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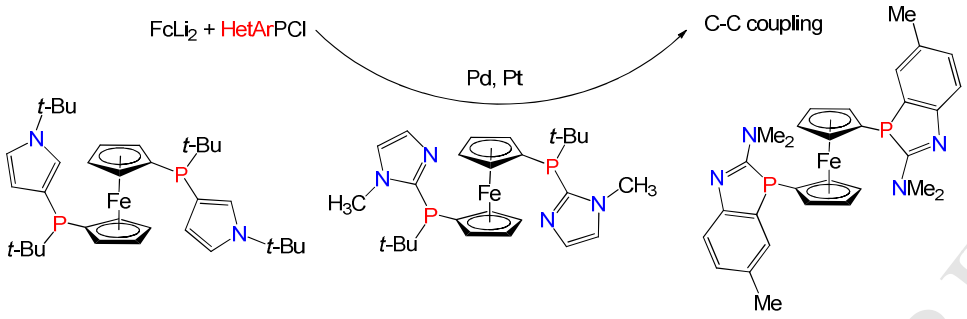
Graphical Abstract



Highlights

♦Synthesis of the first ferrocenyl diphosphines holding *N*-containing heterocyclic motifs ♦ X-ray characterization of their palladium and platinum dichloride complexes ♦ Palladium-catalyzed copper-free Sonogashira and Suzuki cross-coupling reactions using bromoarenes and chloroarenes

Ferrocenyl (P,N)-diphosphines incorporating pyrrolyl, imidazolyl or benzazaphospholyl moieties: synthesis, coordination to group 10 metals and performances in palladium-catalyzed arylation reactions

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REVISED VERSION

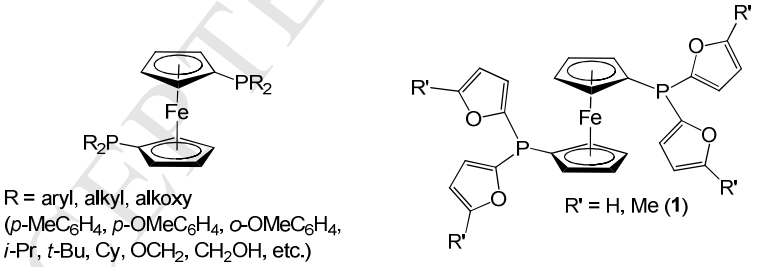
Abstract

Three novel symmetrical ferrocenyl diphosphines with tertiary phosphorus atoms holding respectively nitrogen-containing heterocyclic derivatives of pyrrole, imidazole and benzazaphosphole were synthesized and characterized. Up to now, integration of heteroaromatic fragments, or more generally heterocycles, as substituents on the tertiary phosphines of symmetrical ferrocenyl diphosphines has been limited to the furyl motif. Their coordination to palladium and platinum group 10 transition metals was exemplified, and analyzed using single crystals X-ray diffraction. The performances obtained in palladium-catalyzed copper-free Sonogashira and Suzuki cross-coupling reactions using bromoarenes and chloroarenes are reported for the most efficient system. The unprecedented combination of a *tert*-butyl group and of an imidazolyl motif on the phosphorus atoms led to an air-stable ferrocenyl diphosphine, which allowed in combination with 0.1 to 0.2 mol% of palladium to generate catalytic systems able to couple some activated chloroarenes and most of the bromoarenes examined.

Keywords: Ferrocene • Diphosphine • Heteroaromatic • Palladium • X-ray structure • Cross-coupling

1. Introduction

The discovery of ferrocene and the elucidation of its "sandwich" structure initiated an era of development for organometallic chemistry in the history of chemical science [1]. The selective functionalization of the ferrocene backbone with donor atoms (P, N, S, Se, etc.) has generated many chiral and achiral molecules which are, among other applications, much beneficial as stabilizing ligands for transition metals. Such species have shown for instance important applications in palladium-catalyzed organic synthesis reactions [2]. Based on the impetus provided by the applications of the simple diphosphine 1,1'-bis(diphenylphosphino)ferrocene (dppf), investigations directed towards the synthesis of new ferrocene-based ligands —sterically and/or electronically modified either at the ferrocenyl backbone or at the donor atoms— are of fundamental and applied interest [2a]. Accordingly, a variety of dppf derivatives has been designed and is available for applications in homogeneous metal catalysis (Scheme 1) [3]. Nevertheless, despite the various symmetrical ferrocenyl diphosphine incorporating tertiary phosphines produced and employed as ligands for transition metals, such species are mostly restricted to phosphorus donor atoms substituted with fairly classical aryl and alkyl moieties, as shown in Scheme 1 (left).



Scheme 1. Typical symmetrical ferrocenyl diphosphine employed as ligand in palladium-catalysis.

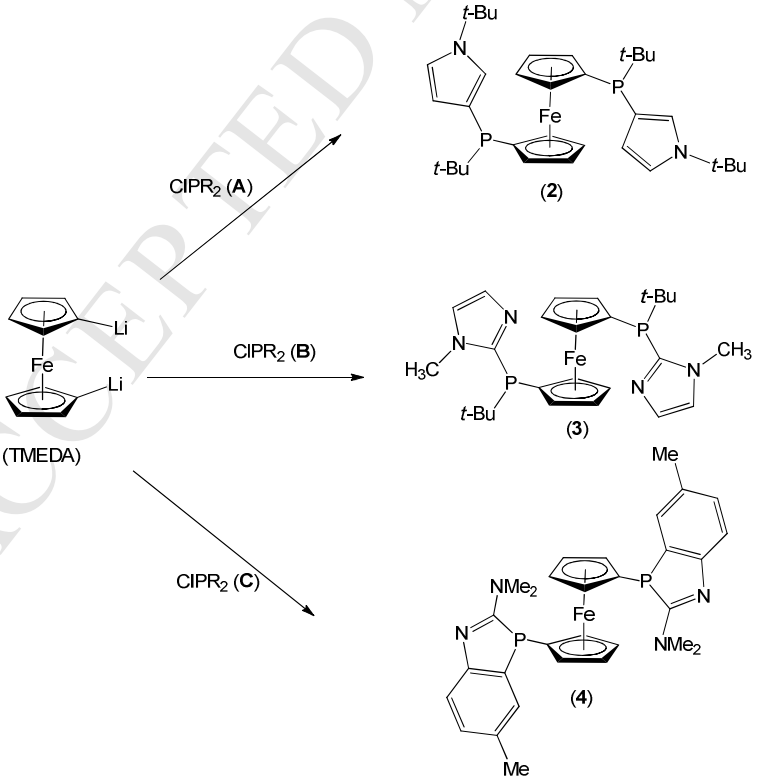
To the best of our knowledge, the incorporation of heteroaromatic fragments, or more generally heterocycles, as substituents on the tertiary phosphines of symmetrical ferrocenyl diphosphines has been limited to the furyl motif, which though led to unique catalytic performances [4,5]. For instance, the ligand 1,1'-bis[di(5-methyl-2-furyl)phosphino]ferrocene (**1** in Scheme 1, right) reported by some of us was found to promote nucleophilic allylic amination of allylic acetate at room

temperature with excellent turnover frequencies [6]. In the presence of 0.01 mol% [Pd/**1**] catalyst the coupling of aniline with allyl acetate occurred at a turnover frequency TOF above 10,000 h^{-1} leading to a complete conversion of substrates with 96% selectivity in monoallylamine. Under the same conditions, dppf as the ligand gave a conversion of 60% after 40 h at room temperature, TOF 150 h^{-1}. Combined with palladium, diphosphine **1** has also provided an efficient and selective catalytic system for the Heck reaction using hydroxylated styrenes and bromoarenes in a straightforward stilbenes synthesis which circumvents the use of protective groups [7]. The combination in **1** of the steric hindrance from ferrocenyl backbone and of strong electron-withdrawing effect from the four furyl substituents on phosphorus donors clearly outperforms the existence of only one of these features in the parent ligands dppf and P(2-furyl)$_3$ tested in the same reaction [7]. With the view to further study the features and catalytic performances of ferrocenyl diphosphines incorporating phosphorus atoms substituted with heteroaromatic motifs, in the present work the novel ferrocenyl diphosphines **2**, **3** and **4** (Scheme 2), bearing respectively nitrogen-containing heterocycles of pyrrole, imidazole and benzazaphosphole type were synthesized and characterized. Their coordination to palladium and platinum group 10 transition metals was exemplified, and the performances obtained in palladium-catalyzed copper-free Sonogashira and Suzuki cross-coupling reactions using bromoarenes and chloroarenes are reported.

