EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

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To be cited as: Eur. J. Inorg. Chem. 10.1002/ejic.201601262

Link to VoR: https://doi.org/10.1002/ejic.201601262

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Synthesis, Palladium(II) Complexes and Catalytic Use of a Phosphanylferrocene Ligand Bearing a Guanidinium Pendant

Ondřej Bárta,[a] Ivana Císařová,[a] Petr Štěpnička*[a]

Abstract: A polar phosphanylferrocene donor equipped with a hydrophilic guanidinium pendant, $Ph_2PfcCH_2NHC(NH)NH_2$·HCl (**1**·HCl; fc = ferrocene-1,1'-diyl), was prepared from the corresponding amine hydrochloride, $Ph_2PfcCH_2NH_2$·HCl (**2**·HCl), and was studied as a ligand for Pd(II) ions. The reactions of **1**·HCl with $[PdCl_2(MeCN)_2]$ at 1:1 and 1:2 Pd-to-ligand ratios led to an unexpected zwitterionic complex, $[PdCl_3(\mathbf{1}H\text{-}\kappa P)]$ (**3**), and the usual bis-phosphane complex, *trans*-$[PdCl_2(\mathbf{1}H\text{-}\kappa P)_2]Cl_2$ (**4**), which were structurally characterized. The defined and air-stable solvated complex **3**·Me_2CO and an *in situ* generated $Pd(OAc)_2$/**1**·HCl system afforded active catalysts for the Suzuki-Miyaura cross-coupling of anionic triolborates with aryl bromides to give the corresponding biphenyls. This reaction, which does not require the presence of an additional base, was advantageously performed in aqueous ethanol, and the coupling products were isolated in good to excellent yields.

Introduction

Ferrocene phosphanes are frequently used as supporting ligands for various metal-mediated organic transformations.[1] However, their use in green aqueous reaction media[2] is compromised by their generally high hydrophobicity. Few examples of water-soluble phosphanylferrocene ligands have appeared in the literature,[3] which prompted us to prepare and study ferrocene phosphanes modified by hydrophilic polar substituents. During our investigations, we have mainly focused on functional phosphanylamides[4] derived from 1'-(diphenylphosphanyl)ferrocene-1-carboxylic acid (Hdpf)[5] and amines bearing polar terminal substituents.[6] In continuation of these studies, we recently expanded the palette of polar modifying groups and prepared ferrocene-based donors with amide substituents bearing neutral urea[7,8] or cationic guanidinium[9] moieties in their terminal positions (compounds **A**-**C** in Scheme 1), which were evaluated in Pd-catalyzed reactions performed in aqueous reaction media.

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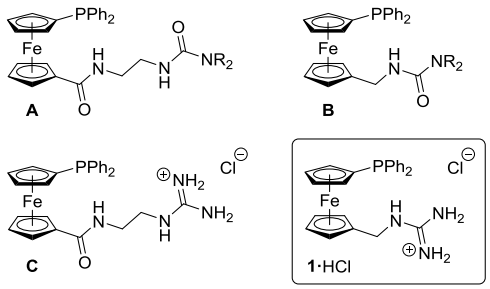


Scheme 1. Examples of phosphanylferrocene donors bearing urea and guanidinium pendants and the newly designed compound **1**·HCl.

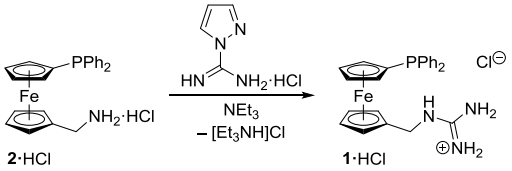
In this contribution, we report another polar donor related to the **B**-type compounds, the phosphanyl guanidinium salt **1** (Scheme 1), wherein the phosphanylferrocene unit and the hydrophilic guanidinium moiety are connected by a flexible methylene linker. Furthermore, we describe Pd(II) complexes prepared with this new functional phosphane and their use in the Pd-catalyzed Suzuki-Miyaura cross-coupling of anionic arylborates with aryl bromides in aqueous solvents.

Notably, N-(ferrocenylmethyl)guanidines are not unprecedented but have been studied predominantly with respect to their supramolecular complexation ability.[10] The application of guanidinium moieties in the design of hydrophilic ferrocene donors remains largely unexplored, in contrast with reports addressing the preparation and catalytic application of water-soluble phosphane ligands bearing guanidinium substituents on their organic backbone.[11]

Results and Discussion

Synthesis of phosphane 1·HCl

The target phosphanylguanidine hydrochloride **1**·HCl was prepared (Scheme 2) by the direct guanylation of 1'-(diphenylphosphanyl)-1-(aminomethyl)ferrocene (**2**), which was generated *in situ* from its hydrochloride[7b] and triethylamine, with 1*H*-pyrazole-1-carboximidamide hydrochloride[12,13] in dry THF. The compound was obtained as a yellow-orange, non-crystallizing solid in 93% yield after the removal of precipitated triethylamine hydrochloride and column chromatography.



