Yield: A, 137 mg (0.34 mmol, 64% based on **39**); B, 102 mg (0.25 mmol, 48% based on **39**). ^{1}H NMR (C_6D_6, δ): 1.37–1.40 (m, 4 H, H3,H4–C_4N), 1.48–1.51 (m, 4 H, H3,H4–C_4N), 2.06 (s, 3 H, CH_3), 3.05–3.13 (m, 4 H, H2,H5–C_4N), 3.16–3.20 (m, 4 H, H2,H5–C_4N), 3.66–3.67 (m, 1 H, C_5H_3), 3.71–3.74 (m, 1 H, C_5H_3), 4.19 (s, 5 H, C_5H_5), 4.75–4.77 (m, 1H, C_5H_3). ^{13}C{^{1}H} NMR (C_6D_6, δ): 12.1 (CH_3), 26.5 (d, $^{3}J_{C,P}$ = 8.7 Hz, C3,C4–C_4N), 26.6 (d, $^{3}J_{C,P}$ = 9.0 Hz, C3,C4–C_4N), 46.8 (d, $^{2}J_{C,P}$ = 4.6 Hz, C2,C5–C_4N), 60.2 (d, $J_{C,P}$ = 1.9 Hz, C_5H_3), 60.7 (C_5H_3), 64.3 (C_5H_3), 70.5 (C_5H_5), 74.0 (d, $^{3}J_{C,P}$ = 5.3 Hz, C_{C5H3}–CH_3), 117.2 (d, $^{2}J_{C,P}$ = 4.0 Hz, C_{C5H3}–O). ^{31}P{^{1}H} NMR (C_6D_6, δ): 22.9. HRMS (ESI-TOF) m/z: [M]$^+$ calcd for $C_{19}H_{27}FeN_2O_2P$ 402.1154; found 402.1158.

*Compound **45**.* Yield: A, 7 mg (0.017 mmol, 3% based on **39**); B, 69 mg (0.165 mmol, 31% based on **39**). ^{1}H NMR (C_6D_6, δ): 1.37–1.40 (m, 4 H, H3,H4–C_4N), 1.48–1.51 (m, 4 H, H3,H4–C_4N), 2.03 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 3.05–3.15 (m, 4 H, H2,H5–C_4N), 3.17–3.21 (m, 4 H, H2,H5–C_4N), 3.64 (pt, $^{3,4}J_{H,H}$ = 2.6 Hz, 1 H, C_5H_3), 3.66–3.70 (m, 1 H, $C_5H_{3/4}$), 4.00–4.02 (m, 1 H, C_5H_3), 4.08–4.11 (m, 3 H, C_5H_4), 4.71 (dd, J = 2.2 Hz, $J_{H,H}$ = 1.8 Hz, 1 H, C_5H_3). ^{13}C{^{1}H} NMR (C_6D_6, δ): 11.8 (CH_3), 13.9 (CH_3), 26.5 (d, $^{3}J_{C,P}$ = 8.7 Hz, C3,C4–C_4N), 26.6 (d, $^{3}J_{C,P}$ = 9.0 Hz, C3,C4–C_4N), 46.8 (d, $^{2}J_{C,P}$ = 5.1 Hz, C2,C5–C_4N), 60.9 (d, $J_{C,P}$ = 1.8 Hz, C_5H_3), 61.4 (C_5H_3), 64.8 (C_5H_3), 69.4 (C_5H_4), 69.6 (C_5H_4), 71.2 (C_5H_4), 71.9 (C_5H_4), 73.9 (d, $^{3}J_{C,P}$ = 5.0 Hz, C_{C5H3}–CH_3), 85.0 (C_{C5H4}–CH_3), 116.8 (d, $^{2}J_{C,P}$ = 3.8 Hz, C_{C5H3}–O). ^{31}P{^{1}H} NMR (C_6D_6, δ): 23.0. HRMS (ESI-TOF) m/z: [M]$^+$ calcd for $C_{20}H_{29}FeN_2O_2P$ 416.1311; found 416.1336.

