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Synthesis, Electrochemistry, Spectroelectrochemistry, and Solid-State Structures of Palladium Biferrocenylphosphines and Their Use in C,C Cross-Coupling Reactions

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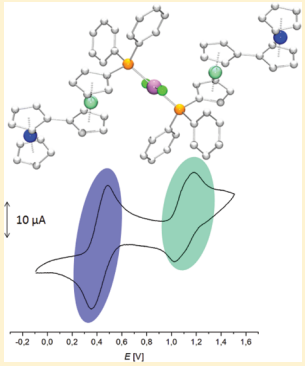
Supporting Information

ABSTRACT: The series of biferrocenyl-functionalized phosphines Bfc(PR_2)/Bfc(Se═PR_2) (R = C_6H_5 (**6**/**14**), C_6H_4-2-CH_3 (**7**/**15**), $^cC_4H_3O$ (**8**/**16**), $^cC_6H_{11}$ (**9**/**17**); Bfc = 1′-biferrocenyl, Fe(η^5-C_5H_5)(η^5-C_5H_4)Fe(η^5-C_5H_4)$_2$) and biferrocenyl diphosphines bfc(PR_2)$_2$/bfc(Se═PR_2)$_2$ (R = C_6H_5 (**10**/**18**), C_6H_4-2-CH_3 (**11**/**19**), $^cC_4H_3O$ (**12**/**20**), $^cC_6H_{11}$ (**13**/**21**); bfc = 1′,1‴-biferrocenyl, (Fe(η^5-C_5H_4)$_2$)$_2$) have been prepared by consecutive synthesis methodologies. The reaction of **6**−**9** with [Pd(Et_2S)$_2Cl_2$] (**22**) gave the appropriate palladium dichloride complexes *trans*-[Pd(Bfc(PR_2))$_2Cl_2$] (R = C_6H_5 (**23**), C_6H_4-2-CH_3 (**24**), $^cC_4H_3O$ (**25**), $^cC_6H_{11}$ (**26**)). The structures of **15**, **16**, **21**, **23**, and **25** in the solid state were determined by single-crystal X-ray diffraction studies, showing that the structural parameters of these molecules correspond to those of related seleno phosphines and phosphino palladium dichloride complexes. Additionally, all complexes were characterized by cyclic voltammetry using [^{n}Bu$_4$N][PF_6] and [^{n}Bu$_4$N][B(C_6F_5)$_4$] as supporting electrolytes. Phosphines **6**−**9** and seleno phosphines **14**−**17** show mostly irreversible redox processes involving the phosphorus and the selenium atom, both being able to form radicals leading to dimerization and other follow-up reactions. In contrast, palladium complexes **23**−**26** show in both electrolyte solutions a reversible behavior, although the iron centers were oxidized at more positive potentials in comparison to free Bfc or bfc phosphines. UV/vis/near-IR spectroelectrochemical measurements were carried out with **25** and **26**. At potentials between 300 and 700 mV IVCT bands typical for [Bfc]$^+$ are observed, reflecting intermetallic communication between the two ferrocene moieties within the biferrocenyl phosphine units, two of which are present. No further bands were found, indicating that no electronic communication between the biferrocenyl moieties along the P−Pd−P unit exists in the mixed-valent species. The palladium complexes are suitable catalysts in the Suzuki reaction of 2-bromotoluene (**27**) or 4′-chloroacetophenone (**28**) with phenylboronic acid (**29**). They can also be applied in the Heck C,C cross-coupling of iodobenzene (**32**) with *tert*-butyl acrylate (**33**). Depending on the steric (estimated by the Tolman cone angle) and electronic properties (estimated by $^1J_{^{31}P^{77}Se}$) of the phosphine ligands, the activity of the corresponding palladium complexes can be predicted. It was found that bulky and electron-rich cyclohexyl- and *o*-tolyl-containing complexes are the most active catalysts in the appropriate Suzuki and Heck reactions.



INTRODUCTION

Palladium-catalyzed C,C cross-coupling reactions, including the Suzuki[1−8] and Heck[1−4,8−11] reactions, are essential transformations in organic and organometallic chemistry. They give access to functionalized biaryls and aryl-substituted alkenes.[12] Therefore, the development of new ligands which effect high conversions at low catalyst loadings under mild reaction conditions have accelerated during the last years. Hitherto, N-heterocyclic carbenes and palladacycles were successfully applied in the synthesis of efficient catalysts.[1−4,13−28] Especially electron-rich and/or bulky palladium-based catalysts, including mono- and bidentate ferrocenyl phosphines, are of great interest, due to the exceptional properties of ferrocene as an electron-rich, stable, and structurally easily modifiable molecule.[28−44] Although palladium complexes with metallocenyl-containing mono- and diphosphine ligands have been well investigated in C,C or C,N bond-forming reactions,[6,34,45−57] less is known about the use of biferrocene derivatives.[58−68] Van Leeuwen and Widhalm applied, for example, enantiopure phosphorus-chiral 2,2′-bis(diarylphosphino)-1,1′-biferrocenyls in palladium-promoted allylic substitution reactions.[58,69,70] 2,2″-Phosphino-substituted biferrocenes were investigated by Weissensteiner in asymmetric hydrogenations.[59] Furthermore, different trans-chelating 2,2″-bis[1-(diphenylphosphino)alkyl]-1,1′-biferrocenes (TRAPs) were used in a wide range of enantioselective catalysis by Ito, Sawamura, and Kuwano.[60−63,65,66]

Catalytic reactions are often affected by relatively small changes in the electronic and/or spatial structure (i.e., Tolman cone angle) of the appropriate palladium-complexed sandwich compounds.[34,71] Since the early work of Allen and Taylor, the existence of a relation between the $^1J_{^{31}P^{77}Se}$ coupling constant and the electronic

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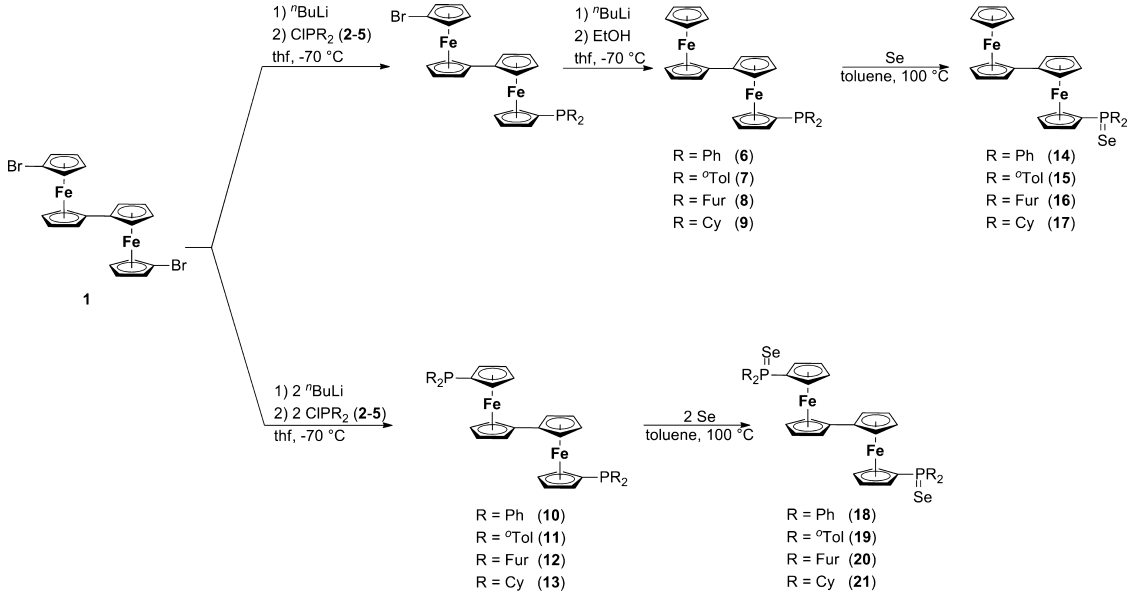
Scheme 1. Synthesis of Mono- and Diphosphanyl Biferrocenes Bfc(PR_2) and bfc(PR_2)$_2$ and the Appropriate Seleno Phosphines Bfc(Se=PR_2) and bfc(Se=PR_2)$_2$, Respectively



properties of phosphines has been well established.[72−77] An increase of $^1J_{^{31}P^{77}Se}$ of the appropriate seleno phosphine corresponds to an increase in the s character of the phosphorus lone-pair orbital, resulting in a decrease of basicity. This allows in a straightforward way the prediction and design of specific, catalytically active transition-metal complexes for homogeneous catalysis.[38,39,44,78,79]

We herein report the synthesis, electrochemistry, structure, and bonding of a series of novel monosubstituted biferrocenylphosphines and their use in selected palladium-promoted C,C cross-coupling reactions.

RESULTS AND DISCUSSION

1. Synthesis and Characterization of Metallocenyl Phosphines (6−13), Phosphine Selenides (14−21), and Palladium Complexes (23−26). The mono- and diphosphanyl biferrocenes Bfc(PR_2) (R = C_6H_5 (**6**), C_6H_4-2-CH_3 (**7**), 2-$^cC_4H_3O$ (**8**), $^cC_6H_{11}$ (**9**); Bfc = 1′-biferrocenyl, Fe($\eta^5C_5H_5$)($\eta^5C_5H_4$)Fe($\eta^5C_5H_4$)$_2$) and bfc(PR_2)$_2$ (R = C_6H_5 (**10**),[80] C_6H_4-2-CH_3 (**11**), $^cC_4H_3O$ (**12**), $^cC_6H_{11}$ (**13**); bfc =1′,1‴-biferrocenyl, (Fe($\eta^5C_5H_4$)$_2$)$_2$) were accessible by consecutive reaction methodologies, as shown in Scheme 1. Treatment of $bfcBr_2$ (**1**)[81] with 1 equiv of ^{n}BuLi in tetrahydrofuran at low temperature followed by an addition of the appropriate chlorophosphine R_2PCl (R = C_6H_5 (**2**), C_6H_4-2-CH_3 (**3**), $^cC_4H_3O$ (**4**), $^cC_6H_{11}$ (**5**)) produced a mixture of Bfc(PR_2) and bfc(PR_2)(Br) compounds. Repeating column chromatography allowed in a time-consuming procedure the separation of the appropriate products from the reaction mixture. For this reason, we developed a consecutive synthesis strategy for the preparation of the monophosphine biferrocenyls **6**−**9** (Scheme 1). This methodology implies the use of an exact ratio of Bfc(PR_2) and bfc(PR_2)(Br) (1:3, respectively). To this mixture was added a slight excess of ^{n}BuLi and EtOH (Experimental Section) to solely give **6**−**9**. After appropriate workup, these orange solid materials could be obtained in moderate yields (40−60%) (Experimental Section). Attempts to obtain higher quantities of monolithiated **1** by lowering the temperature or using solvent mixtures or longer reaction times did not result in significantly higher yields. Monometalation of biferrocene (BfcH) at various temperatures by addition of 1 equiv of ^{n}BuLi or ^{t}BuLi always gave next to the appropriate monometalated species multilithiated products.

In contrast, the symmetric biferrocenes bfc(PR_2)$_2$ (**10**−**13**) are formed in much higher quantities (67−80%) by applying the reaction conditions described above but changing the stoichiometry to 1:2 (Scheme 1). They were even more efficiently accessible when diiodobiferrocene ($bfcI_2$)[82,83] was used as starting material.

The orange biferrocenes **10**−**13** are less soluble than Bfc(PR_2) (**6**−**9**). All molecules Bfc(PR_2) and bfc(PR_2)$_2$ (**6**−**13**) are stable toward air in the solid state and dissolve in common solvents such as dichloromethane. However, solutions containing these molecules oxidize easily to the corresponding phosphino oxides.

To first obtain information on the donor ability of the phosphorus atom in **6**−**13** toward transition-metal fragments, these molecules were converted into the appropriate seleno phosphines Bfc(Se=PR_2) (R = C_6H_5 (**14**), C_6H_4-2-CH_3 (**15**), 2-$^cC_4H_3O$ (**16**), $^cC_6H_{11}$ (**17**)) and bfc(Se=PR_2)$_2$ (R = C_6H_5 (**18**), C_6H_4-2-CH_3 (**19**), 2-$^cC_4H_3O$ (**20**), $^cC_6H_{11}$ (**21**)) on oxidation with selenium in its elemental form in toluene at 100 °C (Scheme 1). Seleno phosphines **14**−**21** could be isolated in almost quantitative yield as orange solids (Experimental Section).

Complexation of phosphines **6**−**9** to palladium dichloride was carried out by reacting them with [Pd(Et_2S)$_2Cl_2$] (**22**) in a molar ratio of 2:1 at ambient temperature in dichloromethane. Thus formed *trans*-[Pd(Bfc(PR_2))$_2Cl_2$] (R = C_6H_5 (**23**), C_6H_4-2-CH_3 (**24**), $^cC_4H_3O$ (**25**), $^cC_6H_{11}$ (**26**)) could be isolated in excellent yield (Experimental Section) (eq 1). As expected, seleno phosphines **14**−**21** and palladium complexes **23**−**26** are stable toward air and moisture both in the solid state and in solution.

The identity of all new compounds was confirmed by elemental analysis, IR and NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}), and ESI TOF mass spectrometry (Experimental Section). Additionally, the electrochemical behavior of these molecules was determined by cyclic voltammetric measurements. Moreover, the spectroelectrochemical behavior of **25** and **26** was determined using UV/vis/near-IR spectroscopy. The molecular structures of **15**, **16**, **21**, **23**, and **25** in the solid state were determined by single-crystal X-ray structure analysis. Suitable crystals for X-ray diffraction were

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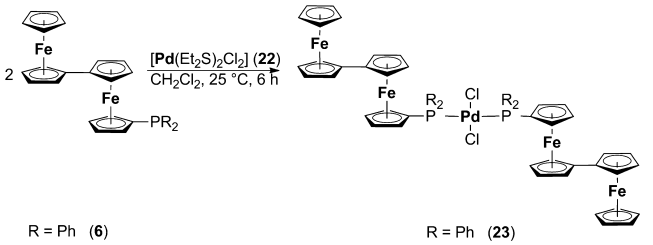

(1)

obtained by slow diffusion of *n*-hexane into a concentrated dichloromethane solution containing **15**, **16**, **21**, **23**, or **25** at ambient temperature. ORTEP diagrams are shown in Figure 1 (**15**, **16**), Figure 2 (**21**), and Figure 3 (**23**, **25**). Selected bond distances (Å) and angles (deg) are given in Tables 1 and 2. The crystal and structure refinement data are summarized in Table S1 (Supporting Information).

Compounds **15** and **16** crystallize in the monoclinic space group $P2_1$ (**15**) or $P2_1/c$ (**16**), whereas **21**, **23**, and **25** crystallize in the triclinic space group $P\bar{1}$. The asymmetric units of **21** and **23** contain half of the molecule with crystallographic C_i symmetry about the center of the fulvalenide connectivity (**21**) or at the palladium atom (**23**). The asymmetric unit of **25** contains 1.5 crystallographic independent molecules (for clarity, Figure 3 shows only one molecule of **25**).

In all compounds the biferrocenyl moieties show a trans configuration; both iron atoms are oriented opposite to each other with respect to the fulvalenide plane. The two C_5H_4 rings of this array are almost coplanar, with interplanar angles of 0.9 (**15**), 10.4 (**16**), 0.0 (**21**), 7.5 (**23**), 14.7 (with Fe1, Fe2), 5.6 (with Fe3, Fe4), and 7.6° (with Fe5, Fe6) (**25**). The cyclopentadienyl rings of individual ferrocenyl building blocks are rotated by 10.4 (Fe1), 20.3 (Fe2) (**15**), 4.8 (Fe1), 3.4 (Fe2) (**16**), 7.6 (**21**), 0.2 (Fe1), 6.3 (Fe2) (**23**), 0.2 (Fe1), 14.9 (Fe2), 12.4 (Fe3), 1.9 (Fe4), 8.2 (Fe5), and 2.4° (Fe6) (**25**), revealing a conformation between fully eclipsed (0°) and staggered (36°). The phosphino substituents and the biferrocenyl units are rotated by 91.3 (**15**), 145.7 (**16**), 153.2 (**21**), 134.9 (**23**), 143.7 (with Fe1, Fe2), 129.9 (with Fe3, Fe4) and 133.7° (with Fe5, Fe6) (**25**) with respect to each other. The coordination geometry of the trans palladium complexes is square planar with an rms deviation of 0.0265 Å (Pd1) (**25**). Due to C_i symmetry no deviation from planarity for **25** (Pd2) and **23** with P−Pd−Cl bond angles between 86.6 and 92.3° is observed.

