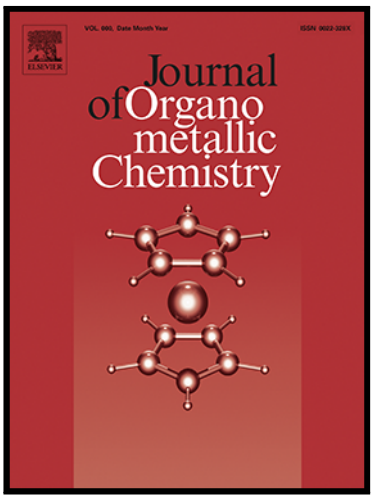

Ferrocenylated imine- and amine(secondary/tertiary)- phosphine P^N ligands and their Pd(II) complexes: synthesis and structural characterization

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Highlights

- A new family of ferrocenylated P^N ligands where nitrogen donor is either of an imine or amine (secondary/tertiary).
- Neutral Pd (II) complexes[(κ^2-P^N)$PdCl_2$] where ligands act in bidentate fashion.
- Characterization of ligands and complexes by spectroscopic methods,
- The crystal structures of ligands and complexes are reported.
- Catalytic evaluation of one of the complexes in Suzuki-Miyaura cross-coupling reaction

Ferrocenylated imine- and amine(secondary/tertiary)- phosphine P^N ligands and their Pd(II) complexes: synthesis and structural characterization

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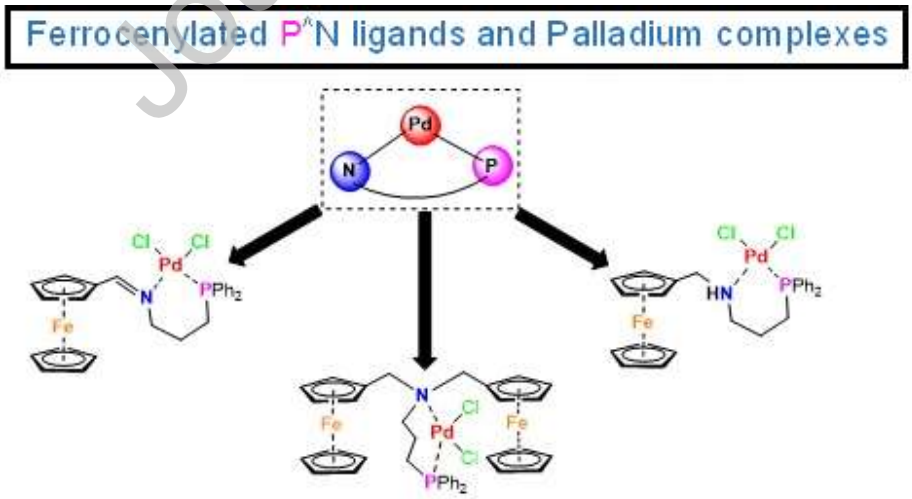
Abstract: A new family of ferrocenylated P^N ligands where the nitrogen donor is either of an imine or amine (secondary/tertiary), was synthesized. The condensation reaction between diphenylphosphino propylamine and formyl ferrocene led to the formation of imine ligand [(η^5-C_5H_5)Fe{(η^5-C_5H_4)CH=N-(CH_2)$_3$-PPh_2)}] (**1**), which on reduction with $NaBH_4$ gave secondary amine ligand [(η^5-C_5H_5)Fe{(η^5-C_5H_4)CH_2-NH-(CH_2)$_3$-PPh_2)}] (**2**). Additionally, nucleophilic substitution reaction of diphenylphosphino ethyl/propyl amine with [$FcCH_2NMe_3^+$][I^-] salt leads to tertiary-amine ligand [(η^5-C_5H_5)Fe(η^5-C_5H_4)CH_2]$_2$-N-(R-PPh_2) where R= C_2H_4 (**3**) and C_3H_6 (**4**). The newly synthesized ferrocenylated ligands were then complexed with Pd(II) giving [*cis*(κ^2-P^N)$PdCl_2$] type complexes (**5**-**8**), where imine, secondary amine, and tertiary amine ligands act as a bidentate ligand. The molecular structures of ligand (**3**), and complexes (**5**), (**6**), and (**7**) have also been determined by X-ray crystallography. In the molecular structures of these complexes, the Pd(II) center presents a distorted square-planar geometry. During the isolation of ligand (**4**), corresponding phosphine oxide (**4A**) along with a phosphonium salt (**4B**) was also isolated as by-products and were characterized by X-ray crystallography. The preliminary catalytic evaluation of complex (**7**) in the Suzuki-Miyaura cross-coupling reaction of arylboronic acids with aryl bromides was performed.

Graphical abstract



Keywords: Ferrocenylated • P^N ligands • Imino, amino phosphines • Pd (II) complexes

1. Introduction

Ligand design remains one of the most important parts of coordination chemistry as these molecules/fragments have a deep impact on the resulting structure and properties of the metal complexes. In particular, the phosphorus-nitrogen mixed donor aminophosphine or iminophosphine P^N ligands are widely used in catalysis due to the presence of both soft (phosphorus) and hard (nitrogen) donor atom [1]. The electron-donating potency of nitrogen can be manipulated by switching from sp^3 to sp^2 hybridized nitrogen atom [2]. The imine-phosphine P^N ligands, in which imine acts as a weak π-acceptor and phosphine as a good σ-donor. These P^N ligands can behave as bridging ligands or as chelating agents with high levels (steric and electronic) control enhanced stability to the complex in a variety of oxidation states and geometries [3].

The P^N linker behavior and chelate ring size might strongly influence: (i) electronic properties of the donor atoms, (ii) the bite angle of the complex, (iii) the spatial array of the terminally disposed donor atom substituents as well as (iv) the conformational flexibility of the chelate, additionally in the case of chiral hetero donor ligands with non-persistent donor atom chirality, (v) the hemilability of the chelate ring, and (vi) the stereoselectivity of the donor atom coordination can also depend on the ring size and change the formation of mono-chelate or non-chelate complexes [4,5].

On the other side, ferrocene is a chemically stable versatile molecule that presents unique structural properties such as adequate rigidity, steric bulkiness, easy derivatization, and redox reversibility. In the last few years, research has focused on monodentate or bidentate ferrocenylated heteroatom donors (P, N, O, and S) that involve different stereoelectronic properties for different applications in materials and catalysis [6-10]. In particular, Ferrocene-based hemilabile ligands functionalized with P^N or P^O donors have a remarkable ability to stabilize low-valent metals. These ligands are electronically, sterically, and stereo geometrically tuneable which provides a fine balance between catalytic and thermodynamic stability [4,11]. Transition metal complexes (Pd, Ni, Rh, and Pt) with these P^N or P^O ligands highly efficient in promoting Suzuki couplings [12].

