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Synthesis, Coordination, and Catalytic Use of 1′-(Diphenylphosphino)ferrocene-1-sulfonate Anion

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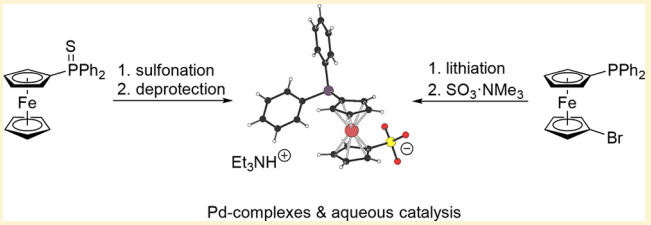
Supporting Information

ABSTRACT: Sulfonation of (diphenylphosphinothioyl)-ferrocene (**1**) with chlorosulfonic acid in acetic anhydride affords the crude sulfonic acid $Ph_2P(S)fcSO_3H$ (**2**; fc = ferrocene-1,1′-diyl), which can be efficiently purified and isolated after conversion to $Ph_2P(S)fcSO_3(HNEt_3)$ (**3**). Methyl triflate/$P(NMe_2)_3$ can be used to convert compound **3** to the stable sulfonate salt $Ph_2PfcSO_3(HNEt_3)$ (**4**) and $Ph_2P(Me)fcSO_3$ (**5**) as a minor, zwitterionic byproduct. Alternatively, compound **4** can be prepared by lithiation of 1′-(diphenylphosphino)-1-bromoferrocene (**6**; Ph_2PfcBr) and trapping of the lithiated intermediate with $SO_3{\cdot}NMe_3$. Reactions of $[(L^{NC})PdX]_2$ and $[(L^{SC})PdX]_2$, where X = Cl, AcO, L^{NC} = 2-[(dimethylamino-κ*N*)methyl]phenyl-κC^1, and L^{SC} = 2-[(methylthio-κ*S*)methyl]phenyl-κC^1, with **4** uniformly produced the bis-chelate complexes $[(L^{NC})Pd(Ph_2PfcSO_3\text{-}\kappa^2O,P)]$ (**7**) and $[(L^{SC})Pd(Ph_2PfcSO_3\text{-}\kappa^2O,P)]$ (**8**), respectively. The reaction of $[PdCl_2(MeCN)_2]$ with **4** afforded the bis(phosphine) complex *trans*-$(Et_3NH)_2[PdCl_2(Ph_2PfcSO_3\text{-}\kappa P)_2]$ (**9**). Complexes **7**–**9** were used as defined catalyst precursors for the Suzuki–Miyaura cross-coupling of boronic acids with acyl chlorides to give ketones. Reactions of aromatic substrates in the presence of Na_3PO_4 and **9**, the base and Pd source that showed the best performance, in a toluene/water biphasic system provided the coupling products in good yields; however, aliphatic substrates typically resulted in poor conversions. Extensive tests of the reaction scope revealed that the transposition of the substituents between the reaction partners can have a substantial effect on the yield of the coupling product in otherwise complementary reactions, which highlights the importance of the judicious choice of starting materials for this particular reaction.



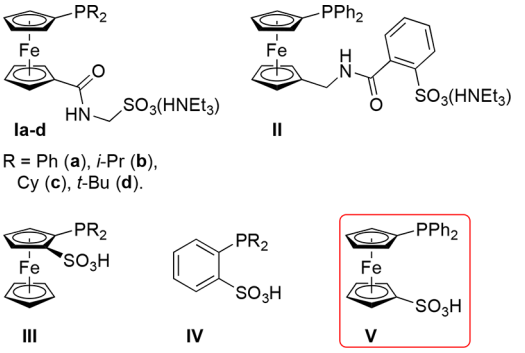
INTRODUCTION

Sulfonated phosphines, such as the iconic 3,3′,3″-phosphinidynetris(benzenesulfonic acid) trisodium salt (TPPTS),[1] are recognized as efficient supporting ligands for a range of transition-metal-catalyzed reactions and, specifically, for reactions conducted in aqueous reaction media.[2] However, their advantages have not been adequately reflected in the chemistry of otherwise widely utilized ferrocene phosphines.[3] Although the synthesis of ferrocenesulfonic acid, $FcSO_3H$ (Fc = ferrocenyl) by the direct sulfonation of ferrocene was described already in 1955,[4,5] the chemistry of sulfonated phosphinoferrocene ligands remained unexplored for decades, likely due to synthetic complications resulting from the facile oxidation of the ferrocene unit during the sulfonation.[6,7]

To avoid the synthetic challenges associated with the use of aggressive sulfonating agents, we initially prepared phosphinoferrocene sulfonates indirectly by the assembly of suitable functional building blocks. The resulting compounds **Ia-d**[8] and **II**[9] (Chart 1), in which the phosphinoferrocene and sulfonate moieties are connected by an amide linkage,[10] not only were highly hydrophilic but also showed favorable catalytic activity.[8,9] In contrast, Erker et al. synthesized a series of 2-phosphinoferrocene-1-sulfonic acids **III**,[11,12] which are indeed closer to the archetypal phosphinosulfonate donors, by utilizing an ortho-lithiation/functionalization approach developed previously for the synthesis of 2-phosphinobenzenesulfonates **IV** from the corresponding sulfonic acids.[13,14] Similar to the studies conducted on **IV**-type ligands, Pd(II) and Ni(II) complexes with these ferrocene ligands were employed as catalysts for various (co)polymerization reactions.[11,15]

Given our longstanding interest[16] in the chemistry of functional, hybrid[17] phosphinoferrocene donors formally resulting through the replacement of one phosphine substituent

Chart 1. Relevant Examples of Phosphinosulfonate Ligands



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Organometallics XXXX, XXX, XXX–XXX

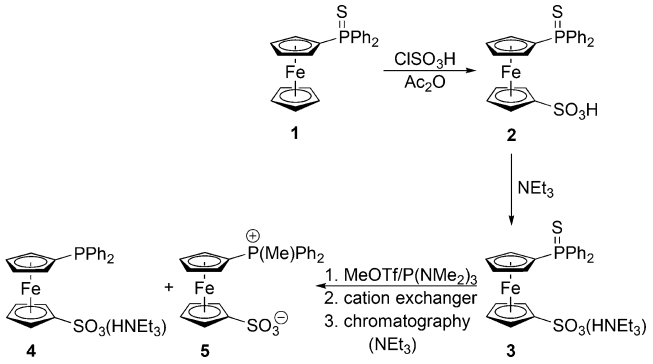
in 1,1′-bis(diphenylphosphino)ferrocene (dppf)[18] with another functional group, we decided to synthesize 1′-(diphenylphosphino)ferrocene-1-sulfonic acid (**V**), which represents a hitherto unknown isomer of compound **III** (R = Ph) and could complement the analogous, previously studied phosphinocarboxylic ligand 1′-(diphenylphosphino)ferrocene-1-carboxylic acid (Hdpf).[19]

This contribution describes the synthesis of triethylammonium 1′-(diphenylphosphino)ferrocene-1-sulfonate, a stable salt of the target acid **V**, the coordination of the 1′-(diphenylphosphino)ferrocene-1-sulfonate anion toward Pd(II) ions bearing different supporting ligands, and the activity of the prepared complexes in Pd-catalyzed Suzuki–Miyaura-type cross-coupling of acyl chlorides with boronic acids to give ketones.

RESULTS AND DISCUSSION

Synthesis of the Target Phosphinoferrocene Sulfonate. Two synthetic routes were designed for the preparation of 1′-(diphenylphosphino)ferrocene-1-sulfonic acid. In the first route (Scheme 1), 1′-(diphenylphosphinothioyl)ferrocene,

Scheme 1. Synthesis of 4 by Sulfonation of 1



$FcP(S)Ph_2$ (**1**; Fc = ferrocenyl), serving as a P-protected starting material, was sulfonated with chlorosulfonic acid in acetic anhydride as previously described for the sulfonation of ferrocene itself.[20] Following hydrolysis and concentration, the formed 1′-(diphenylphosphinothioyl)ferrocene-1-sulfonic acid (**2**) was isolated by chromatography.[21] Screening experiments showed that the outcome of the reaction is strongly dependent on the reaction time and that free acid **2** is relatively unstable. For instance, when the sulfonation was performed at room temperature overnight, the yield of **2** was only 19% with the corresponding phosphine oxide being formed as a side product (approximately 16%). When the reaction time was decreased to 3 h, the yield of **2** increased to 68%, whereas reaction times of 1 h and 30 min resulted in 77% and 64% isolated yields of crude **2**, respectively. Notably, attempts to sulfonate $FcPPh_2$ and $FcPPh_2{\cdot}BH_3$ by a similar procedure were unsuccessful and resulted in the formation of phosphine oxide $FcP(O)Ph_2$ (see ref 6).

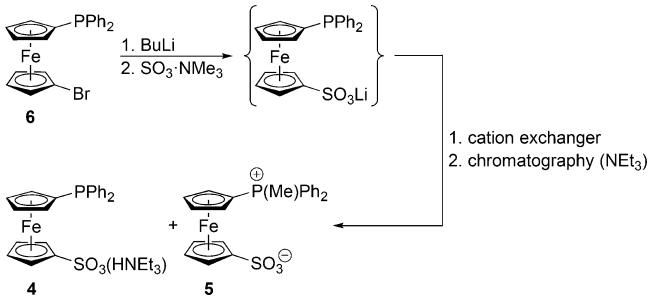
As free acid **2** proved to be prone to decomposition (especially in solution), in subsequent experiments, it was converted to the corresponding triethylammonium salt **3**. This salt is stable enough to be purified by chromatography and can even be crystallized. The optimized procedure described below (see the Experimental Section) reproducibly afforded salt **3** in yields of approximately 75%.

Subsequent deprotection of the phosphine group was performed by reacting salt **3** successively with methyl triflate and tris(dimethylamino)phosphine. Unlike treatment of **3** with only $P(NMe_2)_3$,[22] this deprotection, consisting of sequential *S*-methylation and desulfurization,[23] could advantageously be performed at relatively lower temperatures, which prevents thermal decomposition, and also in a more polar, halogenated solvent that can better dissolve the sulfonate salt. However, the use of MeOTf somewhat complicated the subsequent purification due to partial alkylation[24] of the regenerated phosphine moiety upon the formation of the zwitterionic side product $Ph_2P(Me)fcSO_3$ (**5**) and, more importantly, due to the formation of other counterions (such as $(Me_2N)_3PSMe^+$ and Et_3NMe^+)[25] that had to be replaced with $HNEt_3^+$ to ensure sample homogeneity.

