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Phosphinoferrocene Amidosulfonates: Synthesis, Palladium Complexes, and Catalytic Use in Pd-Catalyzed Cyanation of Aryl Bromides in an Aqueous Reaction Medium

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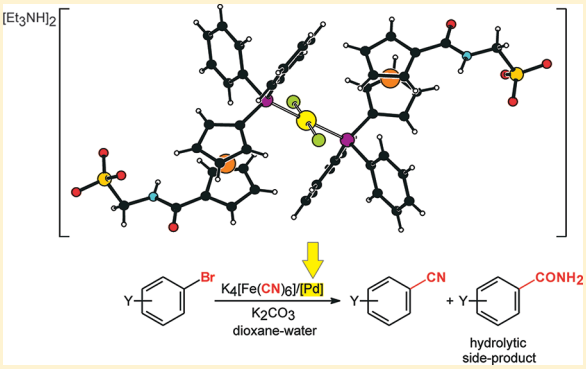
Supporting Information

ABSTRACT: The reaction of pentafluorophenyl 1′-(diphenylphosphino)ferrocene-1-carboxylate (**4**) with ω-aminosulfonic acids $H_2N(CH_2)_nSO_3H$ (n = 1−3) in the presence of 4-(dimethylamino)pyridine and triethylamine affords the respective phosphinoferrocene amidosulfonates as crystalline triethylammonium salts, viz., $(Et_3NH)[Ph_2PfcCONH(CH_2)_nSO_3]$ (**1**, n = 1; **2**, n = 2; **3**, n = 3; fc = ferrocene-1,1′-diyl), in good yields. These ligands react smoothly with $[PdCl_2(cod)]$ (cod = η^2:η^2-cycloocta-1,5-diene) to give the anionic square-planar bis-phosphine complexes *trans*-$(Et_3NH)_2$-$[PdCl_2(Ph_2PfcCONH(CH_2)_nSO_3$-$\kappa P)_2]$ (**5**, n = 1; **6**, n = 2; and **7**, n = 3). The chloride-bridged dimer $[L^{NC}PdCl]_2$, where L^{NC} is 2-[(dimethylamino-κ*N*)methyl]phenyl-κC^1 auxiliary ligand, is cleaved with **1** to give $(Et_3NH)[L^{NC}Pd(Ph_2PfcCONHCH_2SO_3$-$\kappa P)]$ (**8**), in which the amidosulfonate coordinates as a simple phosphine. A similar reaction of $[L^{NC}Pd(OAc)]_2$ and **1** proceeds under a partial elimination of $(Et_3NH)OAc$ to afford a mixture of zwitterionic bis-chelate $[L^{NC}Pd(Ph_2PfcCONHCH_2SO_3$-$\kappa^2O,P)]$ (**9**) and another Pd(II) complex tentatively formulated as $[L^{NC}Pd(OAc)$-$(Ph_2PfcCONHCH_2SO_3$-$\kappa P)]$ (**9a**), from which the former complex separates as an analytically pure crystalline solid. All compounds have been characterized by spectroscopic methods and elemental analysis. The crystal structures of **1**, **3**, **5**·2.5CH_2Cl_2, and **9**·2$CHCl_3$ were determined by single-crystal X-ray diffraction analysis. In addition, complexes **5**−**7** were tested as defined precatalysts for Pd-catalyzed cyanation of aryl bromides with $K_4[Fe(CN)_6]\cdot 3H_2O$ in aqueous dioxane. Complex **5** proved the most active and generally applicable, affording the nitrile products in good to excellent yields.

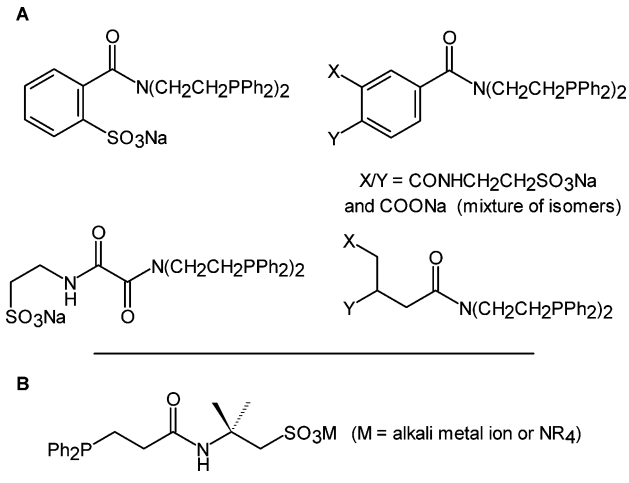


INTRODUCTION

Shortly after the synthesis of the first sulfonated phosphines,[1] it was recognized that the introduction of the highly polar and hydrophilic sulfonate group markedly improves solubility of these donors in water. Since then, there have been reported a number of phosphines sulfonated at their organic backbone. Among these, however, only sulfonated triphenylphosphine derivatives became the real privileged ligands that allowed for transferring numerous important transition metal-catalyzed reactions from organic solvents to water as an environmentally benign reaction medium without compromising their efficacy.[2]

Stimulated very likely by the applications of water-soluble phosphinosulfonate ligands, Whitesides and co-workers designed a series of donors combining extended carboxamido-ω-sulfonate polar tags with a diphosphine ligating unit (Chart 1, A).[3] This concept was later utilized by Sinou et al. in the preparation of water-soluble amidophosphine ligands based on chiral 2-[(diphenylphosphino)methyl]-4-(diphenylphosphino)pyrrolidine.[4] In the mid 1990s, Morteaux, Ziolkowski, et al.[5] and Patin et al.[6] reported the synthesis of another phosphine amidosulfonate ligand (Chart 1, B) by addition of diphenylphosphine or $LiPPh_2$ across the terminal double bond in the readily available

Chart 1



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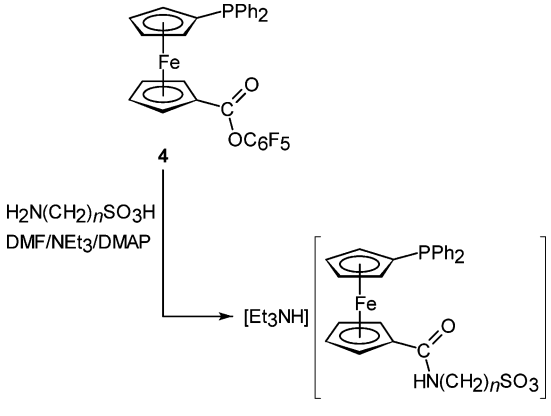
2-acrylamido-2-methyl-1-propanesulfonic acid. The former group further studied this hydrophilic phosphine as a ligand for Rh(I)-catalyzed hydrogenation and hydroformylation reactions in various solvents including water and biphasic mixtures,[5,7] and also for Pd-catalyzed carbonylation of organic halides to the respective acids or esters in water/toluene or water/alcohol mixed solvents.[8]

While exploring the coordination properties and synthetic applications of simple[9] and functional (typically donor-substituted)[10] *phosphinoferrocene carboxamides*, we recently turned also to compounds bearing highly polar amide substituents. So far, we have synthesized phosphinoferrocene amides bearing pendant 2-hydroxyethyl and α-amino acid substituents. The former compounds proved useful ligands for Pd-catalyzed Suzuki–Miyaura cross-coupling in biphasic reaction media,[11] whereas the latter were successfully utilized as ligands for Suzuki–Miyaura cross-coupling in aqueous reaction media (achiral ligands based on glycine)[12] or for enantioselective Cu-catalyzed conjugate addition of diethyl zinc to chalcones[13] and Pd-catalyzed asymmetric allylic alkylation (ligands prepared from chiral amino acids).[14] In a search of other lead structures, we became inspired by the polar phosphine-amides mentioned above and decided to prepare a series of new homologous amides from 1′-(diphenylphosphino)-1-ferrocenecarboxylic acid (Hdpf)[15] and ω-aminosulfonic acids $H_2N(CH_2)_nSO_3H$. This contribution reports the synthesis and structural characterization of three such polar phosphinoferrocene ligands and palladium(II) complexes thereof. Also reported are results of testing of defined Pd(II) diphosphine complexes prepared from these polar donors as catalysts for metal-catalyzed cyanation of aryl bromides in water/dioxane mixtures.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Ligands. Amidosulfonate ligands **1**–**3** were obtained upon reacting the appropriate ω-aminosulfonic acid with Hdpf pentafluorophenyl ester **4**[11] in dry DMF in the presence of triethylamine and a catalytic amount of 4-(dimethylamino)pyridine at room temperature (Scheme 1). Subsequent isolation by column chromatography and recrystallization from hot ethyl acetate afforded the products as air-stable, crystalline triethylammonium salts in good yields. The compounds were characterized by elemental analysis and by spectroscopic methods. In addition, the crystal structures of **1** and **3** have been determined by single-crystal diffraction analysis.

Scheme 1. Preparation of Amidosulfonate Ligands 1–3[a]



1 (n =1), **2** (n =2), **3** (n =3)

[a]DMAP = 4-(dimethylamino)pyridine, DMF = *N*,*N*-dimethylformamide.

Electrospray ionization (ESI) mass spectra of **1**–**3** corroborate the formulation by showing highly abundant signals due to $[Ph_2PfcCONH(CH_2)_nSO_3]^-$ (n = 1–3, fc = ferrocene-1,1′-diyl) and $[Et_3NH]^+$. In NMR spectra, the compounds display characteristic signals of the PPh_2-substituted ferrocene-1,1′-diyl moiety, the $(CH_2)_n$ linking groups, and the triethylammonium counterions. Additional ^{1}H NMR signals due to Et_3NH and the amide protons are observed as broad singlets and CH_2-coupled triplets, respectively, whose positions may change with the temperature and sample concentration. The IR spectra of **1**–**3** show strong amide bands at ca. 1645 (amide I) and 1550 cm^{-1} (amide II); bands due to the terminal sulfonate groups are seen at ca. 1150–1170 ($\nu_{as}(SO_3)$) and 1025–1040 ($\nu_s(SO_3)$).