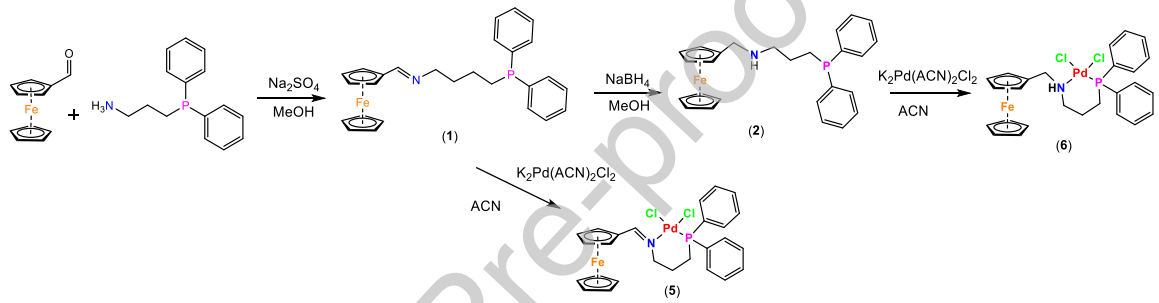
There is a growing interest in the synthesis of different ferrocenylated ligands containing different donor atoms such as P, N, Sb, O, Te, or Se, in our laboratory [13] here we wish to report the synthesis and characterization of new ferrocenylated imine-phosphine and amine-phosphine ligands and their Pd(II) complexes. The preliminary catalytic activity of one of this palladium complex in the Suzuki-Miyaura cross-coupling reaction is also reported.

2. Results and Discussion

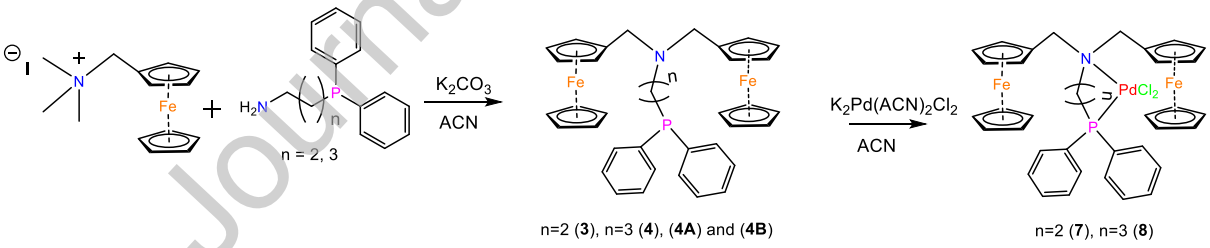
2.1 General Synthesis

New bidentate ferrocenyl imine- or amine- phosphine containing P^N donors were synthesized as shown in **Scheme 1**. The condensation reaction between diphenylphosphino propylamine and ferrocene carboxaldehyde led to the formation of imine ligand $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)CH{=}N\text{-}(C_3H_6\text{-}PPh_2)\}]$ (**1**) which was then reduced by the excess of $NaBH_4$ to obtain secondary amine ligand (**2**). It is to be noted that the ethyl analog of compound (**1**) has already been reported previously.[14]

On the other hand, new ferrocenylated phosphinated tertiary amine ligands $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2]_2$-N-(R-$PPh_2$) where R= C_2H_4 (**3**) and C_3H_6 (**4**) were synthesized by a nucleophilic substitution reaction of (ferrocenylmethyl) trimethylammonium iodide $[FcCH_2NMe_3]^+[I^-]$ salt with phosphinoamine $Ph_2P(CH_2)_nNH_2$ [where n = 2 or 3] respectively (**Scheme 2**). It is worth mentioning that when phosphinoamine $Ph_2P(CH_2)_nNH_2$ reacts with $[FcNMe_3]^+[I^-]$ salt, ligand (**2**) could not be isolated while the ligand (**4**) was isolated though in a low yield. Ligand (**4**) is slightly unstable and gets oxidized faster in comparison to its ethyl analog (**3**). It is also to be mentioned that during the isolation of ligand (**4**), corresponding phosphine oxide (**4A**) and phosphonium salt (**4B**) was also obtained as the by-products. In this work, the newly synthesized ferrocenylated ligands were then reacted with $Pd(CH_3CN)_2Cl_2$, giving *cis*-$[(\kappa^2\text{-P^N})PdCl_2]$ complexes (**5**-**8**) in moderate yields, where these ligands coordinate to palladium center in a bidentate fashion.



Scheme 1. Synthesis of ligands (**1**-**2**) and palladium complexes (**5**-**6**).



Scheme 2. Synthesis of ligands (**3**-**4**) and palladium complexes (**7**-**8**).

2.2 Structural Characterization

The infrared spectra of compound (**1**) show a sharp intense band at 1610 cm^{-1}, which can be assigned to asymmetric stretching of the imine $\nu_{(C=N)}$ group. $^{31}P\{^{1}H\}$-NMR spectra of this ligand (**1**) show a phosphorus resonance at δ -16.52 ppm. Being a phosphine compound, it is sensitive to oxidation of phosphorus and the solution of this ligand shows a new phosphorus resonance also at δ ~33 ppm in $^{31}P\{^{1}H\}$-NMR spectra, because of the formation of the phosphine oxide (**1A**) in the solution, which is also corroborated in the mass spectra as the molecular ion peak corresponding to phosphine oxide is observed in the ligand (**1**) sample. The signal for the imine proton for compound (**1**) appears as singlet δ 8.10 ppm while imine carbon resonance appears at δ 161.38 ppm in the ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of complex (**5**) show an upfield shift of imine hydrogen resonance (δ 7.81 ppm) in comparison to the ligand (**1**) confirm the coordination of the azomethine group. In general, the $^{31}P\{^{1}H\}$-NMR spectra of all the new palladium complexes show a downfield shift of ~30 ppm to the corresponding ligand confirming the coordination of the PPh_2 group to Pd(II) metal center. In Pd-imine complex (**5**), $^{31}P\{^{1}H\}$-NMR resonance is slightly downfield in comparison to the corresponding Pd-amine complex (**6**) which may be due to a higher π acceptor character of the imine group in comparison to an amine group [15].

In the IR spectra, the appearance of a new N-H stretching band at 3324 cm^{-1} and the absence of C=N stretching confirm the formation of ligand (**2**), a secondary amine. In the ^{1}H-NMR spectra, N-H group proton resonance of ligand (**2**) (2.01 ppm) shows a significant downfield shift after complexation to palladium (4.77 ppm). NOESY spectra of complex (**6**) show NOE interactions of *ortho* and *meta* positioned protons of phenyl rings of PPh_2 group with CH_2 (H_h) protons in comparison to the amine ligand (**2**) where only NOE interaction between ortho positioned protons of phenyl rings of PPh_2 group and CH_2 (H_i) protons were observed.

In the ^{1}H-NMR spectra of complex (**6**), the diastereotopic methylene protons (Fc-CH_2) show two different chemical shifts and appear as two *dd*. The appearance of four different chemical shifts [3.87, 4.05, 4.14, and 4.32 ppm] for substituted Cp ring suggests a lack of symmetry and indicates the presence of intramolecular Pd-N coordinative bond. In the IR spectra, a band observed at 3324 cm^{-1} in the free ligand (**2**) has been assigned to $\nu_{(N-H)}$ of the amine group. On complexation, this band shows a hypsochromic shift and appears at 3219 cm^{-1} indicating coordination of the ligand with the metal-ions through the N atom of the amine group.

The $^{31}P\{^{1}H\}$-NMR spectra of the complexes (**7**) and (**8**) show a significant downfield shift in comparison to the ligands (**3**) and (**4**) respectively confirm the coordination of phosphorus atom(-PPh_2) of the ligand in the palladium complex Further, during the synthesis of ligand (**4**), two by-products were also isolated; a) an oxidation product (**4A**) and b) formation of phosphonium salt (**4B**) after the reaction of ligand (**4**) with (Ferrocenylmethyl)trimethylammonium iodide [$FcCH_2NMe_3^+$][I^-] salt. In the $^{31}P\{^{1}H\}$-NMR spectra of compounds (**4A**) and (**4B**), chemical shift at δ_P 32.81 ppm and δ_P 22.52 ppm has appeared, respectively.