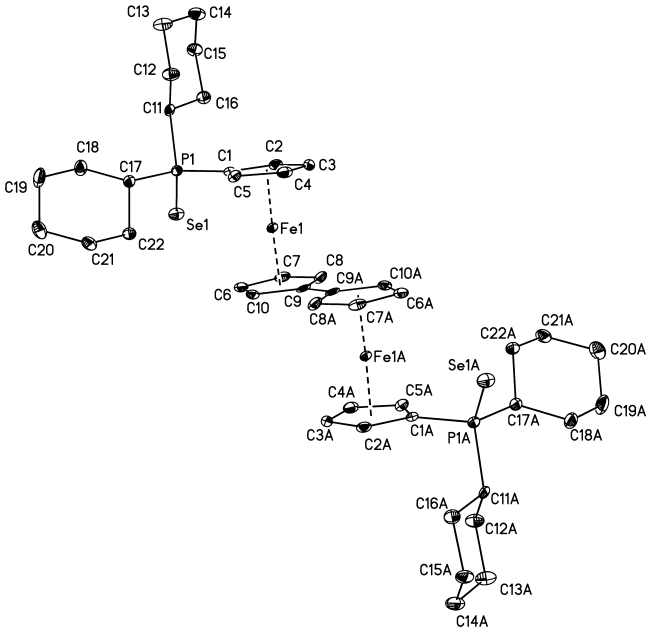

Figure 2. ORTEP diagram (thermal ellipsoids are at the 50% probability level) of the molecular structure of **21** along with the numbering scheme. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x + 1$, $-y$, $-z + 1$ (center of inversion C9−C9A).

The analytical data are consistent with the formation of symmetrically and unsymmetrically substituted biferrocenes.[80,83−85] While IR spectra of the molecules $Bfc(PR_2)/bfc(PR_2)_2$, $Bfc(Se{=}PR_2)/bfc(Se{=}PR_2)_2$, and *trans*-$[Pd(Bfc(PR_2))_2Cl_2]$ are not very distinctive, the ^{1}H NMR spectra of monophosphine

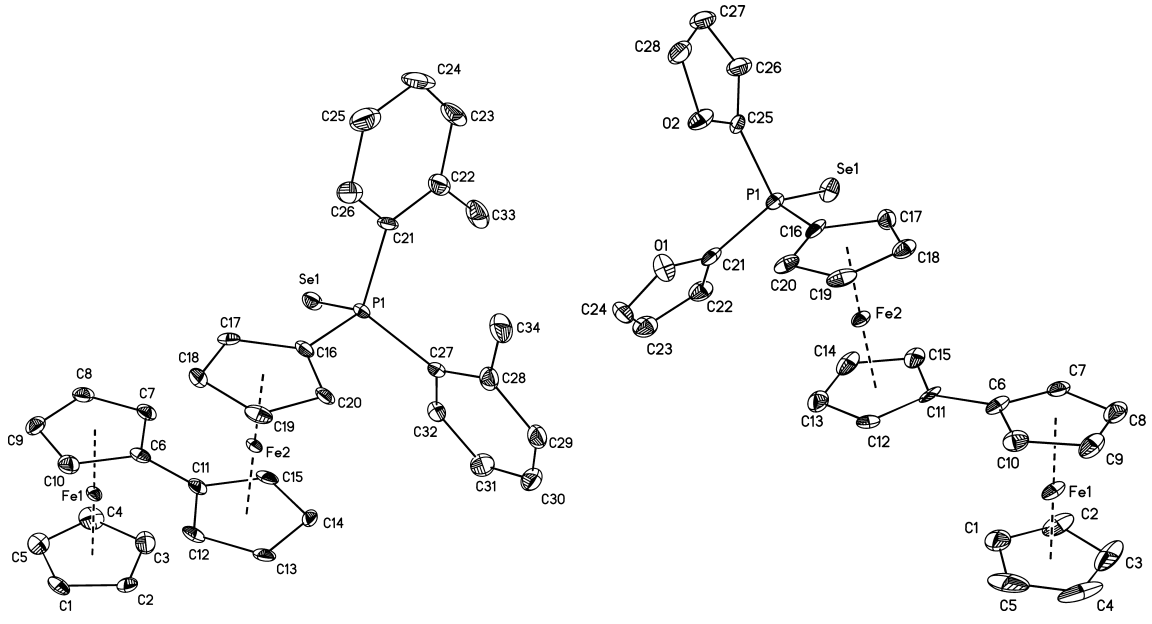

Figure 1. ORTEP diagrams (thermal ellipsoids are at the 50% probability level) of the molecular structures of **15** (left) and **16** (right) along with the numbering scheme. Hydrogen atoms are omitted for clarity.

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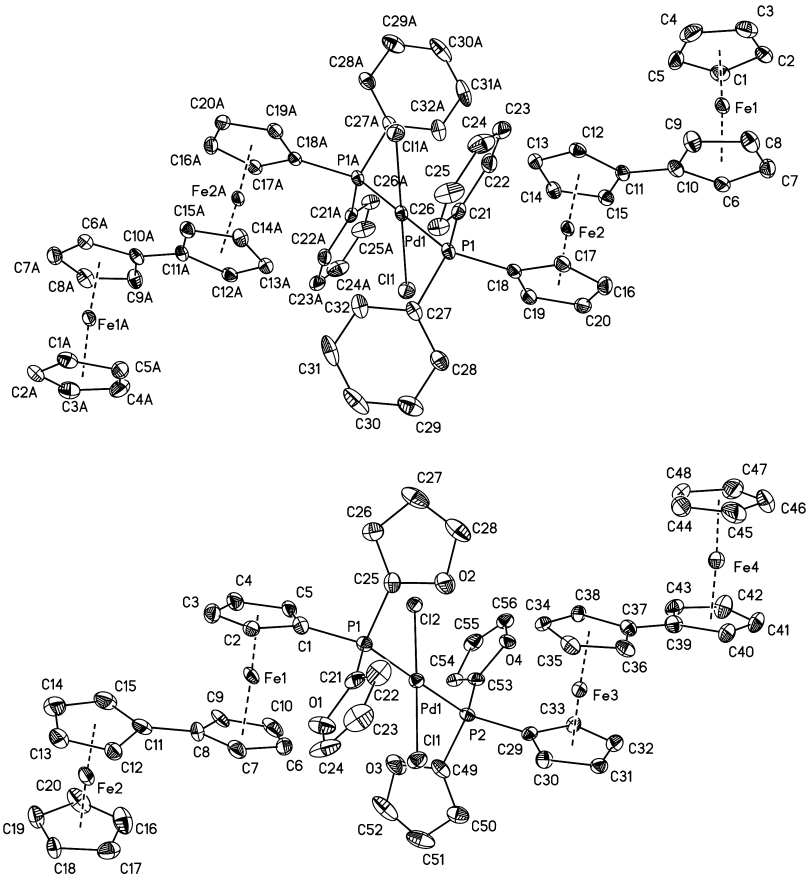

Figure 3. ORTEP diagrams (thermal ellipsoids are at the 50% probability level) of the molecular structures of **23** (top) and **25** (bottom) along with the numbering scheme. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x + 2, -y + 2, -z + 1$ (center of inversion Pd1 (**23**)).

Table 1. Selected Bond Distances (Å) and Angles (deg) of 15, 16, and 21

		Bond Distances			
		Compound **15**[a]			
P1–Se1	2.1204(13)	C16–P1	1.811(5)	C21–P1	1.831(5)
C27–P1	1.830 (5)	C6–C11	1.463(7)	Fe1–D1	1.6548(1)
Fe1–D2	1.6484(1)	Fe2–D3	1.6504(1)	Fe2–D4	1.6434(1)
		Compound **16**[a]			
P1–Se1	2.0864(11)	C16–P1	1.780(4)	C21–P1	1.791(4)
C25–P1	1.810(4)	C6–C11	1.459(5)	Fe1–D1	1.6593
Fe1–D2	1.6409	Fe2–D3	1.6465	Fe2–D4	1.6406
		Compound **21**[b]			
P1–Se1	2.1166(6)	C1–P1	1.801(2)	P1–C17	1.841(2)
C11–P1	1.842(2)	C9–C9A	1.444(4)	Fe1–D1	1.6506(3)
Fe1–D2	1.6450(3)				
		Bond Angles			
		Compound **15**			
C16–P1–C21	104.6(2)	C16–P1–C27	103.6(2)	C21–P1–C27	110.7(2)
Se1–P1–C16	112.59(16)	Se1–P1–C21	110.66(16)	Se1–P1–C27	114.20(18)
		Compound **16**			
C16–P1–C21	106.41(19)	C16–P1–C25	103.72(17)	C21–P1–C25	106.92(18)
Se1–P1–C16	117.24(15)	Se1–P1–C21	111.24(14)	Se1–P1–C25	110.60(14)
		Compound **21**			
C1–P1–C11	104.87(10)	C1–P1–C17	102.97(10)	C11–P1–C17	105.12(10)
Se1–P1–C1	116.62(7)	Se1–P1–C11	111.18(7)	Se1–P1–C17	114.91(8)

[a]D denotes the centroids of C_5H_4 (D2, D3, D4) and the centroids of C_5H_5 (D1). [b]D denotes the centroids of C_5H_4 (D1, D2).

derivatives Bfc(PR_2), Bfc(Se═PR_2), and *trans*-[Pd(Bfc-(PR_2))$_2$$Cl_2$] show multiple resonances due to their unsymmetrical structure. In the ^{1}H NMR spectra of complexes **23**–**26** a total of seven signals were observed, one of which appears as a singlet for

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Table 2. Selected Bond Distances (Å) and Angles (deg) of 23 and 25

Bond Distances					
Compound 23[a]					
P1−Pd1	2.3366(7)	C18−P1	1.800(2)	C21−P1	1.819(2)
C27−P1	1.820(2)	C10−C11	1.463(3)	Pd−Cl1	2.3035(6)
Fe1−D1	1.6547(4)	Fe1−D2	1.6470(4)	Fe2−D3	1.6554(4)
Fe2−D4	1.6487(3)				
Compound 25[a]					
P1−Pd1	2.309(2)	C1−P1	1.787(8)	C21−P1	1.800(8)
C25−P1	1.791(8)	C8−C11	1.467(11)	Pd−Cl1	2.295(2)
Fe1−D1	1.6357(11)	Fe1−D2	1.6447(11)	Fe2−D3	1.656(1)
Fe2−D4	1.647(1)				
Bond Angles					
Compound 23					
Cl1−Pd−Cl1A	180.000(1)	P1−Pd1−P1A	180.000(1)	P1−Pd1−Cl1	86.59(2)
P1−Pd1−Cl1A	93.41(2)	Pd1−P1−C18	115.70(8)	Pd1−P1−C21	117.36(8)
Pd1−P1−C27	110.23(8)				
Compound 25					
Cl1−Pd−Cl2	178.52(8)	P1−Pd1−P2	178.13(8)	P1−Pd1−Cl1	92.28(7)
P1−Pd1−Cl2	88.05(7)	Pd1−P1−C1	116.5(3)	Pd1−P1−C21	117.4(3)
Pd1−P1−C25	111.1(3)	P2−Pd1−Cl1	87.18(7)	P2−Pd1−Cl2	92.53(7)
Pd1−P2−C29	116.9(3)	Pd1−P2−C53	116.9(3)	Pd1−P2−C49	111.5(3)

[a]D denotes the centroids of C_5H_4 (D2, D3, D4) and denotes the centroids of C_5H_5 (D1).

the C_5H_5 unit (Figure 4, *trans*-[Pd(Bfc(PR_2))$_2Cl_2$]). The signals of the biferrocenyl unit ranging from 3.85 to 4.35 ppm (Bfc(PR_2)),

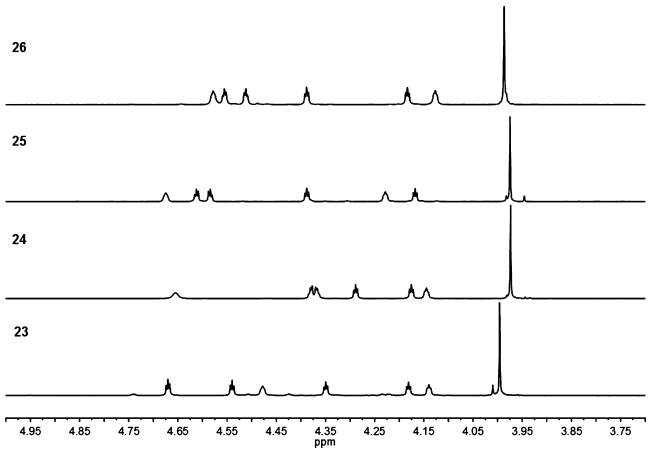

Figure 4. Part of the ^{1}H NMR spectra (in $CDCl_3$, 298 K) of complexes *trans*-[Pd(Bfc(PR_2))$_2Cl_2$] (**23**−**26**).

3.9 to 4.55 ppm (Bfc(Se═PR_2)), and 3.95 to 4.7 ppm ([Pd(Bfc(PR_2))$_2Cl_2$]) show a shift to lower field, due to electron-withdrawing P(V) species (**14**−**21**) or due to coordination of the phosphorus atom to palladium (**23**−**26**). For the different organic substituents bonded at the phosphorus atom, there is no direct electronic influence on the protons of the biferrocenyl core. The $^{13}C\{^1H\}$ NMR spectra of Bfc(PR_2), Bfc(Se═PR_2), and *trans*-[Pd(Bfc(PR_2))$_2Cl_2$] contain the corresponding carbon signals for the unsymmetrically substituted Bfc unit between 60 and 90 ppm.[84] Characteristic for the complexes *trans*-[Pd(Bfc(PR_2))$_2Cl_2$] are the pseudotriplet signals in the $^{13}C\{^1H\}$ NMR spectra due to P−C coupling, indicating the trans arrangement of the phosphine ligands toward each other (Experimental Section).[86−88] For all symmetrically substituted molecules bfc(PR_2)$_2$ and bfc(Se═PR_2)$_2$ four signal sets in the ^{1}H NMR spectra and six resonances in the $^{13}C\{^1H\}$ NMR spectra could be detected in the range expected (Experimental Section). Further signals were found, as is typical for the included organic groups at phosphorus (Experimental Section).[78,79,89]

In the $^{31}P\{^1H\}$ NMR spectra of phosphines Bfc(PR_2) a high-field shift is observed in the series **9** (−7 ppm) > **6** (−16 ppm) > **7** (−36 ppm) > **8** (−64 ppm), of which **9** is most shielded, indicating the strong electron-donating character of the cyclohexyl groups. The progress of the reaction of Bfc(PR_2) (**6**−**9**) with [Pd(Et_2S)$_2Cl_2$] (**22**) could be monitored by $^{31}P\{^1H\}$ NMR spectroscopy, because coordination of the phosphorus atom to palladium is accompanied by a characteristic downfield shift of the phosphorus resonance signal from −64.6 to −7.39 (**6**−**9**) to −14.2 to +18.2 ppm (**23**−**26**) (Experimental Section). Changing the oxidation state of the phosphorus atom from +III in **6**−**13** to +V in **14**−**21** induces a significant shift to lower field (50−65 ppm).

Generally the donor−acceptor character of phosphines toward selenium can be quantified by the $J_{^{31}P-^{77}Se}$ coupling constant. It was found that an increasing $^1J_{^{31}P-^{77}Se}$ coupling constant is significant for electron-withdrawing groups at the phosphorus atom, due to the increased s character of the orbital which is involved in the P−Se bonding.[72−77] A summary of the $^{31}P\{^1H\}$ NMR chemical shifts of molecules **6**−**13** and seleno phosphines **14**−**21** with $^1J_{^{31}P-^{77}Se}$ coupling constants is given in Table 3. From this table it can be seen that the electron-rich Se═P(^{c}C_6H_{11})$_2$ units appear, as expected, at low field (ca. 49 ppm), while Se═P(^{c}C_4H_3O)$_2$ species containing electron-poor furyl units resonate at higher field (ca. −5 ppm). The coupling constants decrease in the series **16**/**20** < **14**/**18** < **15**/**19** < **17**/**21**, demonstrating that the phosphine featuring a furyl ligand acts as an electron-withdrawing group and hence possesses less donor ability (Experimental Section).