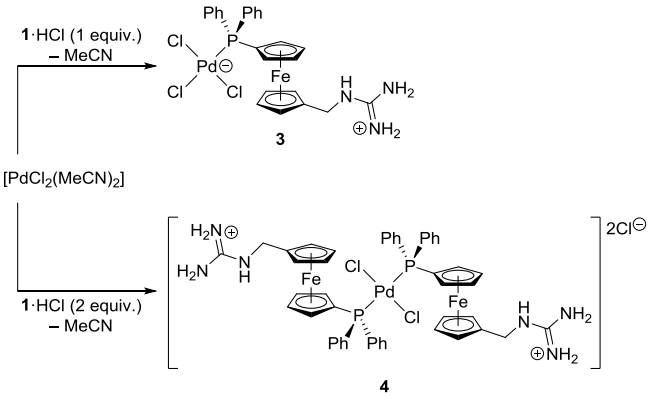
Scheme 2. Synthesis of **1**·HCl.

Phosphane **1**·HCl was characterized by multinuclear NMR spectroscopy, IR spectroscopy and mass spectrometry. Reliable microanalytical data were not obtained, presumably due to the presence of residual solvent in the amorphous material. The ^{1}H, ^{31}P and ^{13}C NMR spectra of **1**·HCl exhibited signals of the phosphanylferrocene moiety within the usual ranges. The ^{13}C NMR signal of the guanidinium unit was observed at δ_C 156.49, while the methylene linking group resonated at δ_H 3.93 (NH-coupled doublet) and δ_C 39.56. The electrospray ionization (ESI) mass spectrum revealed ions attributable to [**1**H]$^+$ (*m/z* 442) and the corresponding phosphane oxide (*m/z* 458). A further peak in the ESI MS spectrum at *m/z* 383 was assigned to the [1′-(diphenylphosphanyl)ferrocenyl]methylium cation, [Ph_2PfcCH_2]$^+$ (or an isomeric species resulting from a rearrangement), in accordance with the relatively easy formation of stabilized ferrocenylmethylium cations.[14,15] Finally, the IR spectrum of **1**·HCl showed absorptions typical of the guanidinium moiety, namely, broad structured bands in the ranges of 2800-3500 cm^{-1} (N-H stretching modes) and 1550-1750 cm^{-1} (N-H bending and C-N stretching vibrations).[16]

Pd(II) complexes with 1·HCl as a P-donor

In view of the anticipated catalytic application, compound **1**·HCl was studied as a ligand in Pd(II) complexes (Scheme 3). The reaction of [$PdCl_2(MeCN)_2$] with **1**·HCl at a 1:1 molar ratio produced a red precipitate, which was insoluble in common organic solvents and was thus difficult to purify and analyze. Nonetheless, when the synthesis was performed using a reactive diffusion approach (*i.e.*, when a methanol solution of the ligand was allowed to diffuse into an acetone solution of the palladium precursor), it produced an orange-red crystalline solid, which was identified by X-ray diffraction analysis as the relatively unusual zwitterionic complex **3**, in which the protonated phosphanylguanidine coordinates as a P-donor, whereas its associated chloride counteranion binds to palladium, forming a negatively charged $PdCl_3^-$ fragment. The compound separates in the form of the defined stoichiometric solvate **3**·Me_2CO.

When the amount of the phosphane was increased to 2 equiv., the reaction afforded the expected bis-phosphane complex **4** (Scheme 3). The coordination of the phosphane moieties and the structural differences between these complexes were clearly manifested in the ^{31}P NMR spectra. While the ^{31}P NMR signal of the free ligand was observed at δ_P –17.5, those of **3**·Me_2CO and **4** were shifted to δ_P 24.7 and 17.1, respectively.



Scheme 3. Preparation of Pd(II) complexes **3** and **4**.

The coordination environment of the Pd(II) ion in **3**·Me_2CO is essentially planar[17] (see Figure 1 and Table 1). However, the Pd-Cl3 bond located *trans* to the phosphane donor is significantly longer that the two remaining Pd-Cl bonds, which corresponds to a greater *trans*-influence[18] of the phosphane donor [P > Cl]. Similarly, the Pd-P bond in **3**·Me_2CO is shortened with respect to the Pd-P bond in the bis-phosphane complex **4** (see below).[19]

The ferrocene unit in **3**·Me_2CO adopts regular geometry with marginally varying Fe-C distances (2.043(2)-2.053(2) Å). Its cyclopentadienyls are mutually tilted by 3.6(1)° and assume an anticlinal eclipsed conformation,[20] which shifts the guanidinium unit away from the P-bound metal center. The protonated guanidine moiety is symmetrical and extensively delocalized, showing similar N-C distances (*N.B.* the bonds to the terminal nitrogens are only approximately 0.01 Å shorter than N1-C24)[21] and N-C-N angles that do not depart much from the ideal 120°.

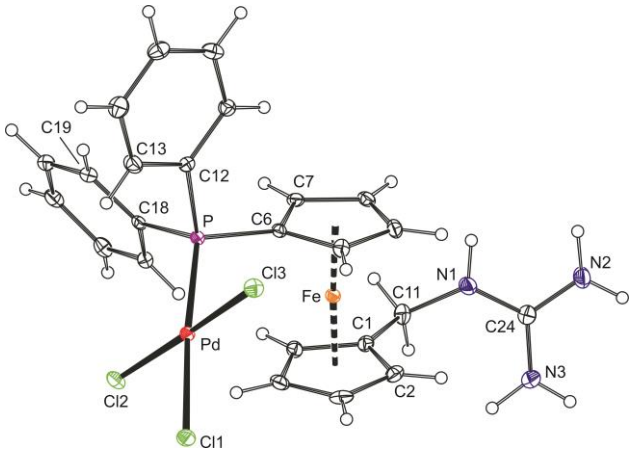


Figure 1. PLATON plot of the complex molecule in the structure of **3**·Me_2CO. Displacement ellipsoids are scaled to the 30% probability level.