Similar to the complex (**6**) in the ^{1}H-NMR and NOESY spectra of complex (**8**) shows methylene protons (Fc-CH_2) as diastereotopic protons and appeared as two doublets. The complex (**8**) proton NMR spectra show a lack of symmetry of substituted cyclopentadienyl ring in comparison to the ligand. This asymmetry of the cyclopentadienyl ring and the NOE interactions of methylene protons with phenyl protons of the -PPh_2 group observed in the NOESY spectra of complex (**8**) suggests the presence of intramolecular Pd-N coordinative bond as mentioned earlier for the complex (**6**).

In general, in the NMR spectra of all the complexes (**5**-**8**), because of *cis* P^N coordination to the palladium metal center, the substituted cyclopentadienyl loses its symmetry. In the MS-FAB$^+$ spectra, molecular ion peak could not be observed but a fragmentation peak corresponding to [M-Cl]$^+$ ion confirms the formation of these complexes (**5**-**8**).[16]

2.3 XRD Analysis

The molecular structures of compounds (**3**), (**4A**), (**4B**), (**5**), (**6**), and (**7**) were confirmed by X-ray crystal structure determination. Crystals of these compounds were obtained by slow diffusion of hexane into a solution of the compounds in $CHCl_3$. Crystal data collection and structural refinement parameters are given in **Table 1**. In the tertiary amine ligand (**3**) crystal structure (**Figure 1**), the torsion angle N(1)-C(23)-C(24)-P(1) 158.2(4)(°) as compared to the corresponding complex (**7**) -46.5(6)(°) after the P^N coordination (**Figure 3**) and complex (**7**) shows square planar geometry around the Pd center. The steric influence of the Cp and Ph groups dictate that Cg1-Pd-Cg2 angle is 131.10° where Cg1 is the centroid of the C(11)-C(15) Cp ring atoms and Cg2 is the centroid of the C(1)-C(5) Cp ring atoms and the Cf1-Pd-Cf2 angle where Cf1 is the centroid of the C(25)-C(30) phenyl ring atoms and Cf2 is the centroid of the C(31)-C(36) phenyl ring atoms is 67.99° and it is seen that aromatic ring systems (Ph or Fc) do not lie face on to the palladium atom and assume non-coplanar conformations, **Figure 3** (**b**).

The structures of complexes (**5**) and (**6**) show the monomeric complexes with slightly distorted square-planar *cis* geometry around the metal center, in which P^N ligand is bonded to the Pd(II) in a bidentate fashion and forms a six-membered ring as shown (**Figure 2** and **Figure 4**). The Pd-P bond length is very similar in both complexes (**5**) and (**6**). Both the complexes show the Pd-Cl bond *trans* to the PPh_2 group [~2.37 (Å)], longer than Pd-Cl bond length *trans* to N atom (imine or amine). Further complex (**6**) shows weak intramolecular contacts of the type C-H···Pd (2.358 Å) **Figure. 4** (**b**). In general, the complexes (**5**), (**6**), and (**7**) show a slightly distorted square planar geometry, where the Pd center is above the coordination N(1)-Cl(2)-Cl(1)-P(1) plane and with a distance of 0.069 Å, 0.09 Å, and 0.006 Å respectively from this plane.

The molecular structures of compounds (**4A**) and (**4B**), are shown in **Figure 5** and **Figure 6** respectively. The geometry around phosphorus in phosphine oxide (**4A**) and phosphonium salt, is approximately tetrahedral and the P-O bond length (1.482(4) Å) in compound (**4A**) coincides with previously reported to the P-O bond lengths in various polymorphs of Ph_3PO (1.484(1) Å).[17] No intramolecular interaction was observed in both the crystal structures. In the compound (**4B**) the distance between the nitrogen and the phosphorus atoms 5.099(4) Å is more than the sum of the van der Waals radii of these atoms (3.4 Å) [18] and the torsión angles P(1)-C(25)-C(24)-C(23) and C(25)-C (24)-C(23)-N(1) are -160.6 (3)° and 161.1 (4)° for compound (**4B**) respectively.

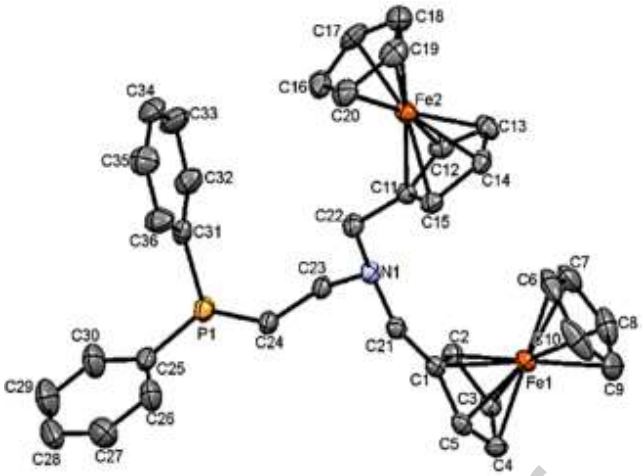


Figure 1. Molecular structure of (**3**) (displacement ellipsoids at 30% probability). H atoms are removed for clarity. Selected bond lengths (Å) = C(22)-N(1), 1.467(6); P(1)-C(31), 1.814(5); P(1)-C(24), 1.836(6); Selected bond angles (°) = C(31)-P(1)-C(24), 99.7(3); P(1)-C(24)-C(23), 108.8(4) C(24)-C(23)-N(1), 117.8(4); C(23)-N(1)-C(22), 112.1(4); (22)-N(1)-C(21), 111.1(4); Selected torsion angles (°) = C(11)-C(22)-N(1)-C(23), -159.0(4); C(1)C(21)-N(1)-C(23), 74.9(5); N(1)-C(23)-C(24)-P(1), 158.2(4); C(31)-P(1)-C(24)-C(23), -79.7(4); C(25)-P(1)-C(24)-C(23), 175.4(4).

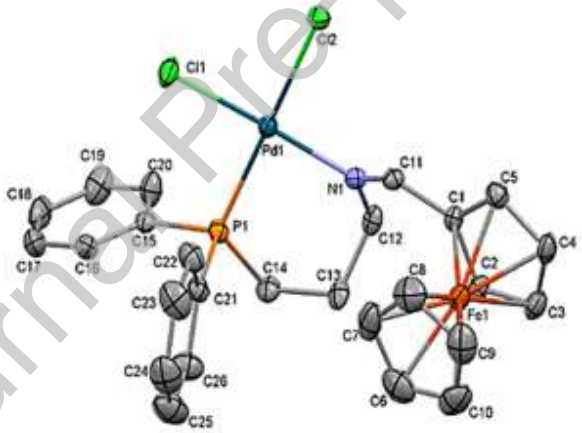
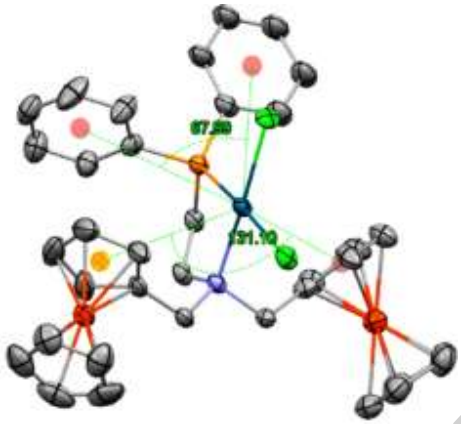
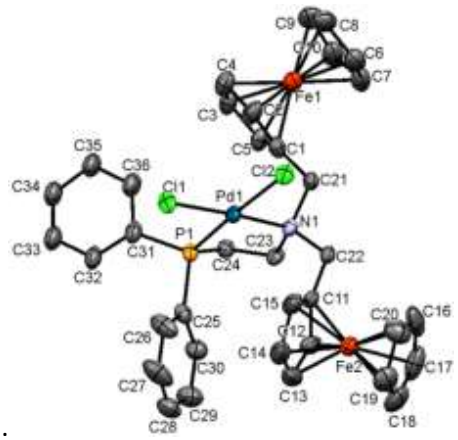


