

1 **New N-pyrazole, P-phosphine hybrid ligands and their reactivity towards Pd(II): X-ray crystal**
2 **structures of complexes with [PdCl₂(N,P)] core**

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50 **ABSTRACT**

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52 Two new N-pyrazole, P-phosphine hybrids ligands: 1-[2-(diphenylphosphanyl)methyl]-3,5-dimethyl
53 pyrazole (LP1) and 1-[2-(diphenylphosphanyl)propyl]-3,5-dimethylpyrazole (LP3) are presented. The
54 reaction of these two ligands and two other ligands reported in the literature: 1-[2-(diphenylphosphanyl)
55 ethyl]-3,5-dimethylpyrazole (LP2) and 1-[2-(diphenylphosphanyl)ethyl]-3,5-diphenylpyrazole (LP4)
56 with [PdCl₂(CH₃CN)₂] yield [PdCl₂(LP)] (LP $\frac{1}{4}$ LP1 (1), LP2 (2), LP3 (3) and LP4 (4)) complexes.
57 All complexes are fully characterised by analytical and spectroscopic methods and the resolution of the
58 crystal structure of complexes 2 and 3 by single crystal X-ray diffraction is also presented. In these
59 complexes the ligands are coordinated to Pd(II) via k²(N,P) forming metallocycles of six (2) and seven
60 (3) members and finish their coordination with two cis-chlorine atoms. Finally, complex 2 is studied in
61 the palladium-catalysed CcC coupling reaction, being active even for aryl chlorides substrates.

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65 **1. INTRODUCTION**

66

67 Pyrazole ligands are widely used as core motifs for a large number of compounds of significant
68 relevancy and they have a variety of applications (i.e. as catalysis, pharmaceuticals, agrochemicals,
69 herbicides, fungicides, among others) [1]. The synthesis of organic ligands containing nitrogen donor
70 atoms and other heteroatoms as N, O and/or S has focused the interest of many research laboratories [2].
71 In particular, the synthesis of nitrogen ligands containing in addition phosphines (N,P-hybrid ligands)
72 and their transition metal complexes has become increasingly attractive in the last years owing to their
73 intrinsic properties, and considerable structural diversity [3]. These complexes are majority focused in
74 the cases where the nitrogen atoms are pyridine [4] or oxazoline groups [5]. Nevertheless, the chemistry
75 of metal complexes with bidentate ligands pyrazole-phosphine has been relatively underexplored [6].

76 During the last years, in our group we have studied hybrid ligands that combine pyrazole and amino-,
77 alcohol-, ether-, thioether-, phosphinite- or phosphine-groups. These hybrid ligands have been studied
78 for their potential hemilabile properties, their applications in catalysis and for the construction of
79 discrete molecular architectures with diversified topologies [7]. It is well known that the
80 coordination/chelation properties of these ligands, and, in consequence, their reactivity and catalytic
81 behaviour, in a complex depend on both (i) kind of heteroatoms (i.e. S, O, N, etc.) and (ii) their relative
82 position in the skeleton of the ligands. Thus, in order to expand the scope of our N-pyrazole, P-phosphine
83 system, we have modulated the length of the link between these and 1-[2-(diphenylphosphanyl)ethyl]-
84 3,5-diphenylpyrazole (LP4) [6f], we have studied their reactivity with $[PdCl_2(CH_3CN)_2]$. The synthesis
85 and characterization of these new ligands and their complexes have been investigated. In particular,
86 NMR experiments and X-ray crystal studies. Finally, complex 2 has been studied as a catalyst in the
87 Heck reaction between phenyl halides and tert-butyl acrylate. heteroatoms.

88 Now, we present herein two new phosphine-ligands 1-[2-(diphenylphosphanyl)methyl]-3,5-
89 dimethylpyrazole (LP1) and 1-[2-(diphenylphosphanyl)propyl]-3,5-dimethylpyrazole (LP3). With these
90 ligands and two ligands previously described in the literature 1-[2-(diphenylphosphanyl)ethyl]-3,5-
91 dimethylpyrazole (LP2) [6e]

92

93 2. RESULTS AND DISCUSSION

94

95 2.1. Synthesis of the ligands

96 Ligand 1-[2-(diphenylphosphanyl)ethyl]-3,5-dimethylpyrazole (LP2) was previously prepared in our
97 group by reaction of 1-(chloroethyl)-3,5-dimethylpyrazole with PPh₂Li in THF at 25 °C [6e]. The
98 ligand 1-[2-(diphenylphosphanyl)ethyl]-3,5-diphenylpyrazole (LP4) was synthesized according to a
99 procedure previously described by Messerle et al. [6f].

100 The new ligands 1-[2-(diphenylphosphanyl)methyl]-3,5-dimethylpyrazole (LP1) and 1-[2-
101 (diphenylphosphanyl)propyl]-3,5-dimethylpyrazole (LP3) were prepared by reaction of 1-
102 (chloromethyl)-3,5-dimethylpyrazole (LC11) [8] or 1-(chloropropyl)-3,5-dimethylpyrazole (LC13) [9],
103 respectively, in presence of PPh₂Li, which is generated in situ by deprotonation of PPh₂H by n-butyl
104 lithium (n-BuLi) in THF as solvent, at 0 °C (Scheme 1a).

105 These new ligands, isolated in a 99% (LP1) and 95% yields (LP3) as yellowish oils, were characterised
106 by C, H, and N elemental analyses, IR, ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectroscopy, and by
107 MS(ESI⁺) mass spectrometry. All of them are in agreement with proposed ligands. In the ³¹P{¹H}
108 NMR spectra, the diphenylphosphanyl moiety gives a singlet at δ^{1/4} 18.4 ppm (LP1) and δ^{1/4} 19.1 ppm
109 (LP3), indicating the presence of the phosphine group [6e,10,12].

110

111 2.2. Synthesis and characterization of the complexes

112 **LP1-LP4** ligands (Scheme 1b) react with one equivalent of [PdCl₂(CH₃CN)₂] in dry CH₂Cl₂ as
113 solvent, to give the complexes [PdCl₂(LP)] (LP ¼ LP1 (1) (11% yield), LP2 (2) (86% yield), LP3 (3)
114 (40% yield) and LP4 (4) (56% yield)) (Scheme 1b). The complexes were analytically and
115 spectroscopically (IR, ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR) characterised.

116 Elemental analyses of the four complexes are consistent with their formulation.

117 MALDI-TOF of 1, 2, and 4 show one peak attributable to [PdCl(LP)]⁺ (m/z values, 437 (100%), 451
118 (100%) and 575 (100%), respectively. ESI(+) of 3 shows two peaks attributable to [PdCl(LP)]⁺ and
119 [PdCl₂(LP) Na]⁺ (m/z values, 465 (100%) and 523 (30%), respectively).

120 Conductivity measurements of 10⁻³ M samples in acetonitrile (between 2 and 8 U_Ω 1cm²mol⁻¹),
121 show the non-ionic behaviour of complexes 1e4 (compared with tabulated values) [11].