Table 1. Selected geometric parameters for **3**·Me_2CO.[a,b]

Distances		Angles	
Pd-Cl1	2.3849(6)	Cl1-Pd-Cl2	89.03(2)
Pd-Cl2	2.3083(5)	Cl1-Pd-Cl3	89.44(2)
Pd-Cl3	2.3170(5)	P-Pd-Cl2	92.65(2)
Pd-P	2.2430(6)	P-Pd-Cl3	89.13(2)
C24-N1	1.335(3)	N1-C24-N2	118.4(2)
C24-N2	1.324(3)	N1-C24-N3	121.2(2)
C24-N3	1.325(3)	N2-C24-N3	120.4(2)
C11-N1	1.457(3)	C1-C11-N1	114.6(2)
Fe-Cg1	1.653(1)	tilt	3.6(1)
Fe-Cg2	1.653(1)	τ	143.3(2)

[a] Definitions: Cg1 and Cg2 are the centroids of the cyclopentadienyl rings C(1-5) and C(6-10), respectively. Tilt is the dihedral angle subtended by the least-squares cyclopentadienyl planes, while τ is the torsion angle C1-Cg1-Cg2-C6. [b] Further data: C1S=O1S = 1.211(4) Å (solvating acetone).

The molecules constituting the structure of **3**·Me_2CO assemble into compact infinite chains oriented along the crystallographic *a* axis by means of N-H···Cl hydrogen bonds (Figure 2). Whereas the Cl1 and Cl2 atoms form such interactions with only one NH proton, Cl3 acts as a bifurcate H-bond acceptor (the N···Cl distances in the range of 3.232(2)-2.320(2) Å). The remaining NH moiety (N3-H5N) forms a hydrogen bridge toward the solvating acetone (N3···O1S = 2.882(3) Å).

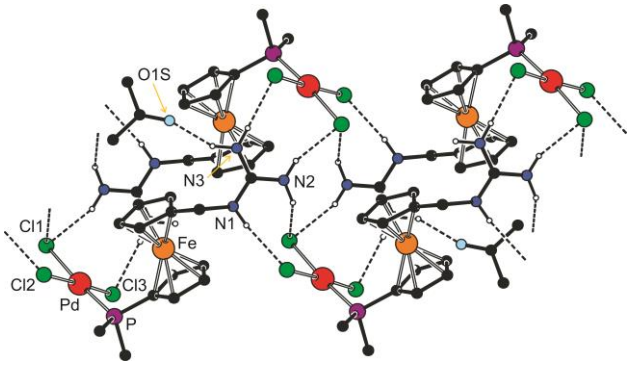


Figure 2. Section of the infinite, one-dimensional hydrogen-bonded array in the crystal structure of **3**·Me_2CO. The hydrogen bonds are shown as dashed lines. For clarity, only the NH hydrogens and pivotal carbons from the phenyl rings are shown.

The bis-phosphane complex crystallizes in solvated form **4**·2MeOH·$2H_2O$ (Figure 4) with the Pd atoms residing on the crystallographic inversion centers (space group *P*–1) and thus with only the half of the molecule structurally independent. The guanidinium groups are directed away from the Pd center (see parameter τ in Table 2), giving rise to hydrophilic layers that accommodate disordered chloride anions and solvating water molecules.[22] Solvating methanol also occupies this space but is fixed in position, serving as a hydrogen bond acceptor to one of the guanidinium NH groups (N3-H5N···O1S hydrogen bond with N···O distance of 2.880(3) Å).

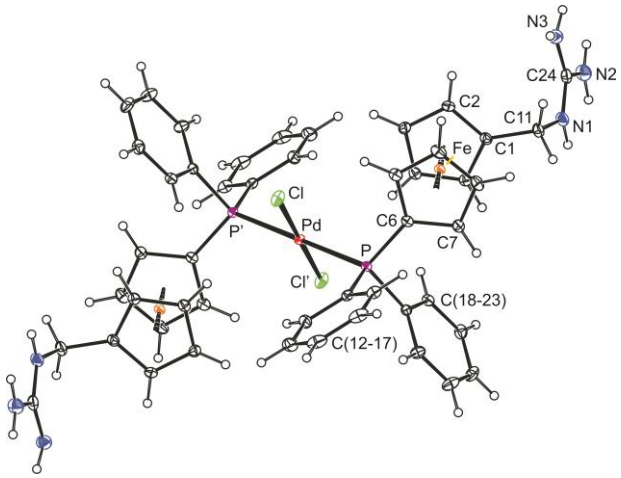


Figure 3. PLATON plot of the complex molecule in the structure of **4**·2MeOH·$2H_2O$. The prime-labeled atoms are generated by crystallographic inversion. Displacement ellipsoids enclose the 30% probability level.