Under the optimized conditions, the crude product obtained after sequential treatment of **3** with MeOTf[26] and $P(NMe_2)_3$ was passed through a cation exchanger (to produce free acid **V**[27]). The obtained crude material was purified by chromatography over silica gel using a NEt_3-containing mobile phase. This procedure was repeated twice, and ultimately, salt **4** was crystallized from dichloromethane/ethyl acetate to produce analytically pure product in 39% yield. Compound **4** thus isolated is an air-stable, rusty orange crystalline solid that is soluble in water, methanol, dichloromethane, and chloroform but is practically insoluble in diethyl ether and hexane. In addition, the combined fractions predominantly containing zwitterion **5** were rechromatographed and crystallized to provide **5** in 8% yield.

The alternative synthesis of **4** was based on a lithiation/functionalization approach commonly used to prepare functionalized ferrocene phosphines[28] (Scheme 2). In the first step, 1′-

Scheme 2. Preparation of 4 by Lithiation/Functionalization of 6



(diphenylphosphino)-1-bromoferrocene (**6**) was lithiated with butyllithium in THF at −78 °C, and the formed lithium salt was (without isolation) reacted with $SO_3{\cdot}NMe_3$.[29] Chromatographic purification afforded (diphenylphosphino)ferrocene, a major side product resulting from protonolysis of the lithiated intermediate (33% yield),[30] and crude salt Ph_2PfcSO_3Li, which was directly converted to the free acid over a cation exchanger and neutralized with NEt_3. Subsequent chromatographic purification followed by crystallization produced salt **4** in 30% yield. Compound **5**, which was detected in only minor amounts in this case, was not isolated.

Both synthetic routes provide the target salt **4** in similar overall yields (approximately 30%). However, the lithiation route is shorter and operationally simpler (especially during the isolation of the product), whereas the sulfonation route uses an easily accessible starting material but requires a more tedious

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Organometallics XXXX, XXX, XXX–XXX

isolation procedure. It is also worth mentioning that, although the sulfonation route does not involve any alkylation step, it still produces zwitterion **5** as a side product (albeit in tiny amounts). Additional experiments revealed that compound **5** is indeed formed during chromatography over a cation exchanger, presumably by acid-catalyzed alkylation of **4** (or free acid **V**) with methanol.[31]

The ^{1}H and ^{13}C NMR spectra of **3**–**5** showed signals typical for a disubstituted ferrocene unit, an attached PPh_2 moiety, and $HNEt_3$ cation (if present). The signals of the *P*-Me group in **5** appear as ^{31}P-coupled doublets at δ_H 3.08 ($^{2}J_{PH}$ = 14.5 Hz) and δ_C 6.67 ($^{1}J_{PC}$ = 59 Hz).[32] The derivatization of the phosphorus substituent is clearly reflected in the ^{31}P NMR spectra, which show distinct singlets at δ_P 42.0, −16.5 and 24.5 for **3**–**5**, respectively. In addition to the downfield shift of the ^{13}C NMR signal of the ferrocene *C*-SO_3 carbon (δ_C ∼94 for **3** and **4**, δ_C ∼99 for **5**), the presence of the sulfonate moiety was further confirmed by IR spectra showing bands due to the $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$ vibrations (ν_{as} ∼1150–1250 cm^{-1}, ν_s ∼1040 cm^{-1}).[8]

The crystal structures of compounds **4** and **5** are displayed in Figure 1 (a structural diagram for compound **3** is available in the Supporting Information). Selected geometric parameters are presented in Table 1.

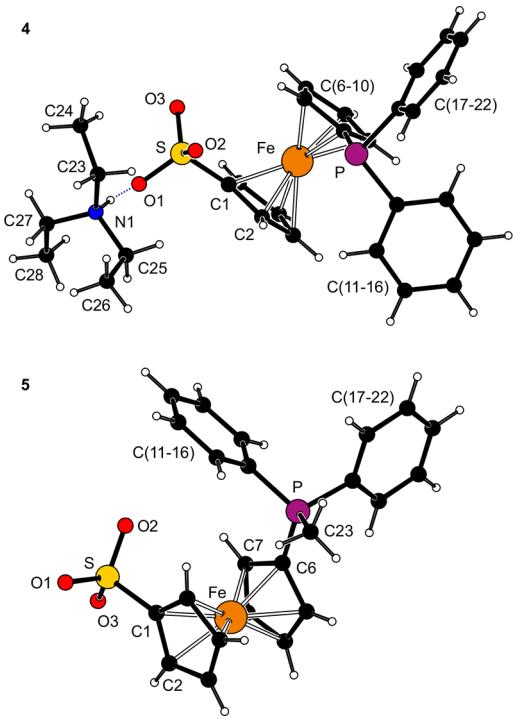


Figure 1. Molecular structures of compounds **4** and **5**. The NH···O hydrogen bond is indicated by a dotted line.

The central ferrocene moieties in the structures of **3**–**5** show almost negligible tilting but different conformations.[18a] In the case of **4** and **5**, the phosphorus and sulfonate substituents assume positions halfway between synclinal eclipsed and anticlinal staggered conformations, whereas in **3**, the substituents are rotated to more distant positions (cf. the τ angles in Table 1). The P–C distances vary noticeably across the series, increasing from **5** via **3** to **4**.[33] This increase can be attributed to the increasing P–C bond orders resulting from the shift of the electron density toward the phosphorus atom upon introduction of the electronegative sulfur atom or quaternization. Additionally, the presence of the fourth substituent on the phosphorus atom in **3** and **5** increases the C–P–C(Ph) angles. In contrast, the geometry of the sulfonate moiety is similar in all three compounds and is comparable to that determined for $(NH_4)_2[fc(SO_3)_2]$[34] and the salts obtained from $FcSO_3H$ and various nitrogen bases.[35] In the structures of **3** and **4**, the sulfonate groups become involved in charge-assisted hydrogen bonding interactions with the $HNEt_3^+$ cations (N1–H1N···O1–S) at identical N1···O1 distances (2.758(2) and 2.759(2) Å, respectively).

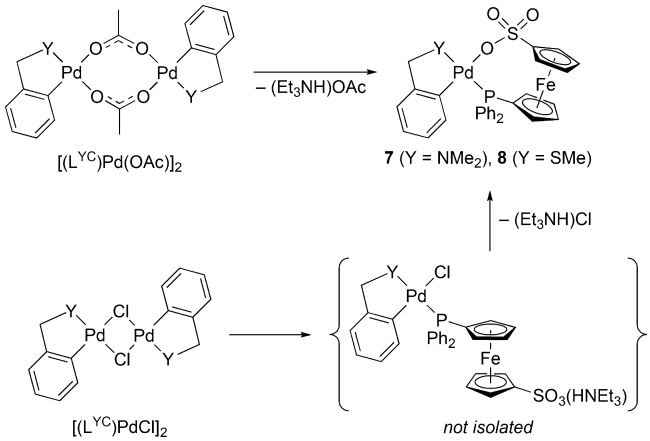
Table 1. Selected Distances (Å) and Angles (deg) for 3–5[a]

param	3	4	5
Y	S1P	void	C23
C1–S1	1.760(2)	1.755(2)	1.775(2)
S–O1	1.470(1)	1.466(2)	1.461(2)
S–O2	1.436(2)	1.445(2)	1.450(2)
S–O3	1.452(2)	1.442(2)	1.454(2)
C6–P	1.787(2)	1.812(2)	1.756(2)
P–Y	1.9614(7)	n.a.	1.790(2)
∠Cp1,Cp2	1.3(1)	2.2(1)	1.8(1)
τ	157.4(1)	86.3(1)	87.8(1)

[a]Definitions: Cp1 and Cp2 are the C(1–5) and C(6–10) cyclopentadienyl rings, respectively. Cg1 and Cg2 are their respective centroids. τ is the torsion angle of C1–Cg1–Cg2–C6. n.a. = not applicable.

Preparation of the Pd(II) Complexes. The coordination properties of the phosphinoferrocene sulfonate anion $Ph_2PfcSO_3^-$ were assessed through reactions of the salt **4** with Pd(II) precursors possessing different supporting ligands. The aim was to prepare a series of compounds in which the anion coordinates in diverse modes, particularly as a P,O-chelating and a P-monodentate ligand. First, we studied the reactions of **4** with acetate-bridged dimers $[(L^{YC})Pd(OAc)]_2$ containing ortho-palladated auxiliary ligands L^{YC} (L^{YC} = 2-[(dimethylamino-κN)methyl]phenyl-κC^1 and 2-[(methylthio-κS)methyl]phenyl-κC^1). These reactions proceeded with cleavage of the dimeric Pd(II) precursors and elimination of $(Et_3NH)OAc$ to produce the structurally analogous complexes **7** and **8**, which feature the phosphinoferrocene sulfonate anion as an O,P-chelating donor (Scheme 3).

Scheme 3. Synthesis of Pd(II) Complexes with Ortho-Palladated Auxiliary Ligands



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Organometallics XXXX, XXX, XXX–XXX

Identical products were isolated from the reactions of **4** with $[(L^{YC})PdCl]_2$ (after crystallization). Indeed, NMR monitoring of the reaction between **4** and $[(L^{NC})PdCl]_2$ (in $CDCl_3$) indicated the formation of two compounds with ^{31}P NMR signals at δ_P 28.4 and 32.8, which correspond to **7** and the plausible bridge cleavage product $(Et_3NH)[(L^{NC})PdCl(Ph_2PfcSO_3\text{-}\kappa P)]$[36] (see Scheme 3), respectively. However, the latter complex, which is the major component in this mixture, is converted to chelate complex **7** during crystallization through the elimination of $(Et_3NH)Cl$.

The signals of the coordinated NMe_2 and SMe fragments in the ^1H and ^{13}C NMR spectra of **7** and **8** appear as characteristic ^{31}P-coupled doublets that suggest a trans-P,Y arrangement, while the coordination of the phosphine moiety is indicated by the shift of the ^{31}P NMR signals to a lower field (δ_P 28.4 and 26.2 for **7** and **8**, respectively). The formulation of **7** and **8** was further supported by the ESI MS spectra showing the respective pseudomolecular ions.