The crystal structures of **1** and **3** are presented in Figure 1. Selected distances and angles are given in Table 1. The molecular structures are rather unexceptional, especially when compared to the crystal structures determined earlier for the related amides $Ph_2PfcCONHR$, where R = H,[9d] $NHCH_2Py$ (Py = pyrid-2-yl),[10a] CH_2CH_2OH,[11] and CH_2CO_2t-Bu.[12] The ferrocene

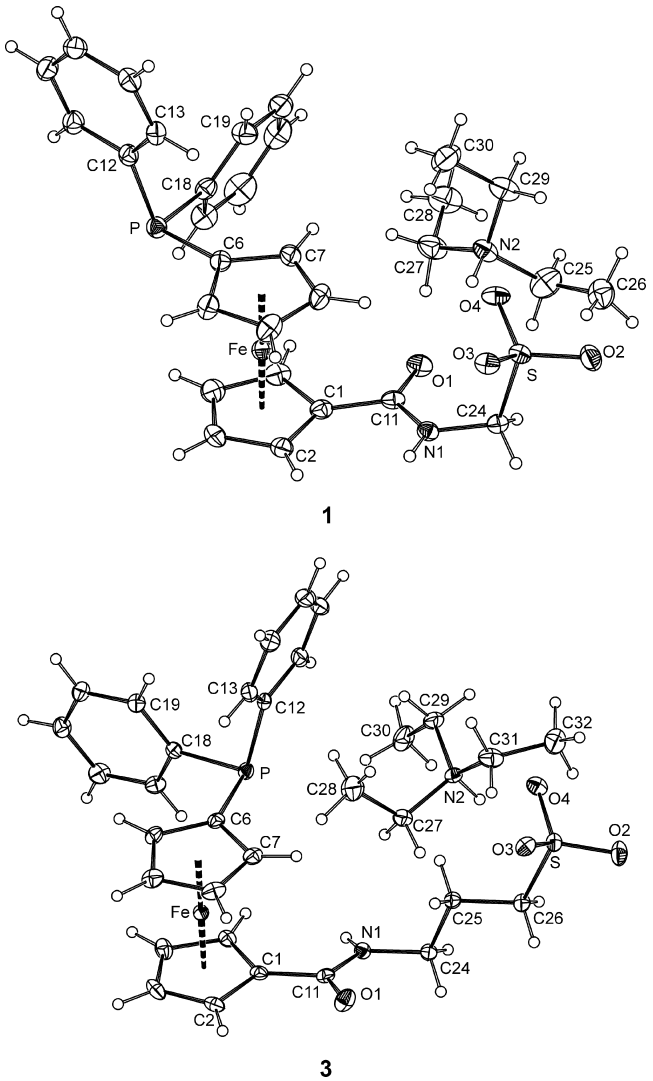


Figure 1. Views of the molecular structures of compound **1** (top) and **3** (bottom). Displacement ellipsoids enclose the 30% probability level.

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Table 1. Selected Distances and Angles for 1 and 3[a]

parameter	1	3
Fe−Cg^P	1.642(1)	1.6397(8)
Fe−Cg^C	1.647(1)	1.6440(8)
∠Cp^C,Cp^P	1.1(2)	3.2(1)
τ[b]	131	78
C11═O1	1.235(3)	1.229(2)
C11−N1	1.352(3)	1.344(2)
N1−C11═O1	122.3(2)	122.6(2)
N1−C24	1.434(3)	1.456(2)
Cp^C vs {CON}[c]	5.0(3)	9.9(2)
CH_2−S	1.799(3)	1.773(2)
S−O	1.449(2)−1.459(2)	1.446(1)−1.470(1)

[a]Definitions: Cp^P and Cp^C are the PPh_2- and amide-substituted cyclopentadienyl rings. Cg^P and Cg^C are the respective centroids. [b]Torsion angle C1−Cg1−Cg2−C6. [c]Dihedral angle of the Cp^C and amide plane {C11,N1,O1}.

units in **1** and **3** are regular with almost identical Fe−ring centroid distances and tilt angles below 5°. In the case of compound **1**, the substituents at the ferrocene unit assume an intermediate conformation close to anticlinal eclipsed (see τ in Table 1). The amide group is rotated by only ca. 5° from the plane of its parent cyclopentadienyl ring (Cp^C), while the attached sulfonatomethyl group is oriented above the Cp^C plane so that the vector of the C24−S bond intersects this ring plane at an angle of 73.5(2)°. The amide pendant in **3** still points toward the PPh_2-substituted cyclopentadienyl ring, but the ferrocene unit adopts a more compact conformation (synclinal eclipsed). The amide plane in **3** is rotated from the Cp^C plane by ca. 10° though without any torsion at the amide pendant (cf. the distance of C24 from the amide plane being only 0.018(2) Å).

Anions in the crystals of **1** and **3** assemble into dimers via N−H···O hydrogen bonds toward one of the sulfonate oxygens (Figure 2; N1···O3 = 2.830(3) Å for **1** and N1···O4 = 2.908(2) Å for **3**). The triethylammonium counterions "decorate" these dimers at the outside, being connected via Et_3N−H···O_3S hydrogen bonds (N2···O4 = 3.044(3) Å for **1** and N2···O3 = 2.704(2) Å for **3**). In the case of **1**, featuring a shorter linking group (methylene), the latter interaction operates synergistically with a relatively shorter (stronger) N−H···O═C contact (N2···O1 = 2.767(3) Å).

Preparation of Pd(II) Complexes. Ligands **1**−**3** react cleanly with [$PdCl_2$(cod)] (cod = η^5:η^5-cycloocta-1,5-diene) to afford the expected square-planar diphosphine complexes **5**−**7** in high yields (Scheme 2). In ^{1}H NMR spectra, these complexes display signals due to the phosphinoferrocene ligands and the ammonium counterions. The $^{31}P\{^1H\}$ NMR spectra of all three complexes comprise one singlet resonance at δ_P 16.9, which is practically identical to that of the related Hdpf complex *trans*-[$PdCl_2$(Hdpf-κP)$_2$][16] and, in turn, suggests the *trans* geometry for all compounds. Indeed, this was confirmed by structure determination for compound **5** as a representative. A view of the complex anion in the crystal structure of solvate **5**·2.5CH_2Cl_2 is presented in Figure 3; a "full" view is available as Supporting Information, Figure S1.

The molecular structure of the complex anion in **5**, particularly the coordination geometry, compares very well with that of *trans*-[$PdCl_2$(Hdpf-κP)$_2$]·2CH_3CO_2H[16] and all other structurally characterized complexes of the type *trans*-[$PdCl_2$(Ph_2PfcY-κP)$_2$], where Y is a *non*chiral[17] functional group.[18,19] Unlike these complexes, however, compound **5** crystallizes without any imposed

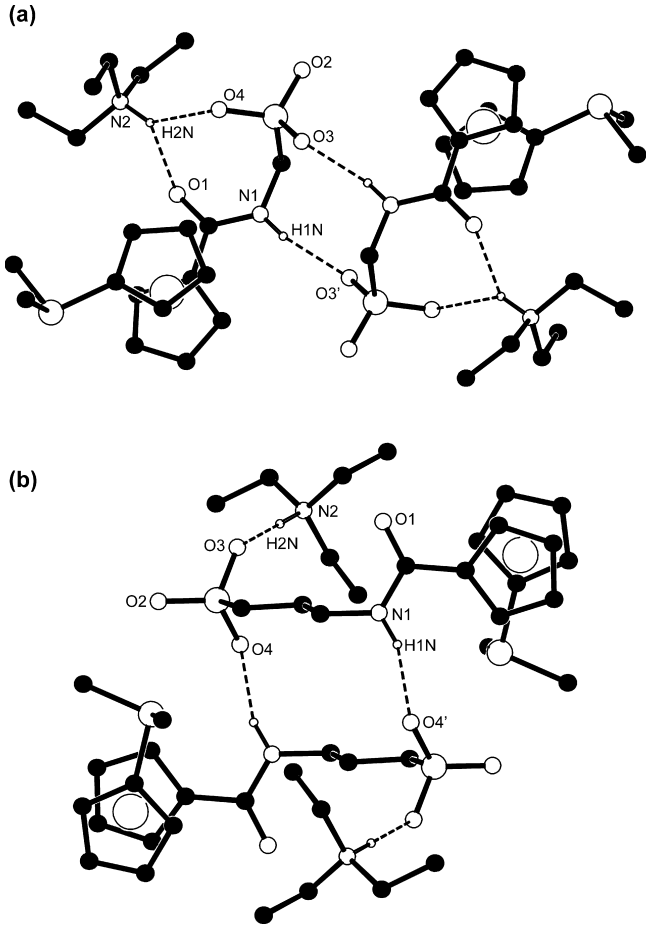
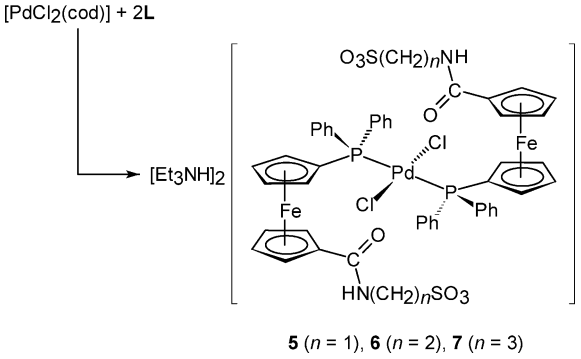


Figure 2. Views of the hydrogen-bonded assemblies in the crystal structures of **1** (a) and **3** (b). Only NH hydrogens and pivotal carbon atoms from the phenyl rings are shown for clarity.

Scheme 2. Preparation of Pd(II) Complexes 5−7[a]



5 (*n* = 1), **6** (*n* = 2), **7** (*n* = 3)

[a]cod = cycloocta-1,5-diene.

symmetry, which can be tentatively attributed to crystal packing effects (most likely to an inefficient packing of the bulky counterions). Nonetheless, the complex anion tends to mimic a higher symmetry with very similar geometry for the two structurally independent $PdCl(Ph_2PfcCONHCH_2SO_3)$ subunits.