Overall, the geometry of the complex molecule (Table 2) resembles that of the analogous compounds resulting from other 1'-functionalized phosphanylferrocene donors, [$PdCl_2$(Ph_2PfcX-κ*P*)$_2$] (fc = ferrocene-1,1'-diyl).[6a-c,23] Because of the imposed symmetry, the coordination environment of the Pd(II) ion is ideally planar but the interligand angles differ slightly from the ideal 90° due to steric reasons. The protonated guanidine units are planar (within ca. 0.01 Å) and display nearly identical N-C distances. Similarly to the mono-phosphane complex **3**·Me_2CO, the N1-C24-N3 angle in the structure of **4**·2MeOH·$2H_2O$ is the most opened among the N-C24-N angles, reflecting the presence of the connecting methylene group, which is positioned *syn* with respect to N3. The guanidine plane is directed away from the ferrocene unit and subtends a dihedral angle of 77.15(7)° with the cyclopentadienyl ring C(1-5).

Table 2. Selected geometric parameters for **4**·2MeOH·$2H_2O$.[a]

Distances		Angles	
Pd-Cl1	2.3008(4)	P-Pd-Cl1	87.66(1)[b]
Pd-P	2.3442(4)	P-Pd-Cl1'	92.34(1)[b]
C24-N1	1.329(2)	N1-C24-N2	118.5(2)

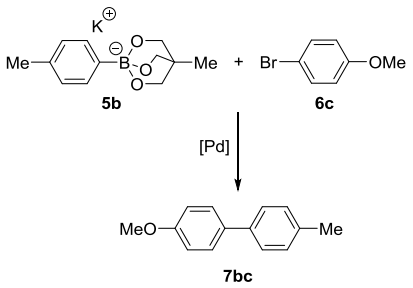
C24-N2	1.334(2)	N1-C24-N3	122.1(2)
C24-N3	1.330(3)	N2-C24-N3	119.5(2)
C11-N1	1.473(2)	C1-C11-N1	111.6(2)
Fe-Cg1	1.6443(8)	tilt	1.8(1)
Fe-Cg2	1.6458(8)	τ	–142.0(1)

[a] The parameters are defined as for **3**·Me_2CO. See footnote [a] in Table 1. [b] The angles P-Pd-Cl1 and P-Pd-Cl1' sum up to 180° due to imposed symmetry.

Catalytic evaluation

Suzuki-Miyaura cross-coupling, one of the most widely used cross-coupling reaction, has numerous practical applications in common laboratory practice and large-scale preparations.[24] As a part of continuous development, anionic aryltriolborates[25]—air-stable boron reagents[26,27] that undergo the coupling reaction without an added base and can be utilized in aqueous reaction media—have recently been introduced. With the new hydrophilic ligand **1**·HCl in hands, we decided to use these reagents and study their reactions mediated by Pd-**1** complexes in organic solvents and their aqueous mixtures.[28]

The initial screening experiments were performed for the reaction of borate **5b** with 4-bromoanisole (**6c**) to give 4-methyl-4'-methoxybiphenyl (**7bc**; Scheme 4) using different solvents and catalysts. In all cases, a slight excess of the borate was used (1.1 equiv.) and the concentration of the reaction components was kept constant (0.2 M for aryl halide). As shown in Table 3, the reactions performed at 50 ºC and with 0.5 mol.% of the defined (complex **3**·Me_2CO) or *in situ* generated ($Pd(OAc)_2$/**1**·HCl) pre-catalyst proceeded with complete conversion within 24 h, irrespective of the solvent used. The isolated yields of **7bc** were satisfactory (above 70%), especially when ethanol and its 1:1 aqueous mixture were used as the reaction solvent.



Scheme 4. The coupling reaction used to screen the reaction conditions.

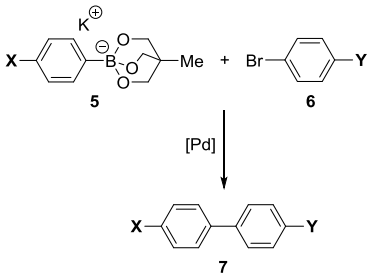
Table 3. The optimization experiments.[a]

Solvent	Conversion[b] (Isolated Yield) of **7bc** [%]	
	$Pd(OAc)_2$/**1**·HCl	**3**
ethanol	100 (87)	100 (80)
ethanol/water (1:1)	100 (87)	100 (89)
water	100 (79)	100 (78)
toluene/water (1:1)	100 (72)	100 (72)

[a] Borate **5b** (1.1 mmol) and aryl bromide **6c** (1.0 mmol) were reacted in the presence of 0.5 mol.% catalyst (generated *in situ* from $Pd(OAc)_2$ and 1.1 molar equiv. of **1**·HCl or complex **3**) in 5 mL of the solvent at 50 ºC for 24 h. The quoted conversions and yields are averages of two independent runs. [b] The conversions were determined by integration of ^{1}H NMR spectra.