Compound **7** crystallized as an ethyl acetate solvate with the solvent molecules disordered in the structural voids and with two structurally independent but similar molecules per the asymmetric unit (the molecules differ mainly in the conformation of the peripheral substituents; see the overlap in the Supporting Information). Views of molecule 1 of this complex and the structure of compound **8**[37] are shown in Figure 2. Selected geometric parameters are given in Table 2.

The molecules of both complexes include two metallocycles sharing the central Pd atom and have the anticipated trans-P,Y geometry. The Pd−donor distances fall into the ranges reported for analogous $(L^{YC})Pd^{II}$ complexes with phosphinoferrocene carboxylate ligands,[16h,i] and the coordination environments of the Pd(II) ions are characteristically angularly distorted. In both structures, the most acute cis-interligand angle is associated with the small and rigid ring constituted by the chelating L^{YC} ligand, whereas the largest interligand angle is the P−Pd−C23 angle in the adjacent position. The P−Pd−O angles associated with the chelating phosphinosulfonate ligand in **7** and **8** (~90°) fall between the values reported for *cis*-$[Pd(2\text{-}Ph_2PC_6H_4SO_3\text{-}\kappa^2O,P)_2]$ (~85°)[38] and $[PdMe(2\text{-}Ph_2PC_6H_4SO_3\text{-}\kappa^2O,P)(C_5H_5N\text{-}\kappa N)]$ (~94−95°).[39] This suggests that the chelate coordination of the $Ph_2PfcSO_3^-$ anion is not compromised by the size and spatial properties of the ferrocene scaffold.

Otherwise, however, the palladium center and its four ligating atoms remain nearly coplanar (within ca. 0.1 Å with respect to the mean plane). The $(L^{YC})Pd$ fragments adopt approximate envelope conformations with the donor atoms Y at the tip position. For both complexes, the coordinated S−O bonds are significantly longer than the remaining, formally S=O bonds. Finally, the ferrocene cylopentadienyl rings in **7** and **8** are tilted by less than 4° and rotated so that their substituents which are involved in chelate coordination assume positions roughly halfway between staggered and eclipsed synclinal (cf. the ideal values: 36 and 72°).

In addition to the neutral complexes with the L^{YC} chelating ligands, we also prepared the anionic bis(phosphine) complex *trans*-$(Et_3NH)_2[PdCl_2(Ph_2PfcSO_3\text{-}\kappa P)_2]$ (**9**), by reacting compound **4** (2 equiv) with $[PdCl_2(MeCN)_2]$ (Scheme 4). This complex was conveniently purified by crystallization from methanol/diethyl ether to afford the red, air-stable stoichiometric solvate **9**·2MeOH. This compound, however, readily loses the solvent of crystallization (under vacuum or even upon prolonged storage under ambient conditions) to produce defined, solvent-free **9**.

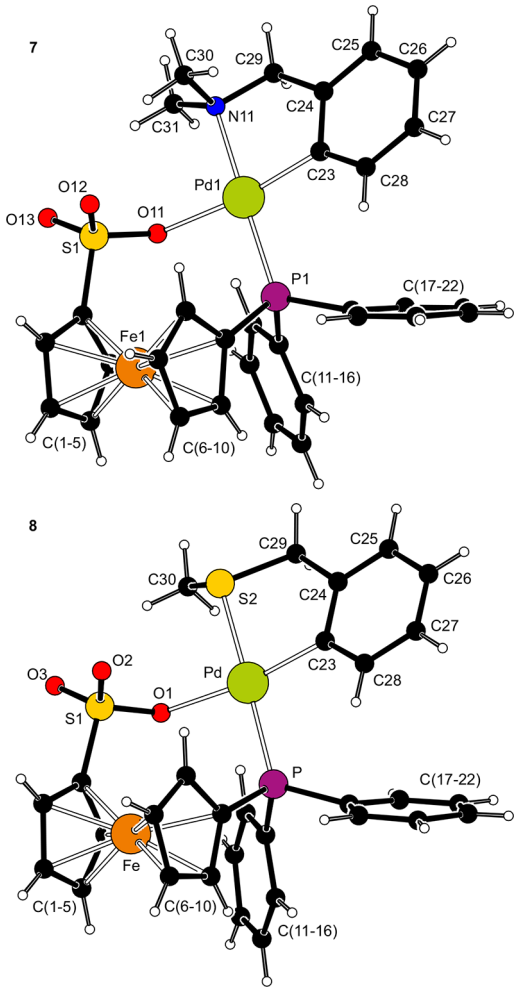

Figure 2. Molecular structures of $(L^{YC})Pd(II)$ complexes **7** (molecule 1) and **8**.

Table 2. Selected Distances (Å) and Angles (deg) for 7 and 8[a]

	complex **6** (Y = N)		
param	molecule 1	molecule 2	**7** (Y = S)
Pd−P	2.2944(6)	2.2626(6)	2.3298(5)
Pd−O	2.152(2)	2.170(2)	2.153(2)
Pd−Y	2.142(2)	2.155(2)	2.3166(5)
Pd−C	2.004(2)	1.979(3)	2.015(2)
P−Pd−O	89.43(5)	90.93(4)	89.64(4)
Y−Pd−C	81.92(9)	81.72(9)	82.67(6)
S−O1	1.484(2)	1.487(1)	1.485(2)
S−O2	1.437(2)	1.444(2)	1.449(2)
S−O3	1.445(2)	1.443(2)	1.443(2)
∠Cp1,Cp2	2.2(2)	3.3(2)	3.8(1)
τ	−49.9(2)	40.5(2)	−54.8(2)

[a]The parameters are defined as they were for **4** (see footnote to Table 1).

Unlike complexes **7** and **8**, compound **9** contains a pair of equivalent phosphinoferrocene sulfonate anions coordinating as monodentate phosphine ligands and two Et_3NH^+ counterions. The formation of a bis(phosphine) complex is indicated by the characteristic downfield shift of the ^{31}P NMR signal (δ_P 15.6 in

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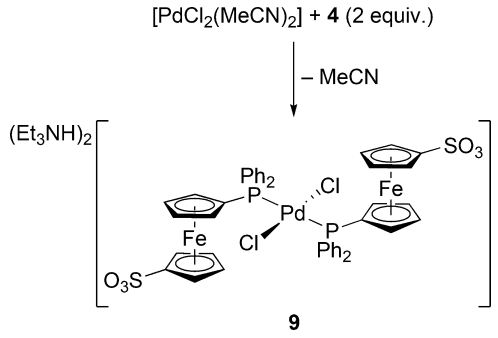
Organometallics XXXX, XXX, XXX−XXX

Scheme 4. Synthesis of Complex 9



$CDCl_3$)[40] and by the appearance of typical apparent triplets for the ^{31}P-coupled ^{13}C NMR signals resulting from virtual coupling in the $^{12}C–^{31}P–Pd–^{31}P–^{13}C$ AA′X spin system.[41]

In the crystal structure of **9**·2MeOH (Figure 3), the individual components are distributed around the crystallographic inversion centers that coincide with the Pd atoms, as is common for complexes of this kind.[42] The coordination geometry of the Pd(II) ion in **9**·2MeOH does not significantly depart from an ideal square-planar geometry because the imposed symmetry renders the coordination sphere ideally planar, the Pd–Cl and Pd–P distances are of rather similar lengths, and finally, the interligand angles differ only negligibly from the ideal 90° (by ±0.7°). The sulfonate moieties, which remain uncoordinated, are rotated away from the ligated metal center (τ = 139.5(1)°) and act as hydrogen bond acceptors for the NH and OH protons of the proximal counter cations and the solvent molecules (see Figure 3; N···O1 2.759(2) Å, O1S···O2 2.791(2) Å).

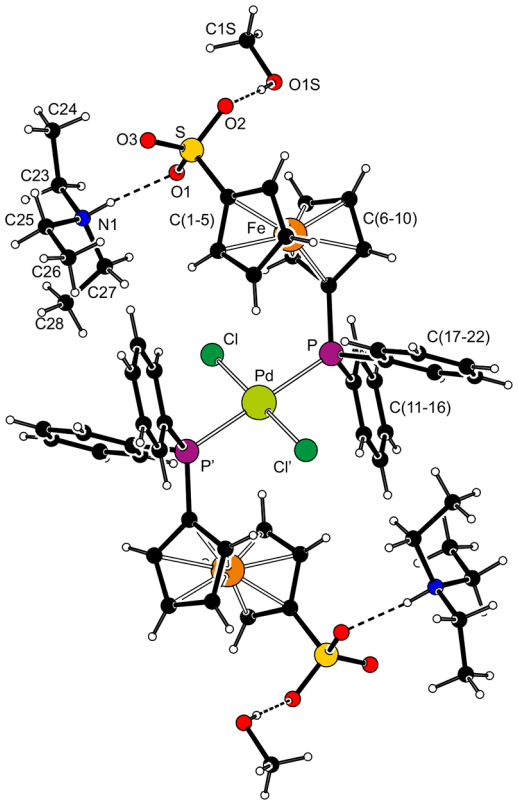


Figure 3. View of the structure of **9**·2MeOH. Hydrogen bonds are indicated by dashed lines. Selected distances (Å) and angles (deg): Pd–Cl 2.3015(5), Pd–P 2.3416(4), Cl–Pd–P 89.30(2), S–O1 1.459(1), S–O2 1.458(1), S–O3 1.448(2), ∠Cp1,Cp2 3.1(1).

Catalytic Tests. Considering the hydrophilic nature of phosphinoferrocene sulfonate **4**, we examined this polar ligand in a Pd-catalyzed Suzuki–Miyaura-type cross-coupling of acyl chlorides with boronic acids to give ketones.[43] Although this reaction may not seem economical in terms of the cost of the starting materials or atom efficiency, it offers a valuable alternative to the conventional acylation reactions because of its selectivity, functional group tolerance and the fact that both acyl chlorides and boronic acids are now readily (often commercially) available. As such, this reaction appears particularly suitable for the selective, small-scale synthesis of specifically substituted functional ketones. In addition, the reaction can be performed under aqueous conditions, which ensures the solubility of both the organic and inorganic components, making them available for the coupling reaction.

