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9-[6-(Diphenylphosphino)pyridin-2-yl]-9*H*-carbazole: synthesis and coordination properties toward Cu^I and Pd^{II}

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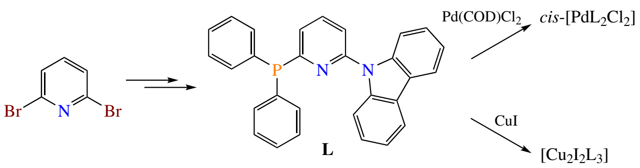
9-[6-(Diphenylphosphino)pyridin-2-yl]-9*H*-carbazole was synthesized in two steps involving cross-coupling of 2,6-dibromopyridine with carbazole followed by treatment of the formed monobromo pyridine derivative with Ph_2PCl. The coordination properties of the synthesized ligand were demonstrated by the reaction with $Pd(COD)Cl_2$ and CuI. The alkylation of the title compound with MeI proceeds selectively at the P atom to afford the corresponding phosphonium salt.

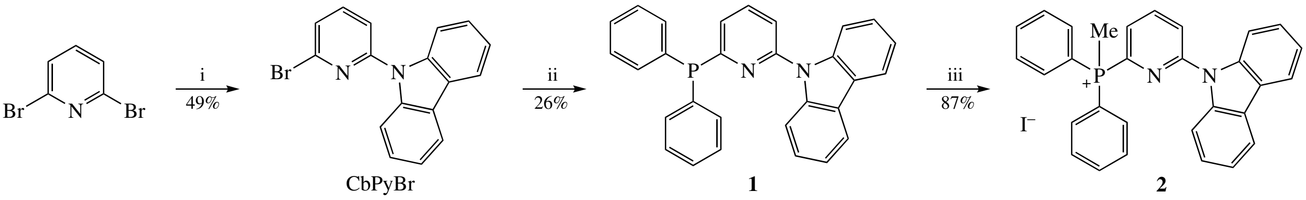


Keywords: 9-[6-(diphenylphosphino)pyridin-2-yl]-9*H*-carbazole, phosphonium salt, copper(I) iodide complexes, palladium(II) chloride complexes, crystal structure.

Pyridylphosphines represent a widely used subclass of *P*,*N*-hybrid ligands in coordination chemistry.[1–3] During the last decades, their metal complexes have been extensively investigated as catalysts and emissive materials.[4–13] Because of the presence of both soft (P) and harder (N) centers, pyridylphosphines exhibit hemilabile character and great structural diversity of the formed coordination compounds.[14–19] Currently, diphenyl(pyridin-2-yl)phosphine is the most common and commercially available representative of pyridylphosphines. Its Pd^{II} complexes were found to be highly effective catalysts for the methoxycarbonylation of propyne,[20] while *cis*-$[Ru(acac)_2(PPh_2Py)_2]$ effectively catalyzes the hydration of nitriles.[21] Diphenyl(pyridin-2-yl)phosphine-based complexes with Cu^I subgroup elements were also investigated due to their promising luminescent characteristics.[22–25] Owing to all the above-mentioned success, initially achieved with diphenyl(pyridin-2-yl)phosphine, many related ligands have also been synthesized and investigated.[26,27] Thus, the derivatization of diphenyl(pyridin-2-yl)phosphine (*e.g.*, *via* introduction of fluorophoric groups) represents an attractive route to new compounds with advanced functional properties.[28,29]

In this work, we report on the synthesis and characterization of previously unknown 9-[6-(diphenylphosphino)pyridin-2-yl]-9*H*-carbazole **1** and its phosphonium salt **2** (Scheme 1). Moreover, **1**-based complexes with $PdCl_2$ and CuI have been obtained and structurally characterized. At the first step of the synthesis, 2,6-dibromopyridine was reacted with 1 equiv. of carbazole in the presence of CuI, K_3PO_4 and *trans*-1,2-diaminocyclohexane system used previously[30] for some analogous reactants. After purification, 9-(6-bromopyridin-2-yl)-9*H*-carbazole (CbPyBr) was isolated in 49% yield (see Scheme 1). At the second step, CbPyBr was lithiated with *n*-BuLi followed by *in situ* treatment with Ph_2PCl. Target **1** was isolated after column chromatography and recrystallization in 26% yield (non-optimized). The alkylation of **1** with MeI (benzene, room temperature) proceeded exclusively at the phosphorus atom to give the corresponding *P*-methylphosphonium salt **2** in 87% yield (see Scheme 1).