122 The IR spectra in the range 4000e400 cm⁻¹ of 1e4 compounds do not show important differences
123 respect free ligands, although the most characteristic bands are attributable to the pyrazolyl and pyridyl
124 groups ν(C)C_{ar} and ν(C)N_{ar} between 1555 and 1552 cm⁻¹ and δ(CeH)_{oop} between 765 and 690
125 cm⁻¹ [12]. The ν(CeP) bands between 798 and 793 cm⁻¹ are characteristic in all Pd complexes [12].
126 On IR spectra in the region 600e100 cm⁻¹, the ν(Pd-N) bands are observed (463e452 cm⁻¹) and the
127 ν(Pd-P) between (332e309 cm⁻¹). Moreover, the spectra of these complexes display two bands
128 (360e347 cm⁻¹) and (345e328 cm⁻¹), corresponding to stretching ν(Pd-Cl), which are typical of
129 compounds with a cis disposition of chlorine ligands around the Pd(II) [13].

130 The ¹H, ¹³C{¹H}, ³¹P{¹H}, HMQC, COSY and NOESY NMR spectra were recorded in CDCl₃ for 1
131 and 3, CD₂Cl₂ for 2 and CD₃CN for 4, due to its low solubility in other deuterated solvents (see
132 Supplementary information). The ¹³C{¹H} NMR spectrum of compound 4, could not be recorded for
133 this complex owing to its low solubility in common solvents. The NMR spectra of 1e4 compounds do
134 not show important differences between free ligands and the complexes in the aromatic and in the
135 methyl region. However, NMR spectra were studied in detail to make the assignment of the N-(CH₂)_x-

136 P signals. The ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were consistent with the proposed formulation
137 and showed the coordination of the ligands (LP1, LP2, LP3 and LP4) to the Pd atom. NMR
138 spectroscopic data are reported in Section 4. The ^1H NMR spectra of complexes 1e4, present one signal
139 between 6.73 and 5.75 ppm, assigned to the protons of the CH(pz). In the ^1H NMR spectrum of 1, the
140 methylene hydrogens appear as one signal, the two protons of the CH₂ group in Npz-CH₂-P chain are
141 equivalent. Thus, the signal can be assigned as a doublet (4.70 ppm, $2J_{\text{PH}} \frac{1}{4} 8.1$ Hz). For 2 and 4, the
142 four protons of the CH₂ groups in Npz-CH₂-CH₂-P chain, appear as two multiplets. The multiplets that
143 correspond to Npz-CH₂ appear at 4.81 (2) and 5.03 (4) ppm, and multiplets of the protons CH₂-P
144 appear at 2.61 (2) and 2.60 (4) ppm. Finally, for compound 3 the ^1H NMR spectrum display four signals
145 as multiplets that corresponds to groups of the signals for Npz-CH₂(a)-CH₂(b)-CH₂(c)-P chain. HMQC
146 spectrum was used to assign the signals of the protons (a), (b) and (c) of the chain. Two of these
147 multiplets appear at 5.69 and 4.25 ppm corresponding to each one of the protons of the fragment Npz-
148 CH₂(a). This behaviour indicates that the two protons are diastereotopic. The other group of signals at
149 1.89 and 1.21 ppm, are attributable to CH₂(b) and CH₂-P(c), respectively. The presence of the
150 multiplets for compounds 1e4 is probably due to the diastereotopic properties of CH₂ groups. This
151 effect is attributable to the rigid conformation of the ligands once they are complexed. The $^{13}\text{C}\{^1\text{H}\}$
152 NMR spectra of 1e3 complexes, show one signal between 109.9 and 107.6 ppm, assigned to the CH(pz).
153 The signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for all complexes appear at lower fields than for the free
154 respectively ligands and permit to know that phosphorus atom is connected to metallic centre. The
155 spectra show a singlet at (δ 35.3 ppm (1), δ 23.9 ppm (2), δ 11.6 ppm (3), and δ 21.0 ppm (4)). Chemical
156 shifts agree with of values of other complexes of Pd(II), Pphosphine complexes described in the
157 literature [6g,6h].

158

159 2.3. Crystal and molecular structure of complexes 2 and 3

160 We were able to obtain X-ray single crystals of complexes 2 and 3, and we performed a crystal structure
161 determination for both complexes.

162 ORTEP pictures and selected bond distances and angles are shown in Fig. 1 (2), Fig. 2 (3) and Table 1.
163 The structures of complexes 2 and 3 consists of discrete Pd(II) molecules. The metal is connected to the
164 pyrazole-phosphine ligands via $k^2(\text{N},\text{P})$ building a metallocycle ring of six (2) and seven (3) members,
165 and finishes its coordination with two chlorine atoms in a cis-disposition. A slightly distorted square-
166 planar geometry is observed around Pd(II) atom in both structures. The distortion of the geometry is
167 observed by the values of distances between Pd(II) and the main plane N1-P-C11-C12 [0.005 Å (2),
168 0.001 Å (3)], the values of the N1-Pd-P bite angles [82.77(8)° (2), 89.07(6)° (3)]. All of them are in
169 agreement with the ones found in the literature [14].

170 The bond distances Pd-N [2.046(3) Å (2), 2.0377(18) Å (3)], Pd-P [2.2325(11) Å (2), 2.2155(7) Å (3)],
171 Pd-C11 [2.3885(12) Å (2), 2.3365(7) Å (3)] and Pd-C12 [2.2752(15) Å (2), 2.2747(7) Å (3)], are in
172 agreement with the values described in the literature: Pd-N [1.953e2.088 Å], Pd-P [2.201e2.285 Å], Pd-
173 C11 [2.282e2.472 Å] and Pd-C12 [2.222e2.294 Å] [14].

174 Due to the different trans effect of the donor atoms in 2 and 3, the Pd-C11 bonds trans to phosphorus, are
175 longer than the Pd-C12 bonds trans to nitrogen [14]. The N1-Pd-P bite angles for 2 and 3 are smaller
176 than 90° C, but are consistent with the reported angles for similar complexes [14]. It is worth noting
177 that in both structures the six (2) and seven-membered rings (3) formed by the bidentate ligands
178 coordinated to palladium adopt a twisted boat conformation.

179 To deeply understand the structure for framework we have explored the connection modes of the metal
180 centers and organic ligands. Thus, we have investigated the self-assembly pattern of [PdCl₂(LP2)] (2)
181 and [PdCl₂(LP3)] (3) complexes in the crystal through intermolecular C-H...Cl hydrogen bonding
182 interactions. In complex 2 (Fig. 3), three of the potentially active H atoms (H13 from phenyl group, H7B

183 and H6A from ethylene chain) are engaged in hydrogen bonds with Cl atoms, which act as the unique
184 receptor for all three intermolecular interactions (C6-H6A\$\$\$Cl2: 3.623 Å, 151.39°; C7-H7B\$\$\$Cl1:
185 3.790 Å, 146.95°; C13-H13\$\$\$Cl1: 3.842 Å, 176.58°). In complex 3 (Fig. 4), each [PdCl2(LP3)] unit
186 is linked to three neighbouring molecules, via also C-H\$\$\$Cl hydrogen bonding (C5-H5C\$\$\$Cl1: 3.627
187 Å, 141.45°; C6-H6B\$\$\$Cl2: 3.639 Å, 128.01°; C8-H8A\$\$\$Cl2: 3.547 Å, 149.18°). All these C-
188 H\$\$\$Cl intermolecular contacts can be considered as “weak” on the basis of the contact distances and
189 angles [15].