Figure 2. Molecular structure of (**5**) (displacement ellipsoids at 30% probability). H atoms are removed for clarity. Selected bond lengths (Å) = P(1)-Pd(1), 2.240(1); Pd(1)-Cl(1), 2.293(1); Pd(1)-Cl(2), 2.368(1); Pd(1)-N(1), 2.044(4); N(1)-C(11), 1.282(5); Selected bond angles (°) = Cl(1)-Pd(1)-N(1), 176.5(1); P(1)-Pd(1)-Cl(2), 176.26(5); C(14)-P(1)-Pd(1), 113.3(2); C(12)-N(1)-Pd(1), 119.7(3); C(14)-C(13)-C(12), 113.9(4); P(1)-Pd(1)-N(1), 90.8(1); Selected torsion angles (°) = N(1)-C(12)-C(13)-C(14), 77.3(5); P(1)-C(14)-C(13)-

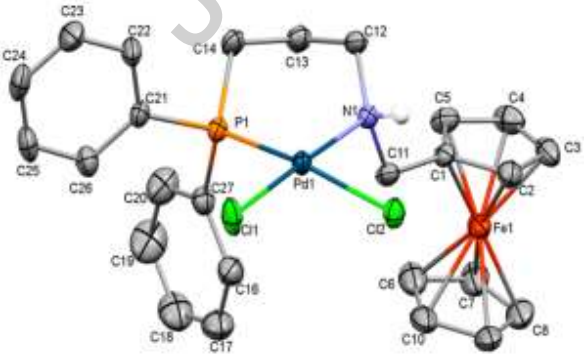
C(12), -59.5(5).

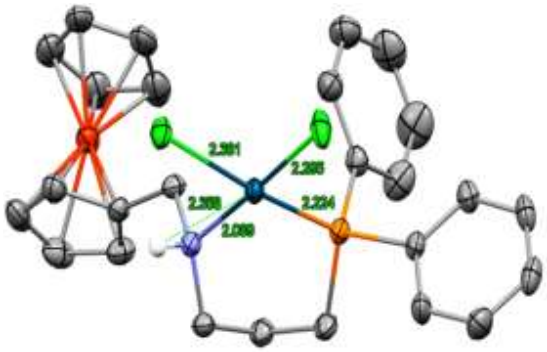




(a) **(b)**

Figure 3. (a) Molecular structure of (**7**) (displacement ellipsoids at 30% probability). H atoms are removed for clarity. (b) compared Cg1-Pd-Cg. Selected bond lengths (Å) = P(1)-Pd(1), 2.200(2); Pd(1)-Cl(1), 2.342(2); Pd(1)-Cl(2), 2.405(2); Pd(1)-N(1), 2.125(5); C(24)-P(1), 1.804(7); C(24)-C(23), 1.494(8); N(1)-C(23), 1.511(7); Selected bond angles (°) = P(1)-Pd(1)-Cl(1), 88.92(6); Cl(2)-Pd(1)-Cl(1), 94.11(6); P(1)-C(24)-C(23), 108.1(4); C(24)-C(23)-N(1), 114.0(5); N(1)-Pd(1)-Cl(2), 90.9(1); P(1)-Pd(1)-N(1), 86.0(1); Cl(1)-Pd(1)-N(1), 174.9(1); Cl(2)-Pd(1)-P(1), 176.79(6); Selected torsion angles (°) = P(1)-C(24)-C(23)-N(1), -46.5(6); C(1)-C(21)-N(1)-Pd(1), -53.8(6); C(11)-C(22)-N(1)-Pd(1), 55.6(6).





(**a**) (**b**)

Figure 4. (a) Molecular structure of (**6**) (displacement ellipsoids at 30% probability). (b) Important bond lengths. Selected bond lengths (Å) = N(1)-Pd(1), 2.089(4); Pd(1)-Cl(2), 2.381(1); Pd(1)-Cl(1), 2.295(1); Pd(1)-P(1), 2.224(1); N(1)-C(12), 1.478(7); N(1)-C(11), 1.494(6); Selected bond angles (°) = Cl(1)-Pd(1)-Cl(2), 92.76(5); C(14)-P(1)-Pd(1), 111.8(2); C(14)-C(13)-C(12), 115.0(5); C(13)-C(12)-N(1), 115.0(4); Cl(1)-Pd(1)-P(1), 89.24(6); Cl(2)-Pd(1)-N(1), 85.1(1); P(1)-Pd(1)-N(1), 92.8(1); Pd(1)-N(1)-C(12), 120.1(3); Pd(1)-N(1)-C(11), 109.3(3); Cl(2)-Pd(1)-P(1), 171.36(5); Cl(1)-Pd(1)-N(1), 177.8(1); Selected torsion angles (°) = P(1)-C(14)-C(13)-C(12), -62.6(6); C(14)-C(13)-C(12)-N(1), 72.3(6).

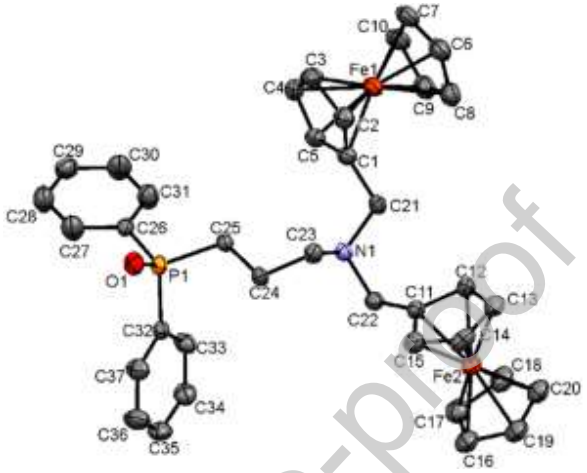


Figure 5. Molecular structure of (**4A**) (displacement ellipsoids at 30% probability). H atoms are removed for clarity. Selected bond lengths (Å) = C(43)-P(1), 1.791(6); P(1)-C(25), 1.800(5); C(25)-C(24), 1.538(6); C(24)-C(23), 1.509(7); C(23)-N(1), 1.508(6); C(11)-N(1), 1.516(7); Selected bond angles (°) = C(22)-N(1)-C(23), 113.1(4); C(11)-N(1)-C(23), 113.3(4); C(26)-P(1)-C(37), 110.9(2); C(37)-P(1)-C(25), 108.0(2); Selected torsion angles (°) = C(12)-C(11)-N(1)-C(23), 55.9(5); N(1)-C(23)-C(24)-C(25), 161.1(4); C(23)-C(24)-C(25)-P(1), -160.6(3), C(24)-C(25)-P(1)-C(43), -171.3(3).