The palladium Pd and its four ligating atoms in **5** are coplanar within ca. 0.03 Å, which is in line with the sum of the interligand angles being 360.0°. The ferrocene units exert tilt angles below ca. 4° and a marginal variation in the Fe−C(Cp) distances (ca. 0.04 Å). Compared to the structure of the free ligand, the ferrocene substituents in **5** are more distant, as

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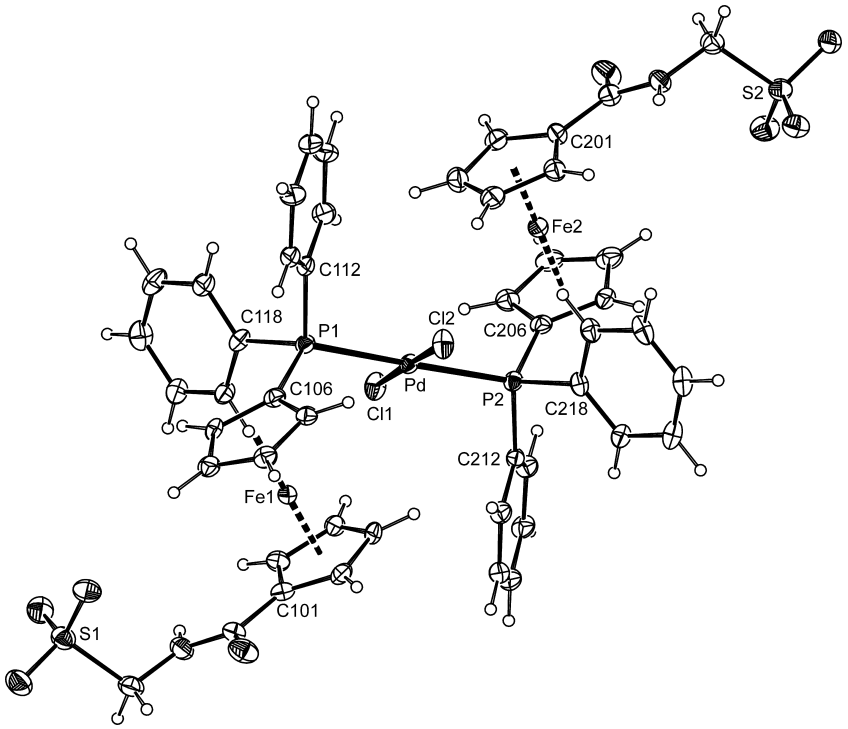


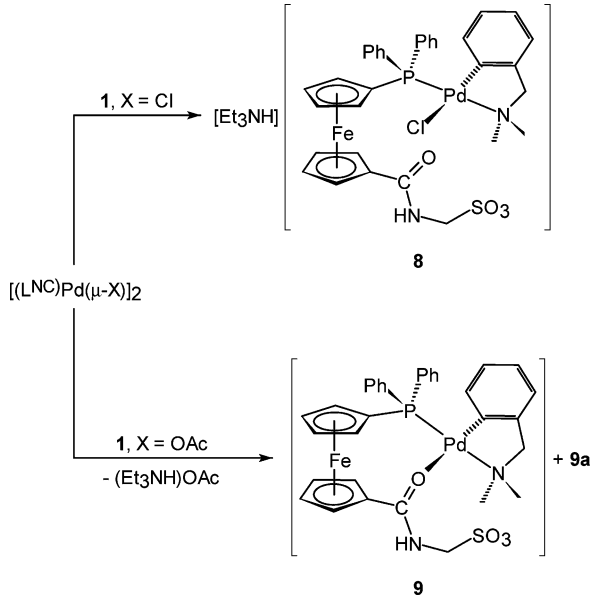
Figure 3. View of the complex anion in the crystal structure of **5**·2.5CH_2Cl_2. Displacement ellipsoids correspond to the 30% probability level.

indicated by the τ angles of 155° and 148° for ferrocene units comprising atoms Fe1 and Fe2, respectively. The amide planes are rotated by 4.4(5)° (moiety 1) and 12.4(5)° (moiety 2) with respect to the planes of their bonding Cp rings.

In the solid state, the molecules of complex **5** aggregate analogously to the free ligand (see Supporting Information, Figure S2). The only notable exception is that the pairs formed through N−H···O_3S hydrogen bonds bind the counterions only via Et_3N−H···O═C interactions (i.e., without supportive Et_3N−H···O_3S contacts such as in **1**) since the cations are shifted with respect to the amidosulfonate chains. Furthermore, because of the presence of two polar chains extending in roughly opposite positions, the anions associate into infinite chains in a brick wall-like fashion.

In another series of experiments, we studied the reactivity of ligand **1** as a representative toward C,N-chelated Pd precursors. Thus, compound **1** reacted with the dimer $[L^{NC}PdCl]_2$ (L^{NC} = 2-[(dimethylamino-κN)methyl]phenyl-κC^1) to afford (Et_3NH)-$[L^{NC}PdCl(Ph_2PfcCONHCH_2SO_3$-$\kappa P)]$ (**8** in Scheme 3) as the sole product. An analogous reaction with the acetate-bridged dimer $[L^{NC}Pd(OAc)]_2$ proved more complicated, producing a mixture of two new Pd complexes and triethylammonium acetate (Scheme 3). The major Pd-containing product (ca. 60%) was found to crystallize preferentially from the reaction mixture (either spontaneously or by addition of a less polar solvent) and was structurally characterized as O,P-chelated zwitterion **9** (see below). This bis-chelate complex apparently results by metathesis-like displacement of the Pd-bound acetate with **1** with concomitant elimination of $(Et_3NH)OAc$. Although the replacement of the acetate ligand is probably assisted by the charge of the terminal sulfonate group, it is the amide oxygen that becomes coordinated to palladium, most likely due to a favorable size of the chelate ring thus formed. A similar motif was found in the structures of $[L^{NC}Pd(Ph_2PfcCONHR$-$\kappa^2O,P)]^+$ salts prepared

Scheme 3. Preparation of Palladium(II) Complexes with L^{NC} Auxiliary Ligand[a]



[a] L^{NC} = 2-[(dimethylamino-κN)methyl]phenyl-κC^1.

from simple (R = Ph)[9b] and functional (R = CH_2CO_2Me)[12] phosphinoferrocene carboxamide ligands.

In view of the literature precedents[20] and our reaction tests (see Experimental Section), the minor component in the reaction mixture was tentatively formulated as the bridge-cleavage product $(Et_3NH)[L^{NC}Pd(OAc)(Ph_2PfcCONHCH_2SO_3$-$\kappa P)]$ (**9a**), representing a plausible reaction intermediate occurring en route from $[L^{NC}Pd(OAc)]_2$ to **9**. Unfortunately, neither *in situ* NMR nor IR spectra of the reaction mixture provided an unambiguous proof for this formulation owing to the presence of broad resonances

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indicating a dynamic system and extensive band overlaps, respectively. Supporting evidence was finally inferred from ESI-MS spectra of the reaction mixture containing **9** and **9a** that clearly showed ions due to $[(L^{NC})Pd(Ph_2PfcCONHCH_2SO_3) + H]^+$ (m/z 747), $[(L^{NC})Pd(Ph_2PfcCONHCH_2SO_3) + Na]^+$ (m/z 769), and $[(L^{NC})Pd(Ph_2PfcCONHCH_2SO_3)(HNEt_3)]^+$ (m/z 848) in positive ion mode and ions attributable to $Ph_2PfcCONHCH_2SO_3^-$ (m/z 506) and $[(L^{NC})Pd(Ph_2Pfc-CONHCH_2SO_3)(X) - H]^+$, where X = Cl ($m/z$ 781) and OAc (m/z 805), in the negative ion mode. The latter species in particular authenticates the formulation of **9a** as an (L^{NC})Pd–acetato complex. Other support came from the model reaction of $[(L^{NC})Pd(OAc)]_2$ with $FcPPh_2$ (Fc = ferrocenyl; Pd:$FcPPh_2$ = 1:1), which cleanly afforded $[(L^{NC})Pd(FcPPh_2)(OAc)]$, showing ions $[(L^{NC})Pd(FcPPh_2)(OAc) + Na]^+$ and $[(L^{NC})Pd(FcPPh_2) + H]^+$ in its ESI$^+$-MS spectrum.

The structure of the solvate **9**·2$CHCl_3$ was determined by X-ray diffraction analysis (Figure 4). It confirms the *trans*-P–N

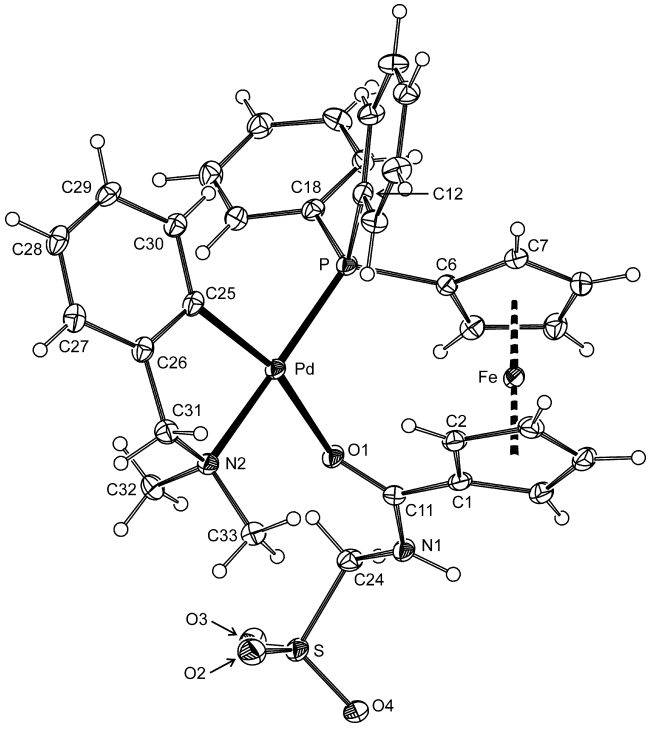


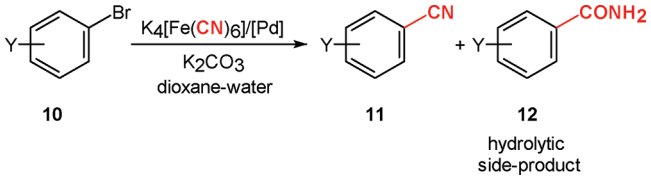
Figure 4. View of the complex molecule in the structure of **9**·2$CHCl_3$. Displacement ellipsoids are drawn at the 30% probability level.

geometry suggested already by the $^4J_{PH}$ coupling constants.[21] The overall coordination geometry is similar to that found in the mentioned cations $[L^{NC}Pd(Ph_2PfcCONHR\text{-}\kappa^2O,P)]^+$ (R = CH_2CO_2Me[12] or Ph[9b]). The coordination plane in **9** is angularly twisted, with the dihedral angle of the in-ring planes {Pd,P,O1} and {Pd,N2,C25} being 13.7(3)°. The donor moieties at the ferrocene unit are brought into proximity by rotation of the Cp rings (τ = 58.4(4)°) and the amide plane, which deviates from coplanarity with its parent Cp^C ring by as much as 26.0(6)°. Otherwise, the geometry of the ferrocene unit remains quite regular.[22] The C11═O1 and C11–N1 bonds are both shorter by 0.01 Å than those in noncoordinated **1**.