190

191 2.4. Heck reactions using [PdCl2(LP2)] (2) complex

192 The Heck reaction is one of the most widely used palladium catalysed reactions in organic synthesis.
193 The reaction consists in the vinylation of aryl halides, and it was first reported by Mizoroki and Heck in
194 the early 1970s. In the following decades, the chemical community has searched for active and stable
195 palladium catalysts, which should be versatile and efficient.

196 Complex [PdCl2(LP2)] (2) has been used as pre-catalyst in the Heck reaction between phenyl halides (I,
197 Cl) and tert-butyl acrylate. The reaction progress was analysed by gaseliquid chromatography (GLC).
198 The results obtained are summarized in Table 2.

199 A characteristic of this complex is the thermal stability, which makes it possible to perform the reactions
200 even at temperature above 140 °C (close to the boiling point of the solvent) under the reaction
201 conditions. In these reactions were used Et3N as base, DMF (Dimethylformamide) as solvent and
202 NBu4Br (TBAB) as additive.

203 The use of complex 2 for the Heck olefination of aryl halides gives rise exclusively to the formation of
204 trans-acrylic acid esters (1H NMR). This complex was sensitive to oxygen or moisture: change in their
205 efficiency was observed if the Heck coupling reactions were carried out under aerobic conditions.
206 During these reactions in the presence of oxygen/moisture a black solid appears from the reaction
207 mixture. This solid was identified as Pd(0) through the mercury poisoning test [16].

208 Catalytic study of complex 2, between phenyl iodide and tertbutyl acrylate, a yield of 100% (0.1 cat.)
209 and 66% (0.01 cat.) were obtained, in 0.16 h and 3.6 h, respectively, with a turnover number (TON) of
210 987 and 6385, respectively (Table 2: entries 1 and 2). Similar palladium complexes synthesised in our
211 group yield similar catalytic behaviour [7h].

212 For several years, aryl bromides and iodides were preferably used as substrates in such reactions,
213 because aryl chlorides are transformed very sluggishly by standard palladium catalysts, due to the
214 strength of the CeCl bond. There has been a growing interest in finding catalytic systems that can
215 successfully catalyse crosscoupling reactions with aryl chlorides, since they are widely available,
216 industrially important, and generally less expensive than their bromide and iodide counterparts. In order
217 to studied the influence of the phenyl halide in our system, we have also studied the catalytic reaction
218 with phenyl chloride as a substrate, yielding 29% (0.1 cat.) and 37% (0.01 cat) in 32 h and 46 h,
219 respectively, with a values of TON of 307 and 3601, respectively (Table 2: entries 3 and 4).

220 In all cases studied the M:L ratio was 1:1. Finally, we have changed this ratio to M:L 1:10. In this case
221 the results were lower, t ¼ 33 h, % conv. ¼ 2, and TON ¼ 269 (Table 2, entry 5).

222

223 **3. CONCLUSION**

224

225 We have presented the synthesis and characterisation of two new ligands (LP1 and LP3), and with these
226 ligands and two other ligands, previously described in the literature (LP2 and LP4), we have assayed the
227 reaction with $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$, obtaining $[\text{PdCl}_2(\text{LP})]$ (LP ¼ LP1 (1), LP2 (2), LP3 (3) and LP4 (4))
228 compounds. All these new complexes have been characterised by elemental analyses, conductivity
229 measurements, infrared and ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies, and MS-ESI(p) and
230 MALDI-TOF spectrometry.

231 The crystal structure of complexes $[\text{PdCl}_2(\text{LP})]$ (LP ¼ LP2 (2) and LP3 (3)) were determined by X-ray
232 diffraction methods showing a square planar geometry where the palladium centre is coordinated to one
233 bidentate LP ligand and two chlorine atoms in a cis disposition.

234 Complex 2 represents an active catalyst in the Heck reaction between phenyl halides and tert-butyl
235 acrylate. The advantages of this practical and efficient catalyst system include its generality and high
236 catalytic activity even for some aryl chlorides under mild conditions.

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238

239 4. EXPERIMENTAL SECTION

240

241 4.1. General details

242 Reactions were carried out under a dinitrogen atmosphere using vacuum line and Schlenk techniques.
243 Solvents were dried and distilled according to standard procedures and stored under nitrogen. All
244 chemicals products were used as received from commercial suppliers, unless otherwise indicated.

245 Elemental Analyses (C, H, N) were performed at Chemical Analyses Service of the Universitat
246 Autònoma de Barcelona, using a Carlo Erba CHNS EA-1108 instrument separated by chromatographic
247 column and thermoconductivity detector. Conductivity measurements were performed at room
248 temperature in 10⁻³ M acetonitrile solutions employing a CyberScan CON 500 (Eutech instrument)
249 conductimeter. Infrared spectra were run in a Perkin Elmer FT-2000 spectrophotometer as KBr pellets
250 or polyethylene films. The ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra and bidimensional NMR spectra
251 were run on a NMR-FT Bruker AC-250 spectrometer. All NMR experiments were recorded on CDCl₃,
252 CD₂Cl₂ or CD₃CN solvents under nitrogen. ¹H and ¹³C{¹H} NMR chemicals shifts (δ) were
253 determinate relative to internal TMS and are given in ppm. ³¹P {¹H} NMR chemical shifts (δ) were
254 determined relative to external 85% H₃PO₄. Electrospray Mass spectra (ESI ⁺) were carried out by the
255 staff of the Chemical Analysis Service of the Universitat Autònoma de Barcelona in an Esquire 3000
256 ion trap mass spectrometer from Bruker Daltonics. Mass experiments were done on acetonitrile solvent.
257 Matrix assisted laser desorption/ionization (MALDI) time-of flight (TOF) mass spectrometry were
258 carried out by the staff of the Institut de Biotecnologia i Medicina of the Universitat Autònoma de
259 Barcelona on a positive ion mode on a Bruker-Daltonics Ultroflex time-of-flight instrument. Ion
260 acceleration was set to 25 KV. All mass spectra were externally calibrated using a standard peptide
261 mixture. The sample was dissolved in CHCl₃ and mixed with 2,5-dihydroxybenzoic acid (DHB)
262 solution matrix (0.5 ml matrix). The mixed solution was applied on a ground steel plate (1 ml). The
263 quantification of the catalytic reaction was carried out using a Hewlett Packard HP5890 gas
264 chromatograph equipped with a flame ionization detector (FID), and a Hewlett Packard HP-5 column
265 (30 m long, 0.32 mm internal diameter and 0.25 mm film thickness). The stationary phase consists of
266 5% diphenyl/95% dimethyl polysiloxane. Thermal stability of complex 2 was evaluated with a blank
267 catalytic experiment (without reagents) at 140 °C, close to the boiling point of the solvent, under the
268 reaction conditions. In these reactions were used Et₃N as base, DMF (Dimethylformamide) as solvent
269 and NBu₄Br (TBAB) as additive.