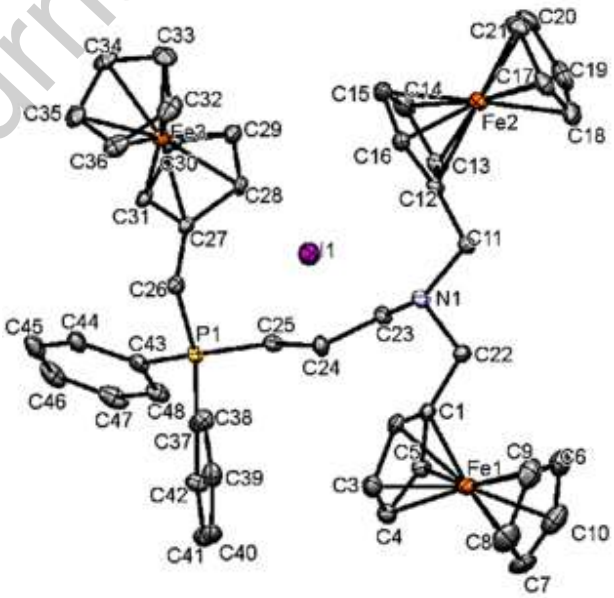
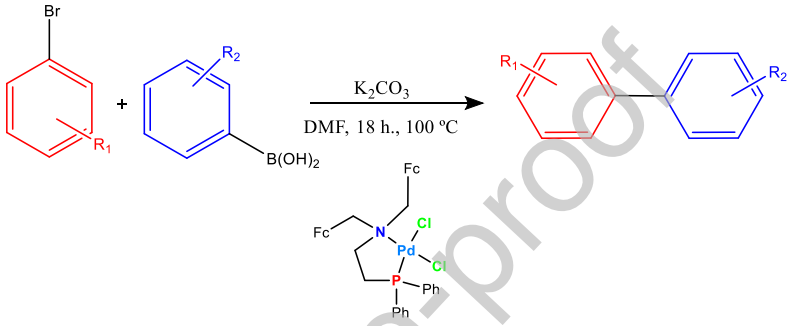


Figure 6. Molecular structure of (**4B**) (displacement ellipsoids at 30% probability). H atoms and solvent molecule are removed for clarity. Selected bond lengths (Å) = N(1)-C(23), 1.500(8); C(23)-C(24), 1.509(8); C(24)-C(25), 1.528(8); C(25)-P(1), 1.802(5); P(1)-O(1), 1.482(4); C(21)-N(1), 1.502(6); Selected bond angles (°) = O(1)-P(1)-C(25), 113.6(2); O(1)-P(1)-C(32), 111.5(2); O(1)-P(1)-C(26), 112.5(2); C(21)-N(1)-C(22), 111.4(4); C(21)-N(1)-C(23), 112.8(4); Selected torsion angles (°) = C(32)-P(1)-C(25)-C(24), -58.2(4); C(26)-P(1)-C(25)-C(24), -170.9(4); P(1)-C(25)-C(24)-C(23), -171.9(4); C(25)-C(24)-C(23)-N(1), -68.2(6).

2.4. Catalytic evaluation for Suzuki-Miyaura cross-coupling

The preliminary catalytic activity of the sufficiently stable complex (**7**) was also evaluated in the Suzuki-Miyaura cross-coupling reaction of aryl bromides with aryl boronic acid with varying steric and electronic properties and the results obtained are shown in **Table 1**.

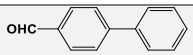
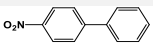


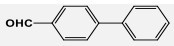
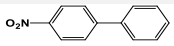
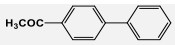
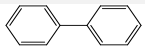
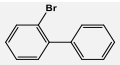
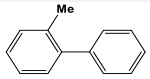
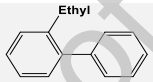
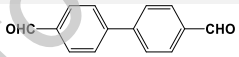
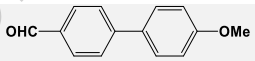
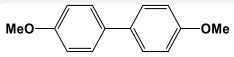
Scheme 3. Suzuki-Miyaura coupling reaction.

All the reactions were carried out in DMF at 100°C for 18h using Na_2CO_3 as a base with 0.5 mol % of Pd(P^N) catalyst loading without the addition of free ligand or any promoting additive. All reactions were performed in the air (**Scheme 3**)[19]. Table 1 summarizes the results obtained in these reactions. The catalyst seems to be air-stable at 100°C, and palladium black, which could probably an indication of the degradation of the catalyst, was not observed. The complex (**7**) shows good activity and corresponding cross-coupling products were obtained in the reaction. (**Table 1**, entry **I**). For the complex (**7**), the normal dependence on the electron-withdrawing property of R_1 of aryl bromide was observed. A decreased catalyst loading (0.25 mol %) does not affect much on the yield of the final product (entries **III** and **IV**). Reactions with ortho and para-substituted bromobenzene exhibited good conversion except entry **VII** (57%. yield) where a low conversion in the reaction using 2-ethyl bromobenzene, is because of the bulkiness of the ethyl group.

The use of 4-methoxy phenylboronic acid gave a good conversion (90%) in comparison with an electron-poor 4-formyl phenylboronic acid where the expected product is obtained in a moderate yield.

Table 1 Suzuki-Miyaura cross-coupling reaction catalyzed by complex (7).

Entry	R_1	R_2	Mol% catal	Product % Conv[b]
I	4-CHO	H	0.5	 96
II	4-NO_2	H	0.5	 96

Ia	4-CHO	H	0.25	 92
IIb	4-NO_2	H	0.25	 90
III	4-$COCH_3$	H	0.5	 93
IV	H	H	0.5	 85
V	2-Br	H	0.5	 91
VI	2-Me	H	0.5	 92
VII	2-Ethyl	H	0.5	 57
VII	4-CHO	4-CHO	0.5	 72
VIII	4-CHO	4-OMe	0.5	 90
IX	4-OMe	4-OMe	0.5	 95

[a] Aryl boronic acid (1.0 mmol), aryl bromide (1.0 mmol), Na_2CO_3 (2.0 mmol), DMF (5 mL), cat. (0.25-0.5 mol%) at 100 °C for 18h. [b] Determined by GC-MS.

3. Conclusion

In summary, new neutral ferrocenylated phosphine imine and amine (secondary and tertiary) ligands were synthesized by different routes and characterized by spectroscopic methods. Further, these ferrocenylated ligands coordinate to palladium as a bidentate ligand and form [(κ^2-P^N)$PdCl_2$] complexes.

The molecular structures of compounds (**3**), (**4**), (**4A**), (**4B**), (**5**), (**6**), and (**7**) were determined. The X-ray studies revealed that the Pd(II) complexes (**6**-**8**) exhibit distorted square-planar geometry. The Pd-Cl bond length *trans* to the PPh_2 group is longer than the Pd-Cl bond length *trans* to the N-(amine or imine) group.

The preliminary catalytic activity of complex (**7**) in the Suzuki-Miyaura coupling reaction was evaluated. The complex showed good activity and conversions up to complete conversion of corresponding cross-coupling products were obtained in the reaction. Reactions with *ortho*- and *para*- substituted bromobenzene exhibited good conversion. Further studies on the coordination chemistry and potential catalytic applications for different C-C and C-N coupling reactions of ferrocenyl methyl imine- or amine-(secondary and tertiary) phosphine ligands are still in progress.

4. Experimental Section

4.1 Materials. The materials were acquired from Sigma-Aldrich and Strem Chemicals and employed without any further purification. All the reactions were performed under an inert atmosphere using conventional Schlenk glassware. Solvents were dried using established procedures.