Likewise **1** and **5**·2.5CH_2Cl_2, the individual molecules of **9**, assemble into centrosymmetric dimers in the crystal (see Supporting Information, Figure S3). In addition, one of the two independent solvating chloroform molecules is connected to two sulfonate oxygens via bifurcate C–H···O contacts (C···O = 3.107(9) and 3.063(8) Å).

Catalytic Tests. Palladium-catalyzed cyanation of aryl halides[23] offers an alternative access to synthetically highly valued benzonitriles. The attractiveness of this reaction, which is complementary to conventional synthetic methods, markedly increased over the past decade, during which time several efficient catalytic systems were discovered, and simultaneously, the hazardous conventional cyanide sources (e.g., alkali metal cyanides, metal cyanides, or Me_3SiCN)[23] were replaced with the practically nontoxic potassium hexacyanoferrate(II).[24] Typically, the cyanations with $K_4[Fe(CN)_6]$ are now performed with ligand-supported[25] or deposited Pd metal[26] catalysts in various polar solvents, their aqueous mixtures, or even in pure water. Having prepared new phosphine ligands with highly polar amidosulfonate tags, we decided to test their defined Pd(II) complexes **5**–**7** as catalysts for this reaction in an aqueous reaction medium (Scheme 4 and Table 2).

Scheme 4. Pd-Catalyzed Cyanation of Aryl Bromides[a]



[a]Substrates: Y = 4-OMe (**a**), 4-Me (**b**), 3-Me (**c**), 2-Me (**d**), 4-CMe_3 (**e**), 4-CF_3 (**f**), 4-C(O)Me (**g**), 4- Ph (**h**), 4-Cl (**i**), 4-NO_2 (**j**), 4-NMe_2 (**k**), 4-CO_2H (**l**), and 4-CH_2CO_2H (**m**). Conditions: 2 mol % of Pd catalyst, 1.0 equiv K_2CO_3, 0.5 equiv $K_4[Fe(CN)_6]\cdot 3H_2O$, dioxane/water, 100 °C/18 h. For catalytic results, see Table 2.

Indeed, the initial screening tests were promising, as the cyanation of 4-bromoanisole as a deactivated substrate performed in the presence of 1 mol % of complex **5**, 0.5 equiv of $K_4[Fe(CN)_6]\cdot 3H_2O$ (corresponds to 3 equiv of CN^-), and 1 equiv of K_2CO_3 as a base in dioxane/water (1:1) afforded the desired nitrile **11a** with a 58% conversion. Rather surprisingly, the homologous compounds **6** and **7** performed considerably worse under strictly analogous conditions (see entries 1–3 in Table 2). Upon increasing the amount of catalyst **5** to 2 mol %, nitrile **11a** was formed with full conversion. On the other hand, lowering the amount of K_2CO_3 to 0.5 equiv resulted in a lower conversion and, in the absence of any base, the reaction stopped entirely (entries 5 and 6 in Table 2).

Additional tests revealed that the reaction outcome depends strongly on the composition of the reaction medium, namely, on the dioxane/water ratio (Figure 5). Whereas the reaction did not proceed in pure dioxane, after the addition of 20 vol % of water to dioxane, **11a** was formed with 77% conversion. Complete conversions were achieved in mixed solvents containing 40, 50, and 60 vol % of water. Any further addition of water incited an unwanted hydrolysis of the initially formed nitrile to amide **12a**. The ratio of **12a**:**11a** increased with the water content, being 17:83 in 20 vol % dioxane and 40:60 in pure water.

A survey of various halide substrates revealed that the cyanation reaction promoted by complex **5** proceeds cleanly and completely with *para*-substituted bromobenzenes bearing simple alkyl, aryl, and acetyl groups and that, in the series of tolyl bromides, it is not affected by the substitution patterns. Substrates with dissociable carboxyl substituents reacted equally

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Table 2. Summary of Catalytic Results in the Pd-Catalyzed Cyanation of Aryl Bromides[a]

			nitrile **11**	amide **12**
enry	substrate **10**	catalyst	^{1}H NMR yield (isolated yield) (%)	^{1}H NMR yield (%)
1	**10a** (4-MeO)	**5**[b]	58	n.d.
2	**10a** (4-MeO)	**6**[b]	20	n.d.
3	**10a** (4-MeO)	**7**[b]	27	n.d.
4	**10a** (4-MeO)	**5**	100 (95)	n.d.
5	**10a** (4-MeO)	**5**[c]	0	n.d.
6	**10a** (4-MeO)	**5**[d]	56	n.d.
7	**10b** (4-Me)	**5**	100 (90)	n.d.
8	**10c** (3-Me)	**5**	100 (76)	n.d.
9	**10d** (2-Me)	**5**	100 (86)	n.d.
10	**10e** (4-CMe_3)	**5**	100 (82)	n.d.
11	**10f** (4-CF_3)	**5**	62	38
12	**10g** (4-C(O)Me)	**5**	100 (93)	n.d.
13	**10h** (4-Ph)	**5**	100 (91)	n.d.
14	**10i** (4-Cl)	**5**	56	44
15	**10j** (4-NO_2)	**5**	<5	n.d.
16	**10k** (4-NMe_2)	**5**	17	n.d.
17	**10l** (4-CO_2H)	**5**[e]	100 (87)	n.d.
18	**10m** (4-CH_2CO_2H)	**5**[e]	100 (89)	n.d.

[a]Conditions: aryl bromide **10** (1.0 mmol), K_2CO_3 (1.0 mmol), and $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.5 mmol) were reacted in the presence of 2 mol % Pd catalyst in dioxane/water (1:1 mixture, 4 mL) at 100 °C for 18 h. n.d. = product was not detected in the reaction mixture. [b]Reaction with 1 mol % of Pd complex. [c]Reaction without added K_2CO_3. [d]Reaction in the presence of 0.50 mmol of K_2CO_3. [e]Reaction in the presence of 2.0 mmol of K_2CO_3 (2 equiv with respect to the substrate). The product was isolated after acidification of the reaction mixture.

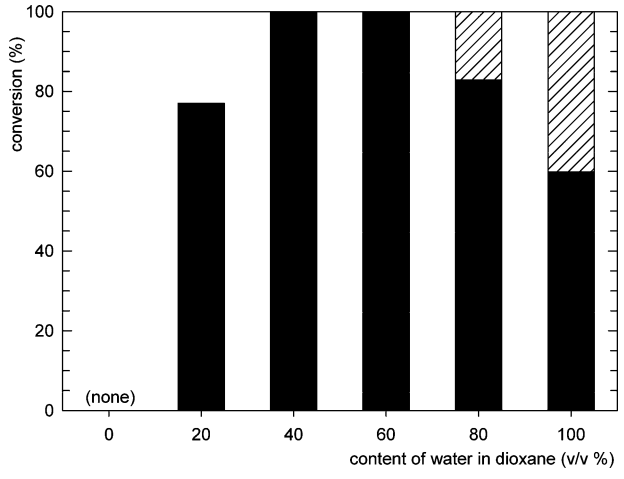

Figure 5. Influence of the amount of water in the water/dioxane reaction medium on the conversion of 4-bromoanisole (**10a**) to 4-cyanoanisole (**11a**, solid bars) and to 4-methoxybenzamide (**12a**, hatched bars). Conditions: **10a** (1.0 mmol), $K_4[Fe(CN)_6)]\cdot 3H_2O$ (0.5 mmol), K_2CO_3 (1.0 mmol), and 2 mol % of **5** in dioxane/water (4 mL), 100 °C/18 h.

well (entries 17 and 18), while a poor conversion was achieved for 4-(dimethylamino)bromobenzene (entry 16). This, however, can be accounted for by a catalyst scavenging effect exerted by the donor group in this substrate, which is present in a large excess. It is also noteworthy that reactions involving substrates bearing electron-withdrawing substituents (4-CF_3 and 4-Cl; −*I*-effect) proceeded still with complete consumptions of the starting bromide but were accompanied by hydrolysis of the initially formed nitrile to the corresponding amide (in dioxane/water, 1:1). Apparently, these substituents reduce electron density at the nitrile group and make it thus more prone toward attack of OH^-, which opens the hydrolytic sequence. Finally, the cyanation of 4-nitrobromobenzene[27] proceeded in only a negligible extent (entry 15), while heterocyclic bromides (2- and 3-bromopyridine and 4-bromopyridine hydrochloride) did not react at all.