2. Results and discussion

One of the remaining challenges offered by palladium-catalyzed cross-coupling arylation reactions is the activation of more reluctant carbon-chloride bonds with robust non air-sensitive ligands [8]. Metal-catalyzed activation of the C–Cl bond of organic chlorides can be promoted by the presence of electron donating fragments in the vicinity of the metal. We thus envisioned that in addition to the heterocyclic substituent attached to phosphorus donor atoms, the introduction of a bulky electron-rich alkyl group, such as *tert*-butyl, on this phosphine group might be helpful for promoting oxidative addition of C–Cl bond onto palladium [8]. On the other hand, due to the predictable heterocyclic π-

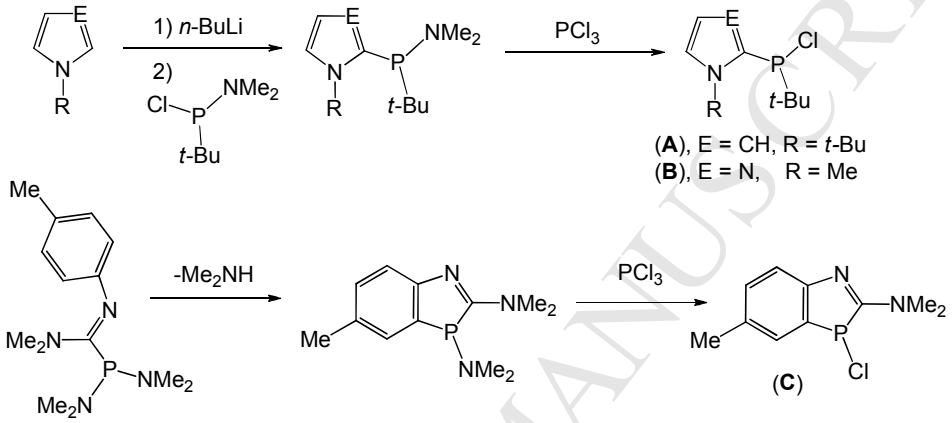
delocalization offered to phosphorus lone pairs, we anticipated for the resulting ferrocenyl diphosphines (**2** and **3** in Scheme 2) a weaker basicity and thus a better stability toward atmospheric oxidation than the one observed for classical trialkyl phosphines such as P(*t*-Bu)$_3$. It is noteworthy that such mixed tertiary phosphines incorporating in addition to the metallocenic fragment both an alkyl and *N*-heterocyclic groups are unprecedented. Pioneering works on 1,1'-bis[phosphino]ferrocene compounds Fe($C_5H_4PR^1PR^2$)$_2$ with two different substituents at the phosphorus atom have been limited to aryl/alkyl groups: R^1 = Ph/R^2 = *t*-Bu [9], R^1= Ph/R^2=*i*-Pr [10], and R^1 = Ph/R^2 = Me [11]. The simple synthetic pathways we choose does not involve any asymmetric induction step, therefore the resulting ligands were expected to be obtained as diastereomeric mixtures (*rac*/*meso* due to asymmetric phosphorus), which may eventually be resolved by fractional crystallization [11]. Finally, we were also interested in introducing a tertiary P-heterocyclic substituent on ferrocene backbone, and a novel heterophosphole of benzazaphosphole type was chosen (**4** in Scheme 2) [12].



Scheme 2. Ferrocenyl (P,N)-diphosphines **2**, **3** and **4**, P-substituted with *N*-heterocycles.

2.1. Synthesis and characterization of ferrocenyl diphosphines incorporating N-heterocyclic moieties

The synthesis of ferrocenyl diphosphine was conducted by dilithiation of the ferrocene followed by quenching with halophosphines $ClPR_2$ (Scheme 2) as early reported by Bishop *et al.* to yield the 1,1'-bis(diphenylphosphino)ferrocene (dppf) [13]. The chlorophosphine precursors **A**, **B**, and **C** of $ClPR_2$ type were synthesized following the routes depicted in Scheme 3.



Scheme 3. Synthesis of pyrrolyl, imidazolyl and benzazaphospholyl chlorophosphines **A**, **B**, and **C**.

The ferrocenyl diphosphines **2**-**4** were isolated by crystallization as mixture of diastereomers with various diastereomeric excess depending on the species and the conditions, as summarized in Table 1. Our success in further improving diastereomeric excess by fractional crystallization was limited since co-crystallization systematically occurred despite our efforts. However, this was not considered as detrimental for our subsequent synthetic applications since we focused on testing achiral palladium-catalyzed cross-coupling reactions. After diastereomeric separation further resolution of the chiral species (*rac*) we formed would be of interest to develop asymmetric cross-coupling reactions. The chemical shifts δ for the phosphorus atoms of **2**-**4** were found ranging between −15 and −30 ppm [14], the imidazolyl group contributes to a greater shielding of phosphorus signal (−29.0 ppm) compared to the pyrrolyl group (−15.6 ppm). A ^{31}P NMR δ chemical shift around −25 ppm was found for the diastereomeric forms of compound **4** holding benzazaphospholyl groups.

Table 1.

Ratio of diastereomers **2**-**4** from fractional crystallization and corresponding ^{31}P NMR shifts.

Diphosphines	Crystallization crop 1 – Enrichment D1:D2	Total yield Cryst. 1	Crystallization crop 2 – Enrichment D1:D2	Total yield Cryst. 2	δ^{31}P NMR D1/D2 (ppm)
2	90:10	55%	/	/	−15.6 / −15.1[a]
3	62:38	52%	22:78	20%	−28.8 / −29.0[b]
4	80:20	33%	58:42	39%	−24.9 / −23.3[b]

Solvent: [a]$CDCl_3$, [b]C_6D_6.

2.2. Coordination of ferrocenyl (P,N)-diphosphines to group 10 metals

Due to the presence of several nitrogen and phosphorus donors on the ferrocenyl ligands **2**-**4** we were eager to check whether phosphorus coordination is prevailing, or if the presence of nitrogen atoms may perturb the Pd/P soft-soft Pearson acid/base preference. The complex [$PdCl_2$(**2**)] in which palladium is embedded into a classical chelating coordination to phosphorus atoms (Fig. 1), was obtained from reacting the dimeric precursor [Pd(II)Cl_2(η^3-C_3H_5)] with diphosphine **2** (diastereomer mixture 90:10) in dichloromethane. After evaporation and treating the residue with diethylether, ^{31}P and ^{1}H NMR indicated that only a single diastereomer was obtained in a final yield of 58%, as evidenced by a single phosphorous signal at 32.45 ppm, and from one set of signal for *H*-Cp at 4.12, 4.19, 4.27 and 4.30 ppm. Methyl protons from *t*-Bu groups on phosphorus atoms are detected as a doublet centered at 1.31 ppm ($^2J_{PH}$= 15.9 Hz), *N*-methyl groups are found at 1.60 ppm and pyrrolyl protons gave signals at 6.41, 6.94 and 8.1 ppm. Single crystals suitable for X-ray diffractions studies allowed us to determine the absolute configuration of the *rac*-[$PdCl_2$(**2**)] complex isolated (Ortep in Fig. 1). We consequently assumed that the diasteromeric phosphine crop used for coordination to palladium was (*rac)*-90:(*meso)*-10.

The molecular structure of *rac*-[$PdCl_2$(**2**)] is of non-crystallographic C_2 symmetry with a distortion of the metallocene backbone. The sandwich conformation is staggered with a torsion angle P1-Ct1-Ct2-P2 of –40.67(8) ° (Ct1 and Ct2 are the centroids of Cp rings). The conformation of the phosphine groups places the *t*-Bu groups roughly perpendicular to the Cp rings in *exo* position relative to ferrocene backbone, pyrrolyl groups are in *endo* position. The palladium center is in a distorted square planar environment with a P1-Pd-P2 bite angle of 101.93(3) ° and a Cl1-Pd-Cl2 angle of 86.18(3) °.

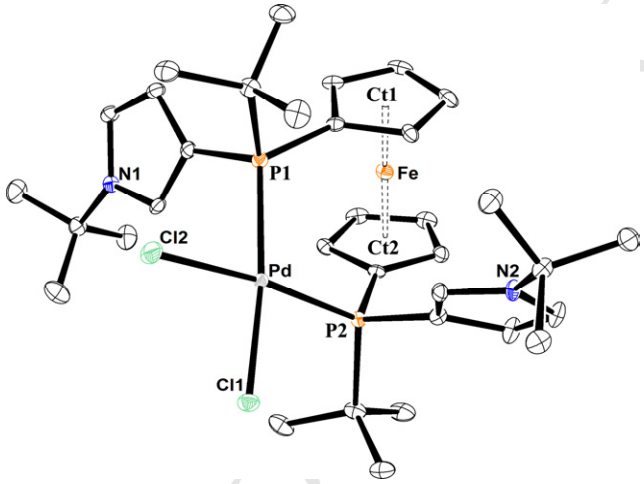


Fig. 1 Molecular structure of *R,R*-[$PdCl_2$(**2**)] (*S,S*-enantiomer is equally present in the unit cell), hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–P1 2.3135(8), Pd–P2 2.3100(8), Pd–Cl1 2.3529(8), Pd–Cl2 2.3296(9), P1-Pd-P2 101.93(3), P1-Pd-Cl1 169.53(3), P2-Pd-Cl2 173.50(3), Cl1-Pd-Cl2 86.18(3), Fe–Ct1 1.631(3), Fe–Ct2 1.632(3); Ct1-Fe-Ct2 175.97(16), P1-Ct1-Ct2-P2 –40.67(8).