Considering the negligible differences in the reaction yields achieved with both tested catalysts at 0.5 mol.% Pd loading, the following experiments were carried out only with the defined and easy-to-handle solvated complex **3**. When the model coupling reaction was conducted with this pre-catalyst at 80 °C in aqueous ethanol, complete conversion to **7bc** was achieved within 3 h, and this outcome did not change after decreasing the catalyst loading to 0.2 mol.% (Note: similar biaryl coupling reactions described in the original article[25] reporting the use of anionic triolborates were performed in the presence of 3 mol.% of $Pd(OAc)_2$ and 6.6 mol.% of supporting phosphine albeit at 20 °C).

In view of the screening results, the following reaction scope tests (Scheme 5) were performed in the presence of 0.2 mol.% **3**·Me_2CO in 50% aqueous ethanol at 80 °C for 3 h. The results given in Table 4 indicate that changing the substituents in the boronate and aryl bromide has a marginal influence under the given reaction conditions. Substrates with both electron-donating and electron-withdrawing substituents reacted efficiently, affording the coupling products in full or nearly complete conversion and with good isolated yield. The lowest, but still very good, conversion of 92%, achieved in the reaction of 4-tolyl boronate **5b** with 1-bromo-4-nitrobenzene (**6h**), can be explained by the lower solubility of the aryl halide in the reaction mixture.



Scheme 5. Reaction scope tests [X/Y = H (**a**), Me (**b**), MeO (**c**), Ph (**d**), CF_3 (**e**), F (**f**), Cl (**g**), NO_2 (**h**), and CN (**i**)].

Table 4. Summary of the reaction scope tests.[a]

Boronate **5**	Bromide **6**	Product **7**	Conversion (Yield)[b] [%]
5b (4-Me)	**6b** (4-Me)	**7bb**	100 (90)
5b (4-Me)	**6c** (4-MeO)	**7bc**	100 (90)
5b (4-Me)	**6e** (4-CF_3)	**7be**	100 (83)
5b (4-Me)	**6g** (4-Cl)	**7bg**	100 (89)
5b (4-Me)	**6h** (4-NO_2)	**7bh**	92 (85)
5b (4-Me)	**6i** (4-CN)	**7bi**	100 (88)
5a (4-H)	**6c** (4-MeO)	**7ac**	98 (89)
5d (4-Ph)	**6c** (4-MeO)	**7cd**	94 (71)
5f (4-F)	**6c** (4-MeO)	**7cf**	100 (89)

[a] The corresponding borate **5** (1.1 mmol) and aryl bromide **6** (1.0 mmol) were reacted in the presence of 0.2 mol.% of complex **3** in 5 mL of ethanol-water (1:1 v/v) at 80 ºC for 3 h. The quoted data are averages of two independent runs. [b] The conversions were determined by integration of ^{1}H NMR spectra.

Conclusions

A new polar phosphanylferrocene donor bearing a cationic guanidinium substituent at the other cyclopentadienyl ring connected through a methylene spacer can be easily prepared from the corresponding amine and isolated as the stable chloride salt **1**·HCl. This compound coordinates Pd(II) ions as a simple phosphane, affording the zwitterionic complex [$PdCl_3$(**1**H-κ*P*)] (**3**) or the usual bis-phosphane complex *trans*-[$PdCl_2$(**1**H-κ*P*)$_2$]Cl_2 (**4**), depending on the Pd-to-ligand ratio. Both the defined complex **3** and a simple catalyst generated *in situ* from palladium(II) acetate and **1**·HCl efficiently mediate the "base-free" coupling of aryl boronate reagents with aryl bromides to afford biphenyls in aqueous solvents.

Experimental Section

Materials and methods. All syntheses were performed under argon using standard Schlenk techniques and with the protection from the direct daylight. Compound **2**·HCl was prepared according to the literature.[7b] Tetrahydrofuran and methanol were dried by PureSolv MD5 (Innovative Technology, USA) solvent purification system. Acetone was dried with anhydrous potassium carbonate and then distilled under argon. Toluene and triethylamine were dried by standing over sodium metal and distilled. Other chemicals and solvents (Lach-Ner, Czech Republic) were used without additional purification.

The NMR spectra were measured at 25 ºC with a Varian INOVA 400 spectrometer operating at 399.95, 100.58, 376.29 and 161.90 MHz for ^{1}H, ^{13}C, ^{19}F and ^{31}P, respectively. The chemical shifts (δ in ppm) are given relative to an internal tetramethylsilane (^{1}H and ^{13}C), external neat $CFCl_3$ (^{19}F) and external 85% aqueous H_3PO_4 (^{31}P). In addition to the usual description of signal multiplicity, vt and vq are used to denote virtual multiplets due to the magnetically non-equivalent protons at the cyclopentadienyl rings (spin systems AA'BB' and AA'BB'X for the methylene- and phosphanyl-substituted rings, respectively, where A, B = ^{1}H, and X = ^{31}P). IR spectra were recorded in Nujol mulls on a Nicolet 6700 FTIR spectrometer over the range of 400-4000 cm^{-1}. ESI+ MS spectra were obtained with a Bruker Esquire 3000 spectrometer for samples dissolved in HPLC-grade methanol. ESI– MS spectra including the high-resolution (HR) measurements were performed with a LTQ Orbitrap XL (Thermo Fisher Scientific) instrument. Elemental analyses were determined with a Perkin-Elmer 2400 Series II CHNS/O analyzer. The presence of residual solvent (if any) was confirmed by NMR analysis.