CONCLUSIONS

Amidosulfonate ligands reported in this paper represent a new entry among the still rather uncommon nonchiral phosphinoferrocene ligands equipped with highly polar functional groups.[28] The particular combination of the donor groups makes them typical hybrid ligands[29] with adaptable coordination properties. Compared to phosphines sulfonated directly at the backbone,[30] they are easier to prepare and, hence, also more structurally versatile (tunable). The presence of a relatively larger hydrophobic group than in sulfonated triphenylphosphines could make compounds **1**−**3** suitable for use in transition metal-catalyzed reactions at water−organic solvent interfaces.[31] This possibility is currently being checked in our laboratory.

EXPERIMENTAL SECTION

Materials and Methods. All syntheses were carried out under an argon atmosphere and with exclusion of direct daylight. Ester **4**,[11] $[PdCl_2(cod)]$,[32] $[(L^{NC})Pd(\mu\text{-}Cl)]_2$,[33] $[(L^{NC})Pd(\mu\text{-}OAc)]_2$,[34] and (diphenylphosphino)ferrocene[35] were synthesized according to literature procedures. Dichloromethane and chloroform were dried over anhydrous potassium carbonate and distilled. (1,4-)Dioxane and triethylamine were freshly distilled from sodium metal. Anhydrous DMF was purchased from Sigma-Aldrich. Other chemicals and solvents used for crystallizations and in chromatography were used as received without any additional purification.

NMR spectra were measured with a Varian UNITY Inova 400 spectrometer at 298 K. Chemical shifts (δ/ppm) are given relative to internal $SiMe_4$ (^{1}H and ^{13}C) or to external 85% H_3PO_4 (^{31}P). In addition to the standard notation of signal multiplicity, vt and vq are used to denote virtual multiplets due to protons of constituting the AA′BB′ and AA′BB′X spin systems in the amide- and PPh_2-substituted cyclopentadienyl rings, respectively (fc = ferrocene-1,1′-diyl). IR spectra were recorded with an FT IR Nicolet Magna 760 instrument. Low-resolution electrospray ionization (ESI) mass spectra were obtained with an LCQ Deca XP (Thermo Finnigan) or an Esquire 3000 (Bruker) spectrometer. High-resolution ESI-MS spectra were recorded with an LTQ Orbitrap XL spectrometer (Thermo Fisher Scientific).

Preparation of Amide 1. Ester **4** (2.0 mmol, 1.160 g), aminomethanesulfonic acid (2.5 mmol, 0.278 g), and 4-(*N*,*N*-dimethylamino)pyridine (0.06 mmol, 7.3 mg) were dissolved in a mixture of anhydrous *N*,*N*-dimethylformamide (10 mL) and triethylamine (1 mL). The resulting mixture was stirred at room temperature for 6 h and then evaporated under reduced pressure. The residue was extracted with dichloromethane (20 mL) in an ultrasonic bath. The extract was filtered and evaporated to afford a crude product, which was purified by column chromatography over silica gel using CH_2Cl_2/MeOH/Et_3N (100:5:2) as the eluent. The first orange band was collected and evaporated. The product was further recrystallized from hot ethyl acetate (ca. 100 mL) to give crystalline **1**, which was isolated by suction and dried under reduced pressure. Yield: 0.998 g (82%,), orange crystalline solid.

^{1}H NMR ($CDCl_3$): δ 1.32 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3 of Et_3NH^+), 3.11 (dq; $^3J_{HH}$ = 7.2 and 3.4 Hz, 6 H, CH_2 of Et_3NH^+), 4.19 (vq, J = 1.8 Hz, 2 H, fc), 4.20 (vt, J = 2.0 Hz, 2 H, fc), 4.47 (d, $^3J_{HH}$ = 6.5 Hz, 2 H, CH_2S), 4.56 (vt, J_{HH} = 1.8 Hz, 2 H, fc), 4.61 (vt, J = 1.8 Hz, 2 H, fc), 6.50 (t, J_{HH} = 6.1 Hz, 1 H, NH), 7.28−7.38 (m, 10 H, PPh_2), 9.97 (br s, 1 H, Et_3NH^+). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 8.64 (CH_3 of Et_3NH^+), 46.19 (CH_2 of Et_3NH^+), 55.65 (CH_2S), 69.16, 72.06, 73.35

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(d, J_{PC} = 4 Hz) and 74.33 (d, J_{PC} = 4 Hz) (4× CH of fc); 75.82 (*C*-CONH of fc), 128.23 (d, $^3J_{PC}$ = 7 Hz, CH_{meta} of Ph), 128.66 (CH_{para} of PPh_2), 133.45 (d, $^2J_{PC}$ = 20 Hz, CH_{ortho} of PPh_2), 138.64 (d, $^1J_{PC}$ = 9 Hz, C_{ipso} of PPh_2), 169.78 (C═O). The signal due to *C*-P of fc was not found. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −17.0 (s). IR (Nujol, cm^{-1}): ν 3269 (s), 1642 (vs), 1550 (vs), 1399 (w), 1345 (vw), 1317 (m), 1308 (m), 1291 (vw), 1242 (w), 1227 (s), 1213 (s), 1197 (vw), 1170 (vs), 1092 (w), 1070 (w), 1037 (vs), 996 (w), 977 (vw), 959 (w), 924 (vw), 894 (w), 842 (vw), 834 (m), 815 (w), 791 (w), 752 (m), 746 (m), 698 (s), 620 (m), 592 (w), 541 (w), 530 (w), 520 (w), 503 (m), 480 (w), 455 (w), 446 (w), 431 (w). ESI^+-MS: *m*/*z* 102 (Et_3NH^+). ESI^--MS: *m*/*z* 506 ($Ph_2PfcCONHCH_2SO_3^-$). Anal. Calcd for $C_{30}H_{37}O_4PFeN_2S$ (608.5): C 59.21, H 6.13, N 4.60. Found: C 58.99, H 6.10, N 4.53.

Preparation of Amide 2. Ester **4** (2.0 mmol, 1.160 g), 2-aminoethane-1-sulfonic acid (taurine; 2.5 mmol, 0.313 g), and 4-(*N*,*N*-dimethylamino)pyridine (0.06 mmol, 7.3 mg) were dissolved in a mixture of *N*,*N*-dimethylformamide (10 mL) and triethylamine (1 mL). After the reaction mixture was stirred at room temperature for 30 min, 0.1 mL of distilled water was introduced via a syringe, and the stirring was continued for another 20 h. Then the mixture was evaporated under reduced pressure, and the solid residue was taken up with dichloromethane (20 mL). The extract was dried over $MgSO_4$ and evaporated, affording a crude product, which was purified by column chromatography on silica with CH_2Cl_2/MeOH/Et_3N (100:5:2) as the eluent. The first minor band was discarded, and the second, orange band was collected and evaporated. The residue was dissolved in boiling ethyl acetate (ca. 60 mL) and slowly cooled to −4 °C to afford a crystalline solid, which was collected by suction and dried *in vacuo*. Yield of **2**: 1.108 g (89%), orange polycrystalline solid.

^1H NMR ($CDCl_3$): δ 1.35 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3 of Et_3NH^+), 3.03 (m, 2 H, CH_2S), 3.13 (dq, $^3J_{HH}$ = 7.4 and 4.8 Hz, 6 H, CH_2 of Et_3NH^+), 3.80 (m, 2 H, CH_2N), 4.14−4.17 (m, 4 H, fc), 4.44 (vt, J' = 1.8 Hz, 2 H, fc), 4.61 (vt, J' = 1.9 Hz, 2 H, fc), 7.25−7.38 (m, 11 H, PPh_2 + NH), 10.02 (br s, 1 H, Et_3NH^+). $^{13}C\{^1H\}$ NMR (DMSO): δ 15.06 (CH_3 of Et_3NH^+), 35.60 (CH_2S), 45.64 (CH_2 of Et_3NH^+), 50.56 (CH_2N), 68.69, 71.06, 72.86 (d, J_{PC} = 4 Hz) and 73.47 (d, J_{PC} = 15 Hz) (4× CH of fc); 76.59 (d, $^1J_{PC}$ = 9 Hz, *C*-P of fc), 77.42 (*C*-CONH of fc), 128.21 (d, $^3J_{PC}$ = 7 Hz, CH_{meta} of PPh_2), 128.53 (CH_{para} of PPh_2), 132.91 (d, $^2J_{PC}$ = 19 Hz, CH_{ortho} of PPh_2), 138.31 (d, $^1J_{PC}$ = 10 Hz, C_{ipso} of PPh_2), 167.86 (C═O). $^{31}P\{^1H\}$ NMR (DMSO): δ −18.1 (s). IR (Nujol, cm^{-1}): ν 3337 (s), 2678 (m), 1649 (vs), 1548 (vs), 1299 (m), 1257 (w), 1229 (m), 1220 (m), 1186 (m), 1162 (s), 1092 (vw), 1067 (vw), 1025 (vs), 839 (m), 807 (w), 749 (m), 701 (m), 669 (w), 617 (w), 570 (vw), 539 (vw), 523 (vw), 504 (m), 468 (w), 456 (w), 444 (w). ESI^+-MS: *m*/*z* 102 (Et_3NH^+). ESI^--MS: *m*/*z* 520 ($Ph_2PfcCONHCH_2CH_2SO_3^-$). Anal. Calcd for $C_{31}H_{39}O_4PFeN_2S\cdot 0.5AcOEt\cdot 0.1CH_2Cl_2$ (675.1): C 58.89, H 6.45, N 4.15. Found: C 58.53, H 6.42, N 4.24. The amount of residual solvents was verified by ^1H NMR spectrum.

Preparation of Amide 3. The synthesis of **3** was carried out exactly as described for **2** starting from ester **4** (2.0 mmol, 1.160 g), 3-aminopropane-1-sulfonic acid (2.5 mmol, 0.348 g), and 4-(*N*,*N*-dimethylamino)pyridine (0.06 mmol, 7.3 mg) in *N*,*N*-dimethylformamide (10 mL) and triethylamine (1 mL). The reaction mixture was stirred for 30 min before distilled water (0.1 mL) was introduced via syringe, and stirring was continued at room temperature for 20 h. Isolation as described above afforded **3** as an orange crystalline solid. Yield: 1.006 g (79%).