Electronic and steric effects are related.[37,71] Therefore, the Tolman cone angle, which is the apex angle of a cylindrical cone centered 2.28 Å from the center of the phosphorus atom which touches the van der Waals radii of the outermost atoms,[79,90,91] is an important value and was calculated for **23** and **25**. Increasing the angle between the phosphine substituents decreases the percentage of s character in the phosphorus lone pair.[37] The Tolman cone angle was calculated from the structural data obtained by X-ray

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Table 3. Chemical Shifts and $^{1}J_{^{31}P-^{77}Se}$ Coupling Constants of Phosphines 6−13 and Corresponding Selenides 14−21 and Ferrocenyl Analogues 35−42, for Comparison

R	compd	Mc[a]	δ(P(III)), ppm	compd	δ(P(V)), ppm	$^{1}J_{^{31}P-^{77}Se}$, Hz	ref
C_6H_5	**6**	Bfc	−16.5	**14**	31.8	732	
	10	bfc	−16.09	**18**	31.7	733	80
	35	Fc	−17.7	**39**	30.8	733	89
2-CH_3-C_6H_4	**7**	Bfc	−36.8	**15**	29.5	715	
	11	bfc	−36.8	**19**	29.4	714	
	36	Fc	−36.5	**40**	29.4	717	79
2-$^{c}C_4H_3O$	**8**	Bfc	−64.6	**16**	−5.2	768	
	12	bfc	−64.7	**20**	−5.4	769	
	37	Fc	−64.4	**41**	−5.3	769	79
$^{c}C_6H_{11}$	**9**	Bfc	−7.3	**17**	49.8	700	
	13	bfc	−7.39	**21**	49.8	700	
	38	Fc	−8.4	**42**	48.8	699	89

[a]Abbreviations and conditions: Bfc = 1′-biferrocenyl, bfc = 1′,1‴-biferrocenyl, Fc = 1′-ferrocenyl; measurements at 298 K in $CDCl_3$.

structure analysis of **23** and **25** using the programm STERIC.[92−94] It was found that the biferrocenyl moiety has an remarkable influence on the size of the Tolman cone angle. The Tolman cone angle was calculated to be 190.4 (**23**) and 167.4° (**25**), indicating that the furyl groups are less sterially demanding than phenyl groups. For molecules **24** and **26** larger values are expected, due to comparison with PR_3 molecules investigated by Tolman[71] and complexes of type $[Pd((FcC{\equiv}C)PR_2)_2Cl_2]$ (R = C_6H_5, C_6H_4-2-CH_3, 2,4,6-$Me_3C_6H_2$, $^{c}C_4H_3O$, tBu, $^{c}C_6H_{11}$).[78] The obtained electronic and steric parameters allow the design of catalytically active palladium transition-metal complexes which can be used, for example, in C,C cross-coupling reactions.[38,39,44,78,79] Our results suggest that in the latter series phosphine **9** and its corresponding palladium dichloride complex **26** should be best suited for Suzuki carbon−carbon couplings, while **8** with its more electron-withdrawing character in **25** is thought to be less active. From Table 3 it can be seen that the related ferrocenyl analogues $Fc(PR_2)$ (R = C_6H_5 (**35**),[79,89] C_6H_4-2-CH_3 (**36**),[79] $^{c}C_4H_3O$ (**37**),[79] $^{c}C_6H_{11}$ (FcCy);[79,89] Fc = ferrocenyl, $(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5))$ and $Fc(Se{=}PR_2)$ (R = C_6H_5 (**39**), C_6H_4-2-CH_3 (**40**), $^{c}C_4H_3O$ (**41**), R = $^{c}C_6H_{11}$ (**42**)) show similar shifts in the $^{31}P\{^{1}H\}$ NMR spectra with almost identical $^{1}J_{^{31}P-^{77}Se}$ coupling constants.[79]

2. Electrochemistry. The redox properties of all new compounds have been studied by cyclic voltammetry (CV), square wave voltammetry (SW), and spectroelectrochemistry (UV/vis/near-IR spectroscopy) in dichloromethane solutions utilizing $[^{n}Bu_4N][PF_6]$ (0.1 M) and $[^{n}Bu_4N][B(C_6F_5)_4]$ (0.1 M), respectively, as supporting electrolyte. The cyclic voltammetric measurements were carried out at 298 K with a scan rate of 100 mV s^{-1}. All data are summarized in Tables 4−7. All potentials are referenced vs a saturated calomel electrode (SCE) with the FcH/FcH^+ redox couple (E_0 = 0.46 V) as internal calibrant.[95]

Figure 5 shows the CVs of **8** in different electrolyte solutions. In both electrolyte solutions compound **8** exhibits multiple redox events, as is characteristic for ferrocenyl phosphines.[79,80,96−103] The assignment of the redox processes to the biferrocenyl unit or to the phosphorus atom cannot be made unequivocally. A similar behavior was found for all phosphines **6**−**13** (Tables 4 and 5). In earlier studies it was stated that follow-up reactions such as dimerization and irreversible oxidations, caused by traces of water or oxygen, can occur at the phosphorus atom.[101] A mechanism for the well-known dppf derivative was recently described by the group of Pilloni.[104] The presence of the lone pair of electrons on each phosphorus atom leads to a phosphorus radical as a result of intramolecular electron transfer processes which can undergo dimerization.[98,105]

Table 4. Redox Potentials of Biferrocenyl Phosphines 6−13[a]

compd	E_{ox}, V	E_{red}, V	$E_{ox,irrev}$, V	$E_{red,irrev}$, V
		Bfc(PR_2)		
6	0.48	0.30	0.74	0.8
			1.2	0.97
7	0.49	0.33	1.26	1.09
	0.84	0.72		0.91
8	0.44	0.35	1.09	0.99
	0.85	0.74		
9	0.42	0.34	0.9	
	0.53	0.47	1.06	
		bfc(PR_2)$_2$		
10[b]	0.49		0.67	1.01
11	0.5	0.4		
	0.78	0.68		
	1.06	0.96		
	1.36	1.26		
12	0.52	0.38	0.84	
			1.17	
13	0.42			0.31
	0.83			0.13
	0.54			−0.8
	1.00			

[a]Conditions: cyclic voltammetric data for 10^{-3} M dichloromethane solutions at 298 K; $[^{n}Bu_4N][PF_6]$ (0.1 M) as supporting electrolyte; scan rate 100 mV s^{-1}; all potentials in V (ΔE_p in V) vs SCE (FcH/FcH^+ as internal standard (E_0 = 0.46 V)).[95] [b]Potentials obtained from ref 80.

Kotz and Nivert reported about a reversible one-electron-redox process for diphenylphosphino ferrocene on measurement to a maximum of 0.8 V.[103] However, irreversible oxidations occur on measurement to higher potentials (1.3 V).[103] Nevertheless, the reversibility of the Fe(II)−Fe(III) oxidation in ferrocenyl phosphines was discussed intensively and many parameters were varied (solvent, scan rate, electrolyte).[98,105−107] Actually, it is known that $[^{n}Bu_4N][PF_6]$ as supporting electrolyte favors the formation of ion pairs of the type $Fc^{+}\cdots PF_6^{-}$.[104,108−112] The negative effect of ion pairing was recently described by Geiger and co-workers.[113−115] They found that the electrolyte had a remarkable influence on the in situ oxidized phosphorus centers. By using a weak coordinating anion (=WCA) such as $[B(C_6F_5)_4]^{-}$ fewer follow-up reactions are

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Table 5. Redox Potentials of Biferrocenyl Phosphines 6−9 and Seleno Phosphines 14−17 under Modified Conditions[a]

compd	E_{ox}, V	E_{red}, V	$E_{ox,irrev}$, V	$E_{red,irrev}$, V
		Bfc(PR_2)		
6	0.45	0.32	0.91	
	0.63	0.49		
7			0.35	0.4
			0.52	0.94
8	0.56	0.47	0.39	
	1.23	1.13	0.93	
9	0.36	0.34	1.03	0.98
	0.62	0.55		
		Bfc(Se═PR_2)		
14	0.42	0.34	1.08	0.65
15	0.43	0.33	0.92	0.69
16	0.28	0.23	0.93	0.57
			0.45	
17	0.42	0.33	0.98	0.69

[a]Conditions: cyclic voltammetric data of 10^{-3} M dichloromethane solutions at 298 K; [^{n}Bu$_4$N][B(C_6F_5)$_4$] (0.1 M) as supporting electrolyte; scan rate 100 mV s^{-1}; all potentials in V (ΔE_p in V) vs SCE (FcH/FcH^+ as internal standard (E_0 = 0.46 V)).[95]

Table 6. Redox Potentials of Complexes 23−26 under Standard Conditions[a]

compd	M	$[M^{n+}]/[M^{(n+1)+}]$ E_0 (ΔE_p), V	$[Fe^{2+}]/[Fe^{3+}]$ (Bfc) E_0 (ΔE_p), V	ΔE_0, mV
23	Pd	−1.2	0.404 (0.088)	466
			0.86 (0.100)	
24	Pd	−1.18	0.413 (0.08)	457
			0.87 (0.11)	
25	Pd	−1.3	0.42 (0.116)	490
			0.91 (0.092)	
26	Pd	−0.74	0.4 (0.12)	380
			0.78 (0.12)	

[a]Conditions: cyclic voltammetric data of 10^{-3} M dichloromethane solutions at 298 K; [^{n}Bu$_4$N][PF_6] (0.1 M) as supporting electrolyte; scan rate 100 mV s^{-1}; all potentials in V (ΔE_p in V) vs SCE (FcH/FcH^+ as internal standard (E_0 = 0.46)).[95]

Table 7. Redox Potentials of Complexes 23−26 under Modified Conditions[a]

compd	$[Fe^{2+}]/[Fe^{3+}]$ E_{01} (ΔE_p), V	E_{02} (ΔE_p), V	$[Fe^{2+}]/[Fe^{3+}]$ E_{03} (ΔE_p), V]	ΔE_{01},[b] mV	ΔE_{02},[c] mV
23	0.42 (0.07)	1.03 (0.05)	1.11 (0.05)	80	650
24	0.40 (0.08)	1.00 (0.05)	1.06 (0.13)	60	630
25	0.41 (0.1)	1.06 (0.1)	1.14 (0.08)	80	690
26	0.38 (0.07)	0.93 (0.03)	1.03 (0.02)	100	600

[a]Conditions: cyclic voltammetric data of 10^{-3} M dichloromethane solutions at 298 K; [^{n}Bu$_4$N][B(C_6F_5)$_4$] (0.1 M) as supporting electrolyte; scan rate 100 mV s^{-1}; all potentials in V (ΔE_p in V) vs SCE (FcH/FcH^+ as internal standard (E_0 = 0.46 V)).[95] [b]$\Delta E_{01} = E_{03} - E_{02}$. [c]$\Delta E_{02} = E_{03} + E_{02}/2 - E_{01}$.

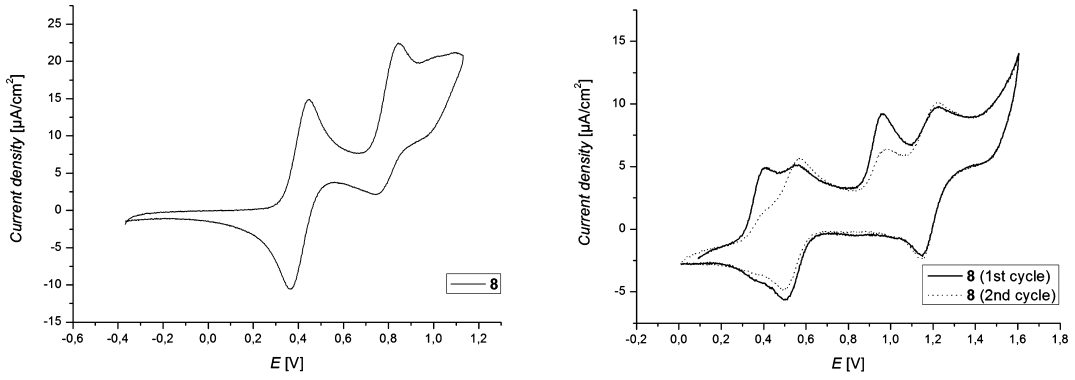
observed, as demonstrated for example for ferrocenyl phosphine selenides and oxides.[99] The combination of a solvent with a low donor character, such as dichloromethane, and a WCA electrolyte such as [^{n}Bu$_4$N][B(C_6F_5)$_4$] gives almost ideal conditions for the investigation of molecules with one or more ferrocenyl moieties because of minimization of the nucleophilic attack and high solubility. Nevertheless, no reversible processes for compounds **6**−**13** were observed using [^{n}Bu$_4$N][B(C_6F_5)$_4$] as supporting electrolyte.

To first get information on the donor ability of the phosphorus atoms in **6**−**13** toward transition-metal fragments, these molecules were converted into the appropriate seleno phosphines **14**−**21**. It was found that such molecules undergo dimerization at the P═Se bond[98,99] in further oxidation processes, resulting from an intramolecular electron transfer from a selenium-centered radical. As expected, seleno phosphines Bfc(Se═PR_2) (**14**−**17**) and bfc(Se═PR_2)$_2$ (**18**−**21**) show irreversible redox events in both electrolyte solutions with an anodic shift, reflecting the fact that seleno phosphines with phosphorus in the oxidation state +V are more difficult to oxidize than the molecules containing phosphorus(III) (for example, see Figure 6, compound **16**). These results illustrate that follow-up reactions take place (Table 5).

When the phosphorus atom is datively bonded to palladium, follow-up processes are inhibited. The complexes *trans*-[Pd(Bfc(PR_2))$_2$$Cl_2$] (**23**−**26**) show, applying standard conditions ([^{n}Bu$_4$N][PF_6]/dichloromethane), two reversible redox events between 0.40 and 0.91 V, supporting the subsequent oxidation of the iron centers exclusively (Table 6). In Figure 7 the cyclic voltammograms of **23**−**26** are depicted. It can be seen that the outer iron atoms (Fe1) are much less influenced by the PR_2 group (E_0 = 0.4−0.42 V) than those of the ferrocenyl units directly bonded to phosphorus (Fe2, E_0 = 0.78−0.91 V). Hence, the peak separation ΔE_0 found for the unsymmetrically substituted biferrocenyl unit is highly dependent on the organic group R at phosphorus. ΔE_0 decreases in the series **25** > **23** > **24** > **26** (Table 7). For E_{red} values between −0.74 and −1.3 V the reduction of Pd(II) to Pd(0) is observed.[116,117] The reduction potential decreases in the series **26** > **24** > **23** > **25**. Furthermore, it can be seen that with increasing electron density at phosphorus the Pd reduction is shifted toward anodic potentials and is thus simplified.

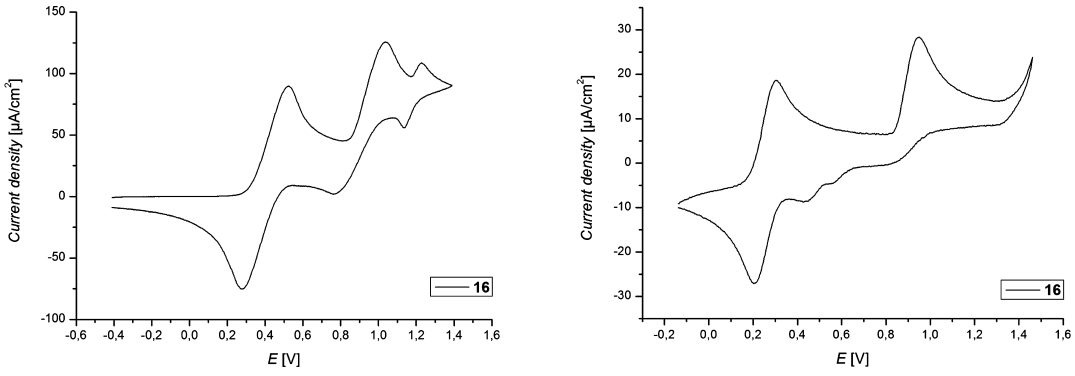
Cyclic voltammograms of **23**−**26** measured in electrolytes with WCAs ([^{n}Bu$_4$N][B(C_6F_5)$_4$]) are depicted in Figure 8. Different from the aforementioned measurements, the second redox process is split. This observation leads to the assumption that both outer iron centers (Fe1) are oxidized at the same potential, while the inner iron centers (Fe2) are oxidized at different potentials (Figure 8). The separation ΔE_{01} between the third and fourth redox processes depends on the organic groups at phosphorus and increases in the series **24** < **25** ≈ **23** < **26**. ΔE_{02} values found for the biferrocenyl unit in **23**−**26** increase in the opposite direction (Table 7). For an explanation of ΔE_{01} and ΔE_{02}, see Figure 9.