*O-Ferrocenyl(2-methoxyferrocenyl)1H-pyrrol-1-ylphosphinate (**49**).* Phosphonate **46** (100 mg, 0.194 mmol), diisopropylamine (0.16 mL, 1.165 mmol), BuLi (0.46 mL, 1.15 mmol), and dimethyl sulfate (0.11 mL, 1.16 mmol) were reacted according to the general procedure for apFr at −70 °C for 4 h as described above. Purification was realized by column chromatography (silica, column size 2.5 × 15 cm) using dichloromethane for the elution of FcOMe (13 mg, 0.060 mmol, 31% based on **46**), a 98:2 dichloromethane/ethyl acetate mixture (v/v) for **46** (42 mg, 0.082 mmol, 42%) and a 95:5 dichloromethane/ethyl acetate mixture (v/v) for the elution of **49** as the eluents. The title compound was obtained as a mixture of two diastereomers in a ratio of 1:0.89 as an orange solid, which rapidly decomposes in solution. Yield: 25 mg (0.047 mmol, 24% based on **46**). Anal. Calcd for $C_{25}H_{24}Fe_2NO_3P$ (529.13 g/mol): C, 56.75; H, 4.57; N, 2.65. Found: C, 57.34; H, 5.40; N, 2.10 (*best match). Mp: 182–188 °C. ^{1}H NMR ($CDCl_3$, δ): 3.70 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 3.80–3.83 (m, 3 H, C_5H_4), 3.85 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_4), 4.08 (dd, $J_{H,P}$ = 5.7 Hz, $J_{H,H}$ = 2.8 Hz, 1 H, C_5H_3), 4.11–4.15 (m, 4 H, C_5H_4, C_5H_3), 4.19 (s, 5 H, C_5H_5), 4.20 (s, 5 H, C_5H_5), 4.21–4.22 (m, 1 H, C_5H_4), 4.23 (s, 5 H, C_5H_5), 4.27 (ddd, $J_{H,P}$ = 3.2 Hz, $J_{H,H}$ = 2.8 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 4.28–4.30 (m, 1 H, C_5H_3), 4.33–4.34 (m, 1 H, C_5H_4), 4.38 (s, 5 H, C_5H_5), 4.43 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,P}$ = 2.0 Hz, $J_{H,H}$ = 1.4, 1 H, C_5H_3), 6.30–6.32 (m, 2 H, H3,4), 6.34–6.36 (m, 2 H, H3,4), 7.15–7.16 (m, 2 H, H2,5), 7.26–7.28 (m, 2 H, H2,5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.7 (d, $J_{C,P}$ = 11.6 Hz, C_5H_3), 55.9 (d, $J_{C,P}$ = 11.7 Hz, C_5H_3), 57.1 (d, $^{1}J_{C,P}$ = 207.7 Hz, C–P), 57.9 (d, $^{1}J_{C,P}$ = 206.3 Hz, C–P), 58.24 (OCH_3), 58.25 (OCH_3), 59.74 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 59.77 (d, $J_{C,P}$ = 3.7 Hz, C_5H_4), 59.82 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 60.1 (d, $J_{C,P}$ = 3.7 Hz, C_5H_4), 62.76 (C_5H_4), 62.83 (C_5H_4), 62.85 (C_5H_4), 64.3 (d, $J_{C,P}$ = 14.2 Hz, C_5H_3), 64.6 (d, $J_{C,P}$ = 15.1 Hz, C_5H_3), 66.8 (d, $J_{C,P}$ = 15.8 Hz, C_5H_3), 67.8 (d, $J_{C,P}$ = 13.2 Hz, C_5H_3), 69.58 (C_5H_5), 69.60 (C_5H_5), 70.0 (C_5H_5), 70.3 (C_5H_5), 112.05 (d, $^{3}J_{C,P}$ = 9.7 Hz, C3,4), 112.13 (d, $^{3}J_{C,P}$ = 10.0 Hz, C3,4), 116.73 (d, $^{2}J_{C,P}$ = 7.3 Hz, C_{C5H4}–O), 116.76 (d, $^{2}J_{C,P}$ = 7.1 Hz, C_{C5H4}–O), 122.3 (d, $^{2}J_{C,P}$ = 6.2 Hz, C2,5), 122.5 (d, $^{2}J_{C,P}$ = 6.3 Hz, C2,5), 128.1 (d, $^{2}J_{C,P}$ = 11.1 Hz, C_{C5H3}–O), 128.7 (d, $^{2}J_{C,P}$ = 9.9 Hz, C_{C5H3}–O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 17.8 (major), 18.3 (minor). HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{25}H_{24}Fe_2NO_3P$ + H 530.0266; found 530.0269.