Synthesis of 1·HCl. Compound **2**·HCl (871 mg, 2.0 mmol) and commercial 1*H*-pyrazole-1-carboxamidine hydrochloride (322 mg, 2.2 mmol) were mixed in dry THF (30 mL). Anhydrous triethylamine (0.59 mL, 4.2 mmol) was added, and the reaction mixture was stirred at room temperature overnight. The resulting mixture was filtered to remove precipitated triethylammonium chloride, and the orange filtrate was evaporated under vacuum. The crude orange oily product was purified by column chromatography using silica gel and dichloromethane-methanol (10:1) as the eluent. The first minor band was discarded. The following (major) band was collected, evaporated and the residue was chromatographed again over a *short* silica gel column with ethyl acetate-methanol (4:1). Following evaporation, hydrochloride **1**·HCl was isolated as a yellow-orange glassy solid. Yield: 893 mg (93%).

^{1}H NMR (DMSO-d_6): δ = 3.93 (d, $^3J_{HH}$ = 5.6 Hz, 2 H, CH_2), 3.98 (vt, *J'* = 1.8 Hz, 2 H, fc), 4.12 (vq, *J'* = 1.9 Hz, 2 H, fc), 4.17 (vt, *J'* = 1.9 Hz, 2 H, fc), 4.51 (vt, *J'* = 1.7 Hz, 2 H, fc), 7.28-7.41 (m, 10 H, Ph), 7.81 (t, $^3J_{HH}$ = 5.6 Hz, 1 H, CH_2NH) ppm. ^{13}C{^{1}H} NMR (DMSO-d_6): δ = 39.56 (s, CH_2), 68.84 (s, CH of fc), 69.05 (s, CH of fc), 71.73 (d, J_{PC} = 4 Hz, CH of fc), 73.10 (d, J_{PC} = 15 Hz, CH of fc), 75.70 (d, $^1J_{PC}$ = 7 Hz, *C*-PPh_2 of fc), 84.10 (s, *C*-CH_2 of fc), 128.18 (d, $^2J_{PC}$ = 7 Hz, CH^{ortho} of PPh_2), 128.50 (s, CH^{para} of PPh_2), 132.91 (d, $^3J_{PC}$ = 20 Hz, CH^{meta} of PPh_2), 138.61 (d, $^1J_{PC}$ = 10 Hz, C^{ipso} of PPh_2), 156.49 (s, guanidinium C^{ipso}) ppm. ^{31}P{^{1}H} NMR (DMSO-d_6): δ = –17.5 (s) ppm. IR (Nujol): ν = 3296 s, 3238 s, 3133 s, 3057 s, 2725 w, 2670 w, 1648 s, 1609 s, 1560 w, 1433 m, 1414 w, 1338 m, 1304 w, 1238 w, 1197 w, 1159 m, 1088 w, 1039 w, 1026 m, 844 w, 832 m, 746 s, 696 s, 580 m, 511 w, 496 s, 487 sh, 451 m cm^{-1}. ESI+ MS: *m/z* = 383 (dominant, $[Ph_2PfcCH_2]^+$), 442 ($[\mathbf{1}H]^+$), 458 ($[Ph_2P(O)fcCH_2NHC(NH_2)_2]^+$). ESI– MS: *m/z* = 476 ($[\mathbf{1} + Cl]^-$), 512 ($[\mathbf{1}\cdot HCl + Cl]^-$). HR MS calc. for $C_{24}H_{24}ClFeN_3P$ ($[\mathbf{1} + Cl]^-$): 476.0751, found: 476.0743.

Preparation of 3·Me$_2$CO. $[PdCl_2(CH_3CN)_2]$ (25.9 mg, 0.10 mmol) was dissolved in dry acetone (5 mL), and the solution was filtered through a PTFE syringe filter (pore size 0.45 μm) into a test tube. A solution of **1** (47.8 mg, 0.10 mmol) in anhydrous methanol (5 mL) was carefully added as a top layer, and the sealed test tube was set aside for crystallization by liquid-phase diffusion. The red crystals that separated during 2 d (the solution was nearly colorless) were filtered off, washed with cold acetone and pentane, and dried under vacuum to give analytically pure **3**·Me_2CO as a deep red crystalline solid. Yield: 52.1 mg (79%).

^{1}H NMR (DMSO-d_6): δ = 2.09 (s, 6 H, Me_2CO), 4.51 (d, $^3J_{HH}$ = 5.7 Hz, 2 H, CH_2), 4.55 (vq, *J'* = 1.9 Hz, 2 H, fc), 4.61 (vt, *J'* = 1.8 Hz, 2 H, fc), 4.64 (vq, *J'* = 1.6 Hz, 2 H, fc), 4.80 (vt, *J'* = 1.8 Hz, 2 H, fc), 7.40-7.52 (m, 10 H, Ph), 7.60 (t, $^3J_{HH}$ = 6.0 Hz, 1 H, CH_2NH) ppm. ^{31}P{^{1}H} NMR (DMSO-d_6): δ