^1H NMR ($CDCl_3$): δ 1.34 (t, $^3J_{HH}$ = 7.4 Hz, 9 H, CH_3 of Et_3NH^+), 2.09 (quintet, J = 6.6 Hz, 2 H, CH_2CH_2S), 2.98 (t, $^3J_{HH}$ = 6.8 Hz, 2 H, CH_2S), 3.11 (dq, $^3J_{HH}$ = 7.4 and 4.8 Hz, 6 H, CH_2 of Et_3NH^+), 3.51 (q, J = 6.2, 2 H, CH_2N), 4.13 (vq, J' = 1.8 Hz, 2H, fc), 4.16 (vt, J' = 2.0 Hz, 2 H, fc), 4.42 (vt, J' = 1.8 Hz, 2 H, fc), 4.64 (vt, J' = 1.9 Hz, 2 H, fc), 6.86 (t, $^3J_{HH}$ = 5.5 Hz, 1 H, N*H*), 7.30−7.39 (m, 10 H, PPh_2), 10.38 (br s, 1 H, Et_3NH^+). $^{13}C\{^1H\}$ NMR (DMSO): δ 9.04 (CH_3 of Et_3NH^+), 25.42 (CH_2CH_2S), 38.34 (CH_2S), 45.63 (CH_2 of Et_3NH^+), 49.47 (CH_2N), 68.78, 71.06, 72.91 (d, J_{PC} = 5 Hz) and 73.35 (d, J_{PC} = 15 Hz) (4× CH of fc); 76.30 (d, $^1J_{PC}$ = 8 Hz, C−P of fc), 77.42 (C−CONH of fc), 128.20 (d, $^3J_{PC}$ = 7 Hz, CH_{meta} of PPh_2), 128.52 (CH_{para} of PPh_2), 132.91 (d, $^2J_{PC}$ = 20 Hz, CH_{ortho} of PPh_2), 138.35 (d, $^1J_{PC}$ = 11 Hz, C_{ipso} of PPh_2), 167.91 (C═O). $^{31}P\{^1H\}$ NMR (DMSO): δ −18.1 (s). IR (Nujol, cm^{-1}): ν 3314 (s), 2692 (s), 1648 (vs), 1545 (vs), 1398 (w), 1343 (vw), 1314 (m), 1296 (m), 1272 (w), 1238 (m), 1222 (w), 1214 (m), 1181 (s), 1150 (vs), 1092 (vw), 1035 (vs), 835 (m), 823 (w), 747 (s), 697 (s), 596 (m), 561 (m), 525 (m), 506 (m), 503 (m), 491 (m), 448 (w), 416 (w). ESI^+-MS: *m*/*z* 102 (Et_3NH^+). ESI^--MS: *m*/*z* 534 ($Ph_2PfcCONHCH_2CH_2CH_2SO_3^-$). Anal. Calcd for $C_{32}H_{41}O_4PFeN_2S$ (636.5): C 60.38, H 6.49, N 4.40. Found: C 60.23, H 6.58, N 4.33.

Preparation of $[HNEt_3]_2[PdCl_2(Ph_2PfcCONHCH_2SO_3$-$\kappa P)_2]$ (5). Ligand **1** (0.20 mmol, 122 mg) was dissolved in dichloromethane (5 mL), and the solution was mixed with a solution of $[PdCl_2(cod)]$ (0.10 mmol, 28.5 mg) in the same solvent (5 mL). After the resulting red reaction mixture was stirred for 1 h, the formed precipitate was collected by suction, washed with diethyl ether and pentane, and dried *in vacuo*. Yield: 123 mg (88%), orange powder.

^1H NMR ($CDCl_3$): δ 1.17 (t, $^3J_{HH}$ = 7.2 Hz, 9 H, CH_3 of Et_3NH^+), 3.08 (q, $^3J_{HH}$ = 7.2 Hz, 6 H, CH_2 of Et_3NH^+), 4.04 (d, J = 6.4 Hz, 2 H, CH_2N), 4.51 (br s, 2 H, fc), 4.68 (vt, J' = 1.7 Hz, 2 H, fc), 4.79 (br s, 2 H, fc), 5.08 (vt, J' = 1.8 Hz, 2 H, fc), 7.44−7.59 (m, 10 H, PPh_2), 8.17 (t, $^3J_{HH} \approx$ 7 Hz, 1 H, NH). $^{31}P\{^1H\}$ NMR (DMSO): δ 16.9 (s). IR (Nujol, cm^{-1}): ν 3306 (s), 2694 (m), 1663 (m), 1652 (m), 1623 (w), 1544 (s), 1399 (w), 1341 (vw), 1311 (m), 1280 (w), 1251 (m), 1238 (vw), 1203 (m), 1183 (m), 1165 (s), 1100 (w), 1071 (w), 1037 (vs), 999 (vw), 964 (vw), 896 (vw), 838 (m), 756 (m), 698 (s), 625 (w), 609 (m), 570 (vw), 541 (w), 526 (w), 517 (m), 504 (m), 474 (m), 461 (w), 435 (w). Anal. Calcd for $C_{60}H_{74}Cl_2Fe_2N_4O_8P_2PdS_2\cdot 0.2CH_2Cl_2$ (1411.3): C 51.23, H 5.31, N 3.97. Found: C 51.24, H 5.25, N 3.83. The presence of residual solvent was confirmed by ^1H NMR spectrum.

Preparation of $[HNEt_3]_2[PdCl_2(Ph_2PfcCONHCH_2CH_2SO_3$-$\kappa P)_2]$ (6). Ligand **2** (0.20 mmol, 124.5 mg) was dissolved in dry dichloromethane (5 mL), and the solution was added to a solution of $[PdCl_2(cod)]$ (0.10 mmol, 28.5 mg) in the same solvent (5 mL). The resulting red solution was stirred for 24 h, concentrated to ca. 5 mL under reduced pressure, and precipitated with diethyl ether/pentane (20 mL, 1:1). The brown-red precipitate was filtered off, washed with diethyl ether and pentane, and dried *in vacuo*. Yield: 139 mg (98%), brown-red powder.

^1H NMR (DMSO-d_6): δ 1.18 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3 of Et_3NH^+), 2.63 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2S), 3.09 (m, 6 H, CH_2 of Et_3NH^+), 3.41−3.50 (m, CH_2N; overlapping with H_2O signal), 4.48−4.55 (m, 4 H, fc), 4.65 (vt, J' = 1.8 Hz, 2 H, fc), 4.88 (vt, J' = 1.8 Hz, 2 H, fc), 7.43−7.59 (m, 10 H, PPh_2), 7.96 (t, $^3J_{HH}$ = 5.5 Hz, 1 H, NH), 8.99 (br s, 1 H, Et_3NH^+). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 16.9 (s). IR (Nujol, cm^{-1}): ν 3329 (vs), 2715 (s), 1636 (s), 1542 (s), 1303 (m), 1246 (w), 1193 (s), 1165 (s), 1099 (m), 1060 (w), 1036 (vs), 999 (vw), 839 (m), 796 (w), 747 (m), 725 (w), 708 (w), 695 (m), 623 (m), 516 (m), 505 (m), 482 (w). Anal. Calcd for $C_{62}H_{78}Cl_2Fe_2N_4O_8P_2PdS_2\cdot 0.8CH_2Cl_2$ (1481.8): C 50.61, H 5.38, N 3.76. Found: C 50.82, H 5.40, N 3.78. The presence of residual solvent was confirmed by ^1H NMR spectrum.

Preparation of $[HNEt_3]_2[PdCl_2(Ph_2PfcCONHCH_2CH_2CH_2SO_3$-$\kappa P)_2]$ (7). Ligand **3** (0.20 mmol, 127.3 mg) and $[PdCl_2(cod)]$ (0.10 mmol, 28.5 mg) were reacted in dichloromethane (total 10 mL) as described above. The reaction mixture deposited a precipitate, which was filtered off, washed with diethyl ether and pentane, and dried *in vacuo*. Yield: 132 mg (91%), orange powder.

^1H NMR (DMSO-d_6): δ 1.17 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3 of Et_3NH^+), 1.80 (p, $^3J_{HH}$ = 7.7 Hz, 2 H, CH_2CH_2S), 2.47−2.53 (m, CH_2S overlapping with the DMSO resonance), 3.09 (q, $^3J_{HH}$ = 7.3 Hz, 6 H, CH_3 of Et_3NH^+), 3.23 (q, $J \approx$ 6.3 Hz, 2 H, CH_2N), 4.46−4.52 (m, 4 H, fc), 4.66 (vt, J' = 1.9 Hz, 2 H, fc), 4.97 (vt, J' = 1.9 Hz, 2 H, fc), 7.43−7.59 (m, 10 H, PPh_2), 8.10 (t, $^3J_{HH}$ = 5.6 Hz, 1 H, NH), 8.95 (bs, 1 H, Et_3NH^+). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 16.9 (s). IR (Nujol, cm^{-1}): ν 3322 (s), 2689 (s), 1655 (m), 1646 (m), 1549 (s), 1344 (vw), 1295 (m), 1268 (w), 1236 (m), 1227 (m), 1206 (w), 1196 (w), 1166 (s), 1099 (m), 1070 (w), 1032 (vs), 999 (vw), 835 (m), 789 (w), 742 (m), 730 (m), 708 (w), 696 (w), 691 (m), 627 (w), 598 (m), 563 (vw), 542 (w), 526 (w), 517 (m), 506 (m), 495 (w), 477 (m), 443 (w). Anal. Calcd for $C_{64}H_{82}Cl_2Fe_2N_4O_8P_2PdS_2\cdot 0.3CH_2Cl_2$ (1475.9):

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C 52.32, H 5.64, N 3.80. Found: C 52.03, H 5.49, N 3.68. The presence of residual solvent was confirmed by ^{1}H NMR spectrum.