*O,O′-Diferrocenyl(1H-pyrrol-2-yl)phosphonate (**52**).* Phosphonate **46** (100 mg, 0.194 mmol), diisopropylamine (0.16 mL, 1.165 mmol), BuLi (0.46 mL, 1.15 mmol), and dimethyl sulfate (0.11 mL, 1.16 mmol) were reacted according to the general procedure for apFr at −40 °C for 4 h as described above. Purification was realized by column chromatography (silica, column size 2.5 × 15 cm) using a 98:2 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **52** was obtained as a yellow, weakly soluble solid. Thus, the sample was suspended in DMSO-d_6 and 10% $CDCl_3$ was added to optimize the solubility. Yield: 27 mg (0.052 mmol, 27% based on **46**). Anal. Calcd for $C_{24}H_{22}Fe_2NO_3P$ (515.10 g/mol): C, 55.96; H, 4.30; N, 2.72. Found: C. 55.71; H, 4.25; N, 2.82. Mp: >250 °C. ^{1}H NMR ($CDCl_3$, δ): 3.87 (br, m, 4 H, C_5H_4), 4.20 (br, m, 10 H, C_5H_5), 4.34 (br, m, 4 H, C_5H_4), 6.35 (br, m, 1 H, C_4H_4N), 6.84 (br, m, 1 H, C_4H_4N), 7.06 (br, m, 1 H, C_4H_4N), 9.08 (br, s, 1 H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.9 (d, $J_{C,P}$ = 3.7 Hz, C_5H_4), 60.1 (d, $J_{C,P}$ = 4.0 Hz, C_5H_4), 62.8 (C_5H_4), 62.9 (C_5H_4), 69.6 (C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 4.3. ^{1}H NMR (DMSO-d_6, δ): 3.87 (br, m, 4 H, C_5H_4), 4.14 (br, m, 10 H, C_5H_5), 4.31 (br, m, 4 H, C_5H_4), 6.24 (br, m, 1 H, C_4H_4N), 6.80 (br, m, 1 H, C_4H_4N), 7.13 (br, m, 1 H, C_4H_4N), 11.93 (br, s, 1 H, NH). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 59.3* (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 59.4* (d, $J_{C,P}$ = 4.5 Hz, C_5H_4), 62.3 (C_5H_4), 62.4 (C_5H_4), 69.1 (C_5H_5), 109.2* (d, $J_{C,P}$ = 16.1 Hz, C_4H_3N), 114.7 (d, $^{1}J_{C,P}$ = 235.8 Hz, $C1_{C4H3N}$–P), 116.6 (d, $^{2}J_{C,P}$ = 4.8 Hz, C_{C5H4}–O), 120.2* (d,

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$J_{C,P}$ = 20.2 Hz, C_4H_3N), 125.3* (d, $J_{C,P}$ = 13.5 Hz, C_4H_3N). $^{31}P\{^1H\}$ NMR (DMSO-d_6, δ): 4.5. (*Obtained from DEPT90 measurements). HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{22}Fe_2NO_3P$ + Na 537.9929; found 537.9913.