To investigate a possible electronic interaction between the biferrocenyl moieties over the P−Pd−P bridge,[79,118,119] spectroelectrochemical experiments were carried out on electron-poor **25** and electron-rich **26**, as examples. Figure 10 displays that both species show absorption bands at low energies at potentials above 300 mV, which reach a maximum at around 700 mV. They can be assigned to the dicationic species [**25**]$^{2+}$ and [**26**]$^{2+}$, respectively, reflecting the existence of two separate mono-oxidized biferrocenium species, one per phosphane unit. Gaussian-shaped bands in the near-IR region (5941 cm^{-1} ([**25**]$^{2+}$) and 4746 cm^{-1} ([**26**]$^{2+}$)) could be fitted by deconvolution (Figure 11) representing the experimental spectra. Their extinction coefficients and widths at half-height are indicative of class II mixed-valent systems.[120] Because of the unsymmetrical structure, delocalization is less favored.[121−124] Therefore, the intensities are lower compared to those of [bfc]$^+$ [125]



(a) [^{n}Bu$_4$N][PF$_6$] (0.1 M) (b) [^{n}Bu$_4$N][B(C$_6$F$_5$)$_4$] (0.1 M)

Figure 5. Cyclic voltammograms of **8** (10^{-3} M dichloromethane solutions at 298 K; scan rate 100 mV s^{-1}).[95]



(a) [^{n}Bu$_4$N][PF$_6$] (0.1 M) (b) [^{n}Bu$_4$N][B(C$_6$F$_5$)$_4$] (0.1 M)

Figure 6. Cyclic voltammograms of **16** (10^{-3} M dichloromethane solutions at 298 K; scan rate 100 mV s^{-1}).[95]

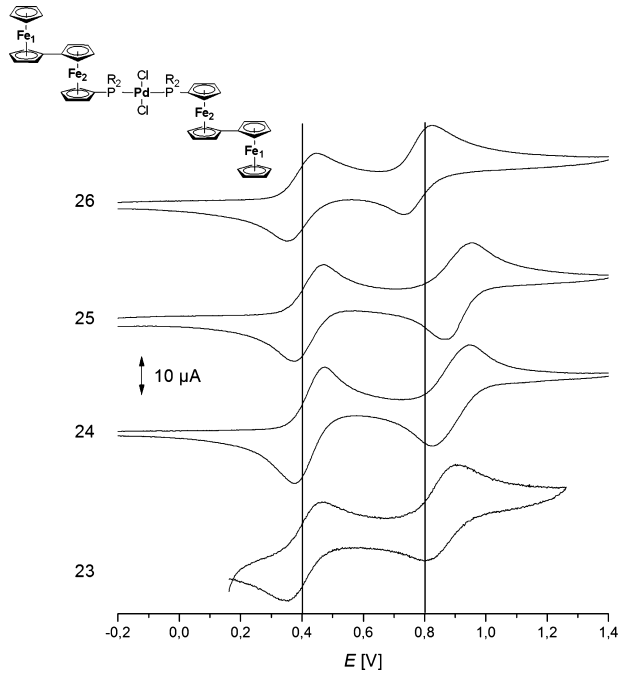


Figure 7. Cyclic voltammograms of **23**–**26** (10^{-3} M dichloromethane solutions at 298 K; [^{n}Bu$_4$N][PF$_6$] (0.1 M) as supporting electrolyte; scan rate 100 mV s^{-1}).[95]

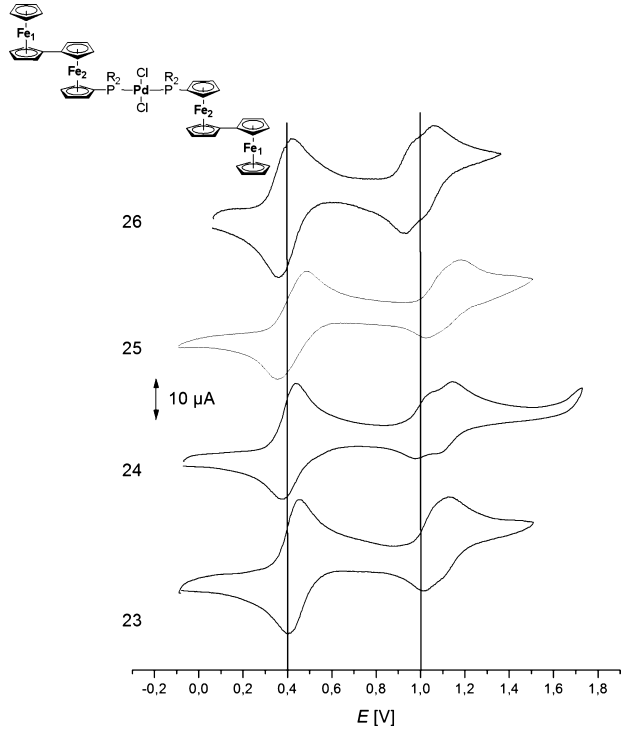


Figure 8. Cyclic voltammograms of **23**–**26** (10^{-3} M dichloromethane solutions at 298 K; [^{n}Bu$_4$N][B(C$_6$F$_5$)$_4$] (0.1 M) as supporting electrolyte; scan rate 100 mV s^{-1}).[95]

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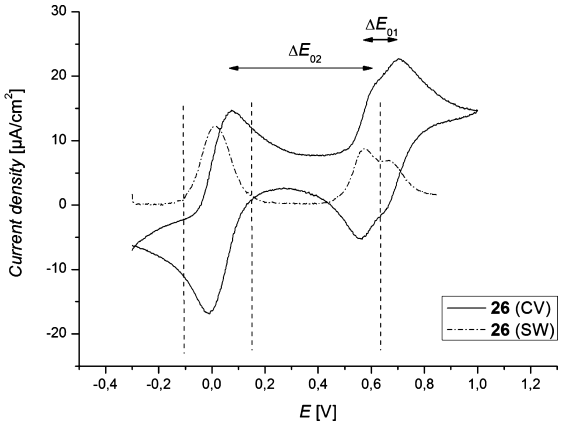


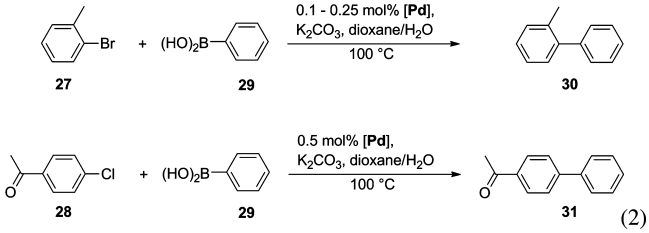
Figure 9. Cyclic voltammogram and square wave voltammogram of **26** (10^{-3} M dichloromethane solutions at 298 K; $[^nBu_4N][B(C_6F_5)_4]$ (0.1 M) as electrolyte; scan rate 100 mV s^{-1}; unreferenced).

and symmetrically substituted biferrocenes[83,85,125] and the absorptions possess broader bandwidths at half-height. Comparison of both absorption bands reflects that the electronic interaction between the two iron centers of each biferrocenyl moiety strongly depends on the substituents at the phosphorus atom. While absorptions for the electron-poor furyl derivative are located at higher energies with low ε values (655 L mol^{-1} cm^{-1}) (Figure 10a), absorptions of the more electron-rich cyclohexyl complex are red-shifted with a significantly higher intensity (ε = 1100 L mol^{-1} cm^{-1}, Figure 10b). In conclusion, the peak separation (ΔE_{01}), which was found only in electrolytes with WCAs ($[^nBu_4N][B(C_6F_5)_4]$), does not result from an electronic interaction between the iron centers over the palladium bridge because no additional IVCT transition was observed for the appropriate tricationic species (Figure 10, spectral series at the top). Therefore, this separation most likely corresponds to electrostatic effects. Similar observations were made for analogous ferrocenyl phosphine palladium complexes.[79]

4. Catalysis. The reactions of 2-bromotoluene (**27**) and 4′-chloroacetophenone (**28**) with 1.3 equiv of phenylboronic acid (**29**) to give the C,C cross-coupled biaryls 2-methylbiphenyl (**30**) and 4-acetylbiphenyl (**31**), respectively, were used as standard reactions to compare the catalytic activity of the newly synthesized palladium complexes **23**–**26** (eq 2). The conversions were performed in presence of 3 equiv of potassium carbonate as base in a solvent mixture of dioxane and water (ratio of 2/1 v/v) with a catalyst loading of 0.1–0.25 mol % Pd at 100 °C in analogy to literature procedures published by Beletskaya (Experimental Section).[34]

From parts a and b of Figure 12 it can be seen that all biferrocenyl phosphines show a good performance at catalyst loadings of 0.25 and 0.1 mol % with almost quantitative conversions (Table 8). Complexes **25** and **26** are somewhat less productive then **23** and **24**. At lower catalyst loadings a reduced activity for the furyl-containing system is found, which is in agreement with the electron density at the phosphorus atom (Table 3, Figure 12b). Due to the electronic and steric properties of phosphines **6**–**9**, palladium complexes **24** and **26** should show the highest performance in Suzuki cross-couplings, since they possess large Tolman cone angles and high Lewis basicity.[37,71,78,79] The obtained results are in accordance with the general statement that electron-rich and bulky phosphines are suitable ligands in Suzuki C,C couplings.[40,41]

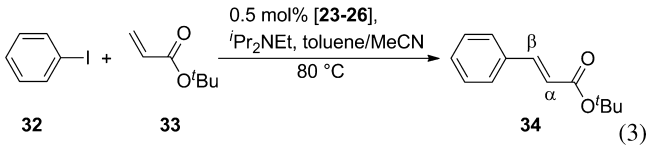
In comparison with the analogous ferrocenylphosphine-based complexes *trans*-$[Pd(Fc(PR_2))_2Cl_2]$ (R = C_6H_5 (**43**), C_6H_4-2-



(2)

CH_3 (**44**), $^cC_4H_3O$ (**45**), $^cC_6H_{11}$ (**46**); Fc = 1′-ferrocenyl, $Fe(\eta^5C_5H_4)(\eta^5C_5H_5)$), complexes **23**–**26** are less active; however, a similar dependence of the catalytic performance and the organic group at the phosphorus atom is characteristic.[79] The bidentate system $[Pd(fc(P(C_6H_4\text{-}2\text{-}CH_3)_2)_2)Cl_2]$ (fc = $Fe(\eta^5C_5H_4)_2$) shows similar conversions at 100 °C with catalyst loadings of 1 mol %.[34]

Due to the fact that the investigated palladium complexes **23**, **24**, and **26** show similar catalytic behavior for the conversion of



(3)

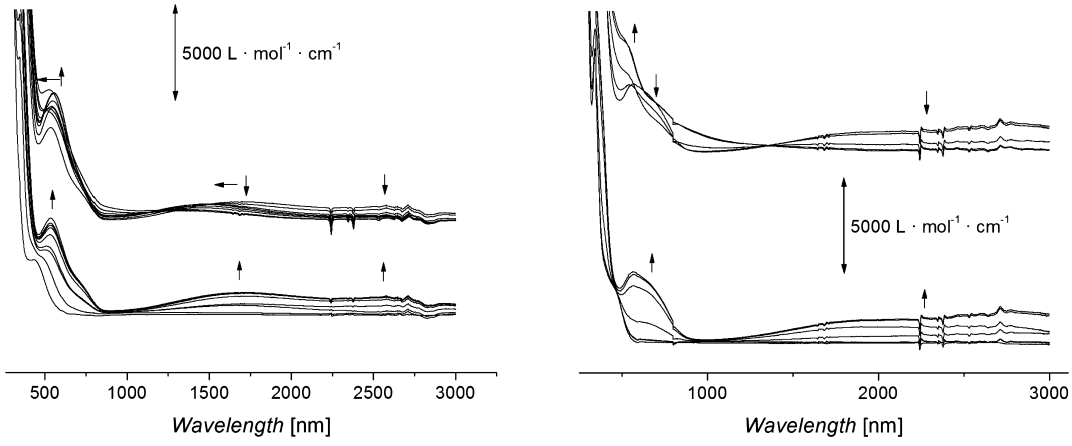


Figure 10. UV/vis/near-IR spectroelectrochemical measurements of **25** (left) and **26** (right), recorded in an OTTLE (optically transparent thin-layer electrode) cell. Potentials are vs Ag/AgCl (10^{-3} M dichloromethane solutions at 298 K; $[^nBu_4N][B(C_6F_5)_4]$ (0.1 M) as supporting electrolyte).

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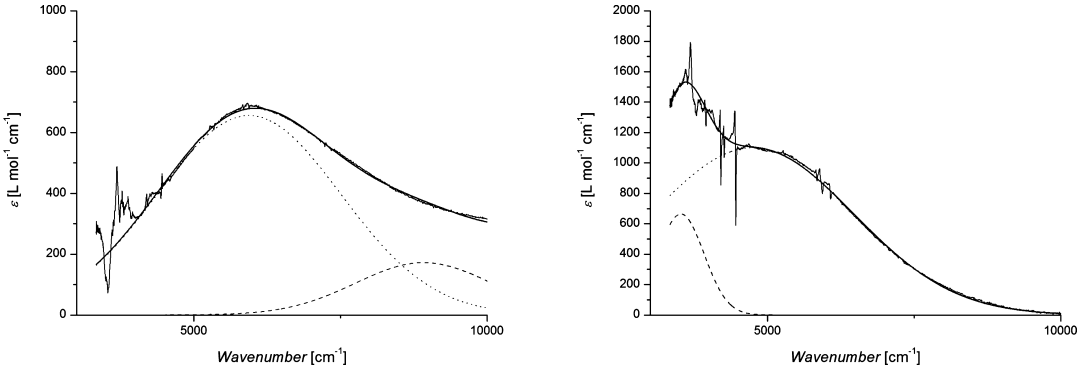

Figure 11. Deconvolution of near-IR absorptions of $[\mathbf{25}]^{2+}$ (left) and $[\mathbf{26}]^{2+}$ (right) using two Gaussian-shaped bands determined by spectroelectrochemical measurements in an OTTLE cell.