The complex [$PdCl_2$(**3**)] (Fig. 2) was obtained from reacting [$PdCl_2(PhCN)_2$] in stoichiometric amount with diphosphine **3** (diastereomer mixture 62:38) in dichloromethane. In the crude mixture this ratio was conserved. After evaporation and treating the residue with diethyl ether, the complex was crystallized and diastereomeric resolution led to isolate *rac*-[$PdCl_2$(**3**)] in 45% yield, with a corresponding δ ^{31}P NMR at 22.7 ppm and ^{1}H NMR δ *H*-Cp at 3.91, 4.16, 4.38 and 4.81 ppm. We easily deduced that the original diasteromeric phosphine crop used for coordination to palladium

was (*rac*)-62:(*meso*)-38 since the obtained yield (45%) of the complex is more than 38 %. (The X-ray structure characterization (see Ortep in Fig. 2) revealed features comparable to *rac*-[$PdCl_2$(**2**)]. However, this complex presents a torsion angle P1-Ct1-Ct2-P2 equal to –28.96(9) °, and in contrast to *rac*-[$PdCl_2$(**2**)], the imidazolyl groups adopt two different orientations with respect to the ferrocene backbone (Pd…C18 = 3.933 (4) and Pd…C26 = 3.605 (4)) and hence the C_2 axis is lost in this solid state conformation.

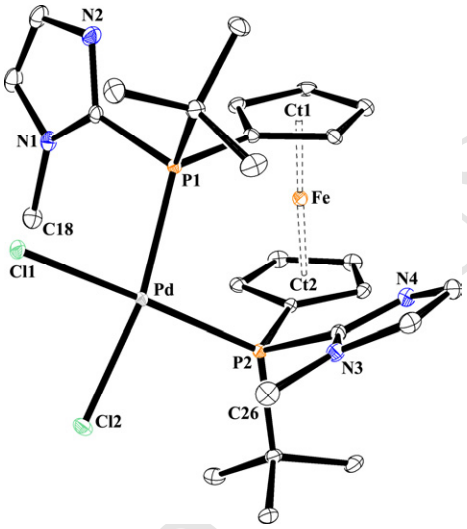


Fig. 2 Molecular structure of *R,R*-[$PdCl_2$(**3**)] (S,S-enantiomer is equally present in the unit cell), hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd−P1 2.3190(9), Pd−P2 2.3100(9), Pd−Cl1 2.3547(9), Pd−Cl2 2.3425(9), P1-Pd-P2 98.62(3), P1-Pd-Cl1 83.39(3), P2-Pd-Cl2 91.92(3), Cl1-Pd-Cl2 86.35(3), Fe−Ct1 1.637(3), Fe−Ct2 1.633(3); Ct1-Fe-Ct2 177.34(17), P1-Ct1-Ct2-P2 –28.96(9).

The synthesis of the related *rac*-[$PtCl_2$(**3**)] was also easily achieved from reacting in stoichiometric amount $PtCl_2(PhCN)_2$ with diphosphine **3**. Crystals suitable for X-Ray diffraction were isolated in 61% yields from a pentane/dichloromethane mixture. ^{31}P NMR in CD_2Cl_2 indicates a signal at 5.2 ppm with a $^1J_{PtP}$ of 3604 Hz typical of a *cis*-coordination of chelating phosphorus atoms with chloride atoms in *trans* position [15]. The complex *rac*-[$PtCl_2$(**3**)] is isostructural with *rac*-[$PdCl_2$(**3**)] complex with no C_2 axis in this solid state conformation (for instance Pt…C18 = 3.638 (4) and Pt…C26 = 4.035 (4)).

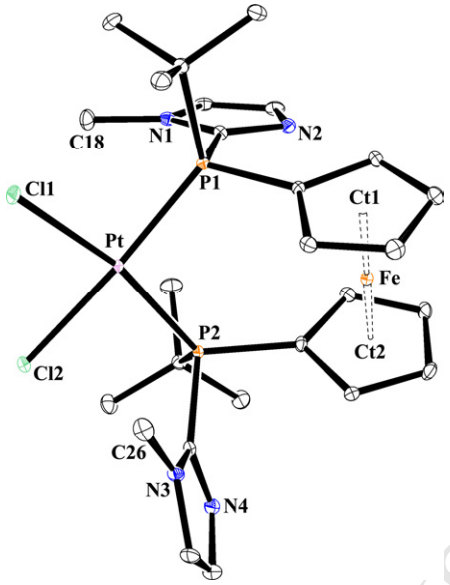


Fig. 3 Molecular structure of *R,R*-[$PtCl_2$(**3**)] (S,S-enantiomer is equally present in the unit cell), hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt–P1 2.2788(12), Pt–P2 2.2863(13), Pt–Cl1 2.3486(13), Pt–Cl2 2.3598(12), P1-Pt-P2 98.74(5), P1-Pt-Cl1 92.65(4), P2-Pt-Cl2 84.13(4), Cl1-Pt-Cl2 84.63(4), Fe–Ct1 1.631(4) , Fe–Ct2 1.637(4); Ct1-Fe-Ct2 177.1(2), P1-Ct1-Ct2-P2 –28.84(12).

The complex [$PdCl_2$(**4**)] (Fig. 4) was obtained from reacting [$PdCl_2(PhCN)_2$] in stoichiometric amount with diphosphine **4** (Scheme 2) from a diastereomer mixture 58:42 in dichloromethane. In the crude mixture this ratio was conserved with the presence of two phosphorus signals in NMR at 28.95 and 32.92 ppm. Crystals were obtained by slow diffusion of pentane in a solution of the complex in $CHCl_3$ (87% yield, major isomer 58%). This complex presents a pseudo-symetry plane, the [$PdCl_2$(**4**)] molecule structure conformation is *meso*. The sandwich conformation is staggered with a torsion angle P1-Ct1-Ct2-P2 equal to –21.3(4). The conformation of the phosphorus atoms places the planar benzazaphospholyl groups roughly perpendicular to the Cp rings in *exo* position relative to ferrocene backbone.

Finally, the synthesis of the platinum complex [$PtCl_2$(**4**)] was also achieved in very good yield (86%) from dichloro(1,5-cyclooctadiene) platinum(II) as a mixture of diastereomers (major isomer 58%).

The phosphorous ^{31}P NMR signal from the major isomer signal is found at 8.14 ppm with a high $^{1}J_{PtP}$ = 3626 Hz constant (minor isomer 10.20 ppm, $^{1}J_{PtP}$ = 3622 Hz), attesting for a *cis*-coordination of chelating phosphorus atoms.

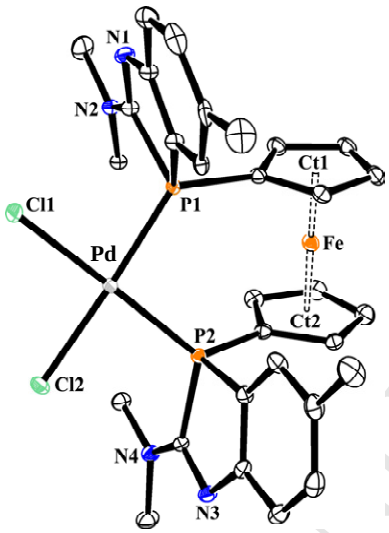


Fig. 4 Molecular structure of *R,S*-[$PdCl_2$(**4**)], hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd−P1 2.26(2), Pd−P2 2.2443(9), Pd−Cl1 2.348(1), Pd−Cl2 2.340(1), P1-Pd-P2 96.8(5), P1-Pd-Cl1 84.2(5), P2-Pd-Cl2 86.52(4), Cl1-Pd-Cl2 92.22(3), Fe−Ct1 1.650(4) , Fe−Ct2 1.643(4); Ct1-Fe-Ct2 179.2(2), P1-Ct1-Ct2-P2 –21.3(4).

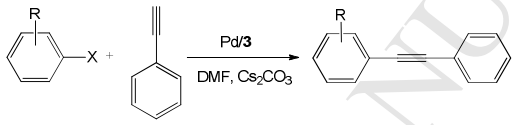
2.3. Cross-coupling reactions catalyzed by palladium/ferrocenyl diphosphine complexes