*O-Ferrocenyl(1H-indol-1-yl)(2-methoxyferrocenyl)phosphinate (**50**).* Compound **47** (100 mg, 0.177 mmol), diisopropylamine (0.15 mL, 1.06 mmol), BuLi (0.43 mL, 1.08 mmol), and dimethyl sulfate (0.10 mL, 1.06 mmol) were reacted at −40 °C for 3 h according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 22 cm) using a 95:5 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **50** was obtained along with compound **53** in a ratio of 1:0.78 (**53**/**50**) as a mixture of two diastereomers. Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by evaporation of a $CHCl_3$ solution containing the mixture of **53** or **50** at ambient temperature. Yield: 25 mg (0.043 mmol, 24% based on **47**). ^1H NMR ($CDCl_3$, δ): 3.56 (s, 3 H, OCH_3), 3.77−3.79 (m, 2 H, C_5H_4), 3.80−3.81 (m, 5 H, OCH_3, C_5H_4), 3.95−3.96 (m, 1 H, C_5H_3), 4.00−4.02 (m, 1 H, C_5H_3), 4.12−4.14 (m, 6 H, C_5H_5, C_5H_3), 4.17−4.19 (m, 7 H, C_5H_5, C_5H_4), 4.22−4.24 (m, 1 H, C_5H_3), 4.28−4.29 (m, 1 H, C_5H_3), 4.30−4.32 (m, 6 H, C_5H_5, C_5H_4), 4.35 (s, 5 H, C_5H_5), 4.40−4.42 (m, 1 H, C_5H_4), 4.48−4.49 (m, 1 H, C_5H_3), 6.64 (ddd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 0.8 Hz, 1 H, H3), 6.66 (ddd, $^3J_{H,H}$ = 3.4 Hz, $^4J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 0.8 Hz, 1 H, H3), 7.16−7.17 (m, 1 H, H4), 7.18−7.20 (m, 1 H, H4), 7.20−7.23 (m, 2 H, H5/6), 7.25−7.28 (m, 2 H, H5/6), 7.53 (dd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{H,P}$ = 2.8 Hz, 1 H, H2), 7.55 (dd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{H,P}$ = 2.8 Hz, 1 H, H2), 7.92 (dd, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 1.2 Hz, 1 H, H7), 8.02 (dd, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 1.1 Hz, 1 H, H7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.8 (d, $J_{C,P}$ = 11.4 Hz, C_5H_3), 56.0 (d, $J_{C,P}$ = 11.8 Hz, C_5H_3), 57.5 (d, $^1J_{C,P}$ = 207.5 Hz, C−P), 57.7 (d, $^1J_{C,P}$ = 206.4 Hz, C−P), 58.28 (OCH_3), 58.31 (OCH_3), 59.8−60.2 (m, C_5H_4), 62.79 (C_5H_4), 62.81 (C_5H_4), 62.83 (C_5H_4), 64.4 (d, $J_{C,P}$ = 13.6 Hz, C_5H_3), 64.5 (d, $J_{C,P}$ = 14.9 Hz, C_5H_3), 66.7 (d, $J_{C,P}$ = 16.0 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 12.3 Hz, C_5H_3), 69.5 (C_5H_5), 69.54 (C_5H_5), 70.1 (C_5H_5), 70.3 (C_5H_5), 107.0 (d, $^3J_{C,P}$ = 7.4 Hz, C3), 107.4 (d, $^3J_{C,P}$ = 7.5 Hz, C3), 114.3 (C7), 114.5 (C7), 116.7 (d, $^2J_{C,P}$ = 7.0 Hz, C_{C5H4}−O), 116.9 (d, $^2J_{C,P}$ = 7.5 Hz, C_{C5H4}−O), 120.9, 121.8, 121.9, 122.2, 123.0, 123.2, 128.1 (d, $^2J_{C,P}$ = 6.6 Hz, C2), 128.6 (d, $^2J_{C,P}$ = 6.4 Hz, C2), 128.8 (d, $^2J_{C,P}$ = 9.7 Hz, C_{C5H3}−O), 128.9 (d, $^2J_{C,P}$ = 11.9 Hz, C_{C5H3}−O), 130.9 (d, $^3J_{C,P}$ = 8.3 Hz, C3a), 131.1 (d, $^3J_{C,P}$ = 8.6 Hz, C3a), 137.3 (d, $^2J_{C,P}$ = 5.0 Hz, C7a), 137.7 (d, $^2J_{C,P}$ = 4.6 Hz, C7a). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 16.8, 18.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{29}H_{26}Fe_2NO_3P$ + H 580.0423; found 580.0430.