Structure **1** has been confirmed by NMR spectroscopy (^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^1H–^{13}C HSQC, ^1H–^{13}C HMBC, ^1H–^{31}P HMBC, ^1H–^1H COSY) and microanalysis data. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a sharp singlet with $\delta_P = -2.91$ ppm (see Online Supplementary Materials, Figure S2). The $^{31}P\{^1H\}$ NMR resonance of phosphonium salt **2** appears as a singlet at 20.75 ppm (Figure S9) that is significantly downfield shifted as compared to **1**. In the ^1H NMR spectrum of **2**, methyl protons resonate as a doublet at 3.25 ppm with the typical $^2J_{P-H}$ coupling constant of 14.9 Hz (Figure S8).



Scheme 1 *Reagents and conditions*: i, carbazole, CuI, K_3PO_4, *trans*-1,2-diaminocyclohexane, 110 °C, 1,4-dioxane (*cf.* ref. 30); ii, Bu^nLi, –80 °C, Et_2O–hexane, then Ph_2PCl, –80 °C; iii, MeI, benzene, room temperature.

To demonstrate coordination properties of synthesized ligand **1**, its reactions with Pd(COD)Cl_2 and CuI have been performed. The choice of Pd(COD)Cl_2 as a source of Pd^{II} was due to its good solubility in CH_2Cl_2 and ability to readily exchange the COD ligand. The reaction of 2 equiv. of **1** with Pd(COD)Cl_2 in CH_2Cl_2 produces a precipitate, recrystallization of which from DMF affords single crystals of square planar complex **3** of composition PdL_2Cl_2 (L = **1**). Reacting 3 equiv. of **1** with 2 equiv. of CuI in the MeCN at ambient temperature leads to the formation of a poorly soluble white precipitate. Recrystallization of the latter from MeCN gives crystals of complex **4** $Cu_2L_3I_2$ (L = **1**). Crystal structures for isolated complexes were determined by single crystal X-ray diffraction (SC-XRD) analysis (Figure 1).[†] According to the SC-XRD data, complex **3** crystallizes as a solvate with DMF, and its asymmetric unit contains one molecule of **3**. The Pd atom adopts a nearly square planar coordination environment (τ_4 ~ 0.079)[31] of *cis*-configuration. Each phosphine ligand is coordinated to the Pd atom through the P atom, while the N atom of the pyridine ring remains uncoordinated. The Pd–P (~2.25 Å) and Pd–Cl (~2.35 Å) bond lengths are typical for the similar complexes.[32–34] The averaged planes of the pyridine and carbazole systems of **1** are twisted relative to each other (twisted angles 38.03° and 40.34°). Complex **4** crystallizes with one molecule per asymmetric unit. Each molecule of **4** consists of a dimeric butterfly-shaped $\{Cu_2I_2\}$ unit and three P-coordinated ligands **1**. One of the two Cu atoms adopts a distorted $\{Cu@P_2I_2\}$ tetrahedral geometry (τ_4 ~ 0.90)[31] with Cu–I and Cu–P bond lengths being comparable to those known for similar complexes.[35,36] The second Cu atom of the $\{Cu_2I_2\}$ unit has a distorted $\{Cu@PI_2\}$ trigonal coordination geometry with Cu–P and Cu–I bond lengths of ~2.22 and ~2.54–2.55 Å, respectively. The fact that the interatomic distance between the Cu atoms of the $\{Cu_2I_2\}$ moiety [3.008(2) Å] is significantly longer than the double Bondi's vdW radius for Cu (2.80 Å)[37] rules out metallophilic interaction. The twist angle between the averaged planes of pyridine and carbazole rings of **1** ligands varies from 35.61° to 38.58°. An absence of coordination of pyridine rings toward metal centers is most probably due to the presence of a carbazole substituent in ligand **1**, which creates steric hindrances.