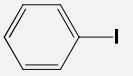
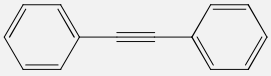
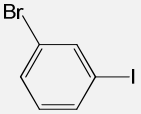
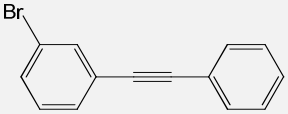
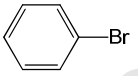
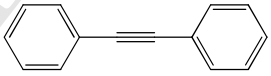
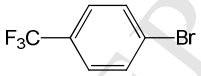
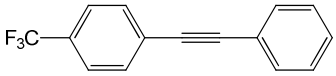
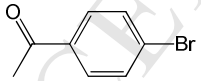
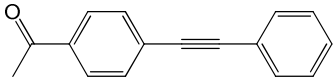
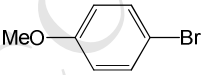
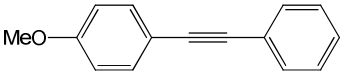
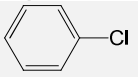
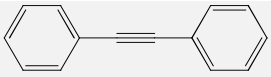
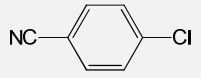
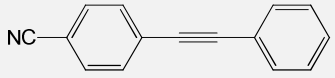
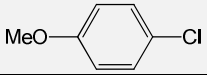
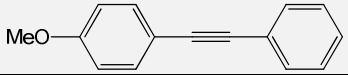
In order to assess the influence of the novel ferrocenyl (P,N)-diphosphines bearing heterocyclic groups on palladium-catalyzed cross-coupling reactions we started our investigations with the arylation of terminal alkynes by using *in situ* formed precatalyst [$PdCl_2$(**3**)] under copper-free conditions. Among palladium-catalyzed C−C bond formation this reaction is known to be significantly ligand-dependent [16], and rather challenging. The palladium-catalyzed arylation of terminal alkynes in the absence of copper render the activation of alkynes even more difficult (since no Cu→Pd transmetalation step of acetylide occurs), but is preferable to obviate the formation of undesired alkyne dimerization side-products [17]. In preliminary screening experiments the coupling of phenyl acetylene with aryl iodides was easily achieved in 20 h in the presence of 4 mol% of catalyst (Table 2,

entries 1 and 2). Interestingly, when 3-bromo-1-iodobenzene is used, thus in the presence of both a bromo and an iodo function on the substrate, the cross-coupling selectively occurred at the more reactive C–I bond. We then examined the coupling reactions using aryl bromide substrates in the presence of a lower catalyst loading at 1 mol%. Bromobenzene and 4-trifluorobromobenzene were quantitatively coupled within 20 h (Table 2, entries 3 and 4). Under the same experimental conditions the coupling of 4-bromoacetophenone was found less effective with a yield of 77% after 20 h (entry 5).

Table 2.

Palladium-catalyzed copper-free arylation of phenyl acetylene from aryl halides using [$PdCl_2$(**3**)].[a]



entry	aryl halide	product	Pd/**3** loading (%)	yield[b] (%)
1			4	>95
2			4	>95
3			1	>95
4			1	>95
5			1	77
6			4	44
7			1	>95
8			1	29
9			1	<5

[a] Conditions: catalyst [$PdCl_2(PhCN)_2$]/**3** (0.01 to 0.04 mmol) , aryl halide (1 mmol), phenyl acetylene (2 mmol), Cs_2CO_3 (2 mmol), DMF, 100 °C, 20 h under Ar. [b] Average of two or more runs determined by GC and GC-MS (±5%).

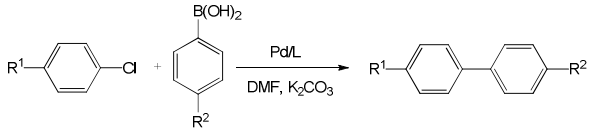
The electron-rich 4-bromoanisole was converted in a moderate 44% yield by using 4 mol% of catalyst (entry 6). The cross-coupling of aryl chlorides was also tested with chlorobenzene and substrates holding electron-donating or electron-withdrawing groups in *para* position. The non-substituted chlorobenzene was efficiently coupled (yield >95%, entry 7), while the functionalization of aryl chloride significantly hampers the reactivity of these species by using [$PdCl_2$(**3**)]. The presence of one donating *t*-Bu group on the phosphorus atoms is apparently insufficient to ensure very fast oxidative addition of electron-rich aryl halides on palladium under our conditions. This might possibly be due to the electron-withdrawing effect of the imidazolyl group. Nevertheless, we tested the arylation of chlorobenzene following Suzuki-Miyaura reaction, this cross-coupling reaction being known to be generally less-demanding than copper-free arylation of alkynes due to preformed organometallic reactive nucleophile.

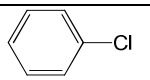
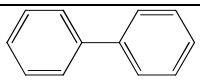
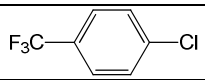
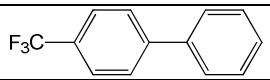
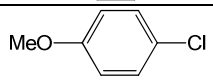
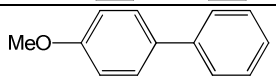
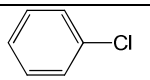
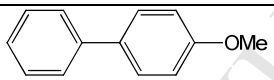
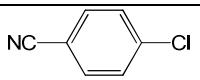
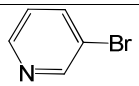
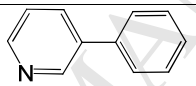
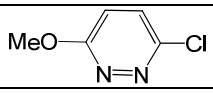
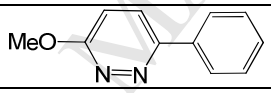
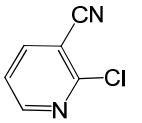
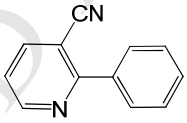
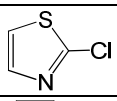
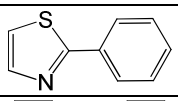
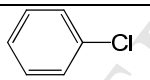
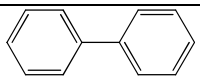
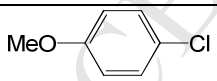
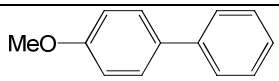
Various aryl chlorides were tested and the optimization of catalyst loading at 0.2 mol% was found appropriate for such couplings. As reported in Table 3, under these conditions the coupling of chlorobenzene was efficiently achieved (entry 1). In contrast to alkyne arylation reactions, substitution on aryl chlorides did not completely inhibit the coupling. For instance, electron-deficient 4-trifluoromethylchlorobenzene was converted in 82% yield (entry 2). Conversely, the presence of the electron-donating methoxy group was a severe limitation when positioned on the aryl chloride with only 7% yield of coupling product (entry 3). The coupling of 4-metoxyphenyl boronic acid to chlorobenzene was also tested but was unsuccessful (entry 4). In contrast, 4-cyano-4'-methoxybiphenyl was obtained in satisfactory 72% yield under these low palladium loading conditions at 100 °C (entry 5).

These results in phenyl arylation from aryl chlorides position fairly favorably ferrocenyl diphosphine **3** among the numerous auxiliary ligands used for Suzuki cross-coupling, in particular if is considered that this phosphine can be kept under air [18].

Table 3.

Palladium-catalyzed arylation of aryl boronic acids from aryl chlorides.[a]



entry	aryl chloride	product	Pd/**L** loading (%)	yield [b] (%)
1			0.2	>95
2			0.2	82
3			0.2	7
4			0.2	<5
5			0.2	76
6			0.2	100
7			0.2	26
8			0.2	26
9			0.2	<5
10			0.2%	>95[c]
11			0.2%	6[c]

[a] Conditions: catalyst $[PdCl_2(PhCN)_2]$/**3** (0.002 mmol) , aryl halide (1 mmol), aryl boronic acid (2 mmol), K_2CO_3 (2 mmol), DMF, 100 °C, 20 h under Ar. [b] Average of two or more runs determined by GC, GC-MS and NMR (±5%). [c] Catalyst $[PdCl_2(PhCN)_2]$/**4** (0.002 mmol).

Such type of cross-coupling reactions has been much less studied with heteroaryl chlorides. Due to the usual prevalence of phosphorus coordination over nitrogen coordination in group 10 metal complexes, as confirmed from our X-ray structure characterizations, we hypothesized that

heteroaromatic substrates containing nitrogen or other donor atoms should not bring undesired coordinative perturbation to our catalytic systems. The results of our investigation of the Suzuki coupling reaction of a selection of heteroaromatic substrates are reported in Table 3, entries 6 to 9. The quantitative coupling of 3-bromopyridine indeed proceeded easily. However, the coupling of chloroheteroarenes was found more difficult and only moderate conversions of 3-cyano-2-chloropyridine (26% yield) and 6-methoxy-3-chloropyridazine (26% yield) were obtained in 20 h. The five membered-ring 2-chlorothiazole was found poorly reactive (entry 9). We also tested the coupling of chloroarenes with [Pd/**4**] (see for instance Table 3, entries 10 and 11) but we obtained either similar or inferior performances. Clearly, the robustness and steric and electronic features of these ligands are demonstrated to be useful in homogeneous catalysis but activating organic chlorides remains a limitation.

3. Summary and conclusions

Three novel ferrocenyl (P,N)-diphosphines **2**, **3** and **4** incorporating phosphorus atoms substituted with *N*-heteroaromatic pyrrolyl, imidazolyl or benzazaphospholyl motifs have been synthesized and characterized, completing the previously reported two sole examples of symmetrical ferrocenyl diphosphines holding heteroaromatic groups (furyl heterocycles). The group 10 coordination complexes formed from coordination of these diphosphines display a classical chelating (P,P)-behavior, even though two to four accessible nitrogen donors are present on the modified ferrocenes. An apparent preference for crystallization of the *rac*-diastereomer has been observed in some cases. In the solid state the diphosphines are not air-sensitive (no phosphine oxide formed after several months under air) despite the presence on the phosphorus atoms of an electron-rich *t*-Bu group. In the palladium-catalyzed arylation of terminal alkynes and phenyl boronic acids the influence of ligand **3** has been specifically examined showing that arene and heteroarene bromides are suitable substrates, while only activated chlorides can be efficiently employed in the presence of 0.2 to 1.0 mol% catalyst. Further works aiming at exploring the properties of these ligands might

address copper coordination chemistry possibly *via* nitrogen atoms and related Ullmann catalysis as arylation reactions.