= 24.7 (s). IR (Nujol): v = 3368 s, 3301 s, 3261 s, 3191 s, 3079 m, 2725 w, 1702 s, 1670 s, 1648 s, 1617 s, 1589 m, 1435 m, 1404 w, 1366 m, 1327 m, 1305 w, 1233 m, 1193 w, 1170 m, 1095 m, 1041 w, 1032 m, 1024 sh, 846 w, 828 w, 750 s, 710 m, 690 s, 635 w, 620 w, 549 m, 525 s, 496 s, 473 m cm^{-1}. ESI+ MS: *m/z* = 383 ($[Ph_2PfcCH_2]^+$), 546 ($[Pd\{Ph_2PfcCH_2(CH_3N_3)\}]^+$), 582 ($[PdCl\{Ph_2PfcCH_2NHC(NH)NH_2\}]^+$). ESI– MS: *m/z* = 654 ([**3** – H]$^-$). HRMS calc. for $C_{24}H_{24}Cl_3FeNPPd$ ([**3** – H]$^-$): 651.9163, found: 651.9148 (monoisotopic). $C_{24}H_{25}Cl_3FeN_3PPd{\cdot}Me_2CO$ (713.15): C 45.47, H 4.38, N 5.89%; found: C 45.20, H 4.73, N 5.70%.

Preparation of *trans*-[$PdCl_2$(1-κ*P*)$_2$]·2HCl (4). [$PdCl_2(CH_3CN)_2$] (13.0 mg, 0.050 mmol) and **1**·HCl (47.8 mg, 0.10 mmol) were dissolved in dry methanol (5 mL) to give a red solution, which was stirred for 1 h and partially evaporated on a rotary evaporator. Methyl *tert*-butyl ether was added (*ca*. 8 mL), causing the product to separate as a red solid. The precipitate was filtered off, washed with methyl *tert*-butyl ether, and dried under vacuum to afford solvated complex **5** as a red-brown solid. Yield: 52.3 mg (91%).

^{1}H NMR (DMSO-d_6): δ = 4.08 (d, $^3J_{HH}$ = 5.9 Hz, 2 H, CH_2), 4.47 (vt, *J′* = 1.8 Hz, 2 H, fc), 4.50 (br s, 2 H, fc), 4.54 (vt, *J′* = 1.8 Hz, 2 H, fc), 4.64 (vt, *J′* = 1.8 Hz, 2 H, fc), 7.40-7.59 (m, 10 H, Ph), 7.85 (t, $^3J_{HH}$ = 5.8 Hz, 1 H, CH_2NH) ppm. $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ = 17.1 (s) ppm. IR (Nujol): v = 3308 s, 3132 s, 3049 s, 2725 w, 2671 w, 1663 s, 1648 s, 1620 s, 1436 m, 1341 w, 1303 w, 1266 w, 1195 w, 1164 m, 1098 m, 1072 w, 1029 m, 999 w, 838 m, 746 m, 709 w, 694 s, 570 w, 539 m, 516 m, 498 s, 474 m cm^{-1}. ESI+ MS: *m/z* = 546 ($[Pd\{Ph_2PfcCH_2(CH_3N_3)\}]^+$), 582 ($[PdCl\{Ph_2PfcCH_2NHC(NH)NH_2\}]^+$), 987 ([**4** – 3HCl – Cl]$^+$), 1023 ([**4** – 2HCl – Cl]$^+$). ESI– MS: *m/z* = 1131 ([**4** – H]$^-$), 1167 ([**4** + Cl]$^-$). HR MS calc. for $C_{48}H_{49}Cl_4Fe_2N_6P_2Pd$ ([**4** – H]$^-$): 1128.9987, found: 1128.9978 (monoisotopic). $C_{48}H_{50}Cl_4Fe_2N_6P_2Pd{\cdot}MeOH{\cdot}2H_2O$ (1200.9): C 49.01, H 4.87, N 7.00%; found: C 49.10, H 4.56, N 6.95%.

General procedure for the catalytic experiments. An oven-dried Schlenk tube was charged with the respective aryl bromide (1.0 mmol), borate (1.1 mmol) and catalyst (0.2 or 0.5 mol.% $Pd(OAc)_2$/**1**·HCl (1.1 equiv.) or complex **3**). A stirring bar was inserted, and the reaction flask was flushed with argon and sealed with a rubber septum. Then, the solvent was introduced (5 mL), and the reaction vessel was transferred to an oil bath maintained at 50 or 80 ºC and stirred for 3 or 24 h. The reaction mixture was diluted with water (5 mL) and extracted with diethyl ether (4× 5 mL). The organic extracts were dried over anhydrous $MgSO_4$ and evaporated with silica gel. The crude pre-adsorbed product was transferred to a silica gel column. Elution with hexane-ethyl acetate (30:1) and evaporation under vacuum afforded pure coupling product.

This procedure was modified in the case of **7cd** due to the low solubility of this compound. Thus, following the quenching by the addition of water, the reaction mixture was extracted with toluene (*ca.* 100 mL). The toluene solution was washed with water (3× 25 mL), and the aqueous washings were back-extracted with toluene (2 × 25 mL). The combined toluene layers were washed with brine (25 mL), dried over $MgSO_4$, and evaporated to afford a white residue, which was crystallized from boiling methanol. The product, which separated upon cooling, was filtered off, washed with cold methanol and dried under vacuum.