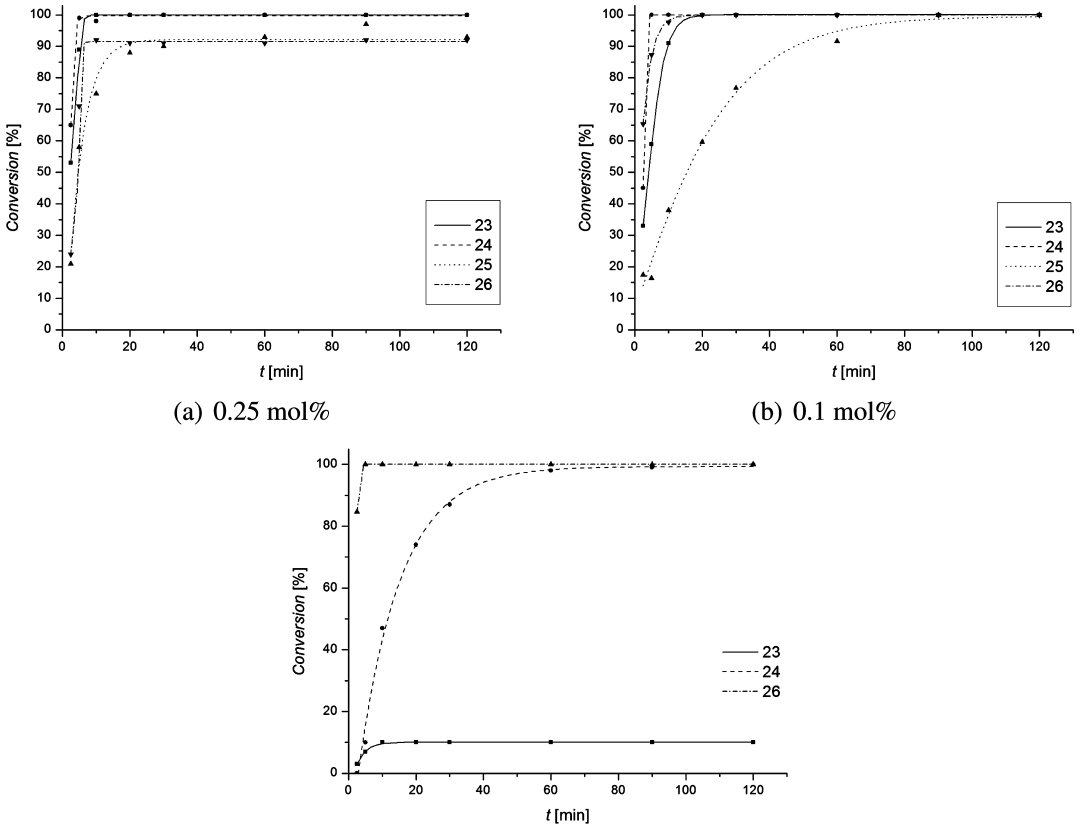

Figure 12. Kinetic investigation of **23**–**26** in the Suzuki C,C cross-coupling of **27** with **29** (a, b) and of **23**, **24**, and **26** in the coupling of **28** with **29** (c).

bromoarenes, a less reactive substrate was applied, and hence **28** was reacted with $PhB(OH)_2$ in presence of 0.5 mol % of palladium catalyst. From Figure 12c it can be seen that **23** shows only a conversion of 10%; however, the palladium complexes **24** and **26** proved to be more efficient. After 90 min a complete conversion of **28** with **29** to **31** was observed for catalysts **24** and **26** the latter complex of which shows the highest activity with full conversion after 10 min (Table 8).

In addition to Suzuki C,C cross-couplings the performance of transition-metal complexes **23**–**26** in the Heck reaction of iodobenzene (**32**) with *tert*-butyl acrylate (**33**) to give (*E*)-*tert*-butyl cinnamate (**34**) following the method described by Boyes and Butler was studied[36] (eq 3, Figure 13).

The reactions were carried out in 1/1 (v/v) toluene/acetonitrile mixtures at 80 °C in the presence of diisopropylethylamine as base with catalyst loadings of 0.5 mol % Pd to investigate the productivity of **23**–**26**. The data given in Figure 13a reveal that the highest productivity is obtained with catalyst **24**, while the highest activity was found for **26**. It can be seen that, as for Suzuki couplings, sterically demanding and electron-rich phosphines are best suited for the Heck reaction. A similar behavior was found for appropriate monoferrocenyl phosphine palladium complexes of the type $[Pd(Fc(PR_2))_2Cl_2]$ (**43**–**46**) (Figure 13b).[79] In comparison with these species the biferrocenyl derived catalysts possess a similar activity. With regard to previous dppf-based catalysts reported by Butler and Boyes, which are supported by addition of [CuI] and show high activity at low catalyst loadings, the systems described here do not require addition of [CuI].[36]

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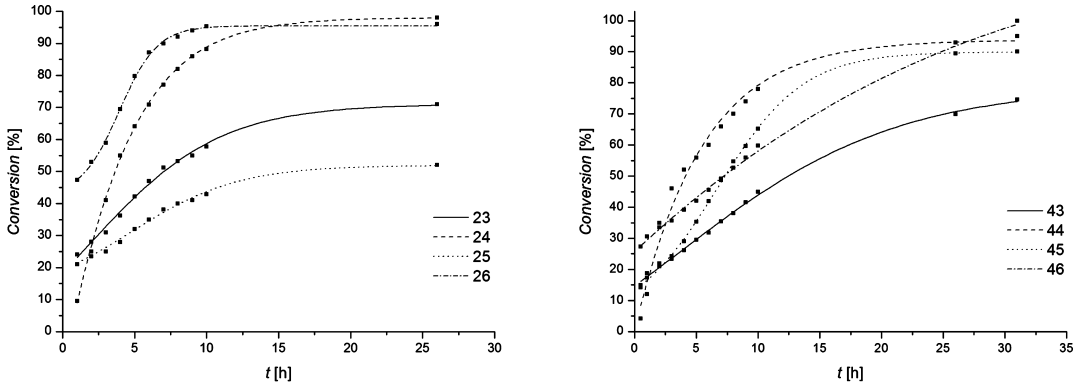
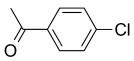


(a) 0.5 mol% $[Pd(R_2PBfc)_2Cl_2]$ (b) 0.5 mol% $[Pd(R_2PFc)_2Cl_2]$

Figure 13. Kinetic investigation of **23**–**26** (a) as well as **43**–**46**[79] (b) in the Heck reaction of **32** with **33** to give **34**.

Table 8. Suzuki Reaction of Br-tol or Cl-AcPh with PhBOH using Catalyst Loadings of 0.25 and 0.1 mol % and 23–26 as the Palladium Source[a]

Compd.	Aryl halide	Catalyst loading	Yield [%]	TOF [h^{-1}]
23		0.25 mol%	100	2400
24			100	1200
25			93	186
26			92	180
23		0.1 mol%	100	3000
24			100	12000
25			100	666
26			100	3000
23		0.5 mol%	10	120
24			100	96
26			100	2400

[a]Results after 2 h.

In summary, in comparison with the bidentate ferrocenyl phosphines reported by Beletskaya, our catalysts are active in the Suzuki reaction at lower catalyst loadings.[34] Nevertheless, compared with the catalyst systems to date based on, for example, N-heterocyclic carbenes,[13,15,23,25–28] palladacycles,[21,22,126–130] or bulky, electron-rich phosphines[2,14,19,24,29–33,131] they are less active.

CONCLUSIONS

Within this study a series of new biferrocenyl phosphine-based transition-metal complexes of the type *trans*-$[Pd(Bfc(PR_2))_2Cl_2]$ (R = C_6H_5, C_6H_4-2-CH_3, $^cC_4H_3O$, $^cC_6H_{11}$; Bfc = 1′-biferrocenyl) are reported. They have been synthesized by reacting the phosphines $Bfc(PR_2)$ with $[Pd(Et_2S)_2Cl_2]$. Phosphines $Bfc(PR_2)$ together with their symmetric analogues $bfc(PR_2)_2$ (bfc = 1′,1‴-biferrocenyl) are accessible by a consecutive synthesis methodology starting from $bfcBr_2$. For the classification of the σ donor ability of the appropriate phosphines $Bfc(PR_2)$ the corresponding phosphine selenides $Bfc(Se{=}PR_2)$ have been synthesized upon addition of selenium in its elemental form to $Bfc(PR_2)$. High $^1J_{^{31}P-^{77}Se}$ values are distinctive for electron-poor phosphines with less donor capability.[72–77] Electrochemical studies of all bimetallocenyl-functionalized phosphines were carried out with two different supporting electrolytes ($[^nBu_4N][PF_6]$, $[^nBu_4N][B(C_6F_5)_4]$) for comparison of the electrochemical behavior under different conditions. In both electrolytes phosphines $Bfc(PR_2)$/$bfc(PR_2)_2$ possess multiple redox processes as are typical for ferrocenyl phosphines.[79,80,96–103] At higher potentials follow-up reactions were detected, which most likely correspond to processes at the phosphorus atom.

For prevention of follow-up reactions during electrochemical measurements, palladium complexes were investigated in which the lone pair of electrons is part of the P–Pd bond. The palladium complexes *trans*-$[Pd(Bfc(PR_2))_2Cl_2]$ show a reversible redox behavior in both supporting electrolytes and are, as expected, more difficult to oxidize in comparison to phosphines $Bfc(PR_2)$. E_0 values of the iron centers next to the phosphine moiety decrease in the series **25** > **24** > **23** > **26**, due to an increase of electron density in the molecules. The outer iron centers are much less influenced by the organic groups at phosphorus. Measurements in $[^nBu_4N][B(C_6F_5)_4]$/dichloromethane solutions result in a separation of the second redox event, which is attributed to the WCA (weak coordinating anion) effect.[99] In conclusion, the outer iron centers were oxidized at the same potential, while the inner, phosphorus-bonded iron centers were oxidized separately. In addition, UV/vis/near-IR spectroelectrochemical measurements were carried out with electron-poor **25** and electron-rich **26**. IVCT bands could be observed in both cases, reflecting intermetallic communication between the two ferrocene units within the biferrocenyl phosphine moieties for the dicationic species.[125] During further oxidation no additional IVCT bands were observed, which leads to the conclusion that electronic communication over the P–Pd–P connectivity does not take place. The IVCT band of electron-rich **26** in comparison to electron-poor **25** is located at lower energy but with higher extinction coefficients, revealing that the communication between the iron centers in **26** is stronger than in **25**.

All palladium complexes were tested as catalysts in C,C cross-couplings. In the palladium-promoted Suzuki reaction of 2-bromotoluene or 4′-chloroacetophenone with phenylboronic acid all complexes are active; however, the highest activity was observed with the cyclohexyl- or *o*-tolyl-substituted phosphines. This can be explained by their bulkiness and high σ donor capability. Furthermore, it could be demonstrated that all palladium species are active in the Heck reaction of iodobenzene with *tert*-butyl acrylate. In comparison to other species in the literature[37] the same dependence on the basicity of the phosphines as for the Suzuki reaction was observed. In summary, the catalysts reported within this work are, in comparison with current catalytic systems,[2,13–15,23,24,26–33,129–131] less active but,

in comparison with other metallocenyl diphosphine palladium catalysts, show a higher activity under similar reaction conditions.[34,36] The corresponding monodentate ferrocenyl phosphines *trans*-[Pd(Fc(PR_2))$_2Cl_2$] show a somewhat higher (for Suzuki) or quite similar activity (for Heck) under the same conditions.[79]

EXPERIMENTAL SECTION

General Data. All reactions were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. Tetrahydrofuran, toluene, *n*-hexane, and *n*-pentane were purified by distillation from sodium/benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride.

Instruments. Infrared spectra were recorded with a FT-Nicolet IR 200 spectrometer. The ^{1}H NMR spectra were recorded with a Bruker Avance III 500 spectrometer operating at 500.303 MHz in the Fourier transform mode; the $^{13}C\{^1H\}$ NMR spectra were recorded at 125.800 MHz. Chemical shifts are reported in δ (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^{1}H NMR, $CDCl_3$, 7.26; $^{13}C\{^1H\}$ NMR, $CDCl_3$, 77.00). $^{31}P\{^1H\}$ NMR spectra were recorded at 101.255 MHz in $CDCl_3$ with $P(OMe)_3$ as an external standard (δ 139.0 ppm, relative to H_3PO_4 (85%) with δ 0.00 ppm). The abbreviation pt in the ^{1}H NMR spectra corresponds to pseudotriplet. The melting points of analytically pure samples (sealed off in nitrogen-purged capillaries) were determined using a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed using a Thermo FLASHEA 1112 Series instrument. Cyclic voltammograms were recorded in a dried cell purged with purified argon. Platinum wires served as working and counter electrodes. A saturated calomel electrode in a separate compartment served as reference electrode. For ease of comparison, all electrode potentials are converted using the redox potential of the ferrocene–ferrocenium couple [FcH]/[FcH$^+$] (FcH = Fe(η^5-C_5H_5)$_2$, E_0 = 0.46 V) as internal standard.[95] Electrolyte solutions were prepared from dichloromethane and [^{n}Bu$_4$N][PF_6] (Fluka, dried under oil-pump vacuum). Measurements on 1.0 mmol/dm^3 solutions of **6**–**9**, **14**–**17**, and **23**–**26** in dry dichloromethane containing 0.1 mol/dm^3 of [^{n}Bu$_4$N][B(C_6F_5)$_4$] as supporting electrolyte were conducted in a three-electrode cell, which utilized a Pt auxiliary electrode, a glassy-carbon working electrode (surface area 0.031 cm^2), and an Ag/Ag$^+$ (0.01 mmol/dm^3 [$AgNO_3$]) reference electrode (mounted on a Luggin capillary). The working electrode was treated by polishing on a Buehler microcloth first with 1 μm and then with 1/4 μm diamond paste. The reference electrode was constructed from a silver wire inserted into a solution of 0.01 mmol/dm^3 [$AgNO_3$] and 0.1 mol/dm^3 [^{n}Bu$_4$N][B(C_6F_5)$_4$] in acetonitrile, in a Luggin capillary with a Vycor tip. This capillary was inserted into a second Luggin capillary with Vycor tip filled with a 0.1 mmol/dm^3 [^{n}Bu$_4$N][B(C_6F_5)$_4$] solution in dichloromethane. Experimental potentials were referenced against [FcH]/[FcH$^+$]. Data were manipulated on a Microsoft Excel worksheet to set the formal reduction potentials of the [FcH]/[FcH$^+$] couple to E_0 = 0.46 V. Under our conditions the [FcH]/[FcH$^+$] couple was at around 0.21 V vs Ag/Ag$^+$. Cyclic voltammograms were recorded in the negative direction at the starting potentials using a Voltalab 3.1 potentiostat (Radiometer) equipped with a DEA 101 digital electrochemical analyzer and an IMT 102 electrochemical interface. Spectroelectrochemical measurements were carried out in an OTTLE cell similar to that described previously by Hartl,[132] from solutions in dichloromethane containing 0.1 mol/dm^3 of [^{n}Bu$_4$N][B(C_6F_5)$_4$] as supporting electrolyte using a Varian Cary 5000 spectrometer. High-resolution mass spectra were recorded using a micrOTOF-QII Bruker Daltonik workstation (ESI-TOF).

Reagents. All starting materials were obtained from commercial suppliers and used without further purification. Dibromobiferrocene,[81] bis(diphenylphosphanyl)biferrocene,[80] chlorophosphines (**3**–**5**),[133–135] and [Pd(Et_2S)$_2Cl_2$][136] were prepared according to published procedures.

General Procedure for the Synthesis of Bfc(PR_2). To a solution of 1.0 g (1.89 mmol) of 1′,1‴-dibromobiferrocene (**1**) dissolved in 50 mL of dry tetrahydrofuran was added 1 equiv of a 2.5 M solution of *n*-butyllithium (1.89 mmol, 0.76 mL, 2.5 M in *n*-hexane) dropwise at −70 °C. After the solution was stirred for 60 min at this temperature, 1 equiv of the appropriate chlorophosphine **2**–**5** was added. The reaction mixture was stirred for 12 h at ambient temperature, and then the solvent was removed under vacuum. The resulting residue was purified by column chromatography and dried under vacuum. A mixture of the title complexes and disubstituted bfc(Br)(PR_2) (R = C_6H_5, C_6H_4-2-CH_3, $^cC_4H_3O$, $^cC_6H_{11}$) was obtained in a molar ratio of 1:3 and was used without further purification in a second lithiation process (vide supra). Therefore, the appropriate mixture was dissolved in 50 mL of tetrahydrofuran and was treated with an excess of a 2.5 M solution of *n*-butyllithium at −70 °C. After 30 min of stirring at this temperature, 1 equiv of EtOH was added in a single portion. The reaction mixture was stirred for 1 h at ambient temperature. Afterward, all volatile materials were evaporated. The resulting residue was purified by column chromatography on alox and dried under vacuum. Complexes **6**–**9** were isolated as orange solid materials.