For initial screening of the factors that might affect the course of the catalytic reaction, we chose the model coupling reaction of benzoyl chloride (**10a**, used in 20 mol % excess) with 4-methoxyphenylboronic acid (**11f**), which can be easily monitored by ^{1}H NMR spectroscopy (Scheme 5). The results

Scheme 5. Coupling Reaction Used for the Initial Screening Experiments

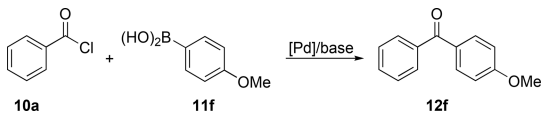


Table 3. Summary of the Screening Experiments[a]

entry	catalyst	base	solvent	NMR yield (%)
1	**9**	Na_2CO_3	H_2O	15
2	**9**/Q*	Na_2CO_3	H_2O	23
3	**9**	Na_2CO_3	C_6D_6	40
4	**9**/Q*	Na_2CO_3	C_6D_6	43
5	**9**	Na_2CO_3	C_6D_6/H_2O	90 (75)[b]
6	**9**/Q*	Na_2CO_3	C_6D_6/H_2O	89
7[c]	**9**	Na_2CO_3	C_6D_6/H_2O	52
8[c]	**9**/Q*	Na_2CO_3	C_6D_6/H_2O	50
9	**7**	Na_2CO_3	C_6D_6/H_2O	48
10	**7**/Q*	Na_2CO_3	C_6D_6/H_2O	52
11	**8**	Na_2CO_3	C_6D_6/H_2O	72
12	**8**/Q*	Na_2CO_3	C_6D_6/H_2O	79
13	**9**	K_2CO_3	C_6D_6/H_2O	69
14	**9**	$NaHCO_3$	C_6D_6/H_2O	34
15	**9**	NaOH	C_6D_6/H_2O	16
16	**9**	Na_3PO_4	C_6D_6/H_2O	96
17	**9**	NaOAc	C_6D_6/H_2O	5
18	none	Na_2CO_3	C_6D_6/H_2O	0

[a]Unless specified otherwise, 4-methoxyphenylboronic acid (**11f**; 1.0 mmol) and benzoyl chloride (**10a**; 1.2 mmol) were reacted in the presence of the specified catalyst (1.0 μmol, 0.1 mol %) and base (1.0 mmol) in 3 mL of the indicated solvent (water or a C_6D_6/H_2O (1/1) mixture) at 50 °C for 3 h. Some reactions were performed in the presence of hexadecyltrimethylammonium bromide (Q*) as a phase transfer reagent (1.0 μmol). The yields are an average of two or three independent runs. [b]Reaction with 0.05 mol % of the catalyst. [c]Reaction performed at 25 °C.

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Organometallics XXXX, XXX, XXX–XXX

outlined in Table 3 indicate that considerably better yields of coupling product **12f** (at 0.1 mol % Pd loading and 50 °C) were obtained in the organic solvent–water mixture than in either pure organic solvent or water and that the reaction is not substantially affected by the presence of hexadecyltrimethylammonium bromide as a phase transfer reagent (Table 3, entries 1–6). Both decreasing the catalyst amount to 0.05 mol % and lowering the reaction temperature to 25 °C had detrimental effects on the reaction outcome (note: the coupling reaction did not proceed in the absence of a Pd catalyst).

Complex **9** performed the best among the Pd(II) complexes evaluated in this study (Table 3, entries 5, 6, and 9–12) and was therefore selected for further experiments. The superiority of this catalyst is difficult to explain. However, tentatively it may be ascribed to a better stabilization of the catalytic metal center (two soft phosphine ligands) and/or its better solubility (or the active catalyst formed thereof) in the aqueous reaction system due to the presence of two sulfonate groups per metal center. In contrast, the presence of more easily leaving L^{YC} ligands in complexes **7** and **8** can result in a faster catalytic activation but,[44] simultaneously, also to a faster decomposition. In addition, these complexes can be expected to be less hydrophilic than **9**.

Of the tested conventional bases, only Na_3PO_4 afforded a better yield of the coupling product than Na_2CO_3, which was the base initially chosen (Table 3, entries 13–17). Hence, Na_3PO_4 was used along with **9** in all following experiments.

Having performed the screening tests in a C_6D_6/water mixture, we turned our attention to identifying a more practical solvent mixture (Table 4). Surprisingly, replacing C_6D_6 with its

Table 4. Additional Screening Experiments[a]

entry	catalyst	solvent	yield of **12f** (%)
1	**9**	C_6D_6/H_2O	95
2	**9**	C_6H_6/H_2O	80
3	**9**	toluene/H_2O	80
4[b]	**9**	toluene/H_2O	80
5[c]	**9**	toluene/H_2O	68
6	$[PdCl_2(MeCN)_2]$	toluene/H_2O	15
7	**13**	toluene/H_2O	22

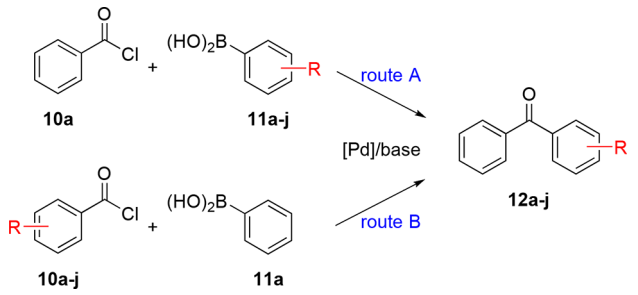
[a]Unless specified otherwise, 4-methoxyphenylboronic acid (**11f**; 1.0 mmol) and benzoyl chloride (**10a**; 1.2 mmol) were reacted in the presence of the specified catalyst (1.0 μmol Pd, 0.1 mol %) and Na_3PO_4 (1.0 mmol) in 3 mL of the indicated solvent (1/1 mixture) at 50 °C for 3 h. Isolated yields are an average of two independent runs. [b]Reaction with 0.2 mol % of catalyst. [c]Reaction performed in air.

nondeuterated counterpart or toluene resulted in reproducibly lower yields of **12f**, which did not increase even when the catalyst loading was increased to 0.2 mol % (cf. entries 1–4). Performing the coupling reaction without an inert atmosphere had a similar negative effect and further decreased the yield of the coupling product (entry 5).

Further tests nonetheless confirmed the beneficial influence of the hydrophilic sulfonate groups in **9** for the coupling reaction in the biphasic system. The model reactions conducted under the optimized conditions but with $[PdCl_2(MeCN)_2]$ or *trans*-$[PdCl_2(FcPPh_2)_2]$ (**13**), which is an analogue of complex **9** that lacks the sulfonate groups (the synthesis and crystal structure of this compound in a solvated form are described in the Supporting Information), both resulted in significantly lower yields of **12f**.

Next, we turned our attention to evaluating the reaction scope. In view of our previous studies,[45] we compared the efficacy of complementary routes leading to the same *monosubstituted* products but from starting materials with inverted substitution patterns (routes A and B in Scheme 6)

Scheme 6. Reaction Scope Tests Using Complementary Routes to Ketones 12



under rather stringent conditions (0.1 mol % Pd, 3 h reaction time). The results summarized in Table 5 indicate that only in

Table 5. Reaction Scope Tests[a]

		yield of **12** (%)	
entry	R	route A	route B
1	H (**a**)	36	
2	2-Me (**b**)	72	10
3	3-Me (**c**)	90	57
4	4-Me (**d**)	87	69
5	4-*t*Bu (**e**)	66	47
6	4-MeO (**f**)	80	8
7	4-F (**g**)	61	68
8	4-Cl (**h**)	95	>95
9	4-NO_2 (**i**)	5	87
10	4-CN (**j**)	<5	27

[a]The respective boronic acid (**11**; 1.0 mmol) and benzoyl chloride (**10**; 1.2 mmol) were reacted in the presence of **9** (1.0 μmol, 0.1 mol %) and Na_3PO_4 (1.0 mmol) in 3 mL of toluene/water (1/1) at 50 °C for 3 h. Isolated yields are an average of two independent runs. Reaction products obtained in low yields were typically contaminated by unreacted benzoyl chloride, which is not included in the tabulated yield.

some cases did the two routes perform equally well (entries 7 and 8), while more often, one of the routes provided a considerably better yield than the complementary one. For substrates bearing 3-Me, 4-Me, and 4-*t*-Bu groups, the yields achieved using route A were ~20–30% higher (in absolute terms) than those achieved using route B. Even more pronounced differences between the two routes were observed for substrates with a 2-Me substituent (where steric effects can play a role) and especially with a 4-MeO substituent. In contrast, benzophenones with 4-NO_2 and 4-CN substituents could be accessed in better yields using route B, in which the substituent comes from the acyl chloride coupling partner.

The same trends were noted also for the reactions leading to the 4,4′-disubstituted products (Table 6; note that the substrates were chosen to include both easily reacting and unreactive compounds and those with minimal steric influence from the substituents). Among the symmetrically disubstituted products, only 4,4′-dichlorobenzophenone (**12hh**) and 4,4′-dimethylbenzophenone (**12dd**) were obtained in good yields,

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Organometallics XXXX, XXX, XXX–XXX

Table 6. Results of the Coupling Reactions Providing 4,4′-Disubstituted Benzophenones 12[a]

X in 4-$XC_6H_4B(OH)_2$ (**11**)	4-$YC_6H_4C(O)Cl$ (**10**)			
	Y = Me (**d**)	Y = MeO (**f**)	Y = Cl (**h**)	Y = NO_2 (**i**)
Me (**d**)	76	5	94	85
MeO (**f**)	70	<5	91	83
Cl (**h**)	86	8	>95	94
NO_2 (**i**)	<5	0	5	<5

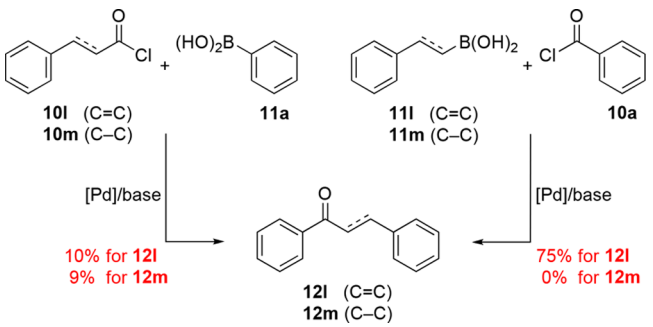
[a]The experiments were performed as described for the substrate scope tests (see footnote *a* to Table 4).

whereas those bearing a pair of methoxy and nitro groups (**12ff**,**ii**) were formed in only trace amounts (<5%). Of the six *unsymmetrical* derivatives, only 4′-methyl-4-chlorobenzophenone (**12dh**) could be obtained in good yields by both routes. In reactions leading to 4-methoxy-substituted benzophenones, the reactions involving 4-methoxyphenylboronic acid consistently produced substantially better yields than those using 4-methoxybenzoyl chloride. The opposite trend holds true for the coupling reactions providing 4-chloro- and 4-nitro-substituted compounds. Especially in the case of reactions involving 4-nitrophenylboronic acid, the yields were consistently very low (Table 5, the bottom row).