X-ray crystallography. Crystals suitable for X-ray diffraction analysis were selected directly from the preparative batch (**3**·Me_2CO) or were grown by layering a solution of complex **4** in wet methanol with methyl *tert*-butyl ether and crystallization by liquid-phase diffusion over several days (**4**·2MeOH·$2H_2O$). Full set diffraction data (±*h*±k±*l*, θ ≤ 27.5°, data completeness 99.9%) were recorded with a Nonius Kappa CCD diffractometer equipped with a Bruker Apex II detector (**3**·Me_2CO) or a Bruker D8 VENTURE Kappa Duo diffractometer with a PHOTON100 detector (**4**·2MeOH·$2H_2O$) at 150(2) K. The data were corrected for absorption using methods included in the diffractometer software.

Both structures were solved by direct methods and were refined by full-matrix least-squares based on F^2 (SHELXL97 and SHELX-2014).[29] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms residing on the N and O atoms were identified on the difference electron density maps and were refined as riding atoms with U_{iso}(H) assigned to 1.2U_{eq} of their bonding N/O atom. Hydrogen atoms bonded to carbon atoms were placed in their calculated positions and similarly refined. The solvating water molecules and chloride anions in the structure of **4**·2MeOH·$2H_2O$ were disordered within channels defined by the bulky complex cations $[PdCl_2\{Ph_2PfcCH_2NHC(NH_2)_2\}_2]^{2+}$ and were refined over two equally populated positions (50:50). The water molecules were modelled only as isolated oxygen atoms because the OH hydrogens could not be unequivocally located on the difference electron density maps. Selected crystallographic data and refinement parameters are given in Table 5.

A recent version of the PLATON program[30] was used for the graphical representation of the structures and all geometric calculations. The numeric values are rounded with respect to their estimated deviations (ESDs) given to one decimal place. Parameters pertaining to atoms in constrained positions are given without ESDs.

Table 5. Crystal data and refinement parameters for the crystal structures of **3**·Me_2CO and **4**·2MeOH·$2H_2O$.

Parameter	**3**·Me_2CO	**4**·2MeOH·$2H_2O$
Formula	$C_{27}H_{31}Cl_3FeN_3OPPd$	$C_{50}H_{58}Cl_4Fe_2N_6O_4P_2Pd$
M [g mol^{-1}]	713.12	1228.86
Crystal system	triclinic	triclinic
Space group	*P*–1 (no. 2)	*P*–1 (no. 2)
a [Å]	10.0157(2)	9.2204(4)
b [Å]	10.0774(2)	9.5490(4)
c [Å]	14.5935(3)	17.0889(6)
α [°]	95.4051(9)	73.965(1)
β [°]	94.0863(9)	76.393(1)
γ [°]	108.2048(8)	69.922(1)
V [$Å^3$]	1385.09(5)	1341.64(9)
Z	2	1
D_{calc} [g cm^{-3}]	1.710	1.521
F(000)	720	628
Diffractions collected	17448	50551
Independent diffractions	6351	6158
R_{int} [%][a]	2.29	1.46

Observed diffractions[b]	5361	5656
No. of parameters	336	332
R (observed diffrns) [%][c]	2.52	2.22
R, wR (all data) [%][c]	3.47, 5.63	2.57, 5.36
$\Delta\rho$ [e Å^{-3}]	–0.29, 0.43	–0.49, 0.54

[a] $R_{int} = \Sigma \left| F_o^2 - F_o^2(\text{mean}) \right| / \Sigma F_o^2$, where F_o^2(mean) stands for the average intensity of symmetry-equivalent diffractions. [b] Diffractions with $I_o \geq 2\sigma(I_o)$. [c] $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$, where $w = [\sigma^2 F_o^2 + (w_1P)^2 + w_2P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$.

CCDC 1508804 (for **3**·Me_2CO) and 1508805 (for **4**·2MeOH·$2H_2O$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Acknowledgements

The research reported in this article received support from the Czech Science Foundation (project no. 13-08890S).

Keywords: phosphane ligands • N,P-ligands • ferrocene ligands • guanidine substituents • cross-coupling • palladium

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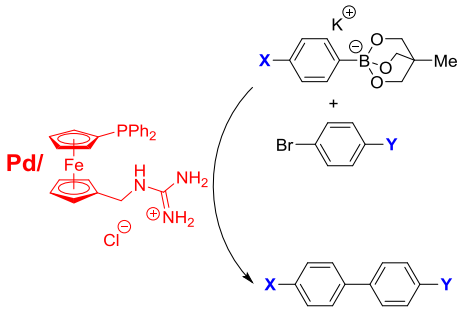
FULL PAPER

A phosphanylferrocene donor with a hydrophilic guanidinium substituent, $Ph_2PfcCH_2NHC(NH)NH_2 \cdot HCl$ (fc = ferrocene-1,1'-diyl), was synthesized and utilized as a ligand for Pd(II) complexes. Both the defined complexes and their *in situ* generated analogues were evaluated as pre-catalysts for the Suzuki-Miyaura cross-coupling of aryl boronates with aryl bromides in polar reaction solvents.



Ferrocene phosphanes*

*Ondřej Bárta, Ivana Císařová, Petr Štěpnička**

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Synthesis, Palladium(II) Complexes and Catalytic Use of a Phosphanylferrocene Ligand Bearing a Guanidinium Pendant