270 The compound [PdCl₂(CH₃CN)₂] was prepared according to literature methods [17], 1-[2-
271 (diphenylphosphanyl)ethyl]-3,5- dimethylpyrazole (LP2) [6e] and 1-[2-(diphenylphosphanyl) ethyl]-3,5-
272 diphenylpyrazole (LP4) [8] ligands were synthesized as we previously reported.

273

274 4.2. Synthesis of the ligands

275 4.2.1. Synthesis of 1-[2-(diphenylphosphanyl)methyl]-3,5- dimethylpyrazole (LP1) and 1-[2-
276 (diphenylphosphanyl)propyl]-3,5-dimethylpyrazole (LP3)

277 A solution of nBuLi (16 ml, 25.3 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of
278 PPh₂H (1.38 ml, 8.0 mmol) in dry THF (10 ml) at -77 °C (acetone/CO₂). After 30 min, the solution of
279 PPh₂Li was added dropwise to a stirred solution of 1-(chloromethyl)-3,5-dimethylpyrazole (LC1HCl)
280 (1.16 g, 8 mmol) for LP1 or 1-(chloropropyl)-3,5-dimethylpyrazole (LC3HCl) (1.39 g, 8 mmol) for
281 LP3, in THF (20 ml) at -77 °C. The mixture was maintained at -77 °C for 1 h. The temperature was
282 then raised to room temperature and after 12 h of stirring the solvent was evaporated under vacuum. 40
283 ml of dichloromethane were added to the residue and the salts were extracted with 3 × 10 ml of distilled
284 water. Evaporation of the solvent from the organic phase gives 1-[2-(diphenylphosphanyl)methyl]-3,5-

285 dimethylpyrazole (LP1) and 1-[2-(diphenylphosphanyl)propyl]-3,5-dimethylpyrazole (LP3) as a
286 yellowish oils.

287 **LP1:** (Yield: 99%, 2.33 g). Anal. Calc. for C₁₈H₁₉N₂P: C, 73.45, H, 6.51; N, 9.52. Found: C, 73.81; H,
288 6.44; N, 9.39%. MS (ESI⁺): m/z (%): 295 (97%) [LP1 p H]_p, 311 (100%) [LP1(O) p H]_p (LP1(O) ¼
289 oxidized ligand). IR: (NaCl, cm⁻¹): 3051 n(CeH)ar, 2922 n(CeH)al, 1552 n(C) C/C]N)ar, 1433
290 d(C]C/C]N)ar, 787 n(PeC), 739, 695 d(CeH)oop. 1H NMR (CDCl₃ at 298 K, 250 MHz) d: 7.47 (m,
291 10H, C₆H₅), 5.65 (s, 1H, pz-CH), 4.61 (d, 2H, 2JPH ¼ 4.7 Hz, pz-CH₂-P), 2.18 (s, 3H, pz-CH₃), 1.83
292 (s, 3H, pz-CH₃) ppm. 13C{1H} NMR (CDCl₃ at 298 K, 63 MHz) d: 148.3, 139.9 (pz-CCH₃), 136.9 (d,
293 1JPC ¼ 14.9 Hz, P-C₆H₅), 133.8e128.3 (C₆H₅), 105.7 (pz-CH), 50.6 (d, 1JPC ¼ 14.6, pz-CH₂-P), 14.0
294 (pz-CH₃), 11.5 (d, 4JPC ¼ 3.3 Hz, pz-CH₃) ppm. 31P{1H} NMR (CDCl₃ at 298 K, 81 MHz) d: 18.4
295 (s, P-C₆H₅) ppm.

296 **LP3:** (Yield: 95%, 2.45 g). Anal. Calc. for C₂₀H₂₃N₂P: C, 74.51, H, 7.19; N, 8.69. Found: C, 74.95; H,
297 7.23; N, 8.33%. MS (ESI⁺): m/z (%): 323 (46%) [LP3 p H]_p, 339 (100%) [LP3(O) p H]_p (LP3(O) ¼
298 oxidized ligand). IR: (NaCl, cm⁻¹): 3047 n(CeH)ar, 2919 n(CeH)al, 1551 n(C) C/C]N)ar, 1433
299 d(C]C/C]N)ar, 778 n(PeC), 742, 698 d(CeH)oop. 1H NMR (CDCl₃ at 298 K, 250 MHz) d: 7.45 (m,
300 10H, C₆H₅), 5.66 (s, 1H, pz-CH), 3.96 (m, 2H, pz-CH₂-CH₂-CH₂-P), 1.87 (m, 2H/2H, pz-CH₂-CH₂-
301 CH₂-P), 2.12 (s, 3H, pz-CH₃), 2.08 (s, 3H, pz-CH₃) ppm. 13C{1H} NMR (CDCl₃ at 298 K, 63 MHz)
302 d: 147.6, 139.0 (pz-CCH₃), 138.7 (d, 1JPC ¼ 12.6 Hz, P-C₆H₅), 134.4 (d, 1JPC ¼ 17.1 Hz, P-
303 C₆H₅), 133.6e128.5 (C₆H₅), 105.3 (pz-CH), 49.7 (d, 3JPC ¼ 14.1 Hz, pz-CH₂-CH₂-CH₂-P), 27.2 (d,
304 1JPC ¼ 16.8 Hz, pz-CH₂-CH₂-CH₂-P), 25.2 (d, 2JPC ¼ 12.0 Hz, pz-CH₂-CH₂-CH₂-P), 13.9 (pz-
305 CH₃), 7.1 (pz-CH₃) ppm. 31P{1H} NMR (CDCl₃ at 298 K, 81 MHz) d: 19.1 (s, P-C₆H₅) ppm.

306

307 4.3. Synthesis of the complexes

308 4.3.1. Complexes [PdCl₂(LP)] (LP ¼ LP1 (1), LP2 (2), LP3 (3) and LP4 (4))

309 The appropriate ligand (0.270 mmol: LP1, 0.079 g; LP2, 0.083 g; LP3, 0.087 g; LP4, 0.117 g) dissolved
310 in dry CH₂Cl₂ (10 ml) was added to a solution of the palladium complex [PdCl₂(CH₃CN)₂] (0.270
311 mmol, 0.070 g) in dry CH₂Cl₂ (15 ml). The orange solutions were stirred at room temperature for 12 h.
312 The resulting solutions were concentrated until 5 ml. For solution that contain the LP2 ligand, a yellow
313 pure solid was obtained by precipitation. Cold dry diethyl ether (5 ml) was added dropwise to the
314 solution of LP1, LP3 and LP4. After one hour at 4 °C an orange pure solid was obtained for LP1 and
315 yellow solids were obtained for LP3 and LP4. The solids were washed with cold dry diethyl ether.