4.2 Apparatus.

Analytical thin-layer chromatography (TLC) was performed using silica gel plates ($60GF_{254}$). The developed chromatogram was analyzed by a UV lamp (254 nm). The silica gel column chromatography was performed with 70-230 and 230-400 mesh and neutral alumina column chromatography were performed with 70-230 mesh. Melting points (mp) were determined using a Mel-Temp Melting Point apparatus. Infrared (IR) spectra were recorded on a Bruker Alpha-P FTIR spectrophotometer with an attenuated total reflectance (ATR) technique. The ^{1}H-NMR (300 MHz), ^{13}C-NMR (75.432 MHz), and ^{31}P-NMR (121.442 MHz) spectra were recorded on a Bruker Avance™ spectrometer at a frequency of 300 MHz, in Methanol-d^4 or $CDCl_3$ using TMS as an internal standard. Chemical shift values are reported in parts per million δ(ppm) and J values are in Hertz. The data collection and refinement parameters for compounds were recorded by Bruker Smart APEX spectrometer using graphite monochromated MoKα radiation (0.71073 Å). The crystal structure of the compound (**4A**) has a chloroform molecule as a solvent of crystallization. The Cp ring is disordered in crystal structures of (**6**), (**7**), and disordered Ph ring. In compound (**4B**) the molecular structure was disordered in one of the Cp ring and the iron atom of Ferrocene. Conversions of all known organic products for Suzuki-Miyaura cross-coupling reaction were determined by GC-MS analyses employing an Agilent Technologies 6890 N coupled with JMS-GC/MS at 70 eV instruments employing a capillary column DB-1MS (0.25mm x 0.25 mm x 30 m) and He as a carrier gas

4.1.1 Synthesis of Compound (η^5-C_5H_5)Fe{(η^5-C_5H_4)CH=N-(C_3H_6-PPh_2)} (1).

In a Schlenk tube under N_2, to a solution of , 0.78 mmol (0.189g) of 2-(diphenylphosphino)propylamine was added 0.78 mmol (0.167 g) of ferrocenecarboxaldehyde with excess of Na_2SO_4 and 10 mL of dry MeOH. The solution was stirred for a 5 h at room temperature, after this time the solution was filtered through cannula and the solution was concentrated under vacuum. Compound (**1**) was isolated by column chromatography on silica gel using hexane/ethyl acetate as eluant under N_2 and was obtained with quantitative yield as an orange solid, Yield 45% (0.159g). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.81 (*p*, $J_{H\text{-}H}$ = 7.68 Hz, 2H, H_h), 2.09 (*m*, 2H, H_i), 3.54 (*t*, $J_{H\text{-}H}$ = 6.75 Hz, 2H, H_g), 4.14 (*s*, 5H, H_d), 4.35 (*d*, $J_{H\text{-}H}$ = 1.91 Hz, 2H, H_b), 4.61 (*t*, $J_{H\text{-}H}$ = 1.91 Hz, 2H, H_c), 7.31 (*m*, 6H, $H_{l,m}$), 7.43 (*ddd*, $J_{H\text{-}H}$ = 7.1, 4.8, 1.8 Hz, 4H, H_k), 8.10 (*s*, 1H, H_e). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 25.85 (*d*, $J_{C\text{-}P}$ = 19.4 Hz, C_i), 27.5 (*d*, $J_{C\text{-}P}$ = 25.5 Hz, C_h), 62.78 (*d*, $J_{C\text{-}P}$ = 20.64 Hz, C_g), 68.51 C_b, 69.19 C_d, 70.46 C_c, 80.79 C_a, 128.51 C_m, 128.63 (*d*, $J_{C\text{-}P}$ = 8.50 Hz C_l), 132.88 (*d*, $J_{C\text{-}P}$ = 29.1 Hz, C_k), 138.81 (*d*, $J_{C\text{-}P}$ = 20.6 Hz, C_j), 161.38C_e. ^{31}P-NMR (121.495 MHz, $CDCl_3$): δ -16.52 ppm. IR (ATR): *v* 3074, 2097, 1610, 1434, 1100 cm^{-1}. MS FAB$^+$ (m/z): 439 [M^+].

4.1.2 Synthesis of Compound (η^5-C_5H_5)Fe{(η^5-C_5H_4)CH_2-NH-(C_3H_6-PPh_2)} (2).

In a Schlenk tube under N_2, to a solution0.78 mmol (0.353 g) of the previously synthesized ligand (**1**) in 10 mL of dry MeOH; was added 10 mmol. of sodium borohydride ($NaBH_4$) and stirring for 3 h. Distilled water 20mL was added and the mixture was extracted with CH_2Cl_2 and separated organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting yellow oil (**2**) was purified, by column chromatography on neutral Alumina using ethyl acetate/hexane as an eluent under N_2, and compound (**2**) was obtained in 50% (0.172g) yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.65 (*q*, $J_{H\text{-}H}$ = 8.34, 7.64

Hz, 2H, H_h), 2.01 (*s*, 1H, H_f), 2.09 (*m*, 2H, H_i), 2.74 (*t*, J_{H-H} = 7.05 Hz, 2H, H_g), 3.50 (*s*, 2H, H_e), 4.12 (*m*, 7H, $H_{d,b}$), 4.17 (*d*, J_{H-H} = 1.83 Hz, 2H, H_b), 7.37-7.31 (*m*, 6H, $H_{l,m}$), 7.47-7.40 (*m*, 4H, H_k). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 25.66 (*d*, J_{C-P} = 19.4 Hz, C_i), 26.14 (*d*, J_{C-P} = 25.5 Hz, C_h), 48.66 C_e, 50.22 (*d*, J_{C-P} = 21.86 Hz, C_g), 67.76 C_b, 68.34 C_d, 68.46 C_c, 86.29 C_a, 128.30 C_m, 128.43 (*d*, J_{C-P} = 21.85 Hz C_l), 132.65 (*d*, J_{C-P} = 30.35 Hz, C_k), 138.63 (*d*, J_{C-P} = 20.64 Hz, C_j). ^{31}P-NMR (121.495 MHz, $CDCl_3$): δ -16.09 ppm. IR (ATR): *v* 3324, 3049, 2811, 1432, 1103 cm^{-1}. MS FAB$^+$: *m/z* 441 [M$^+$]; HRMS: *(m/z)* Found: 441.1312, calcd for $C_{26}H_{28}NPFe$: 441.1309.

4.1.3 Synthesis of Compound $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2]_2\text{-}N\text{-}(C_2H_4\text{-}PPh_2)$ (3).

In a Schlenk tube under N_2, a solution of 2-(diphenylphosphino)ethylamine 0.78 mmol (0.178 g) in 10 ml of dry acetonitrile was added to a solution of $FeCH_2NMe_3[^-I]$ salt 1.56 mmol (0.6 g) with an excess of K_2CO_3 in acetonitrile. The mixture was refluxed for 6 h and turn its color to brown, the solution was concentrated under vacuum and the compound (**3**) was isolated by column chromatography on neutral Alumina using ethyl acetate/hexane as an eluent, as a solid yellow, yield 30 % (0.145g). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.06 (*m*, 2H, H_g), 2.36 (*m*, 2H, H_f), 3.31 (*s*, 4H, H_e), 4.01-3.94 (*m*, 18H, $H_{b,c,d}$), 7.19-7.32 (*m*, 10H, $H_{i,j,k}$). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 26.43 (d, J_{C-P} = 20.6 Hz, C_g), 48.42 (d, J_{C-P} = 37.6 Hz, C_f), 52.64 C_e, 67.95 C_b, 68.52 C_d, 70.20 C_c, 83.49 C_a, 128.47 (*d*, J_{C-P} = 19.4 Hz C_j), 128.51 C_k, 132.88 (d, J_{C-P} = 30.3 Hz, C_i), 138.71 (d, J_{C-P} = 20.6 Hz, C_h). ^{31}P-NMR (121.495 MHz, $CDCl_3$): δ -19.80 ppm. IR (ATR): *v* 3072, 2924, 2854, 1434, 1182 cm^{-1}. MS FAB$^+$: *m/z* 625. [M$^+$]; HRMS: *(m/z)* Found: 626.1372, calcd for $C_{36}H_{37}NPFe$: 626.1362.