*O-Ferrocenyl 9H-Carbazol-9-yl(2-methoxyferrocenyl)phosphinate (**51**).* Compound **48** (100 mg, 0.163 mmol), diisopropylamine (0.14 mL, 0.98 mmol), BuLi (0.39 mL, 0.98 mmol), and dimethyl sulfate (0.09 mL, 0.98 mmol) were reacted at −60 °C for 3 h according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 16 cm) using a 95:5 dichloromethane/ethyl acetate mixture (v/v) as the eluent. The title compound was obtained as an orange solid and as a mixture of both diastereomers in a ratio of 1:0.28 (de = 0.56). Crystals, suitable for single-crystal X-ray diffraction analysis, were obtained by evaporation of a dichloromethane solution at ambient temperature containing **51**. Yield: 58 mg (0.092 mmol, 56% based on **48**). Anal. Calcd for $C_{33}H_{28}Fe_2NO_3P$ (629.24 g/mol): C, 62.99; H, 4.49; N, 2.23. Found: C. 62.98; H, 4.56; N, 2.25. Mp: 206 °C. ^1H NMR ($CDCl_3$, δ): 3.35 (s, 3 H, OCH_3, ma), 3.59 (ddd, $J_{H,H}$ = 2.7 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 1.5 Hz, 0.3 H, C_5H_3, mi), 3.73 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.4 Hz, 0.3 H, C_5H_4, mi), 3.76 (ddd, $J_{H,H}$ = 2.7 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_4, ma), 3.77−3−78 (m, 0.3 H, C_5H_4, mi), 3.79 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_4, ma), 3.83 (s, 0.9 H, OCH_3, mi), 3.89 (dpt, $J_{H,P}$ = 2.8 Hz, $^{3,4}J_{H,H}$ = 2.8 Hz, 0.3 H, C_5H_3, mi), 4.10−4.11 (m, 6 H, C_5H_5, C_5H_3, ma), 4.13 (s, 1.5 H, C_5H_5, mi), 4.15 (ddd, $J_{H,P}$ = 3.5 Hz, $J_{H,H}$ = 2.7 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3, ma), 4.19−4.20 (m, 0.3 H, C_5H_4, mi), 4.21−4.22 (m, 1 H, C_5H_4, ma), 4.27 (s, 1.5 H, C_5H_5, mi), 4.28 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,P}$ = 2.8 Hz, $J_{H,H}$ = 1.4 Hz, 0.3 H, C_5H_3, mi), 4.41−4.42 (m, 1 H, C_5H_4, ma), 4.44 (s, 5 H, C_5H_5, ma), 4.51−4.53 (m, 0.3 H, C_5H_4, mi), 4.54 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,P}$ = 2.8 Hz, $J_{H,H}$ = 1.4 Hz, 1 H, C_5H_3, ma), 7.29 (ddd, $J_{H,H}$ = 7.9 Hz, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 1.0 Hz, 2 H, $C_{12}H_8$, ma), 7.34 (ddd, $J_{H,H}$ = 7.9 Hz, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 1.0 Hz, 0.6 H, $C_{12}H_8$, mi), 7.40 (ddd, $J_{H,H}$ = 8.5 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.3 Hz, 2 H, $C_{12}H_8$, ma), 7.45 (ddd, $J_{H,H}$ = 8.5 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.4 Hz, 0.6 H, $C_{12}H_8$, mi), 7.96−7.98 (m, 2 H, $C_{12}H_8$, ma), 8.02−8.04 (m, 0.6 H, $C_{12}H_8$, mi), 8.16−8.17 (m, 2 H, $C_{12}H_8$, ma), 8.28−8.30 (m, 0.6 H, $C_{12}H_8$, mi). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.8 (d, $J_{C,P}$ = 11.2 Hz, C_5H_3, mi), 56.0 (d, $J_{C,P}$ = 12.0 Hz, C_5H_3, ma), 58.3 (s, OCH_3, ma), 58.4 (s, OCH_3, mi), 58.5 (d, $^1J_{C,P}$ = 206.1 Hz, C−P, ma), 59.8 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4, ma), 60.0 (d, $J_{C,P}$ = 4.0 Hz, C_5H_4, ma), 60.3 (d, $J_{C,P}$ = 3.7 Hz, C_5H_4, mi), 62.7 (C_5H_4, mi), 62.8 (C_5H_4, mi), 62.82 (C_5H_4, ma), 62.84 (C_5H_4, ma), 64.1 (d, $J_{C,P}$ = 15.1 Hz, C_5H_3, mi), 64.2 (d, $J_{C,P}$ = 13.8 Hz, C_5H_3, ma), 66.5 (d, $J_{C,P}$ = 15.6 Hz, C_5H_3, mi), 67.0 (d, $J_{C,P}$ = 11.6 Hz, C_5H_3, ma), 69.47 (C_5H_5, ma), 69.52 (C_5H_5, mi), 70.27 (C_5H_5, mi), 70.29 (C_5H_5, ma), 115.3 (CH, ma), 115.4 (CH, mi), 116.6 (d, $^2J_{C,P}$ = 7.5 Hz, C_{C5H4}−O, ma), 119.6 (CH, ma), 119.7 (CH, mi), 121.8 (CH, ma), 122.1 (CH, mi), 126.15 (d, $^2J_{C,P}$ = 7.2 Hz, C_{C5H3}−O, ma), 126.22 (CH, ma), 126.4 (CH, mi), 129.4 (d, $^3J_{C,P}$ = 12.6 Hz, 4a/ab, ma), 140.7 (d, $^2J_{C,P}$ = 5.6 Hz, 8a/9a, ma), 141.0 (d, $^2J_{C,P}$ = 5.5 Hz, 8a/9a, ma). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 17.0 (ma), 19.3 (mi). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{33}H_{28}Fe_2NO_3P$ 629.0501; found 629.0510.