316 **1** (Yield: 11%, 0.014 g). Anal. Calc. for C₁₈H₁₉N₂PCl₂Pd: C, 45.84; H, 4.06; N, 5.94. Found: C,
317 45.60; H, 3.83; N, 6.21%. MS (MALDITOF): m/z (%): 437 (100%) [PdCl(LP1)]_p. Conductivity (1.02
318 10⁻³ S cm⁻¹ mol⁻¹ in acetonitrile): 2 U 1 cm² mol⁻¹. IR: (KBr, cm⁻¹): 3053 n(CeH)ar, 2958, 2915
319 n(CeH)al, 1555 n(C]C/C]N)ar, 1436 d(C]C/C]N)ar, 798 n(PeC), 744, 690 d(CeH)oop; (polyethylene,
320 cm⁻¹) 463 n(Pd-N), 358, 342 n(Pd-Cl), 325 n(Pd-P). 1H NMR (CDCl₃ at 298 K, 250 MHz) d: 7.63 (m,
321 10H, C₆H₅), 5.86 (s, 1H, pz-CH), 4.70 (d, 2H, 2JPH ¼ 8.1 Hz, pz-CH₂-P), 2.56 (s, 3H, pz-CH₃), 2.28
322 (s, 3H, pz-CH₃) ppm. 13C{1H} NMR (CDCl₃ at 298 K, 63 MHz) d: 148.1, 139.9 (pz-CCH₃), 136.8 (d,
323 1JPC ¼ 14.7 Hz, P-C₆H₅), 135.2e128.5 (C₆H₅), 109.5 (pz-CH), 49.2 (d, 1JPC ¼ 37.4, pz-CH₂-P), 15.2
324 (pz-CH₃), 12.4 (d, pz-CH₃) ppm. 31P{1H} NMR (CDCl₃ at 298 K, 81 MHz) d: 35.3 (s, P-C₆H₅) ppm.

325 **2** (Yield: 86%, 0.113 g). Anal. Calc. for C₁₉H₂₁N₂PCl₂Pd: C, 46.74; H, 4.20; N, 5.66. Found: C,
326 47.07; H, 4.64; N, 5.61%. (MALDI-TOF): m/z (%): 451 (100%) [PdCl(LP2)]_p. Conductivity (1.12 10⁻³
327 S cm⁻¹ mol⁻¹ in acetonitrile): 7 U 1 cm² mol⁻¹. IR: (KBr, cm⁻¹): 3046 n(CeH)ar, 2923 n(CeH)al, 1552
328 n(C]C/C]N)ar, 1436 d(C]C/C]N)ar, 793 n(PeC), 746, 693 d(CeH)oop; (polyethylene, cm⁻¹) 452 n(Pd-
329 N), 347, 328 n(Pd-Cl), 314 n(Pd-P). 1H NMR (CD₂Cl₂ at 298 K, 250 MHz) d: 7.55 (m, 10H, C₆H₅),
330 5.75 (s, 1H, pz-CH), 4.81 (m, 2H, pz-CH₂-CH₂-P), 2.61 (m, 2H, pz-CH₂-CH₂-P), 2.37 (s, 3H, pz-

331 CH₃), 2.19 (s, 3H, pz-CH₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂ at 298 K, 63 MHz) δ: 152.9, 134.4, 127.2
332 (C₆H₅), 107.6 (pz-CH), 45.5 (pz-CH₂-CH₂-P), 27.6 (d, 1JPC ¼ 32.4 Hz, pz-CH₂-CH₂-P), 14.7 (pz-
333 CH₃), 11.0 (pz-CH₃) ppm. ³¹P{¹H} NMR (CD₂Cl₂ at 298 K, 81 MHz) δ: 23.9 (s, P-C₆H₅) ppm.

334 3 (Yield: 40%, 0.054 g). Anal. Calc. for C₂₀H₂₃N₂PCl₂Pd: C, 47.93; H, 4.41; N, 5.30. Found: C,
335 47.72; H, 4.13; N, 5.59%. MS (MALDI-TOF): m/z (%): 465 (100%) [PdCl(LP3)]⁺, 523 (30%)
336 [PdCl(LP3) + Na]⁺. Conductivity (1.05 × 10⁻³ M in acetonitrile): 6 U × 1 cm² mol⁻¹. IR: (KBr,
337 cm⁻¹) 3055 n(CeH)_{ar}, 2959 n(CeH)_{al}, 1554 n(C)C/C]N_{ar}, 1435 d(C)C/C]N_{ar}, 798 n(PeC), 743, 691
338 d(CeH)_{oop}; (polyethylene, cm⁻¹) 457 n(Pd-N), 355, 337 n(Pd-Cl), 309 n(Pd-P). ¹H NMR (CDCl₃ at
339 298 K, 250 MHz) δ: 7.63 (m, 10H, C₆H₅), 5.99 (s, 1H, pz-CH), 5.69/4.25 (m, 1H/1H, pz-CH₂-CH₂-
340 CH₂-P), 1.89/1.21 (m, 2H/ 2H, pz-CH₂-CH₂-CH₂-P), 2.44 (s, 3H, pz-CH₃), 2.23 (s, 3H, pz-CH₃) ppm.
341 ¹³C{¹H} NMR (CDCl₃ at 298 K, 63 MHz) δ: 135.3, 128.4 (C₆H₅), 109.9 (pz-CH), 47.6 (pz-CH₂-
342 CH₂-CH₂-P), 24.9, 23.4 (pz-CH₂-CH₂- CH₂-P), CH₂-CH₂-CH₂-P), 15.7 (pz-CH₃), 12.0 (pz-CH₃)
343 ppm. ³¹P{¹H} NMR (CDCl₃ at 298 K, 81 MHz) δ: 11.6 (s, P-C₆H₅) ppm.

344 4 (Yield: 56%, 0.092 g). Anal. Calc. for C₂₉H₂₅N₂PCl₂Pd: C, 57.12; H, 4.13; N, 4.59. Found: C,
345 56.95; H, 4.05; N, 4.63%. (MALDI-TOF): m/z (%): 575 (100%) [PdCl(LP4)]⁺. Conductivity (1.08 ×
346 10⁻³ M in acetonitrile): 8 U × 1 cm² mol⁻¹. IR: (KBr, cm⁻¹) 3056 n(CeH)_{ar}, 2907 n(CeH)_{al}, 1552
347 n(C)C/C]N_{ar}, 1436 d(C)C/C]N_{ar}, 802 n(PeC), 765, 693 d(CeH)_{oop}; (polyethylene, cm⁻¹) 461 n(Pd-
348 N), 360, 345 n(Pd-Cl), 332 n(Pd-P). ¹H NMR (CD₃CN at 298 K, 250 MHz) δ: 7.71 (m, 20H, C₆H₅),
349 6.73 (s, 1H, pz-CH), 5.03 (m, 2H, pz-CH₂-CH₂-P), 2.60 (m, 2H, pz-CH₂-CH₂-P), 2.21 (s, 3H, pz-
350 CH₃), 1.79 (s, 3H, pz-CH₃) ppm. ³¹P{¹H} NMR (CD₃CN at 298 K, 81 MHz) δ: 21.0 (s, P-C₆H₅)
351 ppm.