Preparation of [HNEt$_3$][(L^{NC})PdCl(Ph$_2$PfcCONHCH$_2$SO$_3$-κ*P*)] (8). A solution of ligand **1** (0.10 mmol, 61 mg) in dry dichloromethane (5 mL) was added to solid [(L^{NC})PdCl]$_2$ (0.050 mmol, 27.5 mg). The resulting solution was stirred for 1 h and then concentrated to ca. 1 mL on a rotary evaporator. The concentrated solution was added dropwise into boiling ethyl acetate (10 mL), and the mixture was slowly cooled to room temperature. The separated crystalline material was isolated by suction and dried *in vacuo*. Yield: 73 mg (83%), ruby red crystals.

^{1}H NMR ($CDCl_3$): δ 1.32 (t, $^3J_{HH}$ = 7.4 Hz, 9 H, CH_3 of Et_3NH^+), 2.85 (d, $^4J_{PH}$ = 2.7 Hz, 6 H, CH_3N), 2.99 (q, $^3J_{HH}$ = 7.4 Hz, 6 H, CH_3CH_2), 4.12 (d, $^4J_{PH}$ = 2.2 Hz, 2 H, CH_2NMe_2), 4.46–4.51 (m, 4 H, $C_{10}H_8$ + CH_2S), 4.63 (bs, 2 H, fc), 4.84 (br s, 2 H, fc), 4.90 (br s, 2 H, fc), 6.24 (td, *J* = 6.4, 1.1 Hz, 1 H, C_6H_4), 6.38 (td, *J* = 7.5, 1.3 Hz, 1 H, C_6H_4), 6.83 (td, *J* = 7.4, 1.1 Hz, 1 H, C_6H_4), 6.90 (unresolved t, 1 H, NH), 6.38 (dd, *J* = 7.4, 1.5 Hz, 1 H, C_6H_4), 7.30–7.44 (m, 6 H, PPh_2), 7.50–7.60 (m, 4 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 8.70 (CH_3 of Et_3NH^+), 46.19 (CH_2 of Et_3NH^+), 50.16 (d, $^3J_{PC}$ = 2 Hz, NCH_3), 53.43, 55.72 (CH_2S and CH_2NMe_2); 69.69, 73.62, 74.20 (CH of fc); 74.34 (d, J_{PC} = 7 Hz, CH of fc), 74.98 (C_{ipso} of fc), 122.49 (CH of C_6H_4), 123.77 (CH of C_6H_4), 124.92 (d, J_{PC} = 5 Hz, CH of C_6H_4), 127.99 (d, J_{PC} = 11 Hz, CH of PPh_2), 130.82 (CH of PPh_2), 131.41 (d, $^1J_{PC}$ = 49 Hz, C_{ipso} of PPh_2), 134.34 (d, J_{PC} = 12 Hz, CH of PPh_2), 138.39 (d, J_{PC} = 11 Hz, CH of C_6H_4), 148.10 (d, J_{PC} = 2 Hz, *C*-Pd of C_6H_4), 152.17 (*C*-CH_2 of C_6H_4), 169.58 (C═O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 32.8 (s). IR (Nujol, cm^{-1}): ν 3293 (s), 2695 (s), 1738 (m), 1650 (m), 1633 (m), 1580 (w), 1535 (s), 1305 (m), 1288 (m), 1246 (m), 1214 (m), 1174 (vs), 1098 (m), 1068 (w), 1041 (s), 996 (vw), 969 (vw), 845 (m), 814 (vw), 751 (m), 744 (m), 696 (m), 622 (m), 543 (w), 522 (m), 509 (m), 487 (vw), 471 (w), 437 (m). ESI$^-$-MS: *m*/*z* 783 ([(L^{NC})PdCl($Ph_2PfcCONHCH_2SO_3$)]$^-$). Anal. Calcd for $C_{39}H_{39}N_3PdClPFeO_4S{\cdot}0.3CH_2Cl_2{\cdot}0.3AcOEt$ (936.5): C 51.94, H 5.60, N 4.49. Found: C 51.35, H 5.60, N 4.31. The amount of clathrated solvents was corroborated by ^{1}H NMR spectroscopy.

Preparation of [(L^{NC})Pd(Ph$_2$PfcCONHCH$_2$SO$_3$-κ^2*P,O*)] (9). Ligand **1** (0.10 mmol, 61 mg) was dissolved in chloroform (3 mL), and the solution was added to a solution of [(L^{NC})Pd(OAc)]$_2$ (0.050 mol, 28 mg) in the same solvent (2 mL). The resulting mixture was stirred for 24 h and concentrated to ca. 1 mL. The solution was filtered through a pad of Celite, and the filtrate containing **9** and **9a** was carefully layered with diethyl ether. Subsequent crystallization by liquid-phase diffusion over several days gave a crystalline material, which was filtered off, washed with diethyl ether, and carefully dried to afford analytically pure **9**. Yield: 43 mg (58%), orange crystals.

^{1}H NMR ($CDCl_3$): δ 2.84 (d, $^4J_{PH}$ = 2.5 Hz, 6 H, CH_3N), 3.98 (vq, *J*′ = 2.0 Hz, 2 H, fc), 4.09 (br s, 2 H, fc), 4.44 (d, $^3J_{HH}$ = 6.5 Hz, 2 H, CH_2S), 4.50 (vt, *J*′ = 2.0 Hz, 2 H, fc), 4.56 (br s, 2 H, fc), 5.69 (s, 2 H, CH_2NMe_2), 6.26 (t, *J* = 6.7 Hz, 1 H, C_6H_4), 6.36 (dt, *J* = 7.6, 1.2 Hz, 1 H, C_6H_4), 6.83 (dt, *J* = 7.2, 0.6 Hz, 1 H, C_6H_4), 6.96 (dd, *J* = 7.5, 1.5 Hz, 1 H, C_6H_4), 7.34–7.47 (m, 6 H, PPh_2), 7.67–7.76 (m, 4 H, PPh_2), 9.09 (t, $^3J_{HH}$ = 6.5 Hz, 1 H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 49.88 (d, $^3J_{PC}$ = 2 Hz, NCH_3), 56.34 (CH_2S), 72.10 (d, $^3J_{PC}$ = 4 Hz, CH_2NMe_2), 72.19 (d, $^1J_{PC}$ = 57 Hz, *C*-P of fc), 72.87, 73.35 (unresolved d) and 73.40 (CH of fc); 74.98 (*C*-CONH of fc), 76.37 (d, J_{PC} = 10 Hz, CH of fc), 122.76 (CH of C_6H_4), 124.58 (CH of C_6H_4), 125.40 (d, J_{PC} = 5 Hz, CH of C_6H_4), 128.64 (d, $^3J_{PC}$ = 11 Hz, CH_{meta} of PPh_2), 129.96 (d, $^1J_{PC}$ = 49 Hz, C_{ipso} of PPh_2), 131.34 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_2), 128.20 (d, $^2J_{PC}$ = 13 Hz, CH_{ortho} of PPh_2), 138.65 (d, J_{PC} = 13 Hz, CH of C_6H_4), 143.23 (d, J_{PC} = 4 Hz, C_{ipso} of C_6H_4), 148.21 (d, J_{PC} = 2 Hz, C_{ipso} of C_6H_4), 173.07 (C═O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 30.4 (s). IR (Nujol, cm^{-1}): ν 3238 (s), 1588 (m), 1578 (vs), 1556 (vs), 1402 (m), 1338 (w), 1323 (m), 1294 (vw), 1250 (m), 1214 (s), 1195 (vw), 1180 (vs), 1157 (vw), 1095 (m), 1072 (vw), 1037 (vs), 1002 (w), 978 (vw), 964 (vw), 898 (w), 870 (w), 845 (w), 830 (vw), 752 (m), 746 (m), 706 (w), 697 (m), 630 (m), 596 (m), 540 (w), 518 (m), 491 (m), 479 (m), 456 (vw), 445 (m), 440 (w). ESI$^+$-MS: *m*/*z* 769 ([(L^{NC})Pd($Ph_2PfcCONHCH_2SO_3$) + Na]$^+$), 747 ([(L^{NC})Pd-($Ph_2PfcCONHCH_2SO_3$) + H]$^+$). Anal. Calcd for $C_{33}H_{33}O_4PFeN_2S$ (746.9): C 53.06, H 4.45, N 3.75. Found: C 52.69, H 4.57, N 3.57.

***In Situ* NMR Study.** A solution of ligand **1** (0.02 mmol, 12.2 mg in 0.8 mL of deuterated solvent) was added to solid [(L^{NC})Pd(OAc)]$_2$ (0.01 mmol, 6.0 mg). The resulting mixture was stirred for 24 h in the dark and analyzed by ^{1}H and ^{31}P{^{1}H} NMR spectrometry. The reactions in dmso-d_6 (δ_P 28.9 major, 30.6 minor), CD_3CN (δ_P 29.4 major, 32.7 minor), or $CDCl_3$ (δ_P ca. 29.6 major, 30.1 minor; broad signals) produced mixtures of two Pd complexes in ca. 60:40 molar ratio. When the reaction was conducted in CD_3OD, pure **9** separated directly from the reaction mixture as a microcrystalline solid.

Reaction of [(L^{NC})Pd(OAc)]$_2$ with (Diphenylphosphino)-ferrocene. A solution of $FcPPh_2$ (74 mg, 0.20 mmol) in THF (5 mL) was added to solid [(L^{NC})Pd(OAc)]$_2$ (60 mg, 0.10 mmol). The reaction mixture was stirred for 1 h and evaporated, and the solid residue was dried *in vacuo*. Yield: 134 mg (quant.), yellow compound.