4. Experimental

All procedures with air and moisture sensitive compounds were performed under an atmosphere of dry argon in oven or flame-dried glassware. Solvents were purified and dried by standard methods. ^{1}H spectra were recorded on a Bruker Avance DRX 500 (500.13 MHz) or Varian VXR-300 (299.94 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 (125.75 MHz) spectrometer. ^{31}P NMR spectra were recorded on a Varian VXR-300 (80.95 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million downfield relative to internal TMS (for ^{1}H, ^{13}C) and external 85% H_3PO_4 (for ^{31}P). Coupling constants are reported in hertz. Chromatography was performed on silica gel Gerudan SI60. Elemental analyses were performed at the "*Micro analytical laboratory of the Institute of Organic Chemistry of the National Academy of Sciences of Ukraine*". Alternatively, the identity and purity (≥95%) of the compounds were established at the "*Plateforme d'Analyses Chimiques et de Synthèse Moléculaire de l'Université de Bourgogne*" using high-resolution mass spectrometry and multinuclear NMR. The exact mass of the complexes was obtained on a Bruker micrOTOF-Q ESI-MS. ^{1}H (300.13, 500.13, or 600.13MHz), ^{13}C (75.5, 125.8, or 150.9 MHz), and ^{31}P (121.5, 202.5, or 242.9 MHz) NMR spectra were recorded on a Bruker 300 Avance, a Bruker 500 Avance DRX spectrometer, or on a Bruker 600 Avance II spectrometer at ICMUB. X-ray analysis of compounds were conducted with intensity data collected on a Bruker-Nonius APEX II diffractometer equipped with an Oxford Cryosystem low-temperature device operating at 115 K. 1-*tert*-butylpyrrol-3-ylphosphorous dichloride [19] and dimethylaminophosphole [20] were synthesized following literature procedures. Coupling product yields were determined by GC, GC-MS and NMR. The *rac* or *meso* configuration was determined when possible after selective crystallization of a palladium complex from a single diastereomer, determination of the yield, X-ray diffraction and $^{31}P/^{1}H$ NMR of the crystals.

*4.1. Synthesis of chlorophosphines (**A**), (**B**) and (**C**)*

*4.1.1. tert-Butylchloro(1-tert-butyl)-1H-pyrrol-3-ylphosphine, **A***

To a solution of 14.3 g of 1-*tert*-butylpyrrol-3-ylphosphorous dichloride (14.3 g, 63.8 mmol) in 60 mL of diethyl ether was added dropwise over 30 min under dry argon *tert*-butylmagnesium chloride (46 mL in 1.6 M solution in diethyl ether, 0.0736 mol). The mixture was then heated under reflux for 1 hour. After the solvent was removed in vacuum, and 200 mL of dry benzene was added to the

residue (*alternatively less toxic toluene can be used in 300 mL*), and insoluble parts were filtered, washed with benzene (2x30 mL). The filtrate was concentrated under vacuum and distilled. The crop boiling between 79 and 90 °C at 0.05 mmHg was collected. A second distillation between 83 and 85 °C at 0.05 mmHg, gives the phosphine **A** as a colorless oil in 34% yield (5.2 g, 21.1 mmol). Chlorophosphine **A** is very sensitive to air and moisture. ^{1}H NMR (C_6D_6, δ ppm) 7.02 (m, 1H, pyrrol), 6.59 (m, 2H, pyrrol), 1.21 (d, 9H, $^{3}J_{PH}$ = 14 Hz, *t*-BuP), 0.99 (s, 9H, *t*-BuN). ^{31}P NMR (C_6D_6, δ ppm) 100.7. ^{13}C NMR (C_6D_6, δ ppm) 124.9 (d, $^{2}J_{CP}$ = 49.0 Hz, C_2), 119.7 (s, C_5), 115.4 (d, $^{1}J_{CP}$ = 34.0 Hz, C_3), 111.8 (d, $^{2}J_{CP}$ = 8.8 Hz, C_4), 54.7 (s, N-*C*(CH_3)), 34.1 (d, $^{1}J_{CP}$ = 26.4 Hz, P-*C*(CH_3)), 30.0 (s, N-C(*C*H_3)), 25.5 (d, $^{2}J_{CP}$ = 17.1 Hz, P-C(*C*H_3)).

*4.1.2. tert-Butylchloro(1-methyl)-1H-imidazol-2-ylphosphine, **B***

To a solution of imidazole (3.24 g, 39.5 mmol) in 55 mL of THF maintained at –90 °C under argon was added dropwise, over 10 min, 16 mL of a solution of *n*-BuLi 2.5 M in hexane (40 mmol). The reaction mixture was warmed up and stirred for 30 min at –70 °C. After cooling back to –80 °C a solution of dimethylamino-*tert*-butylchlorophosphine (6.23 g, 39.5 mmol) in 10 mL of hexane was added dropwise over 10 min. The reaction mixture was warmed up and stirred for 30 min at 20 °C. After solvent evaporation under vacuum, the resulting yellow suspension was cooled to –30 °C and 9 g of dimethylamine (200 mmol) was added. After 10 min stirring the mixture was evaporated to dryness and the residue was treated with 60 mL of hot pentane (glassware in a boiling water bath). The non-soluble solid residue was filtered off under argon and rinsed twice with 30 mL of pentane. The filtrate was evaporated and the oily residue was distilled (b. p. 75-85 °C/0.05 mmHg) to give the target *tert*-butyl-(1-methyl)-1H-imidazol-2-yl-dimethylaminophosphine in 73% yield (6.18 g, 29.0 mmol). ^{1}H NMR (C_6D_6, δ ppm): 1.40 (d, 9H, *J* = 14 Hz, C(CH_3)$_3$), 2.64 (d, 6H, *J* = 8 Hz, N(CH_3)$_2$), 3.16 (s, 3H, NCH_3), 6.47 (s, 1H, Im), 7.24 (s, 1H, Im). ^{31}P NMR (C_6D_6, δ ppm): 50.0. ^{13}C NMR (C_6D_6): δ (ppm) 27.2 (d, *J* = 18 Hz, C(CH_3)$_3$), 32.75 (d, *J* = 15Hz, NCH_3), 35.5 (d, *J* = 13 Hz, C(CH_3)$_3$), 43.2 (d, *J* = 15 Hz, N(CH_3)$_2$), 121.9 (C-5), 129.1 (d, *J* = 1 Hz, C-4), 147.6 (d, *J* = 13 Hz, C-2).

The *tert*-butyl-(1-methyl)-1H-imidazol-2-yl-dimethylaminophosphine is easily converted in chlorophosphine **B**. To a solution of *tert*-butyl-(1-methyl)-1H-imidazol-2-yl-dimethylaminophosphine (6.18 g, 29 mmol) in 10 mL benzene (*alternatively less-toxic toluene can be used in 15 mL amount*) was added to phosphorous trichloride (8.0 g, 60 mmol) at 20 °C. The reaction mixture was stirred for 1 h, then the solvent was first removed under vacuum (14 mmHg), and distillation gave as a second fraction (b. p. 80-82 °C/0.05 mmHg) 5.81 g of chlorophosphine **B** (98%, 28.4 mmol). ^{1}H NMR (C_6D_6, δ ppm): 1.39 (d, 9H, *J* = 15 Hz, C(CH_3)$_3$), 3.08 (s, 3H, NCH_3), 6.31 (s, 1H, Im), 7.17 (s, 1H, Im). ^{31}P NMR (C_6D_6, δ ppm): 79.7. ^{13}C NMR (C_6D_6, δ ppm): 25.6 (d, *J* = 19 Hz, C(CH_3)$_3$), 33.1 (d, *J* = 14Hz, NCH_3), 34.6

(d, *J* = 24 Hz, $C(CH_3)_3$), 123.85 (C-5), 130.4 (C-4), 144.65 (*J* = 40 Hz, C-2). Elemental analysis $C_8H_{14}ClN_2P$ (204.64): calcd. Cl 17.32, N 13.69, P 15.14 found: Cl 16.87, N 13.51, P 15.19.

4.1.3. 3-Chloro-5-methyl-3H-benzo[1,3]azaphosphol-2-yldimethylamine, ***C***

To a solution of dimethylaminophosphole [20] (3.37 g, 14 mmol) in 5 mL of benzene was added phosphorous trichloride (5.9 g, 43 mmol). The reaction mixture was stirred at 25 °C for 3 h. The phosphorous trichloride excess and benzene were then evaporated under vacuum (14 mmHg). Dimethylaminodichlorophosphine was removed under a lower pressure vacuum of 0.05 mmHg. The residue was then distilled (b. p. 130-140 °C/0.05 mmHg) to give **C** as deep red crystals (3.09 g, yield 95%). ^{1}H NMR (C_6D_6, δ ppm): 1.97 (s, 3H, CH_3), 2.64 (br s, 3H, $N(CH_3)_2$), 2.75 (br s, 3H, $N(CH_3)_2$), 6.88 (d, 1H, *J* = 8 Hz, H_{Ar}), 7,16 (br s, 1H, H_{Ar}), 7.33 (d, 1H, *J* = 8 Hz, H_{Ar}). ^{31}P NMR (C_6D_6, δ ppm): 57.4. ^{13}C NMR (C_6D_6, δ ppm) 20.3, 37.5 (br s, $N(CH_3)_2$), 40.8 (br s, $N(CH_3)_2$), 119.5 (CH), 130.46 (d, *J* = 16 Hz), 130.48 (d, *J* = 29 Hz, CH), 131.2 (d, *J* = 5 Hz), 134.3 (CH), 160.1 (d, *J* = 5 Hz), 174.9 (d, *J* = 33 Hz, CN). Elemental analysis $C_{10}H_{12}ClN_2P$ (226.64): calcd. Cl 15.64, N 12.36, P 13.67 found: Cl 15.17, N 12.27, P 13.41.