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353 4.4. X-ray crystal structure for complexes 2 and 3

354 Crystals of complexes 2 and 3 suitable for X-ray diffraction were obtained through recrystallization
355 from CH₂Cl₂/diethyl ether mixtures. Prismatic crystals were selected and mounted on a MAR 345
356 diffractometer with an image plate detector. Unit cell parameters were determined from 47 reflections
357 for 2 and 17380 reflections for 3 (3 < q < 31 °) and refined by least-squares method. Intensities were
358 collected with graphite monochromatized Mo K_α radiation. 24329 reflections were measured in the
359 range 2.56 ° < q < 30.00 for 2, which 5646 were non-equivalent by symmetry (R_{int} (on I) ¼ 0.035). 5619
360 reflections were assumed as observed applying the condition I > 2s. 5717 reflections were measured in
361 the range 2.63 ° < q < 32.88 for 3 which 5330 were assumed as observed applying the condition I > 2s(I).
362 Three reflections were measured every two hours as orientation and intensity control, significant
363 intensity decay was not observed. Lorenz-polarization and absorption corrections were made.

364 For 2 and 3, the structure was solved by direct methods, using SHELX-97 computer program [18] and
365 refined by full matrix leastsquares method with SHELXL-97 computer program [19], using 24329
366 reflections for 2 and 5717 reflections for 3. The function minimized was $w \sum [s_2(I) + 4.8616P]^2$, where $w = 1/4$
367 $[s_2(I) + 4.8616P]^2$, and $P = 1/4 (r_{Fo}^2 + 2 r_{Fc}^2)/3$ for 2, and $w = 1/4 [s_2(I) + (0.0567P)^2 + 0.4027P]^2$ for
368 3. For 2, all H atoms are computed and refined, using a riding model, with an isotropic temperature
369 factor equal to 1.2 times the equivalent temperature factor of the atom which is linked. For 3, 2H atoms
370 were located from a difference synthesis and refined with isotropic temperature factor and 21H atoms
371 were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times
372 the equivalent temperature factor of the atom which is linked.

373 The parameters refined and other details concerning the refinement of the crystal structures are gathered
374 in Table 3.

375

376

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378
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455 **Legends to figures**

456

457 **Figure 1** ORTEP drawing of [PdCl₂(LP₂)] (2), showing all non-hydrogen atoms and the atom
458 numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

459

460 **Figure 2.** ORTEP drawing of [PdCl₂(LP₃)] (3), showing all non-hydrogen atoms and the atom
461 numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

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463 **Figure 3** Supramolecular view of two [PdCl₂(LP₂)] (2) units generated by intermolecular C-H...Cl
464 hydrogen bondings. C-H...Cl hydrogen bonding interactions are indicated with dashed lines..

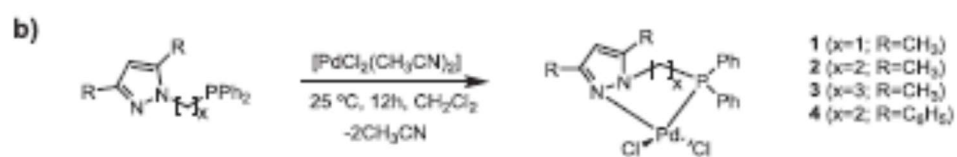
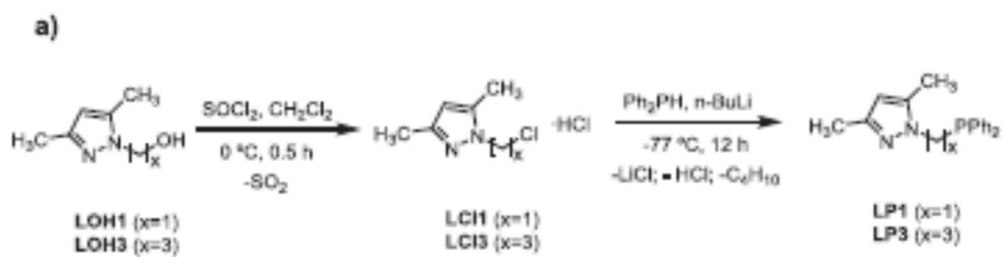
465

466 **Fig. 4** Supramolecular view of four [PdCl₂(LP₃)] (3) units generated by intermolecular C-H...Cl
467 hydrogen bondings. C-H...Cl hydrogen bonding interactions are indicated with dashed lines.

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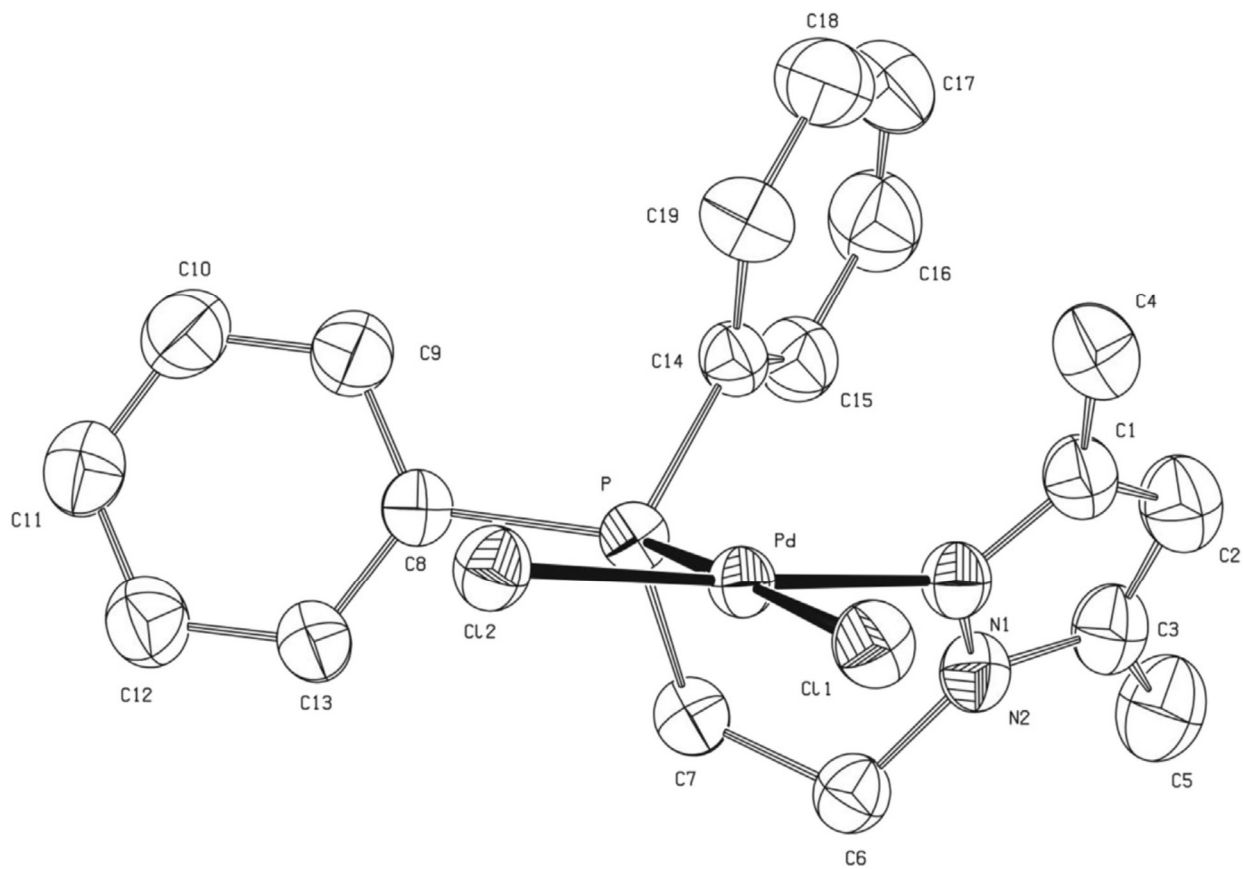
SCHEME 1