4.1.4 Synthesis of Compound $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2]_2\text{-}N\text{-}(C_3H_6\text{-}PPh_2)$ (4).

In a Schlenk tube under N_2, a solution of 2-(diphenylphosphino)propylamine 0.78 mmol (0.189 g) in a 10 ml of dry acetonitrile was added 1.56 mmol of $FeCH_2NMe_3[^-I]$ salt 1.56 mmol (0.6g) with an excess of K_2CO_3 in acetonitrile. The mixture was refluxed for 6 h and turn its color to brown, the solution was concentrated under vacuum and the compound (**4**) was isolated by column chromatography on neutral Alumina using ethyl acetate/hexane as eluent, as a solid yellow, yield 35% (0.175g). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.54 (*m*, 2H, H_g), 1.95 (*m*, 2H, H_m), 2.36 (*t*, 2H, H_h), 3.36 (*s*, 2H, H_e), 4.06 (*s*, 10H, H_d), 4.10 (*m*, 8H, $H_{b,\ c}$), 7.47-7.28 (*m*, 10H, $H_{j,k,l}$). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 25.70 C_g, 31.05 C_f, 41.97 C_h, 52.58 C_e, 68.0 C_b, 68.65 C_d, 70.35 C_c, 128.48 C_k, 128.56 C_k, 128.64 C_l, 132.79 C_j, 133.03 C_j. ^{31}P-NMR (121.495 MHz, $CDCl_3$): δ -15.75 ppm. IR (ATR): *v* 3089, 2932, 2811, 1434, 1104 cm^{-1}. MS-FAB$^+$: *m/z* 639 [M$^+$].

4.1.5 Synthesis of Compound $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2]_2\text{-}N\text{-}(C_3H_6\text{-}P(=O)Ph_2)$ (4A).

Following the synthesis from the reaction to isolate (**4**), the compound (**4A**) phosphine oxide as yellow solid was obtained from one of the fractions in the column chromatography. Yield 10% (0.050g). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.89 (*m*, 2H, H_i), 2.24 (*m*, 2H, H_h), 2.70 (*m*, 2H, H_g), 3.73 (*s*, 4H, H_e), 3.92-4.40 (*m*, 18H, $H_{b,c,d}$), 7.33-7.9 (*m*, 10H, $H_{l,m,k}$). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 18.41 (d, J_{C-P} = 6.1 Hz, C_h), 26.99 C_i, 27.94 $C_{i'}$, 30.09 C_g, 53.27 C_e, 69.27 C_d, 69.67 C_b, 71.33 C_c, 88.26 C_a, 129.19 (*d*, J_{C-P} = 18.2 Hz C_l), 131.18 (*d*, J_{C-P} = 14.5 Hz C_k), 132.32 C_m, 133.56 C_j, 134.57 $C_{j'}$. ^{31}P-NMR (121.495 MHz, $CDCl_3$): δ 32.81 ppm. IR (ATR): *v* 3070, 2924, 2855, 1437, 1180 cm^{-1}. MS-FAB$^+$: *m/z* 655 [M$^+$].

4.1.6 Synthesis of Compound $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2]_2\text{-}N\text{-}(C_3H_6\text{-}P(\text{-}CH_2\text{-}Fc)Ph_2)$ (4B).

Following the synthesis from the reaction to isolate (**4**), the compound (**4B**) phosphonium salt as yellow solid was obtained from one of the fractions in the column chromatography. Yield 12% (0.078g). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.65 (*s*, 2H, H_g), 2.06 (*s*, 2H, H_h), 3.10 (*s*, 2H, H_o), 3.36 (*s*, 2H, H_f), 3.91 (*s*, 2H, H_e), 4.03 (*s*, 2H, H_e), 4.15 (*s*, 10H, H_d), 4.22 (*s*, 4H, H_c), 4.24 (*s*, 4H, H_s), 4.30 (*d*, 2H, H_b), 4.44 (*s*, 2H, H_q), 4.73 (*s*, 2H, H_r), 7.61-7.77 (*m*, 10H, $H_{j,k,l}$). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 18.86 (d, $J_{C\text{-}P}$ = 24.3 Hz, C_h), 19.64

C_o, 26.14 (d, $J_{C\text{-}P}$ = 71.68 Hz, C_g), 51.87 (d, $J_{C\text{-}P}$ = 32.80 Hz, C_f), 54.88 C_e, 69.32 C_d, 69.87 C_s, 70.17 C_c, 70.47 C_b, 71.92 C_q, 72.42 C_r, 73.16 C_p, 73.39 C_a, 116.47 C_i, 117.56 C_i, 130.37 (d, $J_{C\text{-}P}$ = 19.44 Hz, C_j), 133.76 (d, $J_{C\text{-}P}$ = 15.8 Hz, C_k), 135.15 (d, $J_{C\text{-}P}$ = 4.86 Hz, C_l). ^{31}P-NMR (121.495 MHz, $CDCl_3$): δ 22.52 ppm. IR (ATR): *v* 2921, 2851, 1458, 1161 cm^{-1}. MS-FAB$^+$: *m/z* 839 [M^+]; HRMS: *(m/z)* Found: 838.1679, calcd for $C_{48}H_{49}NPFe_3$: 838.1651.

4.1.7 Synthesis of Compound (η^5-C_5H_5)Fe{(η^5-C_5H_4)CH=N-(C_3H_6-PPh_2)$PdCl_2$} (5).

In a Schlenk tube under N_2, to a solution 0.2733 mmol (0.120 g) of ligand (**1**) in 10 mL of dry acetonitrile was added 0.2733 mmol (0.071 g) of Bis(acetonitrile)dichloropalladium(II), and refluxed for 4h, the solution turned into a red color solution. The solution was concentrated under vacuum and the compound (**5**) and was isolated as an orange solid using column chromatography. Yield 30 % (0.047g). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.94-1.44 (*m*, 2H, H_h), 2.52-2.64 (*m*, 2H, H_i), 3.64-3.57 (*m*, 2H, H_g), 4.28 (*s*, 5H, H_d), 4.53 (*d*, $J_{H\text{-}H}$ = 2.29 Hz, 2H, H_c), 4.73 (*m*, 1H, H_b), 6.46 (*m*, 1H, $H_{b'}$), 7.47-7.31 (*m*, 6H, $H_{k,l}$), 7.74 (*m*,2H, H_m), 7.81 (*s*, 1H, H_e). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 23.91 (*d*, $J_{C\text{-}P}$ = 52.20 Hz, C_i), 25.42 C_h, 61.26 (*d*, $J_{C\text{-}P}$ = 6.07 Hz, C_g), 70.51 C_d, 71.68 C_c, 73.02 C_c, 74.16 C_b, 75.62 $C_{b'}$, 77.63 C_a, 124.74 C_j, 125.42 C_j, 128.45 (*d*, $J_{C\text{-}P}$ = 19.42 Hz C_l), 129.01 (*d*, $J_{C\text{-}P}$ = 17 Hz C_l), 131.30 C_m, 132.16 C_m, 132.74 (*d*, $J_{C\text{-}P}$ = 17 Hz, C_k), 133.76 (*d*, $J_{C\text{-}P}$ = 18.21 Hz, C_k) 172.01 C_e. ^{31}P-NMR (121.495 MHz, $CDCl_3$): δ 16.75 ppm. IR (ATR): *v* 3050, 2918, 1616, 1483, 1101 cm^{-1}. MS FAB$^+$: *m/z* 580 [M^+-Cl]; HRMS: *(m/z)* Found: 579.9866, calcd for $C_{26}H_{26}ClNPFePd$: 579.9876.