The differences in the yields of the complementary reactions, which were sometimes quite significant, can be partially attributed to the different reactivities of the substrates. However, other factors, such as side reactions (in particular hydrolysis of the acyl chlorides, which proceed at different rates for different substrates) and, more importantly, solubility issues (4-nitrophenylboronic acid is poorly soluble in the solvent mixture used), can also play an important role. From a wider perspective, the combined results clearly indicate that both complementary routes should always be considered to obtain the coupling products in the highest possible yield.

As further exemplified by the results presented in Scheme 7, the coupling reaction is not suitable for aliphatic substrates,

Scheme 7. Coupling Reactions Involving Aliphatic Substrates

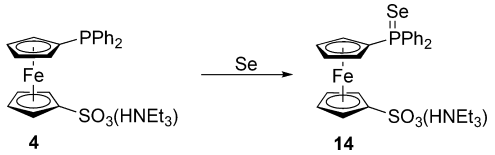


which generally fail to afford satisfactory yields of the coupling products (albeit under rather strict conditions). A notable exception is the reaction of styrylboronic acid (**11l**) with benzoyl chloride, which furnished *trans*-chalcone (**12l**) in a good yield (75% isolated).

The catalytic performance of complex **9** and the trends in reactivity are comparable to those noticed in reactions mediated by catalysts based on other phosphinoferrocene donors.[45] Hence, the favorable catalytic properties of the particular Pd(II) complex **9** may well arise from the polar nature (solubility) and possible hemilabile coordination[17] of the supporting phosphinoferrocene sulfonate ligand rather than from its peculiar stereoelectronic properties. The Tolman cone angle (θ)[46] and the solid angle (Ω)[47] calculated[48] for the anion $Ph_2PfcSO_3^-$ from the structural data determined for **9**·2MeOH were 182 and 147°, respectively. While the former value (θ) is identical with that determined for P(*t*-Bu)$_3$,[46] it is significantly smaller than the cone angle estimated for phosphinoferrocene amide $Ph_2PfcCONHMe$ (~200°).[49] In contrast, the value of the solid angle Ω, which represents the minimum steric demands, is similar to that of triphenylphosphine (~145°)[47] and compares well to the value calculated for the mentioned amide $Ph_2PfcCONHMe$ (~150°).[49]

The stereoelectronic properties of the anion $Ph_2PfcSO_3^-$ were further assessed through the $^{77}Se-^{31}P$ coupling constant ($^1J_{SeP}$), which is known to reflect both phosphine basicity and steric properties (the latter via C–P–C angles).[46,50] The $^1J_{SeP}$ value determined for phosphine selenide **14**, obtained by conventional selenylation of **4** with elemental selenium (Scheme 8), was 732 Hz. This value is very similar to that

Scheme 8. Synthesis of Phosphine Selenide 14



determined for $FcP(Se)Ph_2$ (731 Hz),[50b] suggesting that the introduced sulfonate moiety does not affect much the donor ability of the phosphinoferrocene moiety.

CONCLUSION

This report describes the synthesis of a new polar, anionic phosphinoferrocene sulfonate ligand, which extends the family of functional ligands structurally related to 1,1′-bis(diphenylphosphino)ferrocene (dppf), the archetypal ferrocene phosphine donor. Two reliable synthetic approaches for the preparation of this anionic species, which can be conveniently isolated, stored, and further utilized in the form of the stable ammonium salt **4**, are described and discussed. In addition, preliminary experiments focused on the coordination behavior of this hybrid anionic ligand toward Pd(II) ions were carried out, and as a result, two types of complexes featuring the title phosphinoferrocene sulfonate anion as either a monodentate P-donor or an O,P-chelating ligand with the sulfonate moiety also involved in coordination as a secondary donor group were prepared. Catalytic tests with the isolated complexes in the Pd-catalyzed cross-coupling of acyl chlorides with boronic acids in water/organic solvent biphasic systems to form ketones showed that bis(phosphine) complex **9** gives rise to the most active catalyst. Further catalytic experiments aimed at exploring the scope of this catalytic reaction revealed that the coupling of aromatic substrates to generate selectively substituted benzophenones is controlled by the substituents on both reaction partners, which suggests that the careful selection of starting materials (mainly in terms of possible transposition of the substituents on the aromatic rings) is essential for obtaining good yields of the coupling products. The coupling of aliphatic reagents, especially those where sp^3 carbons are supposed to couple, proceeds much less willingly.

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Organometallics XXXX, XXX, XXX–XXX

EXPERIMENTAL SECTION

General Considerations. The syntheses were performed under an argon atmosphere using standard Schlenk techniques and oven-dried glassware. Compounds **1**,[51] **6**,[52] $[Pd(OAc)(L^{NC})]_2$,[53] $[PdCl(L^{SC})]_2$,[54] and $[Pd(OAc)(L^{SC})]_2$[55] were prepared according to previously published procedures. Anhydrous dichloromethane, methanol, and tetrahydrofuran were obtained from an in-house PureSolv MD5 solvent purification system (Innovative Technology, MA, USA). $CHCl_3$ was dried over CaH_2 and distilled under argon. Acetic anhydride was distilled under argon. Other chemicals (Sigma-Aldrich and Alfa-Aesar) and solvents (Lach-Ner, Czech Republic) employed for crystallizations and chromatography were of reagent grade and were used without further purification. Cation exchange resin (Dowex 50WX4, Sigma-Aldrich) in its protonated form was washed with a large volume of methanol prior to use. This cation exchanger was used for all experiments.

Analytical measurements aimed at confirming the identity and purity of the prepared compounds were performed for bulk samples isolated as described below. The NMR spectra were recorded at 25 °C on a Varian UNITY Inova 400 spectrometer. Chemical shifts (δ in ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C) and to external 85% H_3PO_4 (^{31}P). In addition to the standard notation for the signal multiplicity,[56] vt and vq are used to distinguish virtual multiplets arising from the AA′BB′ and AA′BB′X spin systems of the ferrocene protons at the sulfonate- and PPh_2-substituted cyclopentadienyl rings, respectively (fc = ferrocene-1,1′-diyl). Infrared spectra were recorded on a Nicolet 6700 FTIR spectrometer over the 400−4000 cm^{-1} range. Low-resolution electrospray ionization (ESI) mass spectra were measured with an Esquire 3000 (Bruker) spectrometer using samples dissolved in HPLC-grade methanol. The assignment of the observed ions was confirmed by comparison of the theoretical and experimentally determined isotopic patterns. Elemental analyses were conducted with a PerkinElmer PE 2400 CHN analyzer.

Synthesis of 4 by Sulfonation of 1. Neat chlorosulfonic acid (0.73 mL, 11 mmol) was added dropwise to a suspension of phosphine sulfide **1** (4.024 g, 10 mmol) in acetic anhydride (50 mL) with stirring and cooling in a water bath. After the addition was complete (ca. 5 min), the mixture was stirred at ambient temperature for 1 h, during which time all of the starting material dissolved to give a deep green solution. The reaction mixture was then poured onto crushed ice (100 g) and stirred for another 1 h. The obtained cloudy orange mixture was filtered through a Büchner funnel (which was washed with water and acetic acid), and the filtrate was evaporated under vacuum at 40 °C. The orange solid residue was evaporated three times with dichloromethane (100 mL) and then stored over NaOH in a desiccator overnight to remove residual acetic acid and acetic anhydride.

The crude product was mixed with chloroform (100 mL), and the stirred mixture was treated with triethylamine (15 mL) while being cooled in an ice bath (30 min). Crude salt **3** obtained after evaporation of the solvent was twice dissolved in chloroform, evaporated, and then purified by silica gel chromatography using a dichloromethane/methanol/NEt_3 mixture (20/1/1) as the eluent. The main orange band (without the yellow forerun and the red tail) was collected and evaporated. The solid product was evaporated three times with chloroform and dried over H_2SO_4 overnight. Then, it was dissolved in dichloromethane (50 mL), and the solution was diluted with hot ethyl acetate (50 mL), treated with charcoal, filtered, and evaporated. Next, the residue was dissolved in hot dichloromethane (5 mL), and the solution was diluted with hot ethyl acetate (50 mL). The product, which crystallized upon slow cooling to 4 °C, was isolated by filtration, washed with ethyl acetate, and dried under vacuum to give analytically pure salt **3**. Yield: 4.463 g (76%), orange crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3 of $HNEt_3$), 3.11 (br dq, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 2.6 Hz, 6 H, CH_2 of $HNEt_3$), 4.27 (vt, J' = 1.9 Hz, 2 H, fc), 4.50 (vt, J' = 1.9 Hz, 2 H, fc), 4.58 (vq, J' = 2.0 Hz, 2 H, fc), 4.81 (vq, J' = 1.8 Hz, 2 H, fc), 7.39−7.49 (m, 6 H, PPh_2), 7.67−7.74 (m, 4 H, PPh_2), 10.38 (br s, 1 H, *H*NEt_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 42.0 (s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 8.65 (s, CH_3 of $HNEt_3$), 46.09 (s, CH_2 of $HNEt_3$), 68.96 (s, CH of fc), 71.61 (s, CH of fc), 74.21 (d, $^2J_{PC}$ = 13 Hz, CH of fc), 75.69 (d, $^1J_{PC}$ = 98 Hz, C−P of fc), 75.87 (d, $^3J_{PC}$ = 10 Hz, CH of fc), 94.49 (s, C−SO_3 of fc), 128.20 (d, J_{PC} = 13 Hz, CH of PPh_2), 131.19 (d, $^4J_{PC}$ = 3 Hz, CH_{para} of PPh_2), 131.59 (d, J_{PC} = 11 Hz, CH of PPh_2), 134.48 (d, $^1J_{PC}$ = 87 Hz, C_{ipso} of PPh_2). IR (Nujol): ν_{max}/cm^{-1} 3052 (m), 2630 (br m), 2503 (m), 1671 (br w), 1414 (m), 1401 (m), 1309 (w), 1246 (vs), 1178 (m), 1170 (m), 1161 (s), 1151 (s), 1105 (m) 1072 (m), 1057 (m), 1037 (vs), 1021 (m), 1009 (m), 997 (m), 946 (vw), 922 (vw), 901 (w), 891 (w), 827 (m), 817 (m), 807 (m), 794 (w), 767 (m), 716 (s), 703 (m), 697 (m), 653 (vs), 629 (m), 614 (m), 563 (m), 544 (m), 534 (w), 500 (s), 487 (s), 471 (m), 456 (m), 427 (m). ESI+ MS: *m*/*z* 102 ($[HNEt_3]^+$), 584 ($[M + H]^+$), 685 ($[M + HNEt_3]^+$); ESI− MS: *m*/*z* 481 ($[Ph_2P(S)fcSO_3]^-$). Anal. Calcd for $C_{28}H_{34}FeNO_3PS_2$ (583.5): C, 57.63; H, 5.87; N, 2.40. Found: C, 57.56; H, 5.80; N, 2.34.