*O,O′-Diferrocenyl (1H-indol-2-yl)phosphonate (**53**) (**A**).* Compound **47** (100 mg, 0.177 mmol), diisopropylamine (0.15 mL, 1.06 mmol), BuLi (0.43 mL, 1.08 mmol), and dimethyl sulfate (0.10 mL, 1.06 mmol) were reacted at −40 °C for 3 h according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 22 cm) using a 95:5 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **53** was obtained in a mixture with compound **50** of ratio 1:0.78 (**53**/B). Yield: 31 mg (0.055 mmol, 31% based on **47**). ^1H NMR ($CDCl_3$, δ): 3.86−3.87 (m, 4 H, C_5H_4), 4.21 (s, 10 H, C_5H_5), 4.36−4.38 (m, 2 H, C_5H_4), 4.38−4.40 (m, 2 H, C_5H_4), 7.16−7.18 (m, 1 H, H3), 7.33 (ddt, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 7.0 Hz, $J_{H,H}$ = 1.0 Hz, 1 H, H5/H6), 7.46 (dd, $^3J_{H,H}$ = 8.4 Hz, $J_{H,H}$ = 1.1 Hz, 1 H, H7), 7.57−7.60 (m, 1 H, H5/H6), 7.70 (dd, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 1.1 Hz, 1 H, H4), 9.01 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.9−60.1 (m, C_5H_4), 62.9 (d, $J_{C,P}$ = 4.5 Hz, C_5H_4), 69.6 (C_5H_5), 112.1 (d, $^4J_{C,P}$ = 1.9 Hz, C7), 113.7 (d, $^2J_{C,P}$ = 17.5 Hz, C3), 117.2 (d, $^2J_{C,P}$ = 4.9 Hz, C_{C5H4}−O), 120.8 (C5/6), 122.1 (C4), 122.0 (d, $^1J_{C,P}$ = 227.4 Hz, C_{C2}−P), 125.1 (C5/6), 127.5 (d, $^3J_{C,P}$ = 16.5 Hz, C3a), 138.2 (d, $^3J_{C,P}$ = 13.0 Hz, C7a). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 4.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{24}Fe_2NO_3P$ + H 566.0266; found 566.0295.

*Crystal Data for **53**:* $C_{28}H_{24}Fe_2NO_3P \times CHCl_3$, M = 684.52 g mol^{-1}, crystal dimensions 0.40 × 0.20 × 0.02 mm, monoclinic, $P21/n$, λ = 0.71073 Å, a = 14.5249(6) Å, b = 10.2459(5) Å, c = 19.6024(8) Å, β = 107.309(4)°, V = 2785.1(2) Å^3, Z = 4, ρ_{calcd} = 1.632 Mg m^{-3}, μ = 1.420 mm^{-1}, T = 115.00(10) K, θ range 2.991−24.998°, 17 335 reflections collected, 4887 independent reflections (R_{int} = 0.0506), R_1 = 0.0468, wR_2 = 0.1069 ($I > 2\sigma(I)$).

*Ferrocenyl-1H-indol-2-yl-(2-methoxyferrocenyl)phosphinate (**54**).* Compound **47** (100 mg, 0.177 mmol), diisopropylamine (0.15 mL, 1.06 mmol), BuLi (0.43 mL, 1.08 mmol), and dimethyl sulfate (0.10 mL, 1.06 mmol) were reacted at 0 °C for 4 h according to the general procedure described above. Purification was realized by column chromatography (silica, column size 2.5 × 12 cm) using a 85:15 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **54** was obtained as a mixture of both diastereomers in a ratio of 1:0.098 (de = 0.82). Yield: 69 mg (0.119 mmol, 67% based on **47**). Anal. Calcd for $C_{29}H_{26}Fe_2NO_3P$ (579.19 g/mol): C, 60.14; H, 4.52; N, 2.42. Found: C. 59.61; H, 4.30; N, 2.60. Mp: ∼25 °C. ^1H NMR ($CDCl_3$, δ): 3.73−3.75 (m, 2 H, C_5H_4), 3.82 (s, 3 H, OCH_3), 3.89 (s, 0.3 H, OCH_3, mi), 3.98 (s, 5 H, C_5H_5), 4.14−4.16 (m, 6 H, C_5H_5, C_5H_3), 4.18−4.20 (m, 1 H, C_5H_4), 4.23 (s, 0.5 H, C_5H_5, mi), 4.24−4.26 (m, 1 H, C_5H_4), 4.32 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 4.43 (s, 0.5 H, C_5H_5, minor), 4.57 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 7.17 (ddd, $^3J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 7.0 Hz, $J_{H,H}$ = 0.9 Hz, 1 H, H5/6), 7.32 (ddt, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 7.1 Hz, $J_{H,H}$ = 0.8 Hz, 1 H, H5/6), 7.36 (ddd, $^3J_{H,P}$ = 4.3 Hz, $J_{H,H}$ = 1.9 Hz, $J_{H,H}$ = 0.8 Hz, 1 H, H3), 7.50 (dd, $^3J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 0.7 Hz, 1 H, H7), 7.75 (dd, $^3J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 0.5 Hz, 1 H, H4),