*Synthesis of Bfc(PPh_2) (**6**).* Using the general procedure described above, molecule **1** was reacted with *n*-butyllithium followed by the dropwise addition of 417 mg (1.89 mmol) of **2**. The resulting residue was purified by column chromatography on alumina (column dimension 2.5 × 30 cm) using a diethyl ether/*n*-hexane mixture in a ratio of 1/5 (v/v). At first, unreacted **1** and then a mixture of the title complex and bfc(Br)(PPh_2) (ratio 1/3) was eluted as a red oil. Yield: 800 mg (average molecular weight 613.39 g/mol, 1.3 mmol), $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −16.6 ppm. An 800 mg portion (1.3 mmol) of the obtained mixture was dissolved in tetrahydrofuran and was subsequently lithiated with 0.62 mL of *n*-butyllithium (1.56 mmol, 2.5 M in *n*-hexane) and reacted afterward with 120 mg of EtOH at −70 °C. The obtained crude product was subjected to column chromatography on alumina (column dimension 2.5 × 30 cm) using diethyl ether/*n*-hexane (ratio 1/5, v/v) as eluent. After removal of all solvents, compound **6** could be obtained as an orange solid. Yield: 690 mg (1.24 mmol, 65.8% based on **1**). Anal. Calcd for $C_{32}H_{27}Fe_2P$ (554.22 g/mol): C, 69.34; H, 4.91. Found: C, 69.22; H, 4.91. Mp: 136 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1436 (w, ν_{P-C}); 1457, 1473 (w, $\nu_{C=C}$). ^{1}H NMR ($CDCl_3$, δ): 3.90 (pq, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 3.96 (s, 5 H, C_5H_5), 4.04 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.13 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.15 (pt, J_{HH} = 1.74 Hz, 2 H, C_5H_4), 4.25–4.26 (dt, J_{HH} = 4.2 Hz, 1.8 Hz, 4 H, C_5H_4), 7.3–7.31 (m, 6 H, C_6H_5), 7.33–7.37 (m, 4 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 66.43 (C_5H_4), 67.32 (C_5H_4), 67.73 (C_5H_4), 69.06 (C_5H_4), 69.17 (s, C_5H_5), 72.7, 72.73 (d, J_{CP} = 3.87 Hz, C_5H_4–P), 73.88, 74 (d, J_{CP} = 14.69 Hz, C_5H_4–P), 75.82, 75.87 (d, J_{CP} = 6.2 Hz, C_i/C_5H_4), 83.0 (C_i/C_5H_4), 84.84 (C_i/C_5H_4), 128.07, 128.12 (d, J_{CP} = 6.67 Hz, C_m/C_6H_5), 128.39 (C_p/C_6H_5), 133.42, 133.57 (d, J_{CP} = 19.17 Hz, C_o/C_6H_5), 139.26, 139.34 (d, J_{CP} = 9.6 Hz, C_i/C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −16.55 ppm (s). This compound was stirred for 1 week in acetone in air to prove its oxidation sensitivity, yielding a 1/1 mixture of Bfc(PPh_2) and Bfc(O═PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 28.94 ppm (s).

*Synthesis of Bfc[P(2-$CH_3C_6H_4$)$_2$] (**7**).* Acoording to the general procedure described earlier, compound **1** was reacted with *n*-butyllithium followed by the addition of 470 mg (1.89 mmol) of **3** in a single portion. The resulting residue was purified by column chromatography on alumina (column dimension 2.5 × 30 cm) using a 1/2 (v/v) toluene/*n*-hexane mixture. At first, **1** was eluted. Then the title complex together with bfc(Br)(P(2-$CH_3C_6H_4$)$_2$) in a 1/3 molar ratio was eluted as a red oil. Yield: 600 mg (average molecular weight 641 g/mol, 0.93 mmol), $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −36.9 ppm. A 600 mg portion (0.93 mmol) of the mixture was lithiated with 0.44 mL of *n*-butyllithium (1.22 mmol, 2.5 M in *n*-hexane) and was then reacted with 85 mg of ethanol as described earlier. The obtained residue was subjected to column chromatography on alumina (column dimension 2.5 × 30 cm) using toluene/*n*-hexane (ratio 1/2, v/v) as eluent. After removal of all volatiles, **7** was obtained as an orange solid. Yield: 520 mg (0.89 mmol, 47% based on **1**). Anal. Calcd for $C_{34}H_{31}Fe_2P$ (582.27 g/mol): C, 70.13; H, 5.36. Found: C, 69.99; H, 5.33. Mp: 146–148 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1446 (m, ν_{P-C}); 1559 (m, $\nu_{C=C}$). ^{1}H NMR ($CDCl_3$, δ): 2.53 (s, 6 H, CH_3), 3.94 (s, 5 H, C_5H_5), 3.95 (pq, J_{HH} = 3.7 Hz, 1.8 Hz, 2 H, C_5H_4), 4.06 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.1 (pt,

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J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.17 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.19 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.22 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 6.9−7.06 (m, 4 H, $C_6H_4CH_3$), 7.15−7.21 (m, 4 H, $C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 21.42 (d, J_{CP} = 21.79 Hz, CH_3), 66.32 (C_5H_4), 67.13 (C_5H_4), 67.68 (C_5H_4), 68.84 (C_5H_4), 69.14 (s, C_5H_5), 72.8, 72.85 (d, J_{CP} = 4.16 Hz, C_5H_4−P), 74.46, 74.58 (d, J_{CP} = 15.44 Hz, C_5H_4−P), 75.64, 75.68 (d, J_{CP} = 5.4 Hz, C_i/C_5H_4), 83.04 (C_i/C_5H_4), 84.7 (C_i/C_5H_4), 125.5 (s, $C_6H_4CH_3$), 128.3 (s, $C_6H_4CH_3$), 129.79, 127.83 (d, J_{CP} = 5.08 Hz, $C_6H_4CH_3$), 133.4, ($C_6H_4CH_3$), 137.85, 137.94 (d, J_{CP} = 10.7 Hz, $C_i/C_6H_4CH_3$), 141.54, 141.75 (d, J_{CP} = 26.36 Hz, $C_i/C_6H_4CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −36.84 ppm (s). HRMS (ESI-TOF): m/z calcd for $C_{34}H_{31}Fe_2P$ ($[M]^+$) 582.0858, found 582.0822 (100%).

*Synthesis of Bfc(P(2-$^cC_4H_3O$)$_2$) (**8**).* Compound **1** was reacted with *n*-butyllithium followed by the dropwise addition of 380 mg (1.89 mmol) of **4** as described for the preparation of **6**. The resulting residue was purified by column chromatography on alumina (column dimension 2.5 × 30 cm) using toluene/*n*-hexane (ratio 1/2, v/v). Along with **1**, a mixture of the title complex and bfc(Br)(P(2-$^cC_4H_3O)_2$) in a 1/3 molar ratio was eluted as a red oil. Yield: 700 mg (average molecular weight 593.3 g/mol, 1.17 mmol). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −64.79 ppm. A 700 mg portion (1.17 mmol) of the obtained mixture was dissolved in tetrahydrofuran and was lithiated with 0.56 mL of *n*-butyllithium (1.4 mmol, 2.5 M in *n*-hexane). Afterward, it was reacted with 107 mg of ethanol. The obtained crude product was purified by column chromatography on alumina (column dimension 2.5 × 30 cm) using toluene/*n*-hexane (ratio 1/2, v/v) as eluent. After removal of all volatiles compound **8** was obtained as an orange solid. Yield: 609 mg (1.14 mmol, 60.3% based on **1**). Anal. Calcd for $C_{28}H_{23}Fe_2O_2P$ (534.14 g/mol): C, 62.96; H, 4.34. Found: C, 63.03; H, 4.375. Mp: 179 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1006 (m, ν_{C-O}); 1457 (w, ν_{P-C}); 1559 (w, $\nu_{C=C}$); 3094 (m, $\nu_{C(sp^2)-H}$). ^1H NMR ($CDCl_3$, δ): 3.96 (s, SH, C_5H_5), 4.0 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.12 (pt, J_{HH} = 1.5 Hz, 2 H, C_5H_4), 4.15 (pt, J_{HH} = 1.7 Hz, 2 H, C_5H_4), 4.22 (pt, J_{HH} = 1.7 Hz, 4 H, C_5H_4), 4.3 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 6.38 (m, 2 H, C_4H_3O), 6.66 (m, 2 H, C_4H_3O), 7.62 ppm (d, J_{HH} = 1.6 Hz, 2 H, C_4H_3O). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 65.4 (C_5H_4), 66.21 (C_5H_4), 66.73 (C_5H_4), 67.9 (C_5H_4), 68.1 (s, C_5H_5), 71.7, 71.9 (d, J_{CP} = 5.54 Hz, C_5H_4−P), 73.52, 73.67 (d, J_{CP} = 18.2 Hz, C_5H_4−P), 109.5 (d, J_{CP} = 6 Hz, C_4H_3O), 118.5, 118.7 (d, J_{CP} = 23 Hz, C_4H_3O), 145.5 (d, J_{CP} = 2 Hz, C_4H_3O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −64.6 ppm (s).

*Synthesis of Bfc(P($^cC_6H_{11}$)$_2$) (**9**).* Using the procedure described above, compound **1** was reacted with *n*-butyllithium followed by dropwise addition of 440 mg (1.89 mmol) of chlorodicyclohexylphosphine (Cy). The crude product was purified by column chromatography on alumina (column dimension 2.5 × 30 cm) using toluene/*n*-hexane (ratio 1/2, v/v). At first, **1** was eluted. Then a 1/3 mixture of the title complex and bfc(Br)(P($^cC_6H_{11}$)$_2$) was eluted as a red oil. Yield: 680 mg (average molecular weight 625.47 g/mol, 1.08 mmol), $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −7.46 ppm. A 680 mg portion (1.08) of the mixture was dissolved in tetrahydrofuran as described above and was than lithiated with 0.5 mL of *n*-butyllithium (1.3 mmol, 2.5 M in *n*-hexane) and reacted with 100 mg of ethanol. The crude product was subjected to column chromatography on alumina (column dimension 2.5 × 30 cm) using a toluene/*n*-hexane mixture (ratio 1/2, v/v) as eluent. After removal of all volatile materials compound **9** could be obtained as an orange solid. Yield: 500 mg (0.88 mmol, 46% based on **1**). Anal. Calcd for $C_{32}H_{39}Fe_2P.^1/_2C_6H_{14}$ (566.31 g/mol): C, 68.90; H, 7.60. Found: C, 68.82; H, 7.70. Mp: 157 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1447.5 (m, ν_{P-C}). ^1H NMR ($CDCl_3$, δ): 0.88 (CH_3/C_6H_{14}), 1.26 (CH_2/C_6H_{14}), 1.14−1.28 (m, 10 H, C_6H_{11}), 1.64−1.77 (m, 10 H, C_6H_{11}), 1.87−1.9 (m, 2 H, C_6H_{11}), 3.96 (2 H, C_5H_4), 3.98 (s, 5 H, C_5H_5), 4.06 (pt, J_{HH} = 1.7 Hz, 2 H, C_5H_4), 4.14 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.17 (pt, J_{HH} = 1.7 Hz, 2 H, C_5H_4), 4.32 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.38 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 14.14 (CH_3/C_6H_{14}), 22.70 (CH_2/C_6H_{14}), 25.45 (CH_2/C_6H_{11}), 26.26, 26.32 (d, J_{CP} = 7.2 Hz, CH_2/C_6H_{11}), 26.33, 26.4 (d, J_{CP} = 8.3 Hz, CH_2/C_6H_{11}), 29.21, 29.32 (d, J_{CP} = 14 Hz, CH_2/C_6H_{11}), 29.32, 29.39 (d, J_{CP} = 7.7 Hz, CH_2/C_6H_{11}), 32.4, 32.49 (d, J_{CP} = 11.3 Hz, CH/C_6H_{11}), 65.51 (C_5H_4), 66.35 (C_5H_4), 66.67 (C_5H_4), 68.71 (s, C_5H_5), 68.4 (C_5H_4), 70.33 (C_5H_4−P), 71.52, 71.61 (d, J_{CP} = 11 Hz, C_5H_4−P), 75.28, 75.41 (d, J_{CP} = 16.4 Hz, C_i/C_5H_4), 82.52 (C_i/C_5H_4), 83.42 (C_i/C_5H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −7.39 ppm (s). HRMS (ESI-TOF): m/z calcd for $C_{32}H_{39}Fe_2P$ ($[M + nH]^+$) 567.1562, found 567.1544.

General Procedure for the Synthesis of bfc(PR$_2$)$_2$. To 50 mL of a tetrahydrofuran solution containing 1.0 g (1.89 mmol) of **1** was added 2 equiv of a 2.5 M solution of *n*-butyllithium (3.78 mmol, 1.5 mL, 2.5 M in *n*-hexane) dropwise at −70 °C. After the reaction mixture was stirred for 60 min at −70 °C, 2 equiv of the appropriate chlorophosphine was added. The reaction mixture was stirred for 12 h at ambient temperature and was then concentrated in vacuo to dryness. The resulting residue was purified by column chromatography on alumina using toluene as eluent.

*Synthesis of bfc(P(2-$CH_3C_6H_4$)$_2$)$_2$ (**11**).* According to the general procedure described above, molecule **1** was reacted with *n*-butyllithium followed by addition of 940 mg (3.78 mmol) of chlorodi-*o*-tolylphosphine (**3**) in a single portion. The title complex was obtained as an orange solid. Yield: 1.0 g (1.2 mmol, 66% based on **1**). Anal. Calcd for $C_{48}H_{44}Fe_2P_2$ (794.5 g/mol): C, 72.56; H, 5.58. Found: C, 72.78; H, 5.44. Mp: 210 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1449 (m, ν_{P-C}); 1559 (m, $\nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 2.44 (s, 12 H, CH_3), 3.83 (pq, J_{HH} = 3.7, 1.8 Hz, 4 H, C_5H_4), 3.92 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.00 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.05 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 6.89−6.97 (m, 8 H, $C_6H_4CH_3$), 7.06−7.12 (m, 8 H, $C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 21.32, 21.49 (d, J_{CP} = 22 Hz, CH_3), 67. 07 (C_5H_4), 68.95 (C_5H_4), 72.81, 72.84 (d, J_{CP} = 3.8 Hz, C_5H_4−P), 74.35, 74.47 (d, J_{CP} = 15.6 Hz, C_5H_4−P), 75.65, 75.7 (d, J_{CP} = 6 Hz, C_i/C_5H_4), 83.86 (C_i/C_5H_4−P), 125.54 ($C_6H_4CH_3$), 128.36 ($C_6H_4CH_3$), 129.78, 129.82 (d, J_{CP} = 4.7 Hz, $C_6H_4CH_3$), 133.41 ($C_6H_4CH_3$), 137.8, 137.89 (d, J_{CP} = 4.7 Hz, $C_6H_4CH_3$), 141.52, 141.73 (d, J_{CP} = 26.3 Hz, $C_6H_4CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −36.8 ppm (s). HRMS (ESI-TOF): m/z calcd for $C_{48}H_{44}Fe_2P_2$ ($[M]^+$) 794.1614, found 794.1586 (100%).

*Synthesis of bfc(P(2-$^cC_4H_3O$)$_2$)$_2$ (**12**).* As described earlier, compound **1** was reacted with *n*-butyllithium and then 760 mg (3.78 mmol) of chlorodifurylphosphine (**4**) were added dropwise. The product was obtained as an orange solid. Yield: 1.0 g (1.43 mmol, 75% based on **1**). Anal. Calcd for $C_{36}H_{28}Fe_2O_4P_2$ (698.24 g/mol): C, 61.92; H, 4.04. Found: C, 62.03; H, 3.997. Mp: 180 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1007 (m, ν_{C-O}); 1458 (m, ν_{P-C}); 1556 (w, $\nu_{C=C}$), 3091 (w, $\nu_{C(sp^2)-H}$). ^1H NMR ($CDCl_3$, δ): 3.98 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.09 (pt, J_{HH} = 1.5 Hz, 4 H, C_5H_4), 4.18−4.2 (m, 8 H, C_5H_4), 6.38−6.39 (m, 4 H, C_4H_3O), 6.65−6.66 (m, 4 H, C_4H_3O), 7.62 (d, J_{HH} = 1.5 Hz, 4 H, C_4H_3O). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 67.47 (C_5H_4), 69.2 (C_5H_4), 72.6 (C_i/C_5H_4), 72.88, 72.92 (d, J_{CP} = 5.3 Hz, C_5H_4−P), 74.68, 74.83 (d, J_{CP} = 18 Hz, C_5H_4−P), 84.07 (C_i/C_5H_4), 110.65 (d, J_{CP} = 6 Hz, C_4H_3O), 119.8 (d, J_{CP} = 23.3 Hz, C_4H_3O), 146.7 (s, C_i/C_4H_3O), 152.68 ppm (d, J_{CP} = 8.4 Hz, C_4H_3O. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −64.74 ppm (s).