4.2. Synthesis of 1,1'-bis(*tert*-Butyl(1-*tert*-butyl)-1H-pyrrol-3-ylphosphanyl) ferrocene ***(2)***

To a solution of ferrocene (1.0 g, 5.4 mmol) and *N,N,N,N*-tetramethylethylenediamine (TMEDA, 2 mL, 12.8 mmol) in 40 mL of hexane was added dropwise at 0 °C a solution of *n*-BuLi 1.6 M in hexane (7.9 mL, 12.8 mmol). The reaction mixture was allowed to warm and stirred overnight at room temperature. A solution of chlorophosphine **A** (2.66 g, 10.8 mmol) in 30 mL of hexane was added dropwise to the red suspension of ferrocenyl dilithium salt at –40°C. The reaction mixture was allowed to warm and stirred at room temperature for 3 h. The mixture was then filtered through Celite®, the filtrate was evaporated to dryness and the residue was dried under vacuum at 60 °C for TMEDA removal. The resulting solid was twice crystallized from a 2:3 *vol.* mixture of CH_2Cl_2/hexane to yield 1.8 g of diphosphine **2** (3 mmol, 55%). The major diastereomer (*rac*) is obtained in 9:1 ratio. ^{1}H NMR ($CDCl_3$, ppm): δ 0.90 (d, 18H, $^2J_{PH}$ = 12 Hz, $PC(CH_3)_3$), minor isomer 1.05 (d, $^2J_{PH}$ = 12 Hz), 1.55 (s, 18H, $NC(CH_3)_3$), minor isomer 1.49, 3.67 (br s, 2H, Cp), 3.92 (br s, 2H, Cp), 3.99 (br s, 2H, Cp), 4.26 (br s, 2H, Cp), 6.36 (m, 2H, pyrrol), 6.91 (m, 2H, pyrrol), 7.15 (m, 2H, pyrrol). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –15.6 ppm (minor isomer –15.1). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.0 (d, 2C, $^2J_{PC}$ = 15.0 Hz, $PC(CH_3)_3$), 29.80 (s, $NC(CH_3)_3$), 44.60 (s, $PC(CH_3)_3$), 53.76 (s, $NC(CH_3)_3$), 66.89 (s, Cp), 67.89 (s, Cp), 71.03 (d, Cp, *J* = 7.5 Hz), 74.71 (d, Cp, *J* = 7.5 Hz), 76.24 (s, Cp), 112.20 (s, pyrrol), 117.38 (m, pyrrol), 125.34 (s, pyrrol), 126.07 (s, pyrrol). $C_{36}H_{56}FeN_2P_2$ (634.64): calcd. C 68.13 , H 8.89, N 4.41, found: C 68.22, H 8.56, N 4.48.

*4.3. Synthesis of 1,1'-bis(tert-Butyl(1-methyl)-1H-imidazol-2-ylphosphanyl)ferrocene (**3**)*

To a suspension of ferrocene (4.26 g, 23 mmol) and TMEDA (51 mmol) in 110 mL of hexane maintained at 0 °C was added via syringe a solution of 20.5 mL of *n*-BuLi at 2.5 M in hexane (51 mmol). The reaction mixture was allowed to warm up and stirred overnight at 20 °C. The resulting red-orange precipitate was filtered under argon, rinsed twice with 20 mL hexane and was dried under vacuum (5.11 g, 71%). This ferrocene dilithium salt (2.73 g, 8.7 mmol) was dispersed in 50 mL of toluene at 5 °C, and a solution of chlorophosphine **B** (3.12 g, 15.3 mmol) in 12 mL of toluene was added. The reaction mixture was stirred for 1 h, and the precipitate was filtered off under argon. The filtrate was evaporated in high vacuum to dryness. The reddish-brown oil residue was treated with 90 mL of degassed hot pentane. The solution was filtered under argon, the solid residue was washed with pentane (2x15 mL) and the gathered liquid phase filtrate was evaporated to 70 mL to precipitate 2.08 g of the targeted ferrocenyl diphosphine as a 1.6:1 mixture of diastereoisomers (total yield 52%). The mother solution was concentrated to 20 mL, and then crystals formed at 18 °C were separated to give 710 mg of a 1:3.6 mixture of diastereoisomers (total yield 20%). Major isomer (*rac*): m. p. 160-161 °C. ^{1}H NMR (C_6D_6): δ (ppm) 1.10 (d, 9H, $^{2}J_{PH}$ = 14.0 Hz, $C(CH_3)_3$), 3.47 (s, 3H, NCH_3), 3.86 (2H, Cp), 3.97 (s, 2H, Cp), 4.03 (s, 2H, Cp), 5.49 (s, 2H, Cp), 6.51 (ps, 2H, Im), 7.38 (s, 2H, Im). ^{31}P NMR (C_6D_6): δ (ppm) –28.8. ^{13}C NMR (C_6D_6): δ (ppm) δ 27.54 (d, *J* = 15 Hz, $C(CH_3)_3$), 31.6 (d, *J* = 4Hz, NCH_3), 33.7 (d, *J* = 23 Hz, $C(CH_3)_3$), 71.1 (d, *J* = 10 Hz, Cp), 71.69 (Cp), 74.7(d, *J* = 6 Hz, Cp), 77.1(s, Cp), 77.4(s, Cp), 121.8 (s, ImC-5), 130.1 (s, ImC-4), 146.5 (d, *J* = 4Hz, ImC-2). Minor isomer (*meso*). ^{1}H NMR (C_6D_6): δ(ppm) 1.11 (d, 9H, *J* = 12 Hz, $C(CH_3)_3$), 3.54 (s, 3H, NCH_3), 3.82 (s, 2H, Cp), 3.94 (s, 2H, Cp), 4.03 (s, 2H, Cp), 5.54 (s, 2H, Cp), 6.51 (s, 2H, Im), 7.37 (s, 2H, Im). ^{31}P NMR (C_6D_6): δ (ppm) –29.0. ^{13}C NMR (C_6D_6): δ 27.5 (d, *J* = 15Hz, $C(CH_3)_3$), 31.6 (d, *J* = 5Hz, NCH_3), 33.6 (d, *J* = 20Hz, $C(CH_3)_3$), 73.2 (d, *J* = 6.3Hz, Cp), 74.7 (d, *J* = 6.3Hz, Cp), 77.8 (s, Cp), 78.1 (s, Cp), 121.8 (ImC-5), 130.1 (ImC-4), 146.56 (d, *J* = 6.3Hz, ImC-2). Elemental analysis N, 10.72; C, 59.77; H, 6.89 Found: N, 10.01; C, 59.19; H, 6.82 (residual toluene solvent). HR-MS ($C_{26}H_{37}N_4FeP_2$) ESI: $[M+H]^+$ m/z theo = 523.18374, exp =523.18306, δ 1.297 ppm.

*4.4. Synthesis of 1,1'-bis((2-dimethylamino)-5-methyl-benzo[1,3]azaphosphol-3-yl-)ferrocene (**4**)*

A solution of chlorophosphine **C** (3.10 g, 13.7 mmol) in 35 mL of degassed benzene was added to a dark red suspension of ferrocene dilithium salt (2.36 g, 7.5 mmol) in 70 mL of degassed benzene at 5 °C. The reaction mixture was allowed to warm up and was stirred overnight at 20 °C. The precipitate was filtered off under argon and washed twice with 20 mL of benzene. The filtrate was evaporated to dryness. The residue was crystallized from 55 mL of degassed benzene. After 72 h at 20 °C, the crystals formed were collected to give 1.3 g of **4** as a 1:4 mixture of diastereoisomers (total yield