^{1}H NMR ($CDCl_3$): δ 1.38 (s, 3 H, CH_3CO_2), 2.75 (d, $^4J_{PH}$ = 2.7 Hz, 6 H, NMe_2), 4.00 (virtual q, *J*′ = 2.0 Hz, 2 H, fc), 4.05 (d, $^4J_{PH}$ = 2.3 Hz, 2 H, NCH_2), 4.32 (m, 2 H, fc), 4.40 (s, 5 H, fc), 6.49 (dd, *J* = 5.5, 1.3 Hz, 1 H, C_6H_4), 6.55 (td, *J* = 7.7, 1.6 Hz, 1 H, C_6H_4), 6.92 (td, *J* = 7.3, 1.2 Hz, 1 H, C_6H_4), 7.05 (dd, *J* = 7.4, 1.5 Hz, 1 H, C_6H_4), 7.36–7.47 (m, 6 H, PPh_2), 7.69 (m, 4 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 24.05 (CH_3CO_2), 49.91 (d, $^3J_{PC}$ = 2 Hz, NMe_2), 70.21 (s, CH of fc), 71.15 (d, J_{PC} = 7 Hz, CH of fc), 72.51 (d, $^3J_{PC}$ = 3 Hz, NCH_2), 72.72 (d, J_{PC} = 57 Hz, *C*-P of fc), 74.51 (d, J_{PC} = 10 Hz, CH of fc), 122.76, 123.88, 124.62 (d, J_{PC} = 5 Hz) (3× CH of C_6H_4); 127.84 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.24 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_2), 131.34 (d, $^1J_{PC}$ = 49 Hz, C_{ipso} of PPh_2), 134.39 (d, J_{PC} = 12 Hz, CH of PPh_2), 138.02 (d, J_{PC} = 10 Hz, CH of C_6H_4), 146.25 (d, J_{PC} = 5 Hz, *C*-Pd of C_6H_4), 148.63 (d, J_{PC} = 2 Hz, *C*-CH_2 of C_6H_4), 176.92 (CH_3CO_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 29.6 (s). ESI$^+$-MS: *m*/*z* 692 ([M + Na]$^+$), 611 ([(L^{NC})Pd($FcPPh_2$) + H]$^+$).

Pd-Catalyzed Cyanation of Aryl Bromides. A General Procedure. A reaction vessel was charged with aryl bromide (1.0 mmol), potassium carbonate (138 mg, 1.0 mmol), potassium hexacyanoferrate(II) trihydrate (212 mg, 0.5 mmol), and a palladium source (2 mol % with respect to the aryl bromide). The flask was equipped with a magnetic stirring bar, flushed with argon, and sealed. The solvent (1,4-dioxane/water, 1:1; 4 mL) was added via syringe, and the sealed flask was transferred into an oil bath maintained at 100 °C. After stirring for 18 h, the reaction mixture was cooled and quenched with water (2 mL), ethyl acetate (5 mL), and mesitylene (120 mg, 1.0 mmol) as an internal standard. After the organic layer was analyzed by NMR spectroscopy, it was separated and washed with brine (10 mL). The aqueous layer was extracted with ethyl acetate (3× 5 mL). The organic extracts were combined, dried over magnesium sulfate, and evaporated under reduced pressure. The crude product was purified by flash column chromatography over silica using an ethyl acetate/hexanes mixture to give pure nitriles after evaporation. Carboxylic acids **11k** and **11l** were isolated similarly after acidification of the reaction mixture with 3 M HCl.

Characterization Data. 4-Cyanoanisole (11a): ^{1}H NMR ($CDCl_3$): δ 3.86 (s, 3 H, CH_3O), 6.96 (dm, $^3J_{HH}$ = 6.8 Hz, 2 H, C_6H_4), 7.59 (dm, $^3J_{HH}$ = 7.0 Hz, 2 H, C_6H_4) (ref 36). **4-Cyanotoluene (11b):** ^{1}H NMR ($CDCl_3$): δ 2.42 (s, 3 H, CH_3), 7.27 (dm, $^3J_{HH}$ = 7.9 Hz, 2 H, C_6H_4), 7.54 (dm, $^3J_{HH}$ = 8.1 Hz, 2 H, C_6H_4) (ref 36). **3-Cyanotoluene (11c):** ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 3 H, CH_3), 7.32–7.49 (m, 4 H, C_6H_4) (ref 37). **2-Cyanotoluene (11d):** ^{1}H NMR ($CDCl_3$): δ 2.55 (s, 3 H, CH_3), 7.27 (tm, $^3J_{HH}$ = 8.2 Hz, 1 H, H^5 of C_6H_4), 7.32 (dm, $^2J_{HH}$ = 7.3 Hz, 1 H, H^6 of C_6H_4), 7.48 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H^4 of C_6H_4), 7.60 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H^3 of C_6H_4) (ref 36). **4-*tert*-Butylbenzonitrile (11e):** ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 9 H, CH_3), 7.48 (dm, $^3J_{HH}$ = 8.8 Hz, 2 H, C_6H_4), 7.59 (dm, $^3J_{HH}$ = 8.8 Hz, 2 H, C_6H_4) (ref 38). **4-(Trifluoromethyl)benzonitrile (11f):** ^{1}H NMR (DMSO-d_6): δ 7.84 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, C_6H_4), 8.06 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, C_6H_4). Spectra recorded in $CDCl_3$ corresponded with the literature data (ref 36). **4-Cyanoacetophenone (11g):** ^{1}H NMR ($CDCl_3$): δ 2.65 (s, 3 H, CH_3), 7.78 (dm, $^3J_{HH}$ = 8.0 Hz, 2 H, C_6H_4), 8.05 (dm, $^3J_{HH}$ = 8.1 Hz, 2 H, C_6H_4) (ref 39). **4-Cyanobiphenyl (11h):** ^{1}H NMR ($CDCl_3$): δ 7.42–7.51 (m, 3 H, $C_{12}H_9$), 7.57–7.61 (m, 2 H, $C_{12}H_9$), 7.66–7.74 (m, 4 H, $C_{12}H_9$) (ref 38). **4-Chlorobenzonitrile (11i):** ^{1}H NMR ($CDCl_3$): δ 7.47 (dm, $^3J_{HH}$ = 8.8 Hz, 2 H, C_6H_4),

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7.61 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, C_6H_4) (ref 36). **4-(Dimethylamino)-benzonitrile (11k):** ^{1}H NMR ($CDCl_3$): δ 3.04 (s, 6 H, NMe_2), 6.64 (d, $^3J_{HH}$ = 9.2 Hz, 2 H, C_6H_4), 7.47 (d, $^3J_{HH}$ = 9.0 Hz, 2 H, C_6H_4) (ref 36). **4-Cyanobenzoic acid (11l):** ^{1}H NMR (DMSO-d_6): δ 7.99 (dm, $^3J_{HH}$ = 8.0 Hz, 2 H, C_6H_4), 8.09 (dm, $^3J_{HH}$ = 8.1 Hz, 2 H, C_6H_4), 13.56 (br s, 1 H, CO_2H) (ref 37). **(4-Cyanophenyl)acetic acid (11m):** ^{1}H NMR (DMSO-d_6): δ 3.72 (s, 2 H, CH_2), 7.48 (dm, $^3J_{HH}$ = 8.0 Hz, 2 H, C_6H_4), 7.78 (dm, $^3J_{HH}$ = 8.4 Hz, 2 H, C_6H_4) (ref 40). 4-Nitrobenzonitrile (**11j**)[41] and the amides (**12a**, **12f**, and **12i**)[42] were identified upon comparing ^{1}H NMR spectra of the reaction mixture with the literature data.

X-ray Crystallography. Single crystals suitable for X-ray diffraction analysis were grown from hot ethyl acetate (**1**: yellow plate, 0.08 × 0.20 × 0.38 mm^3; **3**: orange prism, 0.25 × 0.44 × 0.47 mm^3) or by liquid-phase diffusion from diethyl ether/dichloromethane (**5**·2.5CH_2Cl_2: brown plate, 0.05 × 0.25 × 0.30 mm^3) and from diethyl ether/chloroform (**9**·2$CHCl_3$: orange plate, 0.08 × 0.13 × 0.33 mm^3).

Full-set diffraction data ($\pm h \pm k \pm l$; θ_{max} = 26.0−27.6°, data completeness ≥97%) were collected with a KappaCCD or Apex2 diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) at 150(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by the direct methods (SIR-97[43] or SHELXS-87[44]) and refined by full-matrix least-squares on F^2 (SHELXL-97[44]). Unless noted otherwise, the non-hydrogen atoms were refined with anisotropic displacement parameters. The NH hydrogens were identified on difference density maps and refined either freely (**1**) or as riding atoms with U_{iso} = 1.2 U_{eq}(N) (all other structures). All CH hydrogen atoms were included in calculated positions and refined as riding atoms. Selected crystallographic data and structure refinement parameters are available as Supporting Information, Table S1. Particular details on structure refinement are as follows.

One of the Et_3NH^+ cations in the structure of **5**·2.5CH_2Cl_2 is disordered and was refined with isotropic displacement parameters for the carbon atoms. In addition, the solvent of crystallization in the same structure was found to be severely disordered, and its contribution to the scattering was numerically removed using the SQUEEZE[45] routine as incorporated in the PLATON program.[46]

Geometric data and structural drawings were obtained with a recent version of the PLATON program. The numerical values are rounded with respect to their estimated deviations (esd's) given in one decimal. Parameters relating to atoms in constrained positions are given without esd's.

■ ASSOCIATED CONTENT

Supporting Information

Additional structural drawings, summary of crystallographic data (Table S1), and CIF files for all structurally characterized compounds are available free of charge via the Internet at http://pubs.acs.org.

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(20) Dimer $[(L^{NC})Pd(OAc)]_2$ was shown react with stoichiometric amounts of phosphines to afford mononuclear complexes of the type $[(L^{NC})Pd(OAc)(PR_3)]$: Ciba Specialty Chemicals (Van Der Schaaf, P. A.; Kolly, R.; Tinkl, M.) Patent WO 200301372, 2003.

(21) $(L^{NC})Pd$ complexes with simple phosphinocarboxylic ligands: (a) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115. (b) Braunstein, P.; Matt, D.; Nobel, D.; Bouaoud, S.-E.; Grandjean, D. *J. Organomet. Chem.* **1986**, *301*, 401. Representative examples for phosphinoferrocene donors: (c) Štěpnička, P.; Císařová, I. *Organometallics* **2003**, *22*, 1728. (d) Štěpnička, P.; Lamač, M.; Císařová, I. *Polyhedron* **2004**, *23*, 921. (e) Lamač, M.; Císařová, I.; Štěpnička, P. *Collect. Czech. Chem. Commun.* **2007**, *72*, 985, and refs 9b, 10c, 12, 19f.

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