4.1.8 Synthesis of Compound (η^5-C_5H_5)Fe{(η^5-C_5H_4)CH_2-NH-(C_3H_6-PPh_2)$PdCl_2$} (6).

In a Schlenk tube under N_2, to a solution 0.27 mmol (0.12 g) of ligand (**2**) in 10 mL of dry acetonitrile was added 0.27 mmol (0.07 g) of Bis(acetonitrile)dichloropalladium(II) and refluxed for 4h solution turned into a red color solution. The solution was concentrated under vacuum and the compound (**6**) and was isolated as an orange solid using column chromatography. Yield 40 % (0.063g). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.47-2.00 (*m*, 4H, $H_{h,l}$), 2.79 (*m*, 2H, H_g), 3.07 (*dd*, $J_{H\text{-}H}$ = 13.8, 11.0 Hz, 1H, H_e), 3.87 (*m*, 1H, H_c), 4.00 (*s*, 5H, H_d), 4.08-4.04 (*m*, 1H, H_c), 4.18-4.09 (*m*, 1H, H_b), 4.32 (*m*, 1H, H_b), 4.39 (*d*, $J_{H\text{-}H}$ = 14 Hz, 2H, H_e), 4.77 (*d*, $J_{H\text{-}H}$ = 10.8, 1H, H_f), 7.29-8.31 (10H, $H_{k,l,m}$). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 19.41 C_h, 22.69 (*d*, $J_{C\text{-}P}$ = 49.77 Hz, C_i), 44.73 (*d*, $J_{C\text{-}P}$ = 10.93 Hz, C_g), 50.47 C_e, 68.90 C_b, 68.95 C_d, 69.77 C_c, 70.38 C_b, 79.47 C_a, 125.17 C_j, 125.86 C_j, 128.59 (*d*, $J_{C\text{-}P}$ = 19.4 Hz C_k), 129.74 (*d*, $J_{C\text{-}P}$ = 18.2 Hz C_k), 131.13 C_m, 132.51 (*d*, $J_{C\text{-}P}$ = 17.0 Hz, C_l), 132.74 (*d*, $J_{C\text{-}P}$ = 3.6 Hz, C_m), 134.64(*d*, $J_{C\text{-}P}$ = 17.0 Hz, C_l). ^{31}P-NMR (121.495 MHz, $CDCl_3$): δ 13.81 ppm. IR (ATR): *v* 3219, 3083, 2922, 1081, 918, cm^{-1}. MS FAB$^+$ (m/z): 584 [M^+-Cl].

4.1.9 Synthesis of Compound [(η^5-C_5H_5)Fe(η^5-C_5H_4)CH_2]$_2$-N-(C_2H_4-PPh_2)$PdCl_2$ (7).

In a Schlenk tube under N_2, to a solution 0.27 mmol (0.169 g) of ligand (**3**) in 10 mL of dry acetonitrile was added 0.27 mmol (0.07 g) of Bis(acetonitrile)dichloropalladium(II), with refluxed for 4h, solution turned into a red color solution. The solution was concentrated under vacuum and the compound (**7**) and was isolated as an orange solid using column chromatography. Yield 25% (0.052g). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.44-2.29 (*m*, 2H, H_g), 2.81-2.65 (*m*, 1H, H_f), 2.86 (*s*, 2H, H_e), 3.13-2.99 (*m,* 1H, hf), 4.42-3.71 (*m*, 18H, $H_{b,c,d}$), 5.04-4.74 (*m*, 2H, He), 8.30-7.29 (*m*, 10H, $H_{l,m,k}$). ^{31}P-NMR (121.495 MHz, $CDCl_3$): δ -19.80 ppm. IR (ATR): *v* 3057, 2923, 2852, 1645 cm^{-1}. MS FAB$^+$: *m/z* 766 [M^+-Cl].

4.1.10 Synthesis of Compound [(η^5-C_5H_5)Fe(η^5-C_5H_4)CH_2]$_2$-N-(C_3H_6-PPh_2)$PdCl_2$ (8).

In a Schlenk tube under N_2, to a solution 0.27 mmol (0.172 g) of ligand (**4**) in 10 mL of dry acetonitrile was added 0.27 mmol (0.07 g) of Bis(acetonitrile)dichloropalladium(II) and refluxed for 4h solution turned into a red color solution. The solution was concentrated under vacuum and the compound (**8**)

and was isolated as an orange solid using column chromatography. Yield 30% (0.083 g). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.58-1.64 (*m*, 4H, $H_{g,h}$), 2.66 (*s*, 2H, H_f), 3.49 (d, $J_{H\text{-}H}$ = 12.75 Hz, H_e), 4.12-4.14 (*m*, 2H, $H_{b'}$), 4.16-4.18 (*td*, $J_{H\text{-}H}$ = 2.44, 1.25 Hz, 2H, $H_{c'}$), 4.21 (*d*, 10H, H_d), 4.26-4.28 (*td*, 2H, H_c), 7.27-7.33 (*m*, 4H, H_k), 7.38-7.44 (*dd*, $J_{H\text{-}H}$ = 2.08, 7.51 Hz, 2H, H_l), 7.46-7.54 (*ddd*, $J_{H\text{-}H}$ = 1.34, 8.28, 12.18 Hz, 4H, H_j). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 22.8 (*d*, $J_{C\text{-}P}$ = 6.07 Hz, C_h), δ 25.41 (*d*, $J_{C\text{-}P}$ = 43.73 Hz, C_g), 57.27 (d, $J_{C\text{-}P}$ = 9.71 Hz, C_f), 68.70 $C_{b'}$, 69.22 C_d, 69.99 C_c, 69.99 C_c, 71.46 $C_{c'}$, 73.36 C_b, 80.54 C_a, 128.31 (*d*, $J_{C\text{-}P}$ = 18.22 Hz C_k), 129.46 C_i, 130.26 C_i, 131.06 (d, $J_{C\text{-}P}$ = 4.85 Hz, C_l), 133.89 (d, $J_{C\text{-}P}$ = 17 Hz, C_j). ^{31}P-NMR (121.495 MHz, $CDCl_3$): δ 14.69 ppm. IR (ATR): *v* 3196, 2888, 1629, 1435, 1103 cm^{-1}. MS FAB$^+$: *m/z* 782 [M^+-Cl].

General procedure for the Suzuki-Miyaura cross-coupling reactions

In a Schlenk tube under N_2 1.0 mmol of aryl bromide, 1.0 mmol of aryl boronic acid, and 0.5 or 0.25% mol of catalyst in 5 mL of DMF were introduced into a Schlenk tube. The tube was charged with a magnetic stir bar and an equimolar amount of base (Na_2CO_3, 2 mmol), and sealed, then fully immersed in a 100°C oil bath. After 18 hrs, the mixture was cooled to room temperature. Water was added (20 mL). The white suspension was extracted with dichloromethane (3 x 50 mL). The organic phase was washed once again with water, separated and treated with anhydrous $MgSO_4$, filtered, and analyzed by gas chromatography (GC-MS). The results presented are the average of two runs.

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Declarations of interest

None

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