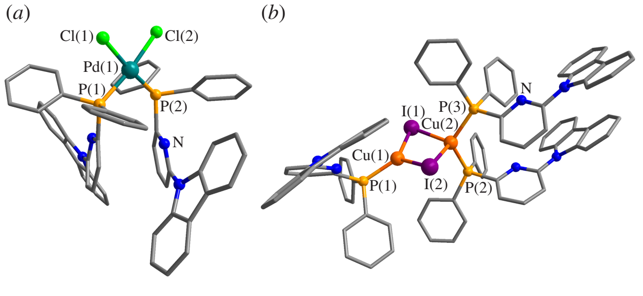


Figure 1 (*a*) X-ray derived structure of **3**. Selected interatomic distances and angles: Pd(1)–P(2) 2.2461(11), Pd(1)–P(1) 2.2559(12), Pd(1)–Cl(2) 2.3419(12), Pd(1)–Cl(1) 2.3511(11), P(2)–Pd(1)–P(1) 101.39(4), P(2)–Pd(1)–Cl(2) 84.44(4), P(1)–Pd(1)–Cl(2) 173.39(4), P(2)–Pd(1)–Cl(1) 175.49(4), P(1)–Pd(1)–Cl(1) 83.10(4), Cl(2)–Pd(1)–Cl(1) 91.11(4). (*b*) X-ray derived structure of **4**. Selected interatomic distances and angles: I(1)–Cu(1) 2.5490(17), I(1)–Cu(2) 2.7328(17), I(2)–Cu(1) 2.5385(16), I(2)–Cu(2) 2.7322(16), Cu(1)–P(1) 2.218(3), Cu(1)–Cu(2) 3.003(2), Cu(2)–P(2) 2.281(3), Cu(2)–P(3) 2.293(3), Cu(1)–I(1)–Cu(2) 69.21(5), Cu(1)–I(2)–Cu(2) 69.36(5), P(1)–Cu(1)–I(2) 122.59(9), P(1)–Cu(1)–I(1) 122.29(9), I(2)–Cu(1)–I(1) 114.61(6), P(2)–Cu(2)–P(3) 121.26(11), P(2)–Cu(2)–I(2) 107.05(9), P(3)–Cu(2)–I(2) 106.67(9), P(2)–Cu(2)–I(1) 105.67(9), P(3)–Cu(2)–I(1) 111.54(8), I(2)–Cu(2)–I(1) 103.15(5).

In conclusion, 9-[6-(diphenylphosphino)pyridin-2-yl]-9*H*-carbazole, a new promising ligand, has been synthesized and characterized. The alkylation of this novel pyridylphosphine with MeI occurs exclusively at the phosphorus atom. In order to demonstrate coordination behavior of the synthesized ligand, its complexes with $PdCl_2$ and CuI were obtained and characterized by SC-XRD analysis. This study contributes to the synthetic chemistry of organophosphines and the coordination chemistry of *P*,*N*-donor ligands.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7548.

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[†] *Crystal data* for **3**. The crystals were grown by slow diffusion of Et_2O vapors into DMF solution at room temperature. $C_{58}H_{42}Cl_2N_4P_2Pd$, $M = 1034.19$, monoclinic, space group $P2_1/n$, 200 K, $a = 10.6584(6)$, $b = 19.1610(8)$ and $c = 26.4113(16)$ Å, $\beta = 97.577(2)°$, $Z = 4$, $V = 5346.8(5)$ Å^3. A crystal with a size of 0.35×0.05×0.02 mm was selected and intensities with 10519 reflections were measured. μ(MoKα) = 0.55 mm^{-1}, $R_{int} = 0.113$, which were used in all calculations. The final R_1 was 0.053 [$F^2 > 2\sigma(F^2)$] and $wR(F^2)$ was 0.133. The free solvent accessible volume in compound **3** derived from PLATON routine analysis was found to be 16.9% (902.0 Å^3). This volume is occupied by highly disordered solvent molecules that could not be modeled as a set of discrete atomic sites. We employed the PLATON/SQUEEZE procedure to calculate the contribution to diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. The most probable solvent for **3** is DMF.

Crystal data for **4** [$Cu_2I_2L_3$]. The crystals were grown by slow evaporation of MeCN solution at room temperature. $C_{87}H_{63}Cu_2I_2N_6P_3$, $M = 1666.22$, monoclinic, space group $P2_1/c$, 200 K, $a = 11.658(3)$, $b = 59.789(16)$ and $c = 10.702(3)$ Å, $\beta = 107.259(4)°$, $Z = 4$, $V = 7124(3)$ Å^3. A crystal with a size of 0.20×0.15×0.10 mm was selected and intensities with 12545 reflections were measured. μ(MoKα) = 1.58 mm^{-1}, $R_{int} = 0.068$, which were used in all calculations. The final R_1 was 0.087 [$F^2 > 2\sigma(F^2)$] and $wR(F^2)$ was 0.197.

The data for crystals of **3** and **4** were collected on a Bruker Kappa Apex II CCD diffractometer using ϕ,ω-scans of narrow (0.5°) frames with MoKa radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The structures were solved by SHELXT 2014/5 and refined by a full matrix least-squares anisotropic-isotropic (for H atoms) procedure using the SHELXL-2018/3 programs set.[38] Absorption corrections were applied using the empirical multiscan method with the SADABS[39] program. The positions of the hydrogen atoms were calculated with the riding model.

CCDC 2361234 and 2361235 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

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