*Synthesis of bfc(P($^cC_6H_{11}$)$_2$)$_2$ (**13**).* Using the procedure described above, molecule **1** was reacted with *n*-butyllithium and then with 880 mg (3.78 mmol) of chlorodicyclohexylphosphine (**5**). The title compound **13** was obtained as an orange solid. Yield: 1.1 g (1.14 mmol, 76% based on **1**). Anal. Calcd for $C_{44}H_{60}Fe_2P_2$ (762.58 g/mol): C, 69.30; H, 7.93. Found: C, 69.05; H, 7.86. Mp: 192 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1448 (m, ν_{P-C}). ^1H NMR ($CDCl_3$, δ): 1.02−1.08 (m, 4 H, C_6H_{11}), 1.13−1.29 (m, 18 H, C_6H_{11}), 1.63−1.67 (m, 7 H, C_6H_{11}), 1.7−1.76 (m, 11 H, C_6H_{11}), 1.85−1.87 (m, 4 H, C_6H_{11}), 3.94 (4 H, C_5H_4), 4.04 (4 H, C_5H_4), 4.13 (4 H, C_5H_4), 4.33 (4 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 26.46 (CH_2/C_6H_{11}), 27.28, 27.33 (d, J_{CP} = 6.2 Hz, CH_2/C_6H_{11}), 27.35, 27.41 (d, J_{CP} = 7.6 Hz, CH_2/C_6H_{11}), 30.23, 30.34 (d, J_{CP} = 13.3 Hz, CH_2/C_6H_{11}), 30.34, 30.43 (d, J_{CP} = 11.3 Hz, CH_2/C_6H_{11}), 33.42, 33.51 (d, J_{CP} = 11.6 Hz, CH/C_6H_{11}), 67.56 (C_5H_4), 69.42 (C_5H_4), 71.37, 71.39 (d, J_{CP} = 2.5 Hz, C_5H_4−P), 73.54, 72.63 (d, J_{CP} = 11.4 Hz, C_5H_4−P), 84.07 (C_i/C_5H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −7.39 ppm (s). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{60}Fe_2P_2$ ($[M + nH]^+$) 763.2944, found 763.2915 (90%); ($[M + nH]^{2+}$) 382.1508, found 382.1485 (100%).

General Procedure for the Preparation of Bfc(Se═PR$_2$) and bfc(Se═PR$_2$)$_2$. To a toluene solution (20 mL) containing 100 mg of monophosphines **6**−**9** (0.18 mmol) or diphosphines **10**−**13** (0.13 mmol) was added 1.2 (for monophosphines) or 2.4 equiv (for diphosphines) of elemental selenium in a single portion, and the reaction mixture was stirred for 5 h at 100 °C. After the respective reaction mixture was cooled to

ambient temperature, it was filtered through a pad of Celite to remove the excess elemental selenium. After filtration all volatile materials were removed under vacuum to afford the appropriate compounds as orange solids.

*Synthesis of Bfc(Se═PPh$_2$) (**14**).* Using the general procedure described above, **6** was reacted with 21.3 mg (0.27 mmol) of selenium. Molecule **14** was obtained as an orange solid. Yield: 100 mg (0.15 mmol, 87.79% based on **6**). Anal. Calcd for $C_{32}H_{27}Fe_2PSe\cdot{}^1/_6CH_2Cl_2$ (633.18 g/mol): C, 59.82; H, 4.26. Found: C, 59.79; H, 4.26. Mp: 215 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 574 (m, $\nu_{P=Se}$); 1433 (w, ν_{P-C}); 1475 (w, $\nu_{C=C}$). ^{1}H NMR ($CDCl_3$, δ): 3.95 (s, 5 H, C_5H_5), 4.16 (4 H, C_5H_4), 4.25 (pq, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.33 (2 H, C_5H_4), 4.35 (pt, J_{HH} = 1.8 Hz, C_5H_4), 4.54 (pt, J_{HH} = 2.4, 1.98 Hz, 2 H, C_5H_4), 5.30 (CH_2/CH_2Cl_2), 6.47−6.48 (m, 2 H, C_6H_5), 7.07−7.09 (m, 2 H, C_6H_5), 7.68 (2 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 53.52 (CH_2/CH_2Cl_2), 65.36 (C_5H_4), 66.81 (C_5H_4), 66.90 (C_5H_4), 68.19 (C_5H_5), 69.5 (C_5H_4), 70.38 (C_i/C_5H_4), 73, 73.09 (d, J_{CP} = 10 Hz, C_5H_4−P), 73.17, 73,27 (d, J_{CP} = 12.5 Hz, C_5H_4−P), 80.98 (C_i/C_5H_4), 85.03 (C_i/C_5H_4), 127.10, 127.20 (d, J_{CP} = 12.6 Hz, C_o/C_6H_5), 130.13, 130.16 (d, J_{CP} = 3.4 Hz, C_m/C_6H_5), 131.03, 131.12 (d, J_{CP} = 10.9 Hz, C_p/C_6H_5), 132.37, 133 (d, J_{CP} = 78.6 Hz, C_i/C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 31.8 ppm ($J_{^{31}P^{77}Se}$ = 731.18 Hz). HRMS (ESI-TOF): m/z calcd for $C_{32}H_{27}Fe_2PSe$ ([M]$^+$) 633.9713, found 633.9690 (100%).

*Synthesis of Bfc(Se═P(2-CH$_3$C$_6$H$_4$)$_2$) (**15**).* According to the procedure earlier described, **7** was reacted with 20.35 mg (0.25 mmol) of selenium. The title compound **15** was obtained as an orange solid. Yield: 100 mg (0.15 mmol, 89% based on **7**). Anal. Calcd for $C_{34}H_{31}Fe_2PSe$ (661.23 g/mol): C, 61.757; H, 4.725. Found: C, 61.37; H, 4.85. Mp: 185 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 558, 575 (m, $\nu_{P=Se}$); 1448 (m, ν_{P-C}); 1559 (m, $\nu_{C=C}$). ^{1}H NMR ($CDCl_3$, δ): 1.99 (s, 6 H, CH_3), 3.93 (s, 5 H, C_5H_5), 4.1 (2 H, C_5H_4), 4.13 (bs, 2 H, C_5H_4), 4.24 (2 H, C_5H_4), 4.29 (2 H, C_5H_4), 4.3 (bs, 2 H, C_5H_4), 7.11−7.18 (m, 4 H, $C_6H_4CH_3$), 7.37 (bm, 4 H, $C_6H_4CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 21.75 (m, CH_3), 65.27 (C_5H_4), 66.83 (C_5H_4), 66.9 (C_5H_4), 68.19 (s, C_5H_5), 70.07 (C_5H_4), 72.9 (C_5H_4−P), 73.03 (C_5H_4−P), 75 (C_i/C_5H_4), 81.08 (C_i), 84.88 (C_i), 125.27, 125.37 (d, J_{CP} = 12.5 Hz, $C_6H_4CH_3$), 127.21 ($C_6H_4CH_3$), 130.33 ($C_6H_4CH_3$), 130.61, 130.7 (d, J_{CP} = 10.19 Hz, $C_6H_4CH_3$), 138.9, 139 (d, J_{CP} = 8.1 Hz, $C_i/C_6H_4CH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 29.5 ppm ($J_{^{31}P^{77}Se}$ = 715 Hz).

*Synthesis of Bfc(Se═P(2-^{c}C$_4$H$_3$O)$_2$) (**16**).* As described earlier, **8** was reacted with 22 mg (0.28 mmol) of selenium. **16** was obtained as an orange solid. Yield: 110 mg (0.179 mmol, 99.6% based on **8**). Anal. Calcd for $C_{28}H_{23}Fe_2O_2PSe$ (613.10 g/mol): C, 54.85; H, 3.78. Found: C, 55.0; H, 3.9. Mp: 200 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 585, 595 (m, $\nu_{P=Se}$); 1002 (m, ν_{C-O}); 1454 (w, ν_{P-C}); 1556 (w, $\nu_{C=C}$), 3084 (m, $\nu_{C(sp^2)-H}$). ^{1}H NMR ($CDCl_3$, δ): 3.95 (s, 5 H, C_5H_5), 4.16 (pq, J_{HH} = 1.7, 3.0 Hz, 2 H, C_5H_4), 4.26 (pq, J_{HH} = 1.8, 3.6 Hz, 2 H, C_5H_4), 4.33 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.36 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.55 (pq, J_{HH} = 2, 4.4 Hz, 2 H, C_5H_4), 6.48−6.49 (m, J_{HH} = 1.6, 3.3 Hz, 2 H, C_4H_3O), 7.09−7.1 (m, 2 H, C_4H_3O), 7.68−7.7 ppm (m, 2 H, C_4H_3O). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 65.44 (C_5H_4), 66.85 (C_5H_4), 66.96 (C_5H_4), 68.21 (C_5H_5), 69.43 (C_5H_4), 69.93 (C_i/C_5H_4), 70.73 (C_i/C_5H_4), 72.7, 72.8 (d, J_{CP} = 14.8 Hz, C_5H_4−P), 73.06, 73.15 (d, J_{CP} = 11.5 Hz, C_5H_4−P), 80.96 (C_i/C_5H_4, C_5H_4−P), 85.29 (C_i/C_5H_4, C_5H_4−P), 109.05, 109.98 (d, J_{CP} = 9.6 Hz, C_4H_3O), 120.89, 121.07 (d, J_{CP} = 21.8 Hz, C_4H_3O), 145.89, 146.79 (d, J_{CP} = 114.2 Hz, C_i/C_4H_3O), 147.11, 147.17 (d, J_{CP} = 6.9 Hz, C_4H_3O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −5.2 ppm ($J_{^{31}P^{77}Se}$ = 768 Hz). HRMS (ESI-TOF): m/z calcd for $C_{28}H_{23}Fe_2O_2PSe$ ([M]$^+$) 613.9298, found 613.9278 (100%).

*Synthesis of Bfc(Se═P(^{c}C$_6$H$_{11}$)$_2$) (**17**).* Molecule **9** was reacted with 21 mg (0.26 mmol) of selenium as stated earlier. Compound **16** was obtained as an orange solid. Yield: 100 mg (0.15 mmol, 91% based on **9**). Anal. Calc. for $C_{32}H_{39}Fe_2PSe$ (645.27 g/mol): C, 59.56; H, 6.091. Found: C, 59.8; H, 6.05. Mp: 165 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 554, 533 (m, $\nu_{P=Se}$); 1448 (m, ν_{P-C}). ^{1}H NMR ($CDCl_3$, δ): 1.22−1.27 (m, 9 H, C_6H_{11}), 1.64−1.66 (m, 2 H. C_6H_{11}), 1.79−1.82 (m, 4 H, C_6H_{11}), 1.9−1.98 (m, 7 H, C_6H_{11}), 3.97 (s, 5 H, C_5H_5), 4.15 (pq, J_{HH} = 1.59, 1.66 Hz, 2 H, C_5H_4), 4.18 (pt, J_{HH} = 1.76 Hz, 2 H, C_5H_4), 4.23 (pq, J_{HH} = 1.6, 1.7 Hz, 2 H, C_5H_4), 4.38 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.39 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4), 4.47 (pt, J_{HH} = 1.8 Hz, 2 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 24.8 (CH_2/C_6H_{11}), 25.37, 25.38 (d, J_{CP} = 1.7 Hz, CH_2/C_6H_{11}), 25.41, 25.45 (d, J_{CP} = 5.4 Hz, CH_2/C_6H_{11}), 25.52, 25.55 (d, J_{CP} = 4.6 Hz, CH_2/C_6H_{11}), 26.25, 26.27 (d, J_{CP} = 2.8 Hz, CH_2/C_6H_{11}), 36.05, 36.4 (d, J_{CP} = 44.5 Hz, CH/C_6H_{11}), 65.54 (C_5H_4), 66.93 (C_5H_4), 66.95 (C_5H_4), 68.26 (s, C_5H_5), 69.95 (C_5H_4), 71.2 (C_i/C_5H_4), 71.69, 71.76 (d, J_{CP} = 8.1 Hz, C_5H_4−P), 71.77, 71.83 (d, J_{CP} = 6.5 Hz, C_5H_4−P), 81.33 (C_i/C_5H_4), 84.81 (C_i/C_5H_4). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 49.87 ppm ($J_{^{31}P^{77}Se}$ = 700 Hz). HRMS (ESI-TOF): m/z calcd for $C_{32}H_{39}Fe_2PSe$ ([M]$^+$) 646.0652, found 646.0634.

*Synthesis of bfc(Se═PPh$_2$)$_2$ (**18**).* According to the procedure described above, molecule **10** was reacted with 25.6 mg (0.325 mmol) of selenium. Compound **18** was obtained as an orange solid. Yield: 100 mg (0.11 mmol, 85.8% based on **10**). Anal. Calcd for $C_{44}H_{36}Fe_2P_2Se_2$ (896.31 g/mol): C, 58.96; H, 4.05. Found: C, 59.12; H, 3.98. Mp: 150 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 572, 531 (m, $\nu_{P=Se}$); 1432 (w, ν_{P-C}); 1475 (w, $\nu_{C=C}$). ^{1}H NMR ($CDCl_3$, δ): 4.13 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.2 (pt, J_{HH} = 1.9 Hz, 4 H, C_5H_4), 4.22 (pq, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.25 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 7.38−7.41 (m, 8 H, C_6H_5), 7.44−7.46 (m, 4 H, C_6H_5), 7.65−7.69 (m, 8 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 66.97 (C_5H_4), 69.74 (C_5H_4), 72.93, 73.01 (d, J_{CP} = 10 Hz, C_5H_4−P), 73.19, 73.29 (d, J_{CP} = 12.5 Hz, C_5H_4−P), 83.07 (C_i/C_5H_4), 127.13, 127.23 (d, J_{CP} = 12.2 Hz, C_o/C_6H_5), 130.19, 130.22 (d, J_{CP} = 3 Hz, C_m/C_6H_5), 131, 131.09 (d, J_{CP} = 10.8 Hz, C_p/C_6H_5), 132.26 (C_i/C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 31.7 ppm ($J_{^{31}P^{77}Se}$ = 733 Hz).

*Synthesis of bfc(Se═P(2-CH$_3$C$_6$H$_4$)$_2$)$_2$ (**19**).* Compound **11** was reacted with 24.8 mg (0.31 mmol) of selenium. Compound **19** was obtained as an orange solid. Yield: 110 mg (0.11 mmol, 92% based on **11**. Anal. Calcd for $C_{48}H_{44}Fe_2P_2Se_2\cdot{}^1/_2CH_2Cl_2$ (952.42 g/mol): C, 58.55; H, 4.55. Found: C, 58.3; H, 4.62. Mp: 200 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 574, 558 (m, $\nu_{P=Se}$); 1448 (m, ν_{P-C}); 1559 (m, $\nu_{C=C}$). ^{1}H NMR ($CDCl_3$, δ): 1.97 (bs, 12 H, CH_3), 4.2 (bs, 8 H, C_5H_4), 4.23 (bs, 8 H, C_5H_4), 5.30 (CH_2/CH_2Cl_2), 7.09−7.12 (m, 4 H, $C_6H_4CH_3$), 7.15−7.17 (m, 4 H, $C_6H_4CH_3$), 7.24 (bs, 4 H, $C_6H_4CH_3$), 7.36 (bs, 4 H, $C_6H_4CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 21.6 (m, CH_3), 53.52 (CH_2/CH_2Cl_2), 67.96 (C_5H_4), 71.3 (C_5H_4), 73.95 (C_5H_4−P), 74.0 (C_5H_4−P), 74.4 (C_i/C_5H_4, 84.0 (C_i), 126.3, 126.39 (d, J_{CP} = 13 Hz, $C_6H_4CH_3$), 128.2 ($C_6H_4CH_3$), 129.0 ($C_6H_4CH_3$), 131.66, 131.74 (d, J_{CP} = 10.1 Hz, $C_6H_4CH_3$), 139.9, 140 (d, J_{CP} = 9.3 Hz, $C_i/C_6H_4CH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 29.42 ppm ($J_{^{31}P^{77}Se}$ = 718 Hz).