Deprotection of 3 and Synthesis of 4. Methyl triflate (2.4 mL, 22 mmol) was added to a solution of compound **3** (5.829 g, 10 mmol) in dichloromethane (100 mL), causing the reaction mixture to warm slightly and change in color from orange to red. After the mixture was stirred at room temperature for 3 h, the solvent was evaporated under vacuum at 35 °C. The oily residue was redissolved in dichloromethane (100 mL) and treated with neat $P(NMe_2)_3$ (2.5 mL, 14 mmol), whereupon the color reverted from red to deep orange. After it was stirred for 3 h, the mixture was concentrated under vacuum (at 35 °C), and the residue was dissolved in methanol (50 mL) and transferred to a column containing a cation exchange resin (ca. 100 mL of Dowex 50WX4 in H^+ cycle) in methanol. After it was equilibrated for 30 min, the column was washed with methanol, and the orange eluate was concentrated under reduced pressure at 40 °C.

The residue was dried over NaOH overnight before being dissolved in a dichloromethane/methanol/NEt_3 mixture (20/1/1; ca. 5 mL; at 0 °C) and purified by silica gel chromatography with the same mobile phase as eluent. Three orange bands were collected and concentrated. The residues were evaporated three times with chloroform and dried over H_2SO_4. The band that eluted first (2.78 g) contained the crude triethyl(methyl)ammonium salt of acid **V**, the second band (5.93 g) contained salt **4** contaminated by another triethylammonium salt (presumably $(Et_3NH)Cl$), and the third band contained crude compound **5** (1.18 g). The first and second fractions were combined and chromatographed again through a cation exchange resin and silica gel as described above to afford crude salt **4** (4.93 g) as the first fraction and compound **5** as the second fraction (0.95 g). The crude **4** containing $(Et_3NH)Cl$ was dissolved in hot dichloromethane (7 mL; with sonication), and the solution was diluted with hot ethyl acetate (70 mL). Slow cooling to 4 °C furnished orange crystals of the pure salt, which were isolated by suction filtration, washed with ethyl acetate, and dried under vacuum. Yield of **4**: 2.167 g (39%), rusty orange, crystalline solid.

Fractions containing mostly zwitterionic compound **5** were combined and rechromatographed over silica gel with a dichloromethane/methanol/NEt_3 mixture (20/1/1). The main band from the product was collected and concentrated. The solid residue was evaporated three times with chloroform, dried over H_2SO_4, and finally crystallized by dissolving in dichloromethane (30 mL), adding hot ethyl acetate (30 mL), and slowly cooling to 4 °C. The crystalline product was isolated using the procedure described for **4**, which yielded compound **5** as a rusty brown, crystalline solid (0.364 g, 8%).

Analytical Data for 4. Mp: 157 °C (CH_2Cl_2/AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3 of $HNEt_3$), 3.12 (dq, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 4.8 Hz, 6 H, CH_2 of $HNEt_3$), 4.05 (vt, J' = 1.9 Hz, 2 H, fc), 4.24 (vq, J' = 1.9 Hz, 2 H, fc), 4.51 (vt, J' = 1.9 Hz, 2 H, fc), 4.68 (vt, J' = 1.7 Hz, 2 H, fc), 7.28−7.38 (m, 10 H, PPh_2), 10.52 (br s, 1 H, *H*NEt_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −16.5 (s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 8.63 (s, CH_3 of $HNEt_3$), 46.03 (s, CH_2 of $HNEt_3$), 68.32 (s, CH of fc), 70.33 (s, CH of fc), 74.35 (d, $^2J_{PC}$ = 15 Hz, CH of fc), 74.54 (d, $^3J_{PC}$ = 4 Hz, CH of fc), 76.70 (d, $^1J_{PC}$ = 6 Hz, C−P of fc), 94.01 (s, C−SO_3 of fc), 128.10 (d, $^3J_{PC}$ = 7 Hz, CH_{meta} of PPh_2), 128.43 (s, CH_{para} of PPh_2), 133.45 (d, $^2J_{PC}$ = 20 Hz, CH_{ortho} of PPh_2), 138.99 (d, $^1J_{PC}$ = 10 Hz, C_{ipso} of PPh_2).

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Organometallics XXXX, XXX, XXX−XXX

IR (Nujol): ν_{max}/cm^{-1} 3065 (m), 2676 (br m), 2506 (m), 1672 (br w), 1397 (m), 1340 (w), 1308 (m), 1242 (vs), 1189 (m), 1163 (vs), 1155 (s), 1089 (m), 1058 (m), 1039 (vs), 1010 (m), 922 (w), 898 (w), 882 (vw), 854 (w), 827 (m), 811 (m), 754 (m), 748 (m), 701 (m), 653 (vs), 563 (m), 534 (w), 524 (m), 494 (s), 458 (m), 442 (m), 432 (w). ESI+ MS: m/z 102 ($[HNEt_3]^+$), 451 ($[M - NEt_3 + H]^+$), 552 ($[M + H]^+$); ESI− MS: m/z 449 ($[Ph_2PfcSO_3]^-$). Anal. Calcd for $C_{28}H_{34}FeNO_3PS$ (551.4): C, 60.98; H, 6.21; N, 2.54. Found: C, 60.89; H, 6.11; N, 2.45.

Analytical Data for **5**. ^1H NMR (400 MHz, dmso-d_6): δ 3.08 (d, $^2J_{PH}$ = 14.5 Hz, 3 H, PMe), 4.01 (vt, J' = 1.9 Hz, 2 H, fc), 4.30 (vt, J' = 1.9 Hz, 2 H, fc), 4.77 (vq, J' = 1.9 Hz, 2 H, fc), 4.94 (vq, J' = 1.9 Hz, 2 H, fc), 7.67−7.73 (m, 4 H, PPh_2), 7.76−7.84 (m, 6 H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, dmso-d_6): δ 24.5 (s). $^{13}C\{^1H\}$ NMR (101 MHz, dmso-d_6): δ 6.67 (d, $^1J_{PC}$ = 59 Hz, PMe), 60.78 (d, $^1J_{PC}$ = 103 Hz, C−P of fc), 69.35 (d, J_{PC} = 19 Hz, 2 CH of fc), 74.33 (d, J_{PC} = 13 Hz, CH of fc), 75.88 (d, J_{PC} = 11 Hz, CH of fc), 98.66 (s, C−SO_3 of fc), 122.59 (d, $^1J_{PC}$ = 90 Hz, C_{ipso} of PPh_2), 129.57 (d, $^3J_{PC}$ = 13 Hz, CH_{meta} of PPh_2), 132.24 (d, $^2J_{PC}$ = 11 Hz, CH_{ortho} of PPh_2), 134.15 (d, $^4J_{PC}$ = 3 Hz, CH_{para} of PPh_2). IR (Nujol): ν_{max}/cm^{-1} 3091 (m), 2723 (br w), 2670 (br w), 1415 (w), 1405 (w), 1326 (w), 1315 (m), 1230 (vs), 1195 (vs), 1184 (s), 1173 (s), 1122 (m), 1114 (m), 1077 (w), 1052 (m), 1042 (vs), 1013 (m), 999 (w), 938 (vw), 914 (m), 893 (m), 882 (m), 871 (w), 848 (m), 827 (m), 815 (w), 787 (w), 760 (m), 749 (m), 720 (m), 696 (m), 649 (vs), 624 (vw), 615 (vw), 554 (w), 538 (m), 500 (m), 491 (s), 473 (m), 449 (w). ESI+ MS: m/z 465 ($[M + H]^+$), 487 ($[M + Na]^+$), 503 ($[M + K]^+$); ESI− MS: m/z 449 ($[M - H]^-$). Anal. Calcd for $C_{23}H_{21}FeO_3PS{\cdot}0.1CH_2Cl_2$ (472.8): C, 58.68; H, 4.52. Found: C, 58.44; H, 4.37.

Synthesis of 4 by Lithiation of 6. A stirred solution of bromide **6** (4.766 g, 10 mmol, purity 95%) in anhydrous THF (80 mL) was cooled in a dry ice/ethanol bath to ca. −78 °C and treated with LiBu (4.4 mL 2.5 M in hexanes, 11 mmol). After it was stirred for 15 min, the solution was poured onto solid $Me_3N{\cdot}SO_3$ (1.672 g, 12 mmol) in another flask attached to the reaction vessel by a glass connecting tube. The resulting orange suspension was stirred at −78 °C for 15 min and then at room temperature overnight (16 h; all of the $Me_3N{\cdot}SO_3$ dissolved during this time). The orange reaction mixture was concentrated under vacuum, leaving a residue, which was chromatographically purified (silica gel, CH_2Cl_2). After the first band containing $FcPPh_2$ (1.210 g, 33%) was removed, the eluent was gradually changed to dichloromethane/methanol (5/1), which led to the development of an orange band. This band was collected and concentrated. The residue (4.77 g) was dissolved in methanol and passed through the cation exchanger. The eluate was concentrated, and the residue was dissolved in a minimum of a CH_2Cl_2/MeOH/NEt_3 mixture (20/1/1, ca. 5 mL) at 0 °C and then chromatographed over silica gel using the same solvent mixture as the eluent. The main orange band was collected and concentrated, and the residue was evaporated with chloroform three times and dried over H_2SO_4.

Crude **4** containing some $(Et_3NH)Cl$ was dissolved in warm CH_2Cl_2 (5 mL) under sonication. The solution was treated with charcoal, diluted with ethyl acetate (50 mL), and cooled to room temperature. The colorless crystals of $(Et_3NH)Cl$ that had formed were isolated by decantation, and the mother liquor was evaporated. The residue was crystallized from dichloromethane and ethyl acetate (5 + 50 mL) as described above, and pure **4** (1.663 g, 30%) was isolated by suction filtration.