33%). The mother liquor was then concentrated to 20 mL and the precipitate formed was collected and crystallized to give 1.5 g of **4** as a 1:1.4 mixture of diastereoisomers (yield 39%). Major isomer: ^{31}P NMR (C_6D_6, δ ppm): –24.9. ^{1}H NMR (C_6D_6, δ ppm): 2.19 (s, 6H, CH_3), 2.74 (s, 12H, $N(CH_3)_2$), 3.63 (s, 2H, Cp), 4.05 (s, 2H, Cp), 4.28 (s, 2H, Cp), 4.43 (s, 2H, Cp), 7.06-7.09 (m, 2H, H_{Ar}), 7.53 (br s, 2H, H_{Ar}), 7.61 (m, 2H, H_{Ar}). Minor isomer: ^{31}P NMR (C_6D_6, δ ppm): –23.3. ^{1}H NMR (C_6D_6, δ ppm): 2.25(s, 6H, CH_3), 2.77 (s, 12H, $N(CH_3)_2$), 3.79 (s, 1H, Cp), 4.05 (s, 1H, Cp), 4.18 (s, 1H, Cp), 4.33 (s, 1H, Cp), 7.06-7.09 (m, 2H, H_{Ar}), 7.53 (br s, 2H, H_{Ar}), 7.59-7.62 (m, 2H, H_{Ar}). For the diastereoisomers: ^{13}C NMR (C_6D_6, δ ppm): 20.83, 20.89 (CH_3), 39.0, (NCH_3), 70.4 (d, *J* = 4 Hz), 70.6 (d, *J* = 4 Hz), 71.23, 71.58, 74.97, 75.09, 75.13, 75.33, 119.3 (CH), 119.4 (CH), 129.77 (d, *J* = 7.5 Hz), 129.71 (d, *J* = 7.5 Hz), 129.97 (d, *J* = 24 Hz), 130.08 (d, *J* = 21 Hz), 130. 67 (d, *J* = 6.3 Hz), 130.62 (d, *J* = 5 Hz), 131.14 (CH), 131.21 (CH), 159.49 (d, *J* = 5 Hz), 159.65 (d, *J* = 5 Hz, N-C_{Ar}), 177.93 (d, *J* = 18 Hz, CN), 178.07 (d, *J* = 18 Hz, CN). Elemental analysis N, 9.89: C, 63.60; H, 5.65; Found: N, 8.59, C, 60.78, H, 5.64. HR-MS ($C_{30}H_{33}N_4FeP_2$) ESI: $[M+H]^+$ m/z theo = 567.15244, exp = 567.15149, δ 1.673 ppm.

N. B.: For all the compounds above described and characterized at IOC-NASU, ^{1}H NMR was conducted on Bruker Avance DRX 500 (500.13 MHz) or Varian VXR-300 (299.94 MHz) spectrometer; ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 (125.75 MHz) spectrometer; ^{31}P NMR spectra were recorded on a Varian VXR-300 (121.42 MHz) spectrometer.

*4.5. Synthesis of the palladium complex [$PdCl_2$(**2**)]*

To a solution of 0.50 g of ferrocenyl diphosphine **2** (0.83 mmol, 90:10 *rac*/*meso*) in 15 mL of freshly distilled CH_2Cl_2 was added 0.15 g of palladium η^3-allyl chloride dimer (0.41 mmol). The reaction mixture was stirred overnight and the solvent was evaporated. The brown oily residue was treated with 5 mL of Et_2O and the resulting precipitate was collected by filtration and dried. Single crystals of *rac*-[$PdCl_2$(**2**)] suitable for X-ray diffraction were obtained by slow diffusion of pentane in a saturated solution of complex in CH_2Cl_2 (0.38 g, 0.48 mmol, yield 58%). ^{1}H NMR ($CDCl_3$, 300 MHz, 300 K): δ 1.31 (d, 18H, $^{2}J_{PH}$ = 15.9 Hz, $PC(CH_3)_3$), 1.60 (s, 18H, $NC(CH_3)_3$), 4.12 (br s, 2H, Cp), 4.19 (br s, 2H, Cp), 4.27 (br s, 2H, Cp), 4.30 (br s, 2H, Cp), 6.41 (m, 2H, pyrrol), 6.94 (m, 2H, pyrrol), 8.11 (m, 2H, pyrrol). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 32.5 ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.23 (s, $PC(CH_3)_3$), 30.74 (s, $NC(CH_3)_3$), 30.81 (s, $PC(CH_3)_3$), 40.82 (s, $PC(CH_3)_3$), 55.83 (s, $NC(CH_3)_3$), 67.91 (s, Cp), 71.24 (s, Cp), 74.86 (d, Cp, *J* = 7.5Hz), 75.18 (d, Cp, *J* = 7.5Hz), 86.14 (s, Cp), 111.79 (s, pyrrol), 113.15 (m, pyrrol), 119.43 (s, pyrrol), 132.69 (s, pyrrol). $C_{36}H_{56}FeN_2P_2PdCl_2$ (811.53): calcd. C 53.28, H 6.96; found: C 53.42, H 6.65. HR-MS (ESI) analysis were unsatisfactory.

*4.6. Synthesis of the palladium complex [$PdCl_2$(**3**)]*

To a solution of 0.05 g of ferrocenyl diphosphine **3** (0.095 mmol, 62:38 *rac*/*meso*) in 5 mL of freshly distilled toluene was added 0.036 g of bis(benzonitrile) palladium dichloride (0.095 mmol). The reaction mixture was stirred for 4 hours at room temperature, filtrated on silica, and the solvent was removed from the filtrate to give [$PdCl_2$(**3**)] as a red powder (0.05 g, 0.007 mmol, yield 75 %). Single crystals of *rac*-[$PdCl_2$(**3**)] suitable for X-ray diffraction were obtained by slow evaporation of a solution of the complex in CH_2Cl_2 (0.03 g, 0.0042 mmol, total yield 45%). ^{1}H NMR (C_6D_6, 600 MHz, 300 K, δ ppm): 1.56 (d, 18 H, $^3J_{PH}$ = 16 Hz, C(C*H*$_3$)$_3$), 3.91 (s, 2H, Cp), 4.16 (s, 2H, Cp), 4.38 (s, 2H, Cp), 4.50 (s, 6H, NC*H*$_3$), 4.81 (s, 2H, Cp), 7.21 (s, 2H, Im), 7.22 (s, 2H, Im). ^{31}P {^{1}H} NMR (C_6D_6, 242 MHz, 300 k, δ ppm): 22.72. ^{13}C {^{1}H} NMR (C_6D_6, 150 MHz, 300 K, δ ppm): 29.36 (s, C(*C*H$_3$)$_3$), 29.91 (s, N*C*H$_3$), 40.6 (s, *Cipso*(CH$_3$)$_3$), 71.51 (s, Cp), 74.3 (m, Cp), 76.23 (m, Cp), 78.43 (s, Cp), 125.31 (d, J_{PC} = 7 Hz, Im), 129.71 (d, J_{PC} = 7 Hz, Im). N.B: NMR in CD_2Cl_2 or $CDCl_3$ of **3** gives an oxide product at 25.22 ppm due to the sensitiveness of the diphosphine in solution. Anal Calcd for $C_{26}H_{36}N_4P_2FePdCl_2$: C 44.63, H 5.19, N 8.01; found C 44.63, H 5.18, N 8.00. HR-MS ($C_{26}H_{36}N_4ClFeP_2Pd$) ESI: $[M\text{-}Cl]^+$ m/z theo = 663.04919, exp = 663.05048, δ 3.364 ppm.

*4.7. Synthesis of the platinum complex [$PtCl_2$(**3**)]*

To a solution of 0.10 g of ferrocenyl diphosphine **3** (0.19 mmol, 62:38 *rac*/*meso*) in 5 mL of freshly distilled CH_2Cl_2 was added 0.090 g of bis(benzonitrile) platinum dichloride (0.19 mmol). The reaction mixture was stirred at room temperature overnight, then the solvent was evaporated and the resulting red powder was treated with 5 mL of Et_2O. The red precipitate was isolated by filtration and dried under vacuum to give [$PtCl_2$(**3**)] as a red solid (0.14 g, 0.17 mmol, yield 94 %). Orange single crystals of *rac*-[$PtCl_2$(**3**)] suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane in a solution of the complex in CH_2Cl_2 (0.09 g, 0.11 mmol, yield 61 %). ^{1}H NMR (CD_2Cl_2, 600 MHz, 300 K, δ ppm): 1.24 (d, 18 H, $^3J_{PH}$ = 16 Hz, C(C*H*$_3$)$_3$), 4.28 (s, 2H, Cp), 4.56 (s, 2H, Cp), 4.57 (s, 2H, Cp), 4.62 (s, 6H, NC*H*$_3$), 4.63 (s, 2H, Cp), 7.17 (s, 2H, Im), 7.2 (s, 2H, Im). ^{31}P {^{1}H} NMR (CD_2Cl_2, 242 MHz, 300 K, δ ppm): 5.2 ($^1J_{PtP}$ = 3604 Hz). ^{13}C {^{1}H} NMR (CD_2Cl_2, 121 MHz, 300 K, δ ppm): 28.9 (s, C(*C*H$_3$)$_3$), 38.0 (s, N*C*H$_3$), 40.9 (s, *C*(CH$_3$)$_3$), 72.3 (s, Cp), 74.3 (t, J = 5 Hz, Cp), 76.3 (m, Cp), 78.1 (s, Cp), 125.7 (s, Im), 129.6 (d, J_{PC} = 7 Hz, Im), 137.4 (C-*ipso*, Im), 137.9 (C-*ipso*, Im). Quaternary carbons of Cp were not detected. Unsatisfactory elemental analysis was obtained, presumably due to residual solvent in the crystals. HR-MS ($C_{26}H_{36}N_4P_2FePtCl$) ESI $[M\text{-}Cl]^+$ m/z theo = 752.10954, exp = 752.11157, δ 2.698 ppm.