*Synthesis of bfc(Se═P(2-^{c}C$_4$H$_3$O)$_2$)$_2$ (**20**).* As described earlier, **12** was reacted with 28.2 mg (0.35 mmol) of selenium. Compound **20** was obtained as an orange solid. Yield: 119 mg (0.14 mmol, 99.2% based on **12**). Anal. Calcd for $C_{36}H_{28}Fe_2O_4P_2Se_2\cdot{}^1/_2$(*n*-hexane) (856.16 g/mol): C, 52.08; H, 3.98. Found: C, 51.99; H, 4.05. Mp: 200 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 578, 569 (m, $\nu_{P=Se}$); 1014 (m, ν_{C-O}); 1458 (m, ν_{P-C}); 1559 (w, $\nu_{C=C}$), 3096 (m, $\nu_{C(sp^2)-H}$). ^{1}H NMR ($CDCl_3$, δ): 0.88 (CH_3/C_6H_{14}), 1.26 (CH_2/C_6H_{14}), 4.16 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.23 (pq, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.36 (pt, J_{HH} = 1.8 Hz, 8 H, C_5H_4), 4.5 (pq, J_{HH} = 2.4 Hz, 1.9 Hz, 4 H, C_5H_4), 6.47−6.49 (m, 4 H, C_4H_3O), 7.08 (pt, J_{HH} = 2.6 Hz, 4 H, C_4H_3O), 7.68 ppm (4 H, C_4H_3O). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 14.14 (CH_3/C_6H_{14}), 22.70 (CH_2/C_6H_{14}), 32.01 (CH_2/C_6H_{14}), 67.14 (C_5H_4), 69.7 (C_5H_4), 70.23 (C_i/C_5H_4), 72.78, 72.9 (d, J_{CP} = 14.5 Hz, C_5H_4−P), 72.96, 73.0 (d, J_{CP} = 11.4 Hz, C_5H_4−P), 83.35 (C_i/C_5H_4), 110.01, 110.08 (d, $3J_{CP}$ = 9.5 Hz, C_4H_3O), 120.9, 121.12 (d, $2J_{CP}$ = 21.9 Hz, C_4H_3O), 145.78, 146.68 (d, J_{CP} = 114 Hz, C_i/C_4H_3O), 147.18, 147.23 (d, J_{CP} = 7 Hz, C_4H_3O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −5.4 ppm ($J_{^{31}P^{77}Se}$ = 769 Hz).

*Synthesis of bfc(Se═P(^{c}C$_6$H$_{11}$)$_2$)$_2$ (**21**).* Applying the general procedure described earlier, **13** was reacted with 25.8 mg (0.32 mmol) of selenium. **21** was obtained as an orange solid. Yield: 100 mg (0.108 mmol, 83.6% based on **13**). Anal. Calcd for $C_{44}H_{60}Fe_2P_2Se_2$ (920.5 g/mol): C, 57.41; H, 6.56. Found: C, 57.50; H, 6.60. Mp: 160 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 549 (m, $\nu_{P=Se}$); 1441 (m, ν_{P-C}). ^{1}H NMR ($CDCl_3$, δ): 1.22−1.27 (m, 18 H, C_6H_{11}), 1.54 (2 H, C_6H_{11}), 1.65−1.67 (m, 4 H, C_6H_{11}), 1.80−1.83 (m, 8 H, C_6H_{11}), 1.93−1.97 (m, 12 H, C_6H_{11}), 4.16 (4 H, C_5H_4), 4.22 (4 H, C_5H_4), 4.41 (pt, J_{HH} = 1.78 Hz, 4 H, C_5H_4), 4.55 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 24.79 (CH_2/C_6H_{11}), 25.35, 25.36 (d, J_{CP} = 1.4 Hz, CH_2/C_6H_{11}), 25.40, 25.45 (d, J_{CP} = 5.7 Hz, CH_2/C_6H_{11}), 25.51, 25.55 (d, J_{CP} = 5 Hz, CH_2/C_6H_{11}), 26.23, 26.26 (d, J_{CP} = 3.2 Hz, CH_2/C_6H_{11}), 36.02, 36.37 (d, J_{CP} = 44.5 Hz, CH/C_6H_{11}), 67.34 (C_5H_4), 70.26 (C_5H_4), 71.77, 71.8 (d, J_{CP} = 3.6 Hz, C_5H_4−P), 71.84, 71.88

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(d, J_{CP} = 4.8 Hz, C_5H_4–P), 83.3 (C_i/C_5H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 49.8 ppm ($J_{^{31}P^{77}Se}$ = 700.5 Hz). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{60}Fe_2P_2Se_2$ ($[M]^+$) 922.1207, found 922.1199.

General Procedure for the Synthesis of [Pd(Bfc(PR$_2$))$_2$Cl$_2$]. To a dichloromethane solution (50 mL) containing 1 equiv of the phosphines **6**–**9** was added 0.5 equiv of $[Pd(Et_2S)_2Cl_2]$ (**22**) in a single portion, and the reaction mixture was stirred for 5 h at 25 °C. Subsequently, the solvent was reduced in volume to 3–5 mL and addition of *n*-hexane (20 mL) caused the precipitation of the appropriate product, which was then washed with *n*-hexane (2 × 10 mL) and dried under oil pump vacuum.

*Synthesis of [Pd(Bfc(PPh$_2$))$_2$Cl$_2$] (**23**).* Using the general procedure described above, 64.5 mg (0.18 mmol) of **22** were reacted with 200 mg (0.36 mmol) of **6**. Complex **23** was obtained as a red solid. Yield: 210 mg (0.16 mmol, 90.7% based on **22**). Anal. Calcd for $C_{64}H_{54}Fe_4P_2PdCl_2 \cdot {}^1/_2CH_2Cl_2$ (1285.76 g/mol): C, 58.32; H, 4.17. Found: C, 58.56; H, 4.27. Mp: 214.5 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1436 (w, ν_{P-C}); 1474, 1483 (m, $\nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 3.99 (s, 10 H, C_5H_5), 4.14 (4 H, C_5H_4), 4.18 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.35 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.47 (4 H, C_5H_4), 4.54 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.67 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 5.30 (CH_2/CH_2Cl_2), 7.35–7.44 (m, 12 H, C_6H_5), 7.61–7.65 (m, 8 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 53.52 (CH_2/CH_2Cl_2), 65.19 (C_i/C_5H_4), 66.6 (C_5H_4), 67.89 (C_5H_4), 67.94 (C_5H_4), 69.2 (C_5H_5), 71.04 (C_5H_4), 774.32 (C_5H_4), 76.04 (C_5H_4), 127.7 (pt, J_{CP} = 5.4 Hz, C_6H_5), 129.9 (C_6H_5), 130.04 (C_6H_5), 134.19 (C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 15.42 ppm (s).

*Synthesis of [Pd(Bfc(P(2-CH$_3$C$_6$H$_4$)$_2$))$_2$Cl$_2$] (**24**).* Following the general procedure stated earlier, 76.7 mg (0.21 mmol) of **22** were reacted with 250 mg (0.43 mmol) of **7**. Complex **24** was obtained as a red solid. Yield: 230 mg (0.17 mmol, 81.6% based on **22**). Anal. Calcd for $C_{68}H_{62}Fe_4P_2PdCl_2$ (1341.87 g/mol): C, 60.86; H, 4.65. Found: C, 59.84; H, 4.601. Mp: 173 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1448 (m, ν_{P-C}); 1559 (m, $\nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 2.37 (s, 12 H, CH_3), 3.97 (s, 10 H, C_5H_5), 4.14 (4 H, C_5H_4), 4.17 (pt, J_{HH} = 1.6 Hz, 4 H, C_5H_4), 4.28 (pt, J_{HH} = 1.7 Hz, 4 H, C_5H_4), 4.36–4.37 (m, 8 H, C_5H_4), 4.65 (4 H, C_5H_4), 7.14–7.20 (m, 8 H, $C_6H_4CH_3$), 7.30–7.33 (m, 4 H, $C_6H_4CH_3$), 7.9–7.94 (m, 4 H, $C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.96 (pt, J_{CP} = 3.5 Hz, CH_3), 66.44 (C_5H_4), 67.88 (C_5H_4), 68.01 (C_5H_4), 69.25 (s, C_5H_5), 72.2 (C_5H_4), 74.4 (pt, J_{CP} = 4.48 Hz, C_5H_4), 77.4 (pt, J_{CP} = 6 Hz, C_5H_4), 82.74 (C_i/C_5H_4), 85.3 (C_i/C_5H_4), 124.9 (pt, J_{CP} = 5.2 Hz, $C_6H_4CH_3$), 130.2 (s, $C_6H_4CH_3$), 131 (pt, J_{CP} = 4 Hz, $C_6H_4CH_3$), 134.9 (s, $C_6H_4CH_3$), 142.31, 142.35 (d, J_{CP} = 5.65, $C_i/C_6H_4CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 11.42 ppm (s).

*Synthesis of [Pd(Bfc(P(2-^{c}C$_4$H$_3$O)$_2$))$_2$Cl$_2$] (**25**).* A 67 mg portion (0.187 mmol) of **22** was reacted with 200 mg (0.374 mmol) of **8**, applying the procedure described above. Complex **25** was obtained as a red solid. Yield: 230 mg (0.181 mmol, 97% based on **22**). Anal. Calcd for $C_{56}H_{46}Fe_4O_4P_2PdCl_2 \cdot {}^1/_4CH_2Cl_2$ (1266.84 g/mol): C, 53.32; H, 3.69. Found: 53.25, 3.76. Mp: 126.6 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1007 (m, ν_{C-O}); 1455 (m, ν_{P-C}); 1555 (m, $\nu_{C=C}$); 3104 (m, $\nu_{C(sp^2)-H}$). ^1H NMR ($CDCl_3$, δ): 3.97 (s, 10 H, C_5H_5), 4.16 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.22 (4 H, C_5H_4), 4.38 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.58 (pt, J_{HH} = 1.7, 1.8 Hz, 8 H, C_5H_4), 4.61 (pt, J_{HH} = 1.7, 1.8 Hz, 4 H, C_5H_4), 4.67 (4 H, C_5H_4), 5.30 (CH_2/CH_2Cl_2), 6.47 (m, 4 H, C_4H_3O), 7.04, 7.05 (d, J_{HH} = 3.4 Hz, 4 H, C_4H_3O), 7.71 (m, 4 H, C_4H_3O). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 53.52 (CH_2/CH_2Cl_2), 65.6 (C_5H_4), 66.8 (C_5H_4), 66.98 (C_5H_4), 68.2 (C_5H_5), 69.9 (C_5H_4), 70.81 (C_i/C_5H_4), 71.33 (C_i/C_5H_4), 73.2 (C_5H_4–P), 74.1 (C_5H_4–P), 85 (C_i/C_5H_4), 109.7 (C_4H_3O), 122.3 (C_4H_3O), 146.4 (pt, J_{CP} = 3.2 Hz, C_4H_3O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −14.2 ppm (s).

*Synthesis of [Pd(Bfc(P(^{c}C$_6$H$_{11}$)$_2$))$_2$Cl$_2$] (**26**).* A 79 mg portion (0.22 mmol) of **22** was reacted with 250 mg (0.44 mmol) of **9** as described earlier. Complex **26** was obtained as a red solid. Yield: 250 mg (0.19 mmol, 86.7% based on **22**). Anal. Calcd for $C_{64}H_{78}Fe_4P_2PdCl_2 \cdot {}^1/_4CH_2Cl_2$ (1309.95 g/mol): C, 57.96; H, 5.94. Found: C, 58.06; H, 6.17. Mp: 220 °C dec. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1447 (m, ν_{P-C}). ^1H NMR ($CDCl_3$, δ): 1.26–1.33 (m, 16 H, C_6H_{11}), 1.69–1.8 (m, 16 H, C_6H_{11}), 2.05–2.08 (m, 4 H, C_6H_{11}), 2.33–2.35 (m, 4 H, C_6H_{11}), 2.5–2.6 (m, 4 H, C_6H_{11}), 3.98 (s, 10 H, C_5H_5), 4.12 (4 H, C_5H_4), 4.18 (pt, J_{HH} = 1.76 Hz, 4 H, C_5H_4), 4.38 (pt, J_{HH} = 1.78 Hz, 4 H, C_5H_4), 4.51 (pt, J_{HH} = 1.75 Hz, 4 H, C_5H_4), 4.55 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 4.57 (4 H, C_5H_4), 5.30 (CH_2/CH_2Cl_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 26.37 (CH_2/C_6H_{11}) 27.55 (CH_2/C_6H_{11}), 27.68 (CH_2/C_6H_{11}), 28.85 (CH_2/C_6H_{11}), 30.07 (CH_2/C_6H_{11}), 36.75 (pt, J_{CP} = 11 Hz, CH/C_6H_{11}), 53.52 (CH_2/CH_2Cl_2), 66.43 (C_5H_4), 67.74 (C_5H_4), 67.82 (C_5H_4), 69.24 (C_5H_5), 71.02 (C_5H_4), 72.86 (C_5H_4–P), 75.14 (pt, J_{CP} = 4.6 Hz, C_i/C_5H_4–P), 83.2 (C_i/C_5H_4), 85.07 (C_i/C_5H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 18.2 ppm (s). HRMS (ESI-TOF): m/z calcd for $C_{64}H_{78}Fe_4P_2PdCl_2$ ($[M]^+$) 1308.1409, found 1309.1366; ($[M]^{2+}$) 655.0696, found 655.0665; $C_{64}H_{78}Fe_4P_2PdCl$ ($[M]^+$) 1273.1722, found 1273.1560.

General Procedure for the Suzuki Reaction. A 500 mg portion (2.92 mmol) of 2-bromotoluene or 464 mg (3.00 mmol) of 4′-chloroacetophenone, 470 mg (3.85 mmol) of phenylboronic acid, 1.21 g (8.76 mmol) of K_2CO_3, and 114 mg (0.50 mmol) of acetylferrocene were dissolved in 12 mL of a dioxane/water mixture (ratio 2/1, v/v). After addition of 0.25 or 0.1 mol % (reaction of 2-bromotoluene) or 0.5 mol % (reaction of 4′-chloroacetophenone) of the appropriate catalyst **23**, **24**, **25**, or **26**, the reaction mixture was stirred for 2 h at 100 °C. Samples (1 mL) were taken after 2.5, 5, 10, 20, 30, 60, 90, and 120 min and filtered through silica gel with diethyl ether as eluent. All volatiles were evaporated under reduced pressure, and the conversions were determined by ^1H NMR spectroscopy.

General Procedure for the Heck Reaction. A 612 mg portion (3.0 mmol) of iodobenzene, 397 mg (3.1 mmol) of *tert*-butyl acrylate, 415 mg (3.2 mmol) of EtN^iPr_2, and 114 mg (0.50 mmol) of acetylferrocene were dissolved in 15 mL of a toluene/acetonitrile mixture (1/1 (v/v)). After addition of 0.5 mol % of the appropriate catalyst **23**, **24**, **25**, or **26**, the reaction mixture was stirred for 10 h at 80 °C. Samples (1 mL) were taken every 1 h, and all volatiles were evaporated under reduced pressure and the conversions determined by ^1H NMR spectroscopy.

Crystallography. Crystal data for **15**, **16**, **21**, **23** and **25** are presented in the Supporting Information. All data were collected on a Oxford Gemini S diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) (**21**, **23**, **25**) and graphite-monochromated Cu Kα radiation (λ = 1.541 84 Å) (**15**, **16**) at 100 K using oil-coated shock-cooled crystals. The structures were solved by direct methods using SHELXS-97 or SIR-92 and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.[137,138] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data for the three reported X-ray crystal structures and tabulated crystal and intensity collection data for **15**, **16**, **21**, **23**, and **25**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for complexes **15**, **16**, **21**, **23**, and **25** have also been deposited with the Cambridge Crystallographic Data Centre (CCDC: 838776 (**23**), 838777 (**21**), 838778 (**25**), 838779 (**15**) and 838780 (**16**)) and can be obtained free of charge from the CCDC via http://www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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