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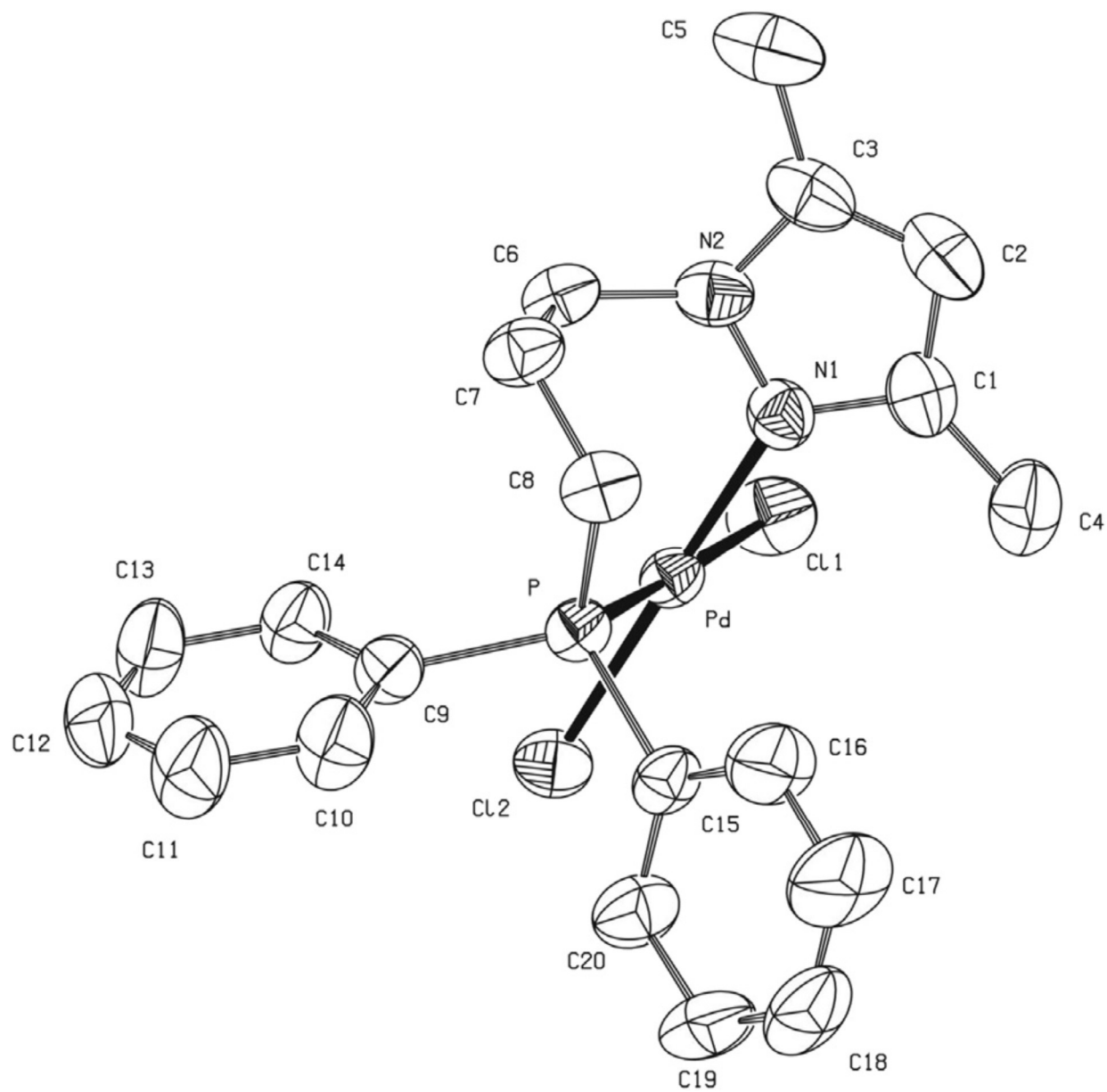
FIGURE 1



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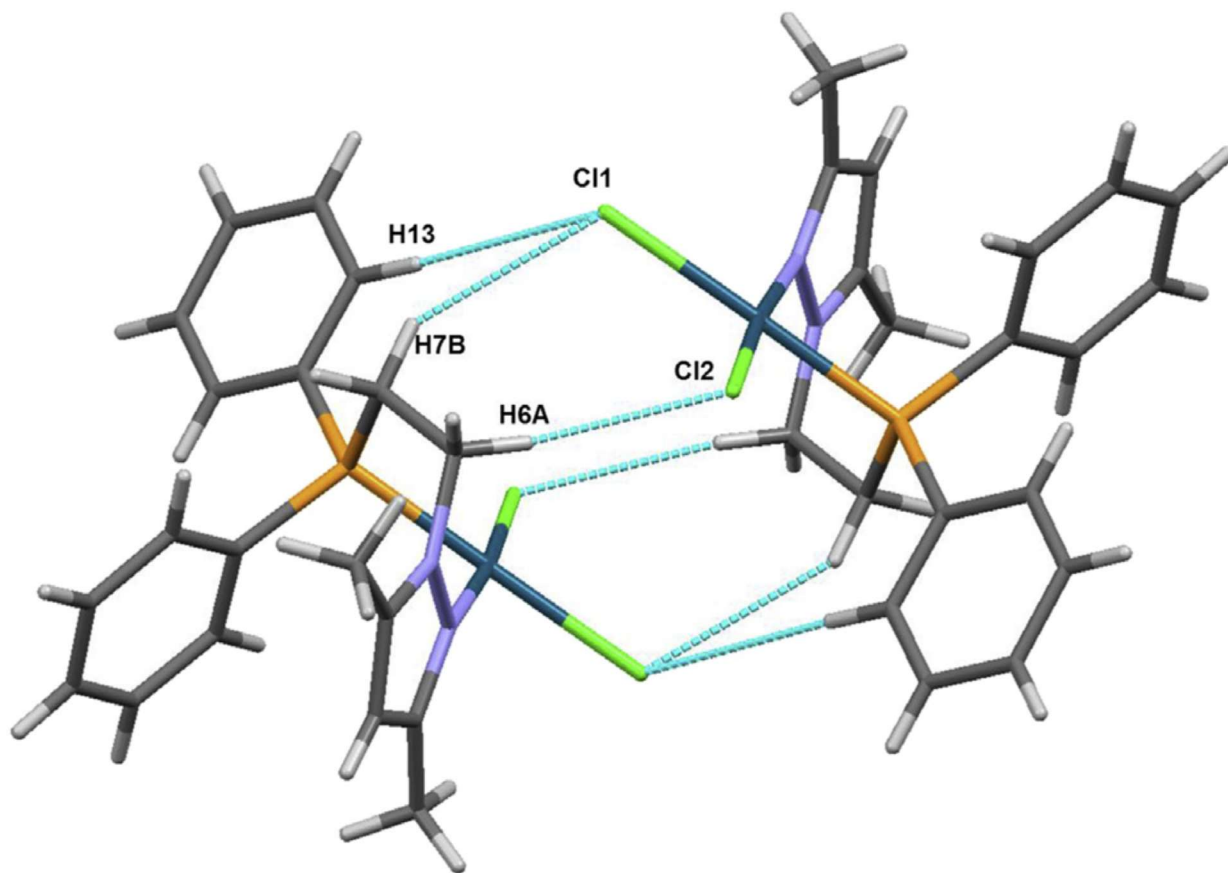
FIGURE 2