Synthesis of [(L^{NC})Pd(Ph_2PfcSO_3-κ^2O,P)] (7). A solution of salt **4** (55.1 mg, 0.10 mmol) in chloroform (2 mL) was added to $[Pd(OAc)(L^{NC})]_2$ (30.0 mg, 0.050 mmol) dissolved in the same solvent (1 mL), and the mixture was stirred for 3 h and then evaporated under vacuum. The residue was dissolved in ethyl acetate (5 mL) and crystallized by adding hexane (20 mL) as a top layer. Crystals of **7**, which formed upon mixing of the solvents during several days, were isolated by filtration, washed with hexane and pentane, and dried under vacuum. Yield: 57.5 mg (83%), orange, crystalline solid.

Alternatively, **4** (55.1 mg, 0.10 mmol) and $[PdCl(L^{NC})]_2$ (27.6 mg, 0.050 mmol) were reacted in $CHCl_3$ (3 mL) for 3 h. Evaporation and recrystallization from methanol (2 mL) and diethyl ether (8 mL) produced rusty orange crystals, which were isolated by suction filtration, washed with diethyl ether, and dried under vacuum. Yield of **7**: 44.7 mg (65%).

^1H NMR (400 MHz, $CDCl_3$): δ 2.96 (d, $^4J_{PH}$ = 2.9 Hz, 6 H, NMe_2), 4.06 (br d, $^4J_{PH}$ = 2.0 Hz, 2 H, NCH_2), 4.07 (vt, J' = 2.0 Hz, 2 H, fc), 4.41 (vt, J' = 2.0 Hz, 2 H, fc), 4.70 (dvt, J = 1.9, 0.8 Hz, 2 H, fc), 4.86 (dvt, J' = 2.9, 1.9 Hz, 2 H, fc), 5.86 (ddd, J = 7.9, 6.5, 1.2 Hz, 1 H, C_6H_4), 6.23 (br td, J = 7.7, 1.6 Hz, 1 H, C_6H_4), 6.72 (td, J = 7.3, 1.1 Hz, 1 H, C_6H_4), 6.88 (br dd, J = 7.4, 1.6 Hz, 1 H, C_6H_4), 7.27−7.33 (m, 4 H, PPh_2), 7.36−7.41 (m, 2 H, PPh_2), 7.52−7.58 (m, 4 H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 28.4 (s). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 50.06 (d, $^3J_{PC}$ = 2 Hz, NMe_2), 69.79 (s, CH of fc), 70.31 (s, CH of fc), 72.08 (d, $^1J_{PC}$ = 52 Hz, C−P of fc), 72.13 (d, $^3J_{PC}$ = 3 Hz, NCH_2), 73.33 (d, $^3J_{PH}$ = 8 Hz, CH of fc), 77.18 (d, partly overlapping with the solvent signal, CH of fc), 92.95 (s, C−SO_3), 122.54 (s, CH of C_6H_4), 123.98 (s, CH of C_6H_4), 124.97 (d, $^4J_{PC}$ = 6 Hz, CH of C_6H_4), 128.16 (d, J_{PC} = 11 Hz, CH of PPh_2), 130.56 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_2), 132.77 (d, $^1J_{PC}$ = 53 Hz, C_{ipso} of PPh_2), 134.34 (d, J_{PC} = 12 Hz, CH of PPh_2), 136.88 (d, $^3J_{PC}$ = 11 Hz, CH of C_6H_4), 144.50 (d, $^2J_{PC}$ = 4 Hz, C_{ipso} of C_6H_4), 148.00 (d, $^3J_{PC}$ = 2 Hz, C_{ipso} of C_6H_4). IR (Nujol): ν_{max}/cm^{-1} 1586 (vw), 1407 (vw), 1306 (w), 1256 (vs), 1196 (m), 1181 (m), 1156 (vs), 1117 (vw), 1097 (m), 1051 (m), 1031 (s), 1003 (s), 978 (vw), 935 (w), 888 (w), 867 (w), 841 (m), 822 (m), 813 (m), 755 (vw), 744 (s), 701 (m), 694 (m), 657 (m), 642 (s), 595 (vw), 579 (w), 544 (m), 529 (m), 498 (m), 487 (s), 472 (m), 454 (w), 438 (w). ESI+ MS: m/z 690 ($[M + H]^+$), 712 ($[M + Na]^+$), 728 ($[M + K]^+$). Anal. Calcd for $C_{31}H_{30}FeNO_3PPdS$ (689.8): C, 53.97; H, 4.38; N, 2.03. Found: C, 53.91; H, 4.39; N, 1.89.

Synthesis of [(L^{SC})Pd(Ph_2PfcSO_3-κ^2O,P)] (8). Compound **4** (55.1 mg, 0.10 mmol) and $[Pd(OAc)(L^{SC})]_2$ (30.2 mg, 0.50 mmol) were reacted in chloroform (3 mL) as described for complex **7**. Evaporation of the chloroform and crystallization from ethyl acetate (10 mL) and hexane (15 mL; liquid phase diffusion) afforded orange-brown crystals, which were isolated by filtration, washed with hexane and pentane, and dried under vacuum to afford analytically pure **8**. Yield: 54.8 mg (79%).

Like the previous procedure, the same product (**8**) was also isolated from the reaction of $[PdCl(L^{SC})]_2$ (27.9 mg, 0.050 mmol) with **4** (55.1 mg, 0.10 mmol) in $CHCl_3$ (3 mL) and crystallization from methanol (2 mL) and diethyl ether (8 mL). Yield of **8**: 43.8 mg (63%).

^1H NMR (400 MHz, $CDCl_3$): δ 2.68 (d, $^4J_{PH}$ = 3.8 Hz, 3 H, SMe), 4.11 (br vt, J' = 1.9 Hz, 2 H, fc), very br s centered at 4.2 (2 H, SCH_2), 4.47 (br s, 2 H, fc), 4.74 (br s, 2 H, fc), 4.91 (br s, 2 H, fc), 6.10 (br td, J = 7.7, 1.1 Hz, 1 H, C_6H_4), 6.18 (br td, J = 7.6, 1.6 Hz, 1 H, C_6H_4), 6.65 (td, J = 7.3, 1.2 Hz, 1 H, C_6H_4), 6.89 (br dd, J = 7.5, 1.7 Hz, 1 H, C_6H_4), 7.27−7.33 (br m, 4 H, PPh_2), 7.36−7.42 (br m, 2 H, PPh_2), 7.52 (br s, 4 H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 26.2 (s). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 20.11 (d, $^3J_{PC}$ = 2 Hz, SMe), 45.55 (d, $^3J_{PC}$ = 1 Hz, SCH_2), 69.82 (s, CH of fc), 70.24 (s, CH of fc), 71.90 (d, $^1J_{PC}$ = 49 Hz, C−P of fc), 73.44 (d, $^3J_{PH}$ = 8 Hz, CH of fc), 77.22 (d, partly overlapping with the solvent signal, CH of fc), 92.97 (s, C−SO_3 of fc), 123.88 (s, CH of C_6H_4), 124.45 (s, CH of C_6H_4), 125.49 (d, $^4J_{PC}$ = 6 Hz, CH of C_6H_4), 128.23 (d, J_{PC} = 11 Hz, CH of PPh_2), 130.63 (s, CH_{para} of PPh_2), 132.13 (d, $^1J_{PC}$ = 51 Hz, C_{ipso} of PPh_2), 134.26 (d, J_{PC} = 11 Hz, CH of PPh_2), 138.94 (d, $^3J_{PC}$ = 13 Hz, CH of C_6H_4), 145.69 (d, $^2J_{PC}$ = 1 Hz, C_{ipso} of C_6H_4), 150.03 (d, $^3J_{PC}$ = 1 Hz, C_{ipso} of C_6H_4). IR (Nujol): ν_{max}/cm^{-1} 1735 (w), 1577 (vw), 1317 (w), 1310 (w), 1293 (vw), 1250 (vs), 1195 (s), 1187 (m), 1170 (m), 1159 (m), 1148 (vs), 1111 (vw), 1097 (m), 1071 (vw), 1063 (w), 1055 (vw), 1033 (s), 1019 (m), 1002 (s), 969 (m), 940 (w), 925 (vw), 888 (vw), 859 (vw), 847 (w), 837 (m), 825 (m), 807 (w), 761 (m), 741 (s), 704 (m), 695 (m), 657 (m), 639 (s), 579 (w), 540 (m), 533 (m), 501 (m), 490 (s), 470 (m), 451 (w), 437 (w). ESI+ MS: m/z 715 ($[M + Na]^+$), 731 ($[M + K]^+$). Anal. Calcd for $C_{30}H_{27}FeO_3PPdS_2$ (692.9): C, 52.00; H, 3.93. Found: C, 51.73; H, 3.97.

Synthesis of $(Et_3NH)_2$[$PdCl_2$(Ph_2PfcSO_3-κP)$_2$] (9). A solution of compound **4** (275 mg, 0.50 mmol) in chloroform (2 mL) was added to $[PdCl_2(MeCN)_2]$ (65 mg, 0.25 mmol) dissolved in the same solvent (1 mL), and the reaction mixture was stirred for 1 day. The product precipitated as a red solid, which was then stored at −20 °C