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9.59 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 56.4 (d, $J_{C,P}$ = 9.7 Hz, C_5H_3), 58.5 (OCH_3), 59.9 (d, $^1J_{C,P}$ = 167.6 Hz, C_{C5H3}–P), 60.03 (C_5H_4), 60.06 (C_5H_4), 60.08 (C_5H_4), 60.12 (C_5H_4), 62.56 (C_5H_4), 62.57 (C_5H_4), 64.4 (d, $J_{C,P}$ = 12.1 Hz, C_5H_3), 67.8 (d, $J_{C,P}$ = 11.1 Hz, C_5H_3), 69.5 (C_5H_5), 70.1 (C_5H_5), 111.7 (d, $^4J_{C,P}$ = 1.5 Hz, C7), 112.4 (d, $^2J_{C,P}$ = 16.1 Hz, C3), 117.3 (d, $^2J_{C,P}$ = 6.6 Hz, C_{C5H4}–O), 120.5 (C5/6), 122.3 (C4), 124.6 (C5/6), 127.0 (d, $^2J_{C,P}$ = 10.2 Hz, C_{C5H3}–O), 127.3 (d, $^3J_{C,P}$ = 10.2 Hz, C3a), 128.9 (d, $^1J_{C,P}$ = 172.2 Hz, C_{C2}–P), 137.9 (d, $^3J_{C,P}$ = 11.0 Hz, C7a). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 25.3 (minor), 25.9 (major). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{29}H_{26}Fe_2NO_3P$ 579.0344; found 579.0370.

Synthesis of Chloro Phosphates: General Procedure. The respective alcohols were dissolved in 10 mL of tetrahydrofuran followed by the addition of an equal volume of diethyl ether. The mixture was cooled to −30 °C, and BuLi (2 equiv) was added dropwise, resulting in the formation of a colorless precipitate. After the mixture was stirred for an additional 10 min at −30 °C, $POCl_3$ (1 equiv) was slowly added and the solution was warmed to ambient temperature and stirred overnight. All volatiles were removed under reduced pressure. The resulting residue was suspended in diethyl ether and filtered through a plug of Celite (minimum 5 cm) with diethyl ether to remove the lithium salt. After removal of all volatiles, the respective chlorophosphates **2a**–**o** were obtained as colorless oils or solids and were used without further purification, as long as solely one signal in the $^{31}P\{^1H\}$ NMR was present.

*Dichloro(pyridine-3-yl)phosphate (**2f**).* 3-Hydroxypyridine (2.50 g, 26.3 mmol), BuLi (10.5 mL, 26.3 mmol), and $POCl_3$ (**2a**, 7,2 mL, 78.86 mmol) were reacted in tetrahydrofuran according to the general procedure, described above. The title compound was obtained as a colorless solid. Yield: 3.12 g (14.7 mmol, 56% based on 3-hydroxypyridine). ^1H NMR ($CDCl_3$, δ): 7.43–7.50 (m, 1 H), 7.72–7.78 (m, 1 H), 8.61–8.72 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 127.8, 135.4 (d, $^3J_{C,P}$ = 5.0 Hz), 136.6 (d, $^3J_{C,P}$ = 7.1 Hz), 141.9, 147.9 (d,, $^2J_{C,P}$ = 10.2 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 4.5.

*(11bR)-4-Chlorodinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepine 4-oxide (**2g**).* 1,1′-(*R*)-Binaphthol (2.00 g, 7.0 mmol), BuLi (2.8 mL, 6.25 mmol), and $POCl_3$ (1.9 mL, 20.7 mmol) were reacted in diethyl ether according to the general procedure, described above. The title compound was obtained as a colorless solid. The spectroscopic data are in agreement with those reported in literature.[82] Yield: 1.68 g (4.6 mmol, 65% based on 1,1-(*R*)-binaphthol). ^1H NMR ($CDCl_3$, δ): 7.04–7.07 (m, 2 H), 7.13–7.30 (m, 4 H), 7.39–7.52 (m, 2 H), 7.77–7.78 (m, 1 H), 7.84–7.89 (m, 2 H), 7.94–7.98 (m, 1 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 10.9.