*4.8. Synthesis of the palladium complex [$PdCl_2$(**4**)]*

To a solution of 0.10 g of ferrocenyl phosphine **4** (0.17 mmol, 42:58, N.B.: from this mixture *rac*/*meso* attribution could not be determined since co-crystallization occurs even for single crystals crops, as checked by ^{31}P NMR of the crystals) in 5 mL of freshly distilled CH_2Cl_2 was added 0.067 g of bis(benzonitrile) palladium dichloride (0.17 mmol). The reaction mixture was stirred at room temperature overnight, then the solvent was evaporated and the resulting red powder was treated with 5mL of Et_2O. The red precipitate was isolated by filtration and dried in vacuum to give [$PdCl_2$(**4**)] (0.11 g, 0.15 mmol, yield 87%) as a mixture of diastereomers corresponding to the starting ligand **4** (42:58). Crystals were obtained by slow diffusion of pentane in a solution of the complex in $CHCl_3$ (0.08 g, 0.1 mmol, total yield 66%). Major isomer (58%): ^{1}H (CD_2Cl_2, 600 MHz, 300 K, δ ppm): 2.49 (s, 6H, CH_3), 3.71 (br s, 12H, NMe_2), 4.03 (s, 2H, Cp), 4.28 (s, 2H, Cp), 4.82 (s, 2H, Cp), 5.08 (s, 2H, Cp), 7.18 (d, 2H, J_{AB} = 8 Hz, CH_{Ar}), 7.37 (d, 2H, J_{AB} = 8 Hz, CH_{Ar}), 7.63 (d, 2H, J_{PH} = 7 Hz, CH_{Ar}). ^{31}P {^{1}H} (CD_2Cl_2, 242 MHz, 300 K, δ ppm): 28.95 ppm. ^{13}C {^{1}H} (CD_2Cl_2, 150 MHz, 300 K, δ ppm): 21.49 (s, CH_3), 72.35 (s, Cp), 72.95 (t, *J* = 8 Hz, Cp), 77.29 (t, *J* = 3 Hz, Cp), 77.73 (s, Cp), 120.87 (s, CH), 130.13 (t, *J* = 9 Hz), 132.75 (d, *J* = 6 Hz, C-ipso CCH_3), 135.36 (s, CH), 156.57 (C-ipso, CN), 168 (C-ipso, CP). Minor isomer (42%): ^{1}H (CD_2Cl_2, 600 MHz, 300 K, δ ppm): 2.51 (s, 6H, CH_3), 3.16 (br s, 12H, NMe_2), 4.39 (s, 2H, Cp), 4.59 (s, 2H, Cp), 4.66 (s, 2H, Cp), 4.81 (s, 2H, Cp), 7.13 (d, 2H, J_{AB} = 8 Hz, CH_{Ar}), 7.13 (d, 2H, J_{AB} = 8 Hz, CH_{Ar}), 7.87 (br s, 2H, CH_{Ar}). ^{31}P {^{1}H} (CD_2Cl_2, 242 MHz, 300 K, δ ppm): 32.92 ppm.^{13}C {^{1}H} (CD_2Cl_2, 150 MHz, 300 K, δ ppm): 21.36 (s, CH_3), 72.68 (t, *J* = 3 Hz, Cp), 74.40 (s, Cp), 74.64 (t, *J* = 7 Hz, Cp), 75.71 (t, *J* = 3 Hz, Cp), 120.72 (s, CH), 129.82 (t, *J* = 9 Hz, CH), 133.09 (d, *J* = 6 Hz, C-ipso, CCH_3), 135.05 (s, CH), 155 (C-ipso, CN), 167 (C-ipso, CP). Quaternary carbons of Cp and $(CH_3)_2N$ were not detected. Anal Calcd for $C_{30}H_{32}N_4P_2FePdCl_2$: C 48.45, H 4.34, N 7.53; found: C 48.28, H 3.94, N 7.12. HR-MS ($C_{30}H_{33}N_4Cl_2FeP_2Pd$) ESI: $[M+H]^+$ m/z theo = 742.99445, exp = 742.99695, δ 4.472 ppm.

*4.9. Synthesis of the platinum complex [$PtCl_2$(**4**)]*

To a solution of 0.10 g of ferrocenyl phosphine **4** (0.17 mmol, 58:42) in 5 mL of freshly distilled CH_2Cl_2 was added 0.066 g of dichloro(1,5-cyclooctadiene)platinum(II) (0.17 mmol). The reaction mixture was stirred at room temperature overnight, then the solvent was evaporated and the resulting orange powder was treated with 5mL of Et_2O. The orange precipitate was isolated by filtration and dried in vacuum to give [$PtCl_2$(**4**)] (0.12 g, 0.14 mmol, yield 86%) as a mixture of diastereomers corresponding to the starting ligand **4** (42:58). Major isomer (58 %): ^{1}H (CD_2Cl_2, 600 MHz, 300 K, δ ppm): 2.47 (s, 6H, CH_3), 3.78 (br s, 12H, NMe_2), 3.98 (s, 2H, Cp), 4.31 (s, 2H, Cp), 4.76 (s, 2H, Cp), 5.03 (s, 2H, Cp), 7.17 (d, 2H, J_{AB} = 8 Hz, CH_{Ar}), 7.34 (d, 2H, J_{AB} = 8 Hz, CH_{Ar}), 7.54 (d, 2H, J_{PH} = 7 Hz, CH_{Ar}). ^{31}P {^{1}H} (CD_2Cl_2, 242 MHz, 300 K, δ ppm): 8.14 ($^1J_{PtP}$ = 3626 Hz). ^{13}C {^{1}H} (CD_2Cl_2, 150 MHz,

300 K, δ ppm): 21.50 (s, CH_3), 72.22 (d, *J* = 16 Hz, Cp), 73.03 (d, *J* = 8 Hz, Cp), 71.91 (d, *J* = 6 Hz, Cp), 76.97 (d, *J* = 8 Hz, Cp), 120.67 (d, *J* = 4 Hz, CH), 130.14 (d, *J* = 15 Hz), 132.88 (d, *J* = 11 Hz, C-ipso CCH_3), 135.42 (s, CH), 156.78 (C-ipso, CN). Minor isomer (42%): ^{1}H (CD_2Cl_2, 600 MHz, 300 K, δ ppm): 2.49 (s, 6H, CH_3), 3.15 (br s, 12H, NMe_2), 4.37 (s, 2H, Cp), 4.56 (s, 2H, Cp), 4.57 (s, 2H, Cp), 4.74 (s, 2H, Cp), 7.12 (d, 2H, J_{AB} = 8 Hz, CH_{Ar}), 7.29 (d, 2H, J_{AB} = 8 Hz, CH_{Ar}), 7.74 (br s, 2H, CH_{Ar}). ^{31}P {^{1}H} (CD_2Cl_2, 242 MHz, 300 K, δ ppm): 10.20 ($^1J_{PtP}$ = 3622 Hz).^{13}C {^{1}H} (CD_2Cl_2, 150 MHz, 300 K, δ ppm): 21.37 (s, CH_3), 73.10 (d, *J* = 8 Hz, Cp), 74.00 (d, *J* = 13 Hz, Cp), 74.48 (d, *J* = 7 Hz, Cp), 74.95 (d, *J* = 9 Hz, Cp), 120.57 (d, *J* = 5 Hz, CH), 129.85 (d, *J* = 15 Hz, CH), 132.58 (d, *J* = 11 Hz, C-ipso, CCH_3), 135.03 (s, CH), 156,78 (C-ipso, CN). Quaternary carbon of Cp and C-P and (CH_3)$_2$N were not detected. HR-MS (ESI) analysis were unsatisfactory. Anal Calcd for $C_{30}H_{32}N_4P_2FePtCl_2$: C 43.29, H 3.87; found: C 42.02, H 4.32.

4.10. Catalytic cross-coupling reactions

Copper-free alkyne arylation. An oven-dried Schlenk flask was charged with the acetylenic compound (2 mmol), 1:1 [$PdCl_2(PhCN)_2$]/ligand (1 mol %), Cs_2CO_3 (2 mmol), and the aryl halide (1 mmol). A magnetic stirring bar was added, and the flask was purged. 5 ml of DMF was then added. The reaction was heated at 100 °C for 20 h. Reactions were monitored by GC, GC-MS and ^{1}H NMR, and yields were calculated from NMR and GC.

Suzuki-Miyaura arylation. An oven-dried Schlenk flask was charged with the aryl boronic acid (2 mmol), 1:1 [$PdCl_2(PhCN)_2$]/ligand (0.2 mol %), K_2CO_3 (2 mmol), and the aryl halide (1 mmol). A magnetic stirring bar was added, and the flask was purged and placed under inert atmosphere. 5 ml of DMF was then added. The reaction was heated to 100 °C for 20 h. Reactions were monitored by GC, GC-MS and ^{1}H NMR and yields were calculated from NMR and GC.

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Appendix A. Supplementary material

CCDC 922383 – 922386 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/

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