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Organometallics XXXX, XXX, XXX−XXX

overnight. The precipitate was isolated by filtration, washed with $CHCl_3$ (1 mL), and dissolved in methanol (3 mL). The solution was filtered through a PTFE syringe filter (0.25 μm pore size) and layered with a minimum of a 1/1 methanol/diethyl ether mixture and then with diethyl ether (20 mL). The red crystals (**9**·2MeOH), which formed within several days, were isolated by filtration, washed with diethyl ether, and dried under vacuum to afford unsolvated **9**. Yield of **9**: 244 mg (76%), brick red, crystalline powdery solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3 of $HNEt_3$), 3.11 (q, $^3J_{HH}$ = 7.3 Hz, 6 H, CH_2 of $HNEt_3$), 4.68 (br vt, J' = 1.8 Hz, 2 H, fc), 4.72−4.75 (br m, 6 H, fc), 7.33−7.42 (m, 6 H, PPh_2), 7.59−7.64 (m, 4 H, PPh_2), 10.36 (br s, 2 H, $HNEt_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 15.6 (s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 8.67 (s, CH_3 of $HNEt_3$), 46.10 (s, CH_2 of $HNEt_3$), 69.10 (s, CH of fc), 71.71 (vt, J_{PC} = 27 Hz, C−P of fc), 72.20 (s, CH of fc), 75.55 (vt, J_{PC} = 4 Hz, CH of fc), 76.67 (vt, $^2J_{PC}$ = 5 Hz, CH of fc), 94.70 (s, C−SO_3 of fc), 127.72 (vt, J_{PC} = 5 Hz, CH of PPh_2), 130.19 (s, CH_{para} of PPh_2), 131.25 (vt, J_{PC} = 25 Hz, C_{ipso} of PPh_2), 134.14 (vt, J_{PC} = 6 Hz, CH of PPh_2). IR (Nujol): ν_{max}/cm^{-1} 3537 (br m), 3462 (br m), 2706 (br m), 2530 (br w), 1629 (br vw), 1300 (w), 1220 (s), 1180 (br vs), 1097 (m), 1057 (m), 1043 (vs), 1013 (m), 999 (w), 893 (vw), 847 (m), 838 (m), 821 (m), 750 (m), 709 (m), 698 (m), 652 (vs), 626 (m), 557 (w), 540 (m), 502 (vs), 474 (s), 464 (m), 437 (w), 425 (w). ESI+ MS: m/z 1005 ($[M - 2HNEt_3 - 2Cl + H]^+$), 1027 ($[M - 2HNEt_3 - 2Cl + Na]^+$), 1043 ($[M - 2HNEt_3 - 2Cl + K]^+$), 1106 ($[M - HNEt_3 - 2Cl]^+$); ESI− MS: m/z 1039 ($[M - 2HNEt_3 - Cl]^-$). Anal. Calcd for $C_{56}H_{68}Cl_2Fe_2N_2O_6P_2PdS_2$·2MeOH (1344.3): C, 51.82; H, 5.70; N, 2.08. Found: C, 51.69; H, 5.38; N, 2.08.

Synthesis of Compound 14. Compound **4** (113 mg, 0.20 mmol) and gray selenium (17 mg, 0.22 mmol) were reacted in dichloromethane (10 mL) overnight. The solvent was evaporated under vacuum, and the residue was purified by chromatography over silica gel using dichloromethane/methanol/NEt_3 (20/1/1) as the eluent. The eluate was evaporated, dissolved in chloroform, and evaporated. This procedure was repeated once again with dichloromethane and ethyl acetate (2 mL each). Next, the crude product was dissolved in a minimum of dichloromethane (few drops) and mixed with hot ethyl acetate (∼2 mL). The crystalline product, which separated upon cooling, was filtered off, washed with ethyl acetate and pentane, and dried under vacuum. Yield of **14**: 107 mg (85%), orange crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3 of $HNEt_3$), 3.11 (dq, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 4.2 Hz, 6 H, CH_2 of $HNEt_3$), 4.31 (vt, J' = 1.9 Hz, 2 H, fc), 4.51 (vt, J' = 1.9 Hz, 2 H, fc), 4.59 (vq, J' = 1.9 Hz, 2 H, fc), 4.84 (vq, J' = 1.9 Hz, 2 H, fc), 7.37−7.75 (m, 10 H, PPh_2), 10.40 (br s, 1 H, $HNEt_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 32.2 (s with ^{77}Se satellites, $^1J_{SeP}$ = 732 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 8.65 (s, CH_3 of $HNEt_3$), 46.09 (s, CH_2 of $HNEt_3$), 69.00 (s, CH of fc), 71.97 (s, CH of fc), 74.61 (d, $^2J_{PC}$ = 13 Hz, CH of fc), 74.67 (d, $^1J_{PC}$ = 89 Hz, C−P of fc), 76.04 (d, $^3J_{PC}$ = 10 Hz, CH of fc), 94.51 (s, C−SO_3 of fc), 128.21 (d, J_{PC} = 13 Hz, CH of PPh_2), 131.24(d, $^4J_{PC}$ = 3 Hz, CH_{para} of PPh_2), 132.03 (d, J_{PC} = 11 Hz, CH of PPh_2), 133.37 (d, $^1J_{PC}$ = 79 Hz, C_{ipso} of PPh_2). IR (Nujol): ν_{max}/cm^{-1} 2671 (br m), 2633 (br m), 2504 (br m), 1413 (w), 1400 (w), 1307 (w), 1292 (vw), 1246 (vs), 1178 (s), 1171 (s), 1162 (s), 1151 (s), 1101 (m), 1072 (w), 1057 (m), 1037 (vs), 1022 (m), 1009 (m), 998 (w), 891 (vw), 827 (m), 817 (w), 794 (vw), 765 (m), 706 (m), 699 (m), 654 (s), 631 (w), 572 (s), 538 (m), 499 (s), 478 (s), 461 (m). ESI+ MS: m/z 102 ($[HNEt_3]^+$); ESI− MS: m/z 529 ($[Ph_2P(Se)$-$fcSO_3]^-$). Anal. Calcd for $C_{28}H_{34}FeNO_3PSSe$ (630.4): C, 53.35; H, 5.44; N, 2.22. Found: C, 52.98; H, 5.28; N, 2.21.

Catalytic Experiments: Reaction Scope Tests. A Schlenk tube was charged successively with the appropriate boronic acid (1.0 mmol), acyl chloride (1.2 mmol), sodium phosphate (164 mg, 1.0 mmol), and a stirring bar, flushed with argon, and sealed with a rubber septum. Toluene (1.5 mL) was introduced, and the reaction flask was transferred to an oil bath maintained at 50 °C. Next, the catalyst (**9**; 1.28 mg, 1.0 μmol) dissolved with sonication in degassed water (1.5 mL) was introduced, and the reaction was allowed to proceed with continuous stirring for 3 h. The resulting mixture was cooled to room temperature and terminated by the addition of saturated aqueous $NaHCO_3$ (9 mL). The mixture was extracted with diethyl ether (20 mL), and the organic layer was separated, washed with saturated aqueous $NaHCO_3$ and NaCl, dried over $MgSO_4$, and finally concentrated onto chromatographic silica gel. The product (preadsorbed on the silica gel) was isolated by silica gel column chromatography using ethyl acetate/hexane as the eluent (1/5, 1/10, or 1/20 depending on the product polarity). The yields given in the text are an average of two independent runs (note: details of the screening reactions are available in the Supporting Information).

X-ray Crystallography. The full-set diffraction data ($\pm h$, $\pm k$, $\pm l$; θ_{max} = 27.5°, data completeness ≥99.6%) were recorded on a Bruker Apex II CCD diffractometer (compounds **4**, **7**, **8**, and **9**·2MeOH) or a Bruker D8 Venture Kappa Duo diffractometer equipped with a PHOTON 100 detector and a IμS 3.0 microfocus source (compounds **3**, **5**, and **13**·2$CHCl_3$). All measurements were performed at 120 or 150 K (Cryostream cooler, Oxford Cryosystems) using Mo Kα radiation (λ = 0.71073 Å). The data were corrected for absorption by the methods included in the diffractometer software.

The structures were solved by direct methods (SHELXS97[57] or SHELXT-2014[58]) and refined by full-matrix least squares based on F^2 (SHELXL-2017[59]). All non-hydrogen atoms were refined with anisotropic displacement parameters. The NH hydrogens were located on the difference density maps and refined as riding atoms with U_{iso} assigned to 1.2 times the U_{eq} value of their bonding atom. Hydrogen atoms bonded to carbons (CH_n) were included in their calculated positions and refined similarly. Disordered solvating ethyl acetate molecules in the structure of **7** were treated as diffuse scattering using PLATON SQUEEZE.[60] Relevant crystallographic data and structural refinement parameters are given in the Table S1 in the Supporting Information.

PLATON[61] was used for the graphical presentation of the structures and all geometric calculations. The numerical values are rounded with respect to their estimated deviations (ESDs) and given to one decimal place. The parameters related to atoms in constrained positions are given without ESDs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00178.

Additional structural drawings including displacement ellipsoid plots of all structurally characterized compounds, summary of the crystallographic and structure refinement parameters, synthesis and crystal structure of **13**·2$CHCl_3$, characterization data for the coupling products **12**, and NMR spectra (PDF)

Accession Codes

CCDC 1832482−1832488 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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Organometallics XXXX, XXX, XXX−XXX

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(25) The presence of $MeNEt_3^+$ can be inferred from the ^{1}H NMR spectra of the reaction mixture, which showed the following signals (in $CDCl_3$): δ 1.35 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, NCH_2CH_3), 3.12 (s, 1 H, NCH_3), 3.45 (q, $^3J_{HH}$ = 7.3 Hz, 2 H, NCH_2CH_3).

(26) Two equivalents of MeOTf is necessary to successfully methylate the phosphine sulfide because of the competitive alkylation of the $HNEt_3$ cation. The subsequent desulfuration can be achieved with only 1 equiv of $P(NMe_2)_3$.

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Organometallics XXXX, XXX, XXX−XXX

(27) Analytical data for Ph_2PfcSO_3H (**V**). ^1H NMR (400 MHz, dmso-d_6): δ 3.91 (vt, J' = 1.8 Hz, 2 H, fc), 4.10 (br d, J' = 1.6 Hz, 2 H, fc), 4.22 (vt, J' = 1.9 Hz, 2 H, fc), 4.50 (vt, J' = 1.7 Hz, 2 H, fc), 7.27−7.39 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, dmso-d_6): δ −17.5 (br s). $^{13}C\{^1H\}$ NMR (101 MHz, dmso-d_6): δ 67.76 (s, CH of fc), 68.98 (s, CH of fc), 73.51 (d, $^2J_{PC}$ = 15 Hz, CH of fc), 73.86 (d, $^3J_{PC}$ = 4 Hz, CH of fc), 75.68 (d, $^1J_{PC}$ = 7 Hz, C-P of fc), 96.58 (s, C-SO_3 of fc), 128.14 (d, J_{PC} = 6 Hz, CH of PPh_2), 128.43 (s, CH of PPh_2), 132.89 (d, J_{PC} = 19 Hz, CH of PPh_2), 138.66 (d, $^1J_{PC}$ = 11 Hz, C_{ipso} of PPh_2). HR MS (ESI+): calcd for $C_{22}H_{20}FeO_3PS$ ($[M + H]^+$), 451.0215; found, 451.0213. HR MS (ESI−): calcd for $C_{22}H_{18}FeO_3PS_2$ ($[M - H]^-$), 449.0069; found, 449.0073.

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Organometallics XXXX, XXX, XXX−XXX