*Dichloro(1H-pyrrol-1-yl)phosphonate (**2m**).* In a Schlenk tube, 1*H*-pyrrole (1 mL, 14.46 mmol) and 30 mL of diethyl ether were cooled to −30 °C. To the solution BuLi (5.8 mL, 14.5 mmol) was dropwise added. In a second Schlenk tube, a solution of 50 mL diethyl ether and $POCl_3$ (**2a**, 5 mL, 54.8 mmol) was cooled to −80 °C. The mixture containing lithiated pyrrole was cooled to −80 °C and was very slowly added to the $POCl_3$ solution by using a transfer cannula. The workup procedure is similar to the general procedure, described above. The title compound was obtained as a colorless oil. Yield: 968 mg (1.88 mmol, 13% based on pyrrole). ^1H NMR ($CDCl_3$, δ): 6.47 (dt, $^4J_{H,P}$ = 5.2 Hz, $J_{H,H}$ = 2.2 Hz, 2 H, H3,4), 7.18 (dt, $^3J_{H,P}$ = 3.4 Hz, $J_{H,H}$ = 2.2 Hz, 2 H, H2,5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 115.1 (d, $^3J_{C,P}$ = 13.2 Hz, C3,4), 122.4 (d, $^2J_{C,P}$ = 7.0 Hz, C2,5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 5.5.

*Dichloro(1H-indol-1-yl)phosphonate (**2n**).* 1*H*-Indole (1.70 g, 14.5 mmol), BuLi (5.8 mL, 14.5 mmol), and $POCl_3$ (4 mL, 43.83 mmol) were reacted according to the general procedure described above. The title compound **2n** was obtained as a colorless oil. The spectroscopic data are in agreement with those reported in literature. ^1H NMR ($CDCl_3$, δ): 6.80 (dd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{H,P}$ = 3.5 Hz, 1 H, H3), 7.35 (td, $^3J_{H,H}$ = 7.3 Hz, $^4J_{H,H}$ = 0.8 Hz, 1 H, H5/6), 7.40 (td, $^3J_{H,H}$ = 7.3 Hz, $^4J_{H,H}$ = 0.8 Hz, 1 H, H5/6), 7.49 (dd, $^3J_{H,H}$ = 3.5 Hz, $^3J_{H,P}$ = 3.5 Hz, 1 H, H2), 7.65–7.66 (m, 1 H, C4/8), 7.93 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, C4/8). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 2.7.

*(9H-Carbazol-9-yl) dichlorophosphonate (**2o**).* 9*H*-Carbazole (2.393 g, 14.31 mmol), BuLi (5.8 mL, 14.5 mmol), and $POCl_3$ (4 mL, 43.83 mmol) were reacted according to the general procedure described above. The title compound **2o** was obtained as a colorless oil. Yield: 2.35 g (8.27 mmol, 58% based on carbazole). ^1H NMR ($CDCl_3$, δ): 7.45 (td, $^3J_{H,H}$ = 8.0 Hz, $J_{H,P}$ = 0.8 Hz, 2 H), 7.53 (dd, $^3J_{H,H}$ = 8.5 Hz, $J_{H,H}$ = 7.4 Hz, $J_{H,P}$ = 1.3 Hz, 2 H), 8.03–8.05 (m, 2 H), 8.16 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 0.5.

Crystallographic data of **4**, **6**, **9**, **10**, **13**, **16a**, **22b**, **24**, **26b**, **27a**, **28b**, **31**, **34**, **40**, **47**, **48**, and **51**–**53** are also available from the Cambridge Crystallographic Database as file numbers: CCDC 1474110 (**4**), 1508129 (**6**), 1474107 (**9**), 1474108 (**10**), 1474109 (**13**), 1474111 (**16a**), 1474112 (**22b**), 1508130 (**24**), 1508131 (**26b**), 1508132 (**27a**), 1508133 (**28a**·$CHCl_3$), 1508134 (**31**), 1508135 (**34**), 1508136 (**40**), 1525260 (**41**), 1508137 (**47**), 1508138 (**48**), 1508139 (**51**·0.9 CH_2Cl_2), 1508140 (**52**), 1508141 (**53**·$CHCl_3$).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00030.

X-ray data for **4**, **6**, **9**, **10**, **13**, **16a**, **22b**, **24**, **26b**, **27a**, **28b**, **31**, **34**, **40**, **47**, **48**, and **51**–**53** (CIF)

Additional details, Tables S1–S7, and Figures S1–S33 (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Gottfried Huttner on the occasion of his 80th birthday.

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