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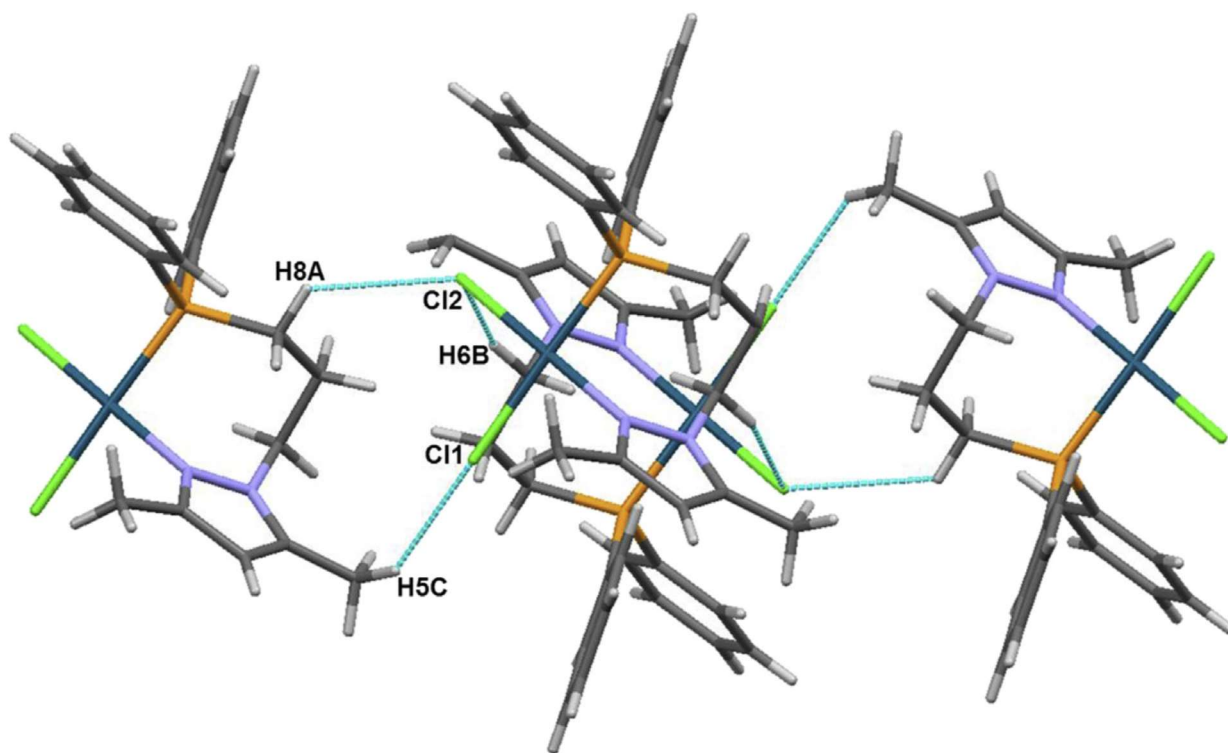
FIGURE 3



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FIGURE 4



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502 **Table 1.** Selected bond lengths (Å) and angles (°) of 2 and 3.

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	2	3
Pd–N(1)	2.046(3)	2.0377(18)
Pd–P	2.2325(11)	2.2155(7)
Pd–Cl(2)	2.2752(15)	2.2747(7)
Pd–Cl(1)	2.3885(12)	2.3365(7)
N(1)–Pd–P	82.77(8)	89.07(6)
P–Pd–Cl(2)	91.80(4)	90.43(3)
N(1)–Pd–Cl(1)	93.27(8)	89.51(6)
P–Pd–Cl(1)	175.22(4)	178.39(2)
Cl(2)–Pd–Cl(1)	92.26(4)	90.99(3)

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509 **Table 2** Heck coupling reaction of Aryl Halides using Pre-Catalysts 2.

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Entry	Ar-X	Cat.	mol%	M:L	Solvent	T (°C)	t (h)	Yield(%)	TON	TOF (h ⁻¹)
1	I	2	0.1	1:1	DMF	140	0.16	100	987	6288
2	I	2	0.01	1:1	DMF	140	3.6	66	6385	1789
3	Cl	2	0.1	1:1	DMF	140	32	29	307	8
4	Cl	2	0.01	1:1	DMF	140	46	37	3601	77
5	Cl	2	0.1	1:10	DMF	140	33	26	269	8

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513

514 **Table 3.** Crystallographic data for 2 and 3.
 515

	2	3
Formula	C ₁₉ H ₂₁ Cl ₂ N ₂ Pd	C ₂₀ H ₂₂ Cl ₂ N ₂ Pd
Formula weight	485.65	499.67
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
System, space group	Monoclinic, P2 ₁ /n	Monoclinic, P2 ₁ /n
a, b, c (Å)	14.300(7), 10.054(5), 15.273(4)	11.857(4), 8.343(3), 21.298(4)
β (°)	113.94(2)	101.22(2)
U (Å ³)/Z	2006.94(15)/4	2066.6(11)/4
D _{calc} (g cm ⁻³)/μ (mm ⁻¹)	1.607/1.275	1.606/1.241
R(000)	976	1008
Crystal size (mm ³)	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
hkl ranges	-19 ≤ h ≤ 21, -14 ≤ k ≤ 13, -23 ≤ l ≤ 23	-15 ≤ h ≤ 15, 0 ≤ k ≤ 12, 0 ≤ l ≤ 30
2θ Range (°)	2.56–30.00	2.63–32.88
Reflections	24329/5646	5717/5717
collected/unique/[R _{int}]	[R _{int}] = 0.0352]	[R _{int}] = 0.0311]
Completeness to θ (%)	96.4	97.1
Absorption correction	Empirical	Empirical
Max. and min. trans.	0.880 and 0.858	0.88 and 0.86
Data/restraints/parameters	5646(3)/227	5717(0)/245
Goodness-of-fit on F ²	1.324	1.140
Final R indices [I > 2σ(I)]	R ₁ = 0.0458, wR ₂ = 0.0839	R ₁ = 0.0379, wR ₂ = 0.0920
R indices (all data)	R ₁ = 0.0460, wR ₂ = 0.0840	R ₁ = 0.0400, wR ₂ = 0.0936
Largest diff. peak and hole (e Å ⁻³)	+0.672, -0.453	+0.747, -0.686

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